3016 *J. Phys. Chem.* **1990**, *94*, 3016-3019

Rates of Reaction of Hydroxyalkyl Radicals with Molecular Oxygen

Akira Miyoshi, Hiroyuki Matsui,

Department of Reaction Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo, 113, Japan

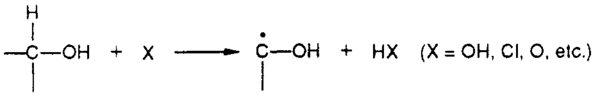
and Nobuaki Washida*

Division of Atmospheric Environment, The National Institute for Environmental Studies, P.O. Tsukuba-gakuen, Ibaraki, 305, Japan *(Received: August 30, 1989; In Final Form: October 30, 1989)*

The rate constants for the reactions of a series of hydroxyalkyl radicals with molecular oxygen have been measured at room temperature (296 ± 4 K) by laser flash photolysis–photoionization mass spectrometry. Measured rate constants are $k[\mathrm{CH_2OH{+}O_2}] = (1.17 \pm 0.12) \times 10^{-11}$, $k[\mathrm{CH_3CH_2CHOH{+}O_2}] = (2.61 \pm 0.41) \times 10^{-11}$, $k[\mathrm{CH_3CHCH_2OH{+}O_2}] = (1.16 \pm 0.22) \times 10^{-11}$, $k[\mathrm{CH_3CH(OH)CH_2{+}O_2}] = (3.82 \pm 0.60) \times 10^{-12}$, and $k[\mathrm{CH_3C(OH)CH_3{+}O_2}] = (3.71 \pm 0.62) \times 10^{-11}$, all in units of $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. These reactions seem to be at high-pressure limits at experimental pressures (1.3–5.5 Torr of He). Although it has been suggested in previous studies that the reaction mechanisms are different between α- and β-hydroxyalkyl radicals (H atom abstractions and recombinations, respectively), the present rates of reaction involving both α- and β-hydroxyalkyl radicals were found to correlate well with the ionization potentials of the radicals. This result suggests that the rate constants for all these reactions are largely controlled by the long-range forces similar to the reactions of alkyl radicals with molecular oxygen.

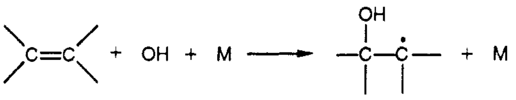
Introduction

Hydroxyalkyl radicals are known to be important intermediates in combustion processes[1] and atmospheric chemistry.[2] α-Hydroxyalkyl radicals are produced in initial steps of alcohol oxidations



$$-\underset{|}{\overset{\overset{\text{H}}{|}}{\text{C}}}-\text{OH} + \text{X} \longrightarrow \underset{|}{\overset{\bullet}{\text{C}}}-\text{OH} + \text{HX} \quad (\text{X} = \text{OH, Cl, O, etc.}) \tag{A}$$

and β-hydroxyalkyl radicals are well-known addition products of reactions of alkenes with OH

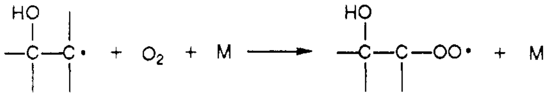


$$\rangle\text{C}=\text{C}\langle + \text{OH} + \text{M} \longrightarrow -\underset{|}{\overset{\overset{\text{OH}}{|}}{\text{C}}}-\underset{|}{\overset{\bullet}{\text{C}}}- + \text{M} \tag{B}$$

Despite the importance of the subsequent reactions of these radicals, there have been very limited studies on these reactions. Though the rate constant and the reaction mechanism for the reaction of hydroxymethyl radical with molecular oxygen have been extensively studied,[3-11] no direct measurements on the reactions of larger hydroxyalkyl radicals with oxygen have been available except for $\mathrm{CH_3CHOH + O_2}$.[12]

Products of the reactions of hydroxyalkyl radicals with $\mathrm{O_2}$ are suggested to be aldehydes (or ketones) + $\mathrm{HO_2}$ [H atom abstractions (C)][13-16] and peroxy radicals [recombinations (D)][13,17] for α- and β-hydroxyalkyl radicals, respectively.

$$-\underset{|}{\overset{\bullet}{\text{C}}}-\text{OH} + \text{O}_2 \longrightarrow -\underset{|}{\text{C}}=\text{O} + \text{HO}_2 \tag{C}$$



$$-\underset{|}{\overset{\overset{\text{HO}}{|}}{\text{C}}}-\underset{|}{\overset{|}{\text{C}}}\bullet + \text{O}_2 + \text{M} \longrightarrow -\underset{|}{\overset{\overset{\text{HO}}{|}}{\text{C}}}-\underset{|}{\overset{|}{\text{C}}}-\text{OO}\bullet + \text{M} \tag{D}$$

In the present study, the rate constants for the reactions of hydroxymethyl radicals ($\mathrm{C_1}$) and four isomers of hydroxypropyl radicals ($\mathrm{C_3}$) with molecular oxygen have been measured:

$$\mathrm{CH_2OH + O_2 \rightarrow products\ [CH_2O + HO_2]} \tag{1}$$

$$\mathrm{CH_3CH_2CHOH + O_2 \rightarrow products\ [CH_3CH_2CHO + HO_2]} \tag{2}$$

$$\mathrm{CH_3CHCH_2OH + O_2\ ({+}M) \rightarrow products\ [CH_3CH(O_2)CH_2OH\ ({+}M)]} \tag{3}$$

$$\mathrm{CH_3CH(OH)CH_2 + O_2\ ({+}M) \rightarrow products\ [CH_3CH(OH)CH_2O_2\ ({+}M)]} \tag{4}$$

$$\mathrm{CH_3C(OH)CH_3 + O_2 \rightarrow products\ [CH_3COCH_3 + HO_2]} \tag{5}$$

This is an extension of our previous study[18] on the reactions of two isomers of hydroxyethyl radicals ($\mathrm{C_2}$) with molecular oxygen.

The interests of the present study were focused on (i) extending our knowledge of the kinetics of these important reactions, (ii) investigating whether these rate constants reflect the difference of the type of reaction between α- and β-hydroxyalkyl radicals [(C) and (D)], and (iii) examining whether there is any systematic trend of the rate constants from $\mathrm{C_1}$ to $\mathrm{C_3}$ hydroxyalkyl radicals, such as the correlation of the rate constants with ionization potentials of the radicals, as was known for alkyl radicals + $\mathrm{O_2}$ reactions.[19]

---

(1) Westbrook, C. K.; Dryer, F. L. *Combust. Sci. Technol.* **1979**, *20*, 125.

(2) Atkinson, R. *Chem. Rev.* **1986**, *86*, 69.

(3) Radford, H. E. *Chem. Phys. Lett.* **1980**, *71*, 195.

(4) Wang, W. C.; Suto, M.; Lee, L. C. *J. Chem. Phys.* **1984**, *81*, 3122.

(5) Grotheer, H. H.; Riekert, G.; Meier, U.; Just, Th. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 187.

(6) Dóbé, S.; Temps, F.; Böhland, T.; Wagner, H. Gg. *Z. Naturforsch.* **1985**, *40A*, 1289.

(7) Payne, W. A.; Brunning, J.; Mitchell, M. B.; Stief, L. J. *Int. J. Chem. Kinet.* **1988**, *20*, 63.

(8) Grotheer, H. H.; Riekert, G.; Walter, D.; Just, Th. *J. Phys. Chem.* **1988**, *92*, 4028.

(9) Nesbitt, F. L.; Payne, W. A.; Stief, L. J. *J. Phys. Chem.* **1988**, *92*, 4030.

(10) Pagsberg, P.; Munk, J.; Anastasi, C.; Simpson, V. J. *J. Phys. Chem.* **1989**, *93*, 5162.

(11) Pagsberg, P.; Munk, J.; Anastasi, C.; Simpson, V. J. *Chem. Phys. Lett.* **1989**, *157*, 271.

(12) Grotheer, H. H.; Riekert, G.; Walter, D.; Just, Th. *Symp. (Int.) Combust.*, [*Proc.*], *22nd*, in press.

(13) Carter, W. P. L.; Darnall, K. R.; Graham, R. A.; Winer, A. M.; Pitts, J. N., Jr. *J. Phys. Chem.* **1979**, *83*, 2305.

(14) Ohta, T.; Bandow, H.; Akimoto, H. *Int. J. Chem. Kinet.* **1982**, *14*, 173.

(15) Washida, N. *J. Chem. Phys.* **1981**, *75*, 2715.

(16) Washida, N. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3757.

(17) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1978**, *82*, 135.

(18) Miyoshi, A.; Matsui, H.; Washida, N. *Chem. Phys. Lett.* **1989**, *160*, 291.

(19) Ruiz, R. P.; Bayes, K. D. *J. Phys. Chem.* **1984**, *88*, 2592.

0022-3654/90/2094-3016$02.50/0

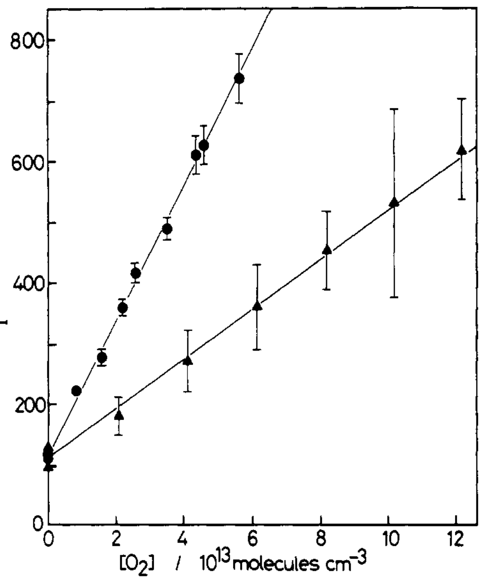


Figure 1. Plots of the first-order decay rates of radicals (k_1) against concentration of molecular oxygen ($[O_2]$). Circles denote experimental data for $CH_2OH + O_2$ reaction at 3.5 Torr. Triangles denote experimental data for $CH_3CH(OH)CH_2 + O_2$ reaction at 4.2 Torr. The error bars represent 2 standard deviations derived from the least-squares analysis. Lines are results of statistically weighted linear least-squares fits.

Experimental Section

The laser flash photolysis–photoionization mass spectrometry apparatus has been described previously.[18] A flowing gas mixture of appropriate precursor molecules for radicals and O_2 diluted in helium was irradiated by a ArF (193 nm) excimer laser (Questek Model 2420S). A small part of the reacting gas was introduced into the photoionization mass spectrometer through a 200-μm pinhole located at the wall of a tubular Pyrex reactor (1.76-cm i.d.). Radicals were ionized by light from a xenon resonance lamp [with a sapphire window (8.44 eV) or with a CaF_2 window (9.57 and 8.44 eV)] powered by a microwave discharge. The ions were mass-selected by a quadrupole mass filter and detected by a Daly type electrode and a scintillation counter. The temporal ion signals were recorded with a LeCroy 9400A digital oscilloscope during a 10-ms period. Signals were transferred to a personal computer after each laser pulse and were discriminated and accumulated for typically 5000–30 000 laser pulses before analysis. Total pressure was monitored by a capacitance manometer (MKS Baratron 170M-35). All gas flows were stabilized by a mass flow controller system (UNIT Model UFC-1100). At a repetition rate of 10–15 Hz, the flow velocity was high enough to completely replace the gas in the reactor between laser pulses. Precursor compound/He mixtures were prepared by passing He through a bubbling saturator, and the partial pressures of precursor molecules were estimated from the vapor pressure of the compounds and the flow rates of precursor compound/He mixtures. The initial radical concentrations were estimated from the laser power, partial pressures, and absorption coefficients of the precursor molecules.

Time profiles of the radical concentrations after laser pulse were fitted to single-exponential functions by the statistically weighted nonlinear least-squares fitting method, and thus the first-order decay rate constants (k_1) were obtained. The analysis revealed that all of the data could be interpreted by a first-order decay mechanism and that no complex radical–radical reactions were needed. Plots of the first-order rate constants vs O_2 concentration ($[O_2]$) gave the bimolecular rate constants (Figure 1).

TABLE I: Summary of the Experimental Rate Constants at 296 ± 4 K

	total press., Torr	$[O_2]$, 10^{13} molecules cm^{-3}	rate const, 10^{-12} cm^3 $molecule^{-1}$ s^{-1}
$CH_2OH + O_2$	1.3	0–6.7	12.9 ± 1.2
	3.5	0–5.7	11.1 ± 0.6
	5.5	0–5.7	12.7 ± 1.1
			11.7 ± 1.2[a]
$CH_3CH_2CHOH + O_2$	1.5	0–1.4	30.6 ± 5.2
	3.3	0–1.6	24.2 ± 2.6
	5.2	0–1.4	28.1 ± 4.3
			26.1 ± 4.1[a]
$CH_3CHCH_2OH + O_2$	3.1	0–3.2	11.7 ± 3.8
	4.2	0–2.5	11.9 ± 3.9
	5.1	0–3.9	11.4 ± 3.5
			11.6 ± 2.2[a]
$CH_3CH(OH)CH_2 + O_2$	2.5	0–12	3.45 ± 0.89
	4.1	0–16	2.51 ± 1.42
	4.2	0–12	4.07 ± 0.40
	5.1	0–12	3.29 ± 1.05
			3.82 ± 0.60[a]
$CH_3C(OH)CH_3 + O_2$	1.8	0–1.1	40.5 ± 6.0
	3.3	0–0.8	43.0 ± 7.4
	4.2	0–0.9	32.9 ± 11.1
	5.3	0–1.5	32.5 ± 5.2
			37.1 ± 6.2[a]

[a] Weighted average.

TABLE II: Precursor Molecules for Radicals

radical	precursor	ΔH_f of radical,[a] kcal mol^{-1}	excess energy,[b] kcal mol^{-1}
CH_2OH	$CH_3CO\text{-}CH_2OH$	-6.2	74.2
CH_3CH_2CHOH	$CH_3CH_2CH(OH)\text{-}COCH_2CH_3$	-23.5	75.1
CH_3CHCH_2OH	$CH_3CH(CH_2OH)\text{-}COCH_3$	-18.6	73.1
$CH_3CH(OH)CH_2$	$CH_3CH(OH)CH_2\text{-}Cl$	-18.8	66.1
$CH_3C(OH)CH_3$	$CH_3C(OH)(CH_3)\text{-}COCH_3$	-29.4	76.9

[a] Quoted from ref 20 or estimated by group additivity rules.[21,22] [b] Excess energy when the precursor molecules are photolyzed by 193-nm light. ΔH_f for precursor molecules were estimated by group additivity rules.[21,22]

Typical experimental conditions were as follows: total pressure = 1.3–5.5 Torr, precursor concentration = 0.3–31 mTorr, and O_2 concentration = 0–5 mTorr. The initial radical concentrations were kept low (~10^{11} and ~10^{12} molecules cm^{-3} for α-hydroxyalkyl radicals and β-hydroxyalkyl radicals, respectively) in order to reduce contributions from radical–radical reactions. Radical concentrations could be increased at least by a factor of 3 before an increase of radical decay rate due to the radical–radical reactions was observed.

He (Nippon Sanso, 99.9999%) and O_2 (Nippon Sanso, 99.99%) were used without further purifications. Hydroxyacetone (Tokyo Kasei), 4-hydroxy-3-hexanone (Tokyo Kasei), 4-hydroxy-3-methyl-2-butanone (Aldrich), 1-chloro-2-propanol (Janssen Chimica), 3-hydroxy-3-methyl-2-butanone (Tokyo Kasei), 3-bromo-1-propanol (Kodak), 3-chloro-1-propanol (Tokyo Kasei), 5-hydroxy-2-pentanone (Tokyo Kasei), and 3-phenyl-1-propanol (Wako Pure Chemical) were used after degassing. All experiments were carried out at room temperature (296 ± 4 K). Indicated error limits are 2 standard deviations.

Results and Discussion

Bimolecular rate constants for the reactions of C_1 hydroxyalkyl and four isomers of C_3 hydroxyalkyl with molecular oxygen,

---

(20) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Data* **1989**, *18*, 881.

(21) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

(22) Group functions are also taken from: Harding, L. B.; Goddard III, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 439.

(23) Calculated from the stabilization energy (−2.2 kcal mol^{-1}) of 3-OH-substituted 1-propyl cation.[24]

(24) Radom, L.; Pople, J. A.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1972**, *94*, 5935.

TABLE III: Comparison of Rate Constant for $CH_2OH + O_2$ at Room Temperature

pressure, Torr	method[a]	rate const, 10^{-12} cm^3 $molecule^{-1}$ s^{-1}	ref
~0.5	DF–LMR[b]	2^{+2}_{-1}	3
~1.5	DF–PE[b]	1.4 ± 0.4	4
0.31–0.94	DF–MS[c]	9.5 ± 2.5	5
0.52–4.88	DF–LMR[b,c]	10.6 ± 2.5	6
~1.0	DF–MS[c]	8.6 ± 0.2	7
760	PR–KA[c]	8.8 ± 0.2	10
1.3–5.5	LP–PIMS[c]	11.7 ± 1.2	this work

[a] DF, discharge flow; LMR, laser magnetic resonance; PE, photofragment emission; MS, mass spectrometry; PR, pulse radiolysis; KA, kinetic absorption; LP, laser flash photolysis; PIMS, photoionization mass spectrometry. [b] Monitoring HO_2. [c] Monitoring CH_2OH.

reactions 1–5, were determined at room temperature (296 ± 4 K). Experimental results are summarized in Table I.

Radical Generation by Photolysis. The precursor molecules for radicals used in the present study are listed in Table II. Hydroxyketones served as good precursor molecules for hydroxyalkyl radicals, and only ion signals stemming from hydroxyalkyl and acetyl (or propionyl) radicals were observed. 3-Hydroxy-1-propyl radical ($CH_2CH_2CH_2OH$), which is another isomer of C_3 hydroxyalkyl, is not listed in Table II. Generation of this radical (IP $\simeq$ 8.26 eV[23]) was also tried photolyzing $BrCH_2CH_2CH_2OH$, $ClCH_2CH_2CH_2OH$, $CH_3COCH_2CH_2CH_2OH$, and $C_6H_5CH_2CH_2CH_2OH$. But no signals at $m/z = 59$ ($^+CH_2CH_2CH_2OH$) were observed with use of either Xe (CaF_2) (9.57 and 8.44 eV) or Kr (MgF_2) (10.64 and 10.03 eV) lamps.

The radicals are produced with a certain amount of excess energy (Table II) by the 193-nm photolysis. In the present experimental conditions, thermalization of the radicals is accomplished within several hundred microseconds,[25] and the effect of hot radical reactions can be neglected.

The isomerizations of the hot radicals (α- to β-hydroxyalkyl, β- to α-hydroxyalkyl or to alkoxy radicals) may occur because the excess energies will be higher than the isomerization barriers (30–50 kcal mol^{-1}, estimated by analogy with the C_2H_5O system[26]). But the observed rate constants for the isomeric α- and β-hydroxyalkyl radicals are apparently different from each other, and they are much larger than the rate constants for the reactions of alkoxy radicals with O_2 ((1.9–8) × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} [20]). If a significant amount of signal from the isomerized species were present, the time profile of radicals would appear to be non-single-exponential due to the mixing of different time constants, which was not experimentally observed in any data. Therefore, isomerizations were not considered to be significant, even though a small amount of isomerization cannot be ruled out. In order to examine this problem further, use of several different precursor molecules (with different excess energy) will be needed. In the previous study,[18] β-hydroxyethyl radicals were generated from two precursor molecules, 2-chloroethanol and 2-bromoethanol[18] (excess energies are 69.8 and 83.3 kcal mol^{-1}, respectively). No difference in the measurement was observed. Thus, only chloroalcohols were used to generate β-hydroxyalkyl radicals in the present study. For α-hydroxyalkyl radicals, no other appropriate precursor compounds could be found.

O_2 molecules may also be photolyzed by 193-nm light and may cause some disturbance to the measurements. Since the ArF excimer laser beam traveled through 2 m of ambient air, the light was selectively filtered to reduce O_2 absorption lines sufficiently.[27]

TABLE IV: Comparison of Rate Constants for Hydroxyalkyl Radicals + O_2 Reactions with Alkyl Radicals + O_2 Reactions

radical[a]	IP,[b] eV	rate const, 10^{-12} cm^3 $molecule^{-1}$ s^{-1}	ref
CH_3	9.84	2.2	28
CH_2OH (α)	7.60[c]	11.7	this work
CH_3CH_2	8.38	4.4	29
CH_2CH_2OH (β)	8.61[d]	3.0	18
CH_3CHOH (α)	6.87[c]	28	18
$CH_3CH_2CH_2$	8.13	5.5	19
$CH_3CH(OH)CH_2$ (β)	8.27[e]	3.82	this work
CH_3CH_2CHOH (α)	6.74[c]	26.1	this work
CH_3CHCH_3	7.55	14.1	19
CH_3CHCH_2OH (β)	7.68[d]	11.6	this work
$CH_3C(OH)CH_3$ (α)	6.48[c]	37.1	this work
$CH_3CHCH_2CH_3$	7.41	16.6	30
$CH_3CHCH(OH)CH_3$ (β)	7.53[e]	28 (±18)	30

[a] (α) denotes α-substitution and (β) denotes β-substitution. [b] From ref 31 otherwise noted. [c] Calculated from the ΔH_f for cations[32] and radicals.[20-22] [d] Calculated from the stabilization energies for OH-substituted alkyl cations[24] (−2.6 kcal mol^{-1} for both CH_2CH_2OH and CH_3CHCH_2OH). [e] Stabilization energies for OH-substituted alkyl cations were estimated to be −2.6 kcal mol^{-1}.

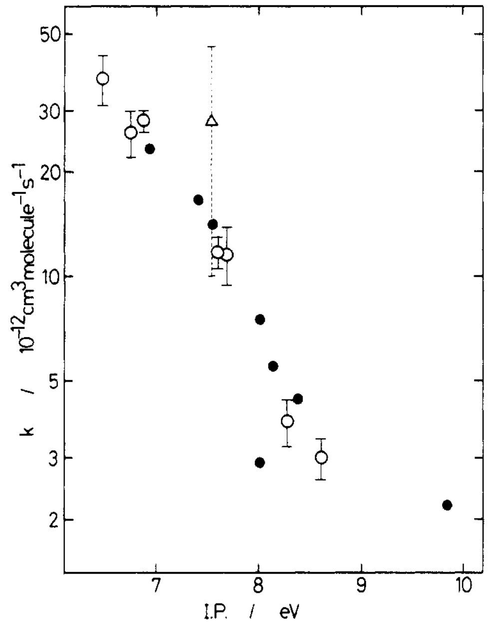


Figure 2. Plot of the rate constant for the hydroxyalkyl + O_2 or alkyl + O_2 reaction vs the ionization potential of the radical. Solid circles denote C_1 to C_4 alkyl radical + O_2 rate constants.[19,28-30,33] Open circles denote hydroxyalkyl radical + O_2 rate constants determined in the previous[18] and present study, and an open triangle denotes $CH_3CHCH(OH)CH_3$ + O_2 rate constant measured by Lenhardt et al.[30]

Rate of Reaction of Hydroxymethyl with Oxygen. Table III compares the previous and present rate constant measurements for reaction 1 at room temperature. Recent measurements monitoring CH_2OH (refs 5–7 and 10 and the present result) are in good agreement. No pressure dependence on this rate constant was found in the pressure region 0.3–760 Torr. The rate constant for this reaction is at the high-pressure limit. No pressure dependence was found for reactions 2–5 in the present pressure region (1.3–5.5 Torr). These reactions involving relatively large molecules also seem to be at or near their high-pressure limits.

OH Substitution Effect of Rate Constants. The OH substitution effects for the high-pressure limiting rate constants are

---

(25) Lambert, J. D. *Vibrational and Rotational Relaxation in Gases*; Oxford University Press: Oxford, 1977.

(26) Sosa, C.; Schlegel, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 7007.

(27) Döbele, H. F.; Rückle, B. *Appl. Opt.* **1984**, *23*, 1040.

(28) Cobos, C. J.; Hippler, H.; Luther, K.; Ravishankara, A. R.; Troe, J. *J. Phys. Chem.* **1985**, *89*, 4332.

(29) Plumb, I. C.; Ryan, K. R. *Int. J. Chem. Kinet.* **1981**, *13*, 1011.

(30) Lenhardt, T. M.; McDade, C. E.; Bayes, K. D. *J. Chem. Phys.* **1980**, *72*, 304.

(31) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. Energetics of Gaseous Ions. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6* (1).

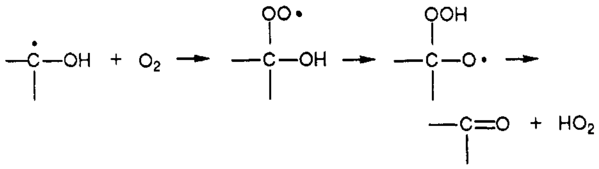
(32) Lossing, F. P. *J. Am. Chem. Soc.* **1977**, *99*, 7526.

(33) Wu, D.; Bayes, K. D. *Int. J. Chem. Kinet.* **1986**, *18*, 547.

summarized in Table IV. The rate constants for α-hydroxyalkyl + O_2 reactions are much larger than the corresponding alkyl + O_2 reactions, while the rate constants for β-hydroxyalkyl + O_2 are close to or a little smaller than the corresponding alkyl + O_2 reactions.

Ionization potentials of the radicals are also listed in Table IV. The high-pressure limiting rate constants for alkyl radicals + O_2 reactions are known to correlate with the ionization potentials of the radicals[19] (solid circles in Figure 2). A similar correlation is found for previous[18,30] and present rates of reaction of hydroxyalkyl radicals (open circles and an open triangle in Figure 2). Similar correlations of rate constants with ionization potentials of radicals (R) have been known for R + O_3,[34] R + Cl_2,[35] and R + O[36] reactions. Bayes and co-workers[19,34] have successfully explained these correlations using attractive entrance potentials for R + X (X = O_2, O_3) perturbed by ionic potentials ($R^+ + X^-$). This result shows that the rates of reaction of OH-substituted alkyl radicals with O_2 are controlled by essentially the same long-range forces as reactions of alkyl radicals with O_2.

This also suggests that the rate-determining steps of both α- and β-hydroxyalkyl + O_2 reactions are recombination processes, which confirms the recombination/isomerization mechanism (not direct abstraction) for α-hydroxylalkyl + O_2 reaction (C′) suggested in previous studies.[6,8,9,11] (This mechanism is suggested[6] from the large rate constant for the reverse reaction of CH_2O with



$$\text{—}\dot{\text{C}}\text{—OH} + O_2 \rightarrow \text{—C(OO}\cdot\text{)—OH} \rightarrow \text{—C(OOH)—O}\cdot \rightarrow \text{—C=O} + HO_2 \quad (C')$$

HO_2[20] and is supported by the temperature dependence of the rate constant for reaction 1[8,9] and the lack of an isotope effect.[8,11]) The rates of reaction do not reflect the difference of the reaction mechanisms whether RO_2 adducts undergo isomerization/dissociation (C′) or stabilization (D).

Conclusions

(i) The rate constants for the reactions of C_1 to C_3 hydroxyalkyl radicals with molecular oxygen have been measured at room temperature (296 ± 4 K) in the pressure region 1.3–5.5 Torr.

(ii) Despite the difference in the reaction mechanisms, the rate constants for the reactions of both α- and β-hydroxyalkyl radicals with O_2 were found to correlate well with the ionization potentials of the radicals. This suggests that the rate-determining steps are the recombination steps for both α- and β-hydroxyalkyl radicals and that the rate constants do not reflect the reaction mechanisms.

(iii) The correlation of rate constants with radical ionization potentials observed previously for R + O_2 reactions was also found to be valid for OH-substituted alkyl radicals.

Registry No. $\dot{C}H_2OH$, 2597-43-5; $H_3CCH_2\dot{C}HOH$, 5723-77-3; $CH_3\dot{C}HCH_2OH$, 7055-10-9; $CH_3CH(OH)\dot{C}H_2$, 7277-18-1; $CH_3\dot{C}(OH)CH_3$, 5131-95-3; O_2, 7782-44-7; H_3CCOCH_2OH, 116-09-6; $H_3CCH_2CH(OH)COCH_2CH_3$, 4984-85-4; $H_3CCH(CH_2OH)COCH_3$, 3393-64-4; $H_3CCH(OH)CH_2Cl$, 127-00-4; $H_3CC(OH)(CH_3)COCH_3$, 115-22-0.

---

[34] Paltenghi, R.; Ogryzlo, E. A.; Bayes, K. D. *J. Phys. Chem.* **1984**, *88*, 2595.

[35] Timonen, R. S.; Russell, J. J.; Sarzyński, D.; Gutman, D. *J. Phys. Chem.* **1987**, *91*, 1873.

[36] Miyoshi, A.; Matsui, H.; Washida, N. *J. Phys. Chem.* **1989**, *93*, 5813.

Excimer Laser Photochemistry of Silane–Ammonia Mixtures at 193 nm

D. B. Beach and J. M. Jasinski*

IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598 *(Received: September 5, 1989; In Final Form: November 13, 1989)*

The ArF excimer laser induced photochemistry of silane–ammonia mixtures has been studied with molecular beam sampling mass spectrometry. The observed products include disilane, trisilane, and all possible aminosilanes, $SiH_x(NH_2)_{4-x}$, x = 0–3. These products are formed under steady-state photolysis conditions and under single-laser-pulse conditions. A mechanism for the formation of these species is proposed and quantitatively evaluated.

The need for low-temperature deposition of dielectric materials in microelectronics has lead to the development of several new methods for the deposition of amorphous silicon nitride thin films from gaseous mixtures of silane and ammonia. These techniques include plasma-enhanced chemical vapor deposition[1,2] (PECVD), mercury-sensitized photochemical deposition,[3] and direct photochemical deposition with use of a 185-nm mercury lamp[4] or a 193-nm ArF excimer laser.[5] Each of these techniques has been explored in film deposition studies, and the results suggest that technologically useful films can be deposited at temperatures as low as 200–300 °C.

Much less is known about the relevant film deposition mechanisms. In each deposition technique, gas-phase silicon- and nitrogen-containing radicals are generated. These species, e.g., SiH_3 and NH_2, may diffuse to surfaces and deposit film directly or they might react in the gas phase to generate silicon–nitrogen-containing compounds, which could then lead to film growth. In order to devise experiments that cleanly differentiate these possible mechanisms, it is first necessary to understand the gas-phase chemistry in some detail. Mechanistic studies of silane–ammonia mixtures under PECVD[6] and Hg-sensitized[7,8] and 185-nm lamp[8] induced deposition conditions have recently been reported, as has a preliminary account[9] of the 193-nm ArF excimer-laser-induced chemistry. In this paper, we present the results of extensive studies of the 193-nm ArF excimer laser induced

---

[1] Morosanu, C. E. *Thin Solid Films* **1980**, *65*, 171 and references therein.

[2] Veprek, S. *Thin Solid Films* **1985**, *130*, 135 and references therein.

[3] Peters, J. W.; Gebhart, F. L.; Hall, T. C. *Solid State Technol.* **1980**, *23*, 121.

[4] Numasawa, Y.; Yamazaki, K.; Hamano, K. *Jpn. J. Appl. Phys.* **1983**, *22*, L792.

[5] Jasinski, J. M.; Meyerson, B. S. *J. Appl. Phys.* **1987**, *61*, 431 and references therein.

[6] Smith, D. L.; Alimonda, A. S.; Chen, C. C.; Jackson, W.; Wacker, B. *Mat. Res. Soc. Symp. Proc.* **1988**, *118*, 107.

[7] Wu, C.-H. *J. Phys. Chem.* **1987**, *91*, 5054.

[8] Allain, B.; Perrin, J.; Guizot, J. L. *Appl. Surf. Sci.* **1989**, *36*, 205.

[9] Jasinski, J. M.; Beach, D. B.; Estes, R. D. *Mat. Res. Soc. Symp. Proc.* **1989**, *131*, 487.

0022-3654/90/2094-3019$02.50/0