The Photodecomposition of CH_2O, CD_2O, CHDO, and CH_2O–CD_2O Mixtures at Xenon Flash Lamp Intensities[1]

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Abstract: The volume and composition of the gaseous products of the photolyses of the pure formaldehydes, CH_2O, CD_2O, and CHDO, and mixtures of CH_2O and CD_2O were determined in experiments at various xenon flash lamp intensities, pressures of aldehyde, temperatures, and at selected wavelength regions of the aldehyde absorption. The data are consistent with the occurrence of two primary photodissociative processes, $CH_2O^* \rightarrow H + HCO$ (I) and $CH_2O^* \rightarrow H_2 + CO$ (II), and the dominance of radical–radical reactions following process I for these conditions. In CH_2O, $\phi_I + \phi_{II} \cong 1.0$ over the entire absorption band; for CD_2O and CHDO the sum is less than unity at the long-wavelength region. From the H_2, HD, and D_2 product distribution in CH_2O–CD_2O mixture photolyses and from the photolyses of CHDO, it was found that the relative efficiencies of processes I and II show a marked dependence on the wavelength of absorbed light; ϕ_I/ϕ_{II} varies from near zero at the longest wavelengths (3550 Å) to a value over unity at the shortest wavelengths employed in this work (2800 Å). On the basis of certain reasonable assumptions concerning the mechanism of the secondary reactions, estimates were derived for ϕ_I and ϕ_{II} for each major absorption band for CH_2O and CD_2O. The temperature and pressure independence of the ϕ_I/ϕ_{II} estimates from the photolyses limited to the long-wavelength bands of formaldehyde shows that process III, $CH_2O^* + CH_2O \rightarrow CH_2OH + HCO$, is unimportant for these conditions. Although process II is the dominant mode of formaldehyde photodecomposition for these conditions, process I does occur measurably on the absorption of light by formaldehyde vapor in the band near 3385 Å. From these observations it is concluded that $D_{HCO-H} \leq 85$ kcal/mole.

The photochemistry of formaldehyde is of special interest to several areas of the scientific community. Because of its structural simplicity and the rather extensive knowledge of its spectroscopy, formaldehyde offers the photochemist an unparalleled opportunity to search for relations between the photophysical and photochemical primary processes and to develop theories of photochemical reactions. A detailed knowledge of the photochemistry of formaldehyde is not only of theoretical interest, but it is of great practical value to the area of air pollution control. Formaldehyde is a major contaminant in urban atmospheres, and the evaluation of its role in atmospheric reactions and in photochemical smog formation must await a more detailed knowledge of its photochemistry. For example, the important rates of H and HCO formation resulting from the photodecomposition of formaldehyde in the sunlight cannot be estimated satisfactorily with the presently available information.

The photolysis of formaldehyde has been interpreted in terms of two distinct primary photodissociative processes

$$H_2CO + h\nu \longrightarrow H + HCO \qquad (I)$$

$$\longrightarrow H_2 + CO \qquad (II)$$

The attempts which have been made to determine the relative importance of the two processes as a function of photon energy have led to conflicting conclusions. Gorin[2] studied the iodine-inhibited photolysis of formaldehyde and concluded that process I was the only important reaction at 2537 and 3130 Å, while process II accounted for about 30% of the formaldehyde photodecomposition at 3650 Å. If one interprets Gorin's limited results according to the present view of the stoichiometry of the formyl radical reaction with iodine [$HCO + I_2 \rightarrow (HCOI + I) \rightarrow HI + CO + I$], then for the iodine-inhibited product rate data, $\phi_I/\phi_{II} \cong (R_{CO} - R_{H_2})/R_{H_2}$. Using this method of estimation, $\phi_I/\phi_{II} \geq 129, 51$ at 2537 Å; 69, 91, 115 at 3130 Å; 1.2, 1.1, 1.4 at 3650 Å. On the other hand, Schoen[3] estimated that $\phi_I/\phi_{II} \geq 5$ from CH_2O–D_2 mixture photolyses at 3650 Å. In later work Klein and Schoen[4] determined the H_2, HD, and D_2 yields in the photolysis of CH_2O–CD_2O mixtures; they concluded that $\phi_I/\phi_{II} \cong 5$ at 3130 Å and about 0.5–5 at 3650 Å. Harrison and Lossing[5] used a specially constructed mass spectrometer system to determine the primary processes in the 2537-Å mercury-photosensitized decomposition of CH_2O. They found that $\phi_I/\phi_{II} \cong 1.5$ for their conditions. In the most recent work concerned with the determination of the extent of the primary processes in formaldehyde photolysis, DeGraff and Calvert[6] inhibited the photolysis with olefin addition and estimated that $\phi_{II} \cong 0.41, 0.48, 0.81$, and 0.85 at 3340, 3130, 2654, and 2537 Å, respectively; this is a trend in ϕ_{II} which is opposite to that suggested in the earlier work.

The energy requirements for process I have been estimated by a variety of methods, but there is a substantial disagreement between the various results. The work of Gorin,[2] Schoen,[3] Klein and Schoen,[4] and

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[1] Presented in part at the Symposium on Structure and Photochemistry of Excited States, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965. Submitted by R. D. M. in partial fulfillment of the requirements for the Ph.D. degree in chemistry, The Ohio State University, 1964. The authors acknowledge gratefully the support of this work through a research grant from the National Center for Air Pollution Control, U. S. Department of Health, Education, and Welfare, Public Health Service, Arlington, Va., and a Petroleum Research Fund Fellowship for R. D. M. during the term of this study.

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Venugopalan and Kutschke[7] established that free radicals could be generated through 3650-Å light absorption by formaldehyde. This has been interpreted as proof of the occurrence of process I at 3650 Å. However, the possible primary process III offers an alternative to this interpretation; see Discussion. If primary process I is assumed to be the origin of radicals in photolysis at

$$CH_2O^* + CH_2O \longrightarrow CH_2OH + HCO \qquad \text{(III)}$$

3650 Å and account is taken of the absorption of light by a vibrationally excited molecule at this wavelength, then the photodissociation data suggest that $D_{HCO-H} \leq 81.5$ kcal/mole. The kinetic data from aldehyde photolyses[8] and the CH_2O-I_2 thermal reaction[9] point to a somewhat higher estimate of D_{HCO-H}. The most accurate of the kinetic data which were derived by Walsh and Benson give $D_{HCO-H} = 87.0 \pm 1.0$ kcal/mole. Electron impact experiments gave the estimates, $D_{HCO-H} = 74.7 \pm 2.3$,[10a] 73.1 ± 2.3,[10b] and 79.5 ± 3[10c] kcal/mole, consistent with the photodissociation limit data. However, Murad and Inghram[11] have indicated errors in the interpretation of these electron impact experiments which discount the claimed accuracy, and they find from their photoionization studies that $D_{CH_3CO-H} = 85.1 \pm 1.4$ kcal/mole. One would expect this value to be very near to that for the equivalent bond in formaldehyde. Hence the Murad and Inghram data suggest $D_{HCO-H} = 85 \pm 2$ kcal/mole.

It has been suggested that the absence of emission from the 1^+ level of the $^1A_2$ excited state of H_2CO indicates that this level is predissociated.[12] Since the 1^+ level lies at 82.1 kcal/mole above the zero point level of the ground state, the data are consistent with the low value of D_{HCO-H} derived from photodissociation limit data. However, the agreement may be fortuitous, as Venugopalan and Kutschke have pointed out, since they have observed free radical formation in CD_2O at 3650 Å while the spectroscopic data for CD_2O show no evidence for predissociation from any known levels of the $^1A_2$ state.

In view of the uncertainties regarding the relative importance of processes I and II as a function of wavelength and the disparity between the various estimates of the energy requirements for process I, we have initiated a study of the flash photolysis of CD_2O-CH_2O mixtures and CHDO. We reasoned that the isotopic scrambling in these systems at high radical concentration should be the result of radical–radical interactions alone, and hence the data derived from selectively filtered flash photolysis experiments could in principle provide an unambiguous result concerning both the photodissociation limit and the relative extent of primary processes I and II as a function of wavelength. Although our expectations for this system were somewhat naive, the results of these experiments reported here provide some interesting and significant new information concerning these problems and the mechanism of formaldehyde photolysis.

Experimental Section

Experimental Methods. The flash photolysis system used was essentially that described by Dingledy and Calvert[13] with some minor modifications. The 1-m flash tube was a conventional, millisecond, Porter-type system employing xenon at 25.5-cm pressure. In the usual experiment a 10-kV charge on the capacitance bank of 80 μF gave a 4000-J discharge. A single filling of the xenon was used in all of the runs reported here. The flash intensity was very reproducible as evidenced by the near equality of the volumes of gaseous products formed in duplicate experiments. The flash lamp paralleled the 1-m reaction cell (227-ml volume), and the lamp, cell, and filters were housed in a stainless steel, cylindrical reflector. The photolysis cell was in series with a trap and an all-glass circulating pump. Polymerization of formaldehyde was prevented by heating all of the parts of the system in contact with formaldehyde vapors to 80° through the use of heating wire or tapes. Silicone grease was used in stopcocks which were heated. The photolysis cell was controlled at 60, 80, or 100° in the different series of runs. A spoon-gauge and mercury manometer combination permitted measurements of pressure without contact between the aldehyde vapor and mercury and eliminated a potential polymerization site.

Filtering of the continuum emitted by the flash lamp was accomplished by the interposition of calibrated glasses between the flash lamp and the reaction cell. The numbered filter systems to which reference is given in figures and tables were constituted as follows: filter 1, Pyrex glass wall of the reaction vessel; filter 2, Pyrex glass wall in a jacket surrounding the reaction vessel; filter 3, 3-mm thickness of window glass; filter 4, 3-mm thickness of window glass. The transmission characteristics of all glasses used in this work were measured on a Cary Model 14 spectrophotometer. In Figure 1 is shown the wavelength dependence of the flash tube light absorbed by CH_2O, CD_2O, and CHDO vapors using the different filter combinations. These curves were calculated from measured absorption data for the aldehydes and the filters employed. The authors are indebted to Mrs. Veronique McMillan, who determined the absorption coefficient data reported here. She used samples of CH_2O, CD_2O, and CHDO vapors taken from the photochemical system and determined the absorption spectra in a special water-jacketed, 5-cm cell maintained at about 80° using a low-resolution, recording spectrophotometer (Bausch and Lomb 505).

The monomeric isotopic formaldehydes were obtained from their polymers by a procedure patterned after that of Spence and Wild.[14] The polymers were purchased in their Eu-polyoxymethylene forms: $(CH_2O)_n$ from Eastman Organic Chemicals, and $(CD_2O)_n$ and $(CHDO)_n$ from Merck (Canada); the stated isotopic purity of the deuterated formaldehydes was 99 atom %. The purified monomer was stored in traps at −78°. Infrared absorption spectra (measured with a 20-m path cell at 25° and low aldehyde pressures), ultraviolet absorption spectra (measured in a 5-cm cell at about 80°), and mass spectra of the formaldehyde samples indicated that the CH_2O and CD_2O monomers were essentially pure materials. The mass spectral data for CHDO suggested that this sample was impure. From the excess of hydrogen over deuterium photodecomposition products in the experiments using filters 1 and 2, we estimate that the CHDO samples probably contained 10% CH_2O impurity. Because of uncertainties in the isotopic purity of the CHDO sample, the accuracy of the data for this compound is questionable. Standard samples of carbon monoxide (Airco), H_2 (Liquid Carbonic), D_2 (Matheson Co.), and HD (prepared from $LiAlD_4$ and $(CH_3)_3NHCl$) were used in calibration of the mass spectrometer.

For those experiments involving mixtures of D_2CO and H_2CO, the desired amount of D_2CO was bled into the evacuated photolysis system first and condensed in the trap at −195°. The H_2CO monomer was then distilled from its storage trap at −78° to the

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Table I. Data from the Flash Photolysis of Mixtures of CH_2O and CD_2O at 80°

Run no.	Reactant pressure, mm		P_{CD_2O}/P_{CH_2O}	No. flashes (voltage, kV)	Product volume, μl (STP)				$V_{HD}/(V_{H_2}+V_{HD}+V_{D_2})$	Calcd[a] av ϕ_I/ϕ_{II}
	CH_2O	CD_2O			H_2	HD	D_2	CO		
					(a) Filter 1					
1	16.8	9.7	0.58	1 (10)	19.34	3.58	3.49	24.5	0.14	0.73
2	24.8	15.3	0.62	1 (10)	26.53	4.56	4.69	32.3	0.13	0.68
3	12.8	10.3	0.81	1 (10)	12.00	3.52	4.04	18.9	0.18	0.76
4	16.1	17.2	1.07	1 (10)	16.13	5.65	7.02	27.2	0.20	0.78
5	12.1	16.3	1.35	1 (10)	11.94	4.73	6.75	b	0.20	0.64
6	16.8	30.4	1.81	1 (10)	15.44	7.60	10.99	33.3	0.22	0.83
									Av 0.18	0.74
					(b) Filters 1 and 2					
7	31.1	18.0	0.58	1 (9.4)	26.60	2.34	4.12	37.3	0.071	0.36
8	24.8	16.5	0.67	1 (9.4)	13.50	2.02	2.83	20.7	0.11	0.50
9	16.0	16.6	1.04	1 (9.4)	10.77	2.05	3.33	19.3	0.13	0.48
10	12.1	12.9	1.06	1 (8.7)	18.12	1.42	2.55	12.9	0.12	0.42
11	7.3	14.5	1.99	1 (9.7)	7.55	2.01	4.26	14.5	0.14	0.45
									Av 0.11	0.44
					(c) Filters 1, 2, and 3					
12	31.1	18.0	0.58	2 (10)	9.62	0.47	1.23	b	0.041	0.23
13	15.5	11.7	0.76	2 (10)	6.67	0.45	1.25	b	0.054	0.23
14	19.3	17.5	0.91	2 (10)	5.31	0.47	1.30	8.6	0.066	0.24
15	13.3	18.5	1.39	2 (10)	5.24	0.54	2.05	8.2	0.069	0.20
16	22.0	31.4	1.43	2 (10)	7.08	0.62	1.92	10.6	0.064	0.22
17	8.3	18.1	2.18	2 (10)	2.64	0.49	1.89	4.8	0.098	0.25
									Av 0.065	0.23

[a] Calculated as described in the text. [b] Analysis for CO discarded.

Table II. Data from the Flash Photolysis of Mixtures of CH_2O and CD_2O in Experiments Using Filters 1, 2, 3, and 4

Run no.	Temp, °C	Reactant pressure, mm		P_{CD_2O}/P_{CH_2O}	No. flashes (voltage, kV)	Product volume, μl (STP)				$V_{HD}/(V_{H_2}+V_{HD}+V_{D_2})$	Calcd[a] av ϕ_I/ϕ_{II}
		CH_2O	CD_2O			H_2	HD	D_2	CO		
18	60	21.0	12.0	0.57	4 (10)	8.40	0.33	1.28	9.1	0.033	0.15
19	60	13.0	30.0	2.31	4 (10)	4.57	0.41	1.82	7.1	0.060	0.17
20	60	11.7	32.0	2.74	4 (10)	3.68	0.36	2.02	b	0.059	0.15
21	60	8.5	31.0	3.65	4 (10)	2.62	0.26	1.71	b	0.057	0.13
										Av 0.052	0.15
22	80	35.8	13.6	0.38	4 (10)	13.10	0.37	1.35	16.6	0.025	0.16
23	80	39.9	28.2	0.73	4 (10)	10.83	0.39	1.82	13.5	0.030	0.13
24	80	23.5	18.3	0.78	16 (5)	5.64	0.24	1.04	6.8	0.035	0.14
25	80	20.4	28.5	1.40	16 (5)	5.51	0.41	1.93	8.0	0.052	0.15
26	80	12.0	19.5	1.62	4 (10)	4.49	0.29	1.66	6.4	0.045	0.13
27	80	12.2	28.0	2.28	4 (10)	5.99	0.40	2.40	b	0.045	0.12
										Av 0.039	0.14
28	100	13.1	31.1	2.37	3 (10) 1 (8.8)	5.62	0.61	3.15	9.4	0.065	0.16
29	100	12.7	32.0	2.57	4 (10)	4.60	0.46	2.68	8.2	0.059	0.15
30	100	9.5	29.2	3.07	4 (10)	3.79	0.37	2.51	b	0.055	0.13
31	100	9.6	31.0	3.23	3 (10) 1 (9)	2.31	0.28	1.19	4.5	0.074	0.19
32	100	8.3	31.0	3.74	3 (10) 1 (8.4)	2.50	0.24	1.49	3.6	0.057	0.14
										Av 0.062	0.15

[a] Calculated as described in the text. [b] Analysis for CO discarded.

CD_2O-containing trap at −195° in the photolysis system. The amount of aldehyde transferred in a given time was determined so that roughly the desired CH_2O amount could be introduced. The two aldehydes were warmed to 80°, vaporized essentially completely, and CH_2O actually added was determined from the difference of the total pressure of the final mixture and the pressure of the CD_2O measured previously. The reactants were mixed thoroughly for 10 min prior to the photolysis using the all-glass circulating pump in series with the photolysis cell and trap. After the flash discharge or series of discharges, the excess of reactants and any other condensables were frozen out in the trap at −195° and the gaseous products collected with a Toepler pump. No analysis of the condensable fraction was attempted. The total volume of each gaseous sample was measured in a buret and then analyzed in a mass spectrometer (Consolidated Model 21-620). The total decomposition of the reactant formaldehyde was less than 0.2% in all of the experiments. With a 2-μl or larger sample of product gas the method of analysis was reproducible to about 5%. There was no detectable decomposition or polymerization of the formaldehyde in dark runs.

Experimental Results. The only products of the formaldehyde photolysis measured in these experiments were carbon monoxide and hydrogen. The average value of the ratio of the total hydrogen (H_2, HD, and D_2) to carbon monoxide for 57 runs was 0.97 ±

Table III. Data from the Flash Photolysis of CHDO at 80°

Run no.	Pressure CHDO, mm	No. flashes (voltage, kV)	Product volume, μl (STP) H_2	HD	D_2	CO	V_{D_2}/V_{HD}	Calcd[a] ϕ_I/ϕ_{II}
			(a) Filter 1					
33	19.2	1 (10)	3.81	14.36	1.33	17.8	0.092	0.58
34	19.2	1 (10)	4.16	13.02	1.19	*b*	0.091	0.60
35	19.4	1 (10)	4.22	13.66	1.25	19.7	0.091	0.60
36	25.7	1 (9.9)	5.25	17.55	1.63	22.9	0.092	0.60
							Av 0.092	0.60
			(b) Filters 1 and 2					
37	18.0	1 (10)	2.43	6.94	0.63	11.3	0.090	0.57
38	19.2	1 (10)	2.57	7.99	0.63	13.2	0.078	0.48
39	19.2	1 (10)	2.43	8.43	0.67	11.5	0.079	0.47
							Av 0.082	0.51
			(c) Filters 1, 2, and 3					
40	18.4	2 (10)	0.64	3.37	0.13	*b*	0.038	0.20
41	19.0	8 (10)	2.12	14.66	0.39	18.8	0.026	0.16
42	30.5	4 (10)	1.69	10.72	0.41	14.0	0.038	0.19
43	31.3	2 (10)	0.89	5.58	0.19	6.9	0.034	0.17
							Av 0.034	0.18
			(d) Filters 1, 2, 3, and 4					
44	26.3	8 (10)	1.02	7.01	0.24	8.9	0.034	0.16
45	32.5	12 (10)	1.49	14.01	0.28	*b*	0.019	0.09
46	37.4	8 (10)	1.24	11.03	0.27	12.8	0.024	0.12
47	40.9	4 (10)	0.80	5.36	0.18	*b*	0.033	0.16
48	52.6	7 (10) 1 (9.4)	1.89	11.80	0.21	15.8	0.017	0.09
49	52.0	7 (10) 1 (8.8)	1.54	11.32	0.30	15.1	0.026	0.13
							Av 0.026	0.13

[a] Calculated as described in the text; the reactant sample was taken to be 90% CHDO and 10% CH_2O as suggested by mass spectrometric analysis and the deuterium-hydrogen imbalance in the products. [b] Analysis for CO discarded.

0.08 (std dev). There was no detectable trend in the ratio caused by variations in intensity, wavelength, temperature, or reactant isotopic composition over the range studied in this work. In several preliminary experiments at 80° using filters 1 and 2, various pressures of pure CH_2O or CD_2O were given a single 10-kV flash. The volume of the hydrogen product was found to be a linear function of the pressure of the aldehyde used. These data are summarized in Figure 2. They show that less CD_2O decomposes than does CH_2O under the same conditions of pressure, temperature, and incident light intensity. This probably results from a combination of the usual isotopic effect observed when C–H and C–D bonds are broken and the smaller absorption by CD_2O over the spectral regions involved in this study. In further preliminary experiments at 80° using filters 1 and 2, the flash voltage was varied in experiments at fixed aldehyde pressure and the volume of hydrogen measured. These data are given in Figure 3. It is seen that the volume of the hydrogen product from the aldehyde photodecomposition is proportional to the square of the charging voltage (or the flash energy). The data from the flash experiments of CH_2O–CD_2O mixtures at various temperatures and filter combinations are summarized in Tables I and II. Similar data for flash experiments using CHDO are given in Table III.

Discussion

The Mechanism of the Flash Photolysis of Pure CH_2O and CD_2O Vapors. From the previous studies of formaldehyde photolysis one must consider the following reactions as possibly important in the flash photolysis of formaldehyde. CH_2O^* represents some undefined excited state or states of formaldehyde ($^1A_2$, $^3A_2$, $^1A_1{}^v$, etc.). A consideration of the pure formaldehyde results from this work allows some definitive choices to be made between possible alternative reactions.

$$CH_2O + h\nu \longrightarrow CH_2O^*$$

$$CH_2O^* \longrightarrow HCO + H \qquad \text{(I)}$$

$$CH_2O^* \longrightarrow H_2 + CO \qquad \text{(II)}$$

$$CH_2O^* + CH_2O \longrightarrow CH_2OH + HCO \qquad \text{(III)}$$

$$H + HCO \longrightarrow H_2 + CO \qquad (1)$$

$$H + HCO + (M) \longrightarrow H_2CO\ (+M) \qquad (2)$$

$$2H + M \longrightarrow H_2 + M \qquad (3)$$

$$2HCO \longrightarrow CO + CH_2O \qquad (4)$$

$$2HCO \longrightarrow 2CO + H_2 \qquad (5)$$

$$2HCO \longrightarrow (HCO)_2 \qquad (6)$$

$$H + CH_2O \longrightarrow H_2 + HCO \qquad (7)$$

$$H + CH_2O \longrightarrow CH_2OH \qquad (8)$$

$$HCO + M \longrightarrow H + CO + M \qquad (9)$$

$$CH_2OH + R \longrightarrow CH_3OH + R(-H) \qquad (10)$$

(1) The only observed products of the flash photolysis of formaldehyde, carbon monoxide and hydrogen, are formed in equal amounts within the experimental error; the average ratio of hydrogen to carbon monoxide was 0.97 ± 0.08 for 57 runs under a variety of conditions. This result is consistent with the observations of DeGraff and Calvert[6] made in the high-intensity photolysis of formaldehyde with continuous illumination. In their experiments at relatively low intensities, a significant excess of carbon monoxide over hydrogen was seen; this observation was made earlier also by Venugopalan and Kutschke.[7] However, at the highest intensities employed by DeGraff and Calvert (about 10^4 greater than those used in the low-intensity experiments), the CO/H_2 ratio approached unity. These re-

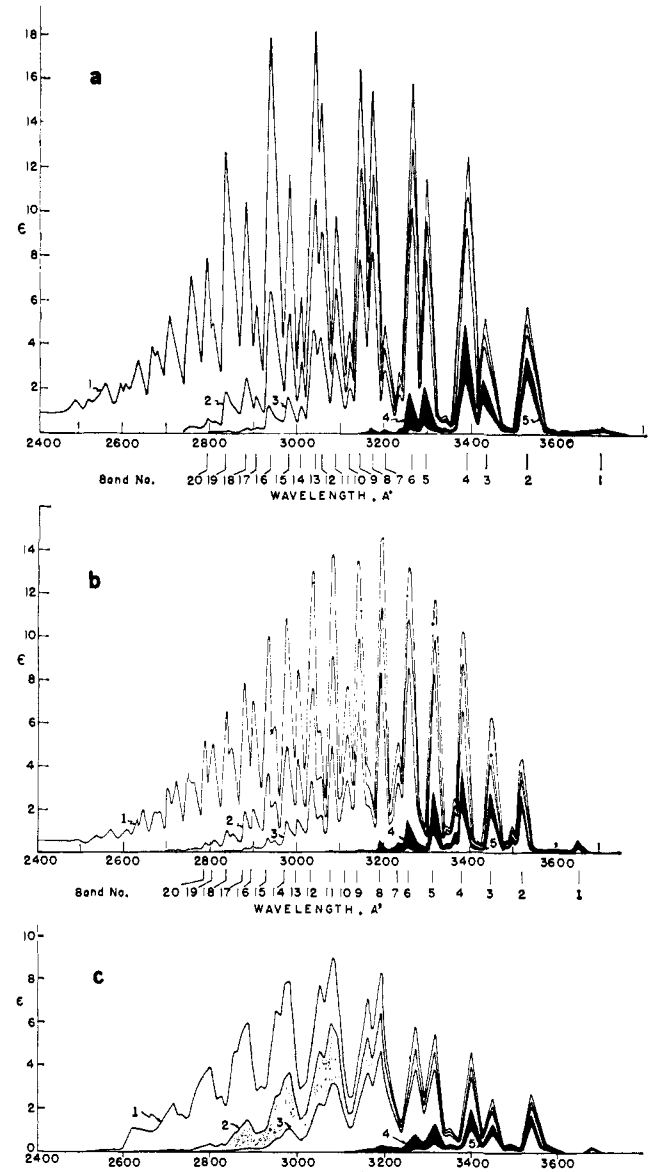

Figure 1. Wavelength dependence of the absorbed intensities of the xenon flash tube light for CH_2O (a), CD_2O (b), and CHDO (c); for each aldehyde, curve 1 is the molar extinction coefficient (l./mole cm); the other curves represent the relative intensities of absorbed light effected by the different filters employed: curve 2, filter 1; curve 3, filters 1 and 2; curve 4, filters 1, 2, and 3; curve 5, filters 1, 2, 3, and 4.

sults show the relative unimportance at flash intensities of reactions such as III, 8, and 10, which lead to a carbon monoxide excess over hydrogen, and reaction 6, which would result in a hydrogen excess. It is unlikely that these reactions occur significantly at rates which fortuitously maintain the balance of carbon monoxide and hydrogen. The occurrence of reaction 6 could not be determined by the analytical procedure used. Blacet and Blaedel[15] found very small quantities of glyoxal from the full Hg-arc photolysis of acetaldehyde. However, Khan, Norrish, and Porter[16] found no evidence for glyoxal formation from the flash photolysis of acetaldehyde. They believed that reaction 5 was an important source of hydrogen and carbon monoxide in that system.

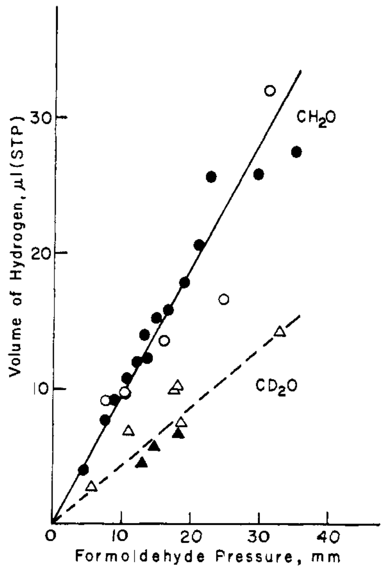

Figure 2. Volume of hydrogen formed as a function of formaldehyde pressure, from photolyses of pure CH_2O or CD_2O vapors and their mixtures; temperature 80°; single flash of 4000 J; filters 1 and 2 employed; the ordinate corresponds to the following: V_{H_2} from pure CH_2O, darkened circles; $V_{H_2} + V_{HD}/2$ from CH_2O–CD_2O mixtures, open circles; V_{D_2}, from pure CD_2O, open triangles; $V_{D_2} + V_{HD}/2$ from CD_2O–CH_2O mixtures, darkened triangles; the abscissa is the partial pressure of the single isotopic species being considered.

(2) The observed direct proportionality between the formaldehyde pressure and the volume of hydrogen formed (Figure 2) disproves the importance of III compared to other decomposition modes in the wavelength range 2900–3600 Å used in these experiments. Walsh and Benson[9] and DeGraff and Calvert[6] suggested that III may be the important reaction leading to radical formation in formaldehyde, particularly at the longer wavelengths. Note that for the relatively small aldehyde pressures and small path lengths (1.7 cm) employed here, the limiting form of the Beer–Lambert absorption law will apply, and the primary processes I and II will occur at a rate proportional to the absorbed light intensity or the pressure of formaldehyde. If III were important in product formation for these conditions, the volume of hydrogen product in Figure 2 would tend toward proportionality to the square of the aldehyde pressure at the higher pressures. This is not the case. A further observation is consistent with the relative unimportance of III for the 2900–3600-Å region. Note in the plot of Figure 2 that there is no significant suppression of the volume of hydrogen ($V_{H_2} + V_{HD}/2$) from the line characteristic of pure CH_2O when CD_2O (13–18 mm) is added. Within the experimental error the open circles ($V_{H_2} + V_{HD}/2$) from the CH_2O–CD_2O mixtures and the darkened circles (V_{H_2} from pure CH_2O) form the same line. The comparison of the volumes of deuterium product formed in experiments using pure CD_2O (open triangles) and the volume of total deuterium ($V_{D_2} + V_{HD}/2$) formed in CD_2O experiments with added CH_2O (darkened triangles in Figure 2) also confirms the unimportance of III for these conditions.

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(15) F. E. Blacet and W. J. Blaedel, *J. Am. Chem. Soc.*, 62, 3374 (1940).

(16) M. A. Khan, R. G. W. Norrish, and G. Porter, *Proc. Roy. Soc.* (London), A219, 312 (1953).

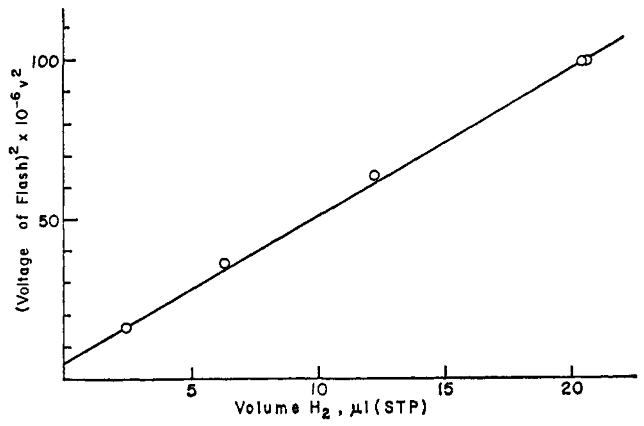

Figure 3. Plot of the volume of hydrogen product of the flash photolysis of CH_2O vapor *vs.* the square of the flash voltage; pressure of CH_2O, 21 mm; temperature, 80°; filters 1 and 2 employed.

(3) The volume of hydrogen product is a linear function of the flash voltage squared (or the energy of the flash); see Figure 3. If one couples this observation with the evidence of the importance of both primary processes I and II to be described in the next section, then the data are consistent with the occurrence of processes I and II followed only by nonchain inducing, radical-radical reactions. This result suggests as well that the flash experiments were essentially isothermal in character. Processes such as 1, 3, 4, and 5 must dominate over 7, 8, and 9 for this system under these conditions. Indeed this is the conclusion which one reaches using reasonable estimates for the rate constants of reactions 1-10 and the various conditions of the flash experiments used here. Since Kutschke and Toby[17] have shown that with the competitive reactions 11 and 12, 11 is favored ($k_{11}/k_{12} \geq 4$), we would expect (1) to be favored over (2) in our reaction sequence.

$$CH_3 + HCO \longrightarrow CH_4 + CO \qquad (11)$$

$$CH_3 + HCO \longrightarrow CH_3CHO \qquad (12)$$

In summary, it is likely that the important reactions in the flash photolysis of formaldehyde are primary processes I and II followed by reactions 1, 3, 4, and 5.

The Flash Photolysis of CH_2O-CD_2O Mixtures. The Estimation of the Wavelength Dependence of $\phi_I + \phi_{II}$ and ϕ_I/ϕ_{II}. The photolysis of mixtures of the isomeric formaldehydes allows an estimation of the variation of the sum and the quotient of the efficiencies of the primary processes I and II as a function of wavelength. The use of different filter systems in this work served to vary the energy distribution absorbed by the reactant. Christie and Porter[18] showed that over the spectral range from 2500 to 4000 Å, the intensities for equal wavelength intervals emitted by the xenon flash lamp are near equal. If one couples this result with the observed dependence of the volume of hydrogen product from CH_2O and CH_2O-CD_2O mixture photolyses on the pressure of formaldehyde and the total energy of the flash employed, then one expects the function F_1 to describe the relation between the product volumes, the experimental variables, and parameters related to the efficiency of light absorption and photodecomposition in the formaldehyde molecule

Table IV. Comparison of *F* Functions (13-15) and the Integrated Absorbed Light Intensity from CH_2O, CD_2O, and CHDO Photolyses

Filters	(1) F, μl deg/(mm V^2) × 10^6	(2) $a\int \epsilon_\lambda Q_\lambda \, d_\lambda$ (arbitrary units)	(3) (1)/(2) × 10^3
	(a) CH_2O	(F_1)	
1	4.59 ± 0.37	1370	3.4 ± 0.3
1, 2	3.77 ± 1.2	846	4.4 ± 1.4
1, 2, 3	0.74 ± 0.24	218	3.4 ± 1.0
1, 2, 3, 4	0.38 ± 0.12	110	3.5 ± 1.0
	(b) CD_2O	(F_2)	
1	2.09 ± 0.30	1102	1.9 ± 0.3
1, 2	1.29 ± 0.26	654	2.0 ± 0.4
1, 2, 3	0.21 ± 0.05	151	1.4 ± 0.3
1, 2, 3, 4	0.089 ± 0.025	71	1.3 ± 0.4
	(c) CHDO	(F_3)[a]	
1	3.66 ± 0.21	787	4.7 ± 0.3
1, 2	2.10 ± 0.12	476	4.1 ± 0.2
1, 2, 3	0.43 ± 0.01	102	4.2 ± 0.1
1, 2, 3, 4	0.15 ± 0.02	51.5	2.9 ± 0.3

[a] These figures include corrections to the experimental data of Table III for the estimated 10% CH_2O impurity of the CHDO samples.

$$F_1 = \frac{V_{H_2} + V_{HD}/2}{(P_{CH_2O}/T)(\Sigma v^2 - v_0^2)} = k\int_{\lambda_1}^{\lambda_2} (\phi_I + \phi_{II})\epsilon_\lambda Q_\lambda \, d\lambda \qquad (13)$$

(P_{CH_2O}/T) is a term proportional to $[CH_2O]$; $(\Sigma v^2 - v_0^2)$ is proportional to the total energy of the flashes used in the given experiment; k is a proportionality constant; $\phi_I + \phi_{II}$ is the sum of the primary quantum yields of processes I and II, respectively; ϵ_λ is the molar extinction coefficient of CH_2O at λ; Q_λ is the transmission at λ of the filter system employed. Expression 13 implies that all of the terms within the integral are wavelength dependent. The limits of integration extend to cover the entire band. The product of $\epsilon_\lambda Q_\lambda$ as a function of λ is shown for CH_2O, CD_2O, and CHDO for various filter combinations in Figure 1. Functions F_2 and F_3, similar to F_1, are expected to describe the total deuterium from CD_2O in CD_2O-CH_2O mixtures and the total hydrogen from CHDO flash photolyses, respectively.

$$F_2 = \frac{V_{D_2} + V_{DH}/2}{(P_{CD_2O}/T)(\Sigma v^2 - v_0^2)} = k\int_{\lambda_1}^{\lambda_2} (\phi_{I'} + \phi_{II'})\epsilon_\lambda{}' Q_\lambda \, d\lambda \qquad (14)$$

$$F_3 = \frac{V_{D_2} + V_{HD} + V_{H_2}}{(P_{CHDO}/T)(\Sigma v^2 - v_0^2)} = k\int_{\lambda_1}^{\lambda_2} (\phi_{I''} + \phi_{II''})\epsilon_\lambda{}'' Q_\lambda \, d\lambda \qquad (15)$$

$\phi_{I'}$ and $\phi_{II'}$ are the primary quantum yields of processes I′ and II′ in CD_2O photolysis, while $\phi_{I''}$ and $\phi_{II''}$

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(17) K. O. Kutschke and S. Toby, *Can. J. Chem.*, 37, 672 (1959).

(18) M. I. Christie and G. Porter, *Proc. Roy. Soc.* (London), A212, 398 (1952).

Table V. Summary of Approximate Primary Quantum Yields as a Function of Wavlength in the Photolyses of CH_2O and CD_2O Vapor at 5–68 mm and 60–100°

$$CH_2O^* \longrightarrow \begin{array}{l} H + HCO \quad (I) \\ H_2 + CO \quad (II) \end{array} \qquad CD_2O^* \longrightarrow \begin{array}{l} D + DCO \quad (I') \\ D_2 + CO \quad (II') \end{array}$$

Absorption band[a]	$\phi_I + \phi_{II}$	ϕ_I/ϕ_{II} (exptl)	ϕ_I/ϕ_{II} $\times 10^2$ (theoret)[b]	ϕ_I/ϕ_{II} (adjusted theory[c])	ϕ_I	ϕ_{II}	$\phi_{I'} + \phi_{II'}$	$\phi_{I'}/\phi_{II'}$	$\phi_{I'}$	$\phi_{II'}$
1	1.0	0.00	0.00	0.00	0.00	1.00	0.31	0.00	0.00	0.31
2	1.0	0.07	0.002	0.01	0.06	0.94	0.35	0.02	0.01	0.34
3	1.0	0.18	0.02	0.09	0.15	0.85	0.39	0.11	0.04	0.35
4	1.0	0.27	0.05	0.17	0.21	0.79	0.43	0.21	0.07	0.36
5	1.0	0.40	0.18	0.40	0.29	0.71	0.47	0.33	0.12	0.35
6	1.0	0.53	0.30	0.57	0.35	0.65	0.51	0.38	0.14	0.37
7	1.0	0.60	0.48	0.80	0.38	0.62	0.54	0.41	0.16	0.38
8	1.0	0.65	0.68	0.99	0.39	0.61	0.57	0.44	0.17	0.40
9	1.0	0.70	0.82	1.17	0.41	0.59	0.61	0.50	0.20	0.41
10	1.0	1.00	0.94	1.28	0.50	0.50	0.65	0.75	0.28	0.37
11	1.0	1.25	1.24	1.56	0.56	0.44	0.69	1.00	0.34	0.34
12	1.0	1.50	1.55	1.83	0.60	0.40	0.73	1.25	0.41	0.32
13	1.0	1.75	1.69	1.95	0.64	0.36	0.77	1.50	0.46	0.31
14	1.0	2.00	2.02	2.22	0.67	0.33	0.81	2.00	0.54	0.27
15	1.0	2.50	2.39	2.50	0.71	0.29	0.85	2.50	0.61	0.24
16	1.0	3.00	3.09	3.00	0.75	0.25	0.89	3.00	0.67	0.22
17	1.0	3.50	3.61	3.36	0.78	0.22	0.93	3.50	0.72	0.21
18	1.0	4.00	4.06	3.66	0.80	0.20	0.97	4.00	0.78	0.19
19	1.0	4.50	5.13	4.32	0.82	0.18	1.00	4.50	0.82	0.18
20	1.0	5.00	6.16	4.92	0.83	0.17	1.00	5.00	0.83	0.17

[a] These bands are the arbitrary numbers assigned to the major absorption peaks as shown in Figure 1. [b] Calculated from the theory of Eyring, *et al.*,[20] using the relation shown in reference 20 and the parameters selected from sources independent of this work.[22] [c] Calculated from relation in reference 18 using E_I and E_{II} as before, but $2\nu_I/\nu_{II} = 106$ and $p = 3.59$, so that the calculated values are forced to match at bands 5 and 15.

are the corresponding quantities for processes I'' and II'' in CHDO photolysis. In Table IV the average

$$\begin{array}{lr} CD_2O^* \longrightarrow D + DCO & (I') \\ CD_2O^* \longrightarrow D_2 + CO & (II') \\ CHDO^* \longrightarrow H + DCO \text{ (or } D + HCO) & (I'') \\ CHDO^* \longrightarrow HD + CO & (II'') \end{array}$$

functions F_1, F_2, and F_3 are given in column 2 as calculated from the data on the left-hand side of the F functions. Also the integrals of the product of $\epsilon_\lambda Q_\lambda$ were calculated for each aldehyde from the data of Figure 1. Note the near constancy of the ratio of columns 1 to 2 observed for CH_2O in Table IV, column 3. This can only result if $\phi_I + \phi_{II}$ is essentially constant as a function of wavelength. Since $\phi_I + \phi_{II}$ is probably near unity for photolyses of CH_2O at the shorter wavelengths, it follows that $\phi_I + \phi_{II} \cong 1.0$ for CH_2O at all wavelengths at the pressures and temperatures employed here. However, in the cases of CD_2O and CHDO apparent decreases in ratio of column 3 of Table IV are seen for the experiments in which the dominant light absorption is in the long-wavelength region. This may be interpreted to show that $\phi_{I'} + \phi_{II'}$ and $\phi_{I''} + \phi_{II''}$ are somewhat less than unity for CD_2O and CHDO photolyses at the long wavelengths. This conclusion is in general agreement with the observed lowered value of $\phi_{II'}$ for CD_2O compared to ϕ_{II} for CH_2O at the longer wavelengths.[6] Through the appropriate assignment of $\phi_{I'} + \phi_{II'}$ values for the various bands of CD_2O it is possible to match the experimental F_2 function with the integral of $(\phi_{I'} + \phi_{II'})\epsilon_\lambda Q_\lambda$ for each of the filter combinations used. Estimates derived in this fashion are shown in Table V.

Since excited molecule–molecule reactions such as III can be eliminated as important for the 2900–3600-Å region as shown above, it follows that the volume of HD formed in CH_2O–CD_2O mixture photolyses should reflect directly on the occurrence of primary process I. Also the total of the volumes of H_2, D_2, and HD should be a measure of the two processes I and II. Thus a qualitative measure of the relative importance of I as a function of wavelength range can be had from the ratios of $V_{HD}/(V_{D_2} + V_{HD} + V_{H_2})$ shown in Tables I and II. Note that the variation of this ratio suggests that process I becomes considerably less important as the percentage of short wavelengths in the flash lamp is lowered. A more quantitative evaluation of the importance of processes I and II can be attempted provided that certain reasonable assumptions are made. We can assume that statistical factors alone determine the isotopic hydrogen species formed by radical–radical reactions from H, HCO, D, and DCO. This is probably a fair approximation since studies of the radical–radical combination reactions, $2A \rightarrow A_2$, $2B \rightarrow B_2$, and $A + B \rightarrow AB$, show for a great variety of radicals that the rates are described well by the function $(R_{AB})^2/(R_{A_2}R_{B_2}) = 4$.[19] Then let us assume that relation 16 describes the volumes of the hydrogen isotopes formed following the free-radical processes I and I'. The subscript I designates that the product volume is only that portion resulting from free-radical processes following reactions I and I'. A further assumption concerning the relation-

$$(V_{HD})_I{}^2/(V_{H_2})_I(V_{D_2})_I = 4 \qquad (16)$$

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(19) (a) J. A. Kerr and A. F. Trotman-Dickenson, *Chem. Ind.* (London), 125 (1959); (b) J. O. Terry and J. H. Futrell, *Can. J. Chem.*, 45, 2327 (1967); (c) J. O. Terry and J. H. Futrell, *ibid.*, 46, 664 (1968).

ship of ϕ_I/ϕ_{II} ratios in CH_2O to those in CD_2O must be made before a detailed calculation of the ratios is possible from the CH_2O–CD_2O data. Application of simple unimolecular rate theory[20] to the photodecomposition processes I and II in formaldehyde predicts that relation 17 should hold for a given wavelength of

$$\phi_I/\phi_{II} \cong \phi_{I'}/\phi_{II'} \tag{17}$$

absorbed light. If one assumes the near correctness of relations 16 and 17 for this system, then relation 18 can be derived. The subscripts I and T refer to volume of

$$\frac{\phi_I}{\phi_I + \phi_{II}} \cong \frac{\phi_{I'}}{\phi_{I'} + \phi_{II'}} \cong \frac{(V_{H_2})_I + (V_{HD})_T/2}{(V_{H_2})_T + (V_{HD})_T/2} \cong \frac{(V_{D_2})_I + (V_{HD})_T/2}{(V_{D_2})_T + (V_{HD})_T/2} \tag{18}$$

hydrogen from process I and total volume, respectively. Average ratios of ϕ_I/ϕ_{II} were calculated from the data of Tables I and II using (18). Within the experimental error these calculated values, shown in the last column of Table I, are independent of the P_{CD_2O}/P_{CH_2O} ratio over a wide range. Note that the extent of process I relative to II decreases regularly as the band of radiation employed contains less and less of the shorter wavelengths. Obviously a nonvibrationally equilibrated formaldehyde molecule is involved for our conditions in this photolysis.

If one assumes that the ϕ_I/ϕ_{II} ratio increases regularly with decrease in wavelength, then it is possible to assign values of ϕ_I/ϕ_{II} to each formaldehyde vibrational band such that the experimentally observed average values of the ratio can be matched. McQuigg[21] followed this procedure and estimated ratios for each band as labeled in Figure 1. He coupled these data and the $\phi_I + \phi_{II}$ estimates, derived as described previously, to determine the individual quantum yields of I and II for the formaldehydes. These data are summarized in Table V. The variation of the experimental ratios of ϕ_I/ϕ_{II} can be matched quite well using the simple theory of Eyring, *et al.*[20] If one uses estimates for the parameters designated in the relation for ϕ_I/ϕ_{II}[20] which are derived from information independent of this work,[22] then the theoretical ratios shown in column 3 of Table V are obtained. The results are striking in that the simple theory predicts well the trend of ϕ_I/ϕ_{II} with wavelength variation. However, the theoretical ratios differ from the experimental values by a constant factor of 10^2. Obviously a good fit between "theory" and experiment can be obtained if the parameters in the equations defining ϕ_I/ϕ_{II} are varied freely. For example, if one takes $E_I \cong 78$ and $E_{II} \cong 45$ kcal/mole as before, the data can be made to fit exactly at bands 4 and 15 through the choice of $2\nu_I/\nu_{II} = 104$ and $p = 3.57$. In column 4 of Table V the values are given of the ϕ_I/ϕ_{II} ratio calculated in this fashion for all the bands. It is apparent that an equation of the simple form, $k = \nu(1 - E_I/E)^m$, often used to describe the rate constant for an energy-rich molecule of total energy E in a reaction with an activation energy E_I, describes qualitatively the reactions of photodecomposition of the formaldehyde molecules. Of course, a much more sophisticated theoretical model can be developed, but the accuracy of the present experimental data does not warrant this treatment now.

A further piece of evidence concerning the relative importance of the possible process III is had from the results summarized in Table II. For these experiments the flash lamp was filtered to restrict the absorbed light to the long wavelengths, 3250–3700 Å. It has been argued[6,9] that because of the deficiency of the quantum energy in the long wavelength photolysis of formaldehyde, the occurrence of process I may be energetically impossible, and process III may be the source of hydrogen scrambling in the long wavelength flash experiments and chain photodecomposition observed in the steady illumination experiments at long wavelengths. If process III were important for the conditions used in these flash experiments, one would expect a temperature dependence of the estimated ratio ϕ_I/ϕ_{II}, since a significant activation energy (about 3 kcal/mole) for III would be expected. To test this hypothesis we have carried out the flash photolyses for the long-wavelength range at several temperatures. No effect of temperature on ϕ_I/ϕ_{II} is seen in the data summarized in Table II. Note that the calculated ratio is essentially constant in experiments at 60, 80, and 100° where $\phi_I/\phi_{II} = 0.15$, 0.14, and 0.15, respectively. Certainly one must conclude that process III is not a major product-forming process in formaldehyde photolysis using the band of wavelengths in the range 3250–3700 Å. It is possible, of course, that the process III is important for photolysis within the longest wavelength bands of formaldehyde for which the absorption in the present experiments was almost negligible (3600–3700 Å). However, all of the results show that within the major absorption bands of formaldehyde vapor, primary process III is relatively unimportant at the usual pressures and temperatures employed.

The Flash Photolysis of CHDO Vapor. The Wavelength Dependence of the Ratio of Efficiencies of the Primary Processes $\phi_{I''}/\phi_{II''}$. The results of the photolysis of CHDO vapor in this study allow a completely independent estimation of the wavelength dependence of the relative efficiencies of the processes I and II in formaldehyde photolysis. In the photolysis of pure CHDO vapor the HD product can arise both from process I'' and process II'', while D_2 and H_2 are formed

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(20) If one considers process I and II to be competitive reactions of the excited formaldehyde molecule, then by the simple unimolecular reaction rate theory of E. M. Eyring, A. Kropf, A. L. Wahrhaftig, and H. Eyring, *J. Chem. Phys.*, **32**, 149 (1960), the ratio ϕ_I/ϕ_{II} is given approximately by

$$\phi_I/\phi_{II} \cong \frac{2\nu_I}{\nu_{II}}\left[\frac{1 - E_I/E}{1 - E_{II}/E}\right]^p$$

ν_I and ν_{II} are the frequencies for the asymmetric C–H stretching and the H–C–H bending modes, respectively, in the excited formaldehyde molecule; E_I and E_{II} are the activation energies for processes I and II, respectively; E is the total energy of the molecule; $p = N - (L/2) - 1$, where N is the total number of internal degrees of freedom and L is the number of internal rotational degrees of freedom ($p = 5$ here); since one expects the energy terms for both CH_2O and CD_2O to be near equal for a given λ, and since $\nu_I \cong \sqrt{2\nu_{I'}}$ and $\nu_{II} \cong \sqrt{2\nu_{II'}}$, then relation 17 follows.

(21) R. D. McQuigg, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1964.

(22) Critical frequencies can be estimated from the data of the $^1A_2$ state of CH_2O: $\nu_I \cong 2930$ cm^{-1} (estimated), $\nu_{II} \cong 1321$ cm^{-1} (D. A. Ramsay, "Determination of Organic Structure by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, Chapter 4); $E_I \cong 78$ kcal/mole (photodissociation limit data[4]); $E_{II} \cong 45$ kcal/mole (experimental E_a presumed to apply to the thermal reaction, $2CH_2O \rightarrow H_2 + CO + CH_2O$: C. J. M. Fletcher, *Proc. Roy. Soc.* (London), **A146**, 357 (1934)); $E = hc/\lambda$; $p = 5$.

only following process I″. In our experiments the interpretation of the data is somewhat complicated by the presence of up to 10% CH_2O in the CHDO sample. However, since D_2 could be formed only following process I″, the ratio of V_{D_2}/V_{HD} should reflect roughly the trend of ϕ_I/ϕ_{II} with wavelength variation. These ratios are shown in Table III. One can conclude that the process I becomes more important relative to II at the shorter wavelengths, the same trend observed for the CH_2O–CD_2O mixture photolysis. As in the previous case we can make further assumptions and estimate the average ratio of $\phi_{I''}/\phi_{II''}$ for the different filter systems used. Using relation 16 it is possible to calculate $(V_{HD})_I$ from the measured V_{D_2} and V_{H_2}.[23] Then $\phi_{I''}/\phi_{II''}$ can be calculated by relation 19.

$$\phi_{I''}/\phi_{II''} = \frac{(V_{HD})_I + 2V_{D_2}}{(V_{HD})_T - (V_{HD})_I} \tag{19}$$

The estimates of $\phi_{I''}/\phi_{II''}$ made in this fashion are summarized in Table III. Although we would consider these values to be somewhat less reliable than the corresponding estimates from the CH_2O–CD_2O data, it is seen that the identical trend of ϕ_I/ϕ_{II} with wavelength is present in both the CHDO and the CH_2O–CD_2O photolysis data. In fact, the values of the ratios derived from the two different aldehyde systems are in reasonable agreement for each filter system employed. The values of ϕ_I/ϕ_{II} and $\phi_{I''}/\phi_{II''}$ are respectively: filter 1, 0.74 and 0.60; filters 1 and 2, 0.44 and 0.51; filters 1, 2, and 3, 0.23 and 0.18; filters 1, 2, 3, and 4, 0.14 and 0.13. The basic assumptions which we have employed to calculate the ϕ_I/ϕ_{II} estimates, eq 16 and 17, are undoubtedly only approximations to the actual case, so it is gratifying to see the degree of agreement between the two sets of data. Although one must use caution in accepting the quantitative aspects of the data for ϕ_I/ϕ_{II} derived in this work, it appears to be well established that the ϕ_I/ϕ_{II} ratio extends from a value near zero at the longest wavelengths absorbed by formaldehyde (3550 Å) to a value over unity for the shortest wavelengths employed in this work (2800 Å).

Comparison of Present ϕ_I/ϕ_{II} Estimations with Those of Previous Workers. The present estimates of ϕ_I and ϕ_{II} and the observed increase in ϕ_I/ϕ_{II} with increase in the energy of the absorbed quantum are consistent with the very limited and qualitative results of Gorin[2] and Klein and Schoen.[3,4] Also the estimated ratio of $\phi_I/\phi_{II} = 1.0$ at 3130 Å is in good agreement with the estimate of $\phi_I/\phi_{II} = 1.1$ from the olefin-inhibited formaldehyde photolyses studied recently by DeGraff and Calvert.[6] However the trend of increasing importance of ϕ_{II} with the increasing energy of the absorbed quantum reported in their work is exactly opposite to that estimated here. It seems impossible to rationalize this difference between the two studies. One such attempt was made by assuming that the observed apparent increase in ϕ_I with increase in quantum energy estimated here could be the result of the increased importance of reaction 7. The fraction of the H atoms having energies in excess of the activation energy for this abstraction reaction would increase at the shorter absorbed wavelengths, and this would effectively enhance the calculated ϕ_I. The largest effect that one can expect from the occurrence of this mechanism is a doubling of the scrambled hydrogen from that expected if purely radical–radical reactions dominate as we have assumed. This is the case since the formyl radical product of a hot H-atom reaction in (7) would be essentially thermally equilibrated and would only undergo radical–radical reactions for these conditions. Thus if one assumes that reaction 7 is unimportant at 3340 Å but occurs with each hot atom formed at the shortest wavelengths used here (band 20 at 2800 Å), then we would estimate that the present data give $\phi_I/\phi_{II} = 0.33$ at 3340 and 2.5 at 2800 Å. The DeGraff and Calvert data suggest $\phi_I/\phi_{II} = 1.4$ at 3340 and 0.41 at 2800 Å (interpolated). Obviously the maximum effect that one can expect from the assumption of the hot atom mechanism does little to bring the two sets of data into accord. In any case there is good evidence that (7) must be unimportant in our experiments. If reaction 7 occurred the ratio (volume of hydrogen product formed in experiments using only filter 1):(the number of quanta of light absorbed in the given experiment) would be much greater than the similar ratio in experiments with filters 1, 2, 3, and 4 employed. The data of Table IV show that this is not the case. It is clear that the incorporation of (7) into our mechanism cannot help to rationalize differences between our results and those of DeGraff and Calvert. It seems likely to us that some error may exist in the DeGraff and Calvert estimations of ϕ_{II} at the wavelengths other than 3130 Å. It is possible that hydrogen formation from H-atom reactions was not completely suppressed in these experiments. A rather unambiguous test proved the complete suppression of such reactions in the 3130-Å experiments, but a similar test was not made in the experiments at the shorter wavelengths. Certainly a redetermination of ϕ_{II} should be made in the radical-inhibited photolyses of formaldehyde at the shorter wavelengths to check for this possible problem.

The HCO–H Bond Dissociation Energy. The present work shows clearly that scrambling of the hydrogen product of the CH_2O–CD_2O photolyses occurred even in experiments which utilized primarily the long wavelength bands of formaldehyde. In the runs with the filters 1–4, only light absorption by bands 1–6 of formaldehyde occurred significantly, and the major contribution to the decomposition was absorption due to bands 2–4; the relative absorbed intensities of these bands were: band 1, 5.5; band 2, 44.0; band 3, 22.3; band 4, 30.3; band 5, 5.0; band 6, 1.8. As shown previously in this work, this scrambling cannot be attributed to the initiation of free radical formation in this system through the excited molecule reactions with formaldehyde. Thus it is likely that the energy of many of the quanta absorbed in these experiments was sufficient to dissociate formaldehyde, since we estimate that 13% of the formaldehyde molecules which absorb light dissociate by I for these conditions. The contribution to the absorbed intensity from the shortest wavelength bands 5 and 6 is only 6.2% of the total energy absorbed, so dissociation must have been induced by

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[23] We have assumed that the sample is 90% CHDO and 10% CH_2O as suggested by mass spectrometric analysis and the deuterium–hydrogen imbalance in the products. Thus a correction is necessary to eliminate H_2 and HD formed following CH_2O photolysis by process I. This was estimated from the hydrogen excess ($V_{H_2} - V_{D_2}$), the estimated values of ϕ_I/ϕ_{II} for CH_2O using the appropriate filter, and relation 16.

light from at least one of the other longer wavelength bands, 4, 3, and 2. Since the quantum energy at band 4 (about 3385 Å) is 84.6 kcal/mole and the average vibrational energy of the formaldehyde molecule at 80° is 0.1 kcal/mole, the present data suggest $D_{\mathrm{HCO-H}} \leq$ 85 kcal/mole.[24]

Of course isotopic scrambling in the 3650-Å direct photolysis of CH_2O–CD_2O mixtures has been observed by Klein and Schoen[3,4] and Venugopalan and Kutschke.[7] This observation has been used to estimate $D_{\mathrm{HCO-H}} \leq 81.5$ kcal/mole. In view of the recent photoionization experiments of Murad and Inghram[11] which lead to $D_{\mathrm{HCO-H}} = 85.1 \pm 1.4$ kcal/mole and the recent kinetic data of Walsh and Benson[9] from which $D_{\mathrm{HCO-H}} = 87.0 \pm 1.0$ kcal/mole, it is necessary to establish the mechanism of hydrogen scrambling in CH_2O–CD_2O mixture photolyses at 3650 Å before accepting the result of $D_{\mathrm{HCO-H}} \leq 81.5$ kcal/mole. In particular the possible contribution of primary process III to the initiation of the scrambling reaction must be determined to establish the relevance of the 3650-Å "photodissocation" experiments to the determination of the $D_{\mathrm{HCO-H}}$ value. We are now studying this mechanism employing a microsecond flash system.

(24) If one assumes that there is a continuous variation of $\phi_{\mathrm{I}}/\phi_{\mathrm{II}}$ with wavelength as was done in deriving the estimates of Table V, then dissociation occurred also at bands 2 and 3 and $D_{\mathrm{HCO-H}} \leq 81$ kcal/mole. Since there is no experimental justification for this treatment the use of the $D_{\mathrm{HCO-H}} \leq 85$ kcal/mole is the only meaningful conclusion that one can form from these experiments.

Decay Kinetics of the Methyl Radical Produced by Ultraviolet Irradiation of Methanol–Water Matrices at 77°K

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Abstract: Methyl radicals have been produced in methanol–water matrices at 77°K by ultraviolet irradiation. The decay of the electron spin resonance spectra of this radical has been studied as a function of methanol concentration. It was found that the decay can best be explained by three parallel reactions, two of these reactions also being series reactions. Three rate constants are determined from this scheme: the methyl radical decay rate constant k_1 (0.8–2.48 × 10^{-3} $\sec^{-1}$) can represent either an abstraction reaction or a diffusion process, while k_2 (0.75–2.83 × 10^{-4} $\sec^{-1}$) and k_3 (1.7 × 10^{-7} $\sec^{-1}$) represent diffusion mechanisms from two different trapping sites T_2 and T_3.

In a previous investigation at the Ballistic Research Laboratories on the decay of $\cdot CH_3$ in ultraviolet-irradiated methanol-water matrices at 77°K, radical lifetimes were found to be a function of methanol concentrations. Since no satisfactory explanation was given for these effects, the present work was initiated to resolve this difficulty. Better results were achieved by using improved techniques, such as longer monitoring times for the $\cdot CH_3$ decays, use of an internal electron spin resonance standard, and a uniform method for irradiating the samples. In 1963 Sullivan and Koski[1] published a report that included the kinetics of the thermal decay of the methyl radical in pure methanol at 77°K. They concluded, as did most other investigators,[2-5] that the decay of $\cdot CH_3$ in 100% methanol and other matrices proceeded by a first-order mechanism.

In this report we will discuss the problem of whether the rate-determining mechanism in the decay of $\cdot CH_3$ in these matrices is primarily chemical or physical.

Experimental Section

Methanol-water samples of 100, 95, 80, 60, 50, 40, 30, and 10% methanol by volume were prepared from Matheson A.C.S. and distilled water. These solutions were used to fill 0.5-mm o.d. quartz sample tubes of 0.5-mm wall thickness. The samples were inserted into a quartz dewar filled with liquid nitrogen and irradiated with a General Electric B-H6 high-pressure mercury lamp using an elliptical reflector to concentrate the light uniformly on the sample (Figure 1). After the samples were irradiated for periods of from 0.75 to 3 hr, they were quickly transferred from the irradiation dewar to a sample dewar cooled to 77°K. The sample dewar was then placed in the X-band cavity of a Varian Associates V-4500 electron paramagnetic resonance spectrometer. In all these runs 100-kHz field modulation was used with a peak amplitude of 2 G. In some preliminary runs strong second-order satellites (lines produced by nuclear "spin flip" type transitions[6]) as well as power saturation of the $\cdot CH_3$ spectra occurred. Later runs were made at a reduced power level of approximately 8 to 12 db below the maximum microwave power of 50 mW (Figure 2), and all rate data were taken from these runs. A Bell Telephone Laboratories electron spin resonance reference standard[7] was used to monitor the stability of the instrument. This standard consisted of powdered phosphorus-doped silicon imbedded in a polyethylene sheet and contained 10^{14} spins. A single-line resonance was produced by the standard at a *g* value of 1.99875 ± 0.0001 with a line width of 1.8 G at 77°K.

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