



Project Summary

Reactivity/Volatility Classification of Selected Organic Chemicals: Existing Data

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This study deals with the classification of 118 organic chemicals according to their involvement in photochemical smog formation. A three-tiered classification system for these chemicals was developed using all available information on their chemical reactivity and volatility, both major determinants of a chemical's oxidant-forming ability. Although the degree of photochemical involvement of chemicals cannot be rigorously compartmentalized into discrete classes, a practical classification system is considered useful from a control strategy viewpoint. Separate three-tiered classification schemes of the reactivity and volatility of these 118 chemicals were also developed. Smog chamber data for low-reactivity organic chemicals may not be directly applicable to ambient conditions. In response to extensive shortcomings in existing information, a number of recommendations and theoretical/experimental protocols designed to bridge current information gaps are presented.

This Project Summary was developed by EPA's Environmental Sciences Research 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

Current strategies to control photochemical air pollution focus on decreasing the emission of volatile organic

compounds (VOCs). VOCs contribute significantly to the production of smog-forming oxidants. A strategy based on the control of such compounds that manifest themselves strongly in smog formation, rather than on indiscriminate control, clearly constitutes a superior technical approach.

Three major factors determine the ozone (O_3)- or oxidant-forming ability of an organic chemical:

- Ambient concentrations (or emissions)
- The ability of the organic chemical and its intermediate products to remain in the gas phase (volatility)
- The ability of the organic chemical to oxidize in the atmosphere (typically, by reacting with hydroxyl [OH] radical or O_3) and the efficiency of the oxidation products to form O_3 (reactivity).

This study deals with the reactivity/volatility classification of 118 organic chemicals (including isomers and mixtures) specified by the U.S. Environmental Protection Agency (EPA). A three-tiered classification system for these chemicals was developed using all available information on their chemical reactivity and volatility. As requested by EPA, separate three-tiered classification schemes of the reactivity and volatility of these chemicals were also developed. The three tiers of the chemical classification system were conceived as follows:

- Class I: Compounds that are unreactive or nonvolatile and do not contribute to smog formation.
- Class II: Compounds that are borderline cases or for which insufficient information is available to draw definitive conclusions.
- Class III: Compounds that are reactive and volatile and contribute to smog formation.

For cases where existing information does not allow any definitive conclusions, a research protocol to bridge many of the shortcomings of the current information needs to be developed. Note that the regulatory objective is to classify chemicals as those that either "contribute to smog" or those that "do not contribute to smog." The middle category of chemicals (Class II) was created as a practical necessity when a compound could not be placed in either of the other two classes because of a lack of reliable information.

Results and Discussion

The reactivity of organic chemicals (OCs) was assessed based on available experimental and theoretical data. Smog chamber data were available for only about one-half the chemicals of interest. Maximum O₃ yield, OC depletion rate, nitric oxide (NO), (or nitrogen dioxide [NO₂]) oxidation rate, and product compositions and concentrations were factors considered in the interpretation of smog chamber data. When smog chamber data were not available, the photochemical potential of OCs was determined based on their reactivity with OH radical. Reactions with O₃ or NO₃ and direct photolysis were considered when appropriate. When experimentally measured OH rate constants were not available, an OH rate constant estimation technique was employed. All the pertinent experimental data and results based on theoretical estimates are summarized in an appendix to the final report. Based on our best interpretation of available data, the following reactivity classification scheme can be derived:

- Class I: Organics where direct (smog chamber) data show O₃ formation significantly less than 0.12 ppm, and the chemical has a measured or calculated depletion rate that is comparable to, or less than, ethane.
- Class II: Direct evidence shows O₃ formation near 0.12 ppm or depletion

rates are 1 to 5 times that of ethane.

- Class III: Chemicals where direct evidence of O₃ formation in excess of 0.12 ppm (initial conditions of OC ≤ 4 ppm and any OC:nitrogen oxides [NO_x] ratio) is available, and/or measured, or calculated depletion rates are larger than 5 times that of ethane, or chemicals for direct or indirect evidence on reactivity exists.

There are a number of exceptions to such a reactivity classification scheme. Typical examples are OCs such as perchloroethylene and carbon disulfide, for which the smog chamber data conflict with kinetic theory and are probably not representative of atmospheric conditions. Another exception is the group of chemicals commonly called "inhibitors" (such as phenols, naphthalene, aniline, and possibly cresols). Such chemicals, although highly reactive, may not produce significant O₃. In assigning reactivity based on the above guidelines, exceptions were kept in mind.

A similar approach was used for the volatility classification scheme. The experimental data, in this case, were highly limited and often conflicting. However, the presence of particulate matter and its composition had a profound effect on the phase distribution of OCs. For the purposes of this study, we assumed a polluted atmosphere. Low-volatility OCs appeared to favor the gas phase in remote unpolluted atmospheres. Vapor pressure was judged as one of the key physical properties in establishing the aerosol/gas phase partitioning of OCs. When measurements were not available, vapor pressures were estimated from boiling-point data. These are summarized in an appendix to the final report. Although uncertainties remain, OC volatility may be classified most conveniently as follows:

- Class I: Organics with clearly greater percent occurrence in the condensed phase (>75% condensed phase) under ambient conditions (vapor pressure < 1 × 10⁻⁸ atm).
- Class II: Organics with intermediate phase distribution in ambient air (1 × 10⁻⁸ atm < vapor pressure < 1 × 10⁻⁶ atm), and organics of uncertain phase distribution or those having insufficient literature information.

- Class III: Organics with clearly greater percent distribution in the gas phase (vapor pressure > 1 × 10⁻⁶ atm).

Based on the above criteria, each of the 118 chemicals was assigned an individual "reactivity" and "volatility" class and an "overall" chemical class based on photochemical involvement (Table 1). For a description of the overall chemical classes, see the scheme outlined in the Introduction.

Conclusions and Recommendations

An important achievement of this study is the compilation of available reactivity and volatility information within a single document. An inherent limitation is the paucity of available data on which to base assessments. Even when data are available, there are often significant inconsistencies among the various studies performed. One source of inconsistency is the incompleteness of data. As an example, OCs found to be quite unreactive at low OC:NO_x ratios (2:5), appear to be quite reactive when this ratio is increased to 20 or more. In many cases, however, the increased reactivity is simply a smog chamber artifact that makes the results unrepresentative of ambient conditions. In addition, several classes of compounds (such as organic acids) have been insufficiently studied. Thus, extreme caution and judgment are required to assess the reliability of a given study.

Available volatility data are also very sparse, and their interpretation is subject to some judgments as well. Because of the paucity of these data, we have made several recommendations to bridge the data gaps.

Table 1. Reactivity/Volatility Classification of Selected Organic Chemicals

Chemical Name	No.	Classification		
		Reactivity	Volatility	Overall
Acetic acid	1	III	III	III
Acetic anhydride	2	II [†]	III	II
Acetaldehyde	3	III	III	III
Acetone	4	III	III	III
Acetone cyanohydrin	5	II [†]	III	II
Acetonitrile	6	I	III	I
Acetylene	7	I	III	I
Acrylic Acid	8	III [†]	III	III
Acrylonitrile	9	III	III	III
Adipic acid	10	III [†]	III	III
Aniline	11	II [*]	III	II
Benzene	12	II	III	II
Bisphenol-A	13	III [†]	I ^{**}	I
1,3-Butadiene	14	III	III	III
n-Butane	15	III	III	III
i-Butane	16	III	III	III
Butenes	17A-C	III	III	III
Isobutylene	18	III	III	III
n-Butanol	19	III	III	III
2-Butoxyethanol	20	III	III	III
n-Butyl acetate	21	III	III	III
s-Butyl acetate	22	III	III	III
t-Butyl alcohol	23	III	III	III
Carbon disulfide	24	II	III	II
Carbon tetrachloride	25	I	III	I
Chloroform	26	I	III	I
Monochlorobenzene	27	II	III	II
p-Dichlorobenzene	28	I	III	I
Dichloropropene (1,3 and 1,2)	29A-B	III [†]	III	III
Cumene	30	III	III	III
Cyclohexane	31	III	III	III
Cyclohexanol	32	III [†]	III	III
Cyclohexanone	33	III	III	III
Diethylene glycol	34	III [†]	III	III
Di-(2-ethylhexyl) phthalate	35	III [†]	I	I
Diisodecyl phthalate	36	III [†]	I	I
Dimethyl terephthalate	37	III [†]	III ^{**}	III
Epichlorohydrin	38	III [‡]	III	III
Ethane	39	I	III	I
Ethanol amine (mono)	40A	III [†]	III	III
Ethanol amine (di)	40B	III [†]	I	I
Ethanol amine (tri)	40C	III [†]	II	II
Ethyl acetate	41	III	III	III
Ethyl alcohol	42	III	III	III
Ethyl benzene	43	III	III	III
Ethyl chloride	44	II [‡]	III	II
2-Ethoxyhexanol	45	III [†]	III	III
Ethylene	46	III	III	III
Ethylene dibromide	47	I [‡]	III	I
Ethylene dichloride	48	I	III	I
Ethyl ether	49	III	III	III
Ethylene glycol	50	III [†]	III	III
Ethylene oxide	51	I	III	I
2-Ethyl hexanol	52	III [†]	III	III
Fluorocarbon 11	53	I	III	I
Fluorocarbon 12	54	I	III	I
Fluorocarbon 22	55	I	III	I
Fluorocarbon 113	56	I	III	I
Fluorocarbon 114	57	I	III	I
Formaldehyde	58	III	III	III
Glycerine	59	II [†]	II	II
Hexamethylenetetramine	60	III [†]	II ^{**}	II
Heptenes	61	III	III	III
1,6-Hexane diamine	62	III [†]	III ^{**}	III

Table 1. (Continued)

Chemical Name	No.	Classification		
		Reactivity	Volatility	Overall
Hydrogen cyanide	63	I [§]	III	I
Isodecyl alcohol	64	III [†]	II	II
Isoprene	65	III	III	III
Isopropyl alcohol	66	III	III	III
n-Propyl alcohol	67	III [§]	III	III
Maleic anhydride	68	III [†]	III	III
Methanol	69	III	III	III
Methyl chloride	70	I [§]	III	I
Methylene chloride	71	I	III	I
Methyl ethyl ketone	72	III	III	III
Methyl isobutyl ketone	73	III	III	III
Methyl methacrylate	74	III	III	III
Solvent naphtha	75	III	III ^{**}	III
Naphthalene	76	II [*]	III	II
Nitrobenzene	77	I	III	I
n-Octyl-n-decylphthalate	78	III [†]	I	I
Nonylphenol (ethoxylated)	79	III [†]	III ^{††}	II
Perchloroethylene	80	I [*]	III	I
Phenol	81	II [*]	III	II
Phosgene	82	I [†]	III	I
Phthalic anhydride	83	III [†]	II	II
Propane	84	III	III	III
Propylene	85	III	III	III
Propylene glycol	86	III [†]	III	III
Propylene oxide	87	III [§]	III	II
Styrene	88	III	III	III
Terephthalic acid	89	III [†]	III	III
Terephthalic acid (dimethyl ester)	90,37	III	III ^{**}	III
Tetrapropylene	91	III [†]	III ^{**}	III
Toluene	92	III	III	III
Toluene diisocyanate	93	III [†]	III	III
1,1,1-Trichloroethane	94	I	III	I
Trichloroethylene	95	III	III	III
Triethylene glycol	96	III [†]	III	III
Vinyl acetate monomer	97	III	III	III
Vinyl chloride monomer	98	III	III	III
m-and mixed Xylenes	99	III	III	III
o-Xylene	100	III	III	III
p-Xylene	101	III	III	III
Dimethyl succinate	102	III [†]	III ^{**}	III
Dimethyl glutarate	103	III [†]	III ^{**}	III
Dimethyl adipate	104	III [†]	III ^{**}	III
2-methoxy ethanol	105	III [†]	III ^{**}	III
Ethylene glycol monomethyl ether	106	III [†]	III	III
Ethylene glycol monoethyl ether	107	III [†]	III	III
Diisoamyl ketone	108	III [†]	III ^{††}	II
Propylene glycol methyl ether	109	III [†]	III	III
Dipropylene glycol methyl ether	110	III [†]	III	III
o,m,p Cresols	111A-C	III [§]	III	III

[†]No smog chamber or measured hydroxyl radical rate constant data were available.

^{*}Exception requiring special interpretation of data (see text).

^{**}Vapor pressure was estimated.

[§]No smog chamber data were available.

^{††}No vapor pressure estimate was possible.

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Basil Dimitriadis is the EPA Project Officer (see below).

The complete report, entitled "Reactivity/Volatility Classification of Selected Organic Chemicals: Existing Data," (Order No. PB 84-232 883; Cost: \$17.50, subject to change) will be available only from:

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The EPA Project Officer can be contacted at:

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