Reactivity Scale for Atmospheric Hydrocarbons Based on Reaction with Hydroxyl Radical

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■ By use of relative and absolute rate constants for the reaction of the hydroxyl radical (OH) with a number of alkanes, alkenes, aromatics, and ketones, a reactivity scale is formulated based on the rate of removal of hydrocarbons and oxygenates by reaction with OH. In this five-class scale, each class spans an order of magnitude in reactivity relative to methane. Thus, assigned reactivities range from <10 for Class I (containing only methane) to $>10^4$ for Class V containing the most reactive compounds (e.g., *d*-limonene). This scale differs in several significant ways from those presently utilized by air pollution control agencies and various industrial laboratories. For example, in contrast to other scales based on secondary manifestations such as yields of ozone and eye irritation, it focuses directly on initial rates of photooxidation. The proposed scale also provides a clearer understanding of the importance of alkanes in the generation of ozone during periods of prolonged irradiation. The present scale can be readily extended to include additional organic compounds (e.g., natural and anthropogenic hydrocarbons, oxygenates, chlorinated solvents), once their rate of reaction with OH is known.

It has been recognized for many years (*1–21*) that all hydrocarbons occurring in polluted atmospheres are not equally effective in producing photochemical oxidant, and hence that the application of cost effective strategies for the control of hydrocarbons requires that more stringent emissions reductions be applied to the more reactive organic compounds (*22–25*). This in turn has led to a continuing requirement for a rational assessment of hydrocarbon reactivity as a basis for control decisions. Such an assessment is particularly critical since attainment of the Federal air quality standard for photochemical oxidant has been sought largely through the stringent control of hydrocarbon emissions (*26–27*).

The first effort to formulate and apply a practical hydrocarbon reactivity scale was taken in 1966 with the implementation by the Los Angeles Air Pollution Control District (LAAPCD) of a regulation, known as Rule 66, to limit solvent organic emissions on the basis of their capacity for promoting photochemical smog formation (*24–25*). This rule and other conceptions of reactivity scales (*28*) represented a major advance in the application of the information then available concerning the mechanisms of photochemical smog formation to the development of practical air pollutant emission control strategies.

Not surprisingly however, both in the past and present, there have been significant differences in hydrocarbon reactivity scales proposed by local, regional, and national air pollution control agencies (*23, 29–31*) as well as by industry (*14, 16*). As shown in Table I, this can lead to very large differences in emission inventory estimates and in approaches to hydrocarbon control (*29, 32, 33*). In this case, reactive hydrocarbon emission inventory levels calculated by Goeller et al. (*32*) using hydrocarbon reactivity definitions of the Environmental Protection Agency (EPA) on the one hand, and the California Air Resources Board (ARB) and LAAPCD on the other, differed by factors of 3 to 4!

A second problem common to virtually all previous reactivity classifications has been their reliance on smog chamber data obtained for relatively short irradiation (~2–6 h) periods. Thus, the recent concern over oxidant formation resulting from longer irradiations during pollutant transport to regions downwind of urban sources introduces additional difficulties both in defining what constitutes a reactive hydrocarbon and in categorizing degrees of reactivity. For example, a compound such as propane, the major component in liquefied petroleum gas (LPG) and often cited as a "clean" fuel, is now known (*34–36*) to contribute to the formation of photochemical oxidants in the later stages of day-long irradiation periods. However, on the basis of data obtained during short-term irradiations, propane has been classified as "unreactive" in a reactivity scale proposed (*23*) by B. Dimitriades of the EPA (hereafter referred to as the EPA reactivity scale).

Altshuller and Bufalini (*9, 17*) have reviewed the various definitions of hydrocarbon reactivity and summarized results of numerous studies up to 1970. The criteria used for evaluating hydrocarbon reactivity include hydrocarbon consumption, the conversion of nitric oxide to nitrogen dioxide, ozone formation, aerosol formation, eye irritation, and plant damage. It is generally agreed that the criteria most suitable with respect to photochemical oxidant control strategies are ozone dosage or maximum ozone concentration (*29*). However, establishing a definitive hydrocarbon reactivity scale to be applied specifically to the control of ozone formation requires an extensive and lengthy experimental program in which the ozone-forming capability of each individual hydrocarbon is determined under simulated atmospheric conditions, including long-term irradiation (i.e., 12–14 h).

An alternative basis for assessing hydrocarbon reactivity, which would appear to have considerable utility and a valid experimental foundation, is the formulation of a reactivity scale based on the rate of disappearance of hydrocarbons due to reaction with the hydroxyl radical, the key intermediate species in photochemical air pollution.

Results and Discussion

It is only in the last six years that the critical role of OH in photochemical smog formation has been generally recognized (*37–40*) and that appreciable rate constant data have become available for the reaction of OH with several classes of hydrocarbons. The importance of OH as a reactive intermediate relative to species such as O_3, $O(^3P)$, and HO_2 has been shown previously (*39–41*) through computer modeling of smog chamber data. For example, Niki et al. (*39*) showed that the reactivity of a number of hydrocarbons, as measured by the rate of conversion of NO to NO_2, correlated significantly better with OH rate constants than with either $O(^3P)$ or O_3 rate constants.

Table I. Comparison of Reactive Hydrocarbon Inventory Levels for Fixed Sources Under Alternative Reactivity Assumptions (from Ref. *32* Based on Pre-1973 Data)

Control strategy	Reactive hydrocarbons, tons/day: Consistent EPA	ARB-LAAPCD	Rand Corp.
1970	876.0	228.3	636.3
1975 nominal	427.3	102.2	239.9
1975 maximal	290.6	57.7	129.9

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The utility of a large environmental chamber in obtaining relative rate constants with an accuracy of ±20% for the reaction of the hydroxyl radical with a variety of hydrocarbons was demonstrated in an earlier study in this laboratory (*41*). This method has recently been extended to an investigation of more than a dozen additional hydrocarbons, including seven compounds for which OH rate constants are not currently available. The detailed kinetic data derived from this investigation have been reported elsewhere (*42*). In these studies we determined the relative rates of disappearance of selected alkanes, alkenes, and aromatic hydrocarbons under simulated atmospheric conditions of temperature, pressure, concentrations, light intensity, and other trace contaminants (NO_x, CO, hydrocarbons, water). These relative rate constants were placed on an absolute basis using the published rate constants for OH + *n*-butane. The assumption that OH was responsible for the hydrocarbon disappearance under the experimental conditions employed (*41*) was subsequently supported by the very good agreement between OH rate constants determined for the individual compounds using flash photolysis–resonance fluorescence techniques (*43, 44*) and those obtained in the initial chamber study (*41*). The general validity of the chamber method for obtaining OH rate constants is illustrated in Figure 1 where the good correspondence between chamber values (*41, 42*) and the available literature values [(*45*) and references in Table IV] is shown graphically.

The importance of the chamber method for the purposes of formulating a reactivity scale is the simultaneous determination of valid rate constants for reactions of OH with a large number and wide variety of atmospherically important hydrocarbons. This substantially expands the number of compounds which can be incorporated, now and in the near future, in the resulting reactivity scale. In this regard we are currently extending (*46*) the chamber method to the determination of rate constants for reactions of OH with natural hydrocarbons, such as terpenes, and solvent hydrocarbons, such as ketones and chloroethenes, for which no data currently exist. Preliminary kinetic data (*46*) for selected natural hydrocarbons and ketones are included in our proposed reactivity scale.

Use of OH Rate Constants as a Reactivity Index. From the successful correlation of OH rate constants with the rates of hydrocarbon disappearance observed in our chamber simulations, we conclude that, to a good approximation, this

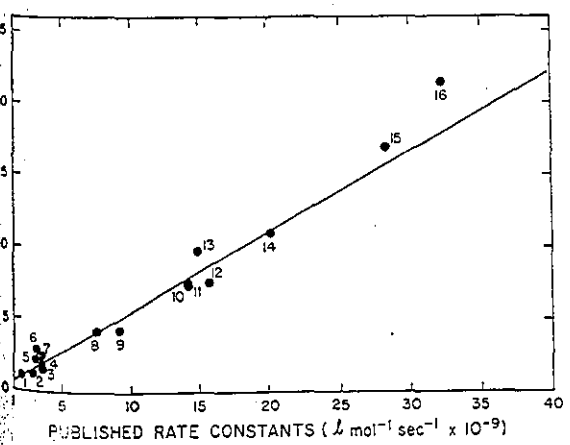

Figure 1. Comparison of relative rates of hydrocarbon disappearance determined by environmental chamber method (refs. *41* and *42*) with selected published rate constants (cited in Table IV) for reaction of those hydrocarbons with OH radicals

The line shown represents one to one correspondence and has slope of (1/1.8) × 10^9 l mol s^{-1}. Compounds shown are: 1, *n*-butane; 2, isopentane; 3, toluene; 4, 2-methylpentane; 5, *n*-hexane; 6, ethene; 7, 3-methylpentane; 8, *p*-xylene; 9, *o*-xylene; 10–11, *m*-xylene; 12, 1,2,3-trimethylbenzene; 13, propene; 14, 1,2,4-trimethylbenzene; 15, 1,3,5-trimethylbenzene; 16, *cis*-2-butene

Table II. Effect of 0.1 PPM Ozone on Calculated Lifetimes of Selected Alkenes Based on Reaction with OH Radicals (1×10^7 Radicals/cm^3) [a] at 300 K

Alkene	OH rate constants, [b] l. mol^{-1} s^{-1}	Half-life [c] for $[O_3] = 0$, h	Half-life [d] for $[O_3] = 0.1$ ppm, h
Ethene	3.8×10^9	3.0	2.8
Propene	1.5×10^{10}	0.76	0.67
cis-2-Butene	3.2×10^{10}	0.36	0.20
1,3-Butadiene	4.6×10^{10}	0.25	0.24

[a] Concentration used in these calculations—see text. [b] See references in Table IV. [c] $t_{1/2} = 0.693/k_{OH}[OH]$ under the assumption of attack only by OH. [d] $t_{1/2} = 0.693/(k_{OH}[OH] + k_{O_3}[O_3])$; k_{O_3} taken from refs. *45* and *59*.

correlation can be extrapolated to the atmosphere for alkenes in ambient air parcels during the early morning hours when ozone levels are generally quite low (≤0.05 ppm), and for alkanes and aromatics at essentially all times and locations. The latter assumption, namely, that an OH rate constant is a good "reactivity index" for alkanes and aromatics throughout an irradiation day (or multiple irradiation days), rests upon the fact that the rates of reaction of these classes of hydrocarbons with species such as ozone, $O(^3P)$ atoms, and hydroperoxyl radicals are several orders of magnitude slower than with OH (*45, 47–49*). For example, even at the highest ozone concentrations experienced in ambient atmospheres, O_3 will not contribute significantly to the photooxidation of alkanes and aromatics.

This is in contrast to the case for alkenes which, although the rate constants for reaction of O_3 with alkenes are not particularly large (*45*), react rapidly with ozone at the average concentrations commonly encountered in polluted ambient air (~0.1–0.2 ppm). The approximate magnitude of the effect of ozone on the atmospheric lifetimes of alkenes is given in Table II. From their OH rate constants (see Table IV), atmospheric lifetimes for four alkenes were obtained by assuming an OH radical concentration in polluted atmospheres of 10^7 radicals cm^{-3}, which is a reasonable value on the basis of both model calculations (*50*) and recent atmospheric measurements (*51–53*). The half-life given in column 3 of Table II is defined as $t_{1/2} = 0.693/k(OH)$, and assumes depletion of the hydrocarbon solely by the hydroxyl radical. When one assumes an average concentration of 0.10 ppm of O_3, the more reactive alkenes show considerably shorter half-lives (column 4). For example, the lifetime of *cis*-2-butene in the atmosphere is 0.36 h assuming only reaction with OH, but this is reduced to 0.20 h when reaction with O_3 at a concentration of 0.1 ppm is considered.

Proposed Reactivity Scale. Under the assumption that hydrocarbon depletion is due solely to attack by OH (with the qualification noted for alkenes), we propose a five-class reactivity scale based on hydrocarbon disappearance rates due to reaction with OH. The ranges of reactivities for the five proposed classes each span an order of magnitude in reactivity relative to methane and are shown in Table III. The hydrocarbon half-lives, as defined above, are also shown for each reactivity range.

Hydroxyl radical rate constant data for a wide range of atmospheric hydrocarbons have been taken from the literature as well as from our own studies and are compiled and referenced in Table IV. The assignment of these compounds in the various classes of our proposed reactivity scale is shown in the last column of Table IV. For interest, carbon monoxide is included in this table since, although it is not a hydrocarbon, it is present in polluted urban atmospheres but is generally regarded as being "unreactive" in ambient air. Thus, carbon

monoxide appears as being somewhat reactive in Class II, which also includes ethane and acetylene. In our current compilation of compounds, methane is the only compound listed which appears in Class I, and 2-methyl- and 2,3-dimethyl-2-butene and *d*-limonene are the only compounds in Class V. Several of the higher alkenes and 1,3-butadiene appear at the upper end of Class IV. Data from our recent study of monoterpene hydrocarbons (*46*) indicate that many of these compounds will appear in Class V (*54*).

Comparison with Other Scales. The ranking of reactivities for the aromatic hydrocarbons in our scale is essentially the same as that obtained by Altshuller et al. (*4*) and by Kopczynski (*7, 17*). Although our proposed scale is based solely on hydrocarbon disappearance rates, Altshuller and Bufalini (*17*) have shown that this measure of reactivity is very similar to the one based on nitric oxide oxidation rates. They showed that the ranking of reactivities of hydrocarbons from the nitric oxide photooxidation studies of Altshuller and Cohen (*6*) and Glasson and Tuesday (*8*) was essentially the same as that obtained from the studies of hydrocarbon consumption carried out by Schuck and Doyle (*1*), Stephens and Scott (*3*), and Tuesday (*5*). We are currently investigating methods of quantitatively relating hydrocarbon consumption to nitric oxide oxidation and ozone formation, the parameter of greatest interest in formulating control strategies for oxidant reduction.

As indicated above, Rule 66 formulated by the LAAPCD in 1966 represented the first hydrocarbon control measure based on photochemical reactivity. Although this regulation has been effective, results from recent studies (*34–36*) indicate that the 4–6 h irradiations (*25*), from which assignments of the degree of reactivity of hydrocarbons were made in formulating Rule 66, did not give sufficient recognition to the ozone-forming potential of slow reactors such as *n*-butane and propane. Consequently, it is now realized that measures more stringent than Rule 66 are necessary to achieve reductions in ozone formation to levels approaching those mandated by the U.S. Clean Air Act Amendments of 1970.

Recognition of such deficiencies in current hydrocarbon control regulations has led to reexamination of present hydrocarbon reactivity classifications. The focus of these re-evaluations has been the five-class reactivity scale (see Table V) proposed by B. Dimitriades at the EPA Solvent Reactivity Conference in 1974 (*23*). Significant changes have been suggested for this reactivity classification by the California ARB (*29, 30*), the LAAPCD (*31*), the EPA (*55*), and by industry. However, since no final conclusions have been reached by any of these agencies at this time, we will restrict comparison of our proposed scale to the 1974 EPA scale.

Table III. Reactivity Scale for Hydrocarbons Based on Rate of Disappearance of Hydrocarbon Due to Reaction with Hydroxyl Radicals

Class	Half-life[a]	Reactivity rel to methane (=1)
I	>9.9 days	<10
II	24 h to 9.9 days	10–100
III	2.4–24 h	100–1000
IV	0.24–2.4 h	1000–10 000
V	<0.24 h	>10 000

[a] $t_{1/2} = 0.693/k_{OH}[OH]$.

Table IV. Proposed Reactivity Classification of Hydrocarbons and CO Based on Reaction with Hydroxyl Radicals

Compound	k_{OH} + Cpd (l. mol^{-1} s^{-1}) × 10^{-9}	Ref[a]	Reactivity rel to methane	Proposed class, see Table III
Methane	0.0048	(*60*)	1	I
CO	0.084	(*45*)	18	II
Acetylene	0.11	(*45, 61, 66*)	23	II
Ethane	0.16	(*62*)	33	II
Benzene	0.85	(*43, 44*)	180	III
Propane	1.3	(*63*)	270	III
n-Butane	1.8	(*41, 42*)	375	III
Isopentane	2.0	(*42*)	420	III
Methyl ethyl ketone	2.1	(*46*)	440	III
2-Methylpentane	3.2	(*42*)	670	III
Toluene	3.6	(*43, 44*)	750	III
n-Propylbenzene	3.7	(*42*)	770	III
Isopropylbenzene	3.7	(*42*)	770	III
Ethene	3.8	(*42, 64–66*)	790	III
n-Hexane	3.8	(*42*)	790	III
3-Methylpentane	4.3	(*42*)	900	III
Ethylbenzene	4.8	(*42*)	1000	III–IV
p-Xylene	7.45	(*41, 43*)	1530	IV
p-Ethyltoluene	7.8	(*42*)	1625	IV
o-Ethyltoluene	8.2	(*42*)	1710	IV
o-Xylene	8.4	(*41, 43*)	1750	IV
Methyl isobutyl ketone	9.2	(*46*)	1920	IV
m-Ethyltoluene	11.7	(*42*)	2420	IV
m-Xylene	14.1	(*41, 43*)	2920	IV
1,2,3-Trimethylbenzene	14.9	(*41, 43*)	3100	IV
Propene	15.1	(*67*)	3150	IV
1,2,4-Trimethylbenzene	20	(*41, 43*)	4170	IV
1,3,5-Trimethylbenzene	29.7	(*41, 43*)	6190	IV
cis-2-Butene	32.3	(*67*)	6730	IV
β-Pinene	42	(*46*)	8750	IV
1,3-Butadiene	46.4	(*42*)	9670	IV–V
2-Methyl-2-butene	48	(*68*)	10 000	V
2,3-Dimethyl-2-butene	67	(*69*)	14 000	V
d-Limonene	90	(*46*)	18 800	V

[a] Where more than one reference is cited, an average value is given for the rate constant.

Table V. Proposed EPA Reactivity Classification of Organics (from Ref. *23*, 1974)

Class I, nonreactive	Class II, reactive	Class III, reactive	Class IV, reactive	Class V, reactive
C_1–C_3 paraffins	Mono-tertiary-alkyl benzenes	C_{4+} paraffins	Primary and secondary alkyl benzenes	Aliphatic olefins
Acetylene	Cyclic ketones	Cycloparaffins	Dialkyl benzenes	α-Methyl styrene
Benzene	Tertiary-alkyl acetates	Styrene	Branched alkyl ketones	Aliphatic aldehydes
Benzaldehyde	2-Nitropropane	*n*-Alkyl ketones	Primary and secondary alkyl alcohols	Tri- and tetra-alkyl benzenes
Acetone		Primary and secondary alkyl acetates	Cellosolve acetate	Unsaturated ketones
Methanol		*N*-methyl pyrrolidone	Partially halogenated olefins	Diacetone alcohol
Tertiary-alkyl alcohols		*N,N*-dimethyl acetamide		Ethers
Methyl acetate		Partially halogenated paraffins		Cellosolves
Methyl benzoate		Partially halogenated paraffins		
Ethyl amines				
Dimethyl formamide				
Perhalogenated hydrocarbons				
Reactivity rating: 1.0	3.5	6.5	9.7	14.3

Briefly, the EPA has proposed, on the basis of previous experimental studies, that methane, ethane, acetylene, propane, and benzene are essentially nonreactive for typical urban ambient hydrocarbon–NO_x ratios (*23*) and these compounds are placed in Class I on their scale. Three other classes have been proposed for mobile source hydrocarbon emissions (*56*)—Class III (C_4 and higher alkanes), Class IV (aromatics less benzene), and Class V (alkenes). When stationary source hydrocarbons, including solvents (Class II), are added to the list, five classes are suggested as shown in Table V.

The reactivity classification proposed here (Tables III and IV) can be compared with that suggested by the EPA (Table V). It is evident that several significant differences emerge:

- The C_1–C_3 alkanes are given equal weighting in the EPA scale, and all are designated unreactive, whereas our scale clearly differentiates among the three compounds from methane in Class I and ethane in Class II to the more reactive propane in Class III.
- According to our proposed classification, benzene and *n*-butane are of similar reactivity, whereas the EPA scale places them in Class I and III, respectively.
- All the alkenes are placed in Class V of the EPA scale, whereas our proposed scale shows a differentiation in reactivity from ethene in Class III to 2,3-dimethyl-2-butene in Class V.
- Our scale gives recognition to the high reactivity of natural hydrocarbons such as β-pinene and *d*-limonene, placing these in Class IV and V, respectively. The present published EPA scale does not give a classification for natural hydrocarbons, although they could be loosely categorized as substituted alkenes in Class V.

In addition to noting these differences, some similarities exist between the two scales. For example, our scale shows that 1,3-butadiene is highly reactive which is consistent with previous studies indicating it to be a facile precursor of eye irritants (*17*) and highly effective in producing oxidant during photolysis of HC–NO_x mixtures (*57*). Also, methanol would appear in the low half of Class II in our scale based on a recent determination of the rate constant for OH attack on methanol (*44*). The value found was $k_{(OH+CH_3OH)}/k_{(OH+CO)} = 0.63$ at 298 K. This reduces to 5.3×10^7 l. mol^{-1} s^{-1} based on $k_{(OH+CO)} = 8.4 \times 10^7$ l. mol^{-1} s^{-1} (*45*). Hence, both our scale and the EPA's show methanol to be relatively unreactive.

It should be emphasized that the classification proposed for our scale is not strictly applicable to compounds which undergo significant photodissociation in the atmosphere, for example, aliphatic aldehydes. In such cases, the compound will be more reactive than predicted from a scale based on hydrocarbon depletion due solely to OH attack. However, our proposed classification emphasizes that most compounds react in polluted atmospheres and suggests that the Class I scale be reserved only for the few compounds which have half-lives greater than about 10 days.

Conclusion

Our proposed reactivity scale based on the depletion of hydrocarbons by reaction with the OH radical has utility in assessing hydrocarbon chemical behavior in polluted ambient air. Since only those organic compounds which participate in atmospheric reactions are of consequence in the chemical transformations in ambient air, their relative reactivity toward OH is a useful and directly measurable index of their potential importance in the production of secondary pollutants.

One advantage of the proposed scale is that, because it is based on the individual rate constants for hydrocarbon reaction with OH, any degree of gradation in reactivity may be used to formulate any desired number of classes—from relatively few to a large number of classes or even an ordered ranking of compounds. A second strength of the present scale is that it can be readily extended to include additional organic compounds once their rate of reaction with OH is known. Finally, the proposed scale gives greater weight than previous reactivity scales to the alkanes and a number of aromatic hydrocarbons, which require a longer period of time to react but can contribute significantly to ozone formation during longer irradiation periods, e.g., during their transport downwind from urban centers—a phenomenon of increasing concern to air pollution control agencies.

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