Figure 5. Infrared transmission spectrum of KBr supported SiO deposited in the presence of 1×10^{-4} torr of H_2O vapor. The film is several thousand angstroms thick.

correspondingly. In any case, it can be demonstrated that water, and not surface hydroxyl, is the required reactant for the formation of W_d and W_c type barriers.

In order to support our model of an SiO + H_2O reaction, we prepared thick (>3000 Å) films of SiO deposited on KBr in the presence of 10^{-4} torr of H_2O vapor. Transmission infrared spectra of these films measured on a Perkin-Elmer 283B showed pronounced structure in the Si–H region, as shown in Figure 5. These bands peak at 2245 and 2135 cm^{-1}, in close agreement to the positions observed by IETS. Using Beckmann's[43] formulas for the relation of observed Si–H intensity to the number of SiH bonds per cm^2 of film, N, and a value of 2 for the index of refraction, one obtains

$$N = 8 \times 10^{16}(e/e_H)^2 \text{ Si–H bonds/cm}^2$$

The fractional charge on the proton, $|e_H/e|$, is less than 0.2[34,43] giving a lower bound of 10^{18} protons/cm^2 of deposited film. If we assume that one water molecule occupies about 2×10^{-16} cm^2 and supplies two protons, a greater than 100 monolayer film of water would be required to produce the observed amount of SiH. Clearly, Si–H formation does not depend on surface OH or previously adsorbed water, but proceeds throughout the deposition processes in the presence of water vapor. We believe these results support our model of SiO + H_2O reaction being the critical step in surface Si–H formation.

Conclusions

Deposition of SiO onto alumina at room temperature under anhydrous conditions [$p(H_2O) < 10^{-6}$ torr] produces well-defined barriers of supported O_ySiH, where $1.5 \leq y \leq 3$ and y is estimated to be closer to 2 than 1.5. By increasing the amount of water present during SiO deposition, a more complex barrier is formed which appears to be more deficient in oxygen than the dry barrier. The barriers, once formed, are exceedingly stable with respect to H $\leftrightarrow$ D exchange and further chemical reaction with water. We see no evidence to support the supposition of Eib et al.[30] that surface OH$^-$ groups are participants in the formation of SiH. We interpret our results to indicate that the Si–H bond is formed by reaction of SiO with water.

Barriers prepared by SiO deposition onto heated substrates gave various combinations of two distinct silicon hydride species. We interpret this to be due to an uncontrolled variation in water vapor pressure in our vacuum system, and not to any intrinsic instability in the heated substrate films. Composite barriers prepared by deposition of SiO in the presence of 10^{-4} torr of O_2 gave reproducible results.

# Reactions of CH₂OO and CH₂(¹A₁) with H₂O in the Gas Phase

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The reactions of peroxymethylene (CH₂OO) and singlet methylene with H₂O were studied in the gas phase by the near-UV photolysis of ketene and diazomethane. Peroxymethylene formed in the reaction of CH₂(³B₁) + O₂ + M → CH₂OO + M was found to react with H₂¹⁸O to produce ¹⁸O-labeled formic acid: CH₂OO + H₂¹⁸O → HC¹⁸OOH, HCO¹⁸OH + H₂O. Singlet methylene was found to react with H₂O to form methanol, CH₂(¹A₁) + H₂O → CH₃OH, competing with the reaction CH₂(¹A₁) + CH₂N₂ → C₂H₄ + N₂.

Introduction

The effect of water vapor on radical reactions is one of the unresolved problems in atmospheric chemistry. Recently, Hamilton and Lii[1] observed that the self-reaction of HO₂ increased in the presence of H₂O and suggested that the reaction of H₂O-complexed HO₂ with HO₂

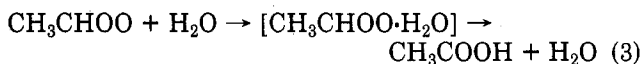$$HO_2 + HO_2 \cdot H_2O \rightarrow H_2O_2 + H_2O + O_2 \quad (1)$$
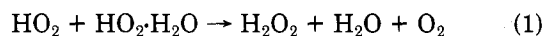
proceeds faster than that between uncomplexed HO₂ by a factor of 8.5.

Cox and Penkett[2] found that the SO₂ oxidation in the *cis*-2-butene–O₃–air system was remarkably inhibited when water vapor existed in the system. Calvert and co-workers[3]

(1) E. J. Hamilton, Jr., and R.-R. Lii, *Int. J. Chem. Kinet.*, **9**, 875 (1977).

(2) R. A. Cox and A. Penkett, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1735 (1972).

argued that the effect might be due to the competitive reactions

$$CH_3CHOO + SO_2 \rightarrow CH_3CHO + SO_3 \quad (2)$$

$$CH_3CHOO + H_2O \rightarrow [CH_3CHOO \cdot H_2O] \rightarrow$$
$$CH_3COOH + H_2O \quad (3)$$

and postulated the complex formation between the so-called Criegee intermediate, CH_3CHOO, and H_2O. Our recent studies on the photooxidation[4a] of the propylene–NO_x–air system and the dark reaction[4b] of O_3 with ethylene and propylene have revealed that the addition of H_2O vapor increased the yield of formic acid markedly. It was suggested that the effect may in part be explained by a reaction analogous to reaction 3

$$CH_2OO + H_2O \rightarrow [CH_2OO \cdot H_2O] \rightarrow HCOOH + H_2O \quad (4)$$
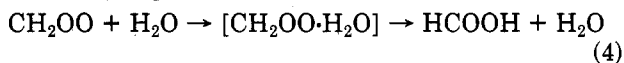
In the present study, the reaction of peroxymethylene (CH_2OO) and singlet methylene ($^1CH_2$) with H_2O are studied in the gas phase by the near-UV photolysis of ketene (CH_2CO) and diazomethane (CH_2N_2).

Production of ^{18}O-labeled formic acid in the reaction of CH_2OO and $H_2^{18}O$ is reported showing the evidence for the reaction

$$CH_2OO + H_2^{18}O \rightarrow [CH_2OO \cdot H_2^{18}O] \rightarrow$$
$$HC^{18}OOH, HCO^{18}OH + H_2O \quad (5)$$
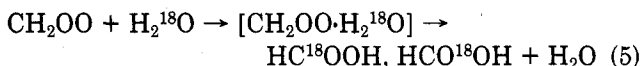
This study also reports the formation of methanol in the reaction of $^1CH_2$ and H_2O:

$$CH_2(^1A_1) + H_2O \rightarrow CH_3OH \quad (6)$$
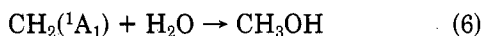
As for the O–H insertion reaction of $^1CH_2$, Kerr et al. reported[5] the insertion of $^1CH_2$ into the alcoholic O–H bond in the gas phase. The relative rates for the insertion of $^1CH_2$ into an O–H bond as compared with insertion into a primary C–H bond are reported to be as follows: CH_3-OH, 21.8; CH_3CH_2OH, 21.2; $(CH_3)_2CHOH$, 14.9; and $(CH_3)_3COH$, 10.9. Thus, the insertion into the O–H bond seems to occur more easily than into a C–H bond. Nevertheless, to the authors' knowledge, the simplest O–H insertion reaction of $^1CH_2$, reaction 6, has never been investigated in the gas phase. In the liquid phase, for a dropwise addition of water to a solution of CH_2N_2 in diethyl ether under the irradiation of sunlight, formation of CH_3OH was reported.[6]

Experimental Section

Ketene was prepared by the pyrolysis of diketene at 550 °C[7] and purified by trap-to-trap distillation. Diazomethane was prepared by decomposition of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in a water–carbitol mixture with 40% KOH aqueous solution.[8] It was stored at –195 °C and distilled from trap (–78 °C) to trap (–195 °C) before use. Gas handling was accomplished with a standard all-glass vacuum system with greaseless stopcocks and

MKS Baratron pressure gauge.

Gases used were pure air (dew point < –70 °C) and N_2 (>99.9995%) supplied from Nippon Sanso Co. The air was used after passing a molecular sieves trap cooled to –40 °C to remove water and CO_2. The N_2 was passed through the trap at –80 °C to remove any trace of O_2. $H_2^{18}O$ (isotope purity, >95%) was supplied by Merck Sharp and Dohme Canada Ltd. CH_3F (PCR Research Chemicals, Inc.) was used after trap-to-trap distillation.

The photochemical reactor used was an 11-L cylindrical quartz vessel (120-mm i.d., 1000 mm long) equipped with multireflection mirrors for long-path Fourier transform infrared spectroscopy (LP-FTIR, Block Engineering Co.–JASCO International Inc. FTS-496S). The light sources for the photolysis of CH_2CO and CH_2N_2 were four "black-light lamps" (Toshiba, FL 20S·BLB, 310 $\lesssim \lambda \lesssim$ 400 nm, $\lambda_{max} \simeq$ 360 nm) and four fluorescent lamps (Toshiba FL20S·W, 360 $\lesssim \lambda \lesssim$ 700 nm), respectively, which surrounded the reactor coaxially.

Ketene (~15 mtorr) or diazomethane (~9 mtorr) was photolyzed in 1 atm of air or N_2 at 30 ± 2 °C. The pressure of added water was varied from 0 to 4 torr. The irradiation times were typically 60 and 30 min for the CH_2CO and CH_2N_2 systems, respectively. The yield of a product as defined by $\Delta(\text{product})/\Delta(CH_2CO \text{ or } CH_2N_2)$ in mole ratio was obtained at a reactant conversion of less than 30% for ketene and 60% for diazomethane.

For the purpose of checking the contribution of the heterogeneous reaction in the CH_2CO–H_2O–air system, two types of smaller volume (~500 mL) Pyrex glass reaction cells with different surface-to-volume (S/V) ratios (one was spherical with $S/V \simeq 0.6$ cm^{-1} and another was made from tubing with $S/V \simeq 2.5$ cm^{-1}) were used. After the irradiation, the reaction mixture was expanded into the reactor with long-path mirrors for IR analysis.

The concentrations of reactants and products were monitored by means of the LP-FTIR. The path length was 40 m, and the spectra were obtained with every 128 scans (scanning time was ~5 min) for the ketene and every 64 scans (3 min) for the diazomethane system at a resolution of 1 cm^{-1}. The absorptivities (base 10, torr^{-1} m^{-1} at 30 °C) used were as follows: CH_2CO, 1.94 (2138 cm^{-1}); HCOOH, 1.24 (1105 cm^{-1}, peak to valley); HCHO, 0.250 (2780 cm^{-1}, peak to valley); O_3, 0.711 (1056 cm^{-1}); C_2H_4, 0.858 (950 cm^{-1}, peak to valley); and CH_3OH, 0.755 (1035 cm^{-1}, peak to valley). The concentrations of CH_2N_2 (2090 cm^{-1}), CO_2 (2362 cm^{-1}), and CO (2204 cm^{-1}) were obtained by use of calibration curves.

For the purpose of identification, a mixture of labeled formic acids was prepared from dried HCOOH and $H_2^{18}O$ by heating them at 90 °C for 3 h. The bands corresponding to ν_{C-O} (1105 cm^{-1} for HCOOH) were considered to be 1101, 1078, and 1074 cm^{-1}, and they were assigned to HC^{18}OOH, HCO^{18}OH, and HC^{18}O^{18}OH, respectively.[9] Isolation of each labeled acid was not performed.

Results

Photolysis of the CH_2CO–H_2O–Air System. Products observed in the photolysis of ketene in 1 atm of air were CO, CO_2, HCOOH, HCHO, O_3, and some unidentified

(3) J. A. Calvert, F. Su, J. W. Bothenheim, and O. P. Strausz, *Atmos. Environ.*, 12, 197 (1978).

(4) (a) H. Akimoto, H. Bandow, F. Sakamaki, G. Inoue, M. Hoshino, and M. Okuda, *Environ. Sci. Technol.*, 14, 172 (1980); (b) H. Bandow, H. Akimoto, and M. Okuda, presented at the 14th International Symposium of Free Radicals, Sanda, Japan, Sept 1979.

(5) J. A. Kerr, B. V. O'Grady, and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 897 (1967).
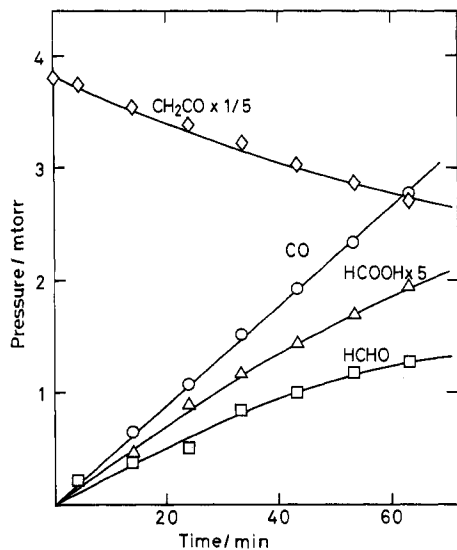
(6) F. C. Palazzo, *Gazz. Chim. Ital.*, 79, 13 (1949).

(7) S. Andreades and H. D. Carlson, "Organic Syntheses", Collected Vol. V, 679 (1973).

(8) J. A. Moore and D. E. Reed, "Organic Syntheses", Collected Vol. V, 351 (1973). Benzene was used for solvent in place of ether, and the distillation procedure was eliminated. Decomposition of precursor was carried out at ~5 °C, and purification of CH_2N_2 was performed by means of trap-to-trap distillation.

(9) The assignments were performed as follows. The concentration ratio of the species which exhibits the C–O stretching band at the lowest frequency (1074 cm^{-1}) was increased as the mixing ratio of $H_2^{18}O$ to HCOOH was increased. Thus, this species was assigned to doubly labeled formic acid. The remaining two should be singly labeled formic acids. Since the C–O stretching frequencies of HCO^{18}OH and HC^{18}OOH are thought to be close to those of HCOOH (1105 cm^{-1}) and HC^{18}O^{18}OH (1074 cm^{-1}), respectively, the species which exhibits the band at 1101 cm^{-1} is presumed to be HC^{18}OOH and the rest (1078 cm^{-1}) is assigned to HCO^{18}OH.

TABLE I: Product Yields in the Photolysis of Ketene in Air

[H$_2$O]$_0$, mtorr	[CH$_2$CO]$_0$, mtorr	Δ[HCOOH]/ Δ[CH$_2$CO]	Δ[CO]/ Δ[CH$_2$CO]	Δ[HCHO]/ Δ[CH$_2$CO]	Δ[O$_3$]/ Δ[CH$_2$CO]
0	18.92	0.022	0.512	0.228	0.035
0	19.29	0.039	0.591	0.312	
260	17.74	0.042	0.430	0.200	
280	19.84	0.042	0.482	0.230	0.057
920	19.03	0.057	0.433	0.244	0.040
920	19.05	0.067	0.434	0.244	0.061
1830	17.02	0.065	0.447	0.287	
1830	16.13	0.068	0.466	0.280	
2750	16.25	0.073	0.483	0.283	
2750	16.25	0.086	0.448	0.271	
3660	17.60	0.096	0.380	0.340	
3660	17.66	0.103	0.440	0.345	0.081

Figure 1. Time profile of concentrations of reactant and products in ketene photolysis with 1 torr of H$_2$O.

Figure 2. (A) IR spectrum of HCOOH, HC^{18}OOH, and HCO^{18}OH produced by the reaction of CH$_2$OO with H$_2$^{18}O. (B) IR spectrum of HCOOH and labeled acids which were prepared authentically: (a) HCOOH, (b) HC^{18}OOH, (c) HCO^{18}OH, (d) HC^{18}O^{18}OH.

Figure 3. Plot of the yield of unlabeled HCOOH vs. pressure of added H$_2$O and H$_2$^{18}O: ($\triangle$) HCOOH produced with H$_2$O, ($\square$) HCOOH produced with H$_2$^{18}O.
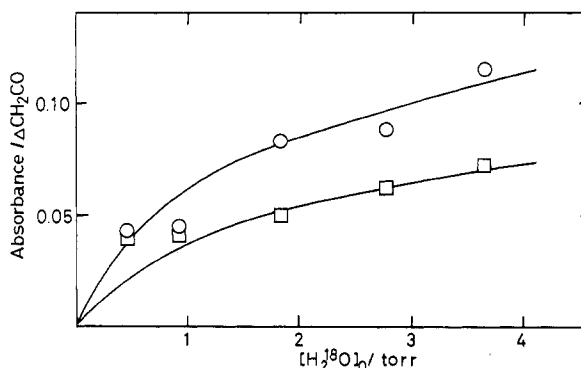
Figure 4. Plot of the absorbance of HC^{18}OOH and HCO^{18}OH divided by the amount of consumed ketene vs. pressure of added H$_2$^{18}O: ($\square$) HCO^{18}OH, (O) HC^{18}OOH.

compound which showed an infrared absorption band at 1162 cm^{-1}. Formation of ozone was confirmed by means of a chemiluminescent ozone analyzer. The formation of HCOOH was found to be enhanced when H$_2$O vapor was added, whereas the yield of CO tended to decrease. The yield of HCHO did not change markedly in the presence of H$_2$O. Unfortunately, due to desorption of CO$_2$ from the reactor wall, the uncertainty of the CO$_2$ concentration is too large to discuss the tendency of its yield as a function of H$_2$O. Figure 1 shows the time profile of the concentration of the reactant and products when ketene was photolyzed in air with ~1 torr of H$_2$O. In the initial stage of the reaction, the increase of HCOOH is linear with irradiation time as are the increases of the other products, which negates the possibility of the secondary formation of HCOOH even in the presence of H$_2$O. Table I presents the product yields.

In order to elucidate the formation mechanism of H$_2$O-enhanced HCOOH, we carried out photolyses of ketene in air in the presence of ^{18}O-labeled water. In the reaction with H$_2$^{18}O, ^{18}O-labeled formic acid was obtained in addition to unlabeled HCOOH as displayed in Figure 2. Either the carbonyl or hydroxyl group was labeled with ^{18}O, but a doubly labeled molecule was not detected. Since no ^{18}O-labeled formic acid was obtained in the irradiation of HCOOH and H$_2$^{18}O in air (without CH$_2$CO), the possibility of the formation of the ^{18}O-labeled formic acid from the exchange of OH between H$_2$^{18}O and HCOOH can be eliminated.

Figure 3 presents the yield of unlabeled HCOOH as a function of added water (H$_2$O and H$_2$^{18}O) pressure. As shown in Figure 3, the yield of unlabeled HCOOH is also enhanced in the presence of H$_2$^{18}O, though the increment
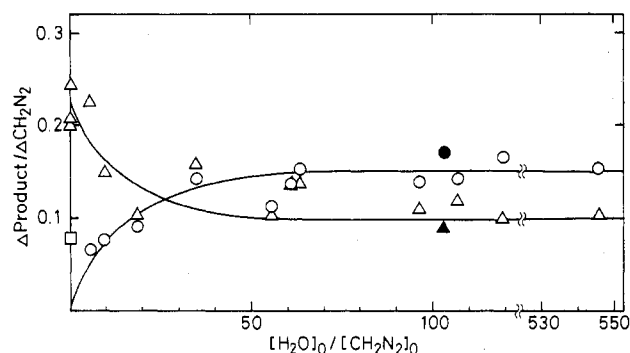
Figure 5. Product yields vs. the ratio of added H_2O to initial pressure of CH_2N_2: (O) CH_3OH, (△) C_2H_4, (□) C_2H_4 in dark run; closed symbols are the yields in the reaction in air.

TABLE II: Yields of C_2H_4 and CH_3OH

$[H_2O]_0$, mtorr	$[CH_2N_2]_0$, mtorr	$\Delta[C_2H_4]/\Delta[CH_2N_2]$	$\Delta[CH_3OH]/\Delta[CH_2N_2]$	$\Phi[C_2H_4]/\Phi[CH_3OH]^a$
0	10.10	0.208		
0	7.70	0.199		
0	7.40	0.244		
50	8.97	0.225	0.065	2.26
100	10.63	0.148	0.076	0.92
210	11.49	0.103	0.091	0.28
300	8.62	0.158	0.142	0.56
460	7.28	0.137	0.152	0.39
460	8.30	0.102	0.110	0.22
460	7.56	0.136	0.137	0.42
920	7.71	0.099	0.165	0.13
920	9.56	0.110	0.138	0.23
920	8.62	0.118	0.141	0.28
3660	6.71	0.104	0.153	0.17
0^b	11.13	0.078		
920^c	9.45	0.089	0.165	

^{a} $\Phi[C_2H_4] = \Delta[C_2H_4]/\Delta[CH_2N_2] - 0.078$. ^{b} Dark run. ^{c} In air.

is much lower than in the case of H_2O addition. In Figure 4, the changes of the absorbances of the $HC^{18}OOH$ and $HCO^{18}OH$ are presented as functions of $H_2^{18}O$ pressure. The enhancement of the ^{18}O-labeled formic acids is clearly demonstrated. Although their absolute concentrations were not determined for lack of the pure, authentic samples, the increment of the ^{18}O-labeled formic acid in the presence of $H_2^{18}O$ is comparable to that of HCOOH in the presence of H_2O.

The increase of unlabeled HCOOH with the addition of $H_2^{18}O$ as shown in Figure 3 suggests that, in addition to "reaction", collisional deactivation also leads to the enhanced formation of formic acid. The effect on collisional deactivation was investigated by photolyzing CH_2CO together with CH_3F instead of H_2O. The yield of formic acid was 0.038, which was nearly the same as that in the case of the reaction without added H_2O. It is indicated that a nonpolar substance such as CH_3F has little effect on the enhancement of HCOOH.

The possibility of a heterogeneous wall reaction to form the ^{18}O-labeled formic acid in the photolysis of the $CH_2CO-H_2^{18}O$-air system was checked in the following experiments. When the photolysis took place in the small vessel (500 mL) with high S/V ratio, the formation of acetic acid, which was supposed to appear by the direct reaction of CH_2CO and H_2O on the wall, exceeded that of formic acid and only a trace of formic acid was observed. In the dark reaction, acetic acid was formed but not formic acid. In contrast to this, the absolute yield of the labeled and unlabeled formic acid was much higher, exceeding that of acetic acid, when the photolysis was carried out in a vessel of a similar volume having a smaller S/V ratio. From these results, it is concluded that the formation of formic acid takes place via a homogeneous reaction and the contribution of the heterogeneous reaction can be excluded as a major source.

Photolysis of the $CH_2N_2-H_2O-N_2$ System. From the photolysis of CH_2N_2 in 1 atm of dry N_2, only ethylene could be detected as a product by means of IR spectroscopy, though its yield was low ($\sim 20\%$). Besides ethylene, methanol was produced in the presence of H_2O. The linear increase of CH_3OH as a function of irradiation time excludes the possibility of its formation via secondary reactions. As the concentration of H_2O increased, the yield of CH_3OH increased, whereas that of C_2H_4 decreased to a constant yield. The changes of the yields of C_2H_4 and CH_3OH as functions of H_2O are shown in Table II and Figure 5.

As a control, a dark run was carried out for a similar concentration of CH_2N_2 in 1 atm of N_2 in the absence of H_2O. A considerable amount of C_2H_4 was found to be produced in the dark decomposition of CH_2N_2. Nearly the

same amount of C_2H_4 as in the dark run was obtained for the photochemical run with a large excess of H_2O and O_2 where both singlet and triplet methylene were mostly scavenged. From these results it was concluded that a constant amount of ethylene was formed by the decomposition of CH_2N_2 on the wall without involving methylene.

Discussion

Reaction of CH_2OO and H_2O. Peroxymethylene (C-H_2OO) is a well-known species believed to be formed in ozone–olefin reactions[10-15] and is supposed[10,14,15] to give CO, CO_2, and formic acid according to the following scheme.

$$CH_2OO^{\ddagger} \longrightarrow \left[CH_2 \overset{O}{\underset{O}{\diamond}} \right] \longrightarrow HCOOH^{\ddagger} \qquad (7)$$

$$HCOOH^{\ddagger} \rightarrow HCOOH \qquad (8)$$

$$\rightarrow CO + H_2O \qquad (9)$$

$$\rightarrow CO_2 + H_2(2H) \qquad (10)$$
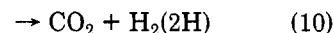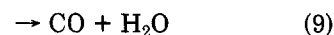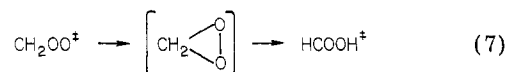
The same species, CH_2OO, is thought to result from a fast reaction of $^3CH_2$ and O_2 in the near-UV photolysis of CH_2CO in the presence of O_2

$$CH_2CO + h\nu \rightarrow {}^3CH_2 + CO \qquad (11)$$

$${}^3CH_2 + O_2 + M \rightarrow CH_2OO + M \qquad (12)$$
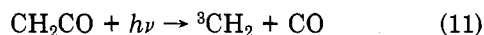
$$\Delta H = -63.2 \text{ kcal/mol}^{16}$$

Hsu and Lin[17] observed the production of a vibrationally excited CO from the reaction of $^3CH_2$ and O_2 and proposed

(10) J. T. Herron and R. E. Huie, *J. Am. Chem. Soc.*, **99**, 5430 (1977).

(11) R. I. Martinez, R. E. Huie, and J. T. Herron, *Chem. Phys. Lett.*, **51**, 457 (1977).

(12) R. D. Suenram and F. J. Lovas, *J. Am. Chem. Soc.*, **100**, 5117 (1978).

(13) H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Chem. Phys. Lett.*, **46**, 327 (1977).
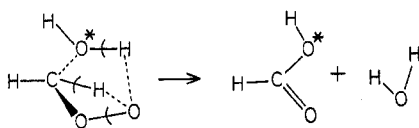
(14) F. Su, J. G. Calvert, and J. H. Shaw, *J. Phys. Chem.*, **84**, 239 (1980).

(15) (a) W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 3004 (1975); (b) L. B. Harding and W. A. Goddard III, *ibid.*, **100**, 7180 (1978).
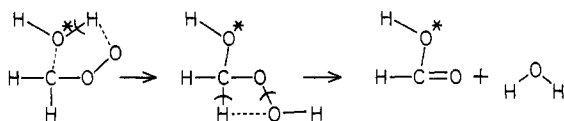
(16) All ΔH_f values are taken from H. Okabe, "Photochemistry of small Molecules," Wiley, New York, 1978, except for $\Delta H_f(CH_2OO) = 29.1$ kcal mol^{-1}, taken from ref 5.

(17) D. S. Y. Hsu and M. C. Lin, *Int. J. Chem. Kinet.*, **9**, 507 (1977).
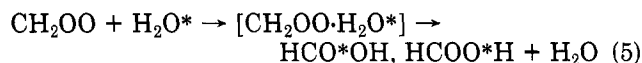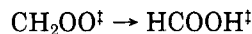
Scheme I

Scheme II

Scheme III

the reaction sequence as reaction 12 followed by reaction 9. Production of HCOOH in the CH₂CO photolysis in the presence of O₂ was noted earlier by Holroyd and Noyes[18] and was explained by the fast reaction of ^{3}CH₂ and O₂. In an analogous reaction system, Murray and Suzui[19] reported that diphenylcarbene (Ph₂C:) and O₂ reacted to give the Criegee intermediate (Ph₂COO) and this yielded ozonide when reacted with aldehyde.

Therefore, the formation of formic acid and its enhancement in the addition of water vapor observed in the present study are considered to be due to the reaction of CH₂OO. There are two possibilities as the HCOOH-forming process from CH₂OO and H₂O:

$$CH_2OO + H_2O^* \rightarrow [CH_2OO \cdot H_2O^*] \rightarrow$$
$$HCO^*OH, HCOO^*H + H_2O \quad (5)$$

or

$$CH_2OO^{\ddagger} \rightarrow HCOOH^{\ddagger}$$

$$HCOOH^{\ddagger} + H_2O^* \rightarrow HCOOH + H_2O^* \quad (8a)$$

$$HCOOH^{\ddagger} + M \rightarrow HCOOH + M \quad (8b)$$

where H₂O* denotes isotopically labeled water. The first process is a "reaction" involving an O atom exchange between CH₂OO and H₂O via a complex formation. The second is merely a vibrational quenching of chemically activated HCOOH competing with the unimolecular decomposition reactions 9 and 10. In either case, the decrease of CO as observed in Table I seems to compensate for the enhancement of HCOOH.

Figure 2 clearly shows that the ^{18}O-labeled formic acids are produced when H₂^{18}O is added. Since the increase of unlabeled formic acid is much less when H₂^{18}O is added as compared to the case when H₂O is added, it can be concluded that the "reaction" of CH₂OO with water, probably via a complex formation, mainly contributes to the enhanced production of formic acid in the presence of water.
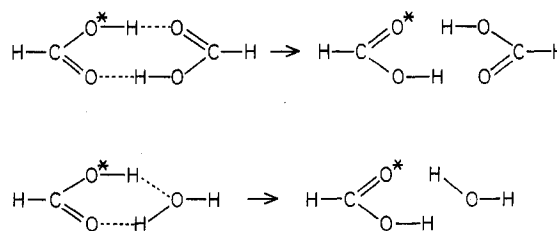
As for the mechanism of the reaction of CH₂OO with H₂O*, the following pathways are possible. One is the pathway as shown in Scheme I.

A similar type of complex between CH₃CHOO and H₂O has been suggested by Calvert et al.[3] in relation to the inhibiting effect of H₂O on the SO₂ oxidation in the O₃-cis-2-butene system.

The other is the one via a hydroxy hydroperoxide as shown in Scheme II.

A similar compound, alkoxy hydroperoxide, was suggested[20] in the reaction of Criegee intermediates with al-

cohol. In both mechanisms, the hydroxyl group of formic acid should be labeled with ^{18}O. However, rapid exchange reactions of an H atom occuring either homogeneously or heterogeneously, as shown in Scheme III, would result in the formation of formic acid labeled on a carbonyl oxygen atom. Thus, neither reaction pathway contradicts the simultaneous formation of HCOO*H and HCO*OH as presented in Figure 2. Since the dipole moment of CH₂OO is calculated[15] to be very large, 3.03 D, complex formation between CH₂OO and H₂O is very plausible.

Figure 3 indicates that HCOOH is also increased, exceeding the amount expected from an isotopic impurity in H₂^{18}O, as the pressure of H₂^{18}O is increased. The increment of HCOOH upon addition of H₂^{18}O is due to the collisional deactivation of HCOOH‡ by H₂^{18}O (reaction 8a). The result in the reaction with CH₃F demonstrates that a nonpolar substance such as CH₃F has little effect on the enhancement of the formation of formic acid. Thus, the vibrational deactivation of HCOOH‡ may also be facilitated by the hydrogen bonding to H₂O.

Reaction of ^{3}CH₂ and O₂. In addition to HCOOH, CO, and CO₂, the formation of HCHO and O₃ was observed in the photolysis of CH₂CO in the presence of O₂. Particularly, the formation of ozone was confirmed for this reaction system for the first time in the present study. This would suggest that the reaction
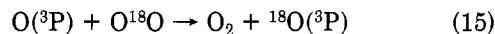
$$^3CH_2 + O_2 \rightarrow HCHO + O(^3P) \quad (13)$$
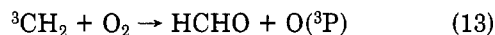
$$\Delta H = -60.1 \text{ kcal/mol}$$

proceeds as well as reaction 12 under atmospheric air pressure, followed by

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (14)$$
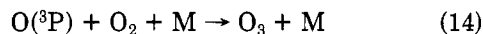
Reaction 13 has been suggested[21] before by analogy with the reaction[22] of O(^{3}P) with O₂ (eq 15). One-step formation

$$O(^3P) + O^{18}O \rightarrow O_2 + {}^{18}O(^3P) \quad (15)$$

mation of O₃ from the reaction of CH₂OO and O₂ (eq 16)

$$CH_2OO + O_2 \rightarrow HCHO + O_3 \quad (16)$$

$$\Delta H = -21.1 \text{ kcal/mol}$$

could be refuted on the basis of the spin conservation rule and the experimental fact that the yield of HCHO did not decrease when H₂O was added (see Table I).

Reaction of ^{1}CH₂ and H₂O. In the photolysis of the CH₂N₂-H₂O-N₂ system, the amount of methanol produced and that of ethylene decreased with the addition of H₂O are nearly the same within experimental error (see Figure 5). Therefore, the ethylene in excess of the dark production and methanol are thought to be formed by the reactions of ^{1}CH₂ with CH₂N₂ and H₂O, respectively. The reaction of ^{3}CH₂ with CH₂N₂ would mainly be a hydrogen atom abstraction as reported by Laufer and Bass.[23]

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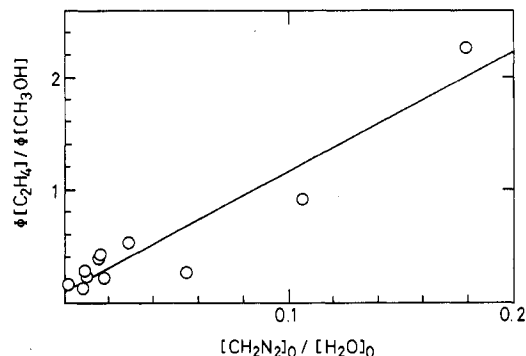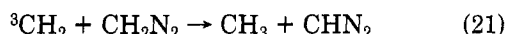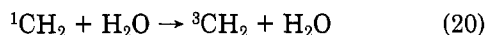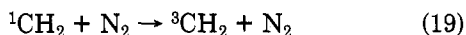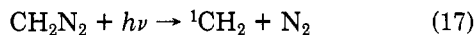
Figure 6. Ratio of the product yield vs. the initial ratio of CH_2N_2 to H_2O.

On the basis of the above arguments, we could consider the mechanism of this reaction as follows:

$$CH_2N_2 + h\nu \rightarrow {}^1CH_2 + N_2 \qquad (17)$$

$$^1CH_2 + CH_2N_2 \rightarrow C_2H_4 + N_2 \qquad (18)$$

$$^1CH_2 + N_2 \rightarrow {}^3CH_2 + N_2 \qquad (19)$$

$$^1CH_2 + H_2O \rightarrow CH_3OH \qquad (6)$$

$$^1CH_2 + H_2O \rightarrow {}^3CH_2 + H_2O \qquad (20)$$

$$^3CH_2 + CH_2N_2 \rightarrow CH_3 + CHN_2 \qquad (21)$$

Singlet methylene underwent a competitive reaction with CH_2N_2 and H_2O. Thus, the ratio of the yield of ethylene to that of methanol can be expressed simply as

$$\Phi[C_2H_4]/\Phi[CH_3OH] = k_{18}[CH_2N_2]/(k_6[H_2O]) \qquad (22)$$

where $\Phi[C_2H_4]$ and $\Phi[CH_3OH]$ are the yields of each product due to the methylene reaction. In order to obtain $\Phi[C_2H_4]$, one subtracts the yield of ethylene due to the dark decomposition of CH_2N_2 from the apparent yield of C_2H_4. Figure 6 shows the plot of eq 22 when the dark yield of C_2H_4 is taken to be 0.08. From the slope of the plot, the rate constant ratio k_{18}/k_6 is found to be 10 ± 2. The error is estimated on the basis of the error in the choice of the dark yield of C_2H_4 and the scattered error in Figure 6. When the rate constant of reaction 18, $k = (3.1 \pm 1.0) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, reported by Bell[24] is used, k_6

is estimated to be $\sim 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. However, it should be noted that the yield of CH_3OH in the present study is much higher than expected when the reported quenching rate constant[25] of $^1CH_2$ by N_2 is used. This problem was not resolved in the present study, and the contribution of the heterogeneous reaction may not entirely be refuted.

It would be interesting to compare the present results with other insertion-type reactions. The relative rate of $^1CH_2$ for insertion into the O–H bond of methanol as compared to the C–H bond is reported[5] to be 21.8. When the value of the rate constant for the insertion of $^1CH_2$ into the C–H bond of methane, 1.9×10^{-12} cm^3 molecule^{-1} s^{-1},[25] is used, the rate of O–H insertion for CH_3OH is estimated to be 4.1×10^{-11} cm^3 molecule^{-1} s^{-1}, which is ~ 1 order of magnitude larger than the rate constant of the insertion reaction of $^1CH_2$ into the O–H bond of H_2O estimated above.

Other than C–H and O–H insertion, an N–H insertion reaction of $^1CH_2$ is known[26] to occur for NH_3

$$CH_2(^1A_1) + NH_3 \rightarrow CH_3NH_2 \qquad \Delta H = -95 \text{ kcal/mol} \qquad (23)$$
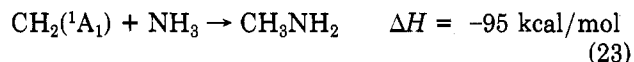
followed by unimolecular decomposition of the product. In the case of reaction 6, the exothermicity ($\Delta H = -89$ kcal/mol) does not exceed the bond dissociation energies of O–H (103 kcal/mol), C–O (93 kcal/mol), and C–H (93 kcal/mol) of CH_3OH, and the unimolecular decomposition of the product, CH_3OH, may not need to be considered.

The isoelectronic species of $^1CH_2$, $O(^1D)$, is known to react with H_2O with a very large rate constant of 1.95×10^{-10} cm^3 molecule^{-1} s^{-1}.[27] The insertion product, H_2O_2, has been detected[28] only in the liquid-phase photolysis of ozone in water. In view of the result of the present study, the gas-phase reaction of $O(^1D)$ with H_2O could also proceed via insertion followed by decomposition of the activated H_2O_2 to form $2OH$.

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