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Potential of Hydrocarbons for Photochemical Conversion of NO to NO_2

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The factor F, the number of NO molecules which are converted photochemically into NO_2 when one hydrocarbon molecule is consumed, was determined for fourteen different hydrocarbons in the photochemical oxidation process. Experiments were carried out in a 67 dm³ Pyrex reaction chamber in which a mixture of hydrocarbon, NO, H_2O, and air was irradiated by a xenon short arc lamp. In the range from low to middle conversion, hydrocarbons and NO decayed nearly exponentially, NO being converted into NO_2. The observed value of F was approximately two for most of the hydrocarbons studied. The value is in line with the long chain mechanism involving OH radicals predicted by Heicklen *et al.* Only *m*-xylene gave a larger F value. Reaction sequences of the long chain mechanism caused by OH radicals were discussed, a generalized kinetic model for the chain mechanism being proposed. This will be useful for the atmospheric modeling of photochemical smog.

When mixtures of hydrocarbons and nitrogen oxides (NO and NO_2) in air are irradiated with ultraviolet radiation, NO is converted into NO_2 as hydrocarbons are consumed.[1,2] After the concentration of NO_2 passes through a maximum, O_3 and other oxidants such as PAN are produced as the NO_2 is consumed.

Heicklen *et al.*[3] proposed a long chain mechanism involving OH radicals for the photochemical conversion of NO into NO_2 in urban atmospheres. According to their mechanism, the conversion is promoted by the reaction of NO with $RO_2\cdot$ radicals which are formed in the reaction of organic free radicals and O_2.

$$RO_2\cdot + NO \longrightarrow RO\cdot + NO_2 \qquad (1)$$

In the reaction with propylene,[4] 2-methylpropene,[3] and butane,[3] Heicklen *et al.* proposed the following overall reactions.

$$C_3H_6 + 2NO + 2O_2 \longrightarrow CH_3CHO + CH_2O + 2NO_2 \qquad (2)$$

$$C_4H_8 + 2NO + 2O_2 \longrightarrow C_3H_6O + CH_2O + 2NO_2 \qquad (3)$$

$$C_4H_{10} + 2NO + 2O_2 \longrightarrow C_4H_8O + H_2O + 2NO_2 \qquad (4)$$

According to their suggestion, two NO molecules should be converted into NO_2 when one hydrocarbon molecule is consumed. However, if the intermediate radicals degrade further to form simpler aldehydes such as CH_2O in Reactions 2, 3, and 4, three to five NO molecules should be converted into NO_2 when one hydrocarbon molecule is consumed.[2]

This report deals with the measurement of the number of NO molecules (factor F) which would be converted into NO_2 when one hydrocarbon molecule is consumed.

Experiments were carried out for fourteen different hydrocarbons. The results would be useful for the computer simulation studies of atmospheric photooxidation processes.

Experimental

Experiments were carried out with use of a Pyrex cylinder as the reaction chamber, inner diam 240 mm, length 1660 mm and volume 67 dm³, which can be evacuated to less than 1×10^{-6} Torr. Each end of the reaction chamber was sealed with a Pyrex window 20 mm thick. The light source was a 500 W xenon short arc lamp and a parallel light beam of 200 mm ϕ was obtained with an elliptic mirror, a lens, and an off-axis parabolic mirror. The effective light intensity for the primary photo-decomposition rate of NO_2 was 0.08 min^{-1}.

An oil free pumping system consisting of an ion pump, titanium getter pump, cryo-sorption pump, and oil rotary pump with a liquid nitrogen cooled foreline trap was used in order to avoid oil contamination of the reaction chamber.

Hydrocarbons and NO were first subjected to pressure reading in a 105 ml flask, and then expanded to the reaction chamber. After that, water vapor and air were introduced through four inlets. In order to verify that all the gases had been mixed homogeneously, four sampling outlets were attached to the chamber, at the center, at one-fourth the distance from one end, and at both ends. After one and a half hours, the contents of sample gases from the four different ports reached the constant values. After this, sampling was done through the center port.

The decay of hydrocarbons were measured by a F.I.D. gas chromatograph, and the concentrations of NO and NO_2 were monitored by a chemiluminescent NO_x analyzer (Monitor Labs. Model 8440). The analyzer is capable of measuring simultaneously the concentrations of NO and total NO_x, where total NO_x is the sum of NO, NO_2, and other nitrogen containing compounds which can be reduced to NO by a molybdenum converter.

The concentration of reactants was 0.5—2 ppm of hydrocarbons and 1—2 ppm of NO in 1 atm of air, the relative humidity being about 60%. The mixture was irradiated until 50—60% of NO was converted into NO_2. In the case of T.M.E. (2,3-dimethyl-2-butene), the reaction proceeded too fast for consecutive GC analysis. Mesh screens were placed between the chamber and the light source in order to reduce the light intensity. The reaction mixture was drawn first into a constant volume glass bulb (700 cm³) and then concentrated in a GC sampling tube cooled by liquid nitrogen. After being subjected to the concentration process, the sampling tube was heated and the sample was fed into the gas chromatograph directly.

Sampling to the GC and to the NO_x analyzer was done every 20 or 30 min. When sampling had been carried out 7—10 times, the pressure of the reaction chamber decreased to *ca.* 600 Torr. The pressure drop effect on the measurements was calibrated in advance and all the data are corrected for the pressure change.

Chemicals (research grade, Wako Pure Chemical Ind.) were used without further purification except degassing. The gases, propylene and *cis*-2-butene (research grade, Takachiho

Kogyo Co.), pure air (pure gas B, Nippon Sanso), and NO (research grade, Matheson) were used without purification.

Before irradiation, the initial concentrations of NO and NO_2 in the mixture were measured by a NO_x analyzer. Usually, *ca.* 0.1 ppm of NO_2 was detected in a mixture containing *ca.* 1 ppm of NO.

The impurity of air and organic compounds adsorbed on the wall of the reaction chamber might convert NO into NO_2 by irradiation. In order to check the impurity effect a mixture of NO, water, and air was irradiated. The effect was found to be negligible.

Results and Discussion

When a dry mixture of hydrocarbon and NO with a small amount of NO_2 is irradiated, the initial decay of hydrocarbon and NO is very slow, showing an induction period, then the decay becomes faster as the reaction proceeds.[1,2] The time dependency of the concentrations of hydrocarbon and NO could not be followed by an exponential decay. On the other hand, if water vapor is added to the mixture, for example, at a humidity of 50%, the decrease of hydrocarbon and NO is much faster than for the dry mixture and is well approximated by an exponential decay up to the middle conversion region.[5] This could be explained by an equilibrium reaction between NO, NO_2, and H_2O and HONO.[6]

$$NO + NO_2 + H_2O \rightleftharpoons 2HONO \tag{5}$$

The HONO formed is photolyzed, giving OH radicals.[7]

$$HONO + h\nu(290\text{—}400\,\text{nm}) \longrightarrow OH + NO \tag{6}$$

Thus, in the wet system the reaction can be initiated by OH radicals and is followed by long chain reactions involving-OH radicals.[3] In this case the steady state concentration of OH radicals will be reached in a shorter reaction time.[8]

The result in the $C_3H_6/NO/H_2O$/air system is shown in Fig. 1. Propylene and NO decay nearly exponentially except for a few points after starting, the total NO_x remaining unchanged. According to reports by Winer *et al.*[9] and Spicer and Miller,[10] the commercial chemiluminescent NO_x analyzer responds to nitrogen containing compounds such as PAN, nitrates and nitrites. Thus we cannot state that all the amount of NO consumed was converted into NO_2. However, since the production of nitrates and nitrites could not be observed by F.I.D. gas chromatography and the conversion of C_3H_6 is not large (30%), the formation of nitrates and nitrite is thought to be very small and the great part of NO consumed would be NO_2. The ratio of the NO consumed to the C_3H_6 consumed is about 2. The net photochemical loss of the NO_2 formed is also negligibly small due to the following reaction sequences:

$$NO_2 + h\nu \longrightarrow NO + O \tag{7}$$

$$O + O_2 + M \longrightarrow O_3 + M \tag{8}$$

$$O_3 + NO \longrightarrow NO_2 + O_2 \tag{9}$$

Figure 2 shows the results of the *m*-xylene/NO/H_2O/air system. In this case the amount of the total NO_x decreases as *m*-xylene and NO are consumed. This could be explained by the formation of nitrates and nitrocompounds which was observed by F.I.D. gas chromatography. NO report seems to have appeared on the response of commercial chemiluminescent NO_x analyzer to aromatic nitrates and nitrocompounds. However, the result in Fig. 2 shows that it should be much lower than that to NO and NO_2. The ratio of the NO consumed to *m*-xylene consumed is *ca.* 3.2.

The amount of NO_2 produced (total NO_x—NO) was almost equal to that of NO consumed in the system of alkenes and alkanes. On the other hand, in the system of aromatic compounds, the amount of NO_2 produced

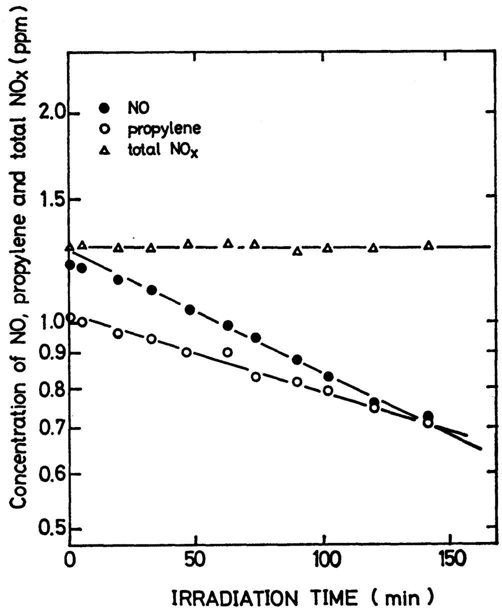


Fig. 1. Concentrations of NO (●), propylene (○), and total NO_x(△) *vs.* irradiation time. The concentration of NO_2 is the difference between total NO_x and NO.

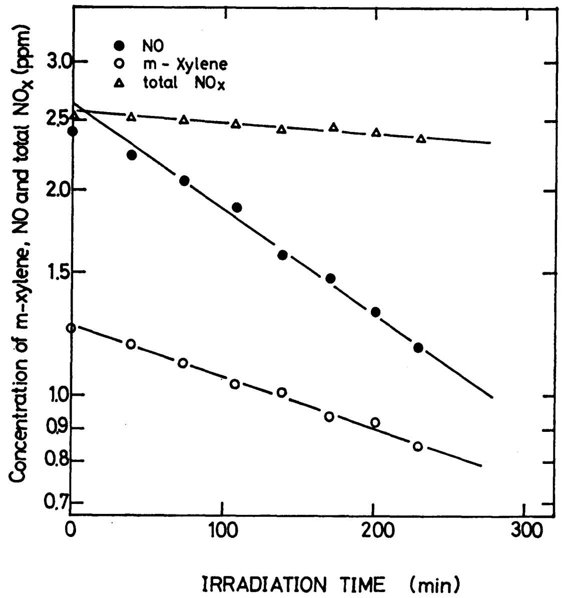


Fig. 2. Concentrations of NO (●), *m*-xylene (○), and total NO_x (△) are plotted against irradiation time.

was always smaller than that of NO consumed. Benzyl nitrate and *m*-nitrotoluene are produced in the photooxidation of the toluene/HONO/air system.[11,12] These nitrates and nitrocompounds are produced in other aromatic compounds. This would account for the loss of NO_2 as compared to the NO consumed in the reaction system involving these compounds.

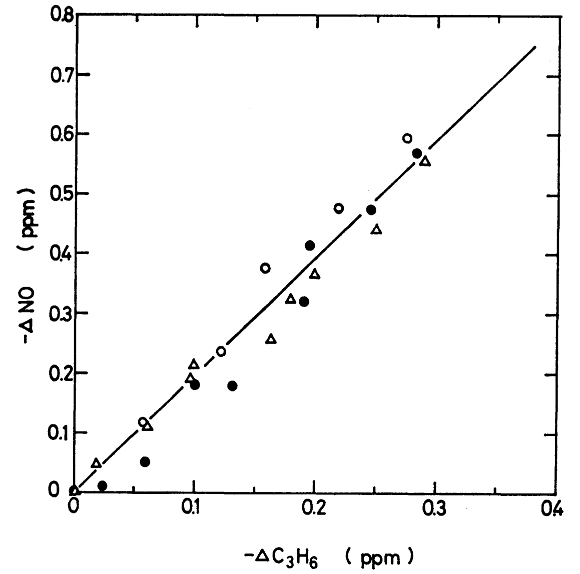


Fig. 3. Consumed NO, $-\Delta NO$, is plotted against comsumed propylene, $-\Delta C_3H_6$, for three different conditions.
Initial conditions are: (○) $[C_3H_6]=1.06$ ppm, $[NO]=1.85$ ppm; (△) $[C_3H_6]=1.01$ ppm, $[NO]=1.20$ ppm; (●) $[C_3H_6]=0.68$ ppm, $[NO]=2.20$ ppm.

In order to obtain the ratio of the NO consumed ($-\Delta NO$) to the hydrocarbons consumed ($-\Delta$H.C.), $-\Delta NO$ was plotted against $-\Delta$H.C. Figure 3 shows an example of propylene. The results under three different initial conditions lie on a straight line. The least-squares method was used in order to obtain factor *F*, *i.e.*, the number of NO molecules converted into NO_2 when one propylene molecule is consumed. The factors thus obtained are given in Table 1. Numbers in parentheses give the error limits, ±, calculated by the least squares standard deviation (5%).

Taking into consideration the error limits, the *F* value is found to be approximately 2 for most of the compounds studied. This value was predicted by Heicklen *et al.* for propylene,[4] 2-methylpropene,[3] and butane[3] and by Niki *et al.* for propylene.[1] Although there is a small difference between the mechanisms proposed by Heicklen *et al.* and Niki *et al.*, the overall reaction for propylene can be described by Reaction 2 in both mechanisms. Referring to the mechanism of Heicklen *et al.* and also that of Niki *et al.*, the reactions for *cis*-2-butene can be explained by the following:

$$C_4H_8 + OH \longrightarrow \cdot C_4H_8OH \tag{10}$$

$$\cdot C_4H_8OH + O_2 \longrightarrow HOC_4H_8O_2\cdot \tag{11}$$

$$HOC_4H_8O_2\cdot + NO \longrightarrow HOC_4H_8O\cdot + NO_2 \tag{12}$$

$$HOC_4H_8O\cdot \longrightarrow CH_3CHO + \cdot C_2H_4OH \tag{13}$$

$$\cdot C_2H_4OH + O_2 \longrightarrow HOC_2H_4O_2\cdot \tag{14}$$

$$HOC_2H_4O_2\cdot + NO \longrightarrow HOC_2H_4O\cdot + NO_2 \tag{15}$$

$$HOC_2H_4O\cdot \longrightarrow OH + CH_3CHO \tag{16}$$

The overall reaction is

$$C_4H_8 + 2NO + 2O_2 \longrightarrow 2CH_3CHO + 2NO_2 \tag{17}$$

Table 1. *F* factors for organic compounds

Compound	Run number	Initial conditions		Final concentration of hydrocarbon(ppm)	*F*(±)
		Hydrocarbon(ppm)	NO(ppm)		
Propylene	1	1.06	1.85	0.08	1.8 (0.2)
	2	1.01	1.20	0.70	2.2 (0.2)
	3	0.68	2.20	0.44	2.3 (0.3)
cis-2-Butene	4	0.92	2.03	0.67	2.0 (0.1)
	5	0.55	1.93	0.34	2.1 (0.3)
T.M.E.[a] (2,3-Dimethyl-2-butene)	6	1.11	1.99	0.78	2.0 (0.3)
Cyclopentene	7	1.08	2.02	0.40	1.9 (0.1)
Cyclohexene	8	1.26	1.71	0.70	2.3 (0.6)
Pentane	9	1.31	2.20	0.93	2.2 (0.3)
Hexane	10	2.00	2.21	1.60	2.0 (0.4)
Cyclopentane	11	0.84	1.83	0.61	2.2 (0.4)
Cyclohexane	12	1.21	2.03	0.92	2.3 (0.5)
	13	1.43	1.67	0.78	1.8 (0.1)
Toluene	14	1.34	1.69	1.00	2.2 (0.2)
	15	1.07	1.72	0.82	2.3 (0.3)
Ethylbenzene	16	1.46	1.96	1.05	1.9 (0.3)
o-Xylene	17	1.00	2.79	0.51	2.3 (0.2)
m-Xylene	18	0.97	2.18	0.76	3.4 (0.5)
	19	1.25	2.42	0.83	3.2 (0.3)
p-Xylene	20	0.91	1.83	0.57	2.4 (0.1)
	21	0.96	1.70	0.50	2.1 (0.3)
Mesitylene	22	0.92	1.75	0.56	2.3 (0.1)

a) Irradiation light intensity reduced to 1/8. Irradiation time 2—4 h for all measurements.

In the case of *cis*-2-butene, Demerjian *et al.*[2] proposed a reaction, which forms formic acid, instead of Reaction 16.

$$HOC_2H_4O\cdot \longrightarrow CH_3\cdot + HCOOH \qquad (18)$$

The reaction sequence is

$$CH_3\cdot + O_2 \longrightarrow CH_3O_2\cdot \qquad (19)$$

$$CH_3O_2\cdot + NO \longrightarrow CH_3O\cdot + NO_2 \qquad (20)$$

$$CH_3O\cdot + O_2 \longrightarrow H_2CO + HO_2\cdot \qquad (21)$$

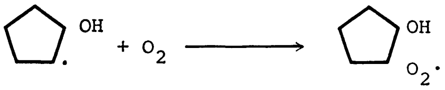
$$HO_2\cdot + NO \longrightarrow OH + NO_2 \qquad (22)$$

In this case four NO molecules should be converted into NO_2 as one *cis*-2-butene molecule is consumed. Our results, (F=2 for *cis*-2-butene), support the mechanism of Heicklen *et al.* and Niki *et al.*, and refute that of Demerjian *et al.* The results for T.M.E. could also be explained by the following overall reaction:

$$(CH_3)_2C_2(CH_3)_2 + 2NO + 2O_2 \longrightarrow 2(CH_3)_2CO + 2NO_2 \qquad (23)$$

For cyclopentene, the sequence would be

(24)



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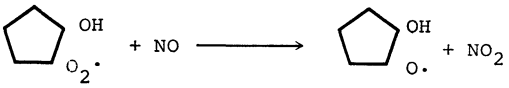

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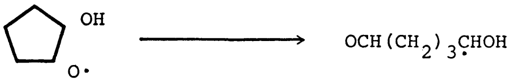


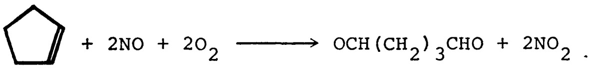
(27)

$$OCH(CH_2)_3\dot{C}H(OH) + O_2 \longrightarrow OCH(CH_2)_3CH(OH)O_2\cdot \qquad (28)$$

$$OCH(CH_2)_3CH(OH)O_2\cdot + NO \longrightarrow OCH(CH_2)_3CH(OH)O\cdot + NO_2 \qquad (29)$$

$$OCH(CH_2)_3CH(OH)O\cdot \longrightarrow OCH(CH_2)_3CHO + OH \qquad (30)$$

The overall reaction is



(31)

The photooxidation of cyclohexene could be explained in a similar way.

For alkanes, Heicklen *et al.*[3] proposed a mechanism for butane.[3] In a similar manner, the sequence for pentane is

$$C_5H_{12} + OH \longrightarrow C_5H_{11}\cdot + H_2O \qquad (32)$$

$$C_5H_{11}\cdot + O_2 \longrightarrow C_5H_{11}O_2\cdot \qquad (33)$$

$$C_5H_{11}O_2\cdot + NO \longrightarrow C_5H_{11}O\cdot + NO_2 \qquad (34)$$

$$C_5H_{11}O\cdot + O_2 \longrightarrow C_5H_{10}O + HO_2\cdot \qquad (45)$$

$$HO_2\cdot + NO \longrightarrow NO_2 + OH \qquad (22)$$

The overall reaction is

$$C_5H_{12} + 2NO + 2O_2 \longrightarrow C_5H_{10}O + H_2O + 2NO_2 \qquad (36)$$

For hexane, the overall reaction is

$$C_6H_{14} + 2NO + 2O_2 \longrightarrow C_6H_{12}O + H_2O + 2NO_2 \qquad (37)$$

Carter *et al.*[14] suggested an isomerization mechanism in the alkane reaction. In the case of pentane, $C_5H_{11}O\cdot$ formed in Reaction 34 can be isomerized in part *via* the following reaction:

$$C_5H_{11}O\cdot \longrightarrow \cdot C_5H_{15}(OH) \qquad (38)$$

The reaction might proceed *via*

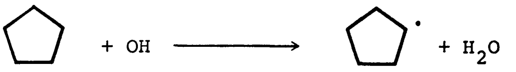
$$\cdot C_5H_{10}(OH) + O_2 \longrightarrow \cdot O_2C_5H_{10}(OH) \qquad (39)$$

$$\cdot O_2C_5H_{10}(OH) + NO \longrightarrow \cdot OC_5H_{10}(OH) + NO_2 \qquad (40)$$

$$\cdot OC_5H_{10}(OH) + O_2 \longrightarrow (OH)C_5H_9O + HO_2 \qquad (41)$$

$$HO_2 + NO \longrightarrow OH + NO_2 \qquad (22)$$

In this case, the value of factor F should be between 2 and 3, according to the competition between Reactions 35 and 38. Considering the error limit in Table 1, the mechanism proposed by Carter *et al.* is also acceptable in the case of pentane and hexane. In the case of cyclopentane, the sequence might be as follows:



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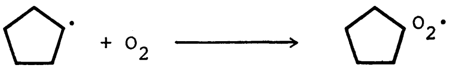

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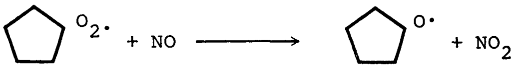
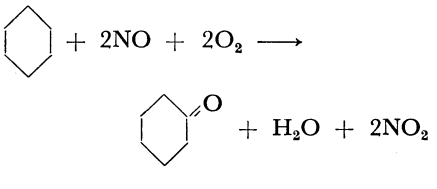


(44)

(45)

$$HO_2 + NO \longrightarrow NO_2 + OH \qquad (22)$$

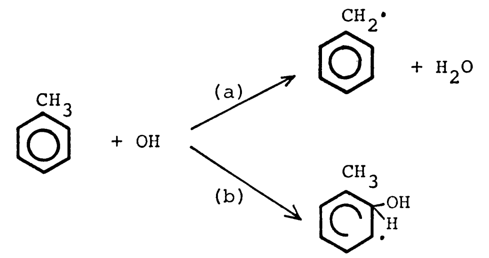
The overall reaction for cyclohexane is



(46)

The above mechanisms might explain the fact that factor F is usually about 2 for alkenes and alkanes.

In the reaction of aromatic hydrocarbons the mechanism is not so simple. For example, for toluene the reaction mechanism[11,12] might be



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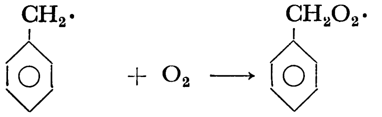
(48)

For path (a)



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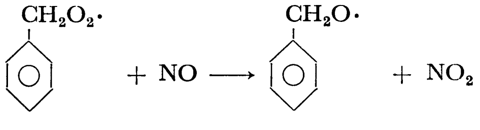

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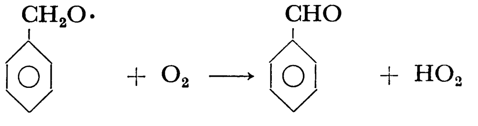
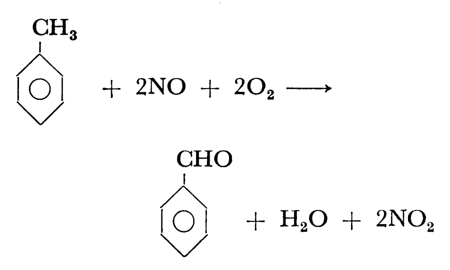


(51)

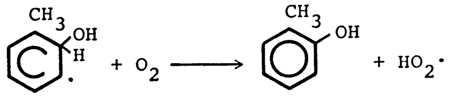
$$HO_2\cdot + NO \longrightarrow NO_2 + OH \qquad (22)$$

The overall reaction for path (a) is



(52)

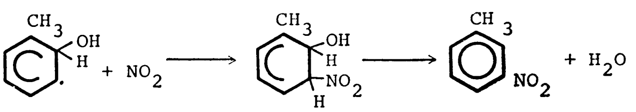
For path (b)



(53)

$$HO_2\cdot + NO \longrightarrow NO_2 + OH \qquad (22)$$

and



(54)

The formation of benzaldehyde, cresols, and m-nitrotoluene has been reported[11,12] in the photooxidation of the toluene/HONO/air system. According to the above mechanism, factor F for toluene should be less than two. However, small amounts of glyoxal and methylglyoxal have been detected in the photooxidation of the toluene/NO_2 system.[15] These products are also found in the photooxidation of the toluene or xylene/NO/H_2O/air systems.[13] The formation mechanism of these compounds is not yet clear, but it is most probable that they are formed after the aromatic ring is opened. Probably factor F for toluene becomes about 2 due to the radicals which are formed by the ring rupture.

The reaction mechanism of other aromatic compounds might be similar to that of toluene. The F factors for aromatic compounds are generally a little larger than 2, except for m-xylene. It is not known why the F factor of only m-xylene is larger than 3. Among the reaction rate constants of OH with xylene, only m-xylene is about twice faster than other o- and p-xylenes.[16] Probably the fraction of aromatic ring opening is larger in m-xylene.

In addition to the compounds listed in Table 1, determination of factor F was made for ethylene, which is of theoretical interest as the simplest alkene. Due to the poor efficiency of liquid nitrogen trapping of ethylene, the value for F scattered from 1.0 to 3.0, and is therefore not given in Table 1.

It has been suggested[17,18] that OH is the most important intermediate species during the initial stages of smog chamber experiments and that the contribution to attack on hydrocarbons by OH is much larger than O_3, HO_2, and $O(^3P)$. The contribution of O_3 to the consumption of hydrocarbons in the present study can be estimated as follows.

According to Reactions 7—9, the final steady state concentration of O_3 in our experiments is given by

$$[O_3]_{ss}^{final} = \frac{k_7[NO_2]^{final}}{k_9[NO]^{final}} \qquad (I)$$

where the value of k_7 is 0.08 min^{-1} except for the case of T.M.E. where it is 0.01 min^{-1}. The most recent value for k_9 is 26.5 ppm^{-1} min^{-1}.[19] The ratio of NO_2 to NO in the final measurement could be obtained experimentally, assuming that the concentration of NO_2 is equal to the value of total NO_x minus NO. The calculated final steady state concentrations of O_3 for several selected hydrocarbons are given in Table 2.

If hydrocarbons are consumed by OH and O_3, the concentration of hydrocarbons is given by the following equation, assuming that the concentrations of OH and O_3 are constant:

$$\frac{\ln[\text{hydrocarbon}]_0 - \ln[\text{hydrocarbon}]}{t} = k_a[OH] + k_b[O_3] \qquad (II)$$

where $[\text{hydrocarbon}]_0$ refers to the initial concentration of hydrocarbons, and k_a and k_b are the rate constants for the reaction of OH and O_3, respectively, with hydrocarbons. Since the initial and final concentrations for hydrocarbons and irradiation time, which is 2—3 h for alkenes, are known, the left hand side of Eq. II can be calculated. The values for k_b are reported for propylene,[20] cis-2-butene,[21] and T.M.E.[21] as 1.56×10^{-2}, 1.85×10^{-1}, and 1.55 ppm^{-1} min^{-1}, respectively. Therefore, the contribution of O_3 to the consumption of hydrocarbons at the final point of measurement can be

Table 2. Calculated values for $[O_3]_{ss}^{final}$, $k_b\,[O_3]_{ss}^{final}$ and the left hand side of Eq. II for selected alkenes given in Table 1

Compound	Run number in Table 1.	Irradiation time (min)	Calculated $[O_3]_{ss}^{final}$ (ppm)	$k_b\,[O_3]_{ss}^{final}$ (min^{-1})	$\frac{1}{t}\cdot\ln\frac{[hydrocarbon]_0}{[hydrocarbon]}$ (min^{-1})
Propylene	1	180	1.64×10^{-3}	2.6×10^{-5}	1.6×10^{-3}
	2	140	2.50	3.9	2.6
	3	140	1.29	2.0	3.1
cis-2-Butene	4	135	1.11	21	2.3
	5	150	1.05	19	3.2
T.M.E.[a] (2,3-Dimethyl-2-butene)	6	160	0.16	25	2.2
Cyclopentene	7	115	4.06	85[b]	8.6

a) Irradiation light intensity reduced to 1/8. b) Calculated using the rate constant for *cis*-2-butene+O_3 as k_b.

calculated by the form of $k_b[O_3]_{ss}^{final}$. The experimental decay rate of hydrocarbons and the calculated contributions of O_3 are given in Table 2 for propylene, *cis*-2-butene and T.M.E. The contribution of O_3 is less than 2 and 10% for propylene and *cis*-2-butene, respectively, and for T.M.E. nearly 10% at the final points in the measurements. These contributions of O_3 to other measured points would be much smaller, since ozone increases exponentially with irradiation time. The value for k_b is unknown for cycloalkanes. The effect on cyclopentene was calculated with use of the value of k_b for *cis*-2-butene. In this case the contribution by O_3 was also less than 10% (Table 2).

The contribution by O_3 should be very small in the case of alkanes and aromatics, because the reaction of ozone with alkanes and aromatics is extremely slow.

The results in Table 1 show that the long chain mechanism proposed by Heicklen *et al.*[3] and by Niki *et al.*[1] may be right and the value of factor F nearly equal to 2 can be used in computer simulation studies of the photooxidation process of a hydrocarbon and NO mixture.

The finding that factor F is approximately 2 regardless of the type and carbon number of hydrocarbons might allow us to propose a generalized oxidation chain mechanism which would be useful for the mathematical modeling of photochemical air pollution in an urban airshed. For alkenes the NO oxidation mechanism could be generalized as follows, referring to the mechanism given for *cis*-2-butene,

$$\begin{aligned}
\text{(A)}\quad & RH + OH \xrightarrow{+O_2} RO_2\cdot + H_2O \\
& RO_2\cdot + NO \longrightarrow RO\cdot + NO_2 \\
& RO\cdot + O_2 \longrightarrow R'_2CO + R''O_2\cdot \\
& R''O_2\cdot + NO \longrightarrow R'''_2CO + NO_2 + OH
\end{aligned}$$

where R'_2CO and R''_2CO represent aldehydes or ketones. Similarly, a generalized model for alkanes can be written as

$$\begin{aligned}
\text{(B)}\quad & RH + OH \xrightarrow{+O_2} RO_2\cdot + H_2O \\
& RO_2\cdot + NO \longrightarrow RO\cdot + NO_2 \\
& RO\cdot + O_2 \longrightarrow RCHO + HO_2\cdot \\
& HO_2\cdot + NO \longrightarrow OH + NO_2
\end{aligned}$$

Model (B) is equivalent to model (A) if $HO_2\cdot$ is recognized as $R'O_2\cdot$ and the difference in the type and the stoichiometric number of carbonyl compounds formed in the chain is ignored. In the case of aromatic hydrocarbons, path (a) initiated by H atom abstraction can be generalized just as for paraffins. However path (b) initiated by the OH addition and aromatic ring rupture path is difficult to be generalized at this stage since the reaction mechanism is far from being clarified. Nevertheless, from the evidence that the overall factor F is approximately 2 for most of the aromatic compounds, it is reasonable to adopt the generalized model of reaction (A) or (B) even for these compounds if the difference in the stoichiometric number and the type of oxidized compounds is ignored.

Thus, we propose a generalized kinetic model (A) or (B) for the NO oxidation chain processes in the presence of alkanes, alkenes, and aromatic hydrocarbons commonly present in the polluted urban atmosphere. This would be useful for the development of atmospheric photochemical air pollution modeling. Sveral reports[22–24] have appeared on the mathematical modeling of photochemical air pollution in an urban airshed. The mathematical modeling requires a kinetic reaction model for atmospheric reactions as well as models for atmospheric diffusion and transport processes. A kinetic model must satisfy certain requirements to be applicable to the atmospheric simulations. First, the model should predict the behavior of a complex mixture of hydrocarbons since a polluted urban atmosphere contains various hydrocarbon species. Second, since an atmospheric simulation model consists of a set of partial differential equations for diffusion and transport, the kinetic model must be compact enough to avoid excessive computation time for numerical integration. Model (A) or (B) satisfies these requirements. Since the models are common for various types of hydrocarbons, the chemical behavior of various hydrocarbon species is characterized only by the reaction rates with OH, O, and O_3. Thus, if it is combined with other typical reactions among NO, NO_2, O_3, RH, OH, and $RO_2\cdot$, the atmospheric simulation could be made by model (A) or (B).

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