PHOTOCHEMISTRY OF THE GASEOUS HYDROGEN PEROXIDE–CARBON MONOXIDE SYSTEM. II: RATE CONSTANTS FOR HYDROXYL RADICAL REACTIONS WITH HYDROCARBONS AND FOR HYDROGEN ATOM REACTIONS WITH HYDROGEN PEROXIDE

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Summary

Previous studies on the photochemistry of the system hydrogen peroxide–carbon monoxide–oxygen–isobutane, from which we obtained the rate constant for the reaction of hydroxyl with isobutane, have been continued with other aliphatic hydrocarbons and additional hydroxyl radical rate constants have been obtained. The constants obtained were: C_3H_6, 13.4×10^{-12}; C_3H_8, 2.2×10^{-12}; $n\text{-}C_4H_{10}$, 2.9×10^{-12}; $c\text{-}C_4H_8$, 1.2×10^{-12}; and $c\text{-}C_6H_{12}$, 6.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

For the reactions:

$$H + H_2O_2 \xrightarrow{k_5} H_2O + OH$$
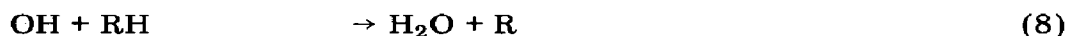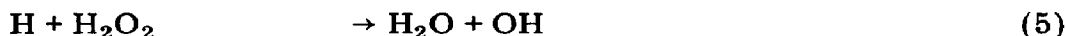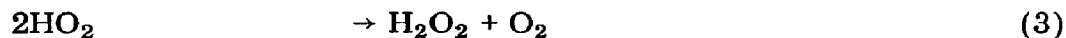$$H + H_2O_2 \xrightarrow{k_6} H_2 + HO_2$$
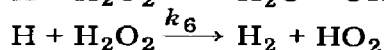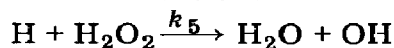
by a treatment of earlier data on the photochemistry of the system hydrogen peroxide–carbon monoxide, we have obtained $k_5 = 5.7 \times 10^{-15}$ and $k_6 = 3.1 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}.

Introduction

In a previous paper we have described a photochemical method for obtaining rate constants for hydroxyl radical reactions based solely on the determination of carbon dioxide [1]. The reaction scheme proposed was:

$$H_2O_2 + h\nu \text{ (254 nm)} \rightarrow 2OH \tag{1}$$
$$OH + H_2O_2 \rightarrow H_2O + HO_2 \tag{2}$$
$$2HO_2 \rightarrow H_2O_2 + O_2 \tag{3}$$
$$OH + CO \rightarrow CO_2 + H \tag{4}$$
$$H + H_2O_2 \rightarrow H_2O + OH \tag{5}$$
$$H + H_2O_2 \rightarrow H_2 + HO_2 \tag{6}$$
$$H + O_2 + M \rightarrow HO_2 + M \tag{7}$$
$$OH + RH \rightarrow H_2O + R \tag{8}$$

If the initial reaction system consisted only of hydrogen peroxide and an inert gas, carbon dioxide, the integrated rate expression was:

$$\ln \frac{[H_2O_2]_0}{[H_2O_2]_0 - 2[O_2]} = 2I_0' t \tag{9}$$

where, for a fixed illumination geometry, I_0' depends only on the incident intensity and was obtained from eqn. (9).

If the initial reaction system consisted of hydrogen peroxide and carbon monoxide, steady state considerations gave:

$$\frac{k_5}{k_6} = \left(\frac{d[CO_2]/dt}{d[H_2]/dt} \right)_0 - 1 \tag{10}$$

From which we obtained k_5/k_6 = 2.0 ± 1.0 at 298 K[*].

If the reaction system contained in addition sufficient oxygen so that the only reaction of hydrogen atom is reaction (7), the derived rate expression was:

$$\frac{2I_0'}{(d[CO_2]/dt)_0} = \frac{1}{[CO]_0} \frac{k_2}{k_4} + \frac{1}{[H_2O_2]_0} = A \tag{11}$$

From which, using a literature value of k_4, we obtained k_2 = 1.2 ± 0.3 × 10^{-12} cm^3 molecule^{-1} s^{-1}.

If, in addition, a hydrocarbon was added to the reaction system, the derived rate expression was:

$$\frac{2I_0'}{(d[CO_2]/dt)_0} = A + \frac{k_8[RH]_0}{k_4[CO]_0[H_2O_2]_0} \tag{12}$$

From which we obtained k_8 = 3.5 ± 0.8 × 10^{-12} cm^3 molecule^{-1} s^{-1} for isobutane.

We have continued experimental studies in the system immediately above and have obtained results for several additional aliphatic hydrocarbons. Also by further consideration of the data from which we obtained k_5/k_6, we have obtained values of the individual rate constants, k_5 and k_6.

Experimental

The experimental procedures were the same as before [1]. Additional compounds used were: propene, Matheson C.P.; propane, Matheson Instrument Grade; n-butane, Matheson C.P.; cyclobutane, a laboratory synthesized product supplied by Professor J. Root; and cyclohexane, Baker and Adamson, Reagent. Except for the cyclobutane, the purity of the hydrocarbons exceeded 99.9%; the cyclobutane contained 6.5% n-butane which, because of the small amount available to us, we did not remove. All of these hydrocarbons are transparent at 254 nm.

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[*] The value reported was 3.0 ± 1.0 but should have been given as 2.0 ± 1.0 because we neglected to subtract unity from the slope ratio as required by eqn. (10).

TABLE 1

Initial rate of CO_2 formation in the H_2O_2—CO—O_2—RH system

[RH]/ Torr	$(10^4 d[CO_2]/dt)/$ Torr s^{-1}
C_3H_6	
0.04	6.0
0.07	6.2
0.15	4.4
0.16	4.0
0.29	3.3
0.30	3.2
C_3H_8	
0.16	6.3
0.34	5.8
0.41	4.7
0.56	5.2
0.75	4.5
1.16	4.2
1.53	4.0
1.54	3.3
n-C_4H_{10}	
0.13	6.8
0.44	5.3
0.77	5.2
1.56	3.2
3.79	2.0
6.20	1.0
c-C_4H_8	
0.16	6.2
0.77	5.2
3.10	3.2
4.67	2.7
c-C_6H_{12}	
0.20	4.67
0.48	3.00
0.79	2.83
1.24	2.00
1.57	1.50
1.59	1.50
1.92	1.67
2.37	1.00

Results

The results obtained at 298 K with the hydrocarbons are given in Table 1. The experimental conditions were: initial hydrogen peroxide, 0.95 Torr;
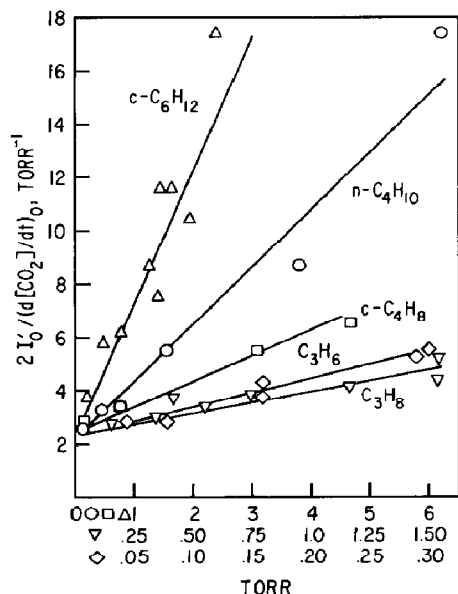
Fig. 1. Photochemical reaction in mixtures of H_2O_2, CO, O_2, and hydrocarbon at 254 nm and 25 °C.

initial carbon monoxide, 9.5 Torr; initial oxygen, 5.4 Torr; I_0', 8.7 × 10^{-4} s^{-1}. With added hydrocarbon, no carbon dioxide was produced in the absence of carbon monoxide.

Discussion

Rate constants for the reaction of hydroxyl with hydrocarbons

To obtain k_8 for the various hydrocarbons, we followed the procedure used in our previous paper for isobutane [1]. The data of Table 1 plotted in conformance with eqn. (12) are shown in Fig. 1. The slopes of the lines yield values of k_8/k_4 from which k_8 may be calculated using, as before, $k_4 = 1.5 \pm 0.3 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. The rate constants obtained are given in Table 2. The error limits given are ± 25%, in all cases greater than the standard deviations calculated from least squares analyses, which we consider a realistic appraisal. The comparison value for propene was obtained by a competitive kinetic scheme similar to ours [2]. The other comparison values were obtained by two different methods of kinetic spectroscopy: flash photolysis followed by optical absorption detection in a flow system [4]; a flow discharge followed by mass spectrometric detection [3, 5]. The three methods give values in reasonable agreement, particularly when it is noted that the values of Greiner [4] have been corrected from somewhat higher values and that there may be reason to believe that the correction is not justified [6].

The rate constants for the reaction of hydroxyl with alkane hydrocarbons are the only values for the reaction of an electrophilic free radical with a significant number of such hydrocarbons in the gas phase. It is, therefore,

TABLE 2

Rate constants for the reaction of hydroxyl with hydrocarbons

Compound	k_8/k_4	$10^{12}k_8/cm^3$ molecule^{-1} s^{-1}		
		This study	Literature value	Ref.
C_3H_6	89.3	13.4 ± 3.4	11.0 ± 3.0	2
			17.0 ± 4.3	3
C_3H_8	14.3	2.2 ± 0.6	1.2 ± 0.1	4
n-C_4H_{10}	19.4	2.9 ± 0.7	2.6 ± 0.1	4
			4.1 ± 1.1	5
i-C_4H_{10}	23.5[a]	3.5 ± 0.9	2.3 ± 0.2	4
c-C_4H_8	[8.47][b]	[1.3][b]		
c-C_4H_8		1.2 ± 0.3[c]		
c-C_6H_{12}	44.8	6.7 ± 1.5	4.8 ± 0.3	3

[a] Value obtained in our earlier work [1].
[b] Uncorrected for n-butane impurity.
[c] Corrected for n-butane impurity.

interesting to compare these rate constants with those obtained with oxygen atom in its ground state, ^{3}P, an even-numbered-electron electrophilic biradical, and with methyl radical, a typical non electrophilic radical. Such a comparison is shown in Table 3 for the hydrocarbons we have studied. Although propene has been included, the reaction with hydroxyl is almost entirely addition to the olefinic bond [3, 7] and eqn. (8) for propene should be modified to reflect this. The values for oxygen atom and methyl radical were calculated from the compilation of Kondratiev [8]. The methyl radical values are subject to considerable error because it was necessary to extrapolate from

TABLE 3

Comparison of rate constants for hydrogen atom abstraction

Compound	Relative rate constants, reaction with		
	OH	O	CH_3
C_3H_6	4.6	2.5	2.5
C_3H_8	0.8	0.8	0.002
n-C_4H_{10}	1.0	1.0	1.0
i-C_4H_{10}	1.2		5.0
c-C_4H_8	0.4	0.8	0.9
c-C_6H_{12}	2.3	6.2	3.0

high temperature data and, in particular, the value for propane is highly uncertain at any temperature. For n-butane, where the relative rates for each abstracting species are taken as unity, the rate constants are: hydroxyl, 2.9×10^{-12}; oxygen atom, 1.8×10^{-14}; and methyl, 6.7×10^{-20} cm^3 molecule^{-1} s^{-1}. For addition to propene, the oxygen atom rate constant is relatively very much greater than for either hydroxyl or methyl radicals, probably due to a quite different addition mechanism. With the exception of the reaction of methyl with propane, which we have pointed out above is a highly uncertain value, there is a fair parallelism among the sets of relative rate constants. Thus, there is no evidence from these data that electrophilicity of the abstracting species has an important effect on the order of reactivity of aliphatic hydrocarbons, alkenes, alkanes, and cyclic.

Rate constants for the reactions of hydrogen atoms with hydrogen peroxide
   As stated in the introduction, we have obtained k_5/k_6 from eqn. (10) and data represented in Fig. 2 of our previous paper [1]. Further considerations of the same data now allow us to obtain values for k_5 and k_6.
   In the system hydrogen peroxide—carbon monoxide, the amounts of carbon dioxide and hydrogen increase monotonically with time while the amount of oxygen reaches a maximum and then decreases. At the maximum the rates of formation and consumption of oxygen are balanced:

$$k_3[HO_2]^2 = k_7[H][O_2][M] \tag{13}$$

and

$$\frac{k_7[M]}{k_5 + k_6} = \left(\frac{1}{1 + k_5/k_6} \frac{d[CO_2]/dt}{d[H_2]/dt} - 1 \right) \frac{[H_2O_2]}{[O_2]} \tag{14}$$

From eqn. (10) and since $(d[CO_2]/dt)/(d[H_2]/dt)$ may be expressed by $(d[CO_2]/d[H_2])_t$, eqn. (14) gives:

$$\frac{k_7[M]}{k_5 + k_6} = \left\{ \left(\frac{d[H_2]}{d[CO_2]} \right)_0 \left(\frac{d[CO_2]}{d[H_2]} \right)_{O_2\,max} - 1 \right\} \left(\frac{[H_2O_2]}{[O_2]} \right)_{O_2\,max} \tag{15}$$

In Fig. 2, the H_2 vs. CO_2 yield has been plotted. The lower portion of the curve gives a straight line extrapolation to the origin, which is also an experimental point. The upper portion of the curve also yields a straight line which passes through the data corresponding to the maximum in the O_2 yield. From the plot $(d[H_2]/d[CO_2])_0 = 0.35$ and, hence, $k_5/k_6 = 1.86 \pm 0.14$, in good agreement with our earlier value. Also $(d[CO_2]/d[H_2])_{O_2\,max} = 4.2$, $[H_2O_2]_{O_2\,max} = 0.58$ Torr, and $[O_2]_{max} = 0.067$ Torr. From the above, $k_7[M]/(k_5 + k_6) = 4.1$. Additional pressures at the maximum in the O_2 yield were H_2, 0.1; CO, 15.7; H_2O, 0.5; and CO_2, 0.4 Torr. With argon as the third body, $k_7 = 2.4 \times 10^{-32}$ cm^6 molecule^{-2} s^{-1} at 298 K; the reported efficiencies of third bodies relative to argon taken as unity are: CO, 2; CO_2, 3; and H_2O, 13 [9]. Assuming that H_2O_2 is about as efficient as H_2O, the third body pressures are equivalent to an effective argon pressure of about 46 Torr. From which $k_5 = 5.7 \pm 1.4 \times 10^{-15}$ and $k_6 = 3.1 \pm 0.8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

To this time, the only values of k_5 which have been reported are gross approximations and, therefore, no realistic comparison with our value is possible. For k_6, however, it is possible to calculate rate constants from recent results on the reaction of deuterium atom with hydrogen peroxide [10]. Rate constants for the reaction:

$$D + H_2O_2 \rightarrow HD + HO_2 \qquad (16)$$

in the range 294 - 464 K were obtained which gave $k_{16} = 1.2 \times 10^{-11}$ exp $(-2100 \pm 200/T)$ cm^3 molecule^{-1} s^{-1}. At a single temperature, 375 K, $k_6/k_{16} = 0.43$ was obtained. This value of k_6/k_{16} is in good agreement with one which may be calculated from the isotope effect. The ratio of pre-exponential factors calculated from collision theory is $A_6/A_{16} = 1.39$. The difference in activation energies, $E_6 - E_{16}$, may be taken as equal to the difference in zero point energies in H_2 and HD, $E_{0(H_2)} - E_{0(HD)} = 3.46$ kJ. These values yield $k_6/k_{16} = 0.46$ at 375 K, in excellent agreement with the experimental value. Therefore, it is reasonable to use isotope effect theory to convert values of k_{16} to values of k_6. From $k_6 = [A_6/A_{16} \exp(E_{0(HD)} - E_{0(H_2)})/RT] \cdot k_{16}$, $k_6 = 1.7 \times 10^{-11} \exp(-2500/T)$ cm^3 molecule^{-1} s^{-1}. At 298 K, $k_6 = 3.9 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, in good agreement with our result.

A calculation of k_6 by Baulch et al. [9], which placed major emphasis on the results of Albers et al. [10] and some emphasis on the results of
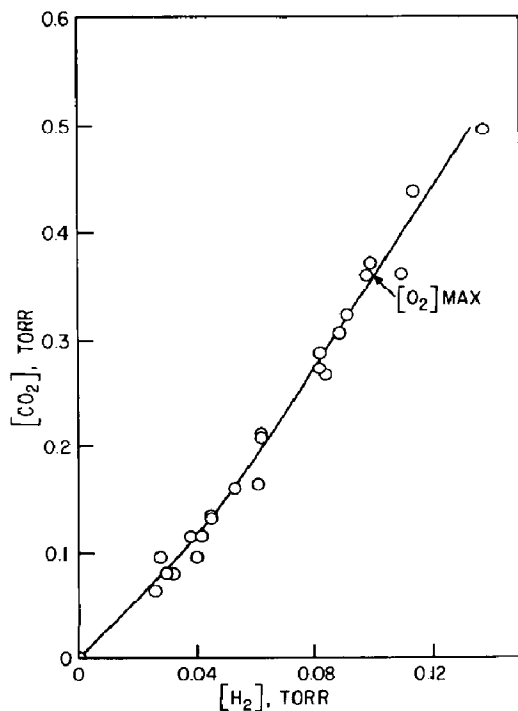

Fig. 2. Production of CO_2 and H_2 from mixtures of H_2O_2 and CO irradiated at 254 nm and 25 °C.

Baldwin *et al.* [11] at temperatures in the range 713 - 773 K, gave $k_6 = 2.8 \times 10^{-12} \exp(-1900/T)$ cm^3 molecule^{-1} s^{-1} and hence $k_6 = 4.8 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K. For this calculation $k_6/k_{16} = 0.43$ was taken as constant over the temperature range 294 - 464 K. However, as shown above, the effect of temperature on this ratio is appreciable and may be calculated with some confidence.

Acknowledgements

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