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RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

# A NEW CARBON-BOND MECHANISM FOR AIR QUALITY SIMULATION MODELING

by

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## ABSTRACT

A new generalized kinetic mechanism for photochemical smog, which incorporates recent information on the atmospheric reactions of aromatic hydrocarbons, has been developed. The mechanism, labeled the Carbon-Bond Mechanism III (CBM-III), is the third lumped-parameter mechanism to be designed in accordance with the carbon-bond reaction concept in which carbon atoms with similar bonding are treated similarly, regardless of the molecules in which they occur. The principal feature that distinguishes CBM-III from previous Carbon-Bond Mechanisms is the updated aromatic hydrocarbon chemistry.

Because of the general nature of the CBM-III, it can be used to model the entire atmospheric mix of hydrocarbons and is suitable for use in Air Quality Simulation Models (AQSMs). Principal features of CBM-III include a separate reaction scheme for ethylene; realistic photochemistry for aromatic hydrocarbons and dicarbonyl compounds; and formation pathways for alkyl nitrates and nitroaromatic compounds.

CBM-III was tested by comparing the predictions obtained with the mechanism against smog chamber data of multi-component hydrocarbon/$NO_x$ mixtures obtained in the indoor chamber facility at the University of California, Riverside, and the outdoor chamber facility of the University of North Carolina.

In addition to a discussion of the development and testing of the CBM-III, information is also provided on the application of the mechanism for urban air quality modeling. Instructions are given on how to partition the emission and atmospheric hydrocarbon data into the various carbon-bond groupings that are used in the CBM-III. Calculated bond groupings are given for several types of hydrocarbon data (including data for several specific urban areas).

CONTENTS

TABLES

## LIST OF ABBREVIATIONS

| | |
|---|---|
| $ACO_3$ | Peroxyacyl radical (two-carbon surrogate for $RCO_3$) |
| APRC | Aromatic product carbon |
| ARO | Aromatic ring |
| ARPI | Aromatic oxidation intermediate product |
| CARB | Carbonyl bond |
| CBM | Carbon-Bond Mechanism |
| CRIG | Criegee intermediate ($H_2CO_2$) |
| $CRO_2$ | Carbonyl peroxy which will produce DCRB |
| DCRB | Dicarbonyl compound |
| EKMA | Empirical Kinetics Modeling Approach |
| ETH | Ethylene or slow olefinic bond |
| GLY | Surrogate for dicarbonyls |
| KET | Ketone |
| MCRG | Surrogate for $RCHO_2$ type Criegee intermediates |
| $MEO_2$ | Peroxy radical (one-carbon surrogate for $RO_2$) |
| NMHC | Non-methane hydrocarbon |
| NPHN | Nitrophenol |
| NRAT | Organic nitrate |
| OLE | Olefinic bond |
| OPEN | Aromatics ring-opening intermediate |
| OZIPM | Same as OZIPP plus mechanism and other options |

| | |
|---|---|
| OZIPP | Ozone Isopleth Plotting Package (computer program used in EKMA) |
| PAN | Peroxyacyl nitrate |
| PAR | Single or paraffinic bond |
| PHEN | Phenolic pathway surrogate in ARO oxidation |
| PHO | Phenoxy radical |
| ... | General organic moiety (R = H, $CH_3$, $C_2H_3$, etc.) |
| $RAO_2$ | Hydroxy peroxyl from OH + OLE |
| RARO | Aromatic radical |
| $RBO_2$ | Hydroxyperoxyl from OH + ETH |
| $RCO_3$ | Peroxyacyl radical |
| RHC | Reactive hydrocarbons |
| RO | Alkoxyl radical |
| $RO_2$ | Peroxy radical |
| W | Carbonyl balancing unit |
| X | Carbon-mass balancing unit |

# SECTION 1

# INTRODUCTION

The Carbon-Bond Mechanism (CBM) is a photochemical kinetic mechanism that has been developed expressly to provide a reasonable compromise between chemical realism and computational efficiency. The CBM is designed to meet stringent validation standards in the simulation of laboratory smog-chamber studies; however, it can also be easily applied to atmospheric studies using a minimum number of assumptions.

The version of the Carbon-Bond Mechanism presented in this manual is the product of two major revisions and is referred to as CBM-III. The original Carbon-Bond Mechanism (CBM-I) is described in Whitten, Hogo, and Killus (1980), and CBM-II is described in Whitten, Killus, and Hogo (1980). The current version (CBM-III) differs from CBM-II principally in the structure of the oxidation mechanism for aromatic hydrocarbons and in some modifications of inorganic reaction-rate constants.

These three Carbon-Bond Mechanisms are so named because they treat the carbon bond, rather than the molecule, as the principal unit of reaction. This concept offers several important advantages. First, the CBM is carbon-conservative. The olefinic bond group, for example, always contains two carbon atoms that must be accounted for in its products. The paraffinic bond contains one carbon atom, and the aromatic bonds, six.* Thus we can eliminate the cumbersome notion of "average molecular weight," which causes considerable difficulty in the application of lumped molecular mechanisms. Furthermore, use of the CBM allows precise calculation of carbon-mass balance in simulations, whereas such calculations can only be approximated when other mechanisms are used.

The second major advantage afforded by the CBM is a considerable reduction in the range of reaction-rate constants that must be averaged for the lumped hydrocarbon species. This is true for paraffins, for example, in which iso-butane has a molecular reaction-rate constant with OH of

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* CBM-I treated aromatic bonds as a sum of three double-bonded carbon atoms. This approximation was changed in the CBM-II.

5000 $ppm^{-1}min^{-1}$, and iso-octane has a reaction rate of 11,500 $ppm^{-1}min^{-1}$. These reactivity rates, normalized to the number of carbon atoms per molecule, are 1250 $ppm^{-1}min^{-1}$ and 1440 $ppm^{-1}min^{-1}$, respectively. The relative difference between these two figures is thus much smaller than the relative difference between the molecular reaction rates.

Finally, because the CBM has been used for a wide variety of laboratory and atmospheric applications, the validation data set is extensive. Past performance has shown the CBM to be an eminently practical simulation tool. Each update of the mechanism is carefully considered in the light of past applications and current knowledge. The newer version of the CBM, therefore, should yield results similar to those obtained in past applications in which the older versions were used, but the recently modified CBM is more representative of current knowledge of the explicit photochemistry of smog formation.

# SECTION 2

# RECOMMENDATIONS

When using the CBM, special attention should be given to the level of carbonyls used in the inputs for emissions and air quality. Also, air monitoring data should be used to verify both the carbonyl inputs and the levels generated by the model using the CBM. Future validation studies for any atmospheric kinetics mechanism should involve comparisons of measured and simulated carbonyl levels.

Future versions of the CBM should include the correct chemistry for natural hydrocarbon species such as isoprene and α-pinene. This improvement will become possible as the explicit chemistry for these species becomes available.

## SECTION 3

## FORMULATION OF THE NEW VERSION OF THE CARBON-BOND MECHANISM

At the time the original CBM (shown in table 1) was formulated, it represented a condensation of existing explicit mechanisms (primarily for propylene and butane). It was also used to simulate a set of smog-chamber experiments with a reasonable degree of success. Knowledge of smog chemistry has expanded to include more molecules, however, and the amount of data derived from smog-chamber experiments has increased. Therefore, we sought to improve the Carbon-Bond Mechanism.

Periodic updating of generalized mechanisms like the CBM is preferable to continuous updating. Changes in one reaction may require compensating changes in other reactions to maintain the overall predictive accuracy of simulations in which the mechanism is used. Consequently, after a reaction change, the mechanism should be tested with an entire set of smog-chamber data to ensure that no special problems have arisen that would make atmospheric applications difficult. The cost of such testing makes it desirable to test the effects of several changes at once. Documentation of any changes is also necessary to keep all users of the mechanism informed.

For many applications (such as the use of the mechanism in a photochemical dispersion model) major changes in the mechanism require extensive program modification. Numerical changes in rate constants can be typically accommodated by such programs, but changes in product yield may involve modification of the steady-state approximations necessary for rapid solution of the chemical equations.

The first update of the CBM (CBM-II), reported by Whitten et al. (1979), reflected the following changes to the CBM formulation:

- Eliminating the peroxyformyl radical ($HCO_3^{\bullet}$).
- Updating the rate constants and excluding HONO and HOOH.
- Including the reactions of intermediate Criegee species formed from ozone-olefin reactions.

TABLE 1. THE ORIGINAL FORMULATION OF THE CARBON-BOND MECHANISM

| | Reaction | Rate Constant ($ppm^{-1}min^{-1}$) |
|---|---|---|
| 1 | $NO_2 + h\upsilon \rightarrow NO + O$ | *† |
| 2 | $O + O_2 (+ M) \rightarrow O_3 (+ M)$ | $2.08 \times 10^{-5}$ |
| 3 | $O_3 + NO \rightarrow NO_2 + O_2$ | 25.2 |
| 4 | $O + NO_2 \rightarrow NO + O_2$ | $1.34 \times 10^{4}$ |
| 5 | $O_3 + NO_2 \rightarrow NO_3 + O_2$ | $5 \times 10^{-2}$ |
| 6 | $NO_3 + NO \rightarrow NO_2 + NO_2$ | $1.3 \times 10^{4}$ |
| 7 | $NO_3 + NO_2 + H_2O \rightarrow 2HNO_3$ | $1.66 \times 10^{-3}$§** |
| 8 | $NO + NO_2 + H_2O \rightarrow 2HNO_2$ | $2.2 \times 10^{-9}$§ |
| 9 | $HNO_2 + h\upsilon \rightarrow NO + OH$ | † |
| 10 | $NO_2 + OH\cdot \rightarrow HNO_3$ | $9 \times 10^{3}$ |
| 11 | $NO + OH\cdot \rightarrow HNO_2$ | $9 \times 10^{3}$ |
| 12 | $CO + OH\cdot \rightarrow CO_2 + HO_2\cdot$ | $2.06 \times 10^{2}$ |
| 13 | $OLE + OH\cdot \xrightarrow{O_2} HCHO + CH_3O_2\cdot$ | $3.8 \times 10^{4}$ |
| 14 | $PAR + OH\cdot \xrightarrow{O_2} CH_3O_2\cdot + H_2O$ | $1.3 \times 10^{3}$ |
| 15 | $ARO + OH\cdot \xrightarrow{O_2} HCHO + CH_3O_2\cdot$ | $8 \times 10^{3}$ |
| 16 | $OLE + O \xrightarrow{2O_2} HC(O)O_2\cdot + CH_3O_2\cdot$ | $5.3 \times 10^{3}$ |
| 17 | $PAR + O \xrightarrow{O_2} CH_3O_2\cdot + OH\cdot$ | 20 |
| 18 | $ARO + O\cdot \xrightarrow{2O_2} HC(O)O_2\cdot + CH_3O_2\cdot$ | 37 |
| 19 | $OLE + O_3 \xrightarrow{O_2} HC(O)O_2\cdot + HCHO + OH\cdot$ | 0.01 |

(continued)

TABLE 1

| | Reaction | Rate Constant ($ppm^{-1}min^{-1}$) |
|---|---|---|
| 20 | $ARO + O_3 \xrightarrow{O_2} HC(O)O_2^{\bullet} + HCHO + OH\bullet$ | 0.002 |
| 21 | $OLE + O_3 \rightarrow$ Ozonide | 0.005 |
| 22 | $HCHO + h\upsilon \xrightarrow{2O_2} HC(O)O_2^{\bullet} + HO_2^{\bullet}$ | † |
| 23 | $HCHO + h\upsilon \rightarrow CO + H_2$ | $4 \times 10^{-4}$* |
| 24 | $HCHO + OH\bullet \xrightarrow{O_2} HC(O)O_2^{\bullet} + H_2O$ | $1 \times 10^{4}$ |
| 25 | $HO_2^{\bullet} + NO \rightarrow OH\bullet + NO_2$ | $2 \times 10^{3}$ |
| 26 | $CH_3O_2^{\bullet} + NO \rightarrow NO_2 + HCHO + HO_2^{\bullet}$ | $2 \times 10^{3}$ |
| 27 | $HC(O)O_2^{\bullet} + NO \rightarrow NO_2 + CO_2 + HO_2^{\bullet}$ | $2 \times 10^{3}$ |
| 28 | $H_2O_2 + h\upsilon \rightarrow OH\bullet + OH\bullet$ | † |
| 29 | $HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$ | $4 \times 10^{3}$ |
| 30 | $CH_3O_2^{\bullet} + HO_2^{\bullet} \rightarrow H_3COOH + O_2$ | $4 \times 10^{3}$ |
| 31 | $HC(O)O_2^{\bullet} + HO_2 \rightarrow HC(O)OOH + O_2$ | $1 \times 10^{4}$ |
| 32 | $HC(O)O_2^{\bullet} + NO_2 \rightarrow PAN$ | 50 |
| 33 | $PAN \rightarrow HC(O)O_2^{\bullet} + NO_2$ | 0.02* |
| 34 | $ARO + NO_3 \rightarrow$ Products | 50 |
| 35 | $HO_2^{\bullet} + NO_2 \rightarrow HNO_2$ | 20 |

* Units of $min^{-1}$.

† Light-dependent.

§ Units of $ppm^{-2}min^{-1}$.

** Rate constant is for the computer simulations of UCR smog-chamber experiments.

(concluded)

- Including new surrogate species representing the addition products of OH• to double bonds.

- Including a new formulation for carbonyl photolysis and oxidation.

- Treating alkyl radicals in long-chain paraffins.

- Treating ethylene as an explicit species.

- Treating internal olefins as carbonyls.

- Using a root-mean-square rate constant for the reactions of OH•, O, and $O_3$ with hydrocarbon mixtures.

- Incorporating a new aromatic chemical reaction scheme.

The rate constants used in the aromatics chemistry were modified by Whitten, Killus, and Hogo (1980). The aromatics scheme developed in CBM-II represented an interim treatment, occasioned by a rapid increase in our understanding of aromatic hydrocarbon oxidation. The second update of the CBM, discussed in this report, reformulates the aromatics chemistry to reflect current understanding of the explicit chemistry of toluene and xylenes. This revision also includes reactions that treat the oxidation of ketones to dicarbonyl compounds. Each of these changes is discussed in the following subsections.

The mechanism reported by Whitten, Killus, and Hogo (1980) (reflecting the first update plus rate-constant changes for aromatics) is known as CBM-II (see table 2); the new version of the Carbon-Bond Mechanism, shown in table 3, is called CBM-III.

## ELIMINATION OF THE PEROXYFORMYL RADICAL

At the time of the original formulation of the CBM, our explicit mechanisms included the peroxyformyl radical ($HCO_3^•$), which no longer appears in our explicit chemistry. To account for this change, we introduced a new species, $ACO_3^•$, which is a surrogate for $RCO_3^•$ radicals (where R has one or more carbon atoms). $ACO_3^•$, which has two carbon atoms, is formed in the CBM from the reaction of OH• with the species CARB, which represents only one carbon atom. Thus some correction must be made to preserve carbon-mass balance. The correction we used is suggested by a reaction of $RCO_3^•$ in the explicit mechanisms. In such mechanisms, $RCO_3^•$ ($R > CH_3$) can react with NO to produce $NO_2$, $CO_2$, and $RO_2^•$. The significance of that reaction is that it initiates the oxidation of the carbon atom adjacent to the $CO_3^•$ group in $RCO_3^•$ without any

TABLE 2. CARBON-BOND MECHANISM-II

| | Reaction | Rate Constant at 298K* ($ppm^{-1}min^{-1}$) | Activation Energy (K) |
|---|---|---|---|
| 1 | $NO_2 + h\upsilon \rightarrow NO + O$ | Experimental† | -- |
| 2 | $O + O_2 + M \rightarrow O_3 + M$ | $2.1 \times 10^{-5}$§ | -- |
| 3 | $O_3 + NO \rightarrow NO_2 + O_2$ | 23.9 | 1,450 |
| 4 | $O_3 + NO_2 \rightarrow NO_3 + O_2$ | $4.8 \times 10^{-2}$ | 2,450 |
| 5 | $O + NO_2 \rightarrow NO + O_2$ | $1.34 \times 10^{4}$ | -- |
| 6 | $O_3 + OH \rightarrow HO_2 + O_2$ | $7.7 \times 10^{1}$ | 1,000 |
| 7 | $O_3 + HO_2 \rightarrow OH + 2O_2$ | 5.0 | 1,525 |
| 8 | $NO_2 + OH \rightarrow HNO_3$ | $1.4 \times 10^{4}$ | -- |
| 9 | $CO + OH \xrightarrow{O_2} HO_2 + CO_2$ | $4.4 \times 10^{2}$ | |
| 10 | $NO + NO + O_2 \rightarrow 2NO_2$ | $7.1 \times 10^{-10}$§ | -- |
| 11 | $NO_3 + NO \rightarrow 2NO_2$ | $2.8 \times 10^{4}$ | -- |
| 12 | $NO_3 + NO_2 + H_2O \rightarrow 2HNO_3$ | $311 \times k(N_2O_5 + H_2O)$** | -10,600 |
| 13 | $HO_2 + NO \rightarrow NO_2 + OH$ | $1.2 \times 10^{4}$ | -- |
| 14 | $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ | $1.5 \times 10^{4}$ | -- |
| 15 | $PAR + O \xrightarrow{O_2} MEO_2 + OH$ | $2 \times 10^{1}$ | 2,100 |
| 16 | $PAR + OH \xrightarrow{O_2} MEO_2 + H_2O$ | $1.5 \times 10^{3}$ | 560 |
| 17 | $OLE + O \xrightarrow{O_2} MEO_2 + ACO_3 + X$ | $2.7 \times 10^{3}$ | 325 |
| 18 | $OLE + O \rightarrow CARB + PAR$ | $2.7 \times 10^{3}$ | 325 |

(continued)

TABLE 2

| | Reaction | Rate Constant at 298K* ($ppm^{-1}min^{-1}$) | Activation Energy (K) |
|---|---|---|---|
| 19 | $OLE + OH \xrightarrow{O_2} RAO_2$ | $4.2 \times 10^4$ | -540 |
| 20 | $OLE + O_3 \rightarrow CARB + CRIG$ | $8 \times 10^{-3}$ | 1,900 |
| 21 | $OLE + O_3 \rightarrow CARB + MCRG + X$ | $8 \times 10^{-3}$ | 1,900 |
| 22 | $ETH + O \xrightarrow{O_2} MEO_2 + HO_2 + CO$ | $6 \times 10^2$ | 800 |
| 23 | $ETH + O \rightarrow CARB + PAR$ | $6 \times 10^2$ | 800 |
| 24 | $ETH + OH \xrightarrow{O_2} RBO_2$ | $1.2 \times 10^4$ | -382 |
| 25 | $ETH + O_3 \rightarrow CARB + CRIG$ | $2.4 \times 10^{-3}$ | 2,560 |
| 26 | $ACO_3 + NO \xrightarrow{O_2} NO_2 + MEO_2 + CO_2$ | $3.8 \times 10^3$ | -- |
| 27 | $RBO_2 + NO \xrightarrow{O_2} NO_2 + 2\ CARB + HO_2$ | $1.2 \times 10^4$ | -- |
| 28 | $RAO_2 + NO \xrightarrow{O_2} NO_2 + 2\ CARB + HO_2$ | $1.2 \times 10^4$ | -- |
| 29 | $MEO_2 + NO \xrightarrow{O_2} NO_2 + CARB + MEO_2 + X$ | $(1.2 \times 10^4)(A-1)/A$ †† | -- |
| 30 | $MEO_2 + NO \xrightarrow{O_2} NO_2 + CARB + HO_2$ | $(1.2 \times 10^4)/A$ ** | -- |
| 31 | $MEO_2 + NO \rightarrow$ Nitrate | $5 \times 10^2$ | -- |
| 32 | $RBO_2 + O_3 \rightarrow 2\ CARB + HO_2 + O_2$ | 5.0 | -- |
| 33 | $RAO_2 + O_3 \rightarrow 2\ CARB + HO_2 + O_2$ | $2 \times 10^2$ | -- |
| 34 | $MEO_2 + O_3 \rightarrow CARB + HO_2 + O_2$ | 5.0 | -- |
| 35 | $CARB + OH \xrightarrow{O_2} \alpha(HO_2 + CO) + (1 - \alpha)(ACO_3 + X)$ | $(2.4 - \alpha) \times 10^4$ | -- |
| 36 | $CARB + h\upsilon \rightarrow CO + H_2$ | $\alpha k_f$ *§§ | -- |
| 37 | $CARB + h\upsilon \xrightarrow{O_2} (1 + \alpha)HO_2 + (1 - \alpha)(MEO_2 + X) + CO$ | $(\frac{\alpha + 1}{2})k_f$ *†† | -- |
| 38 | $X + PAR \rightarrow$ | $1 \times 10^5$ | -- |

(continued)

TABLE 2

| | Reaction | Rate Constant at 298K* ($ppm^{-1}min^{-1}$) | Activation Energy (K) |
|---|---|---|---|
| 39 | $ACO_3 + NO_2 \rightarrow PAN$ | $2 \times 10^3$ | -- |
| 40 | $PAN \rightarrow ACO_3 + NO_2$ | $2.8 \times 10^{-2\dagger}$ | 12,500 |
| 41 | $ACO_3 + HO_2 \rightarrow$ Stable products | $4 \times 10^3$ | -- |
| 42 | $MEO_2 + HO_2 \rightarrow$ Stable products | $4 \times 10^3$ | -- |
| 43 | $CRIG + NO \rightarrow NO_2 + CARB$ | $1.2 \times 10^4$ | -- |
| 44 | $CRIG + NO_2 \rightarrow NO_3 + CARB$ | $8 \times 10^3$ | -- |
| 45 | $CRIG + CARB \rightarrow$ Ozonide | $2 \times 10^3$ | -- |
| 46 | $MCRG + NO \rightarrow NO_2 + CARB + PAR$ | $1.2 \times 10^4$ | -- |
| 47 | $MCRG + NO_2 \rightarrow NO_3 + CARB + PAR$ | $8 \times 10^3$ | -- |
| 48 | $MCRG + CARB \rightarrow$ Ozonide | $2 \times 10^3$ | -- |
| 49 | $CRIG \rightarrow CO + H_2O$ | $6.7 \times 10^{2\dagger}$ | -- |
| 50 | $CRIG \rightarrow$ Stable products | $2.4 \times 10^{2\dagger}$ | -- |
| 51 | $CRIG \xrightarrow{O_2} 2HO_2 + CO_2$ | $9 \times 10^{1\dagger}$ | -- |
| 52 | $MCRG \rightarrow$ Stable products | $1.5 \times 10^{2\dagger}$ | -- |
| 53 | $MCRG \xrightarrow{O_2} MEO_2 + OH + CO$ | $3.4 \times 10^{2\dagger}$ | -- |
| 54 | $MCRG \xrightarrow{O_2} MEO_2 + HO_2 + CO_2$ | $4.25 \times 10^{2\dagger}$ | -- |
| 55 | $MCRG \xrightarrow{O_2} CARB + 2HO_2 + CO$ | $8.5 \times 10^{1\dagger}$ | -- |
| 56 | $ARO + OH \xrightarrow{O_2} ARPI + ARPI + ARPI + HO_2$ | $6 \times 10^3$ | -- |
| 57 | $ARO + OH \xrightarrow{O_2} HO_2 + GLY + X$ | $1.6 \times 10^3$ | -- |
| 58 | $ARO + OH \xrightarrow{O_2} OH + GLY + W$ | $1.5 \times 10^4$ | -- |
| 59 | $W + CARB \rightarrow$ | $1.0 \times 10^5$ | -- |
| 60 | $ARPI + NO \rightarrow NO + CARB + PAR$ | 30 | -- |



(continued)

TABLE 2

| | Reaction | Rate Constant at 298K* ($ppm^{-1}min^{-1}$) | Activation Energy (K) |
|---|---|---|---|
| 61 | ARPI + NO → $NO_2$ + Aerosol | 15 | -- |
| 62 | ARPI + $NO_3$ → CARB + CARB | $3.5 \times 10^4$ | -- |
| 63 | ARPI + $O_3$ → Aerosol | 0.6 | -- |
| 64 | GLY + OH → $HO_2$ + ARPI + ARPI + ARPI + CO | $10^4$ | -- |
| 65 | GLY $\xrightarrow{O_2}$ $MEO_2$ + $HO_2$ + ARPI + ARPI + ARPI | $k_{GLY}$*** | -- |

* The rate constants shown were those employed at UCR to model eleven experiments in which mixes of seven hydrocarbons were used. For that study the default values $\alpha = 0.5$ and $A = 1.3$ were used.

† Units of $min^{-1}$.

§ Units of $ppm^{-2}min^{-1}$.

** $k(N_2O_5 + H_2O) = 5 \times 10^{-6}$ $ppm^{-1}min^{-1}$ for UCR simulations.

†† A = A is the average number of $RO_2^{\cdot}$-type radicals generated from a hydrocarbon between attack by OH· and generation of $HO_2^{\cdot}$.

§§ $\alpha$ is the fraction of total aldehydes that represents formaldehyde and ketones. $k_f$ is the carbonyl photolysis rate constant.

*** $k_{GLY} \cong 0.036 \times k_{(NO_2 + h\upsilon)}$.

(concluded)

TABLE 3. CARBON-BOND MECHANISM III

| | Reaction | Rate Constant at 298K ($ppm^{-1}min^{-1}$) | Activation Energy (K) |
|---|---|---|---|
| 1 | $NO_2 \rightarrow NO + O$ | * | 0 |
| 2 | $O + (O_2) + (M) \rightarrow O_3$ | $4.40 \times 10^{6}$† | 0 |
| 3 | $NO + O_3 \rightarrow NO_2 + O_2$ | 26.6 | 1450 |
| 4 | $NO_2 + O_3 \rightarrow NO_3 + O_2$ | 0.048 | 2450 |
| 5 | $NO_2 + O \rightarrow NO + O_2$ | $1.3 \times 10^{4}$ | 0 |
| 6 | $OH + O_3 \rightarrow HO_2 + O_2$ | 100 | 1000 |
| 7 | $HO_2 + O_3 \rightarrow OH + 2O_2$ | 2.40 | 1525 |
| 8 | $OH + NO_2 \rightarrow HNO_3$ | $1.60 \times 10^{4}$ | 0 |
| 9 | $OH + CO \xrightarrow{O_2} HO_2 + CO_2$ | 440 | 0 |
| 10 | $NO + NO + (O_2) \rightarrow NO_2 + NO_2$ | $1.50 \times 10^{-4}$† | 0 |
| 11 | $NO + NO_3 \rightarrow NO_2 + NO_2$ | $2.80 \times 10^{4}$ | 0 |
| 12 | $NO_2 + NO_3 + H_2O \rightarrow 2HNO_3$ | § | $-1.06 \times 10^{4}$ |
| 13 | $NO + HO_2 \rightarrow NO_2 + OH$ | $1.20 \times 10^{4}$ | 0 |
| 14 | $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ | $1.50 \times 10^{4}$ | 0 |
| 15 | $X + PAR \rightarrow$ | $10^{5}$ | 0 |
| 16 | $OH + PAR \xrightarrow{O_2} MEO_2 + H_2O$ | 1300 | 560 |
| 17 | $O + OLE \xrightarrow{O_2} MEO_2 + ACO_3 + X$ | 2700 | 325 |
| 18 | $O + OLE \rightarrow CARB + PAR$ | 2700 | 325 |
| 19 | $OH + OLE \xrightarrow{O_2} RAO_2$ | $3.70 \times 10^{4}$ | -540 |

(continued)

TABLE 3

| | Reaction | Rate Constant at 298K ($ppm^{-1}min^{-1}$) | Activation Energy (K) |
|---|---|---|---|
| 20 | $O_3$ + OLE → CARB + CRIG | 0.008 | 1900 |
| 21 | $O_3$ + OLE → CARB + MCRG + X | 0.008 | 1900 |
| 22 | O + ETH $\xrightarrow{O_2}$ $MEO_2$ + $HO_2$ + CO | 600 | 800 |
| 23 | O + ETH → CARB + PAR | 600 | 800 |
| 24 | OH + ETH $\xrightarrow{O_2}$ $RBO_2$ | $1.20 \times 10^4$ | -382 |
| 25 | $O_3$ + ETH → CARB + CRIG | 0.0024 | 2560 |
| 26 | NO + $ACO_3$ $\xrightarrow{O_2}$ $NO_2$ + $MEO_2$ | $1.04 \times 10^4$ | 0 |
| 27 | NO + $RBO_2$ $\xrightarrow{O_2}$ $NO_2$ + CARB + $HO_2$ + CARB | $1.20 \times 10^4$ | 0 |
| 28 | NO + $RAO_2$ $\xrightarrow{O_2}$ $NO_2$ + CARB + $HO_2$ + CARB | $1.20 \times 10^4$ | 0 |
| 29 | NO + $MEO_2$ $\xrightarrow{O_2}$ $NO_2$ + CARB + $MEO_2$ + X | 3800 | 0 |
| 30 | NO + $MEO_2$ $\xrightarrow{O_2}$ $NO_2$ + CARB + $HO_2$ | 7700 | 0 |
| 31 | NO + $MEO_2$ → NRAT | 500 | 0 |
| 32 | $O_3$ + $RBO_2$ → CARB + CARB + $HO_2$ + $O_2$ | 5.0 | 0 |
| 33 | $O_3$ + $RAO_2$ → CARB + CARB + $HO_2$ + $O_2$ | 200 | 0 |
| 34 | OH + CARB → $CRO_2$ + X | 500 | 0 |
| 35 | OH + CARB $\xrightarrow{O_2}$ $HO_2$ + CO | 7000 | 0 |
| 36 | OH + CARB $\xrightarrow{O_2}$ $ACO_3$ + X | 6000 | 0 |
| 37 | CARB → CO + $H_2$ | ($\approx$0.001 $K_1$)* | 0 |
| 38 | CARB + ($O_2$) $\xrightarrow{O_2}$ 2/3 ($2HO_2$ + CO) 1/3 ($2MEO_2$ + CO + 2X) | ($\approx$0.002 $K_1$)* | 0 |

(continued)

TABLE 3

| | Reaction | Rate Constant at 298K ($ppm^{-1}min^{-1}$) | Activation Energy (K) |
|---|---|---|---|
| 39 | $NO_2 + ACO_3 \rightarrow PAN$ | 7000 | 0 |
| 40 | $PAN \rightarrow ACO_3 + NO_2$ | 0.022 | $1.35 \times 10^4$ |
| 41 | $HO_2 + ACO_3 \rightarrow$ Stable products | $1.50 \times 10^4$ | 0 |
| 42 | $HO_2 + MEO_2 \rightarrow$ Stable products | 9000 | 0 |
| 43 | $NO + CRIG \rightarrow NO_2 + CARB$ | $1.20 \times 10^4$ | 0 |
| 44 | $NO_2 + CRIG \rightarrow NO_3 + CARB$ | 8000 | 0 |
| 45 | $CARB + CRIG \rightarrow$ Ozonide | 2000 | 0 |
| 46 | $NO + MCRG \rightarrow NO_2 + CARB + PAR$ | $1.20 \times 10^4$ | 0 |
| 47 | $NO_2 + MCRG \rightarrow NO_3 + CARB + PAR$ | 8000 | 0 |
| 48 | $CARB + MCRG \rightarrow$ Ozonide | 2000 | 0 |
| 49 | $CRIG \rightarrow CO + H_2O$ | 670** | 0 |
| 50 | $CRIG \rightarrow$ Stable products | 240** | 0 |
| 51 | $CRIG \xrightarrow{O_2} HO_2 + HO_2 + CO$ | 90** | 0 |
| 52 | $MCRG \rightarrow$ Stable products | 150** | 0 |
| 53 | $MCRG \xrightarrow{O_2} MEO_2 + OH + CO$ | 340** | 0 |
| 54 | $MCRG \xrightarrow{O_2} MEO_2 + HO_2$ | 425** | 0 |
| 55 | $MCRG \xrightarrow{O_2} CARB + HO_2 + CO + HO_2$ | 85** | 0 |
| 56 | $OH + ARO \xrightarrow{O_2} RARO + H_2O$ | 8000 | 600 |
| 57 | $OH + ARO \xrightarrow{O_2} HO_2 + OPEN$ | $1.45 \times 10^4$ | 400 |
| 58 | $NO + RARO \xrightarrow{O_2} NO_2 + PHEN + HO_2$ | 4000 | 0 |

(continued)

TABLE 3

| | Reaction | Rate Constant at 298K ($ppm^{-1}min^{-1}$) | Activation Energy (K) |
|---|---|---|---|
| 59 | $OPEN + NO \xrightarrow{O_2} NO_2 + DCRB + X + APRC$ | 6000 | 0 |
| 60 | $APRC \xrightarrow{O_2} DCRB + CARB + CO$ | $10^{4**}$ | 0 |
| 61 | $APRC \xrightarrow{O_2} CARB + CARB + CO + CO$ | $10^{4**}$ | 0 |
| 62 | $PHEN + NO_3 \rightarrow PHO + HNO_3$ | 5000 | 0 |
| 63 | $PHO + NO_2 \rightarrow NPHN$ | 4000 | 0 |
| 64 | $PHO + HO_2 \rightarrow PHEN$ | $5.00 \times 10^4$ | 0 |
| 65 | $OPEN + O_3 \rightarrow DCRB + X + APRC$ | 40 | 0 |
| 66 | $OH + PHEN \xrightarrow{O_2} HO_2 + APRC + PAR + CARB$ | $3.00 \times 10^4$ | 0 |
| 67 | $DCRB \xrightarrow{O_2} 1/2\ (HO_2 + ACO_3 + CO)$ $1/2\ (MEO_2 + HO_2 + 2CO)$ | $(\approx 0.04\ K_1)^*$ | 0 |
| 68 | $PHEN + OH \rightarrow PHO$ | $10^4$ | 0 |
| 69 | $CRO_2 + NO \xrightarrow{O_2} NO_2 + HO_2 + DCRB$ | $1.20 \times 10^4$ | 0 |
| 70 | $DCRB + OH \rightarrow ACO_3$ | 7000 | 0 |
| 71 | $HONO \rightarrow OH + NO$ | $(\approx 0.06\ K_1)^*$ | 0 |
| 72 | $OH + NO \rightarrow HONO$ | 9770 | 0 |
| 73 | $O_3 \rightarrow O^1D$ | $(\approx 10^{-3} K_1)^*$ | 0 |
| 74 | $O^1D \xrightarrow{+(M)} O$ | $4.44 \times 10^{10}$ | 0 |
| 75 | $O^1D + H_2O \rightarrow OH + OH$ | $3.4 \times 10^5$ | 0 |

* Sunlight-dependent; units of $min^{-1}$.

† Units of $ppm^{-2}min^{-1}$.

§ Heterogeneous; pseudo third order. Equal to $591 \times N_2O_5 + H_2O$.

** Units of $min^{-1}$.

involvement of OH• or O. Thus it corresponds, in the terms used in the CBM, to the conversion of PAR (single or paraffinic bond) to $MEO_2$ (the surrogate for $RO_2^{\bullet}$)by a pathway not previously accounted for in the CBM. In the revised Carbon-Bond Mechanism, $ACO_3^{\bullet}$ reacts with NO to produce $NO_2$, $CO_2$, and $MEO_2$. When this reaction is included in the CBM, one PAR must be subtracted to account for the $MEO_2$ formed (i.e., to maintain carbon-mass balance). We accomplished this by means of a fictitious compound X. Whenever an extra carbon atom appears on the right side of a chemical reaction, one X is produced that immediately removes one PAR by means of the reaction PAR + X→ , which is given a high rate constant. Typically, the appearance of X accounts for the oxidation of a single-bonded carbon atom from the PAR pool by pathways other than direct reaction with OH• (oxidation of paraffins by oxygen atoms has been eliminated in the CBM-III). These other pathways were not accounted for in the original formulation of the CBM.

In using the methodology just described, one may encounter difficulty if X is produced when no saturated carbon atoms remain (i.e., [PAR] = 0). An example of such a case would be one in which the formaldehyde concentration is large compared with that of the paraffins and higher aldehydes. If it is known a priori that such a case exists, the formation rate of $ACO_3^{\bullet}$ can simply be set to a small number. However, it is unlikely that this situation will occur in the atmosphere, where paraffinic hydrocarbons are abundant. Tropospheric methane provides an equivalent minimum [PAR] level of 0.01 ppm.

In the application of complex atmospheric models, we have encountered situations in which a flaw in the numerical transport algorithm artificially reduced [PAR] to a low level (which was reduced to a negative number when the "X chemistry" was employed). However, we do not consider this to be a drawback in the treatment of chemistry. Indeed, in this instance the chemistry subroutine helped to locate an error in the transport algorithm.

## PRODUCTS OF THE OZONE-OLEFIN REACTIONS

Because Criegee intermediates from the ozone-olefin reaction were added to the explicit mechanisms, we included them in the Carbon-Bond Mechanism. The Criegee intermediates are represented by the symbols CRIG for $CH_2O_2$ and MCRG for $CH_3CH_2O_2$, the two Criegee intermediates found in the explicit mechanisms (see Whitten et al., 1979, and Dodge and Arnts, 1979).

## EXPLICIT TREATMENT OF THE OLEFIN HYDROXYL ADDITION PRODUCT

The explicit chemistry of hydroxyl attack on olefins leads to the formation of two aldehydes from the initial addition product, which in air is a $HORO_2$ radical. In CBM-I this radical was treated as a typical $RO_2$ radical

that produces but one aldehyde; the extra aldehyde was added along with the $RO_2$ as a product in the initial OH reaction. However, CBM-II and CBM-III include a special reaction of the $HORO_2$ addition product with $O_3$. Hence, the explicit treatment allows the formation of two aldehydes from the $HORO_2$ or reaction with $O_3$. The $O_3$ reaction is still under investigation, and future versions of the CBM probably will not require this reaction.

## INORGANIC RADICAL SOURCES

Although the chemistries of HONO and $O^1D$ (reactions 70 to 74) are included in CBM-III, these reactions can be deleted from the mechanism for most urban applications. The production and destruction of HONO is a relatively unimportant cycle, and the steady-state concentration of HONO during the day is very low. Small concentrations of HONO (1 to 2 ppb) have been measured at night (Platt et al., 1980), and the compound might be found in small concentrations in emitted $NO_x$. Although HONO is important in the initiation phase of smog-chamber experiments, other radical sources (e.g., HCHO) have been measured at concentrations high enough to overshadow the importance of HONO as a component of polluted air.

Ozone photolyzes to form $O^1D$, a fraction of which then reacts with water to generate OH (reactions 72 to 74). We have found this reaction to be important principally in application to rural areas, where the background concentration of ozone is greater than 10 times the background of carbonyl compounds. In urban applications $O^1D$ chemistry is relatively unimportant and can often be omitted.

## CARBONYL PHOTOLYSIS AND OXIDATION

A necessary part of the formulation of the Carbon-Bond Mechanism is the condensation of the reactions of aldehydes and ketones into two types of reactions, namely, photolysis and oxidation by hydroxyl radical.

In general, aldehydes larger than formaldehyde appear to photolyze as follows:

$$RCHO + h\upsilon \rightarrow R'O_2^{\cdot} + HO_2^{\cdot} + CO \qquad k_{(1)} = \phi k_f \quad . \qquad (1)$$

The photolysis rate constant $\phi k_f$ is defined as follows: $\phi$ is the average quantum yield, and $k_f$ is the photolysis rate constant for formaldehyde producing two radicals.

In the photolysis of formaldehyde under a typical solar spectrum, two reaction pathways occur at approximately equal rates:

$$HCHO + h\upsilon \rightarrow H_2 + CO \qquad k_{(2)} = k_f \quad , \qquad (2)$$

$$HCHO + h\upsilon \rightarrow HO_2^{\bullet} + HO_2^{\bullet} + CO \qquad k_{(3)} = k_f \quad . \qquad (3)$$

Thus the total photolysis rate for formaldehyde is 2 x $k_f$.

For simplicity, CBM-II treated ketone photolysis in the same manner as it would formaldehyde. The lumped reaction set for carbonyl photolysis then became

$$CARB + h\upsilon \rightarrow H_2 + CO \qquad k_{(4)} = \alpha k_f \quad , \qquad (4)$$

$$CARB + h\upsilon \rightarrow (1 + \alpha)HO_2^{\bullet} \qquad (5)$$

$$+ (1 - \alpha)(MEO_2 + X) + CO \qquad k_{(5)} = \left(\frac{\alpha + 1}{2}\right) k_f \quad ,$$

where

$$\alpha = \frac{[\text{formaldehyde}] + [\text{ketones}]}{[\text{total carbonyls}]} \quad ,$$

and

$k_f$ = formaldehyde photolysis to radicals,

= formaldehyde photolysis to stable products

1/2 $k_f$ = photolysis of higher aldehydes.

More realistically, ketone photolysis typically yields two peroxyalkyl radicals:

$$KET + h\upsilon \rightarrow RO_2^{\bullet} + RO_2^{\bullet} + CO \quad . \qquad (5a)$$

Ketones can also yield peroxyacyl as a photolysis product:

$$KET + h\upsilon \rightarrow RO_2^{\cdot} + RCO_3^{\cdot} \quad . \qquad (5b)$$

However, this is a minor formation pathway for peroxyacyl (hydroxyl attack on higher aldehydes has much greater significance). Since $RCO_3^{\cdot}$ yields $RO_2^{\cdot}$ when reduced by NO, equation (5a) is a good approximation of the overall process.

For the new lumped mechanism (CBM-III), we define CARB as the concentration of carbonyls (i.e., the sum of the aldehyde and ketone concentrations):

$$CARB + h\upsilon \rightarrow (H_2 + CO) = CO + H_2 \quad , \qquad (6a)$$

$$CARB + h\upsilon \rightarrow (HO_2^{\cdot} + HO_2^{\cdot} + CO) = 2HO_2^{\cdot} + CO \quad , \qquad (6b)$$

$$CARB + h\upsilon \rightarrow (MEO_2 + 2X + MEO_2^{\cdot} + CO) \quad , \qquad (6c)$$

with the photolysis rate constants,

$$\frac{form}{CARB} \cdot k_{(1)} = k_{(6a)} \quad ,$$

$$\frac{[k_{(3)}]\ form + (0.5\ higher\ aldehydes)k_{(1)}}{CARB} = k_{(6b)} \quad ,$$

$$\frac{[k_{(1)}]\ (0.5\ higher\ aldehydes) + KET[k_{(5a)}]}{CARB} = k_{(6c)} \quad .$$

Thus, the higher aldehyde photolysis pathway is halfway between formaldehyde and ketones in product yield.

The second major reaction of aldehydes is oxidation by hydroxyl radicals:

$$HO_2^{\cdot} + CO + H_2O \quad \text{for formaldehyde} \qquad (7a)$$

$$RCHO + OH^{\cdot} \rightarrow$$

$$ACO_3^{\cdot} + H_2O \quad \text{for higher aldehydes} \qquad (7b)$$

Ketone oxidation is more complex. For example, (MEK)

$$CH_3COCH_2CH_3 + OH \xrightarrow{+O_2} CH_3COCHO_2^{\bullet}CH_3 + (H_2O) \quad , \tag{8}$$

$$CH_3COCHO_2^{\bullet}CH_3 + NO \rightarrow NO_2 + CH_3COCH\dot{O}CH_3 \quad , \tag{9}$$

$$CH_3COCH\dot{O}CH_3 + O_2 \rightarrow HO_2 + CH_3COCOCH_3 \quad \text{(biacetyl, a highly photolytic dicarbonyl compound).} \tag{10}$$

A ketone oxidation pathway can easily be included in CBM-III because the dicarbonyl compounds (DCRB) are already included as part of the new aromatics chemistry.

$$CARB + OH \rightarrow CRO_2 + X \quad , \tag{11}$$

$$CRO_2 + NO \rightarrow NO_2 + HO_2 + DCRB \quad . \tag{12}$$

Aldehyde oxidation pathways are the same for both CBM-II and CBM-III:

$$CARB + OH \rightarrow HO_2 + CO + H_2O \quad , \tag{13}$$

$$CARB + OH \rightarrow ACO_3 + X + H_2O \quad , \tag{14}$$

where X is the previously mentioned negative carbon species used to maintain mass balance.

## ALKYL RADICAL CHEMISTRY

The alkyl radical (RO•) chemistry used in our mechanisms was discussed in detail by Whitten and Hogo (1977). In the propylene and butane explicit mechanisms, only alkyl radicals with four or fewer carbon atoms are important. The following reactions for the primary alkyl radicals are used in these explicit mechanisms:

$$CH_3CH_2CH(O\cdot)CH_3 \xrightarrow{O_2} CH_3CH_2O_2 + CH_3CHO \qquad k = 1.0 \times 10^5\ min^{-1} \quad , \qquad (15)$$

$$CH_3CH_2CH(O\cdot)CH_3 + O_2 \rightarrow CH_3CH_2C(O)CH_3 + HO_2 \qquad k = 1.43\ ppm^{-1}min^{-1} \quad , \qquad (16)$$

$$CH_3CH_2CH_2CH_2O\cdot \xrightarrow{O_2} HOCH_2CH_2CH_2CH_2O_2 \qquad k = 2 \times 10^6\ min^{-1} \quad , \qquad (17)$$

$$CH_3CH_2CH_2CH_2O\cdot + O_2 \rightarrow CH_3CH_2CH_2CHO + HO_2 \qquad k = 3.3\ ppm^{-1}min^{-1} \quad , \qquad (18)$$

$$CH_3CH_2CH_2O\cdot + O_2 \rightarrow CH_3CH_2CHO + HO_2 \qquad k = 3.3\ ppm^{-1}min^{-1} \quad , \qquad (19)$$

$$CH_3CH_2O\cdot + O_2 \rightarrow CH_3CHO + HO_2 \qquad k = 3.3\ ppm^{-1}min^{-1} \quad , \qquad (20)$$

$$CH_3O\cdot + O_2 \rightarrow HCHO + HO_2 \qquad k = 1.2\ ppm^{-1}min^{-1} \quad . \qquad (21)$$

Alkylperoxyl radicals can thus react through a number of pathways that may be represented as follows:

$$RO_2 + NO \rightarrow RO\cdot + NO_2 \quad , \qquad (22)$$

$$RO_2 + NO \rightarrow \text{nitrates} \quad , \qquad (23)$$

$$RO\cdot + O_2 \rightarrow \text{aldehyde} + HO_2 \quad , \qquad (24)$$

$$RO\cdot \xrightarrow{O_2} HORO_2 \text{ (isomerization)} \quad , \qquad (25)$$

$$RO\cdot \xrightarrow{O_2} R'O_2 + \text{aldehyde (decomposition)} \quad , \qquad (26)$$

$$RO_2 + HO_2 \rightarrow \text{stable products} \quad . \qquad (27)$$

Reactions (25) and (26) occur in systems with carbon chains greater than, or equal to, four (e.g., butane and 2,3-dimethylbutane). The isomerization reaction chain (reaction 25) terminates when the $\alpha$-hydroxyl radical reacts with oxygen to form a carbonyl compound--i.e., reaction (24). In the Carbon Bond Mechanism, we write reactions (22) and (24) as a single step:

$$MEO_2 + NO \rightarrow NO_2 + CARB + HO_2^{\cdot} \quad . \tag{28}$$

We have condensed reactions (25) and (26) into the $RO_2^{\cdot}$ scheme as:

$$MEO_2 + NO \rightarrow NO_2 + CARB + (MEO_2 + X) \quad . \tag{29}$$

Reactions (23) and (27) translate directly into:

$$MEO_2 + NO \rightarrow \text{nitrates} \quad , \tag{30}$$

$$MEO_2 + HO_2^{\cdot} \rightarrow \text{stable products} \quad . \tag{31}$$

Reaction (29) condenses the alkyl isomerization and decomposition processes, with the net effect that more than one $RO_2^{\cdot}$ radical is generated per reaction of PAR with OH. The condensed reaction sequence lumps the hydroxy-carbon group into the carbonyl category, an approximation whose validity cannot be assessed without explicit data for the reactivity of hydroxy compounds. However, isomerized hydroxy species have not yet been detected. Since a slow reaction rate would allow the buildup of detectable concentrations of these species, a relatively high reaction rate for such compounds is implied.

If we let "A" equal the number of $RO_2^{\cdot}$ radicals per alkyl oxidation, then

$$k_{(29)} = k_{(28)}(A - 1) \quad .$$

For short-chain hydrocarbons (carbon number <4) A = 1 and $k_{(29)} = 0$. The sum of the rate constants for reactions (28), (29), and (30) equals the reaction rate of $RO_2^{\cdot} + NO$:

$$k_{(28)} + k_{(29)} + k_{(30)} = 12{,}000 \text{ ppm}^{-1}\text{min}^{-1} \quad .$$

Therefore,

$$k_{(29)} = [12{,}000 - k_{(30)}] \frac{A - 1}{A} \quad .$$

Empirically, nitrate formation observed in smog-chamber experiments requires a reaction-rate constant for reaction (30) that falls within the range of 250 $\text{ppm}^{-1}\text{min}^{-1}$ to 1250 $\text{ppm}^{-1}\text{min}^{-1}$, depending on the hydrocarbons involved. For an intermediate urban mix of hydrocarbons, we recommend a rate of 500 $\text{ppm}^{-1}\text{min}^{-1}$. Long chain alkyl radicals tend to react according to the pathways shown in reactions (29) and (30) more often than do molecules having lower molecular weight. Insufficient information is available to set these reaction-rate constants a priori; Carter et al. (1979) suggested some values for individual peroxy radicals on the basis of empirical fits to smog-chamber data.

For some hydrocarbons (e.g., 2,3-dimethylbutane) "A" can be as high as 2. When calculations for butane are based on the detailed reaction sequence, "A" is approximately 1.3. Calculations based on the ratio of hydrocarbon consumed to the oxidation of NO in smog-chamber experiments (Kopczynski, Kuntz, and Bufalini, 1975) yield a value for "A" of 1.5, which we recommend as the default value for "A". Therefore, the nominal rate constants for reactions (28), (29), and (30) are 7700, 3800, and 500, respectively.

## AROMATIC OXIDATION

We have devised an explicit mechanism for treating toluene oxidation (Killus and Whitten, 1981) and have extended our work to include simulation of m-xylene systems. Our studies indicate that aromatic hydrocarbon oxidation differs from olefin and paraffin oxidation in several important ways. Our simulation mechanisms show three major differences between aromatic compounds and a compound such as propylene:

- A high photolysis rate of oxidation products: toluene oxidation products, for example, photolyze at a rate twice that which would result from a 100 percent yield of formaldehyde from toluene decay. This high rate is apparently caused by a fractional yield of methyl glyoxal,

which photolyzes at a rate roughly 15 times that of formaldehyde.

- A low rate of peroxyl radical production: the inefficiency of toluene and other aromatic hydrocarbons in effecting NO-to-$NO_2$ conversions has been observed by other investigators (Kopczynski, Kuntz, and Bufalini, 1975). Empirically, methyl glyoxal photolysis alone is nearly sufficient to explain the number of NO-to-$NO_2$ conversions observed in toluene oxidation. Thus, either the other products of toluene decay are unreactive or there is a mechanism in toluene oxidation that destroys peroxyl or otherwise prevents the peroxyl radicals from reacting with NO.

- After the onset of ozone production, a powerful $NO_x$ sink mechanism occurs that does not appear to consume hydrogen-containing radicals. This sink probably involves $NO_3^{\bullet}$ and can result in nitrophenols or dinitrate compounds.

The mechanism described herein contains the aforementioned features and is based on a condensation of our explicit aromatics mechanisms.

## RING OPENING

The initial step of the ring opening pathway can be easily treated with three reactions:

$$ARO + OH \rightarrow OPEN \quad , \tag{32}$$

$$OPEN + NO \rightarrow NO_2 + HO_2 + DCRB + APRC \quad , \tag{33}$$

$$OPEN + O_3 \rightarrow HO_2 + DCRB + APRC \quad . \tag{34}$$

These reactions are exactly analogous to reactions in our explicit toluene mechanism. The lumped rate constant of initial OH attack depends on the mix of hydrocarbons present.

The species DCRB represents photolyzable dicarbonyl species: methyl glyoxal and biacetyl.

The species APRC (aromatic product carbon) represents the remainder of the aromatic molecule once the dicarbonyl species has been subtracted. In toluene oxidation this would be either the compound cis-2-butenedial (CBD) or two glyoxal molecules, depending on the degree of oxidation of the aromatic molecule prior to ring opening. Since xylene has another methyl group attached to the ring, the ultimate yield of methyl glyoxal is twice that of toluene but depends on the xylene isomer.

We treat the secondary products represented by APRC in a simple way:

$$\text{APRC} \rightarrow \text{DCRB} + \text{GLY} \quad , \tag{35}$$

$$\text{APRC} \rightarrow \text{GLY} + \text{GLY} \quad . \tag{36}$$

Thus far we have obtained the best results using a 50/50 split to pathways (35) and (36) for experiments containing equal amounts of toluene and xylene.

We have the following oxidation sequence for glyoxal:

$$(\text{CHO})_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HCO} + \text{CO} \quad , \tag{37}$$

$$\text{HCO}\cdot \rightarrow \text{HO}_2 + \text{CO} \quad . \tag{38}$$

This sequence is similar to that of formaldehyde oxidation except for the extra yield of 1 molecule of CO. Therefore, we treat the production of glyoxal in the carbon-bond units as

$$\text{GLY} = \text{CARB} + \text{CO} \quad .$$

## PATHWAYS TO PHENOLIC HYDROCARBONS

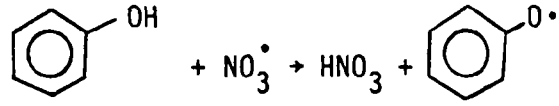
In our toluene mechanism there are two pathways to phenolic hydrocarbons: (1) addition of OH to the aromatic ring, forming cresols, and (2) hydration and nitrification of oxybenzoyl radicals. One example of the second pathway is the terminating reactions of benzaldehyde (BZA) oxidation:

$$\text{BZA} + \text{OH} \xrightarrow{+\text{O}_2} \text{peroxyl benzoyl } (\text{PBZO}_2) \quad , \tag{39}$$

$$\text{PBZO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{oxybenzoyl (PBZO)} \quad , \tag{40}$$

$$PBZO + NO_2 \xrightarrow{+\ water} \text{nitrophenol (NPHN)} \quad . \tag{41}$$

Phenolic hydrocarbons may serve as both radical sinks and $NO_x$ sinks in our reaction scheme. $NO_x$ is lost from the system in the form of nitrophenols and also when $NO_3^{\bullet}$ is converted to nitric acid:




(42)

Hydrogen abstraction from the paraffinic substituents on the aromatic ring is treated in the single-bonded carbon portion of the Carbon-Bond Mechanism. Similarly, the carbonyl portion of benzaldehyde is lumped together with the carbonyl bonds, and peroxybenzoyl nitrate is lumped with other PANS. The phenolic pathway of BZA oxidation is lumped with OH addition to the aromatic ring:

$$ARO + OH \rightarrow RARO \text{ (aromatic radical)} \quad , \tag{43}$$

$$RARO + NO \rightarrow NO_2 + HO_2 + PHEN \quad . \tag{44}$$

The lumped species PHEN can then react with OH or $NO_3$ to form nitrophenols:

$$PHEN + OH \rightarrow PHO_3 \quad , \tag{45}$$

$$PHEN + NO_3 \rightarrow PHO + HNO_3 \quad , \tag{46}$$

$$PHO + NO_2 \rightarrow NPHN \quad . \tag{47}$$

Since nitrophenols have low vapor pressures, it is likely that they also participate in aerosol formation.

The phenoxy radical can also react with $HO_2$:

$$PHO + HO_2 \rightarrow PHEN + O_2 \quad . \tag{48}$$

This reaction can be an important radical sink in aromatic systems. We assume that the reaction rate for this reaction is similar to that of $OH + HO_2$ (Baulch et al., 1980).

# SECTION 4

# USING THE CARBON-BOND MECHANISM

In its current form, the Carbon-Bond Mechanism (CBM-III) treats the reactions of six types of carbon atoms: (1) single-bonded carbon atoms, whose principal constituent is paraffinic carbon molecules (hence the abbreviation PAR), (2) relatively reactive double-bonded carbon (OLE), (3) slow double bonds, which are almost exclusively ethylene (ETH), (4) reactive aromatic rings (ARO), (5) carbonyl compounds such as aldehydes and ketones (CARB), and (6) highly photolytic $\alpha$-dicarbonyl compounds such as methyl glyoxal and biacetyl (DCRB). Some other types of carbon atoms can also be treated within this set. For instance, highly reactive internal double-bonded carbon atoms were shown by Whitten, Killus, and Hogo (1980) to be equivalent to two carbonyls per double bond. Hence three levels of olefin reactivity can be treated in the CBM (slow as ETH, relatively reactive terminal olefins as OLE, and highly reactive internal olefins as 2 CARB per bond). Appendix B lists the CBM fractions recommended for a variety of organics.

The use of the molecular bond rather than the whole molecule as the principal unit may at first seem confusing to those whose experience is solely with molecular reactions. However, several major advantages associated with the bond-group-reaction principle make the conceptual effort involved worthwhile.

The primary advantage is that the Carbon-Bond Mechanism does not require the sometimes uncertain calculation of "average molecular weight." The carbon number of each carbon-bond group is fixed:

| Carbon-Bond Group | Carbon Number (carbon atoms) |
|---|---|
| PAR | 1 |
| ETH | 2 |
| OLE | 2 |
| ARO | 6 |
| CARB | 1 (plus 1 oxygen atom) |
| DCRB | 2 (plus 2 oxygen atoms) |

In a lumped molecular mechanism, chemical reactions might be expected to alter the average molecular weight of each species category. When this phenomenon occurs, it is impossible to perform mass-balance calculations on the reactive organic compounds remaining in the model simulation. The Carbon-Bond Mechanism allows precise hydrocarbon-mass-balance calculations to be made, thus facilitating the estimation of the importance of phenomena like long-range smog precursor transport and day-to-day carry-over of pollutants. Moreover, whereas most lumped molecular mechanisms do not conserve carbon, the Carbon-Bond Mechanism conserves carbon and follows each hydrocarbon fraction to its end products (generally CO or $CO_2$, but occasionally aerosol or nonreactive hydrocarbons).

The range of reactivities of carbon bonds is generally less than that of reactivities of molecules because larger molecules tend to react faster even if each constituent atom is of similar reactivity. Thus the problem of rate-constant averaging is reduced in the Carbon-Bond Mechanism.

The carbon-bond concept has an additional advantage over the molecular concept because it offers a sensible method for dealing with the atmospheric chemistry of many complex or unusual molecules. For example, the molecule cinnamaldehyde ($C_6H_5CH{=}CHCHO$) might be treated as 1 ARO, 1 OLE, and 1 CARB assuming that the double bond is about as reactive as propylene. The double bond can also be treated as 1 ETH or 2 CARB, depending on the extent of its reactivity compared with that of propylene. For mechanisms in which the molecular concept is used, cinnamaldehyde can be described as an aromatic, an olefin, or an aldehyde. In making a choice among the three possibilities, the chemistry associated with the other two parts of the molecule is ignored, whereas the CBM approach offers reasonable chemical pathways for all three parts. Some surrogate mechanisms use a particular blend of propylene and butane to provide a reasonable simulation fit to smog-chamber data in which cinnamaldehyde is used. However, in the absence of smog-chamber data the surrogate and molecular approaches require arbitrary decisions, whereas the

carbon-bond approach provides a simple methodology for handling a large variety of molecules. The current carbon-bond approach allows some flexibility to adjust reactivity should smog-chamber data or other information become available (as in the cinnamaldehyde example).

Another related advantage of the carbon-bond approach over the molecular or surrogate approaches is optimization for simulating complex mixes rather than single molecules. The current CBM is designed to be optimized for simulating urban mixtures of hydrocarbons. If used for single-molecule smog-chamber experiments, the CBM requires certain adjustments that are usually straightforward. Molecular or surrogate mechanisms, on the other hand, are inherently optimized to simulate smog-chamber experiments using only the specific molecules that form the basis of the mechanisms. Thus, simulating complex urban mixes with these mechanisms requires adjustments in both the precursor definitions and the chemistry, and such adjustments are often complicated.

Finally, the Carbon-Bond Mechanism in its present implementation (CBM-III) has several features that enable us to recommend it over other available mechanisms. For example, treating ethylene as a separate species is an improvement over lumping all olefins together, because the behavior of olefins varies greatly with changing olefinic composition. The treatment of aromatic hydrocarbons in CBM-III is more chemically realistic than that in previous mechanisms. However, a realistic treatment of ethylene and aromatic hydrocarbons is not inherent in the carbon-bond concept. Molecular mechanisms can also be designed with similar features; at the present time only the CBM-III has been so designed.

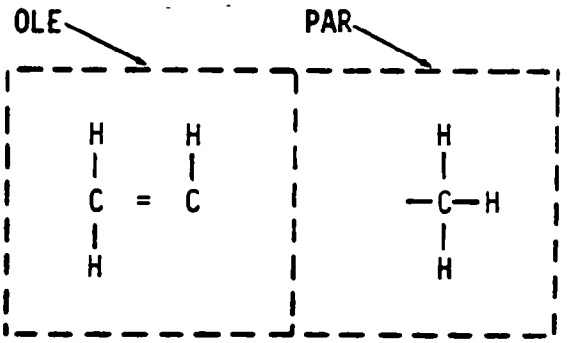
## SPECIATION OF EMISSIONS AND ATMOSPHERIC CONCENTRATIONS INTO BOND CATEGORIES

Several important principles must be remembered in the application of the Carbon-Bond Mechanism. First, all carbon must be accounted for. Thus, if one adds up all of the carbon in each bond category of emissions, the sum should equal the total carbon emitted. Although this principle appears simple and obvious, there are practical complications. Emissions of solvents, for example, are usually given in kilograms of emissions, but methyl alcohol ($H_2COH$) is a solvent in which most of the weight is represented by the oxygen atom in the methanol molecule. Another example is the case of automobile exhaust emissions, which are usually reported in gm/mi. of hydrocarbon as methane--i.e., each carbon atom measured is assumed to have a molecular weight of 16 gm/mole. Evaporative emissions, on the other hand, are reported as straight mass, which means that a lower molecular weight is called for. Accounting for all carbon is further complicated by the fact that the procedures used to obtain automobile exhaust hydrocarbon estimates do not respond efficiently to all reactive species. Aldehydes, for example, are not often measured by standard procedures and must be added to the exhaust emissions estimates.

## THE VOLUMETRIC EQUIVALENCE PRINCIPLE

The second important principle to remember when using the Carbon-Bond Mechanism is that the volumetric concentrations (in ppm) of most species used with the CBM are similar to both the volumetric measurements and the molar concentrations used in other mechanisms. One ppm of aromatic hydrocarbon bonds in the CBM is usually equivalent to 1 ppm of aromatic hydrocarbons in a lumped mechanism.*

We note two exceptions to the equivalence of speciation between the CBM and molecular mechanisms. The major exception is the PAR species, which includes not only the carbon in paraffinic molecules but also single-bonded carbon in other molecules. A molecule of propylene, for example, contains one single-bonded carbon in addition to the olefinic bond:




In other words, the CBM total reactive hydrocarbon (RHC) given in ppmC must equal

$$(OLE \times 2) + (ETH \times 2) + (ARO \times 6) + CARB + (DCRB \times 2) + PAR = RHC \text{ (in ppmC)} \quad .$$

## SURROGATE CARBONYLS

A minor exception to the rule of equivalent speciation lies in the relationship of CARB as a reaction product to other species. Some compounds, especially internal olefins (e.g., trans-2-butene), react much more rapidly than do terminal olefins like propylene. Thus, instead of creating a new species with an atmospheric lifetime of only a few minutes, we chose to treat

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* This is not true, however, for "surrogate mechanisms" in which all hydrocarbons are assumed to be represented by some mixture of surrogate hydrocarbons (e.g., propylene and butane). Comparison of speciation in the CBM with that in a surrogate mechanism is obviously impossible.

internal olefins as if they had already reacted (i.e., as if an internal olefinic bond were already transformed to two carbonyls).

A similar approximation is used for cycloparaffins. No data exist for the reactions and reactivity rates of these compounds; however, we believe that they are more reactive than ordinary paraffinic hydrocarbons. At some point in the reaction scheme the ring structure must break, yielding two reactive sites instead of one. We therefore add one CARB group to the CBM splits for cycloparaffins to account for the extra reactive site.

## SAMPLE CARBON-BOND CALCULATIONS

In appendix B we present the name, molecular weight, carbon number, and carbon-bond groupings for several compounds. This table can be referred to in the preparation of emission inventories for the Carbon-Bond Mechanism.

To show how the CBM bond groupings can be obtained for a variety of user objectives, we present several examples of such calculations. The first example is presented as Table 4.

### Example 1

TABLE 4. CARBON-BOND GROUPINGS

| Hydrocarbon Concentrations (ppm) | | CBM Group/Molecule |
|---|---|---|
| Ethylene | 1.051 | 1 ETH |
| Propylene | 0.108 | 1 OLE + 1 PAR |
| Butane | 1.13 | 4 PAR |
| trans-2-Butene | 0.055 | 2 CARB + 2 PAR |
| 2,3-Dimethylbutane | 0.715 | 6 PAR |
| Toluene | 0.121 | 1 ARO + 1 PAR |
| m-Xylene | 0.108 | 1 ARO + 2 PAR |
| Formaldehyde | 0.03 | 1 CARB |

(continued)

Table 4

Carbon-Bond Calculations

ETH = 1 x 1.051 = 1.051

OLE = 1 x 0.108 = 0.108

ARO = (1 x 0.121) + (1 x 0.108) = 0.229

CARB = (2 x 0.055) + (1 x 0.03) = 0.14

PAR = (1 x 0.108) + (4 x 1.13) + (2 x 0.055)
+ (6 x 0.715) + (1 x 0.121) + (2 x 0.108) = 9.365

Source: University of California at Riverside Smog-Chamber Experiment (EC-231)

Example 2

Example 2 calculates the carbon-bond concentrations that would be used for the ambient hydrocarbon measurements reported by Kopczynski et al. (1972). Gas chromatographic analysis (GCA) accounted for 90 percent of total nonmethane hydrocarbons as identified by flame ionization analysis (FIA). Table 5(a) gives the carbon fraction allocated to each bond category for each molecular species as calculated from the bond-splitting information in appendix B. The calculated molar concentration for each bond group is also given. Table 5(b) gives the sum of each bond category as well as the carbon fraction for each bond category for the measured hydrocarbon mix. This information could be directly input to OZIPM, a computer program designed to generate EKMA-type isopleth diagrams with any kinetic mechanism.

Kopczynski et al. (1972) do not report carbonyl data for aldehydes or ketones. The response of aldehydes and ketones to FIA and GCA is inefficient. The carbon fraction shown for the CARB species in table 5(b) consists exclusively of surrogate carbonyls--compounds such as internal olefins (which form carbonyls rapidly); precise carbonyl data are lacking.

If the hydrocarbon splits in table 5(b) are used without correction for probable carbonyl concentrations, underprediction of the reactivity of the atmospheric mix results. Indeed, Kopczynski, Kuntz, and Bufalini (1975), prepared a "simulated Los Angeles mix" on the basis of measured concentrations in the 1972 study. They found that the simulated mix required the consumption

Example 2

TABLE 5. CARBON-BOND CONCENTRATIONS APPLIED TO AMBIENT HYDROCARBON MEASUREMENTS REPORTED BY KOPCZYNSKI ET AL. (1972)

(a) Carbon-Bond Concentrations in ppb

| Measured Hydrocarbon Olefins | Carbon Fraction ppbC | ETH | OLE | ARO | PAR | CARB | NR | Molar Concentrations ETH | OLE | ARO | PAR | CARB | NR |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ethylene | 151 | 1.0 | | | | | | 75.5 | | | | | |
| Propylene | 60 | | 0.67 | | 0.33 | | | | 20.0 | | 20.0 | | |
| 1-Butene / Isobutene | 47 | | 0.5 | | 0.5 | | | | 11.75 | | 23.5 | | |
| trans-2-Butene / Methylacetylene | 12* | | | | 0.25 | 0.25 | 0.5 | | | | 3.0 | 3.0 | 6.0 |
| cis-2-Butene | 8 | | | | 0.5 | 0.5 | | | | | | 4.0 | |
| 1,3-Butadiene | 11 | | 0.5 | | | 0.5 | | | 2.75 | | | 5.5 | |
| 1-Pentene | 11 | | 0.4 | | 0.6 | | | | 2.2 | | 6.6 | | |
| 2-Methyl-1-butene | 15 | | 0.4 | | 0.6 | | | | 3.0 | | 9.0 | | |
| trans-2-Pentene | 22 | | | | 0.6 | 0.4 | | | | | 13.2 | 8.8 | |
| cis-2-Pentene | 10 | | | | 0.6 | 0.4 | | | | | 6.0 | 4.0 | |
| 2-Methyl-2-butene | 29 | | | | 0.6 | 0.4 | | | | | 17.4 | 11.6 | |
| 1-Hexene | 15 | | 0.33 | | 0.67 | | | | 2.5 | | 10.0 | | |
| Unknown 7† / Unknown 8† | 6 / 3 | 9 | 0.33 | | 0.67 | | | | 1.5 | | 6.0 | | |
| Total | 400 | | | | | | | 75.5 | 43.7 | | 118.7 | 36.9 | 6.0 |

(continued)

TABLE 5

(a) (continued)

| Measured Hydrocarbon | Carbon Fraction | | | | | | | Molar Concentrations | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aromatics | ppbC | ETH | OLE | ARO | PAR | CARB | NR | ETH | OLE | ARO | PAR | CARB | NR |
| Toluene | 271 | | | 0.86 | 0.14 | | | | | 38.7 | 38.7 | | |
| Ethylbenzene | 67 | | | 0.75 | 0.25 | | | | | 8.4 | 16.75 | | |
| p-Xylene | 100 | | | 0.75 | 0.25 | | | | | 12.5 | 25.0 | | |
| m-Xylene | 215 | | | 0.75 | 0.25 | | | | | 26.9 | 53.75 | | |
| o-Xylene | 87 | | | 0.75 | 0.25 | | | | | 10.9 | 21.75 | | |
| n-Propylbenzene | 21 | | | 0.67 | 0.33 | | | | | 2.3 | 7.0 | | |
| m-Ethyltoluene<br>p-Ethyltoluene | 111 | | | 0.67 | 0.33 | | | | | 12.3 | 37.0 | | |
| tert-Butylbenzene<br>o-Ethyltoluene | 23 | | | 0.67 | 0.33 | | | | | 2.6 | 7.7 | | |
| sec-Butylbenzene<br>1,2,4-Trimethylbenzene | 137* | | | 0.63 | 0.37 | | | | | 14.4 | 50.5 | | |
| 1,3,5-Trimethylbenzene | 29 | | | 0.67 | 0.33 | | | | | | | | |
| Isopropylbenzene<br>Styrene | 76 | | | 0.7 | 0.22 | 0.074 | | | | 8.9 | 17.0 | 5.6 | |
| Total | 1137 | | | | | | | | | 137.9 | 275.15 | 5.6 | |

(continued)

TABLE 5

(a) (continued)

| Measured Hydrocarbon | Carbon Fraction | | | | | | | Molar Concentrations | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Paraffins | ppbC | ETH | OLE | ARO | PAR | CARB | NR | ETH | OLE | ARO | PAR | CARB | NR |
| Ethane | 191 | | | | 0.0 | | | | | | | | 191.0 |
| Propane | 140 | | | | 0.5 | | | | | | 70.0 | | 70.0 |
| Isobutane | 65 | | | | 1.0 | | | | | | 65.0 | | |
| n-Butane | 286 | | | | 1.0 | | | | | | 286.0 | | |
| Isopentane | 312 | | | | 1.0 | | | | | | 312.0 | | |
| n-Pentane | 171 | | | | 1.0 | | | | | | 171.0 | | |
| Cyclopentane<br>2-Methylpentane | 138* | | | | 0.91 | 0.09 | | | | | 125.6 | 12.4 | |
| 3-Methylpentane | 68 | | | | 1.0 | | | | | | 68.0 | | |
| n-Hexane | 82 | | | | 1.0 | | | | | | 82.0 | | |
| 2,4-Dimethylpentane | 89 | | | | 1.0 | | | | | | 89.0 | | |
| Cyclohexane | 16 | | | | 0.83 | 0.17 | | | | | 13.3 | 2.7 | |
| 3-Methylhexane | 68 | | | | 1.0 | | | | | | 68.0 | | |
| n-Heptane | 40 | | | | 1.0 | | | | | | 40.0 | | |
| Methylcyclohexane | 49 | | | | 0.86 | 0.14 | | | | | 42.1 | 6.9 | |
| Unknown 1 | 6 | | | | 1.0 | | | | | | 6.0 | | |
| Unknown 2 | 11 | | | | 1.0 | | | | | | 11.0 | | |
| Unknown 3 | 37 | | | | 1.0 | | | | | | 37.0 | | |
| Unknown 4 | 28 | | | | 1.0 | | | | | | 28.0 | | |
| Unknown 5 | 23 | | | | 1.0 | | | | | | 23.0 | | |
| Unknown 6 | 80 | | | | 1.0 | | | | | | 80.0 | | |
| (Acetylene) | 160 | | | | 0.0 | | | | | | | | 160.0 |
| Total | 2060 | | | | | | | | | | 1617.0 | 22.0 | |

* Assume 50/50 split.

† Assume molecular weight of 6.

(continued)

TABLE 5

(b) Carbon-Bond Speciation Category*

| Species | Σ Molar Concentrations (ppb) | Carbon Fraction | Normalized |
|---|---|---|---|
| ETH | 75.5 | 0.042 | 0.048 |
| OLE | 43.7 | 0.024 | 0.027 |
| ARO | 137.9 | 0.23 | 0.26 |
| PAR | 2011.0 | 0.56 | 0.64 |
| CARB | 64.5 | 0.018 | 0.02 |
| Non-Methane Nonreactive | 427.0 | 0.119 | |

* Gas chromatograph accounted for 3597 ppbC (3170 ppbC RHC + 427 ppbC nonreactive). Flame ionization analysis (FIA): TNMHC = 4.0 ppmC (4000 ppb)

(c) Carbon-Bond Speciation Category Corrected for Unmeasured Hydrocarbons and Unmeasured Carbonyls

| Species | Σ Molar Concentrations* (ppb) | Carbon Fraction Normalized† |
|---|---|---|
| ETH | $75.5 \times \frac{4000}{3597} = 84.0$ | 0.044 |
| OLE | $43.7 \times \frac{4000}{3597} = 48.6$ | 0.025 |
| ARO | $137.9 \times \frac{4000}{3597} = 153.4$ | 0.24 |
| PAR | $2011.0 \times \frac{4000}{3597} = 2236.3$ | 0.58 |
| CARB | $64.5 + 360.0^{\S} \times \frac{4000}{3597} = 431.7$ | 0.11 |

* Unmeasured reactive hydrocarbon = $(1 - \frac{3597 \text{ ppbC GCA}}{4000 \text{ ppbC FIA}}) = 10\%$

† Total reactive organic carbon = 3853.6 ppbC

§ Unmeasured carbonyl; see text

(concluded)

of 2.3 moles of carbon per mole of NO oxidized to $NO_2$ in a smog chamber. Kopczynski et al. (1972) found that samples of Los Angeles air required only 1.4 moles of carbon per mole of NO oxidized to $NO_2$. Kopczynski, Kuntz, and Bufalini (1975) suggested that other species, such as aldehydes, were contributing to NO oxidation in Los Angeles.

From these data we can estimate the CARB concentration necessary to replicate the oxidation reactivity observed by Kopczynski et al. (1972). If we multiply the molar bond concentrations shown in table 5(b) by the OH reaction-rate constant for each bond group, we obtain the production rate of peroxyl radicals (which oxidize NO to $NO_2$) from the measured hydrocarbons per OH concentration in the air sample:

| Compound | Bond Concentration (ppm) | OH Reaction-Rate Constant ($ppm^{-1}min^{-1}$) | Peroxyl Radicals per OH Attack | Peroxyl Production Rate per OH ($min^{-1}$) |
|---|---|---|---|---|
| ETH | 0.0755 | 12,000 | 2 | 1,812 |
| OLE | 0.0437 | 37,000 | 2 | 3,234 |
| ARO | 0.1379 | 20,500 | 2 | 5,654 |
| PAR | 2.011 | 1,300 | 2.5* | 6,536 |
| CARB | 0.0645 | 14,000 | 2 | 1,806 |
| (surro-gate) | | | | 19,042 |

* The "A factor" of 1.5 gives 1.5 $RO_2^{\bullet}$ + 1 $HO_2^{\bullet}$ per OH attack on a paraffinic bond.

The observed rate of peroxyl production was 2.3/1.4 = 1.64 times higher in the Los Angeles air sample than in the surrogate mix. Compounds unidentified by GCA for the Los Angeles air sample amounted to 10 percent of the total. If we make the conservative assumption that the unidentified compounds had the same reactivity as the identified mix, then the observed rate becomes 2.07/1.4 = 1.48 times higher than the laboratory mix. This adjustment for 10 percent unmeasured hydrocarbon raises all the calculated bond concentrations by 10 percent and increases the peroxyl production rate to 21160. $min^{-1}$ per OH.

Given the observed "reactivity gap" of 0.48, we may estimate the concentration of carbonyl compounds necessary to account for the additional oxidation of NO to $NO_2$:

$$\frac{21160.\ \text{min}^{-1} \times 0.48}{14000\ \text{ppm}^{-1}\ \text{min}^{-1} \times 2} = 0.36\ \text{ppm (360 ppb)} \quad ,$$

which is equal to 9 percent of the observed hydrocarbon concentration and should be added to the carbon fractions shown in table 5(c).

Example 3

Example 3 also represents ambient sampling in the Los Angeles area (Calvert, 1976). In this case, however, the measurements are reported in molar units. To calculate CBM units from molar units, the appropriate bonds-per-molecule factor (from appendix B) is multiplied by the molar concentration.

Calvert (1976) stated that roughly 85 percent of total carbon atoms were detected as individual species. Thus about 0.58 ppmC remain unaccounted for in the analysis. If this excess carbon is reactive, we must make some assumption regarding its composition. Normalizing to total RHC (see table 6[b]) is equivalent to assuming that the composition of the unidentified carbon is similar to the average of that which was identified. This is what we did in the previous example. Alternatively, if we assume that the unidentified carbon is all paraffinic, the PAR fraction is then increased to 79 percent, and all other categories are reduced by 25 percent. Overall, the normalized carbon fractionation of RHC as shown in table 6(b) is the most conservative approach. However, it is important to bear in mind that only "surrogate carbonyls" are represented in this speciation. The reactivity calculations in example 2 indicate that this approach may underestimate the carbonyl component. We discuss this problem more thoroughly in section 5.

Example 4

Example 4 (Table 7) shows the correspondence between a molecular mechanism and the CBM as each would be used in the OZIPM program. In the OZIPM program two sets of numbers are input: the carbon number of each species and the carbon fraction of emissions represented by that species. In the case of the Carbon-Bond Mechanism, we also need to know the ethylene fraction of the olefinic emissions, because the CBM splits out ethylene from other olefins. This example is taken from a trajectory model study that uses the RAPS data base for St. Louis (Jeffries, 1981, private communication). For that study, ethylene was assumed to equal one-half of the olefinic emissions (internal olefins were ignored). Given that ethylene represents one-half of

Example 3

TABLE 6. LOS ANGELES AMBIENT MEASUREMENTS

(a) Reported in Molar Units

| Compound | [RH],ppm Molar Basis | Bonds per Molecule x Concentration | | | | | |
|---|---|---|---|---|---|---|---|
| | | NR | OLE | ETH | PAR | ARO | CARB |
| $CH_4$ | 2.01 | 2.01 | | | | | |
| $C_2H_6$ | 0.049 | 0.049 | | | | | |
| $C_2H_4$ | 0.043 | | | 0.043 | | | |
| $C_2H_2$ | 0.038 | 0.038 | | | | | |
| $C_3H_8$ | 0.037 | 0.0185 | | | 0.0185 | | |
| $C_3H_6$ | 0.0087 | | 0.0087 | | 0.0087 | | |
| iso-$C_4H_{10}$ | 0.012 | | | | 0.048 | | |
| n-$C_4H_{10}$ | 0.037 | | | | 0.148 | | |
| 1-$C_4H_8$ | 0.0015 | | 0.0015 | | 0.0030 | | |
| iso-$C_4H_8$ | 0.0030 | | 0.0030 | | 0.0060 | | |
| iso-$C_5H_{12}$ | 0.0443 | | | | 0.02215 | | |
| n-$C_5H_{12}$ | 0.0162 | | | | 0.0810 | | |
| Cyclo-$C_5H_{10}$ | 0.0026 | | | | 0.0104 | | 0.0026 |
| 1-$C_5H_{10}$ | 0.004 | | 0.004 | | 0.016 | | |
| 2-Methylbutene | 0.0008 | | | | 0.0032 | | 0.0016 |
| 2,2-Dimethylbutene | 0.0008 | | | | 0.0032 | | 0.0016 |
| 2-Methylpentane | 0.0110 | | | | 0.066 | | |
| 3-Methylpentane | 0.0100 | | | | 0.06 | | |
| 1-Hexene | 0.0017 | | 0.0017 | | 0.0085 | | |
| n-Hexane | 0.0100 | | | | 0.06 | | |
| Cyclohexene | 0.0107 | | | | 0.0428 | | 0.0214 |
| 2,2,3-Trimethylbutane | 0.0077 | | | | 0.0539 | | |
| $C_6H_6$ | 0.0082 | 0.0492 | | | | | |
| 2-Methylhexane | 0.0069 | | | | 0.0483 | | |
| 3-Methylhexane | 0.0063 | | | | 0.0441 | | |

(continued)

TABLE 6

(a) (continued)

| Compound | [RH], ppm Molar Basis | Bonds per Molecule x Concentration | | | | | |
|---|---|---|---|---|---|---|---|
| | | NR | OLE | ETH | PAR | ARO | CARB |
| 1-Heptene | 0.0044 | | 0.0044 | | 0.022 | | |
| n-$C_7H_{16}$ | 0.0043 | | | | 0.0301 | | |
| Methylcyclohexane | 0.0037 | | | | 0.0222 | | 0.0037 |
| 2,2,3- and 2,3,3-Trimethylpentane | 0.0019 | | | | 0.0152 | | |
| 2,2,4-Trimethylpentane | 0.0025 | | | | 0.02 | | |
| Toluene | 0.020 | | | | 0.02 | 0.02 | |
| 1-Methylcyclohexene | 0.0047 | | | | 0.0235 | | 0.0094 |
| 2,2,5-Trimethylhexane | 0.0010 | | | | 0.009 | | 0.001 |
| n-$C_8H_{18}$ | 0.0021 | | | | 0.0168 | | |
| $EtC_6H_5$ | 0.0041 | | | | 0.0082 | 0.0041 | |
| p,m-Xylenes | 0.014 | | | | 0.028 | 0.014 | |
| o-Xylene | 0.0060 | | | | 0.012 | 0.006 | |
| n-$C_9H_{20}$ | 0.0013 | | | | 0.0117 | | |
| n-$PrC_6H_5$ | 0.0010 | | | | 0.003 | 0.001 | |
| sec-$BuC_6H_5$ | 0.0050 | | | | 0.02 | 0.005 | |
| n-$C_{10}H_{22}$ | 0.0011 | | | | 0.011 | | |
| n-$C_{11}H_{24}$ | 0.0010 | | | | 0.011 | | |
| n-$C_{12}H_{26}$ | 0.0003 | | | | 0.0036 | | |
| CO | 1.91 | | | | | | |
| Total | | | 0.0233 | 0.043 | 1.2384 | 0.0501 | 0.040 |

(b) Total RHC Normalized

| Compound | RHC (ppm) | ppmC | Carbon Fraction of RHC |
|---|---|---|---|
| OLE | 0.0233 | 0.0466 | 0.0271 |
| ETH | 0.043 | 0.086 | 0.0501 |
| PAR | 1.2347 | 1.2347 | 0.719 |
| ARO | 0.0501 | 0.306 | 0.178 |
| CARB | 0.044 | 0.044 | 0.0256 |
| Total | | 1.7173 | |

(concluded)

Example 4

TABLE 7. COMPARISON OF MOLECULAR MECHANISM AND THE CBM AS USED IN THE OZIPM PROGRAM

| OZIPM INPUTS | | |
|---|---|---|
| Species | Average Carbon Number | Carbon Fraction of Emissions |
| Olefin* | 3 | 0.193 |
| Aromatic | 8.1 | 0.142 |
| Paraffin | 6.0 | 0.601 |
| Aldehyde | 1 | 0.065 |

| CARBON-BOND MECHANISM | | |
|---|---|---|
| Olefin | 2 | 2/6 x 1/2 x 0.193 = 0.032 |
| Ethylene | 2 | 1/2 x 0.193 = 0.0965 |
| Aromatic | 6 | 6/8.1 x 0.142 = 0.105 |
| Aldehyde | 1 | 0.065 = 0.065 |
| Paraffin | 1 | (2/3 x 1/2 x 0.193) + 2.1/8.1 x 0.142 + 0.601 = 0.70 |

* Ethylene = one-half of the carbon in the olefin category.

the carbon in the olefin category, we can then calculate the average carbon number for the remaining olefinic compounds:

$$\text{carbon number} = \frac{\text{total carbon}}{\text{number of molecules}}$$

$$3 = \frac{0.193}{\underbrace{\frac{0.0965}{2}}_{\text{ethylene}} + \underbrace{\frac{0.0965}{x}}_{\text{other olefins}}}$$

$$\frac{3}{2} \cdot 0.0965 + \frac{3}{x} \cdot 0.0965 = 0.193 \quad ,$$

$$0.2895 = (0.193 - 0.14475)\, x \quad ,$$

$$6 = x \quad .$$

Thus, one-half of the olefinic carbon is ethylene (0.0965 of the total). Of the six carbon atom olefins remaining, one-third are olefinic bonds (two carbons per olefinic bond; six carbons per molecule). Thus the olefinic fraction is 2/6 x 1/2 x 0.193, or 0.032. The other calculations are straightforward: 6/8.1 of the aromatic molecules are aromatic bonds; the aldehydes do not change; and the remaining carbon is made up of PAR.

1 ppmC of emissions then equals:

0.032/2 ppm OLE

0.0965/2 ppm ETH

0.105/6 ppm ARO

0.065 ppm CARB

0.70 ppm PAR

We can also estimate olefin composition from the hydrocarbon data given in examples 2 and 3. From table 8 we see that olefinic carbon is composed of 37 percent ETH, 21 percent OLE, 12 percent internal olefins as CARB, and 30 percent PAR. Similarly, from examples 2 and 3 we estimate that 1.1 percent of primary paraffinic carbon can be placed in the CARB category because of the cyclic paraffins that are included.

TABLE 8. CARBON-BOND COMPOSITION OF OLEFINS

(Based on examples 2 and 3 in this chapter)

| Species | Example 2 | Example 3 | Average |
|---|---|---|---|
| ETH | 0.38 | 0.37 | 0.37 |
| OLE | 0.22 | 0.20 | 0.21 |
| Internal olefin (CARB) | 0.09 | 0.15 | 0.12 |
| PAR | 0.31 | 0.28 | 0.30 |
| Average carbon number | 2.9 | 2.8 | 2.86 |

These data indicate an average carbon number of nearly three, which agrees well with the estimate made on the basis of the RAPS emissions. Ethylene, however, appears equal to 40 percent, rather than 50 percent, of olefinic carbon.

If we use both the olefinic-composition factors in table 8 and the cyclic paraffin carbonyl surrogate for the OZIPM inputs, the CBM carbon splits become

$$OLE = 0.193 \times 0.21 = 0.0405,$$

$$ETH = 0.193 \times 0.37 = 0.0714,$$

$$CARB = 0.065 + (0.193 \times 0.12) + (0.011 \times 0.601) = 0.0948,$$

$$ARO = 0.142 \times 6/8.1 = 0.105,$$

$$PAR = (0.193 \times 0.3) + 2.1/8.1 \times (0.142) + (0.601 \times 0.989) = 0.689.$$

# SECTION 5

# HYDROCARBONS IN URBAN AREAS

In this section we review available data regarding the composition of hydrocarbons in polluted urban air. The study of ambient hydrocarbon composition and the related subject of speciation of pollutant emissions is important to the successful application of kinetic modeling of urban smog.

Any kinetic mechanism is liable to error if the various hydrocarbon species that it treats are improperly specified. This problem does not ordinarily arise in smog-chamber studies, because the experimenter has full control over the introduction of hydrocarbons into the reaction vessel. Nor does the speciation problem arise in the application of a surrogate mechanism such as that used in EKMA, where all hydrocarbons are assumed to be represented by a mixture of propylene and butane. The surrogate approach is inflexible, however, because it does not allow for the differences that do exist among hydrocarbon species.

Because a lumped-species mechanism like the Carbon-Bond Mechanism is more flexible than a surrogate mechanism, there is greater potential for error. An "assumed hydrocarbon speciation" can be supplied for the CBM to set exact proportions for the emitted hydrocarbon species, thereby eliminating the flexibility of the modeling exercise. Instead, we prefer to present information about the probable composition of hydrocarbons within urban areas. Such data allow the user to judge whether or not a particular emissions inventory lies within the limits of variation for hydrocarbon composition. At the end of this section, we provide a default hydrocarbon composition profile, which can be used in the absence of data or when the modeler suspects an error in the speciation data.

## HYDROCARBON SPECIATION FOR THE LOS ANGELES AREA

Killus et al. (1980) prepared estimates of hydrocarbon composition for the Los Angeles area on the basis of the work of Trijonis and Arledge (1975). It should be noted that these estimates, shown in table 9, were prepared prior to the adoption of the methodology in which internal olefins and a fraction of cyclic paraffins are treated as carbonyl emissions. This

TABLE 9. HYDROCARBON EMISSIONS IN THE LOS ANGELES BASIN BY CARBON FRACTION IN CATEGORIES USED IN THE SAI URBAN AIRSHED MODEL

| Source Category | Percentage of Total Hydrocarbon Emissions | Carbon Fraction | | | | | |
|---|---|---|---|---|---|---|---|
| | | Olefins* | Paraffins | Ethylene | Aromatics | Carbonyls† | Nonreactive Hydrocarbons |
| Land motor vehicles† | 67.5 | 0.032 | 0.61 | 0.032 | 0.235 | 0.037 | 0.091 |
| Aircraft | 1.6 | 0.073 | 0.64 | 0.038 | 0.163 | 0.058 | 0.09 |
| Refineries | 1.9 | 0.04 | 0.84 | 0.0 | 0.17 | 0.0 | 0.05 |
| Other | 29.0 | 0.026 | 0.565 | 0.016 | 0.066 | 0.011 | 0.326 |
| Total hydrocarbons from all sources | -- | 0.029 | 0.60 | 0.027 | 0.182 | 0.029 | 0.158 |
| Normalized carbon fraction emissions excluding nonreactive HC | -- | 0.034 | 0.71 | 0.032 | 0.22 | 0.034 | |
| Normalized carbon fractions with "surrogate" carbonyls | -- | 0.024 | 0.70 | 0.032 | 0.22 | 0.055 | |

* Olefins excluding ethylene.

† Carbonyl emissions are estimates only (because they would not have been detected by the measurement methods used); thus the sum of the weight fractions in this row is greater than 1.

"surrogate carbonyl" approximation tends to reduce slightly the olefinic and paraffinic bond groups and to increase the carbonyl emissions. Internal olefins represent between 10 and 15 percent of the carbon in olefin molecules, which is 30 to 40 percent of OLE (as shown in section 4). Additional surrogate carbonyls represent about 1 percent of the remaining emissions. Table 9 also shows the principal effect of the "surrogate carbonyl" approximation--the reduction of olefins to 0.024 of the RHC emissions and the increase of carbonyls to 0.055 of RHC.

The Los Angeles inventory of volatile organic carbon emissions, as used in the SAI Airshed Model, is presently undergoing review and modification (Allen, 1981, private communication). The most recent emissions splits (obtained by application of correction factors to the summation of the emissions data file for the Airshed Model) are given in table 10.

Hydrocarbon speciation for the motor-vehicle emissions shown in table 10 is taken from measurements made by Black and High (1980) for an uncontrolled automobile burning fuel that contains 22 percent aromatics (17 percent in carbon-bond units). However, the average aromatic content measured by Mayrsohn and Crabtree (1976) in a sample of Los Angeles gasolines was 37 percent (26 percent in carbon-bond units). Such speciation for gasoline corresponds well with the measurements made by Kopczynski et al. (1972) [described in example 2 in section 4] in which the aromatic-bond fraction was greater than 20 percent. However, Calvert (1976) [example 3 in section 4] reported hydrocarbon composition estimates in which the aromatic-bond fraction was only 17 percent. The estimates made by Calvert were derived from typical data from the LARPP study in Los Angeles. Thus, the range of emissions estimates for the Los Angeles area is corroborated to some extent by atmospheric measurements (see table 11).

## HYDROCARBON SPECIATION FOR OTHER URBAN AREAS

Table 12 presents data regarding hydrocarbon speciation for several urban areas (Kopczynski et al., 1975). Table 13 indicates the carbon-bond composition for these samples, using the carbon-composition factors outlined in example 4 in section 4. Note that CARB contains "surrogate carbonyl" only. Actual carbonyl concentrations are likely to be higher than what is indicated by these data.

Table 14 presents the data from a study performed by Ferman, Eisinger, and Monson (1977) for the Denver area. The sampling site was 6 km northwest of downtown Denver, and as the table indicates, the fractions for ethylene, olefins, and aromatics are all two-thirds of those derived from the Kopczynski et al. data for a Denver expressway. Surrogate carbonyl for the off-highway data represents an even smaller fraction (relative to the expressway data)

TABLE 10. LOS ANGELES EMISSIONS SPECIATION FOR 1974 EMISSIONS INVENTORY

| Source | OLE | PAR | ETH | ARO | CARB |
|---|---|---|---|---|---|
| Land motor vehicles | 0.1 | 0.59 | 0.124 | 0.19 | 0.046 |
| All sources | 0.049 | 0.705 | 0.090 | 0.154 | 0.046 |

Source: California ARB (1981).

TABLE 11. CARBON-BOND FRACTIONS OF RHC FOR EMISSIONS AND AMBIENT MEASUREMENTS IN THE LOS ANGELES AREA

| Estimate or Measurement | OLE | PAR | ETH | ARO | CARB |
|---|---|---|---|---|---|
| Emissions estimates for 1974 | | | | | |
| Killus et al. (1980) | 0.024 | 0.7 | 0.032 | 0.22 | 0.055 |
| California ARB (1981) | 0.049 | 0.705 | 0.096 | 0.154 | 0.039 |
| Atmospheric measurements | | | | | |
| Kopczynski et al. (1972) | 0.027 | 0.64 | 0.048 | 0.26 | 0.07* |
| Calvert (1976) (LARPP--1974) | 0.027 | 0.72 | 0.05 | 0.18 | 0.026† |

* Calculated from excess reactivity over laboratory surrogate mix (see Example 2 in section 4).

† Surrogate CARB only; aldehydes and ketones not measured.

TABLE 12. RATIOS OF POLLUTANTS TO SUM OF HYDROCARBONS LESS $C_1$ TO $C_3$ PARAFFINS IN ROADWAY SAMPLES

| Pollutant | St. Louis, 1972 Highways | St. Louis, 1972 Downtown | Denver Expressway Interchange 1971 | L.A. Underpass 1970 | Lincoln Tunnel 1970 |
|---|---|---|---|---|---|
| $C_3$ + paraffins | 0.42 | 0.50 | 0.57 | 0.41 | 0.46 |
| Olefins | 0.23 | 0.19 | 0.15 | 0.13 | 0.22 |
| $C_6$ + aromatics | 0.25 | 0.23 | 0.23 | 0.41 | 0.26 |
| Acetylene | 0.068 | 0.068 | 0.056 | 0.053 | 0.067 |
| Carbon monoxide | 5.0 | 5.1 | 4.0 | 3.2 | 4.5 |
| Nitrogen oxides | 0.13 | 0.22 | 0.16 | 0.14 | 0.40 |

Source: Kopczynski, Kuntz, and Bufalini (1975)

TABLE 13. URBAN HYDROCARBON COMPOSITION DATA

(a) Carbon-Bond Splits for Data in Table 12

| Site | From Olefins | | | | From ARO | | From PAR | | Total |
|---|---|---|---|---|---|---|---|---|---|
| | ETH | OLE | CARB | PAR | ARO | PAR | PAR | CARB | PAR |
| St. Louis Highways | 0.085 | 0.048 | 0.028 | 0.069 | 0.19 | 0.06 | 0.404 | 0.006 | 0.533 |
| Downtown | 0.07 | 0.04 | 0.023 | 0.057 | 0.15 | 0.04 | 0.493 | 0.007 | 0.59 |
| Denver Expressway | 0.056 | 0.0315 | 0.018 | 0.045 | 0.15 | 0.04 | 0.562 | 0.008 | 0.65 |
| Los Angeles Underpass | 0.048 | 0.027 | 0.016 | 0.039 | 0.31 | 0.10 | 0.404 | 0.006 | 0.54 |
| Lincoln Tunnel | 0.08 | 0.046 | 0.026 | 0.066 | 0.20 | 0.06 | 0.453 | 0.007 | 0.58 |

(b) Normalized to 100 Percent Carbon

| Site | ETH | OLE | PAR | ARO | CARB |
|---|---|---|---|---|---|
| St. Louis Highways | 0.094 | 0.053 | 0.59 | 0.21 | 0.038 |
| Downtown | 0.076 | 0.044 | 0.64 | 0.16 | 0.033 |
| Denver Expressway | 0.059 | 0.033 | 0.68 | 0.16 | 0.027 |
| Los Angeles Underpass | 0.05 | 0.028 | 0.57 | 0.33 | 0.023 |
| Lincoln Tunnel | 0.085 | 0.049 | 0.62 | 0.21 | 0.035 |

TABLE 14. STATISTICAL SUMMARY OF HYDROCARBON DATA FOR THE DENVER AREA*

(a) Hydrocarbon Concentrations (ppbC)

| Hydrocarbon | Average | 99th Percentile | Maximum |
|---|---|---|---|
| Ethane† | 69 | 447 | 638 |
| Ethylene | 53 | 304 | 508 |
| Acetylene† | 59 | 344 | 530 |
| Propane† | 95 | 785 | 924 |
| Propylene | 25 | 146 | 243 |
| Isobutane | 58 | 557 | 857 |
| n-Butane | 123 | 685 | 979 |
| Isopentane | 111 | 600 | 999 |
| n-Pentane | 68 | 586 | 781 |
| 2-Methylpentane | 53 | 424 | 652 |
| 3-Methylpentane | 37 | 254 | 509 |
| n-Hexane | 55 | 321 | 535 |
| 2,2,3-Trimethylbutane | 32 | 218 | 485 |
| Cyclohexane | 17 | 164 | 547 |
| Benzene† | 18 | 116 | 178 |
| 2-Methylhexane | 34 | 198 | 441 |
| 3-Methylhexane | 38 | 240 | 481 |
| 1-Heptene | 20 | 135 | 301 |
| n-Heptane | 33 | 210 | 420 |
| Methylcyclohexane | 28 | 177 | 272 |
| Toluene | 64 | 338 | 520 |
| 1-Methylcyclohexane | 23 | 120 | 239 |
| n-Octane | 22 | 153 | 766 |
| Ethylbenzene | 15 | 80 | 115 |
| m- and p-Xylene | 47 | 260 | 372 |
| o-Xylene | 24 | 142 | 571 |
| n-Nonane | 19 | 116 | 334 |
| sec-Butylbenzene | 30 | 167 | 419 |
| n-Decane | 22 | 146 | 209 |
| n-Undecane | 14 | 84 | 120 |
| Total | 1112 | 7333 | |

* Based on >500 points for each compound. Compounds listed are the 30 with the highest average concentrations. Minimum concentrations for all are less than 1 ppbC.

† Nonreactive (propane 0.5 reactive).

(continued)

TABLE 14

(b) Carbon-Bond Fractions for Denver Hydrocarbon Data

| | ETH | OLE | CARB | ARO | PAR |
|---|---|---|---|---|---|
| Average | 0.0476 | 0.02 | 0.009 | 0.123 | 0.80 |
| 99th Percentile | 0.0415 | 0.0185 | 0.0095 | 0.1025 | 0.83 |

(concluded)

apparently because of the exclusion of trace compounds like internal olefins. These data represent the least reactive mix of hydrocarbons in any data set that we have analyzed. Use of fractions lower than these for ethylene, olefins, and aromatics is not recommended. Because carbonyl concentrations are usually unmeasured and conjectural, we present later in the section some carbonyl emissions estimates.

Table 15 gives hydrocarbon-composition data for sites in the eastern United States and the carbon-bond fractions calculated from these data. Since no internal olefins were reported and only a small quantity of cyclic paraffins was measured, no fraction of surrogate CARB is calculated. Note also that the fraction of ethylene as carbon in olefin molecules varies from 0.33 to 0.49, with an average of 0.41. This figure is similar to the 0.37 fraction that we have used in the preceding examples.

The data in table 16 are derived from samples taken in September 1973 by Lonneman and Bufalini (private communication) for the Houston, Texas, area. The high ethylene fraction calculated for these samples represents the major discrepancy between them and samples taken from other urban areas. The ethylene concentrations observed were in some cases three to five times the acetylene concentration, which indicates a large nonautomotive source of ethylene in the Houston area. Other data gathered in Houston (Lonneman and Bufalini, private communication; Siddiqi and Worley, 1975) show more common ethylene fractions, with approximately a one-to-one ratio to acetylene.

## CARBONYL COMPOUNDS IN URBAN AIR

In our discussion of hydrocarbon composition thus far, we have not included carbonyl compounds per se. Because aldehydes and ketones require special measurement techniques, they are not included in the available composition data, and only "surrogate carbonyl" can be reported. However, the photochemical reactivity observed in urban air pollution leads to the conclusion that significant concentrations of carbonyl compounds do exist in urban atmospheres, both as primary emissions and as secondary reaction products.

In the following subsection we discuss the importance of carbonyl compounds in the formation of smog, and we then examine some estimates of carbonyls in emissions and ambient air.

## RADICAL SOURCES AND HYDROCARBON REACTIVITY

Smog formation results from the catalytic oxidation of hydrocarbons by hydroxyl radicals (OH). The concentration of hydroxyl radicals in the

TABLE 15. HYDROCARBON COMPOSITION DATA FOR SELECTED SITES IN THE EASTERN UNITED STATES

(a) Ratio* of Sum of Paraffins, Olefins, and Aromatics to Acetylene at New York-New Jersey Station at All Times

| Component | Bayonne | Linden | Manhattan | Brooklyn | Lincoln Tunnel |
|---|---|---|---|---|---|
| $\sum$ Paraffins | 19.50 | 19.08 | 8.51 | 11.29 | 6.81 |
| $\sum$ $C_4$ paraffins | 5.34 | 5.24 | 1.97 | 2.47 | 1.41 |
| $\sum$ $C_5$ paraffins | 6.48 | 5.65 | 2.89 | 3.21 | 1.90 |
| $\sum$ Olefins | 4.83 | 5.75 | 2.21 | 2.97 | 3.24 |
| $\sum$ $C_4$ olefins | 0.99 | 1.35 | 0.39 | 0.50 | 0.59 |
| $\sum$ $C_6$ olefins | 0.11 | 0.14 | 0.05 | 0.05 | 0.08 |
| $\sum$ Aromatics | 12.77 | 11.70 | 6.74 | 11.3 | 3.87 |
| Toluene | 5.20 | 4.84 | 2.16 | 4.77 | 1.27 |
| $\sum$ $C_8$ aromatics | 5.89 | 4.87 | 2.67 | 4.67 | 1.44 |
| $\sum$ $C_9$ + $C_{10}$ aromatics | 1.68 | 1.99 | 1.91 | 1.86 | 1.16 |
| Ethylene | 1.83 | 1.91 | 1.08 | 1.28 | 1.33 |
| Propylene | 0.54 | 0.87 | 0.31 | 0.38 | 0.61 |
| Average acetylene concentration, ppb carbon | 15.9 | 21.7 | 43.7 | 32.1 | |
| Total | 37.1 | 36.5 | 17.46 | 25.56 | 13.92 |

Source: Lonneman et al. (1974)

(continued)

TABLE 15

(b) Average Ratios* of Hydrocarbon to Acetylene in Lincoln Tunnel

| Component | Ratio of Component to $C_2H_2$ and Standard Deviation |
|---|---|
| Ethylene | 1.33 ± 0.14 |
| Isobutane | 0.34 ± 0.05 |
| n-Butane | 0.97 ± 0.12 |
| Propylene | 0.61 ± 0.07 |
| Isopentane | 1.25 ± 0.14 |
| Isobutylene | 0.34 ± 0.04 |
| Butene-1 | |
| Sum of $C_4$ olefins | 0.60 ± 0.07 |
| n-Pentane | 0.62 ± 0.07 |
| Sum of $C_5$ olefins | 0.53 ± 0.08 |
| Cyclopentane | 0.76 ± 0.08 |
| 2-Methylpentane | |
| 3-Methylpentane | 0.34 ± 0.04 |
| n-Hexane | 0.36 ± 0.05 |
| 2,4-Dimethylpentane | 0.34 ± 0.04 |
| 2,2,4-Trimethylpentane | 0.27 ± 0.23 |
| Toluene | 1.27 ± 0.23 |
| Ethyl benzene | 0.22 ± 0.03 |
| p-Xylene | 0.25 ± 0.03 |
| m-Xylene | 0.70 ± 0.15 |
| o-Xylene | 0.28 ± 0.04 |
| Sum of $C_8$ aromatics | 1.44 ± 0.25 |
| 3 & 4-Ethyl toluene | 0.38 ± 0.05 |
| sec-Butyl benzene | 0.40 ± 0.06 |
| 1,2,4-Trimethyl benzene | |
| Sum of paraffins | 6.81 ± 0.92 |
| Sum of olefins† | 3.24 ± 0.32 |
| Sum of aromatics | 3.87 ± 0.58 |
| Total nonmethane hydrocarbons | 13.9 ± 1.5 |
| Carbon monoxide | 63.4 ± 6.1 |

* Ratios were calculated from component concentrations in parts-per-billion carbon.

† Average carbon number for olefins = 2.88
Ethylene = $\sum$ olefin x 0.41.

(continued)

TABLE 15

(c) Carbon-Bond Fractions for Data Presented in Table 15(a) and (b)

| Site | ETH | OLE | ARO | PAR | CARB |
|---|---|---|---|---|---|
| Bayonne | 0.049 | 0.0405 | 0.268 | 0.64 | -- |
| Linden | 0.052 | 0.057 | 0.248 | 0.64 | -- |
| Manhattan | 0.062 | 0.026 | 0.29 | 0.62 | -- |
| Brooklyn | 0.0501 | 0.03 | 0.18 | 0.74 | -- |
| Lincoln Tunnel | 0.0955 | 0.066 | 0.208 | 0.63 | -- |

(concluded)

TABLE 16. COMPOSITION OF HYDROCARBON IN HOUSTON AIR

| | Fraction of Carbon per Bond Category | | | | | |
|---|---|---|---|---|---|---|
| Site | ETH | OLE | PAR | ARO | Surrogate CARB | Nonreactive |
| H01 | 0.11 | 0.022 | 0.43 | 0.2 | 0.016 | 0.22 |
| | 0.14 | 0.028 | 0.55 | 0.26 | 0.02 | -- |
| H05 | 0.107 | 0.057 | 0.57 | 0.16 | 0.026 | 0.08 |
| | 0.12 | 0.062 | 0.62 | 0.17 | 0.0285 | -- |

atmosphere is small (about $10^{-7}$ ppm), but because they are rapidly destroyed, a constant influx of such radicals is necessary to maintain the smog-formation process. Most of the radicals necessary to generate smog are formed by the photolysis of oxygenated hydrocarbons--e.g.:

$$HCHO + h\upsilon \xrightarrow{+O_2} CO + HO_2 + HO_2 \quad ,$$

followed by

$$HO_2 + NO \rightarrow NO_2 + OH \quad .$$

Since photolyzable oxygenates are intermediate products of the process of hydrocarbon oxidation, the smog process is self-perpetuating; however, under some circumstances, it is not self-starting. If a pure hydrocarbon of relatively low reactivity were to be irradiated in an atmosphere free of extraneous sources of radicals, the smog-formation process would never be initiated. Urban air, however, contains numerous initial radical sources. Some oxygenated hydrocarbons are formed in the combustion process, and others are formed when extremely reactive hydrocarbons (like trans-2-butene) are exposed to a background of trace ozone. This process represents one of the sources of "surrogate carbonyl" used in the CBM. Inorganic radical sources are also important in the formation of oxygenated hydrocarbons. Perhaps the most important source for the troposphere is the photolysis of ozone:

$$O_3 + h\upsilon \rightarrow O^1D + O_2 \quad ,$$

$$O^1D + H_2O \rightarrow OH + OH \quad .$$

This process dominates in clean air in which the concentration of hydrocarbons and nitrogen oxides is low.

In urban or industrial areas where the concentration of nitrogen oxides and nitrates is high, nitrous acid (HONO) photolysis can play an important role in smog formation:

$$HONO + h\upsilon \rightarrow H + NO \quad .$$

Nitrous acid, which has been observed in urban air, may be a minor component of automobile exhaust. It can be formed in liquid water droplets (Schwartz and White, 1981) or as part of the denitrification process in vegetation (Anderson et al., 1978).

HONO has been detected in urban air at night near Riverside, California (Platt, et al., 1980) at concentrations of 3 percent to 6 percent of ambient

$NO_2$.· Presumably, HONO is formed in heterogeneous reactions near the emissions source of $NO_x$, in this case automotive exhaust (the sample path in the Riverside study included a section of a freeway). HONO has been observed in direct sampling of auto exhaust under some conditions (Winer, 1981, private communication).

Although total $NO_x$ was not reported in the study of Platt et al., $NO_2$ concentrations are typically one-third of total $NO_x$ in the Los Angeles and San Gabriel basin area (LAAPCD, 1974, Hayes, private communication). This would put emissions of HONO in the range of 1 to 2 percent of total $NO_x$. In our kinetic simulation studies (Whitten et al., 1979; Whitten, Killus, and Hogo, 1980), we have found that one-third of the equilibrium concentration of HONO (calculated from the concentrations of NO, $NO_2$, and water vapor) is generally sufficient to explain initiation phenomena in smog-chamber experiments. For a $NO_2$-to-$NO_x$ ratio of 0.33 and a water vapor concentration of 15,000 ppm, this calculated concentration of HONO equals 1.9 percent--excellent agreement with the atmospheric measurements.

In modeling urban air, one might wish to include the effects of HONO by including the species and specifying its emissions as approximately 2 percent of $NO_x$. However, as mentioned previously, for atmospheric studies the Carbon-Bond Mechanism is usually implemented without the chemistry of HONO. Except for the initiation effects discussed earlier, nitrous acid chemistry has a negligible effect on the calculations.

We have devised a methodology to simulate the effects of HONO emissions by specifying an emission of DCRB, the highly photolytic dicarbonyl species. DCRB has a photolysis rate that is nearly as high as that of HONO. Since the radical yield for DCRB photolysis is twice that of HONO, the emissions rate of DCRB should be only 1 percent that of $NO_x$, one-half the assumed HONO emissions rate. Although DCRB emits peroxyl rather than hydroxyl radicals, the peroxyl radicals are rapidly converted to OH by reaction with NO. The excess NO-to-$NO_2$ conversions produced by this approach amount to only a few percent of total $NO_x$, and the discrepancy in carbon-mass balance is less than 1 percent.

## EMISSIONS OF CARBONYL COMPOUNDS

In addition to their role in the initiation of the smog process, carbonyl compounds are also of major importance to smog chemistry, because a significant fraction of hydrocarbon reactivity* results from the oxidation of carbonyl compounds by the hydroxyl radical. In section 4, when we compared

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* The term "reactivity" has acquired a variety of meanings in smog chemistry. In this context we define it as the oxidative production of peroxyl radicals, a process which then effects a conversion of NO to $NO_2$.

the reactivity rate of an urban air sample with that of a surrogate laboratory smog mixture containing pure hydrocarbons, we found the reactivity rate for the urban air sample to be about 40 percent greater than that of the surrogate. Furthermore, since carbonyls are a principal reaction product of hydrocarbons, a significant fraction of the peroxyl radicals formed in the laboratory hydrocarbon mixture results from the oxidation of carbonyls.

The Carbon-Bond Mechanism is designed to treat explicitly the carbonyl oxidation products of hydrocarbons. However, primary emissions make up a significant fraction of carbonyl compounds, and unless the emissions inventory of such compounds is reasonable, no mechanism, however well designed, will produce acceptable results. Thus, the modeler must have an understanding of the range of plausible values for the carbonyl composition of urban volatile organic compounds.

Dimitriades and Wesson (1972) reviewed available information concerning the relative levels of aldehydes and hydrocarbons found in automobile exhaust. In tests performed by the U.S. Bureau of Mines (Sawicki, Stanley, and Elbert, 1961; Dimitriades and Wesson, 1972), a mole fraction of total aldehyde per mole of hydrocarbon was calculated to range from 0.06 to 0.09. Other studies indicated greater variation, with mole fractions of aldehyde ranging from 0.07 to 0.35 (Oberdorfer, 1967) and from 0.12 to 0.20 (Wadowski and Weaver, 1970). Dimitriades and Wesson (1972) concluded that total aldehyde levels in pre-1970 auto exhaust represented about 10 percent of total hydrocarbon on a molar basis and 5 percent on a carbon basis (the aldehydes being about 60 percent formaldehyde on a molar basis).

Altshuller and McPherson (1963) measured ambient concentrations of formaldehyde and acrolein. Acrolein was found to make up 10 percent to 15 percent of the concentration of formaldehyde, thus indicating the probable importance of carbonyl species other than simple aldehydes. Seizinger and Dimitriades (1972) identified numerous carbonyl compounds in automobile exhaust--notably acrolein, acetone, and the aromatic aldehydes. Although Altshuller and McPherson (1963) did not report aldehydes as a fraction of reactive hydrocarbon, the formaldehyde concentrations observed (0.01 to 0.115 ppm) were consistent with the 5 percent carbon fraction suggested by Dimitriades and Wesson (1972).

In an analysis of monitoring data for the Los Angeles area (Scott Research Laboratories, 1970), Killus et al. (1980) concluded that aldehyde emissions were similar to olefin emissions when calculated on a molar basis. If this assumption is made, the data given in this chapter indicate aldehyde emissions that range from 0.034 to 0.074 as a fraction of emitted reactive carbon.

Data are very sparse for emissions from vehicles having pollution-control devices. However, in a review of recent data, Bulon, Malko, and Taback (1978) found no major differences in the formaldehyde emissions from controlled and uncontrolled vehicles. Reported emission levels were fairly low in these studies: approximately 2 to 3 percent of total RHC. Note that total aldehyde emissions would be expected to be higher and total carbonyls higher still.

The preceding analysis provides an outline of plausible carbonyl emissions in an urban emissions inventory. Formaldehyde emissions alone account for perhaps 2 to 6 percent of the carbon emitted in automobile exhaust; however, formaldehyde would account for only 1 to 4 percent of total emitted reactive carbon, since other emission processes (e.g., evaporation) seldom emit aldehydes per se.

Adding other aldehydes to formaldehyde increases our estimate of carbonyl emissions by approximately 50 percent (since formaldehyde represents 60 percent of aldehyde emissions on a molar basis). The addition of other carbonyl compounds (e.g., acetone, acrolein, and benzaldehyde) increases the carbonyl emissions rate still further, to perhaps twice that of emitted formaldehyde. Finally, surrogate carbonyl in the CBM accounts for perhaps 2 percent of emitted carbon.

In the CBM, carbonyl emissions as a fraction of total reactive carbon emissions would be expected to represent a minimum of 5 percent, which is in agreement with the assumptions used in other mechanisms (e.g., EKMA). Total aldehyde emissions could be as high as 7 percent and total carbonyls as high as 10 percent of reactive carbon (on the basis of reactivity differentials between urban air and laboratory surrogate mixes) [see example 2, section 4]. With the onset of photochemical smog formation, the carbonyl fraction increases because of oxidation of reactive hydrocarbons to aldehydes, ketones, glyoxals, and so forth. This process eventually reaches a photochemical equilibrium in which carbonyl carbon can represent as much as 25 percent of reactive carbon.

## SUMMARY OF URBAN HYDROCARBON COMPOSITION

In this section we have presented a variety of hydrocarbon-composition data reported in carbon-bond units. Since the CBM allows for easy inventory of emissions, ambient data, and modeled concentrations, the ranges of composition data can be used to ascertain whether a particular modeling study is employing a realistic hydrocarbon composition. Ranges are presented in table 17, and a recommended composition is indicated for those studies in which detailed species data are lacking.

TABLE 17. RANGES OF URBAN HYDROCARBON COMPOSITION

(Fractions Normalized to RHC)

| | Carbon Fraction | |
|---|---|---|
| Compound | Range | Recommended |
| ETH | 0.03 → 0.12 | 0.05 |
| OLE | 0.02 → 0.06 | 0.03 |
| ARO | 0.10 → 0.33 | 0.22 |
| PAR | 0.55 → 0.80 | 0.65 |
| CARB* | 0.03 → 0.11 | 0.05 |

* Includes surrogate carbonyl from internal olefins and cyclic paraffins.

# SECTION 6

# SUMMARY

The original publication of the Carbon-Bond Mechanism (CBM-1, given in Whitten, Hogo, and Killus, 1980) introduced the concept of treating the atmospheric chemistry of complex mixtures of organic molecules as if the carbon atoms reacted more or less independently according to their local bonding. Since that introduction, the mechanism has undergone two major updates, and considerable experience with its use in atmospheric models has shown that proper use of the mechanism is essential to produce good results. This report presents the latest version of the Carbon-Bond Mechanism (CBM-III) in section 1, followed by a guide to using virtually any version of the CBM in section 2. In section 3, which also concerns the use of the CBM, specific urban reactivities are illustrated and a recommended set of CBM fractions to represent urban organics is developed for cases where data are lacking (table 17).

The latest CBM update, given in section 1, is mainly concerned with the chemistry of aromatics. Dicarbonyl compounds and nitroaromatic compounds have been shown to play a significant role in the smog chemistry of aromatics. Reactions have therefore been introduced into CBM-III to account for similar reactions identified in the detailed or explicit chemistry of aromatics, especially toluene. The CBM update also includes changes in several rate constants to reflect recent independent measurements and evaluations. Finally, some minor changes in handling ketones have been introduced.

Section 2 explains how the CBM shows key advantages over other mechanisms in actual use. For instance, the averaging of molecular weights is eliminated; carbon conservation is automatic; reactivity averaging is often done over a narrow range; molecules with various functional groups can be handled in a straightforward manner; and the CBM concept tends to work best for complex mixtures, although adjustments can be made to treat individual hydrocarbons. Important principles relating to successful applications of the CBM are also discussed. Some of these principles are the accounting of all reactive carbon, the volumetric equivalence between CBM units and molecular concentrations of certain species, and the surrogate nature of the CBM carbonyl species. Examples of converting specific molecular information into CBM speciation are then presented.

Section 3 has been included to show how proper speciation can be developed for several urban areas. Although the CBM has been formulated to respond correctly to changes in reactivities, this sensitivity can lead to incorrect results if the CBM is improperly utilized. In particular, the CBM is very sensitive to carbonyl levels. A review of some available data is presented. Finally, a set of CBM fractions representative of typical urban reactivity is presented for use in the absence of speciation data. If speciation data appear to give quite different CBM fractions than this representative set, then the data should be checked to ensure that the differences can be explained.

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# Appendix A

## VALIDATION SIMULATIONS FOR CARBON-BOND MECHANISM III

### UNIVERSITY OF CALIFORNIA AT RIVERSIDE--SEVEN COMPONENT RUNS

One of the requirements of a kinetic mechanism is that it respond appropriately to changes in hydrocarbon composition. Three different hydrocarbon mixtures containing varying amounts of olefins, paraffins, and aromatics were used in the eleven modeling experiments performed at UCR (see table A-1). As can be seen from the simulation results shown in figures A-1 through A-11, CBM-III gives reasonable results for all three mixtures of hydrocarbons.

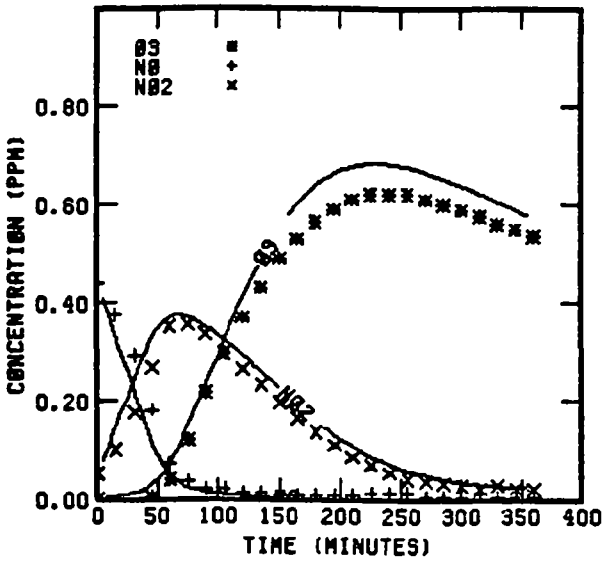
Simulations more accurate than those we have presented can be achieved by adapting CBM-III to the specific hydrocarbons in these experiments rather than using the default values for various rate constants. For example, the mixture of butane and 2,3-dimethylbutane in the paraffin component has an average reaction rate with OH of approximately 1100 $ppm^{-1}min^{-1}$, which is lower than the default value of 1300 $ppm^{-1}min^{-1}$. Similarly, the default speciation of CARB in CBM-III is one-half formaldehyde, one-quarter higher aldehydes, and one-quarter ketones. The actual measured carbonyl compositions in these experiments varied from these ratios.

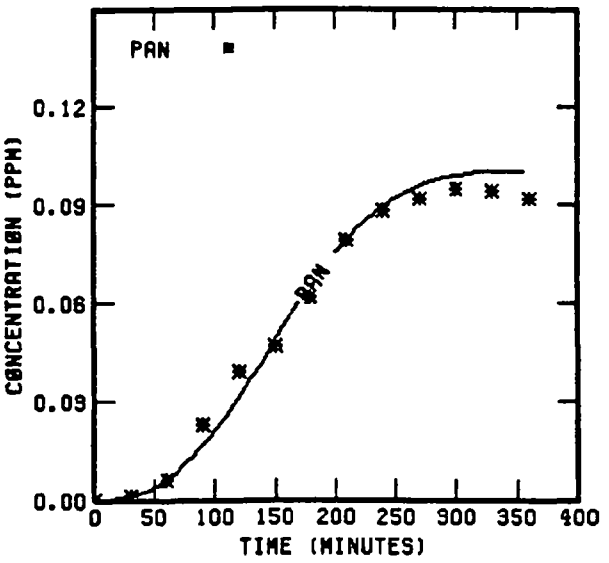
The only variable factor for each experiment was the initial concentration of HONO that was assumed to be formed when the chamber was loaded with $NO_x$. These concentrations are given in table A-1. Initial HONO varies from 0 to 12 ppb. The maximum HONO used is 2.5 percent of $NO_x$, which is similar to the ratios of HONO to $NO_2$ that have been observed in the atmosphere (Platt et al., 1979).

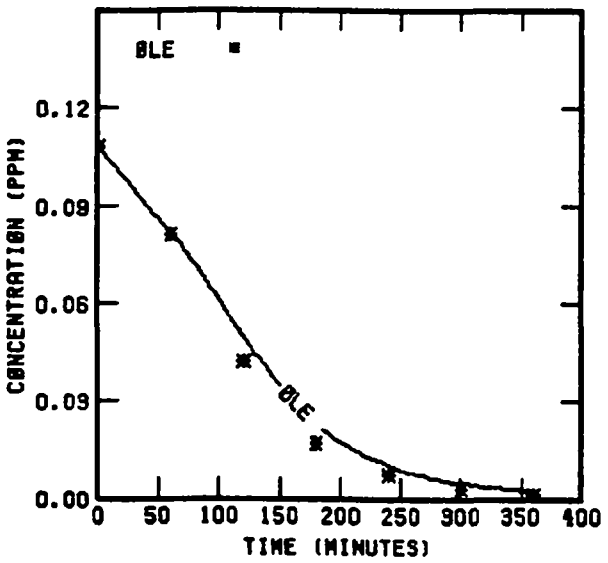
TABLE A-1. INITIAL CONDITIONS AND REACTIVITY DATA FOR SEVEN HYDROCARBON/$NO_x$ EXPERIMENTS

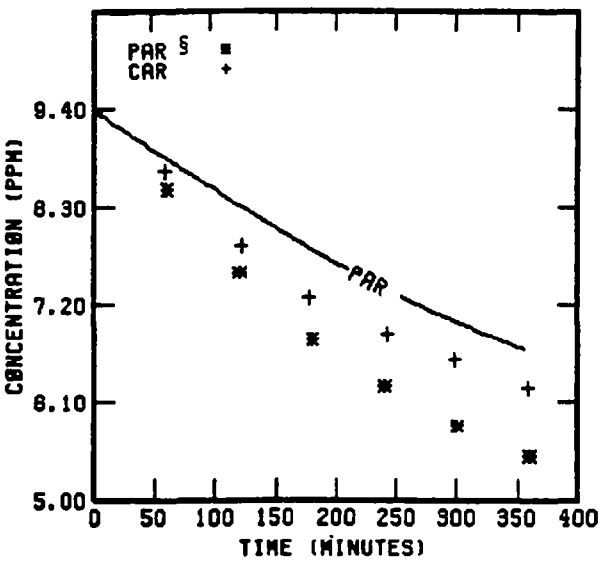
| | Concentration (ppm) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| EC Run No. | 231 | 232 | 233 | 237 | 238 | 241 | 242 | 243 | 245 | 246 | 247 |
| EPA Run No. | 4 | 1 | 2 | 4 | 3 | 5 | 7 | 7A | 6 | 1 | 8 |
| Mixture | B | A | A | B | B | B | C | | C | A | C |
| **Reactant** | | | | | | | | | | | |
| Ethene | 1.051 | 0.258 | 0.260 | 0.875 | 0.982 | 0.484 | 2.014 | 1.939 | 2.055 | 0.253 | 1.025 |
| Propene | 0.108 | 0.051 | 0.051 | 0.100 | 0.093 | 0.045 | 0.109 | 0.109 | 0.104 | 0.049 | 0.054 |
| trans-2-Butene* | 0.055 | 0.026 | 0.025 | 0.050 | 0.047 | 0.024 | 0.108 | 0.110 | 0.102 | 0.026 | 0.053 |
| n-Butane | 1.130 | 1.102 | 1.085 | 1.025 | 0.966 | 0.464 | 0.558 | 0.568 | 0.534 | 1.058 | 0.273 |
| 2,3-Dimethylbutane | 0.715 | 0.612 | 0.648 | 0.463 | 0.420 | 0.211 | 0.203 | 0.084 | 0.185 | 0.538 | 0.080 |
| Toluene | 0.121 | 0.032 | 0.034 | 0.086 | 0.083 | 0.040 | 0.306 | 0.155 | 0.321 | 0.023 | 0.145 |
| m-Xylene | 0.108 | 0.029 | 0.033 | 0.091 | 0.084 | 0.044 | 0.306 | 0.154 | 0.317 | 0.023 | 0.145 |
| Total HC (ppmC) | 13.17 | 9.31 | 9.50 | 10.46 | 10.07 | 4.95 | 12.82 | 9.74 | 12.86 | 8.56 | 6.17 |
| NO | 0.440 | 0.469 | 0.096 | 0.377 | 0.718 | 0.379 | 0.377 | 0.386 | 0.743 | 0.386 | 0.380 |
| $NO_2$ | 0.052 | 0.024 | 0.007 | 0.106 | 0.234 | 0.110 | 0.125 | 0.114 | 0.259 | 0.122 | 0.125 |
| $NO_x$ | 0.492 | 0.492 | 0.103 | 0.483 | 0.952 | 0.489 | 0.503 | 0.502 | 0.992 | 0.506 | 0.505 |
| HONO | 0.006 | 0.004 | 0.004 | 0.008 | 0.010 | 0.008 | 0.010 | 0.010 | 0.020 | 0.012 | 0.010 |
| HCHO | 0.020 | 0.009 | 0.004 | 0.0 | 0.026 | 0.018 | 0.028 | 0.0 | 0.016 | 0.000 | 0.003 |
| **Reactivity** | | | | | | | | | | | |
| $NO_2$ max (ppm) | 0.357 | 0.333 | 0.071 | 0.368 | 0.663 | 0.351 | 0.400 | 0.394 | 0.752 | 0.366 | 0.369 |
| at time (min) | 75 | 150-165 | 30-45 | 60 | 120 | 135 | 30 | 30 | 60 | 135 | 60 |
| $O_3$ max (ppm) | 0.623 | -- | 0.330 | 0.655 | 0.692 | -- | 0.682 | 0.716 | 0.892 | 0.574 | 0.657 |
| at time (min) | 225-255 | -- | 240-345 | 240 | 435 | -- | 105 | 135 | 180 | 570 | 210-240 |
| 6-hr $O_3$ (ppm) | 0.540 | 0.305 | 0.325 | 0.584 | 0.674 | 0.408 | 0.418 | 0.711 | 0.635 | 0.374 | -- |
| PAN max (ppm) | 0.095 | -- | 0.307 | 0.100 | 0.113 | -- | 0.140 | 0.100 | 0.194 | 0.070 | 0.106 |
| at time (min) | 270-330 | -- | 300 | 300 | 495 | -- | 180 | 135-150 | 240 | 570 | 300 |
| 6-hr PAN (ppm) | 0.092 | 0.040 | 0.036 | 0.098 | 0.084 | 0.047 | 0.111 | 0.100 | 0.162 | 0.041 | -- |
| **Physical Parameters (Averages)** | | | | | | | | | | | |
| Temperature (°F) | 85.3 | 85.3 | 85.0 | 86.2 | 86.8 | 86.5 | 86.0 | 85.0 | 86.3 | 86.5 | 86.4 |
| RH (%) | 42.5 | 54.0 | 53.0 | 57.0 | 59.5 | 50.5 | 60.5 | 54.5 | 50.5 | 53.0 | 54.0 |
| Radiometer (mv) | 0.23 | 0.23 | 0.23 | 0.23 | 0.23 | 0.23 | 0.23 | 0.23 | 0.23 | 0.23 | 0.23 |

* In the Carbon-Bond Mechanism, internal olefins are treated as two carbonyl groups, i.e., their reaction times are asumed to be instantaneously fast.



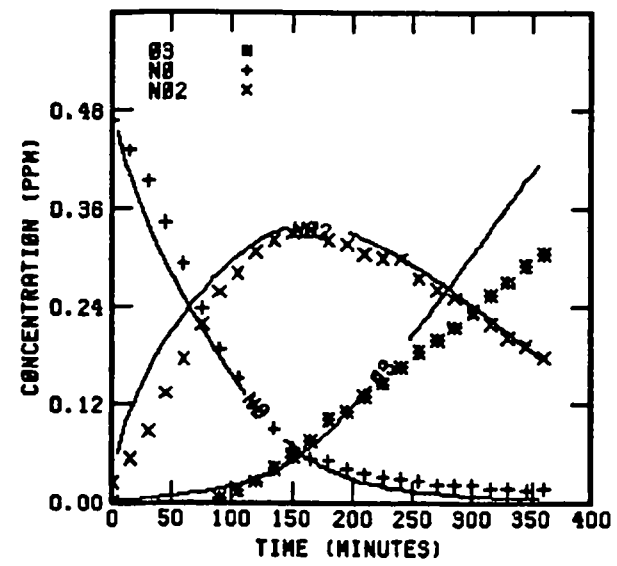



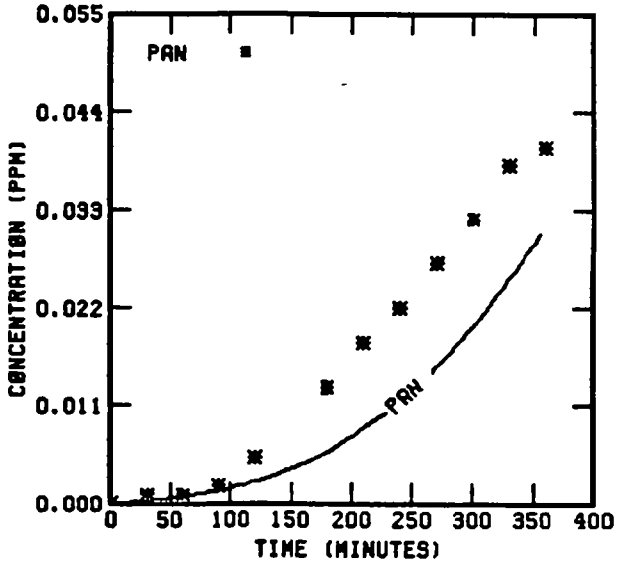



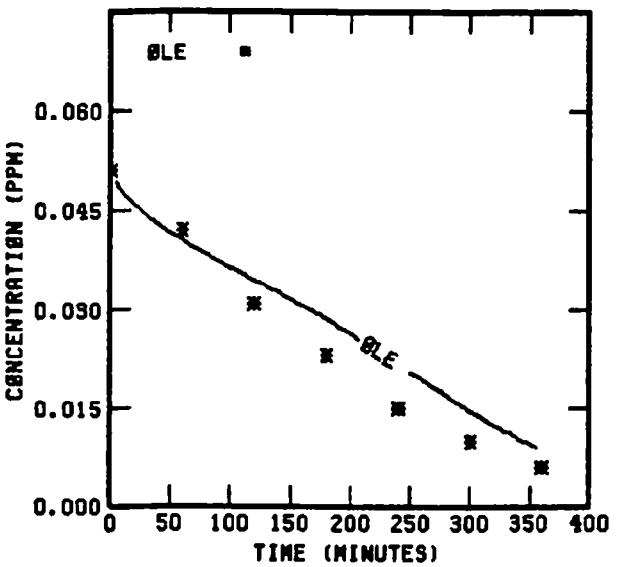



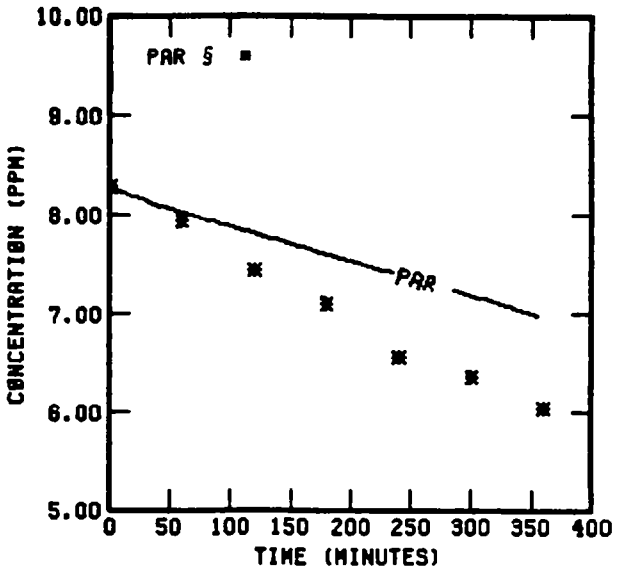

§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

Figure A-1. Simulation results for EC-231.



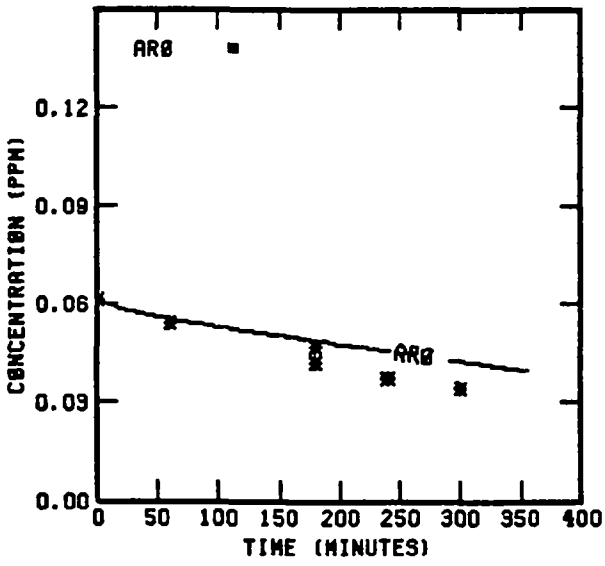



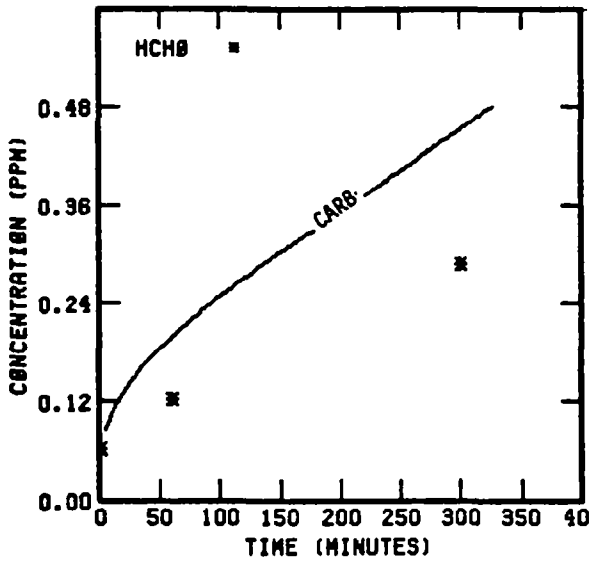




§ Paraffins only.

Figure A-2. Simulation results for EC-232.



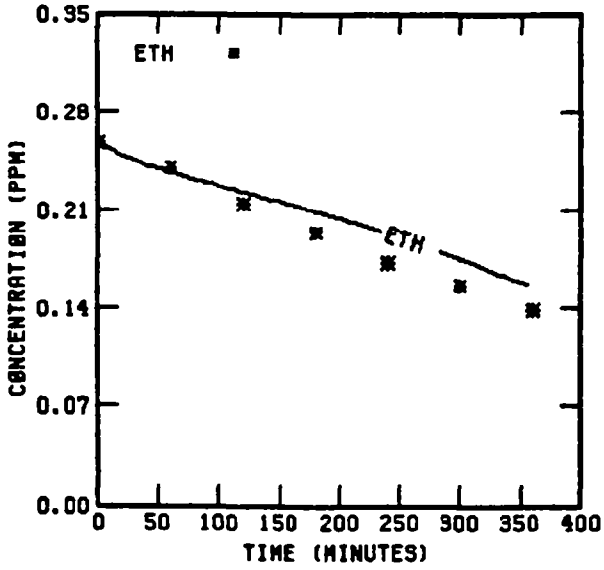
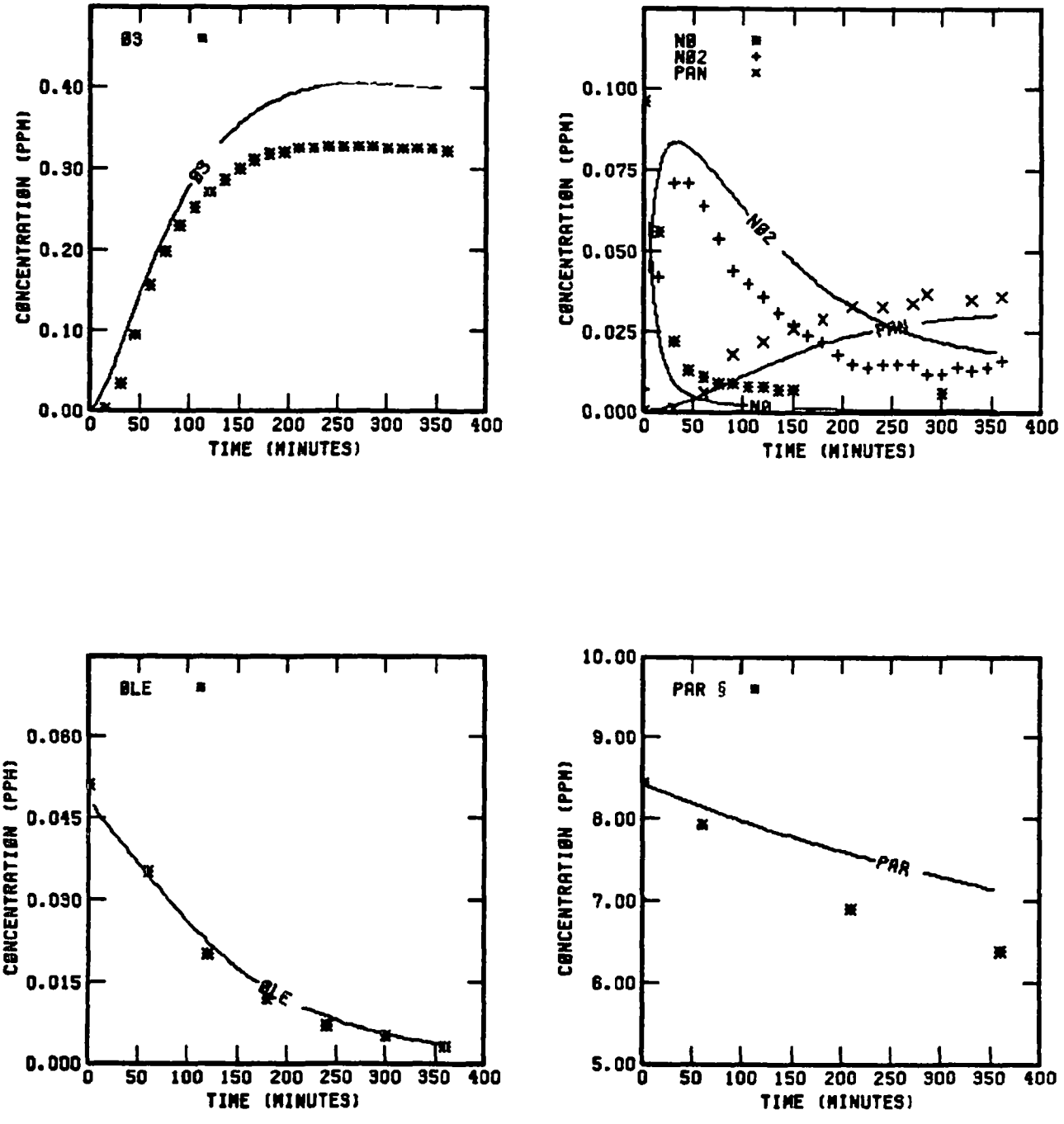
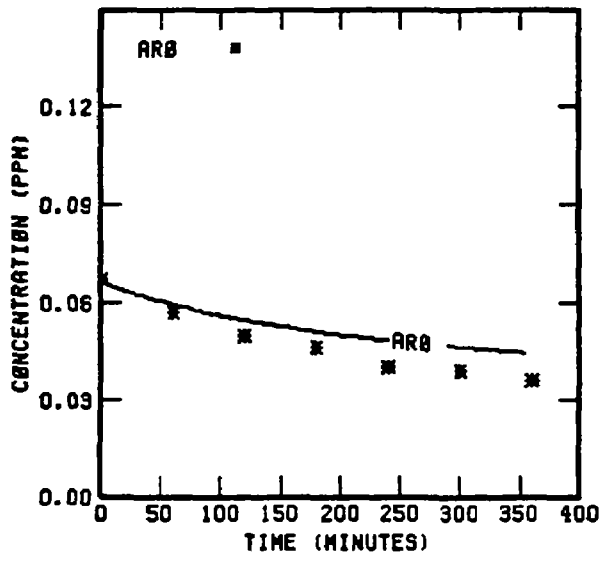



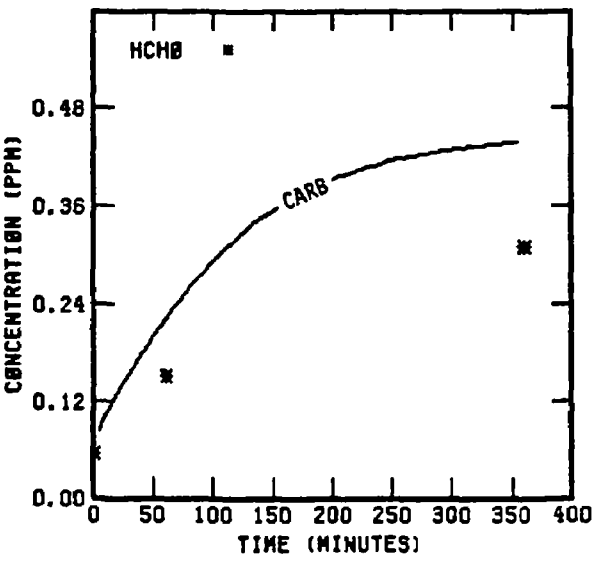

Figure A-2. (concluded)




§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

Figure A-3. Simulation results for EC-233.



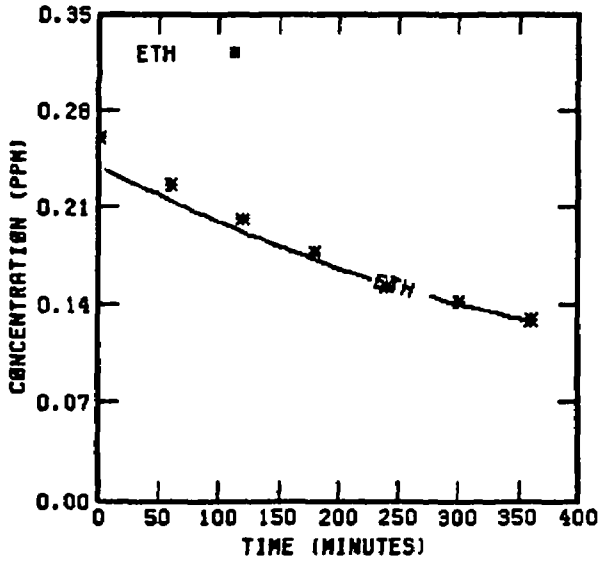
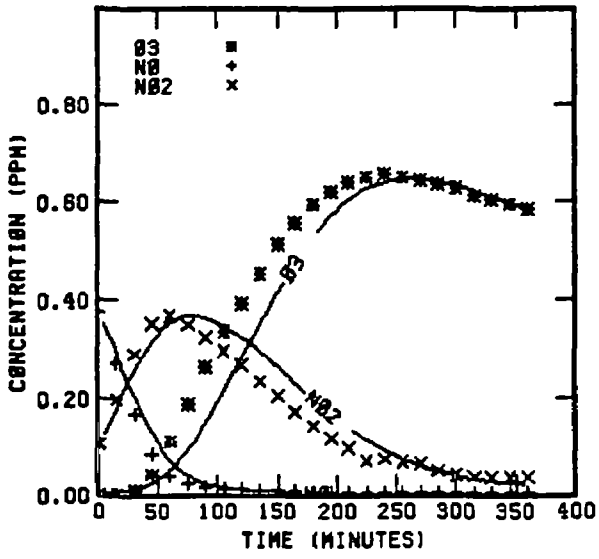
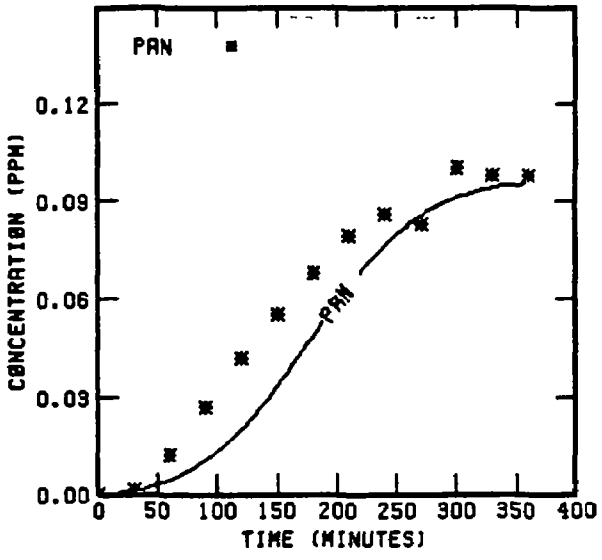
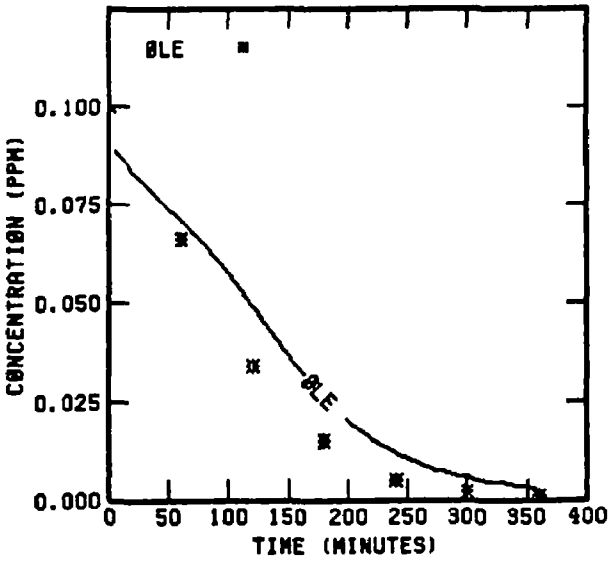
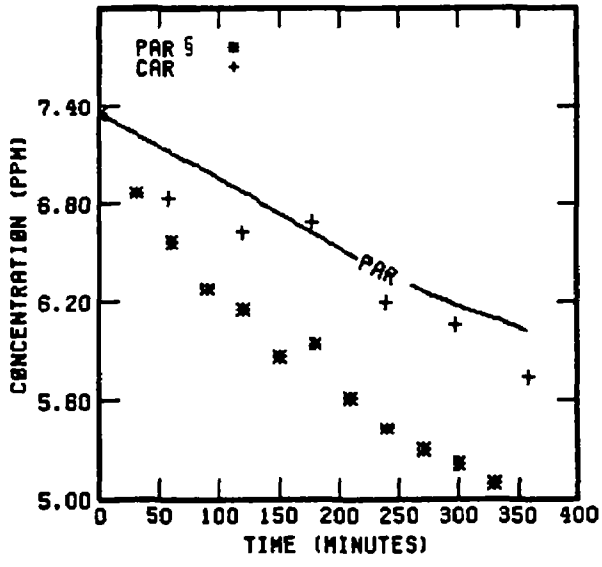




Figure A-3. (concluded)



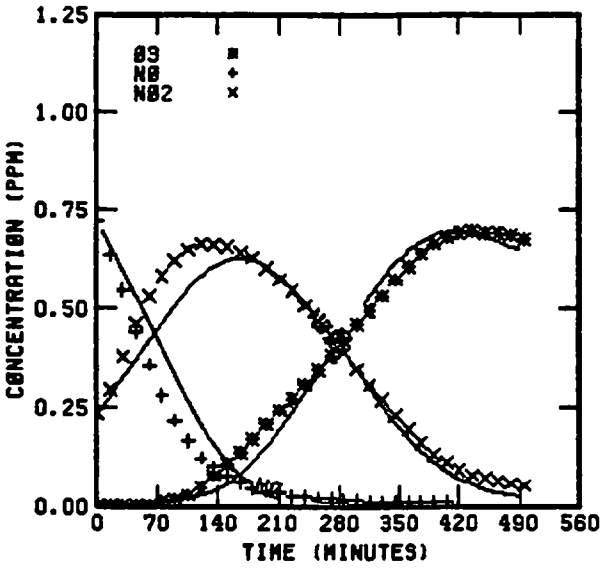



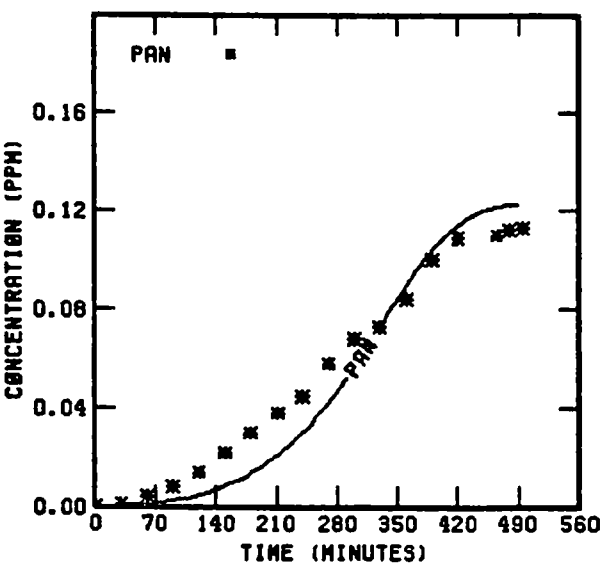



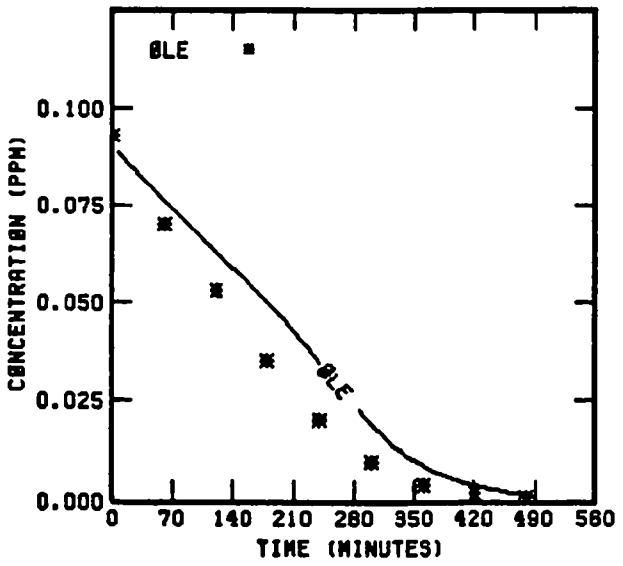



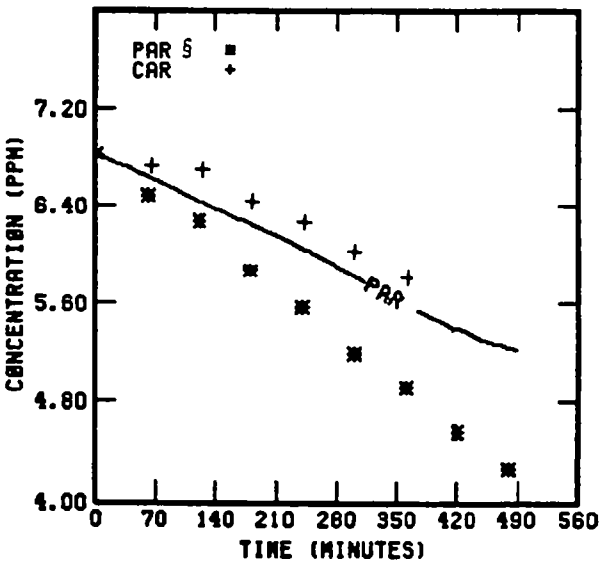

§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

Figure A-4. Simulation results for EC-237.



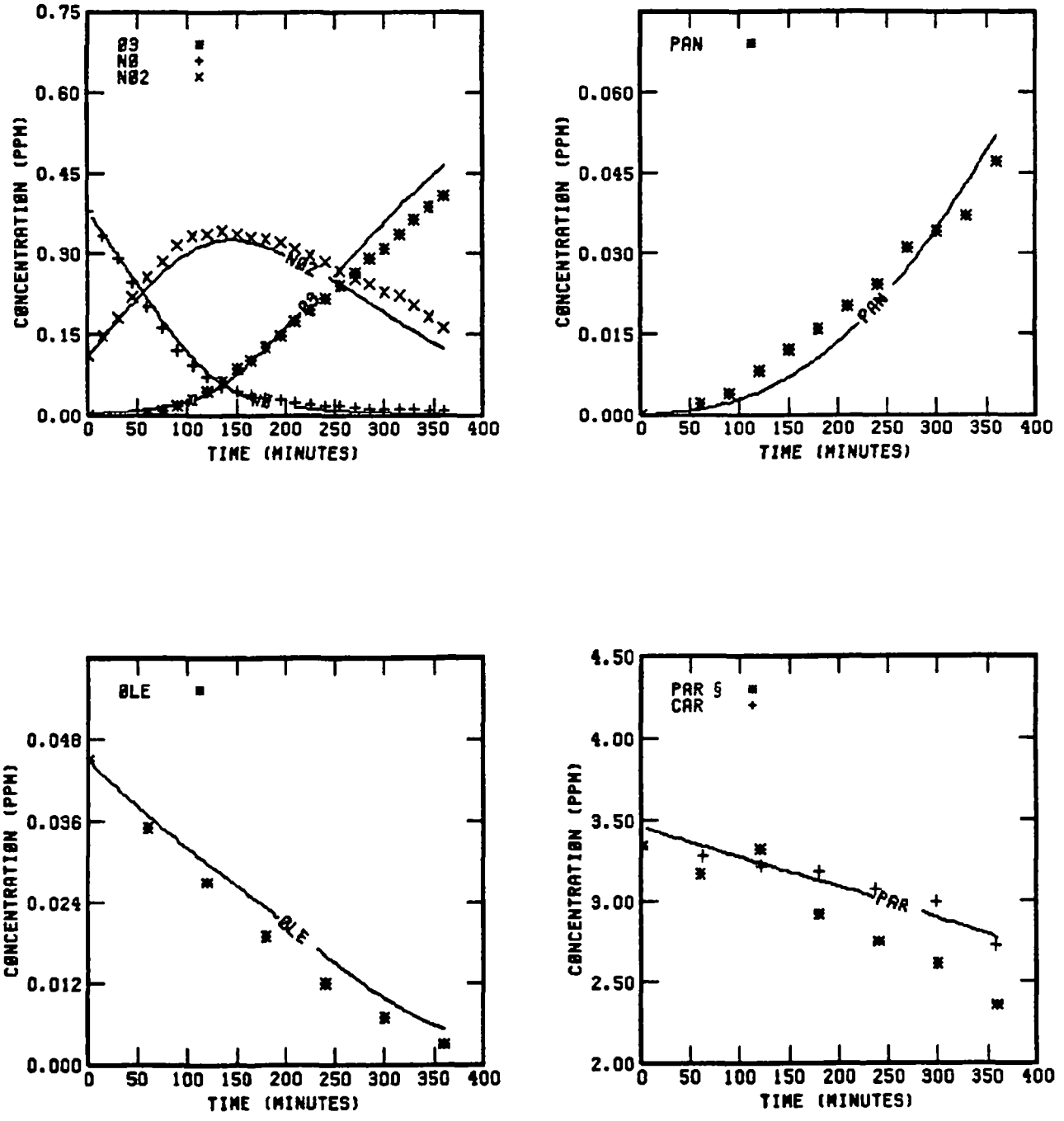



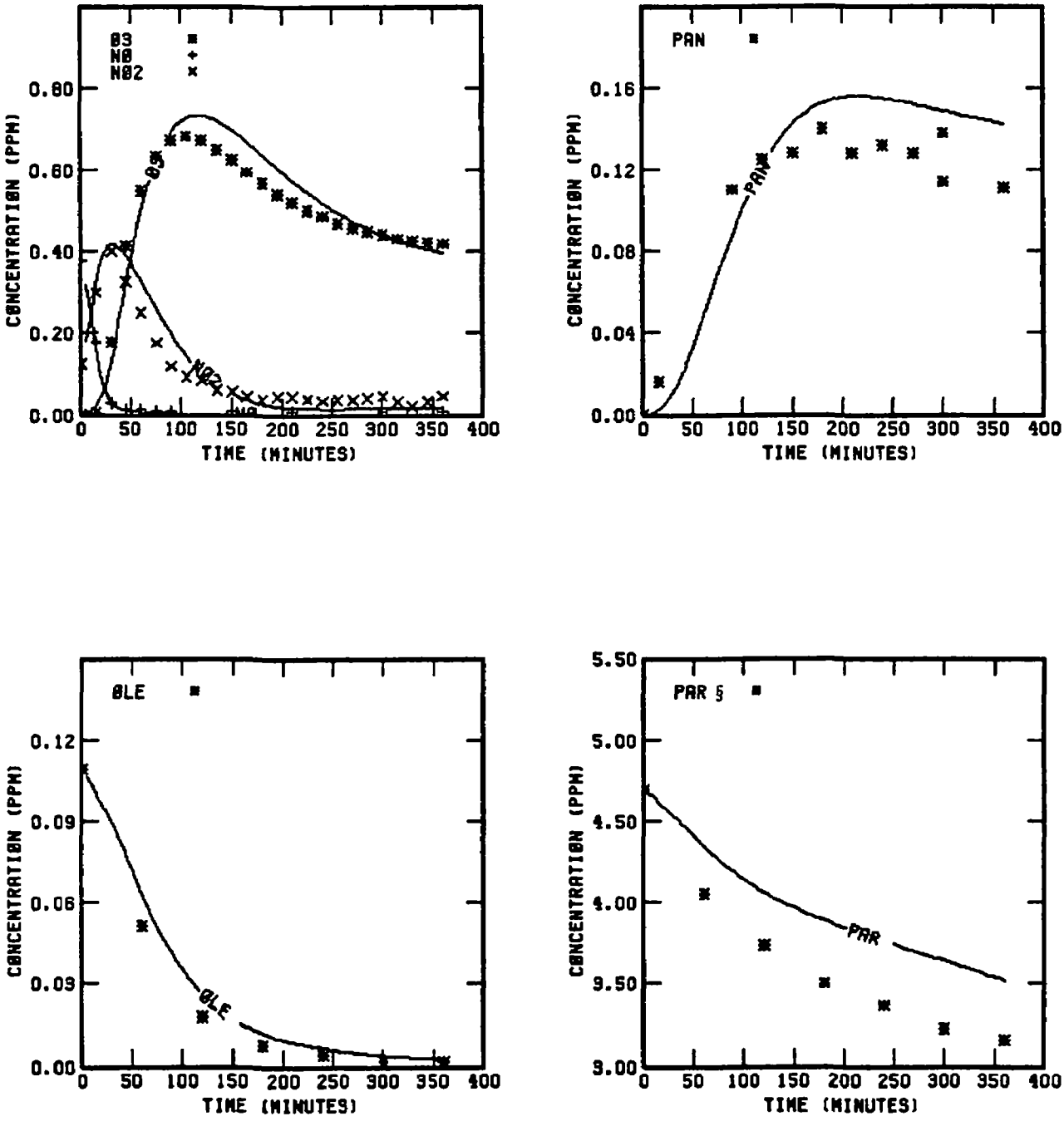

§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

Figure A-5. Simulation results for EC-238.



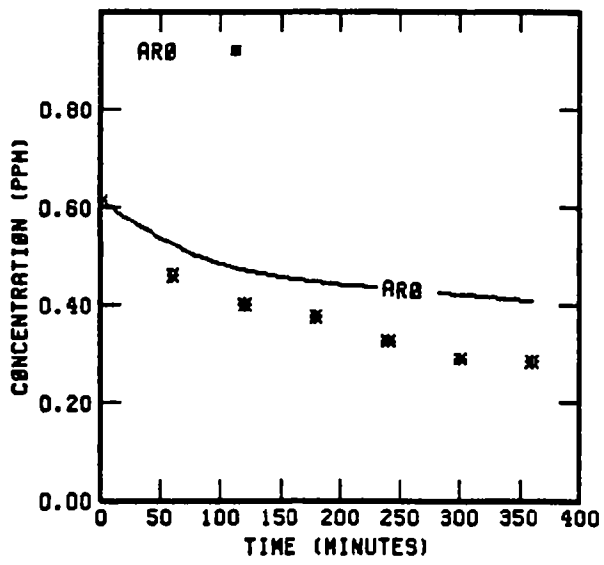

§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

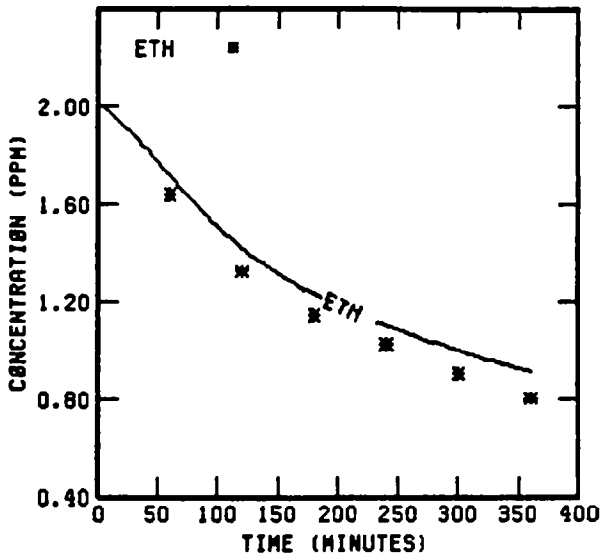
Figure A-6. Simulation results for EC-241.




§Paraffins only.

Figure A-7. Simulation results for EC-242.



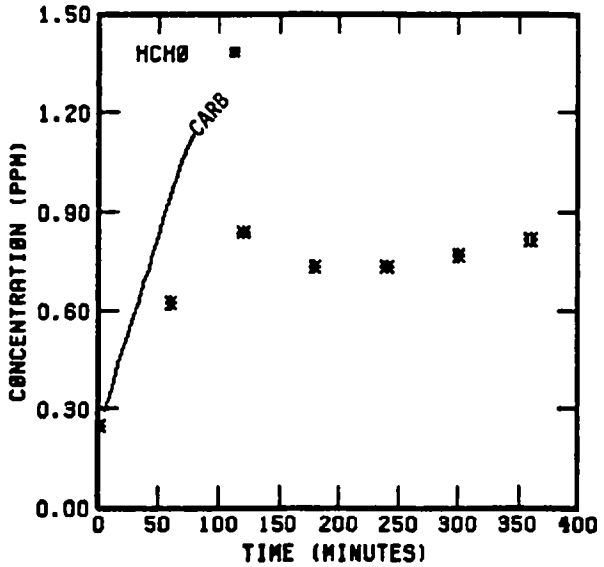
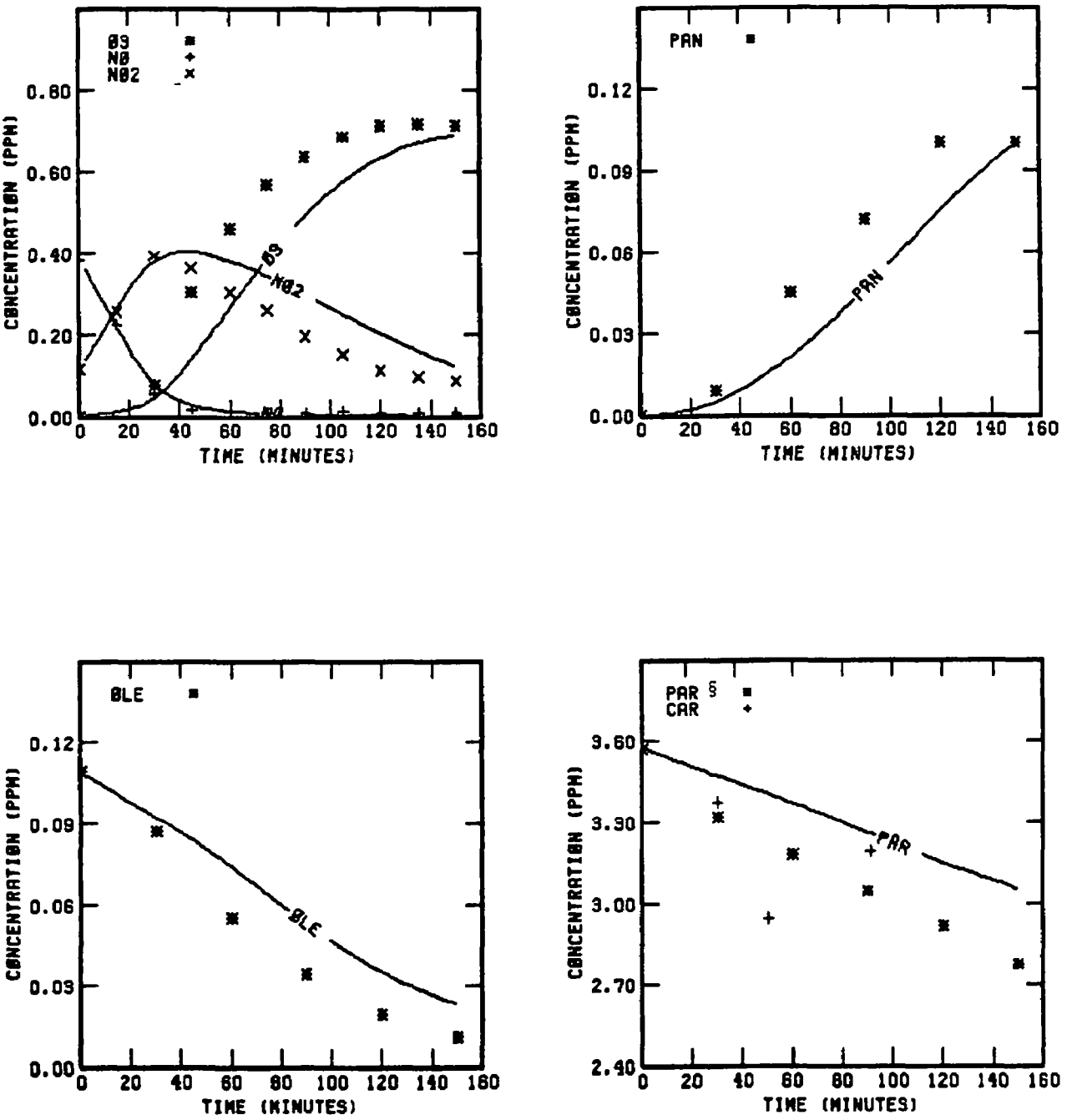
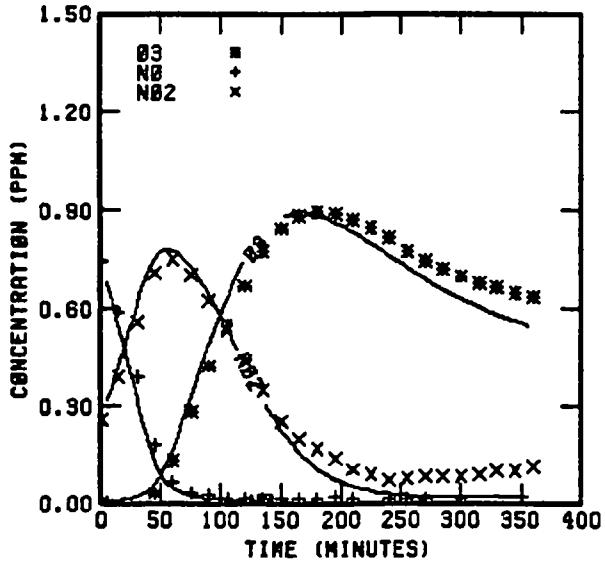



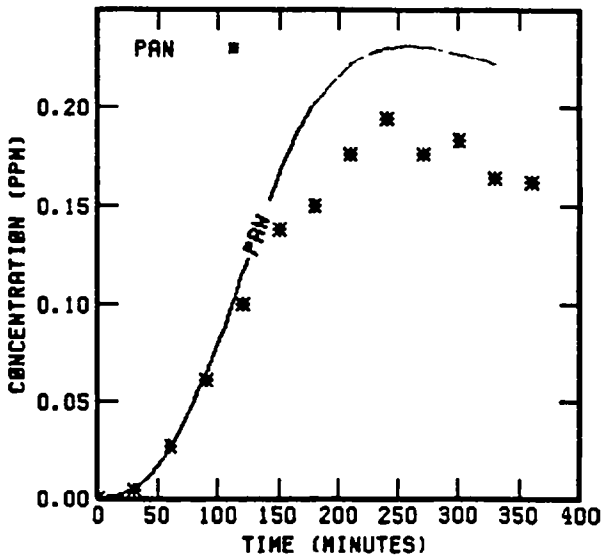

Figure A-7. (concluded)

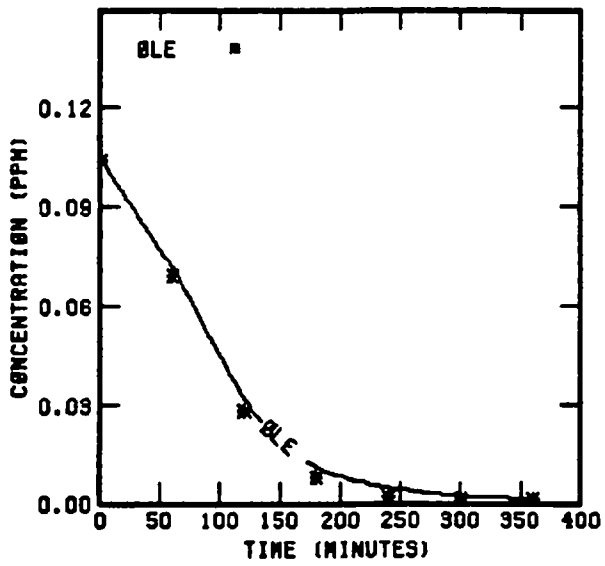


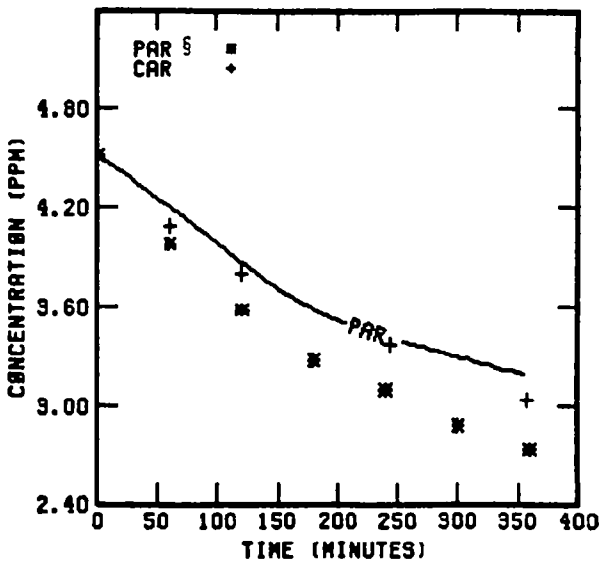

§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

Figure A-8. Simulation results for EC-243.



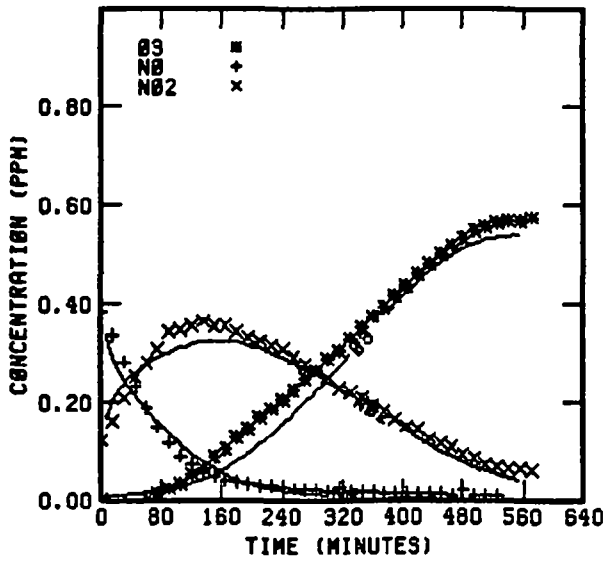



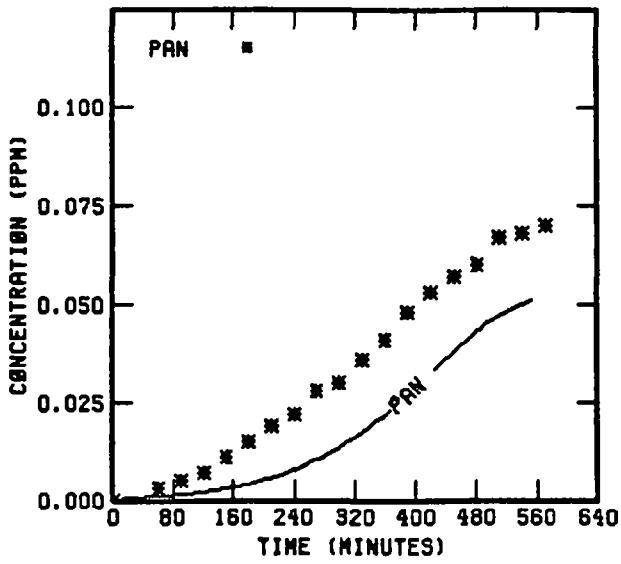



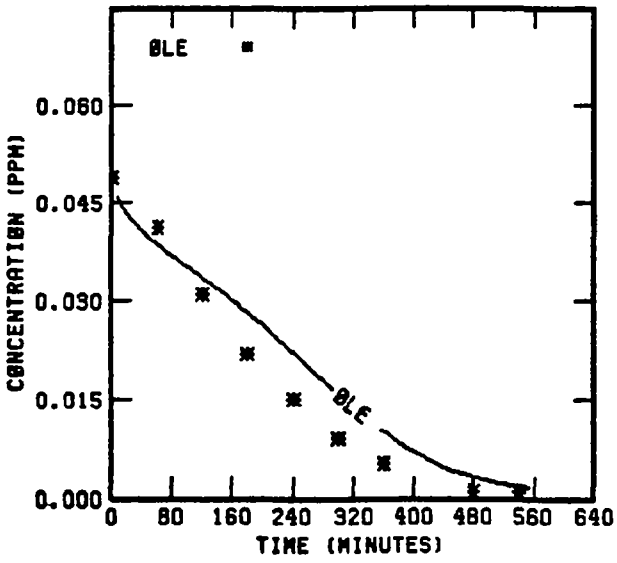



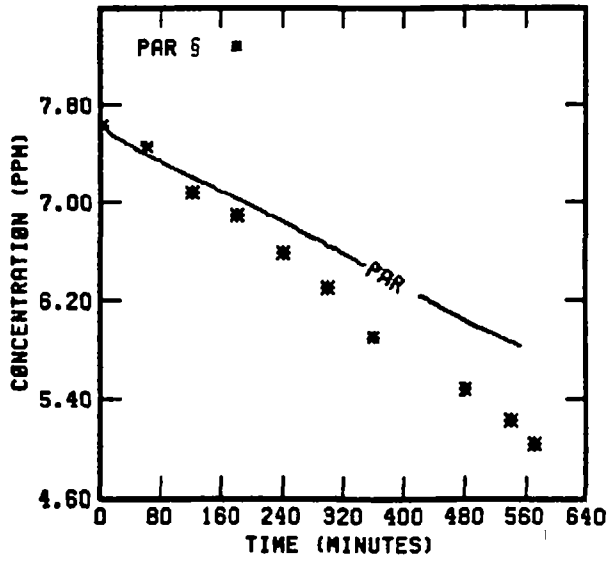

§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

Figure A-9. Simulation results for EC-245.



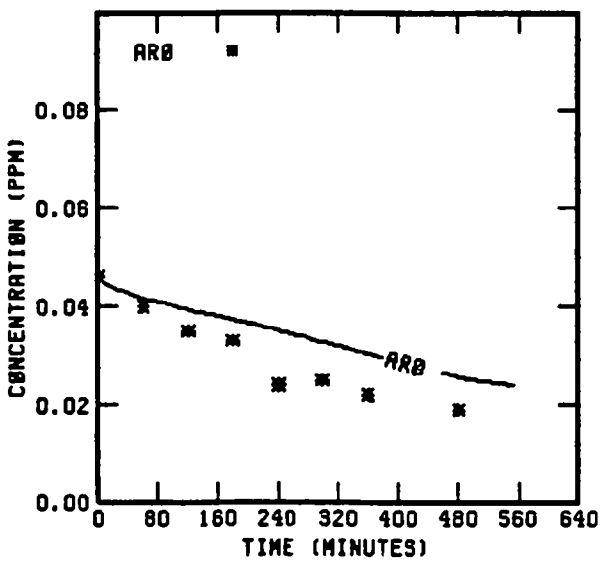



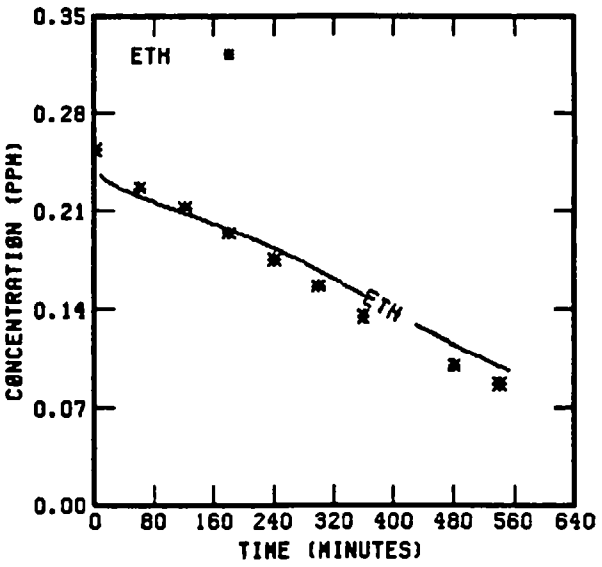




§ Paraffins only.

Figure A-10. Simulation results for EC-246.



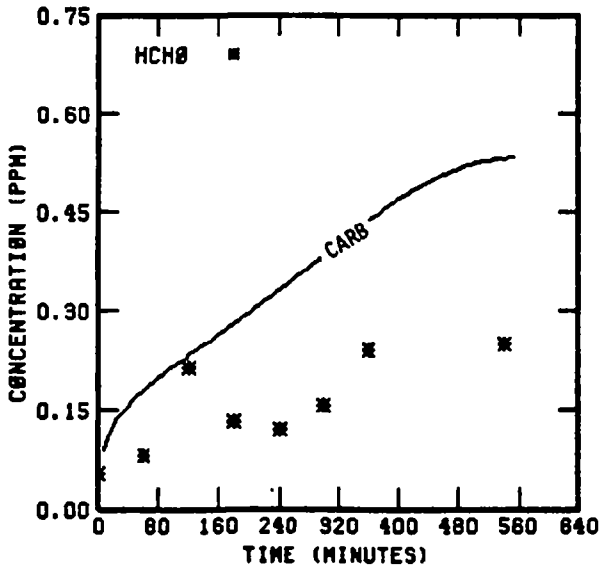
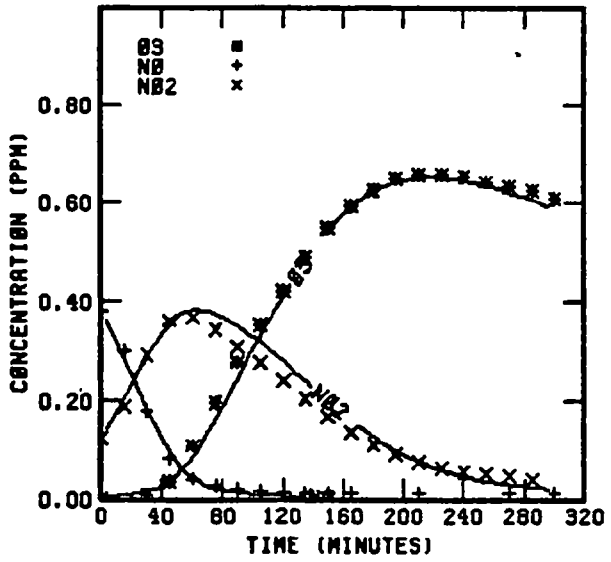
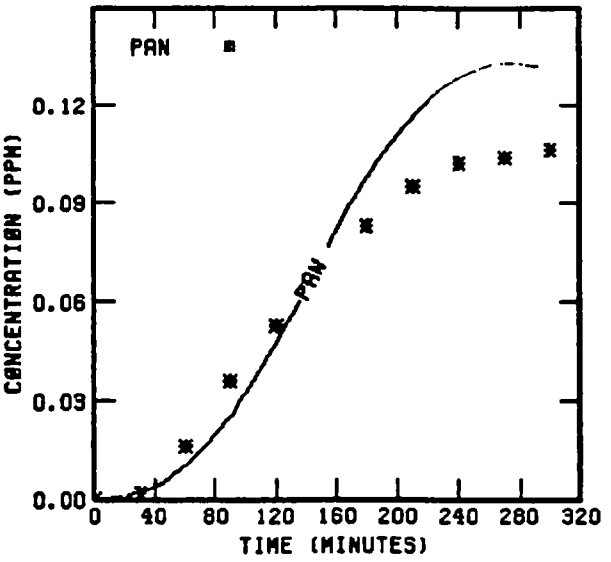
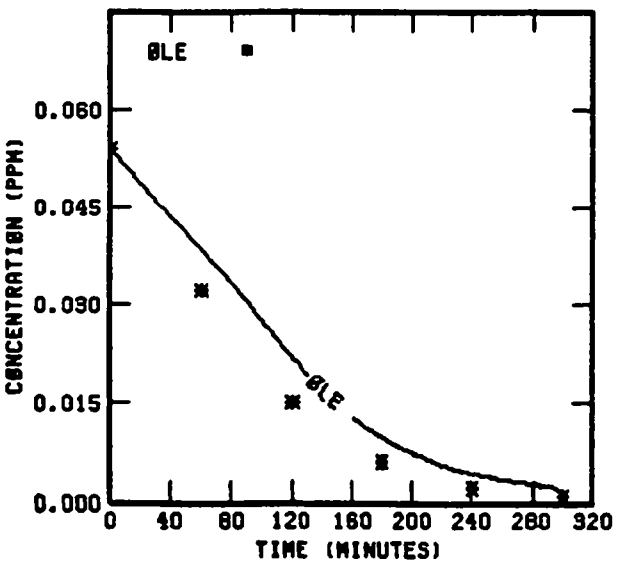
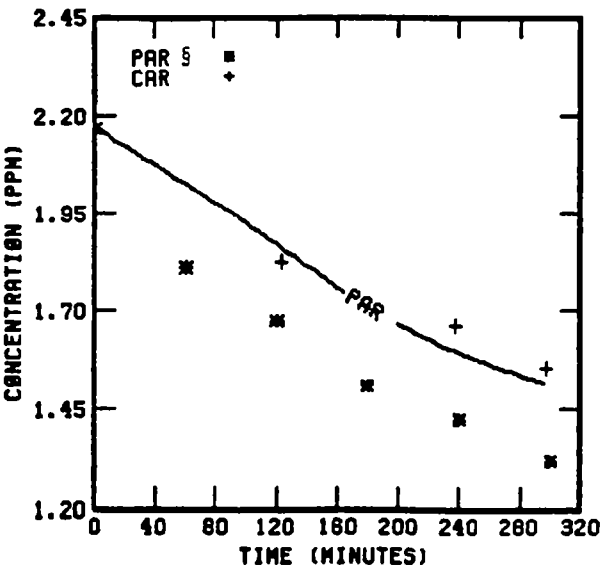




Figure A-10. (concluded)




§ Low concentrations include paraffins only; high concentrations include all measured single-bonded carbon.

Figure A-11. Simulation results for EC-247.

The chamber-dependent reactions used in these simulations are

$$O_3 \text{ and } NO_2 \text{ loss to walls} = 0.0016 \text{ min}^{-1}$$
$$k_{12} = 0.0017 \text{ min}^{-1}$$
$$NO_2 \text{ emission from walls} = 0.1 \text{ ppb min}^{-1}$$

Photolysis rates are

$$k_1 = 0.3 \text{ min}^{-1}$$
$$k_{37} = 2.7 \times 10^{-4} \text{ min}^{-1}$$
$$k_{38} = 5.4 \times 10^{-4} \text{ min}^{-1}$$
$$k_{67} = 0.0135$$
$$k_{78} = 1 \times 10^{-4} \text{ min}^{-1}.$$

UNIVERSITY OF NORTH CAROLINA OUTDOOR SMOG-CHAMBER EXPERIMENT
(URBAN MIX; TWO-DAY SIMULATION)

The UNC two-day, urban-mix experiment has been previously simulated with CBM-I (Whitten, Hogo, and Killus, 1980). The hydrocarbon mix used contained no aromatics (see table A-2). CBM-III gives results that are comparable to those of CBM-I for mixtures containing olefins and paraffins only (see figure A-12).

Rural North Carolina air is used in the UNC chamber experiments. Background reactivity for the air and chamber is simulated by the following reactions:

$NO_2$ offgassing from walls: $5 \times 10^{-4} \times k_1$

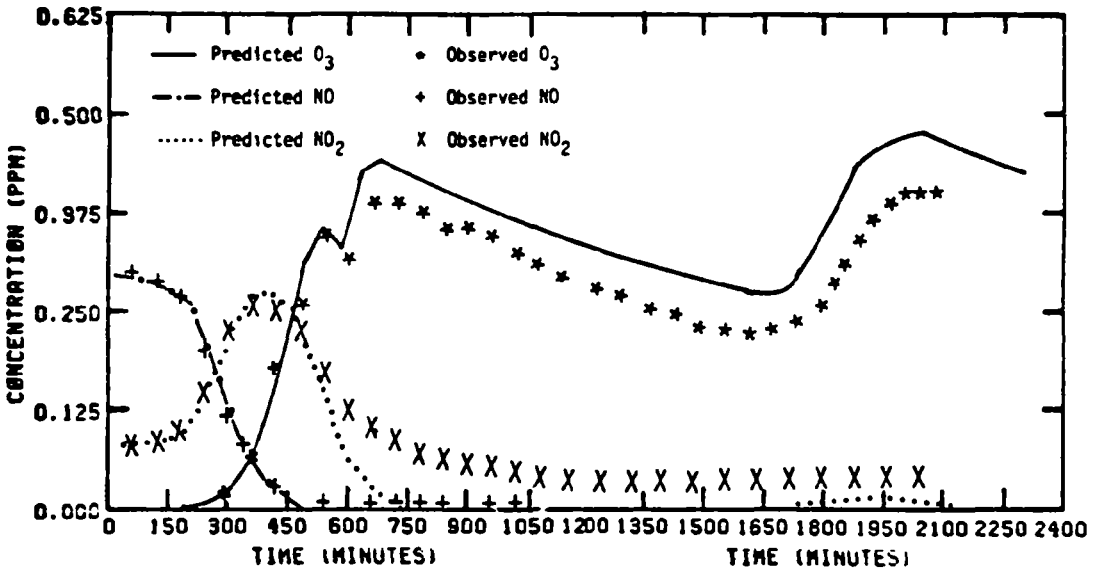
Background reactivity: $OH + MEO_2$ $1000 \text{ ppm}^{-1}\text{min}^{-1}$

$HO_2$ production $1.5 \times 10^{-4} k_1$ .

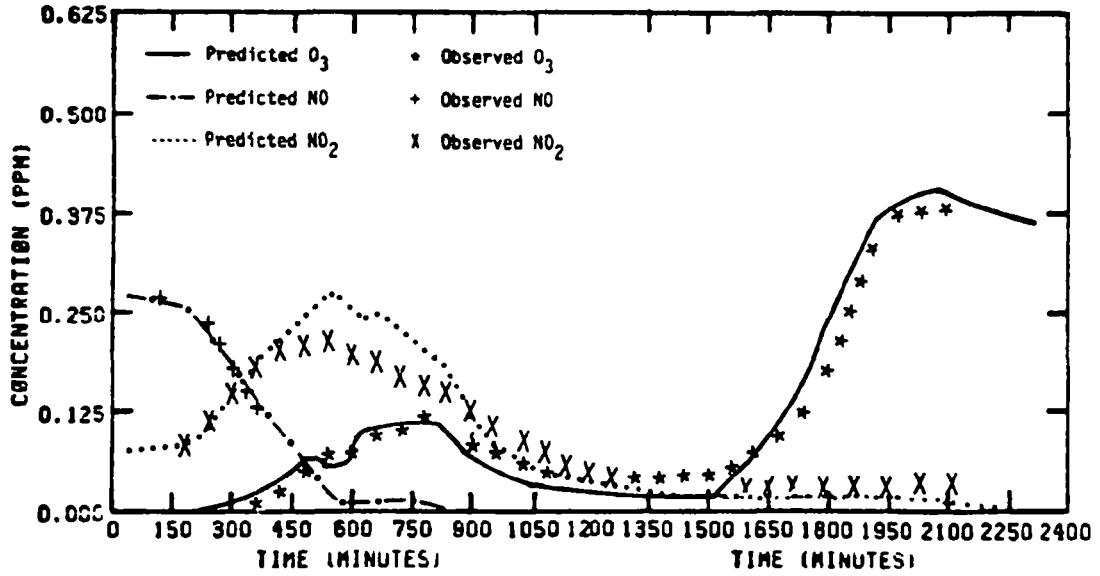
These background reactivity reactions correspond to a hydrocarbon level of about 0.3 ppmC of reactive hydrocarbon and 0.05 ppm formaldehyde. This background reactivity is derived from UNC experiments performed with $NO_x$ added but without added hydrocarbons. Both sides of the chamber were assumed to have an initial condition of 7 ppb HONO.

TABLE A-2. SIMULATED URBAN HYDROCARBON MIXTURE

| Class/Compound | Relative Concentration (ppm) | Relative Concentration (ppmC) | Mole Fraction |
|---|---|---|---|
| Acetylenic | | | |
| Acetylene | 265 | 530 | 0.171 |
| Subtotal | 265 | 530 | 0.171 |
| Paraffins | | | |
| Isopentane | 172 | 860 | 0.111 |
| n-Pentane | 286 | 1430 | 0.184 |
| 2-Methyl pentane | 85 | 510 | 0.055 |
| 2,4-Dimethyl pentane | 69 | 483 | 0.044 |
| 2,2,4-Trimethylene pentane | 76 | 608 | 0.049 |
| Subtotal | 688 | 3891 | 0.444 |
| Average carbon number = 5.7 | | | |
| Olefins | | | |
| Butene-1 | 40 | 160 | 0.026 |
| cis-2-Butene | 43 | 172 | 0.028 |
| 2-Methyl-1-butene | 26 | 130 | 0.017 |
| 2-Methyl-2-butene | 32 | 160 | 0.021 |
| Ethylene | 360 | 720 | 0.232 |
| Propylene | 97 | 291 | 0.062 |
| Subtotal | 598 | 1633 | 0.385 |
| Average carbon number = 2.7 | | | |
| Total | 1551 | 6,054 | 1.000 |

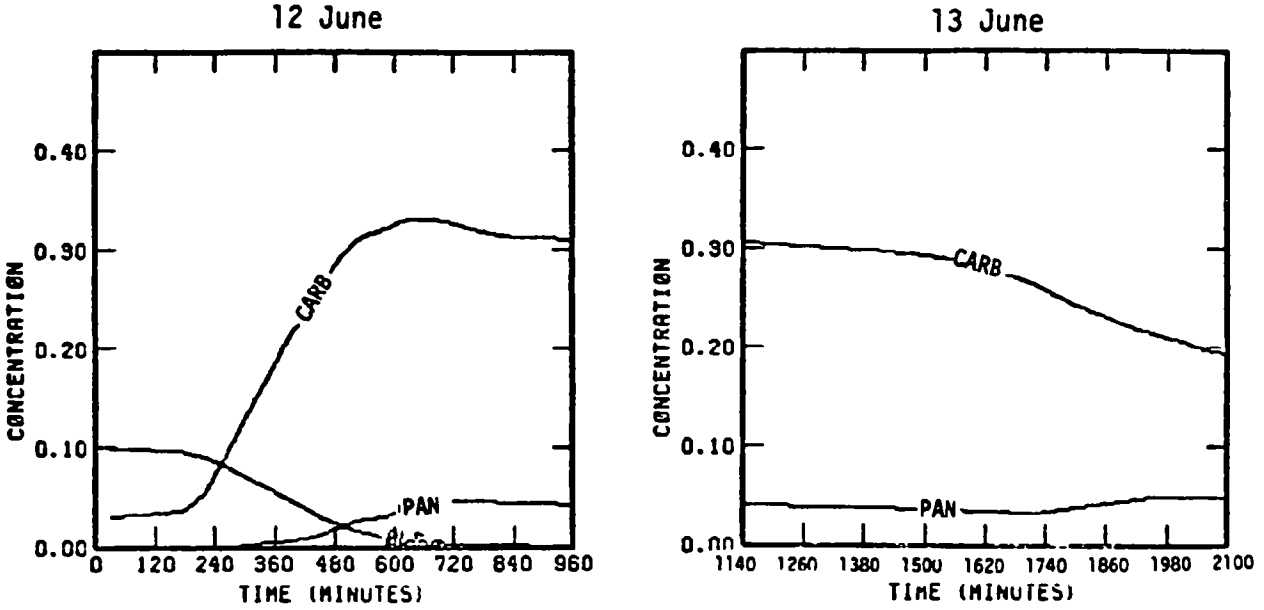



(a) High Hydrocarbon (2.9 ppmC)

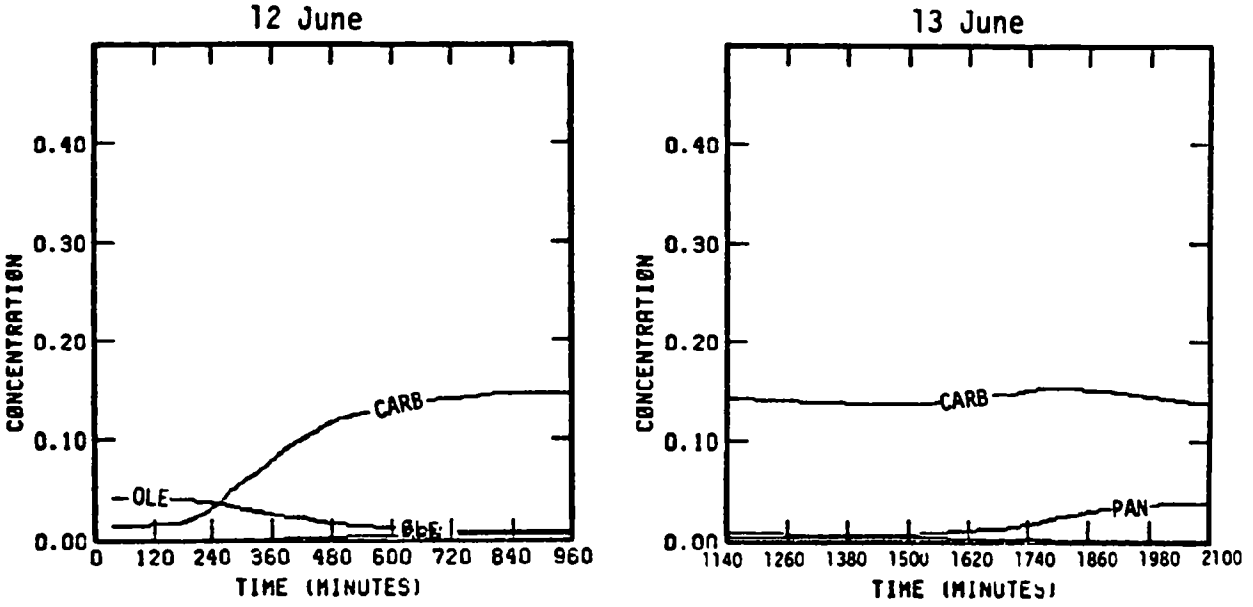



(b) Low Hydrocarbon (1.3 ppmC)

Figure A-12. Results of two-day University of North Carolina smog-chamber run.

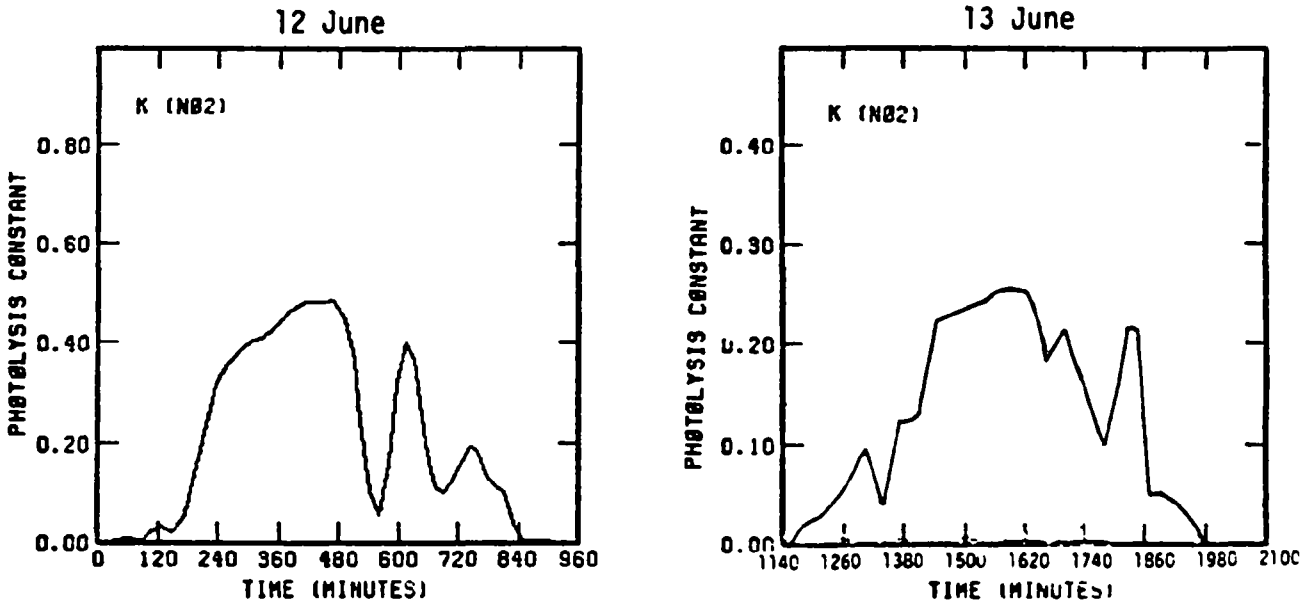



(c) High Hydrocarbon




(d) Low Hydrocarbon

Figure A-12. (continued)




(e) Photolysis Rate

Note: $NO_2$ data = $NO_2$ + PAN

Figure A-12. (concluded)

Appendix B

# MOLECULAR WEIGHTS AND BOND FRACTIONS OF COMMON MOLECULES

## TABLE B-1. MOLECULAR WEIGHTS OF MOLECULES (ORDERED BY SAROAD CODE)

| SPECIES NO. | SAROAD CODE | MOLECULAR WEIGHT | CHEMICAL NAME |
|---|---|---|---|
| 1 | 43000 | 86.00 | UNKNOWN SPECIES |
| 2 | 43105 | 86.17 | ISOMERS OF HEXANE |
| 3 | 43106 | 100.20 | ISOMERS OF HEPTANE |
| 4 | 43107 | 114.23 | ISOMERS OF OCTANE |
| 5 | 43108 | 128.25 | ISOMERS OF NONANE |
| 6 | 43109 | 142.28 | ISOMERS OF DECANE |
| 7 | 43110 | 156.30 | ISOMERS OF UNDECANE |
| 8 | 43111 | 184.35 | ISOMERS OF TRIDECANE |
| 9 | 43112 | 170.33 | ISOMERS OF DODECANE |
| 10 | 43113 | 198.38 | ISOMERS OF TETRADECANE |
| 11 | 43114 | 212.41 | ISOMERS OF PENTADECANE |
| 12 | 43115 | 98.19 | C-7 CYCLOPARAFFINS |
| 13 | 43116 | 112.23 | C-8 CYCLOPARAFFINS |
| 14 | 43117 | 126.26 | C-9 CYCLOPARAFFINS |
| 15 | 43118 | 114.23 | MINERAL SPIRITS |
| 16 | 43119 | 114.23 | LACTOL SPIRITS |
| 17 | 43120 | 56.10 | ISOMERS OF BUTENE |
| 18 | 43121 | 70.13 | ISOMERS OF PENTENE |
| 19 | 43122 | 72.15 | ISOMERS OF PENTANE |
| 20 | 43123 | 136.24 | TERPENES |
| 21 | 43201 | 16.04 | METHANE |
| 22 | 43202 | 30.07 | ETHANE |
| 23 | 43203 | 28.05 | ETHYLENE |
| 24 | 43204 | 44.09 | PROPANE |
| 25 | 43205 | 42.08 | PROPYLENE |
| 26 | 43206 | 26.04 | ACETYLENE |
| 27 | 43207 | 42.08 | CYCLOPROPANE |
| 28 | 43208 | 40.06 | PROPYNE |
| 29 | 43209 | 40.06 | METHYLACETYLENE |
| 30 | 43211 | 84.16 | 3-METHYL-1-PENTENE |
| 31 | 43212 | 58.12 | N-BUTANE |
| 32 | 43213 | 56.10 | BUTENE |
| 33 | 43214 | 58.12 | ISOBUTANE |
| 34 | 43215 | 56.10 | ISOBUTYLENE |
| 35 | 43216 | 56.10 | TRANS-2-BUTENE |
| 36 | 43217 | 56.10 | CIS-2-BUTENE |
| 37 | 43218 | 54.09 | 1,3-BUTADIENE |
| 38 | 43219 | 54.09 | ETHYLACETYLENE |
| 39 | 43220 | 72.15 | N-PENTANE |
| 40 | 43221 | 72.15 | ISOPE NTANE |
| 41 | 43223 | 70.14 | 3-METHYL-1-BUTENE |
| 42 | 43224 | 70.13 | 1-PENTENE |

(continued)

TABLE B-1

| SPECIES NO. | SAROAD CODE | MOLECULAR WEIGHT | CHEMICAL NAME |
|---|---|---|---|
| 43 | 43225 | 70.13 | 2-METHYL-1-BUTENE |
| 44 | 43226 | 70.13 | TRANS-2-PENTENE |
| 45 | 43227 | 70.13 | CIS-2-PENTENE |
| 46 | 43228 | 70.13 | 2-METHYL-2-BUTENE |
| 47 | 43229 | 86.17 | 2-METHYL PENTANE |
| 48 | 43230 | 86.17 | 3-METHYL PENTANE |
| 49 | 43231 | 86.17 | HEXANE |
| 50 | 43232 | 100.20 | HEPTANE |
| 51 | 43233 | 114.23 | OCTANE |
| 52 | 43234 | 84.16 | 2,3-DIMETHYL-1-BUTENE |
| 53 | 43235 | 128.25 | NONANE |
| 54 | 43236 | 142.28 | N-DECANE |
| 55 | 43241 | 156.30 | UNDECANE |
| 56 | 43242 | 70.14 | CYCLOPENTANE |
| 57 | 43245 | 84.16 | 1-HEXENE |
| 58 | 43248 | 84.16 | CYCLOHEXANE |
| 59 | 43255 | 170.33 | N-DODECANE |
| 60 | 43258 | 184.36 | N-TRIDECANE |
| 61 | 43258 | 86.17 | 2,3-DIMETHYLBUTANE |
| 62 | 43259 | 198.38 | N-TETRADECANE |
| 63 | 43260 | 212.41 | N-PENTADECANE |
| 64 | 43260 | 84.16 | 2-ETHYL-1-BUTENE |
| 65 | 43261 | 98.18 | METHYLCYCLOHEXANE |
| 66 | 43262 | 84.16 | METHYLCYCLOPENTANE |
| 67 | 43264 | 98.15 | CYCLOHEXANONE |
| 68 | 43265 | 40.06 | PROPADIENE |
| 69 | 43268 | 84.16 | C-3-HEXENE |
| 70 | 43269 | 84.16 | 2-METHYL-2-PENTENE |
| 71 | 43270 | 84.16 | 3-METHYL-T-2-PENTENE |
| 72 | 43271 | 100.20 | 2,4-DIMETHYLPENTANE |
| 73 | 43272 | 82.14 | METHYLCYCLOPENTENE |
| 74 | 43273 | 82.14 | CYCLOHEXENE |
| 75 | 43274 | 100.20 | 2,3-DIMETHYLPENTANE |
| 76 | 43275 | 100.20 | 2-METHYLHEXANE |
| 77 | 43276 | 114.22 | 2,2,4-TRIMETHYLPENTANE |
| 78 | 43277 | 114.22 | 2,4-DIMETHYLHEXANE |
| 79 | 43278 | 114.22 | 2,5-DIMETHYLHEXANE |
| 80 | 43279 | 114.22 | 2,3,4-TRIMETHYLPENTANE |
| 81 | 43280 | 114.22 | 2,3,3-TRIMETHYLPENTANE |
| 82 | 43281 | 226.44 | HEXADECANE |
| 83 | 43282 | 240.46 | HEPTADECANE |
| 84 | 43283 | 254.49 | OCTADECANE |
| 85 | 43284 | 268.51 | NONADECANE |
| 86 | 43285 | 282.54 | EICOSANE |
| 87 | 43286 | 296.57 | HENEICOSANE |
| 88 | 43287 | 310.59 | DOCOSANE |
| 89 | 43288 | 112.23 | ETHYLCYCLOHEXANE |
| 90 | 43289 | 84.16 | C6 OLEFIN UNK |
| 91 | 43290 | 112.23 | C8 OLEFIN UNK |
| 92 | 43291 | 86.17 | 2,2-DIMETHYLBUTANE |

(continued)

TABLE B-1

| SPECIES NO. | SAROAD CODE | MOLECULAR WEIGHT | CHEMICAL NAME |
|---|---|---|---|
| 93 | 43292 | 68.11 | CYCLOPENTENE |
| 94 | 43293 | 84.16 | 4-METHYL-T-2-PENTENE |
| 95 | 43294 | 98.18 | C7-OLEFIN UNKNOWN |
| 96 | 43295 | 100.20 | 3-METHYLHEXANE |
| 97 | 43296 | 114.23 | 2,2,3-TRIMETHYLPENTANE |
| 98 | 43297 | 114.23 | 4-METHYLHEPTANE |
| 99 | 43298 | 114.23 | 3-METHYLHEPTANE |
| 100 | 43299 | 114.23 | 2,2,5-TRIMETHYLPENTANE |
| 101 | 43301 | 32.04 | METHYL ALCOHOL |
| 102 | 43302 | 46.07 | ETHYL ALCOHOL |
| 103 | 43303 | 60.09 | N-PROPYL ALCOHOL |
| 104 | 43304 | 60.09 | ISOPROPYL ALCOHOL |
| 105 | 43305 | 74.12 | N-BUTYL ALCOHOL |
| 106 | 43306 | 74.12 | ISOBUTYL ALCOHOL |
| 107 | 43307 | 118.17 | BUTYL CELLOSOLVE |
| 108 | 43309 | 74.12 | TERT-BUTYL ALCOHOL |
| 109 | 43310 | 76.11 | METHYL CELLOSOLVE |
| 110 | 43311 | 90.12 | CELLOSOLVE |
| 111 | 43312 | 112.23 | 1-T-2-C-4-TM-CYCLOPENTANE |
| 112 | 43320 | 116.16 | DIACETONE ALCOHOL |
| 113 | 43351 | 74.12 | ETHYL ETHER |
| 114 | 43367 | 106.12 | GLYCOL ETHER |
| 115 | 43368 | 62.07 | GLYCOL |
| 116 | 43369 | 76.00 | PROPYLENE GLYCOL |
| 117 | 43370 | 62.07 | ETHYLENE GLYCOL |
| 118 | 43390 | 72.10 | TETRAHYDROFURAN |
| 119 | 43401 | 60.05 | ACETIC ACID |
| 120 | 43402 | 74.08 | METHYL ACETATE |
| 121 | 43403 | 88.10 | ETHYL ACETATE |
| 122 | 43404 | 102.13 | PROPYL ACETATE |
| 123 | 43405 | 116.16 | N-BUTYL ACETATE |
| 124 | 43438 | 100.11 | ETHYL ACRYLATE |
| 125 | 43443 | 132.00 | CELLOSOLVE ACETATE |
| 126 | 43444 | 104.00 | ISOPROPYL ACETATE |
| 127 | 43445 | 140.00 | METHYL AMYL ACETATE |
| 128 | 43446 | 116.16 | ISOBUTYL ACETATE |
| 129 | 43450 | 73.09 | DIMETHYLFORMAMIDE |
| 130 | 43451 | 144.21 | ISOBUTYL ISOBUTYRATE |
| 131 | 43452 | 132.00 | 2-ETHOXYETHYL ACETATE |
| 132 | 43502 | 30.03 | FORMALDEHYDE |
| 133 | 43503 | 44.05 | ACETALDEHYDE |
| 134 | 43504 | 58.08 | PROPRIONALDEHYDE |
| 135 | 43510 | 72.12 | BUTYRALDEHYDE |
| 136 | 43511 | 58.08 | C3 ALDEHYDE |
| 137 | 43512 | 86.14 | C5 ALDEHYDE |
| 138 | 43513 | 128.21 | C8 ALDEHYDE |
| 139 | 43551 | 58.08 | ACETONE |
| 140 | 43552 | 72.10 | METHYL ETHYL KETONE |
| 141 | 43559 | 100.16 | METHYL N-BUTYL KETONE |
| 142 | 43560 | 100.16 | METHYL ISOBUTYL KETONE |

(continued)

TABLE B-1

| SPECIES NO. | SAROAD CODE | MOLECULAR WEIGHT | CHEMICAL NAME |
|---|---|---|---|
| 143 | 43601 | 44.05 | ETHYLENE OXIDE |
| 144 | 43602 | 58.08 | PROPYLENE OXIDE |
| 145 | 43702 | 41.05 | ACETONITRILE |
| 146 | 43704 | 53.06 | ACRYLONITRILE |
| 147 | 43721 | 45.09 | ETHYLAMINE |
| 148 | 43740 | 59.11 | TRIMETHYL AMINE |
| 149 | 43801 | 50.49 | METHYL CHLORIDE |
| 150 | 43801 | 112.56 | CHLOROBENZENE |
| 151 | 43802 | 84.94 | DICHLOROMETHANE |
| 152 | 43803 | 119.39 | CHLOROFORM |
| 153 | 43804 | 153.84 | CARBON TETRACHLORIDE |
| 154 | 43807 | 331.67 | CARBON TETRABROMIDE |
| 155 | 43811 | 137.37 | TRICHLOROFLUOROMETHANE |
| 156 | 43812 | 64.52 | ETHYL CHLORIDE |
| 157 | 43813 | 98.97 | 1.1-DICHLOROETHANE |
| 158 | 43814 | 133.42 | 1.1.1-TRICHLOROETHANE |
| 159 | 43815 | 99.00 | ETHYLENE DICHLORIDE |
| 160 | 43817 | 165.85 | PERCHLOROETHYLENE |
| 161 | 43819 | 173.85 | METHYLENE BROMIDE |
| 162 | 43820 | 131.66 | 1.1.2-TRICHLOROETHANE |
| 163 | 43821 | 187.38 | TRICHLOROTRIFLUOROETHANE |
| 164 | 43822 | 92.00 | TRIMETHYLFLUOROSILANE |
| 165 | 43823 | 120.92 | DICHLORODIFLUOROMETHANE |
| 166 | 43824 | 131.40 | TRICHLOROETHYLENE |
| 167 | 43860 | 62.50 | VINYL CHLORIDE |
| 168 | 45101 | 114.23 | NAPTHA |
| 169 | 45102 | 106.16 | ISOMERS OF XYLENE |
| 170 | 45103 | 134.21 | DIMETHYLETHYLBENZENE |
| 171 | 45104 | 120.19 | ISOMERS OF ETHYLTOLUENE |
| 172 | 45105 | 134.21 | ISOMERS OF BUTYLBENZENE |
| 173 | 45106 | 134.21 | ISOMERS OF DIETHYLBENZENE |
| 174 | 45107 | 120.19 | ISOMERS OF TRIMETHYLBENZENE |
| 175 | 45108 | 120.19 | ISOMERS OF PROPYLBENZENE |
| 176 | 45201 | 78.11 | BENZENE |
| 177 | 45202 | 92.13 | TOLUENE |
| 178 | 45203 | 106.16 | ETHYLBENZENE |
| 179 | 45204 | 106.16 | O-XYLENE |
| 180 | 45205 | 106.16 | M-XYLENE |
| 181 | 45206 | 106.16 | P-XYLENE |
| 182 | 45207 | 120.19 | 1.3.5-TRIMETHYLBENZENE |
| 183 | 45208 | 120.19 | 1.2.4-TRIMETHYLBENZENE |
| 184 | 45209 | 120.19 | N-PROPYLBENZENE |
| 185 | 45211 | 120.19 | O-ETHYLTOLUENE |
| 186 | 45212 | 120.19 | M-ETHYLTOLUENE |
| 187 | 45215 | 134.21 | TERT-BUTYLBENZENE |
| 188 | 45216 | 134.21 | SEC-BUTYLBENZENE |
| 189 | 45220 | 104.14 | STYRENE |
| 190 | 45221 | 118.15 | A-METHYLSTYRENE |
| 191 | 45225 | 120.19 | 1.2.3-TRIMETHYLBENZENE |
| 192 | 45232 | 134.21 | TETRAMETHYLBENZENE |
| 193 | 45233 | 148.23 | TRI/TETRAALKYL BENZENE |
| 194 | 45234 | 134.21 | ISOMERS OF METHYLPROP. BENZENE |
| 195 | 45300 | 94.11 | PHENOLS |
| 196 | 45401 | 230.00 | XYLENE BASE ACIDS |
| 197 | 46201 | 88.12 | 1.4-DIOXANE |

(concluded)

# TABLE B-2. BOND GROUPS PER MOLECULE (ORDERED BY SAROAD CODE)

| SPECIES NO. | CHEMICAL NAME | SPECIES PROFILES BY BOND GROUP OLE | PAR | ARO | CARB | ETH | UNREACTIVE |
|---|---|---|---|---|---|---|---|
| 1 | UNKNOWN SPECIES | 0.10 | 4.00 | 0.25 | 0.92 | 0.16 | |
| 2 | ISOMERS OF HEXANE | | 6.00 | | | | |
| 3 | ISOMERS OF HEPTANE | | 7.00 | | | | |
| 4 | ISOMERS OF OCTANE | | 8.00 | | | | |
| 5 | ISOMERS OF NONANE | | 9.00 | | | | |
| 6 | ISOMERS OF DECANE | | 10.00 | | | | |
| 7 | ISOMERS OF UNDECANE | | 11.00 | | | | |
| 8 | ISOMERS OF TRIDECANE | | 13.00 | | | | |
| 9 | ISOMERS OF DODECANE | | 12.00 | | | | |
| 10 | ISOMERS OF TETRADECANE | | 14.00 | | | | |
| 11 | ISOMERS OF PENTADECANE | | 15.00 | | | | |
| 12 | C-7 CYCLOPARAFFINS | | 6.00 | | 1.00 | | |
| 13 | C-8 CYCLOPARAFFINS | | 7.00 | | 1.00 | | |
| 14 | C-9 CYCLOPARAFFINS | | 8.00 | | 1.00 | | |
| 15 | MINERAL SPIRITS | | 7.00 | | 1.00 | | |
| 16 | LACTOL SPIRITS | | 0.00 | | | | |
| 17 | ISOMERS OF BUTENE | | 2.00 | | 2.00 | | |
| 18 | ISOMERS OF PENTENE | | 3.00 | | 2.00 | | |
| 19 | ISOMERS OF PENTANE | | 5.00 | | | | |
| 20 | TERPENES | 1.00 | 8.00 | | | | |
| 21 | METHANE | | | | | | 1.00 |
| 22 | ETHANE | | | | | | 2.00 |
| 23 | ETHYLENE | | | | | 1.00 | |
| 24 | PROPANE | | 1.50 | | | | 1.50 |
| 25 | PROPYLENE | 1.00 | 1.00 | | | | |
| 26 | ACETYLENE | | | | | | 1.00 |
| 27 | CYCLOPROPANE | | 2.00 | | 1.00 | | |
| 28 | PROPYNE | | 2.00 | | | | 1.00 |
| 29 | METHYLACETYLENE | | 1.50 | | | | 1.50 |
| 30 | 3-METHYL-1-PENTENE | | 6.00 | | | | |
| 31 | N-BUTANE | | 4.00 | | | | |
| 32 | BUTENE | 1.00 | 2.00 | | | | |
| 33 | ISOBUTANE | | 4.00 | | | | |
| 34 | ISOBUTYLENE | 1.00 | 2.00 | | | | |
| 35 | TRANS-2-BUTENE | | 2.00 | | 2.00 | | |
| 36 | CIS-2-BUTENE | | 2.00 | | 2.00 | | |
| 37 | 1,3-BUTADIENE | 1.00 | | | 2.00 | | |
| 38 | ETHYLACETYLENE | | 4.00 | | | | |
| 39 | N-PENTANE | | 5.00 | | | | |
| 40 | ISOPENTANE | | 5.00 | | | | |

(continued)

# TABLE B-2

SPECIES PROFILES BY BOND GROUP

| SPECIES NO. | CHEMICAL NAME | OLE | PAR | ARO | CARB | ETH | UNREACTIVE |
|---|---|---|---|---|---|---|---|
| 41 | 3-METHYL-1-BUTENE | 1.00 | 3.00 | | | | |
| 42 | 1-PENTENE | 1.00 | 3.00 | | | | |
| 43 | 2-METHYL-1-BUTENE | 1.00 | 3.00 | | | | |
| 44 | TRANS-2-PENTENE | | 3.00 | | 2.00 | | |
| 45 | CIS-2-PENTENE | | 3.00 | | 2.00 | | |
| 46 | 2-METHYL-2-BUTENE | | 3.00 | | 2.00 | | |
| 47 | 2-METHYL PENTANE | | 6.00 | | | | |
| 48 | 3-METHYL PENTANE | | 6.00 | | | | |
| 49 | HEXANE | | 6.00 | | | | |
| 50 | HEPTANE | | 7.00 | | | | |
| 51 | OCTANE | | 8.00 | | | | |
| 52 | 2,3-DIMETHYL-1-BUTENE | 1.00 | 4.00 | | | | |
| 53 | NONANE | | 9.00 | | | | |
| 54 | N-DECANE | | 10.00 | | | | |
| 55 | UNDECANE | | 11.00 | | | | |
| 56 | CYCLOPENTANE | | 4.00 | | 1.00 | | |
| 57 | 1-HEXENE | 1.00 | 4.00 | | | | |
| 58 | CYCLOHEXANE | | 5.00 | | 1.00 | | |
| 59 | N-DODECANE | | 12.00 | | | | |
| 60 | N-TRIDECANE | | 13.00 | | | | |
| 61 | 2,3-DIMETHYLBUTANE | | 6.00 | | | | |
| 62 | N-TETRADECANE | | 14.00 | | | | |
| 63 | N-PENTADECANE | | 15.00 | | | | |
| 64 | 2-ETHYL-1-BUTENE | 1.00 | 4.00 | | | | |
| 65 | METHYLCYCLOHEXANE | | 6.00 | | 1.00 | | |
| 66 | METHYLCYCLOPENTANE | | 5.00 | | 1.00 | | |
| 67 | CYCLOHEXANONE | | 4.00 | | 2.00 | | |
| 68 | PROPADIENE | | 1.00 | | 2.00 | | |
| 69 | C-3-HEXENE | 1.00 | 4.00 | | | | |
| 70 | 2-METHYL-2-PENTENE | | 4.00 | | 2.00 | | |
| 71 | 3-METHYL-T-2-PENTENE | | 4.00 | | 2.00 | | |
| 72 | 2,4-DIMETHYLPENTANE | | 7.00 | | | | |
| 73 | METHYLCYCLOPENTENE | 1.00 | 4.00 | | | | |
| 74 | CYCLOHEXENE | 1.00 | 4.00 | | | | |
| 75 | 2,3-DIMETHYLPENTANE | | 7.00 | | | | |
| 76 | 2-METHYLHEXANE | | 7.00 | | | | |
| 77 | 2,2,4-TRIMETHYLPENTANE | | 8.00 | | | | |
| 78 | 2,4-DIMETHYLHEXANE | | 8.00 | | | | |
| 79 | 2,5-DIMETHYLHEXANE | | 8.00 | | | | |
| 80 | 2,3,4-TRIMETHYLPENTANE | | 8.00 | | | | |

(continued)

TABLE B-2

SPECIES PROFILES BY BOND GROUP

| SPECIES NO. | CHEMICAL NAME | OLE | PAR | ARO | CARB | ETH | UNREACTIVE |
|---|---|---|---|---|---|---|---|
| 81 | 2,3,3-TRIMETHYLPENTANE | | 8.00 | | | | |
| 82 | HEXADECANE | | 16.00 | | | | |
| 83 | HEPTADECANE | | 17.00 | | | | |
| 84 | OCTADECANE | | 18.00 | | | | |
| 85 | NONADECANE | | 19.00 | | | | |
| 86 | EICOSANE | | 20.00 | | | | |
| 87 | HENEICOSANE | | 21.00 | | | | |
| 88 | DOCOSANE | | 22.00 | | | | |
| 89 | ETHYLCYCLOHEXANE | | 7.00 | | 1.00 | | |
| 90 | C6 OLEFIN UNK | 1.00 | 4.00 | | | | |
| 91 | C8 OLEFIN UNK | 1.00 | 6.00 | | | | |
| 92 | 2,2-DIMETHYLBUTANE | | 6.00 | | | | |
| 93 | CYCLOPENTENE | 1.00 | 3.00 | | | | |
| 94 | 4-METHYL-T-2-PENTENE | | 4.00 | | 2.00 | | |
| 95 | C7-OLEFIN UNKNOWN | 1.00 | 5.00 | | | | |
| 96 | 3-METHYLHEXANE | | 7.00 | | | | |
| 97 | 2,2,3-TRIMETHYLPENTANE | | 8.00 | | | | |
| 98 | 4-METHYLHEPTANE | | 8.00 | | | | |
| 99 | 3-METHYLHEPTANE | | 8.00 | | | | |
| 100 | 2,2,5-TRIMETHYLPENTANE | | 8.00 | | | | |
| 101 | METHYL ALCOHOL | | 1.00 | | | | |
| 102 | ETHYL ALCOHOL | | 2.00 | | | | |
| 103 | N-PROPYL ALCOHOL | | 3.00 | | | | |
| 104 | ISOPROPYL ALCOHOL | | 3.00 | | | | |
| 105 | N-BUTYL ALCOHOL | | 4.00 | | | | |
| 106 | ISOBUTYL ALCOHOL | | 4.00 | | | | |
| 107 | BUTYL CELLOSOLVE | | 5.00 | | 1.00 | | |
| 108 | TERT-BUTYL ALCOHOL | | 3.00 | | 1.00 | | |
| 109 | METHYL CELLOSOLVE | | 2.00 | | 1.00 | | |
| 110 | CELLOSOLVE | | 3.00 | | 1.00 | | |
| 111 | 1-T-2-C-4-TM-CYCLOPENTANE | | 7.00 | | 1.00 | | |
| 112 | DIACETONE ALCOHOL | | 5.00 | | 1.00 | | |
| 113 | ETHYL ETHER | | 3.00 | | 1.00 | | |
| 114 | GLYCOL ETHER | | 1.00 | | 1.00 | | |
| 115 | GLYCOL | | 1.00 | | 1.00 | | |
| 116 | PROPYLENE GLYCOL | | 2.00 | | 1.00 | | |
| 117 | ETHYLENE GLYCOL | | 1.00 | | 1.00 | | |
| 118 | TETRAHYDROFURAN | | 3.00 | | 1.00 | | |
| 119 | ACETIC ACID | | 2.00 | | | | |
| 120 | METHYL ACETATE | | | | | | 3.00 |

(continued)

# TABLE B-2

SPECIES PROFILES BY BOND GROUP

| SPECIES NO. | CHEMICAL NAME | OLE | PAR | ARO | CARB | ETH | UNREACTIVE |
|---|---|---|---|---|---|---|---|
| 121 | ETHYL ACETATE | | 3.00 | | 1.00 | | |
| 122 | PROPYL ACETATE | | 4.00 | | 1.00 | | |
| 123 | N-BUTYL ACETATE | | 5.00 | | 1.00 | | |
| 124 | ETHYL ACRYLATE | | 3.00 | | 2.00 | | |
| 125 | CELLOSOLVE ACETATE | | 4.00 | | 2.00 | | |
| 126 | ISOPROPYL ACETATE | | 5.00 | | | | |
| 127 | METHYL AMYL ACETATE | | 8.00 | | | | |
| 128 | ISOBUTYL ACETATE | | 6.00 | | | | |
| 129 | DIMETHYLFORMAMIDE | | | | | | 3.00 |
| 130 | ISOBUTYL ISOBUTYRATE | | 7.00 | | 1.00 | | |
| 131 | 2-ETHOXYETHYL ACETATE | | 4.00 | | 2.00 | | |
| 132 | FORMALDEHYDE | | | | 1.00 | | |
| 133 | ACETALDEHYDE | | 1.00 | | 1.00 | | |
| 134 | PROPRIONALDEHYDE | | 2.00 | | 1.00 | | |
| 135 | BUTYRALDEHYDE | | 3.00 | | 1.00 | | |
| 136 | C3 ALDEHYDE | | 2.00 | | 1.00 | | |
| 137 | C5 ALDEHYDE | | 4.00 | | 1.00 | | |
| 138 | C8 ALDEHYDE | | 7.00 | | 1.00 | | |
| 139 | ACETONE | | 2.00 | | 1.00 | | |
| 140 | METHYL ETHYL KETONE | | 3.00 | | 1.00 | | |
| 141 | METHYL N-BUTYL KETONE | | 5.00 | | 1.00 | | |
| 142 | METHYL ISOBUTYL KETONE | | 5.00 | | 1.00 | | |
| 143 | ETHYLENE OXIDE | | 1.00 | | | | 1.00 |
| 144 | PROPYLENE OXIDE | | 2.00 | | | | 1.00 |
| 145 | ACETONITRILE | | 1.00 | | | | 1.00 |
| 146 | ACRYLONITRILE | 1.00 | 1.00 | | | | |
| 147 | ETHYLAMINE | | 1.00 | | | | 1.00 |
| 148 | TRIMETHYL AMINE | | 3.00 | | | | |
| 149 | METHYL CHLORIDE | | | | | | 1.00 |
| 150 | CHLOROBENZENE | | | | | | 6.00 |
| 151 | DICHLOROMETHANE | | | | | | 1.00 |
| 152 | CHLOROFORM | | | | | | 1.00 |
| 153 | CARBON TETRACHLORIDE | | | | | | 1.00 |
| 154 | CARBON TETRABROMIDE | | | | | | 1.00 |
| 155 | TRICHLOROFLUOROMETHANE | | | | | | 1.00 |
| 156 | ETHYL CHLORIDE | | | | | | 2.00 |
| 157 | 1,1-DICHLOROETHANE | | | | | | 2.00 |
| 158 | 1,1,1-TRICHLOROETHANE | | | | | | 2.00 |
| 159 | ETHYLENE DICHLORIDE | | | | | 1.00 | |
| 160 | PERCHLOROETHYLENE | | | | | | 2.00 |

(continued)

# TABLE B-2

SPECIES PROFILES BY BOND GROUP

| SPECIES NO. | CHEMICAL NAME | OLE | PAR | ARO | CARB | ETH | UNREACTIVE |
|---|---|---|---|---|---|---|---|
| 161 | METHYLENE BROMIDE | | | | | | 1.00 |
| 162 | 1,1,2-TRICHLOROETHANE | | | | | | 2.00 |
| 163 | TRICHLOROTRIFLUOROETHANE | | | | | | 2.00 |
| 164 | TRIMETHYLFLUOROSILANE | | | | | | 3.00 |
| 165 | DICHLORODIFLUOROMETHANE | | | | | | 1.00 |
| 166 | TRICHLOROETHYLENE | | | | | 1.00 | |
| 167 | VINYL CHLORIDE | | | | | 1.00 | |
| 168 | NAPTHA | | 8.00 | | | | |
| 169 | ISOMERS OF XYLENE | | 2.00 | 1.00 | | | |
| 170 | DIMETHYLETHYLBENZENE | | 4.00 | 1.00 | | | |
| 171 | ISOMERS OF ETHYLTOLUENE | | 3.00 | 1.00 | | | |
| 172 | ISOMERS OF BUTYLBENZENE | | 4.00 | 1.00 | | | |
| 173 | ISOMERS OF DIETHYLBENZENE | | 4.00 | 1.00 | | | |
| 174 | ISOMERS OF TRIMETHYLBENZENE | | 3.00 | 1.00 | | | |
| 175 | ISOMERS OF PROPYLBENZENE | | 3.00 | 1.00 | | | |
| 176 | BENZENE | | | | | | 6.00 |
| 177 | TOLUENE | | 1.00 | 1.00 | | | |
| 178 | ETHYLBENZENE | | 2.00 | 1.00 | | | |
| 179 | O-XYLENE | | 2.00 | 1.00 | | | |
| 180 | M-XYLENE | | 2.00 | 1.00 | | | |
| 181 | P-XYLENE | | 2.00 | 1.00 | | | |
| 182 | 1,3,5-TRIMETHYLBENZENE | | 3.00 | 1.00 | | | |
| 183 | 1,2,4-TRIMETHYLBENZENE | | 3.00 | 1.00 | | | |
| 184 | N-PROPYLBENZENE | | 3.00 | 1.00 | | | |
| 185 | O-ETHYLTOLUENE | | 3.00 | 1.00 | | | |
| 186 | M-ETHYLTOLUENE | | 3.00 | 1.00 | | | |
| 187 | TERT-BUTYLBENZENE | | 4.00 | 1.00 | | | |
| 188 | SEC-BUTYLBENZENE | | 4.00 | 1.00 | | | |
| 189 | STYRENE | | 1.00 | 1.00 | 1.00 | | |
| 190 | A-METHYLSTYRENE | | 2.00 | 1.00 | 1.00 | | |
| 191 | 1,2,3-TRIMETHYLBENZENE | | 3.00 | 1.00 | | | |
| 192 | TETRAMETHYLBENZENE | | 4.00 | 1.00 | | | |
| 193 | TRI/TETRAALKYL BENZENE | | 5.00 | 1.00 | | | |
| 194 | ISOMERS OF METHYLPROP. BENZENE | | 4.00 | 1.00 | | | |
| 195 | PHENOL | | | | | | 6.00 |
| 196 | XYLENE BASE ACIDS | | 2.00 | 1.00 | | | |
| 197 | 1,4-DIOXANE | 1.00 | 2.00 | | 2.00 | | |

(concluded)

TABLE B-3. MOLECULAR WEIGHT OF MOLECULES
(IN ALPHABETICAL ORDER)

| SPECIES NO. | SAROAD CODE | MOLECULAR WEIGHT | CHEMICAL NAME |
|---|---|---|---|
| 1 | 43814 | 133.42 | 1.1.1-TRICHLOROETHANE |
| 2 | 43820 | 131.66 | 1.1.2-TRICHLOROETHANE |
| 3 | 43813 | 98.97 | 1.1-DICHLOROETHANE |
| 4 | 45225 | 120.19 | 1.2.3-TRIMETHYLBENZENE |
| 5 | 45208 | 120.19 | 1.2.4-TRIMETHYLBENZENE |
| 6 | 45207 | 120.19 | 1.3.5-TRIMETHYLBENZENE |
| 7 | 43218 | 54.09 | 1.3-BUTADIENE |
| 8 | 46201 | 88.12 | 1.4-DIOXANE |
| 9 | 43245 | 84.16 | 1-HEXENE |
| 10 | 43224 | 70.13 | 1-PENTENE |
| 11 | 43312 | 112.23 | 1-T-2-C-4-TM-CYCLOPENTANE |
| 12 | 43296 | 114.23 | 2.2.3-TRIMETHYLPENTANE |
| 13 | 43276 | 114.22 | 2.2.4-TRIMETHYLPENTANE |
| 14 | 43299 | 114.23 | 2.2.5-TRIMETHYLPENTANE |
| 15 | 43291 | 86.17 | 2.2-DIMETHYLBUTANE |
| 16 | 43280 | 114.22 | 2.3.3-TRIMETHYLPENTANE |
| 17 | 43279 | 114.22 | 2.3.4-TRIMETHYLPENTANE |
| 18 | 43234 | 84.16 | 2.3-DIMETHYL-1-BUTENE |
| 19 | 43258 | 86.17 | 2.3-DIMETHYLBUTANE |
| 20 | 43274 | 100.20 | 2.3-DIMETHYLPENTANE |
| 21 | 43277 | 114.22 | 2.4-DIMETHYLHEXANE |
| 22 | 43271 | 100.20 | 2.4-DIMETHYLPENTANE |
| 23 | 43278 | 114.22 | 2.5-DIMETHYLHEXANE |
| 24 | 43452 | 132.00 | 2-ETHOXYETHYL ACETATE |
| 25 | 43260 | 84.16 | 2-ETHYL-1-BUTENE |
| 26 | 43229 | 86.17 | 2-METHYL PENTANE |
| 27 | 43225 | 70.13 | 2-METHYL-1-BUTENE |
| 28 | 43228 | 70.13 | 2-METHYL-2-BUTENE |
| 29 | 43269 | 84.16 | 2-METHYL-2-PENTENE |
| 30 | 43275 | 100.20 | 2-METHYLHEXANE |
| 31 | 43230 | 86.17 | 3-METHYL PENTANE |
| 32 | 43223 | 70.14 | 3-METHYL-1-BUTENE |
| 33 | 43211 | 84.16 | 3-METHYL-1-PENTENE |
| 34 | 43270 | 84.16 | 3-METHYL-T-2-PENTENE |
| 35 | 43298 | 114.23 | 3-METHYLHEPTANE |
| 36 | 43295 | 100.20 | 3-METHYLHEXANE |
| 37 | 43293 | 84.16 | 4-METHYL-T-2-PENTENE |
| 38 | 43297 | 114.23 | 4-METHYLHEPTANE |
| 39 | 45221 | 118.15 | A-METHYLSTYRENE |
| 40 | 43503 | 44.05 | ACETALDEHYDE |
| 41 | 43404 | 60.05 | ACETIC ACID |
| 42 | 43551 | 58.08 | ACETONE |
| 43 | 43702 | 41.05 | ACETONITRILE |
| 44 | 43206 | 26.04 | ACETYLENE |
| 45 | 43704 | 53.06 | ACRYLONITRILE |
| 46 | 45201 | 78.11 | BENZENE |
| 47 | 43213 | 56.10 | BUTENE |
| 48 | 43308 | 118.17 | BUTYL CELLOSOLVE |
| 49 | 43510 | 72.12 | BUTYRALDEHYDE |
| 50 | 43268 | 84.16 | C-3-HEXENE |

(continued)

TABLE B-3

| SPECIES NO. | SAROAD CODE | MOLECULAR WEIGHT | CHEMICAL NAME |
|---|---|---|---|
| 51 | 43115 | 98.19 | C-7 CYCLOPARAFFINS |
| 52 | 43116 | 112.23 | C-8 CYCLOPARAFFINS |
| 53 | 43117 | 126.26 | C-9 CYCLOPARAFFINS |
| 54 | 43511 | 58.08 | C3 ALDEHYDE |
| 55 | 43512 | 86.14 | C5 ALDEHYDE |
| 56 | 43289 | 84.16 | C6 OLEFIN UNK |
| 57 | 43294 | 98.18 | C7-OLEFIN UNKNOWN |
| 58 | 43513 | 128.21 | C8 ALDEHYDE |
| 59 | 43290 | 112.23 | C8 OLEFIN UNK |
| 60 | 43807 | 331.67 | CARBON TETRABROMIDE |
| 61 | 43804 | 153.84 | CARBON TETRACHLORIDE |
| 62 | 43311 | 90.12 | CELLOSOLVE |
| 63 | 43443 | 132.00 | CELLOSOLVE ACETATE |
| 64 | 43801 | 112.56 | CHLOROBENZENE |
| 65 | 43803 | 119.39 | CHLOROFORM |
| 66 | 43217 | 56.10 | CIS-2-BUTENE |
| 67 | 43227 | 70.13 | CIS-2-PENTENE |
| 68 | 43248 | 84.16 | CYCLOHEXANE |
| 69 | 43264 | 98.15 | CYCLOHEXANONE |
| 70 | 43273 | 82.14 | CYCLOHEXENE |
| 71 | 43242 | 70.14 | CYCLOPENTANE |
| 72 | 43292 | 68.11 | CYCLOPENTENE |
| 73 | 43207 | 42.08 | CYCLOPROPANE |
| 74 | 43320 | 116.16 | DIACETONE ALCOHOL |
| 75 | 43823 | 120.92 | DICHLORODIFLUOROMETHANE |
| 76 | 43802 | 84.94 | DICHLOROMETHANE |
| 77 | 45103 | 134.21 | DIMETHYLETHYLBENZENE |
| 78 | 43450 | 73.09 | DIMETHYLFORMAMIDE |
| 79 | 43287 | 310.59 | DOCOSANE |
| 80 | 43285 | 282.54 | EICOSANE |
| 81 | 43202 | 30.07 | ETHANE |
| 82 | 43433 | 88.10 | ETHYL ACETATE |
| 83 | 43438 | 100.11 | ETHYL ACRYLATE |
| 84 | 43302 | 46.07 | ETHYL ALCOHOL |
| 85 | 43812 | 64.52 | ETHYL CHLORIDE |
| 86 | 43351 | 74.12 | ETHYL ETHER |
| 87 | 43219 | 54.09 | ETHYLACETYLENE |
| 88 | 43721 | 45.09 | ETHYLAMINE |
| 89 | 45203 | 106.16 | ETHYLBENZENE |
| 90 | 43288 | 112.23 | ETHYLCYCLOHEXANE |
| 91 | 43203 | 28.05 | ETHYLENE |
| 92 | 43815 | 99.00 | ETHYLENE DICHLORIDE |
| 93 | 43370 | 62.07 | ETHYLENE GLYCOL |
| 94 | 43601 | 44.05 | ETHYLENE OXIDE |
| 95 | 43502 | 30.03 | FORMALDEHYDE |
| 96 | 43368 | 62.07 | GLYCOL |
| 97 | 43367 | 106.12 | GLYCOL ETHER |
| 98 | 43286 | 296.57 | HENEICOSANE |
| 99 | 43282 | 240.46 | HEPTADECANE |
| 100 | 43232 | 100.20 | HEPTANE |

(continued)

TABLE B-3

| SPECIES NO. | SAROAD CODE | MOLECULAR WEIGHT | CHEMICAL NAME |
|---|---|---|---|
| 101 | 43281 | 226.44 | HEXADECANE |
| 102 | 43231 | 86.17 | HEXANE |
| 103 | 43214 | 58.12 | ISOBUTANE |
| 104 | 43446 | 116.16 | ISOBUTYL ACETATE |
| 105 | 43306 | 74.12 | ISOBUTYL ALCOHOL |
| 106 | 43451 | 144.21 | ISOBUTYL ISOBUTYRATE |
| 107 | 43215 | 56.10 | ISOBUTYLENE |
| 108 | 43120 | 56.10 | ISOMERS OF BUTENE |
| 109 | 45105 | 134.21 | ISOMERS OF BUTYLBENZENE |
| 110 | 43109 | 142.28 | ISOMERS OF DECANE |
| 111 | 45106 | 134.21 | ISOMERS OF DIETHYLBENZENE |
| 112 | 43112 | 170.33 | ISOMERS OF DODECANE |
| 113 | 45104 | 120.19 | ISOMERS OF ETHYLTOLUENE |
| 114 | 43106 | 100.20 | ISOMERS OF HEPTANE |
| 115 | 43105 | 86.17 | ISOMERS OF HEXANE |
| 116 | 45234 | 134.21 | ISOMERS OF METHYLPROP. BENZENE |
| 117 | 43108 | 128.25 | ISOMERS OF NONANE |
| 118 | 43107 | 114.23 | ISOMERS OF OCTANE |
| 119 | 43114 | 212.41 | ISOMERS OF PENTADECANE |
| 120 | 43122 | 72.15 | ISOMERS OF PENTANE |
| 121 | 43121 | 70.13 | ISOMERS OF PENTENE |
| 122 | 45108 | 120.19 | ISOMERS OF PROPYLBENZENE |
| 123 | 43113 | 198.38 | ISOMERS OF TETRADECANE |
| 124 | 43111 | 184.36 | ISOMERS OF TRIDECANE |
| 125 | 45107 | 120.19 | ISOMERS OF TRIMETHYLBENZENE |
| 126 | 43110 | 156.30 | ISOMERS OF UNDECANE |
| 127 | 45102 | 106.16 | ISOMERS OF XYLENE |
| 128 | 43221 | 72.15 | ISOPENTANE |
| 129 | 43444 | 104.00 | ISOPROPYL ACETATE |
| 130 | 43304 | 60.09 | ISOPROPYL ALCOHOL |
| 131 | 43119 | 114.23 | LACTOL SPIRITS |
| 132 | 45212 | 120.19 | M-ETHYLTOLUENE |
| 133 | 45205 | 106.16 | M-XYLENE |
| 134 | 43201 | 16.04 | METHANE |
| 135 | 43432 | 74.08 | METHYL ACETATE |
| 136 | 43301 | 32.04 | METHYL ALCOHOL |
| 137 | 43445 | 140.00 | METHYL AMYL ACETATE |
| 138 | 43310 | 76.11 | METHYL CELLOSOLVE |
| 139 | 43801 | 50.49 | METHYL CHLORIDE |
| 140 | 43552 | 72.10 | METHYL ETHYL KETONE |
| 141 | 43560 | 100.16 | METHYL ISOBUTYL KETONE |
| 142 | 43559 | 100.16 | METHYL N-BUTYL KETONE |
| 143 | 43209 | 40.06 | METHYLACETYLENE |
| 144 | 43261 | 98.18 | METHYLCYCLOHEXANE |
| 145 | 43262 | 84.16 | METHYLCYCLOPENTANE |
| 146 | 43272 | 82.14 | METHYLCYCLOPENTENE |
| 147 | 43819 | 173.85 | METHYLENE BROMIDE |
| 148 | 43118 | 114.23 | MINERAL SPIRITS |
| 149 | 43212 | 58.12 | N-BUTANE |
| 150 | 43435 | 116.16 | N-BUTYL ACETATE |

(continued)

TABLE B-3

| SPECIES NO. | SAROAD CODE | MOLECULAR WEIGHT | CHEMICAL NAME |
|---|---|---|---|
| 151 | 43305 | 74.12 | N-BUTYL ALCOHOL |
| 152 | 43238 | 142.28 | N-DECANE |
| 153 | 43255 | 170.33 | N-DODECANE |
| 154 | 43260 | 212.41 | N-PENTADECANE |
| 155 | 43220 | 72.15 | N-PENTANE |
| 156 | 43303 | 60.09 | N-PROPYL ALCOHOL |
| 157 | 45209 | 120.19 | N-PROPYLBENZENE |
| 158 | 43259 | 198.38 | N-TETRADECANE |
| 159 | 43258 | 184.36 | N-TRIDECANE |
| 160 | 45101 | 114.23 | NAPTHA |
| 161 | 43284 | 268.51 | NONADECANE |
| 162 | 43235 | 128.25 | NONANE |
| 163 | 45211 | 120.19 | O-ETHYLTOLUENE |
| 164 | 45204 | 106.16 | O-XYLENE |
| 165 | 43283 | 254.49 | OCTADECANE |
| 166 | 43233 | 114.23 | OCTANE |
| 167 | 45206 | 106.16 | P-XYLENE |
| 168 | 43817 | 165.85 | PERCHLOROETHYLENE |
| 169 | 45300 | 94.11 | PHENOLS |
| 170 | 43265 | 40.06 | PROPADIENE |
| 171 | 43204 | 44.09 | PROPANE |
| 172 | 43504 | 58.08 | PROPRIONALDEHYDE |
| 173 | 43434 | 102.13 | PROPYL ACETATE |
| 174 | 43205 | 42.08 | PROPYLENE |
| 175 | 43369 | 76.00 | PROPYLENE GLYCOL |
| 176 | 43602 | 58.08 | PROPYLENE OXIDE |
| 177 | 43208 | 40.06 | PROPYNE |
| 178 | 45216 | 134.21 | SEC-BUTYLBENZENE |
| 179 | 45220 | 104.14 | STYRENE |
| 180 | 43123 | 136.24 | TERPENES |
| 181 | 43309 | 74.12 | TERT-BUTYL ALCOHOL |
| 182 | 45215 | 134.21 | TERT-BUTYLBENZENE |
| 183 | 43390 | 72.10 | TETRAHYDROFURAN |
| 184 | 45232 | 134.21 | TETRAMETHYLBENZENE |
| 185 | 45202 | 92.13 | TOLUENE |
| 186 | 43216 | 56.10 | TRANS-2-BUTENE |
| 187 | 43226 | 70.13 | TRANS-2-PENTENE |
| 188 | 45233 | 148.23 | TRI/TETRAALKYL BENZENE |
| 189 | 43824 | 131.40 | TRICHLOROETHYLENE |
| 190 | 43811 | 137.37 | TRICHLOROFLUOROMETHANE |
| 191 | 43821 | 187.38 | TRICHLOROTRIFLUOROETHANE |
| 192 | 43740 | 59.11 | TRIMETHYL AMINE |
| 193 | 43822 | 92.00 | TRIMETHYLFLUOROSILANE |
| 194 | 43241 | 156.30 | UNDECANE |
| 195 | 43000 | 86.00 | UNKNOWN SPECIES |
| 196 | 43860 | 62.50 | VINYL CHLORIDE |
| 197 | 45401 | 230.00 | XYLENE BASE ACIDS |

(concluded)

# TABLE B-4. BOND GROUPS PER MOLECULE (IN ALPHABETICAL ORDER)

| SPECIES PROFILES BY BOND GROUP | | | | | | | |
|---|---|---|---|---|---|---|---|
| SPECIES NO. | CHEMICAL NAME | OLE | PAR | ARO | CARB | ETH | UNREACTIVE |
| 1 | 1.1.1-TRICHLOROETHANE | | | | | | 2.00 |
| 2 | 1.1.2-TRICHLOROETHANE | | | | | | 2.00 |
| 3 | 1.1-DICHLOROETHANE | | | | | | 2.00 |
| 4 | 1.2.3-TRIMETHYLBENZENE | | 9.00 | 1.00 | | | |
| 5 | 1.2.4-TRIMETHYLBENZENE | | 3.00 | 1.00 | | | |
| 6 | 1.3.5-TRIMETHYLBENZENE | | 3.00 | 1.00 | | | |
| 7 | 1.3-BUTADIENE | 1.00 | | | 2.00 | | |
| 8 | 1.4-DIOXANE | 1.00 | 2.00 | | 2.00 | | |
| 9 | 1-HEXENE | 1.00 | 4.00 | | | | |
| 10 | 1-PENTENE | 1.00 | 3.00 | | | | |
| 11 | 1-T-2-C-4-TM-CYCLOPENTANE | | 7.00 | | 1.00 | | |
| 12 | 2.2.3-TRIMETHYLPENTANE | | 8.00 | | | | |
| 13 | 2.2.4-TRIMETHYLPENTANE | | 8.00 | | | | |
| 14 | 2.2.5-TRIMETHYLPENTANE | | 8.00 | | | | |
| 15 | 2.2-DIMETHYLBUTANE | | 6.00 | | | | |
| 16 | 2.3.3-TRIMETHYLPENTANE | | 8.00 | | | | |
| 17 | 2.3.4-TRIMETHYLPENTANE | | 8.00 | | | | |
| 18 | 2.3-DIMETHYL-1-BUTENE | 1.00 | 4.00 | | | | |
| 19 | 2.3-DIMETHYLBUTANE | | 6.00 | | | | |
| 20 | 2.3-DIMETHYLPENTANE | | 7.00 | | | | |
| 21 | 2.4-DIMETHYLHEXANE | | 8.00 | | | | |
| 22 | 2.4-DIMETHYLPENTANE | | 7.00 | | | | |
| 23 | 2.5-DIMETHYLHEXANE | | 8.00 | | | | |
| 24 | 2-ETHOXYETHYL ACETATE | | 4.00 | | 2.00 | | |
| 25 | 2-ETHYL-1-BUTENE | 1.00 | 4.00 | | | | |
| 26 | 2-METHYL PENTANE | | 6.00 | | | | |
| 27 | 2-METHYL-1-BUTENE | 1.00 | 3.00 | | | | |
| 28 | 2-METHYL-2-BUTENE | | 3.00 | | 2.00 | | |
| 29 | 2-METHYL-2-PENTENE | | 4.00 | | 2.00 | | |
| 30 | 2-METHYLHEXANE | | 7.00 | | | | |
| 31 | 3-METHYL PENTANE | | 6.00 | | | | |
| 32 | 3-METHYL-1-BUTENE | 1.00 | 3.00 | | | | |
| 33 | 3-METHYL-1-PENTENE | | 6.00 | | | | |
| 34 | 3-METHYL-T-2-PENTENE | | 4.00 | | 2.00 | | |
| 35 | 3-METHYLHEPTANE | | 8.00 | | | | |
| 36 | 3-METHYLHEXANE | | 7.00 | | | | |
| 37 | 4-METHYL-T-2-PENTENE | | 4.00 | | 2.00 | | |
| 38 | 4-METHYLHEPTANE | | 8.00 | | | | |
| 39 | A-METHYLSTYRENE | | 2.00 | 1.00 | 1.00 | | |
| 40 | ACETALDEHYDE | | 1.00 | | 1.00 | | |

(continued)

TABLE B-4

SPECIES PROFILES BY BOND GROUP

| SPECIES NO. | CHEMICAL NAME | OLE | PAR | ARO | CARB | ETH | UNREACTIVE |
|---|---|---|---|---|---|---|---|
| 41 | ACETIC ACID | | 2.00 | | | | |
| 42 | ACETONE | | 2.00 | | 1.00 | | |
| 43 | ACETONITRILE | | 1.00 | | | | 1.00 |
| 44 | ACETYLENE | | | | | | 1.00 |
| 45 | ACRYLONITRILE | 1.00 | 1.00 | | | | |
| 46 | BENZENE | | | | | | 6.00 |
| 47 | BUTENE | 1.00 | 2.00 | | | | |
| 48 | BUTYL CELLOSOLVE | | 5.00 | | 1.00 | | |
| 49 | BUTYRALDEHYDE | | 3.00 | | 1.00 | | |
| 50 | C-3-HEXENE | 1.00 | 4.00 | | | | |
| 51 | C-7 CYCLOPARAFFINS | | 6.00 | | 1.00 | | |
| 52 | C-8 CYCLOPARAFFINS | | 7.00 | | 1.00 | | |
| 53 | C-9 CYCLOPARAFFINS | | 8.00 | | 1.00 | | |
| 54 | C3 ALDEHYDE | | 2.00 | | 1.00 | | |
| 55 | C5 ALDEHYDE | | 4.00 | | 1.00 | | |
| 56 | C6 OLEFIN UNK | 1.00 | 4.00 | | | | |
| 57 | C7-OLEFIN UNKNOWN | 1.00 | 5.00 | | | | |
| 58 | C8 ALDEHYDE | | 7.00 | | 1.00 | | |
| 59 | C8 OLEFIN UNK | 1.00 | 6.00 | | | | |
| 60 | CARBON TETRABROMIDE | | | | | | 1.00 |
| 61 | CARBON TETRACHLORIDE | | | | | | 1.00 |
| 62 | CELLOSOLVE | | 3.00 | | 1.00 | | |
| 63 | CELLOSOLVE ACETATE | | 4.00 | | 2.00 | | |
| 64 | CHLOROBENZENE | | | | | | 6.00 |
| 65 | CHLOROFORM | | | | | | 1.00 |
| 66 | CIS-2-BUTENE | | 2.00 | | 2.00 | | |
| 67 | CIS-2-PENTENE | | 3.00 | | 2.00 | | |
| 68 | CYCLOHEXANE | | 5.00 | | 1.00 | | |
| 69 | CYCLOHEXANONE | | 4.00 | | 2.00 | | |
| 70 | CYCLOHEXENE | 1.00 | 4.00 | | | | |
| 71 | CYCLOPENTANE | | 4.00 | | 1.00 | | |
| 72 | CYCLOPENTENE | 1.00 | 3.00 | | | | |
| 73 | CYCLOPROPANE | | 2.00 | | 1.00 | | |
| 74 | DIACETONE ALCOHOL | | 5.00 | | 1.00 | | |
| 75 | DICHLORODIFLUOROMETHANE | | | | | | 1.00 |
| 76 | DICHLOROMETHANE | | | | | | 1.00 |
| 77 | DIMETHYLETHYLBENZENE | | 4.00 | 1.00 | | | |
| 78 | DIMETHYLFORMAMIDE | | | | | | 3.00 |
| 79 | DOCOSANE | | 22.00 | | | | |
| 80 | EICOSANE | | 20.00 | | | | |

(continued)

TABLE B-4

SPECIES PROFILES BY BOND GROUP

| SPECIES NO. | CHEMICAL NAME | OLE | PAR | ARO | CARB | ETH | UNREACTIVE |
|---|---|---|---|---|---|---|---|
| 81 | ETHANE | | | | | | 2.00 |
| 82 | ETHYL ACETATE | | 3.00 | | 1.00 | | |
| 83 | ETHYL ACRYLATE | | 3.00 | | 2.00 | | |
| 84 | ETHYL ALCOHOL | | 2.00 | | | | |
| 85 | ETHYL CHLORIDE | | | | | | 2.00 |
| 86 | ETHYL ETHER | | 3.00 | | 1.00 | | |
| 87 | ETHYLACETYLENE | | 4.00 | | | | |
| 88 | ETHYLAMINE | | 1.00 | | | | 1.00 |
| 89 | ETHYLBENZENE | | 2.00 | 1.00 | | | |
| 90 | ETHYLCYCLOHEXANE | | 7.00 | | 1.00 | | |
| 91 | ETHYLENE | | | | | 1.00 | |
| 92 | ETHYLENE DICHLORIDE | | | | | 1.00 | |
| 93 | ETHYLENE GLYCOL | | 1.00 | | 1.00 | | |
| 94 | ETHYLENE OXIDE | | 1.00 | | | | 1.00 |
| 95 | FORMALDEHYDE | | | | 1.00 | | |
| 96 | GLYCOL | | 1.00 | | 1.00 | | |
| 97 | GLYCOL ETHER | | 1.00 | | 1.00 | | |
| 98 | HENEICOSANE | | 21.00 | | | | |
| 99 | HEPTADECANE | | 17.00 | | | | |
| 100 | HEPTANE | | 7.00 | | | | |
| 101 | HEXADECANE | | 16.00 | | | | |
| 102 | HEXANE | | 6.00 | | | | |
| 103 | ISOBUTANE | | 4.00 | | | | |
| 104 | ISOBUTYL ACETATE | | 6.00 | | | | |
| 105 | ISOBUTYL ALCOHOL | | 4.00 | | | | |
| 106 | ISOBUTYL ISOBUTYRATE | | 7.00 | | 1.00 | | |
| 107 | ISOBUTYLENE | 1.00 | 2.00 | | | | |
| 108 | ISOMERS OF BUTENE | | 2.00 | | 2.00 | | |
| 109 | ISOMERS OF BUTYLBENZENE | | 4.00 | 1.00 | | | |
| 110 | ISOMERS OF DECANE | | 10.00 | | | | |
| 111 | ISOMERS OF DIETHYLBENZENE | | 4.00 | 1.00 | | | |
| 112 | ISOMERS OF DODECANE | | 12.00 | | | | |
| 113 | ISOMERS OF ETHYLTOLUENE | | 3.00 | 1.00 | | | |
| 114 | ISOMERS OF HEPTANE | | 7.00 | | | | |
| 115 | ISOMERS OF HEXANE | | 6.00 | | | | |
| 116 | ISOMERS OF METHYLPROP. BENZENE | | 4.00 | 1.00 | | | |
| 117 | ISOMERS OF NONANE | | 9.00 | | | | |
| 118 | ISOMERS OF OCTANE | | 8.00 | | | | |
| 119 | ISOMERS OF PENTADECANE | | 15.00 | | | | |
| 120 | ISOMERS OF PENTANE .. | | 5.00 | | | | |

(continued)

TABLE B-4

SPECIES PROFILES BY BOND GROUP

| SPECIES NO. | CHEMICAL NAME | OLE | PAR | ARO | CARB | ETH | UNREACTIVE |
|---|---|---|---|---|---|---|---|
| 121 | ISOMERS OF PENTENE | | 3.00 | | 2.00 | | |
| 122 | ISOMERS OF PROPYLBENZENE | | 3.00 | 1.00 | | | |
| 123 | ISOMERS OF TETRADECANE | | 14.00 | | | | |
| 124 | ISOMERS OF TRIDECANE | | 13.00 | | | | |
| 125 | ISOMERS OF TRIMETHYLBENZENE | | 3.00 | 1.00 | | | |
| 126 | ISOMERS OF UNDECANE | | 11.00 | | | | |
| 127 | ISOMERS OF XYLENE | | 2.00 | 1.00 | | | |
| 128 | ISOPENTANE | | 5.00 | | | | |
| 129 | ISOPROPYL ACETATE | | 5.00 | | | | |
| 130 | ISOPROPYL ALCOHOL | | 3.00 | | | | |
| 131 | LACTOL SPIRITS | | 8.00 | | | | |
| 132 | M-ETHYLTOLUENE | | 3.00 | 1.00 | | | |
| 133 | M-XYLENE | | 2.00 | 1.00 | | | |
| 134 | METHANE | | | | | | 1.00 |
| 135 | METHYL ACETATE | | | | | | 3.00 |
| 136 | METHYL ALCOHOL | | 1.00 | | | | |
| 137 | METHYL AMYL ACETATE | | 8.00 | | | | |
| 138 | METHYL CELLOSOLVE | | 2.00 | | 1.00 | | |
| 139 | METHYL CHLORIDE | | | | | | |
| 140 | METHYL ETHYL KETONE | | 3.00 | | 1.00 | | |
| 141 | METHYL ISOBUTYL KETONE | | 5.00 | | 1.00 | | |
| 142 | METHYL N-BUTYL KETONE | | 5.00 | | 1.00 | | |
| 143 | METHYLACETYLENE | | 1.50 | | | | 1.50 |
| 144 | METHYLCYCLOHEXANE | | 8.00 | | 1.00 | | |
| 145 | METHYLCYCLOPENTANE | | 5.00 | | 1.00 | | |
| 146 | METHYLCYCLOPENTENE | 1.00 | 4.00 | | | | |
| 147 | METHYLENE BROMIDE | | | | | | 1.00 |
| 148 | MINERAL SPIRITS | | 7.00 | | 1.00 | | |
| 149 | N-BUTANE | | 4.00 | | | | |
| 150 | N-BUTYL ACETATE | | 5.00 | | 1.00 | | |
| 151 | N-BUTYL ALCOHOL | | 4.00 | | | | |
| 152 | N-DECANE | | 10.00 | | | | |
| 153 | N-DODECANE | | 12.00 | | | | |
| 154 | N-PENTADECANE | | | | | | |
| 155 | N-PENTANE | | 5.00 | | | | |
| 156 | N-PROPYL ALCOHOL | | 3.00 | | | | |
| 157 | N-PROPYLBENZENE | | 3.00 | 1.00 | | | |
| 158 | N-TETRADECANE | | 14.00 | | | | |
| 159 | N-TRIDECANE | | | | | | |
| 160 | NAPTHA | | 8.00 | | | | |

(Continued)

TABLE B-4

SPECIES PROFILES BY BOND GROUP

| SPECIES NO. | CHEMICAL NAME | OLE | PAR | ARO | CARB | ETH | UNREACTIVE |
|---|---|---|---|---|---|---|---|
| 161 | NONADECANE | | 19.00 | | | | |
| 162 | NONANE | | 9.00 | | | | |
| 163 | O-ETHYLTOLUENE | | 3.00 | 1.00 | | | |
| 164 | O-XYLENE | | 2.00 | 1.00 | | | |
| 165 | OCTADECANE | | 18.00 | | | | |
| 166 | OCTANE | | 8.00 | | | | |
| 167 | P-XYLENE | | 2.00 | 1.00 | | | |
| 168 | PERCHLOROETHYLENE | | | | | | 2.00 |
| 169 | PHENOLS | | | | | | 8.00 |
| 170 | PROPADIENE | | 1.00 | | 2.00 | | |
| 171 | PROPANE | | 1.50 | | | | 1.50 |
| 172 | PROPRIONALDEHYDE | | 2.00 | | 1.00 | | |
| 173 | PROPYL ACETATE | | 4.00 | | 1.00 | | |
| 174 | PROPYLENE | 1.00 | 1.00 | | | | |
| 175 | PROPYLENE GLYCOL | | 2.00 | | 1.00 | | |
| 176 | PROPYLENE OXIDE | | 2.00 | | | | 1.00 |
| 177 | PROPYNE | | 2.00 | | | | 1.00 |
| 178 | SEC-BUTYLBENZENE | | 4.00 | 1.00 | | | |
| 179 | STYRENE | | 1.00 | 1.00 | 1.00 | | |
| 180 | TERPENES | 1.00 | 8.00 | | | | |
| 181 | TERT-BUTYL ALCOHOL | | 3.00 | | 1.00 | | |
| 182 | TERT-BUTYLBENZENE | | 4.00 | 1.00 | | | |
| 183 | TETRAHYDROFURAN | | 3.00 | | 1.00 | | |
| 184 | TETRAMETHYLBENZENE | | 4.00 | 1.00 | | | |
| 185 | TOLUENE | | 1.00 | 1.00 | | | |
| 186 | TRANS-2-BUTENE | | 2.00 | | 2.00 | | |
| 187 | TRANS-2-PENTENE | | 3.00 | | 2.00 | | |
| 188 | TRI/TETRAALKYL BENZENE | | 5.00 | 1.00 | | | |
| 189 | TRICHLOROETHYLENE | | | | | 1.00 | |
| 190 | TRICHLOROFLUOROMETHANE | | | | | | 1.00 |
| 191 | TRICHLOROTRIFLUOROETHANE | | | | | | 2.00 |
| 192 | TRIMETHYL AMINE | | 3.00 | | | | |
| 193 | TRIMETHYLFLUOROSILANE | | | | | | 3.00 |
| 194 | UNDECANE | | 11.00 | | | | |
| 195 | UNKNOWN SPECIES | 0.10 | 4.00 | 0.25 | 0.32 | 0.16 | |
| 196 | VINYL CHLORIDE | | | | | 1.00 | |
| 197 | XYLENE BASE ACIDS | | 2.00 | 1.00 | | | |

(concluded)

| TECHNICAL REPORT DATA *(Please read Instructions on the reverse before completing)* | | |
|---|---|---|
| 1. REPORT NO. | 2 | 3 RECIPIENT'S ACCESSION NO |
| 4. TITLE AND SUBTITLE<br>A NEW CARBON-BOND MECHANISM FOR AIR QUALITY SIMULATION MODELING | | 5 REPORT DATE<br>6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S)<br>J. P. Killus and G. Z. Whitten | | 8 PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Systems Applications, Inc.<br>101 Lucas Valley Road<br>San Rafael, California 94903 | | 10 PROGRAM ELEMENT NO.<br>CDWA1A/01-0301 (FY-82)<br>11 CONTRACT/GRANT NO.<br>68-02-3281 |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Environmental Sciences Research Laboratory-RTP, NC<br>Office of Research and Development<br>U.S. Environmental Protection Agency<br>Research Triangle Park, North Carolina 27711 | | 13. TYPE OF REPORT AND PERIOD COVERED<br>Interim 6/80 - 6/81<br>14. SPONSORING AGENCY CODE<br>EPA/600/09 |
| 15. SUPPLEMENTARY NOTES | | |


16. ABSTRACT

A new generalized kinetic mechanism for photochemical smog, which incorporates recent information on the atmospheric reactions of aromatic hydrocarbons, has been developed. The mechanism, labeled the Carbon-Bond Mechanism III (CBM III), is the third lumped-parameter mechanism to be designed in accordance with the carbon-bond reaction concept in which carbon atoms with similar bonding are treated similarly, regardless of the molecules in which they occur. Because of the general nature of the CBM III, it can be used to model the entire atmospheric mix of hydrocarbons and is suitable for use in air quality simulation models. Principal features of CBM III include a separate reaction scheme for ethylene, realistic photochemistry for aromatic hydrocarbons and dicarbonyl compounds, and formation pathways for alkyl nitrates and nitroaromatic compounds. CBM III was tested by comparing the predictions obtained with the mechanism against smog chamber data of multi-component hydrocarbon/$NO_x$ mixtures. In addition to a discussion of the development and testing of the CBM III, information is also provided on the application of the mechanism for urban air quality modeling.


| 17. KEY WORDS AND DOCUMENT ANALYSIS | | |
|---|---|---|
| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
| | | -- |
| 18. DISTRIBUTION STATEMENT<br>RELEASE TO PUBLIC | 19 SECURITY CLASS *(This Report)*<br>UNCLASSIFIED<br>20 SECURITY CLASS *(This page)*<br>UNCLASSIFIED | 21. NO OF PAGES<br>118<br>22. PRICE |

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