



Project Summary

Development of Ozone Reactivity Scales for Volatile Organic Compounds

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Methods for developing a numerical scale ranking reactivities of volatile organic compounds (VOCs) towards ozone formation were investigated. Effects of small VOC additions on ozone formation (incremental reactivities) were calculated for 140 types of VOCs in model scenarios representing a variety of single-day pollution episodes. Relative reactivities determined from effects of the VOCs on maximum ozone concentrations (ozone yields) varied widely among the scenarios, but relative reactivities determined from effects on integrated ozone levels were less variable. A "maximum reactivity" scale was derived from ozone yield reactivities in scenarios where NO_x inputs were adjusted so the VOCs had the greatest effect on ozone, and a "maximum ozone" scale was derived from scenarios where NO_x inputs gave maximum ozone concentrations. These scales gave different relative reactivities for many VOCs, particularly aromatics. Several "multi-scenario" scales were derived from the ozone yield and integrated ozone reactivities in the unadjusted scenarios. The maximum ozone scale was more consistent with averages of ratios of ozone yield reactivities. The maximum reactivity scale was more consistent with ratios of integrated ozone reactivities and also corresponded best with multi-scenario scales developed to minimize the total error in ozone predictions. Information concerning effects of NO_x levels, of the composition of base case VOC emissions, and of other scenario conditions on reactivities was also obtained. Although case-by-case analysis is the best method to determine effects of VOC

emission changes on ozone formation, the maximum reactivity scale may be appropriate when a single VOC ranking must be used.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The formation of photochemical ozone continues to be a complex problem in many urban areas. Ozone is formed by the interactions of volatile organic compounds (VOCs) with oxides of nitrogen (NO_x), and control of both is necessary to solve the ozone problem. One of the ozone control strategies being considered is to change the chemical nature of VOC emissions so that they have less of a tendency to promote ozone formation, i.e., so that they are less "reactive." Two example strategies are the conversion of motor vehicles to alternative fuels and the substitution of currently used solvents with less reactive compounds. The development and assessment of such strategies require a means to quantify and compare the ozone formation reactivities of the many types of VOCs that can be emitted.

There are a number of ways to quantify the reactivities of a VOC. The most direct is to measure the change in ozone levels caused by changing the emissions of the VOC in an actual air pollution episode. This can be expressed as the "incremental reactivity" of the VOC, which is defined as the change on ozone caused by adding an arbitrarily small amount of the VOC to the



emissions, divided by the amount of VOC added. This takes into account the effects of all aspects of the organic's reaction mechanism on ozone formation. The incremental reactivities of VOCs in air pollution episodes can be estimated by using computer airshed models, given a representation of the conditions of the episode and of the atmospheric chemical reactions of the VOC.

Previous modeling studies have shown that incremental reactivities of VOCs depend on environmental conditions, particularly on the ratio of total emissions of reactive organic gases (ROG) to NO_x . This means that no single scale can predict incremental reactivities under all conditions. This complicates the development and use of VOC reactivity scales for regulatory and control strategy assessment purposes. The most scientifically justifiable option is not to use a single reactivity scale but to examine the effects of all proposed VOC changes on a case-by-case basis. But this is not practical for screening purposes or when a large number of alternative options need to be considered. For such cases, regulators have the options of either ignoring reactivity altogether or of using a generalized scale. Though not applicable to all conditions, the scale at least provides a practical method for using reactivity considerations in developing ozone control strategy.

If use of an appropriate reactivity scale has the practical effect of achieving better ozone control strategies than ignoring reactivity, then the second option is to be preferred. In this case, the problem becomes developing an optimum scale for such applications. In this work, we investigate and compare alternative approaches for deriving such generalized VOC reactivity scales.

Methods

Representative Pollution Episodes

A set of 62 idealized single-cell, single-day ozone pollution scenarios, representing 12 different urban areas throughout the United States, was taken as a representative distribution of ozone pollution episodes. The "all-city average" mixture of ROG species, taken from ground-level air measurements of VOC species in a variety of urban areas in the United States, was used to represent organic emissions from all sources in these scenarios. (This mixture of VOCs is called the "base ROG mixture" in the subsequent discussion, and its incremental reactivity is used as the standard against which the reactivities of the individual VOCs are compared.) These 62 scenarios may not accurately represent the conditions of any specific episodes, but as

a set they represent a wide distribution of the airshed conditions that might affect VOC reactivity. Therefore, they should be suitable for assessing methods to develop reactivity scales encompassing a wide range of conditions.

A representative subset of 21 of these 62 scenarios, designated the "base case" scenarios, were used to derive several different "base case, multi-scenario" reactivity scales. Because of the wide variation of ROG/ NO_x ratios in these scenarios, VOC reactivities, both absolute and relative, varied widely among these scenarios. To derive reactivity scales for more consistent sets of chemical conditions, two sets of modified scenarios were developed where NO_x inputs were adjusted to yield standard conditions of NO_x availability. For the "maximum reactivity" scenarios, the NO_x inputs for 29 scenarios were adjusted such that the base ROG mixture had the maximum reactivity. For the "maximum ozone" scenarios, the NO_x inputs for 21 scenarios were adjusted to yield the maximum peak ozone concentration. The NO_x inputs yielding maximum reactivity conditions are always higher than those yielding maximum ozone. For example, for a Los Angeles scenario, the maximum reactivity ROG/ NO_x ratio was 6, and the maximum ozone ratio was 8. However, these ratios varied from scenario to scenario.

In addition, two "averaged conditions" scenarios were developed for studying the effects on reactivity of changing the base ROG composition, one for maximum reactivity and one for maximum ozone ROG/ NO_x conditions. The scenario conditions other than NO_x inputs were derived roughly from the average of those for the set of city-specific scenarios discussed above.

Chemical Mechanism for VOCs

The chemical mechanism used in the reactivity calculations was recently developed and is documented in a previously published journal article. It includes separate representations of over 140 types of VOCs. The representation of approximately 20 of these was tested against results of environmental chamber experiments. The representations of the mechanisms for the others were estimated or derived by analogy with mechanisms for the species with better studied mechanisms and by using measured or estimated rate constants. The tabulations of the reactivity results for these species in this work include codes giving the level of uncertainty of the mechanism used for each type of VOC and the extent to which the mechanism for each VOC was tested against environmental chamber data. Although the atmospheric reaction mechanisms of many, if not most, of these VOCs

are highly uncertain, this mechanism incorporates our best present estimates for a wide variety of VOCs that are emitted into the atmosphere.

Quantification of Reactivity in an Individual Scenario

As indicated above, the incremental reactivity of a VOC is the change in ozone formation caused by adding a small amount of the VOC to the emission in a scenario, divided by the amount added. Reactivities are calculated for small amounts of added VOC to remove the dependence of reactivity on the amount added and also so that the incremental reactivities of mixtures can be calculated by linear summations of those of their components. The "ozone formed" quantity can be either the maximum ozone concentration calculated in the scenario or the ozone concentration integrated overtime. In the first case, the incremental reactivities are referred to as "ozone yield" reactivities, while in the latter case, they are referred to as "integrated ozone" reactivities. Both types of reactivity were calculated for the base case and the averaged conditions scenarios, while only ozone yield reactivities were calculated for the maximum reactivity and the maximum ozone scenarios.

The ozone yield reactivities of VOCs can be broken down into two components: the "kinetic reactivity," which is the fraction of the emitted VOC that reacts in the scenario, and the "mechanistic reactivity," which is the amount of ozone formed per molecule of reacting VOC. Separate estimates of these two components were made for the maximum reactivity scenarios and the maximum ozone scenarios.

Reactivity Scales Derived

Six different generalized or multi-scenario reactivity scales were developed from the incremental reactivities calculated for the various types of scenarios. The maximum reactivity (MaxRct) and the maximum ozone (MaxO₃) scales were developed by averaging the kinetic and mechanistic reactivities in the maximum reactivity or the maximum ozone scenarios. These can be thought of as generalized scales for fixed chemical conditions with respect to NO_x but with averaged conditions with respect to the other scenario inputs. Examples of incremental reactivities and reactivities relative to the base ROG mixture are shown for selected VOCs in Table 1.

The incremental reactivities in the maximum ozone scale are always lower than those in the maximum reactivity scale. This is because the efficiency of ozone formation from the reacting VOCs (i.e., the mechanistic reactivities) is higher under maximum

Table 1. Summary of Relative Reactivities for Selected VOC Species in Various Reactivity Scales

| Compound | Relative Reactivity ^a | | | | | |
|-----------------|----------------------------------|-------------------|---|--------|--------|--------|
| | Adj. No. Scales (Ozone Yield) | | Base Case, Multi-Scenario Scales (Ozone Yield) | | | |
| | MaxRct | MaxO ₃ | Avg.R | LS Fit | Avg.R | LS Fit |
| Carbon Monoxide | 0.034 | 0.070 | 0.076 | 0.043 | 0.050 | 0.036 |
| Methane | 0.0052 | 0.0090 | 0.0094 | 0.0060 | 0.0061 | 0.0048 |
| Ethane | 0.065 | 0.108 | 0.116 | 0.078 | 0.072 | 0.058 |
| n-Butane | 0.27 | 0.45 | 0.45 | 0.32 | 0.29 | 0.24 |
| n-Octane | 0.17 | 0.29 | 0.18 | 0.18 | 0.120 | 0.140 |
| Isooctane | 0.29 | 0.42 | 0.35 | 0.30 | 0.24 | 0.24 |
| n-Pentadecane | 0.078 | 0.128 | 0.0077 | 0.074 | -0.022 | 0.043 |
| Ethene | 2.2 | 2.8 | 3.0 | 2.4 | 2.4 | 2.2 |
| Propene | 2.8 | 3.0 | 3.3 | 2.9 | 2.9 | 2.7 |
| trans-2-Butene | 3.0 | 2.9 | 3.1 | 3.1 | 3.7 | 3.3 |
| 1-hexene | 1.25 | 1.20 | 1.10 | 1.26 | 0.92 | 1.13 |
| Benzene | 0.108 | 0.084 | 0.080 | 0.098 | 0.086 | 0.090 |
| Toluene | 0.71 | 0.38 | 0.21 | 0.58 | 0.45 | 0.59 |
| m-Xylene | 2.3 | 1.8 | 1.7 | 2.2 | 2.1 | 2.3 |
| Naphthalene | 0.32 | 0.039 | -0.129 | 0.21 | 0.122 | 0.25 |
| Methanol | 0.37 | 0.53 | 0.53 | 0.40 | 0.38 | 0.35 |
| Ethanol | 0.53 | 0.67 | 0.67 | 0.57 | 0.44 | 0.44 |
| Formaldehyde | 5.6 | 4.5 | 4.9 | 5.2 | 7.3 | 6.7 |
| Acetone | 0.22 | 0.20 | 0.19 | 0.21 | 0.17 | 0.19 |
| Benzaldehyde | -0.24 | -1.06 | -2.0 | -0.64 | -1.27 | -0.54 |

^aIncremental reactivities of the VOCs relative to the incremental reactivity of the base ROG mixture. Reactivity given on a carbon-mole basis. Abbreviations used:

- Ozone Yield - Scale derived from effects of VOCs on ozone yields
- Int'd Ozone - Scale derived from effects on integrated ozone
- MaxRct - Maximum reactivity scale
- MaxO₃ - Maximum ozone reactivity scale
- Avg. R - Scale derived by the average ratio method
- LS Fit - Scale derived by the least-squares fit method

reactivity conditions. More significantly in terms of VOC control strategies, for many types of VOCs the relative reactivities are also different in the two scales. For example, aromatic hydrocarbons have relatively high MaxRct reactivities but have relatively low MaxO₃ reactivities. This is because they have relatively large NO_x sinks in their mechanism, which significantly reduces their reactivities in scenarios where ozone is more NO_x limited. On the other hand, slowly reacting compounds such as CO and methane have higher relative reactivities in the maximum ozone scale. This is because OH radical levels tend to be higher under the lower NO_x maximum ozone scenarios than they are in the higher NO_x maximum reactivity scenarios. The higher radical levels mean that larger fractions of the slower reacting compounds will react. Aldehydes and alkenes have high relative reactivities in both scales.

Four "multi-scenario" relative reactivity scales were derived from the reactivities in the unadjusted or "base case" scenarios. These can be thought of as representing scales that might be appropriate if these base case scenarios represented a realistic distribution of airshed conditions. Two different methods were used to derive the scales from the distribution of reactivities in the individual scenarios, and separate scales were developed for ozone yield reactivities and for integrated ozone reactivities. In the "average ratio" method the scale was derived by averaging the ratios of incremental reactivities of the VOCs to the incremental reactivity of the base ROG mixture for all the scenarios. Each scenario was weighed equally, including the highly NO_x-limited scenarios, where VOC changes had only a small effect on reactivity. In the "least-squares error" method, the relative reactivities were de-

rived to minimize the least-squares error in absolute ozone predictions throughout the entire set of scenarios that would result from using the single scale. This gives greater weight to those scenarios where VOC changes have greater effects on ozone. Examples of the four base case relative reactivity scales are also shown in Table 1.

For most VOCs, the relative reactivities in the multi-scenario scale derived from ozone yield reactivities and the average ratio method corresponded roughly to those in the maximum ozone scale. However, this scale had a high degree of uncertainty because the reactivity ratios being averaged had a high degree of scatter. This is because ozone yield reactivities depend significantly on the ROG/NO_x ratio, which varied widely among the base case scenarios. The multi-scenario scale derived from ozone yield reactivities by the least-squares fit method had less scatter because there was less variability in reactivity ratios in the scenarios that had the largest effect on the scale. This scale corresponded reasonably well to the maximum reactivity scale. This is because the least-squares fit derivation method gives greater weight to scenarios that are closer to maximum reactivity conditions.

Integrated ozone relative reactivities tended to be less variable among the base case scenarios, and the multi-scenario scales derived using them tended to be less dependent on the derivation method. They also corresponded better to the maximum reactivity scale than the maximum ozone scale. This is because integrated ozone concentrations are always affected by the ozone formation rate, which is also the major factor affecting the ozone yield reactivity under maximum reactivity conditions. The ozone formation rate is a less important factor in determining ozone yield reactivities under maximum reactivity conditions. Under maximum ozone conditions, the ultimate ozone formation potential is the most important factor.

Dependence of Reactivities on Scenario Conditions

The level of uncertainty of any reactivity scale and its potential use as an ozone control assessment tool are influenced to a large extent by the sensitivities of reactivities to scenario conditions. The dependence on NO_x is known to be a very important factor. To investigate this further, reactivities relative to the base ROG surrogate were calculated as a function of the NO_x inputs for a series of representative VOCs for the "averaged conditions" scenario. The results indicated that ozone yield reactivities varied continually as the NO_x levels changed and

that there is no single characteristic relative reactivity of a VOC for NO_x -limited conditions. They also indicated that integrated ozone relative reactivities were much less dependent on NO_x levels than ozone yield relative reactivities. Integrated ozone and ozone yield relative reactivities tended to be similar at maximum reactivity NO_x levels and to then diverge from each other as NO_x was reduced. This is consistent with the fact that the multi-scenario, integrated ozone reactivity scales tended to agree better with the maximum ozone scale than with the maximum reactivity scale.

To investigate the effects of non- NO_x -related scenario conditions on reactivity, it is necessary to factor out the effects of these conditions on the effective availability of NO_x . A given NO_x level or ROG/NO_x ratio may correspond to maximum reactivity conditions for one scenario and maximum ozone or even NO_x -limited conditions for another, depending on how the scenario conditions affect ozone formation and NO_x removal rates. Therefore, holding NO_x inputs constant while varying other scenario conditions does not necessarily mean that conditions of NO_x availability are also being held constant. However, if the scenarios being compared have NO_x inputs adjusted to yield either maximum reactivity or maximum ozone conditions, then they have consistent conditions of NO_x availability. Thus, any differences in calculated reactivities for such scenarios would indicate the effects of other non- NO_x -related scenario conditions on reactivity.

The scenarios employed in this study had considerable variation in amounts of dilution, total VOC inputs, integrated light intensity, amounts of pollutants entrained from aloft, and relative amounts of pollutants present initially or emitted during the day. Although a systematic study of the effects of these factors on reactivity was not carried out, the variations in reactivities among the NO_x adjusted (maximum reactivity or maximum ozone) scenarios give an indication of the sensitivities of reactivities to these factors. For most VOCs, this variability caused variations in kinetic and mechanistic reactivities yielding standard deviations of averages on the order of $\pm 30\%$. VOCs with low mechanistic reactivity had much higher relative variability in mechanistic reactivity. These include high-molecular-weight alkanes under all conditions and aromatics under maximum ozone conditions. Except for aromatics, the extent of variability of reactivities tended to be similar for maximum reactivity and maximum ozone conditions.

These results do not indicate the effects of uncertainties or variabilities in the base

ROG mixture on reactivity, because the same mixture was used for all scenarios. Separate calculations were carried out to investigate the effects of uncertainties in the base ROG composition on VOC reactivities. The aldehyde fraction was varied from 0 to 15% of the mixture, and the amounts of alkenes and aromatics, relative to alkanes, were varied by factors of 2 relative to the standard mixture. The largest effect was found to be the effect of reducing the aldehyde fraction on aldehyde reactivity: decreasing it from 5% to 0% increased the formaldehyde reactivity by almost a factor of 2. Other than this, it is hard to make any generalizations concerning the effects of changing the ROD mixture on VOC reactivity — the qualitative effects seemed to vary considerably from case to case. Except for the large aldehyde-on-aldehyde effect, the effects of these rather large variations in the base ROG composition on the NO_x -adjusted incremental reactivities of these representative VOCs can be considered to be relatively small. Factor of 2 changes in alkene or aromatic fractions caused less than 25% changes in reactivities in most cases.

Conclusions

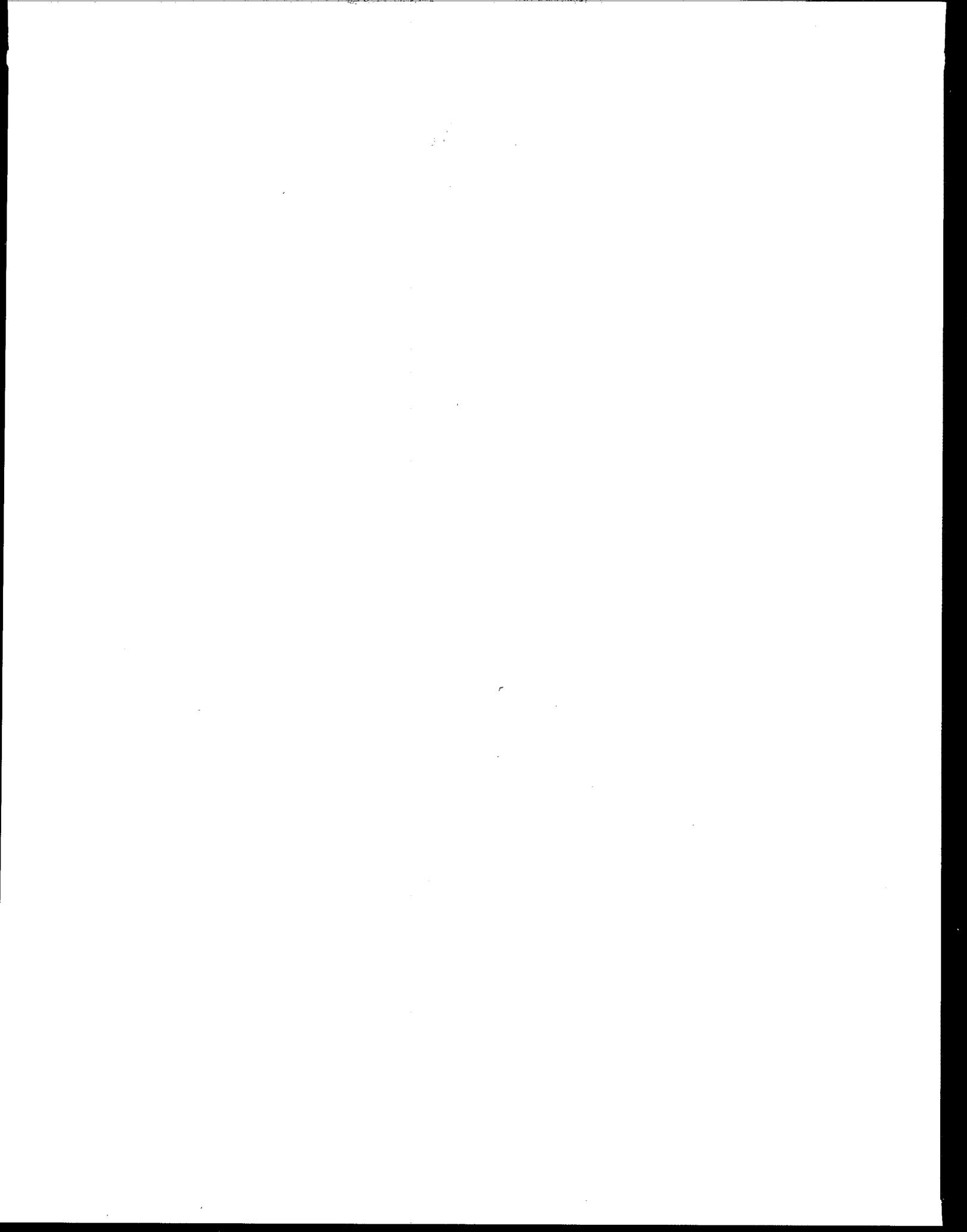
Developing VOC reactivity scales for ozone control strategies results in three types of difficulties: (1) gaps in our knowledge of the gas-phase reaction mechanisms cause major uncertainties in calculated reactivities for many VOCs, (2) uncertainties in airshed conditions also cause uncertainties in reactivity calculations, and (3) the dependence of VOC reactivities on airshed conditions means that there would be uncertainties in any reactivity scale that was developed even if the reactivities of the VOCs in individual airsheds were known. The focus of this work has primarily been on the third problem.

The difference in relative levels of NO_x is the most important reason that VOC reactivities vary from scenario to scenario. NO_x conditions significantly affect ratios of reactivities of VOCs in different chemical classes. It can be argued that the maximum reactivity and the maximum ozone reactivity scales developed in this work represent respectively the high and low limits for conditions of NO_x availability that are appropriate for defining a VOC reactivity scale. Significant concentrations of ozone are not formed if NO_x levels are much higher than those giving maximum reactivity. If NO_x levels are lower than those yielding maximum ozone, then ozone formation is NO_x limited, and NO_x control is much more effective than VOC control in reducing ozone. Therefore, comparison of MaxRct and the

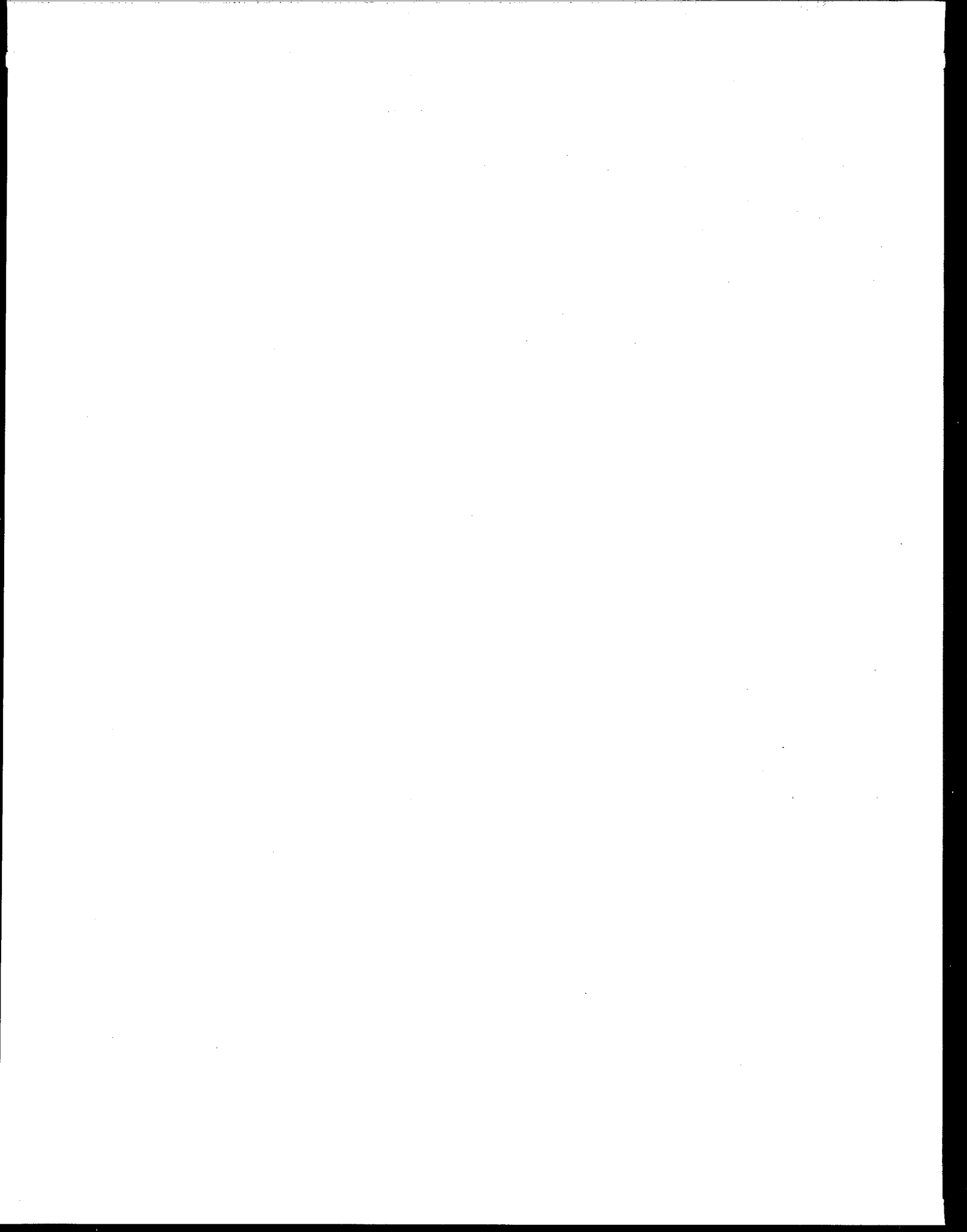
MaxO₃ scales, gives an appropriate indication of the effect on reactivity scales of uncertainties in NO_x conditions that are relevant to ozone control strategies.

Since these two reactivity scales can in some cases give significantly different predictions of benefits of proposed VOC substitutions, it can be questioned whether it is appropriate ever to use reactivity scales in control strategy applications. Obviously, if major substitution strategies are being considered, they should be evaluated as comprehensively as possible, and reliance on a single reactivity scale alone would not be justifiable. However, when this is not practical, it is reasonable to expect that the use of an appropriate reactivity scale would more likely lead to better ozone control strategies than if reactivity were ignored altogether. The problem then is to determine what is the best type of scale for this purpose. While not conclusive (because of the uncertainties in the set of scenarios employed), the results of this study suggest a maximum reactivity scale — such as the MaxRct scale — may give a good approximation to such an "optimum" scale. It gives reasonably good predictions of relative reactivities for airsheds where VOC changes have the largest effect on ozone, and it gives reasonably good predictions of relative integrated ozone reactivities for a wide variety of airsheds. Although these conclusions are based on reactivities calculated for highly simplified, single-day, and perhaps in some cases inaccurate scenarios, they are sufficiently varied that it is not unreasonable to expect that similar results would be obtained if more detailed and accurate scenarios were employed.

However, it is clear that further research is needed to reduce the uncertainties in the derivation of VOC reactivity scales. The uncertainties in airshed conditions obviously need to be reduced. More work is needed on the effects of scenario conditions on reactivity. The chemical mechanisms for many VOCs are highly uncertain, and experimental data are needed to reduce these uncertainties, or at least to test their predictions of maximum reactivity.



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The complete report, entitled "Development of Ozone Reactivity Scales for Volatile
Organic Compounds" (Order No. PB91-243 386/AS; Cost: \$26.00, subject to
change) will be available only from:*

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