

A Study of the Primary Processes in CH₂O and CD₂O Photolyses¹

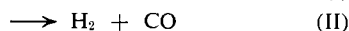
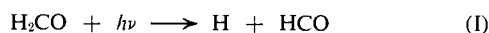
Benjamin A. DeGraff and Jack G. Calvert

Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210. Received November 25, 1966

Abstract: The primary processes occurring on photolysis of CH₂O and CD₂O have been delineated at 3340, 3130, 2654, and 2537 Å, through experiments with added olefin, neopentane, and biacetyl. The data provide estimates of primary quantum efficiencies of the processes: CH₂O + *hν* → H + HCO (I), and CH₂O + *hν* → H₂ + CO (II). Information is also obtained on the nature and the lifetimes of the excited states involved in these processes. The data show process I is favored at the longer wavelengths (3340 Å), while II dominates at the shorter wavelengths (2537 Å). Data from the photolyses of pure formaldehyde and its mixtures with propylene show values of Φ_{CO} - Φ_{H₂}, which are significantly greater than zero. The data are most consistent with the occurrence of a newly postulated reaction sequence (H + CH₂O → CH₃O; CH₃O + CH₂O → CH₃OH + HCO), which leads to methanol formation and a carbon monoxide excess. The additional possibility exists of a contribution to the carbon monoxide excess from a third primary process, CH₂O* + CH₂O → CH₂OH + HCO (III), particularly in photolyses at the very long wavelengths (3660 Å).

The structural simplicity of formaldehyde and the extensive knowledge of its spectroscopy give added interest to the study of the primary processes in formaldehyde photolysis. In this case it should be possible to describe the intimate details of the photochemistry which follow light absorption and precede photodecomposition. Considerable information has been reported on both the singlet-singlet (¹A₂ ← ¹A₁) and the singlet-triplet (³A₂ ← ¹A₁) transitions.²

The photochemistry of formaldehyde has been studied by numerous workers. Particular attention has been given to the secondary or thermal reactions of the hydrogen atom and formyl radical fragments formed in the photolysis.³ However, there is still no general agreement on the activation energies for the formyl radical decomposition and the hydrogen-atom abstraction reactions.⁴ The photolysis of formaldehyde has been interpreted in terms of two distinct primary photodissociative processes⁵



Attempts have been made to determine the relative importance of the two processes using both iodine inhibition⁶ and isotope exchange methods.^{3d} However, the two studies lead to opposite views as to the relative importance of I and II as a function of photon energy. The results of a more recent study using flash photolysis of CH₂O-CD₂O mixtures have been interpreted to show

(1) Presented in part at the Seventh Informal Conference on Photochemistry, Rensselaer Polytechnical Institute, Troy, N. Y., June 1966. Submitted by B. A. D. in partial fulfillment of the requirements for the Ph.D. degree in chemistry, The Ohio State University, Sept 1965. The authors acknowledge gratefully the support of this work through a research grant from the National Center for Air Pollution Control, U. S. Public Health Service, Bethesda, Md.

(2) (a) J. R. Henderson, *J. Chem. Phys.*, **44**, 3496 (1966); (b) W. T. Raynes, *ibid.*, **44**, 2755 (1966). For a review of the earlier work, see (c) D. A. Ramsay, "Determination of Organic Structure by Physical Methods," Vol. 2, Academic Press Inc., New York, N. Y., 1962, p 317; (d) S. F. Mason, *Quart. Rev.* (London), **15**, 191 (1961).

(3) (a) E. I. Akeroyd and R. G. W. Norrish, *J. Chem. Soc.*, 890 (1936); (b) J. G. Calvert and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 176 (1951); (c) F. H. Dorman and A. S. Buchanan, *Australian J. Chem.*, **9**, 41 (1950); (d) R. Klein and L. J. Schoen, *J. Chem. Phys.*, **24**, 1094 (1956).

(4) (a) J. G. Calvert, *J. Phys. Chem.*, **61**, 1206 (1957); (b) R. Klein and L. J. Schoen, *J. Chem. Phys.*, **29**, 953 (1958); (c) W. R. Brennen, I. D. Gay, G. P. Glass, and H. Niki, *ibid.*, **43**, 2569 (1965).

(5) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 371.

(6) E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

that process II is dominant at the lower photon energies.⁷ This is in contrast with the behavior observed for the C₂-C₄ aldehydes, RCHO, where the intramolecular formation of RH and CO is favored over the cleavage to form R and HCO at the higher energies of the absorbed quantum.⁸ However, the treatment of the H-D scrambling produced in the CH₂O-CD₂O mixture flash photolysis experiments, which were used to derive the wavelength dependence of φ_I and φ_{II}, is very complex and required that certain assumptions of questionable validity be made.

In this work we have studied the primary processes occurring on photolysis of formaldehyde at selected wavelengths within the first absorption band through experiments with added olefin, neopentane, and biacetyl. The data provide direct estimates of φ_{II} and also information on the nature and the lifetime of the excited states involved in the formaldehyde photolysis.

Experimental Section

Formaldehyde was prepared from polyoxymethylene according to the procedure of Spence and Wild.⁹ Formaldehyde-*d*₂ obtained in polymeric form from Merck Sharpe and Dohme, Ltd., with a stated purity of 99% deuterium. All hydrocarbon gases were Phillips research grade and were used without further purification. Biacetyl (Eastman White Label product) was outgassed, dried over calcium sulfate, and bulb-to-bulb distilled at reduced pressure with the middle third retained for use.

The apparatus consisted of a quartz photolysis cell mounted in an air thermostat with the usual associated glass pump, traps, and tubing. These were connected to a conventional high-vacuum system by bakable metal valves. Pressures were read with a triple-spoon gauge-manometer combination. All components which had direct contact with formaldehyde were heated to avoid polymerization. The thermostat was such that the average temperature of the cell remained constant to within ±0.2° of a desired temperature over the 3-5-hr photolysis period.

The light source was a Hanovia S-500 medium pressure arc. The various wavelength regions (3340, 3130, 2654, and 2537 Å) were isolated by chemical filters.¹⁰ The spectral distribution of the lines so isolated was checked using a Hilger medium quartz spectrograph and was in accord with the published information on the filters.¹⁰

The bulk of the analyses were performed on a modified Aerograph A-90-P2 gas chromatograph. The product gases were

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

(8) See ref 5, p 369.

(9) R. Spence and W. Wild, *J. Chem. Soc.*, 338 (1935).

(10) See ref 5, pp 729-733.

Table I. Data from the 3130-A Photolyses of Pure Formaldehyde and Its Mixtures with Propylene and Neopentane

Run no.	Temp, °C	—Pressure, mm—			I_a , quanta/cc sec $\times 10^{-11}$	Φ_{CO}	Φ_{H_2}
		CH ₂ O	C ₃ H ₆	C ₅ H ₁₂			
1	156.0	169	23.6	2.70	1.95
2	127.8	161	22.9	1.89	1.43
3	128.5	160.5	47.5	...	22.0	3.17	0.67
4	128.2	159	128.2	...	21.7	3.52	0.56
5	128.7	159	205.5	...	21.7	3.63	0.49
6	128.7	159	308.5	...	21.6	3.68	0.44
7	128.9	160	...	290	21.5	2.50	1.62
8	128.9	159.5	194	116	21.5	3.08	0.46
9	129.2	79	18.4	1.55	1.30
10	129.1	78	10.1	1.58	1.26
11	129.2	78	23.5	...	9.36	2.48	0.59
12	129.3	78	51	...	9.27	3.08	0.49
13	129.2	78	102	...	9.42	3.02	0.48
14	129.0	80.5	103.5	...	18.4	2.52	0.47
15	129.6	78	155.5	...	9.15	2.66	0.44
16	129.6	78	102	53	8.93	2.67	0.45
17	128.7	81	102.5	101	17.9	2.30	0.43
18	129.0	79.5	105	208	18.2	2.31	0.42
19	128.9	80.5	103.5	309	19.0	1.82	0.40
20	129.1	82.5	106	408	18.8	1.76	0.39
21	129.5	78.5	...	205	7.58	2.23	1.92
22	129.5	79	...	102.5	7.65	2.39	1.89
23	104.9	81	52.5	...	18.8	2.04	0.46
24	91.0	80	8.50	...	1.14
25	90.8	78	8.37	1.45	1.16
26	90.9	79	21.2	1.43	1.08
27	91.2	80	21.5	...	8.28	1.99	0.55
28	91.6	80.5	103	...	21.6	1.89	0.45
29	91.0	81.5	105	113.5	7.96	1.84	0.42
30	91.4	81.0	102	206	21.7	1.67	0.39

Table II. Data from the Photolyses of Pure Formaldehyde and Its Mixtures with Propylene at Several Wavelengths

Run no.	Wave-length, A	Temp, °C	Pressure, mm		I_a , quanta/cc sec $\times 10^{-11}$	Φ_{CO}	Φ_{H_2}
			CH ₂ O	C ₃ H ₆			
31	3340	109.1	201	...	4.31	1.67	0.82
32	3340	109.3	113.5	...	3.06	1.28	0.90
33	3340	109.3	63	...	1.56	1.55	1.44
34	3340	109.2	110	95	2.84	1.15	0.41
35	2654	109.1	103.5	...	5.00	1.72	1.37
36	2654	109.1	101	54	4.63	3.01	0.80
37	2654	109.1	119.5	67.5	6.59	3.57	0.82
38	2654	109.1	109	104.5	4.28	3.22	0.81
39	2654	108.7	108	154.5	5.79	3.44	0.81
40	2537	109.0	116	...	2.90	1.99	1.46
41	2537	109.0	110	...	3.87	2.00	1.36
42	2537	109.3	110.5	62	2.70	3.38	0.89
43	2537	109.0	111	87	2.94	3.00	0.81
44	2537	109.2	109	108.5 ^a	3.84	3.21	0.85
45	2537	109.0	105.5	112	2.95	3.37	0.90

^a Isobutene was used in place of propylene in this run.

separated using an 8-ft column of 5A molecular sieve (30–60 mesh) maintained at 105°. Argon was used as the carrier gas. The response of the instrument was calibrated using standard mixtures which closely approximated in both size and composition the samples of product gases.

Mass spectra were obtained using a Consolidated Electro-dynamics Corp. Model 21-620 mass spectrometer. Isotope ratios were determined with a similar mass spectrometer modified for that purpose. The infrared analyses were performed using a Perkin-Elmer Model 21, 40-m long-path spectrometer.

Actinometry was performed at frequent intervals. Acetone was used in experiments at 3130, 2654, and 2537 A with Φ_{CO} taken as

Table III. Data from the Photolyses of Pure CD₂O and Its Mixtures with Propylene

Run no.	Wave-length, A	Temp, °C	Pressure, mm		I_a , quanta/cc sec $\times 10^{-11}$	Φ_{CO}	Φ_{D_2}
			CD ₂ O	C ₃ H ₆			
46	3340	109.2	112	34	2.30	0.25	0.19
47	3130	129.1	87.5	...	30.3	0.83	0.97
48	3130	129.8	82.5	27	28.7	0.89	0.39
49	3130	129.6	84.5	62	28.9	0.86	0.36
50	3130	130.2	87.5	108	29.6	0.83	0.35
51	2654	109.3	107	...	4.53	1.10	1.17
52	2654	109.5	106	...	5.46	1.17	1.21
53	2654	109.2	110.5	65	5.44	1.41	0.70
54	2654	109.1	112	120	5.19	1.43	0.69
55	2654	109.2	104.5	170.5	4.31	1.33	0.70
56	2537	109.5	126	...	2.45	1.05	0.99
57	2537	109.1	104	53	2.33	1.52	0.87
58	2537	109.1	106	87	2.63	1.41	0.86
59	2537	109.1	104.5	89.5 ^a	2.81	1.62	0.88

^a Isobutene was used in place of propylene in this run.

unity for our conditions. At 3340-A azomethane was used with Φ_{N_2} assumed equal to unity. Extinction coefficients were measured at each wavelength and temperature using an RCA 935 phototube whose output was displayed on a strip chart recorder. The light intensity was also monitored continuously during each run using this device.

The experimental conditions and the quantum yields of carbon monoxide and hydrogen products are summarized for pure CH₂O and CH₂O-olefin and/or -neopentane mixtures at 3130 A in Table I; similar experiments for 3340, 2654, and 2537 A are listed in Table II. Data for CD₂O and CD₂O-olefin mixtures at all four wavelengths are given in Table III.

Discussion

The Primary Processes in Formaldehyde Photolysis.

The olefin inhibition studies herein reported allow a determination of ϕ_{II} values and a delineation of the wavelength dependence of the two primary photodissociative processes I and II in formaldehyde photolysis. Free-radical production of molecular hydrogen following I was suppressed in this work through the use of added olefin. The common radical "getters" used in thermal and photochemical studies, NO, O₂, and I₂, are rather unsatisfactory for photochemical applications since their interaction with electronically excited molecules is not well understood. There is evidence that each is capable of strongly perturbing the course of the photolysis.¹¹ Monoolefins are efficient hydrogen-atom scavengers at high pressures, but the possible perturbing influence of the olefin under these conditions should be examined in light of Cundall's work;¹² the possibility of triplet energy transfer to the olefin must be considered. Our experimental conditions were such that the mean time between collisions of an excited molecule and propylene was of the order of 10⁻⁸ sec. From the experiments with added biacetyl described below, we estimate that the longest lived excited state of formaldehyde formed at 3130 A, presumed to be the

(11) (a) C. Reed, *Quart. Rev.* (London), **12**, 205 (1958); (b) G. R. Martin and H. C. Sutton, *Trans. Faraday Soc.*, **48**, 812 (1952); (c) J. N. Pitts, Jr., and F. E. Blacet, *J. Am. Chem. Soc.*, **74**, 455 (1952); (d) G. R. McMillan and J. G. Calvert, "Oxidation and Combustion Reviews," Vol. 1, C. F. H. Tipper, Ed., Elsevier Publishing Co., Amsterdam, 1965, p 83.

(12) (a) R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964); (b) R. B. Cundall and A. S. Davies, *ibid.*, **62**, 2444, 2793 (1966); (c) R. B. Cundall and A. S. Davies, *Proc. Roy. Soc. (London)*, **A290**, 563 (1966).

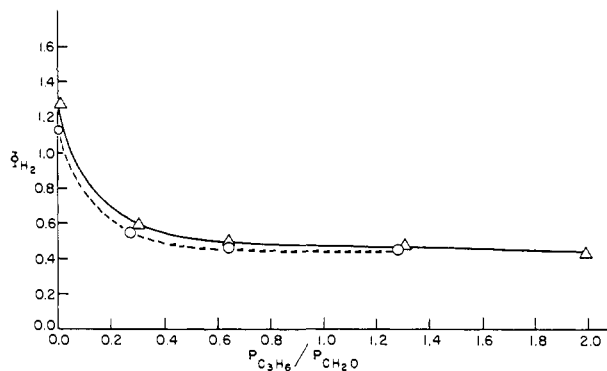


Figure 1. The quantum yield of hydrogen *vs.* the propylene to formaldehyde ratio for photolyses at 3130 Å and temperatures of 91°, O; and 129°, Δ.

triplet state, has a lifetime of about 10^{-8} – 10^{-9} sec. Thus the excited aldehyde will suffer relatively few collisions with propylene before dissociation. The work of Rebert and Ausloos¹³ has suggested that monoolefins are only a factor of about 10^{-5} times as efficient as conjugated olefins in quenching acetone's phosphorescence. Although the work of Cundall's group suggests a much higher efficiency of triplet acetone quenching as measured by isomerization of *cis*-ethylene-*d*₂ and *cis*-2-butene, it is difficult for us to exclude the effects of radical addition to the olefin in their experiments. Direct measurement of acetone phosphorescence as used by Rebert and Ausloos should be a more reliable measure of acetone triplet. If one accepts the results of Rebert and Ausloos and arbitrarily assigns unit energy-transfer probability to the conjugated olefins, a molecule such as propylene is expected to be a very poor triplet energy acceptor for formaldehyde and other similar molecules of very short triplet lifetime.

To test the effectiveness of propylene as a radical scavenger in the photolysis of formaldehyde, several series of experiments were performed. Figure 1 shows graphically the results of propylene inhibition on the quantum yield of hydrogen in experiments at 3130 Å and at two temperatures. The limiting quantum yield of hydrogen is the same within the experimental error for experiments at 91 and 129°. The rather small change in temperature is not expected to alter significantly the value of ϕ_{II} , but the result suggests that the efficient scavenging of radicals occurs for the high olefin pressures which give the limiting value of Φ_{H_2} . The initial pressure of formaldehyde and the incident intensity were both varied by a factor of 2 without changing the limiting value. Mass spectral (isotope ratio) analysis of the product deuterium from the photolysis of CD_2O – C_3H_6 mixtures showed that abstraction from propylene was unimportant under our conditions. Also mixtures of CH_2O , CD_2O , and C_3H_6 at the partial pressures which gave limiting hydrogen quantum yields were photolyzed. On the basis of the very small amounts of HD found for CH_2O and CD_2O photolyses, ϕ_{II} , estimated from limiting Φ_{H_2} data, may be in error due to incomplete scavenging by at most 3–5 and 5–8%, respectively.

(13) R. E. Rebert and P. Ausloos, *J. Am. Chem. Soc.*, **87**, 5569 (1965).

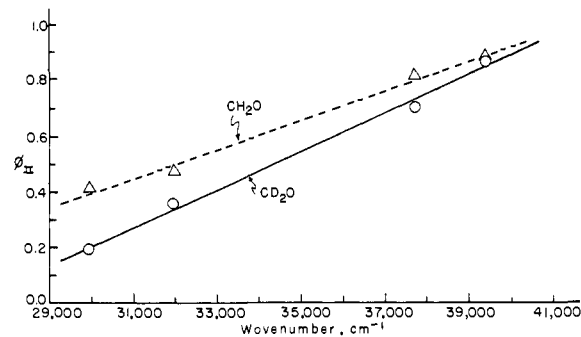


Figure 2. The quantum yields of primary process II, CH_2O (or CD_2O) + $h\nu \rightarrow CO + H_2$ (or D_2), as a function of wavenumber for photolyses of CH_2O and CD_2O in the vapor phase.

The estimates of the primary quantum yields for the molecular process II were obtained from the limiting Φ_{H_2} or Φ_{D_2} values at high olefin concentrations for both CH_2O and CD_2O at four wavelength regions, 3340, 3130, 2654, and 2537 Å. Figure 2 shows the resulting quantum yields as a function of wavenumber. Within the scatter of the data, the primary yield is a linear function of photon energy. The observed monotonic increase in the importance of the molecular mode of dissociation with energy is consistent with the trends found for the other simple aldehydes.¹⁴

McQuigg found that the volume of products from formaldehyde flash photolysis was proportional to the number of quanta absorbed by the formaldehyde, independent of the wavelength of the light absorbed from 2500 to 3300 Å.⁷ If $\phi_I + \phi_{II}$ equal unity at the shorter wavelengths, as seem very likely, then $\phi_I + \phi_{II}$ is near unity over this whole range of wavelengths. Thus a reasonable estimate of ϕ_I may be derived from the relation $\phi_I = 1 - \phi_{II}$. Following this procedure it can be estimated that ϕ_{II}/ϕ_I increases from ~ 0.7 at 3340 to 7.3 at 2537 Å for CH_2O . The question arises as to what factors determine the relative importance of each of these processes. Of course, the two processes may arise simply as competitive reactions which involve the same electronic state or states. Another possible answer to this question is that two different excited states are involved and that the competition between the two decomposition modes is determined by the rates of population of these states and their reactivities. The most obvious choice of states would be the 1A_2 and 3A_2 electronic states. If spin is conserved in processes I and II then triplet decomposition to molecular hydrogen and carbon monoxide is not possible at the photon energies used in this study, and only the free-radical process could originate from the triplet species.

To evaluate the possible role of the triplet formaldehyde in the photolysis of formaldehyde several experiments were performed.

Few aldehydes and ketones show measurable phosphorescence. Formaldehyde phosphorescence has never been reported although it has been searched for in many laboratories. The participation of a triplet state in the photodecomposition of the aldehydes and ketones has been inferred largely from indirect evidence, but this evidence has been rather convincing. Spe-

(14) (a) F. E. Blacet and J. N. Pitts, Jr., *ibid.*, **74**, 3382 (1952); (b) C. S. Parmenter and W. A. Noyes, Jr., *ibid.*, **85**, 416 (1963).

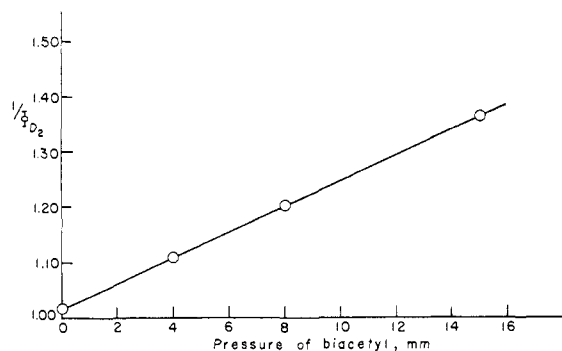
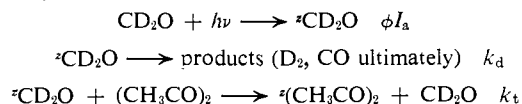


Figure 3. Plot for the biacetyl quenching of the quantum yield of deuterium in the photolysis of CD₂O-biacetyl mixtures at 109° and about 75 mm pressure of CD₂O.

cifically, photosensitized emission from biacetyl and the decomposition of biacetyl have been used as triplet diagnostic tests in the gas phase.¹⁵ The strong emission and low energy (about 2.5 eV) of its first excited triplet state make biacetyl particularly attractive.

In conjunction with a study of the formaldehyde-sensitized emission of biacetyl, to be reported in a subsequent paper, we also studied the effect of biacetyl on the photodecomposition of formaldehyde-*d*₂. The deuterio isomer was used in this study with a knowledge of the longer excited lifetime for the deuterio compound and with the hope of reducing troublesome abstraction reactions. The data summarized in Figure 3 show that the diketone is effective in deactivating some state of the excited aldehyde formed at 3130 Å; Φ_{D₂} decreases with increasing biacetyl pressure. At this wavelength biacetyl is almost transparent. However, experiments with biacetyl alone were performed as an added check, and negligible product formation occurred under these conditions. That energy was being transferred from formaldehyde to the biacetyl in the CD₂O-(CH₃CO)₂ mixture photolyses was shown by the presence of C₂H₆, CH₃D, and excess CO in the products. HD was not found and thus a D-atom sensitized decomposition is unlikely. However the presence of a small quantity of CH₃D indicates that the methyl-sensitized decomposition of formaldehyde may be occurring.

If we write a general mechanism for energy transfer to biacetyl as



one can show that $1/\Phi_{D_2} = k_t[(\text{CH}_3\text{CO})_2]/k_d\phi + \text{constant}$. Here z represents the excited state multiplicity. It is assumed that biacetyl does not interfere with the formation of products by the usual paths which are operative in its absence. With this choice of mechanism, coupled with an assumed energy-transfer rate constant of 10^{14} cc/mole sec, and $\phi = 1$, the data of Figure 3 lead to an estimate of the lifetime of the excited state of about 5×10^{-9} sec. If one assumes that processes I and II originate exclusively from the triplet and singlet excited states, respectively, and that the biacetyl addition does not alter significantly the mechanism of hydrogen formation from the free-radical

(15) (a) H. Okabe and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **79**, 801 (1957); (b) J. Hecklen and W. A. Noyes, Jr., *ibid.*, **81**, 3858 (1959); (c) R. P. Borkowski and P. Ausloos, *ibid.*, **84**, 4044 (1962).

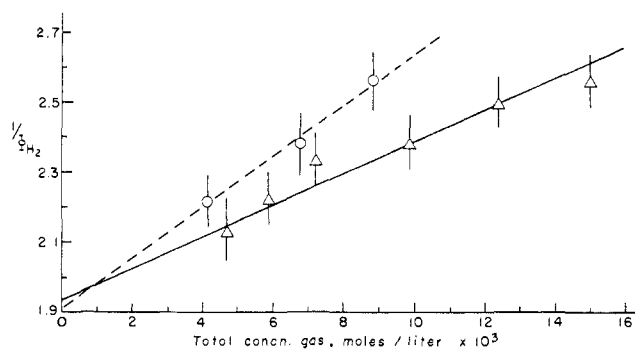


Figure 4. Plots for the quenching of the primary process II in formaldehyde photolysis at 3130 Å for experiments at 91°, O; and 129°, Δ; in each experiment approximately 100 mm of propylene and 80 mm of formaldehyde were present, and varied amounts of neopentane were added to obtain the gas concentration changes.

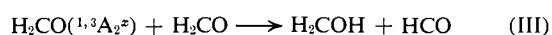
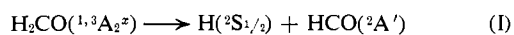
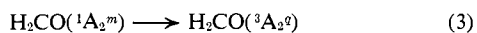
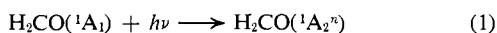
mechanism, then a plot of the function $(1 - \phi_{II})/(\Phi_{D_2} - \phi_I)$ vs. $[(\text{CH}_3\text{CO})_2]$ yields an estimate of $k_t/k_d(\text{triplet})$ from its slope. Assuming $k_t = 10^{14}$ cc/mole sec, then $k_d(\text{triplet}) \cong 1 \times 10^8 \text{ sec}^{-1}$ and $\tau(\text{triplet}) \cong 10^{-8}$ sec. Computations based on the sensitized emission studies yield a similar value.¹⁶ The quenching efficiency is greater than can be accounted for through collisional deactivation (see the results of added neopentane described below), and it is most likely a result of electronic energy transfer. Some care must be used in assigning the donor state since both singlet and triplet energy transfer are possible and would lead to an apparent decrease in the decomposition quantum yield of the donor. However, the companion study of the formaldehyde-sensitized emission of biacetyl conducted under the same experimental conditions as the study reported here shows that formaldehyde preferentially excites biacetyl phosphorescence.¹⁶ This is rather compelling evidence that triplet energy transfer is occurring. Thus it appears probable that triplet formaldehyde is produced and decomposition does originate from this state. As stated previously, spin conservation suggests that this decomposition reaction is the free-radical split (process I); obviously this cannot be tested unambiguously from the data at hand.

Further experiments were designed to elucidate the nature of the state leading to process II, molecular hydrogen formation. The pressure dependence of the quantum yield of hydrogen was studied at 3130 Å and at temperatures of 91 and 129° to evaluate the efficiency of collisional deactivation of this excited state. Hydrogen formation from the free-radical process I was suppressed in all of these runs through the addition of approximately 100 mm of propylene. Neopentane was used as an "inert" gas since it has many degrees of freedom, and under our conditions abstraction reactions involving its primary hydrogens would be unimportant. These results are summarized in Figure 4. It is apparent that some deactivation occurs at each temperature, although rather inefficiently. Of course, partial vibrational relaxation of excited formaldehyde would not eliminate process II completely, but only lower its efficiency. The ϕ_{II} data for 2537 and 3340 Å suggest that relaxation of vibrational energy by 27 kcal/mole lowers ϕ_{II} by 50%. If one assumes that the

(16) From a study which is to be published by A. Zahra of these laboratories.

collision cross section for the deactivation process is $3.6 \times 10^{-15} \text{ cm}^2$, and that each collision is effective in deactivating completely the excited molecule, then the data of Figure 4 lead to an excited state lifetime of about $2 \times 10^{-11} \text{ sec}$. This must represent a minimum lifetime in view of the nature of the assumptions made. However, it seems clear that the lifetime of the excited state responsible for the concerted process II is very short at 3130 Å, and it is probably near 10^{-10} sec .

The present data and the other information on formaldehyde photolysis may be considered in terms of the following general mechanism for the primary processes.



In the mechanism shown, the right-hand superscript denotes the degree of vibrational excitation above the lowest level of that state where $q > p > \dots n > m > \dots$. The observed wavelength dependence of ϕ_{II} (Figure 2) proves that vibrational relaxation of the excited formaldehyde is incomplete before reaction for the conditions employed here. Regardless of the multiplicity of the state or states involved in primary processes I and II, it is evident that the higher the degree of vibrational excitation, the higher is the efficiency of the process II. Of course we expect the rate constant for both processes I and II to be a function of the vibrational level and multiplicity of the particular state involved. Although it is probably an oversimplification, it seems attractive to the authors to suggest that process II originates largely from the excited singlet state, and that I and III are derived largely from the triplet. With this assumption one may rationalize the increase in the extent of II at the shorter wavelengths in terms of the shortened lifetime of the singlet and the increased magnitude of k_{II} compared to k_3 . The primary quantum efficiencies of processes I and II are about equal at 3130 Å. If they originate largely from the different states as suggested, then the rate of intersystem crossing must be about the same as the rate of process II; that is, $k_3 \cong 10^{10} \text{ sec}^{-1}$ a surprisingly high value. In any case the evidence presented here for the short-lived excited states implies that the rate of intersystem crossing of formaldehyde is very fast. For the formaldehyde molecule the similarity in the geometry of the singlet and triplet excited states must favor large Franck-Condon overlap factors.

The molecular orbital picture of the states to which the initially excited n, π^* carbonyl states pass enroute to photodissociation by processes I and II was first put forward by Peters¹⁷ and later expanded by Abrahamson, Littler, and Vo.¹⁸ It depicts the state giving rise to the concerted process as one in which considerable H-H bonding exists, *i.e.*, an $n, \sigma^*_{\text{CH}_2}$ state.¹⁸ The free-radical process may arise from a state in which H-H

antibonding is dominant such as an $n, \sigma^*_{\text{CH}_2}$ state. Unfortunately, the relative energies of these states are not known even approximately, and their energies relative to the n, π^* carbonyl states also are a matter of speculation. Abrahamson has pointed out that, due to the nonplanarity of the excited state, some overlap occurs between the $\sigma^*_{\text{CH}_2}$ orbital and the $2p_y$ orbital of oxygen. This effect may lower the energy of the $\sigma^*_{\text{CH}_2}$ state sufficiently so that the energy necessary for the free-radical process is equal to or less than that required for the molecular decomposition. A quantitative interpretation of the primary processes in terms of the transfer of excitation from the excited carbonyl $^1(n, \pi^*)$ or $^3(n, \pi^*)$ states to intermediate states will certainly add greatly to our understanding of the internal energy-transfer processes involved in molecular photochemistry. However, the meaningful interpretation of these details must await the more accurate determination of the appropriate molecular orbital energies.

Primary process III is included to account for the apparent presence of H atoms in the photolysis of formaldehyde at the long wavelengths.^{3d} At 3600 Å absorption is in the well-known α band which originates from the ground state with 1 quantum of ν_4 excitation. Hence a molecule absorbing in this band is about 81.6 kcal/mole above the ground state. It now appears likely that $87 \pm 1 \text{ kcal/mole}$ is necessary to dissociate formaldehyde,¹⁹ and a process such as III seems necessary to explain the photochemistry of formaldehyde at 3660 Å.^{19,20} In view of the low activation energy associated with H-atom abstraction from formaldehyde, it is quite possible that triplet formaldehyde may abstract an H atom from formaldehyde analogous to the triplet state reactions of carbonyl compounds in liquid systems.²¹ Primary process III is also in accord with the mechanism proposed by Kistiakowsky and co-workers for the high-temperature pyrolysis of formaldehyde.²²

Formaldehyde Photolysis Mechanism and the Excess of Carbon Monoxide over Hydrogen in the Products.

During the course of this study, sufficient data accumulated to allow some interesting and new observations on the mechanism of the secondary reactions in the photolysis of formaldehyde. For the usual conditions employed in this study, notably high formaldehyde pressures and low light intensities, the quantum yield of carbon monoxide exceeded that of hydrogen by an amount far outside the experimental error (see the data of Tables I and II). The product imbalance was much smaller for the CD_2O data (see Table III). Kutschke and Venugopalan also found a carbon monoxide excess at 3130 Å for both CH_2O and CD_2O photolysis at high temperatures which was inversely dependent on the absorbed light intensity.²³ However, McQuigg found the ratio of products $\text{H}_2/\text{CO} \cong 1.0$ for CD_2O and CH_2O photolyses at the high intensities of flash photolysis.⁷ In view of these apparently conflicting results, we

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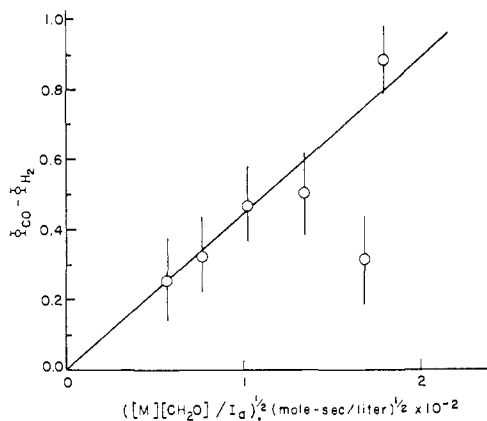
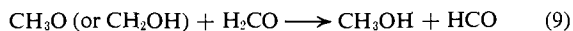
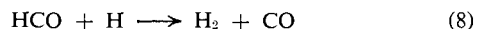
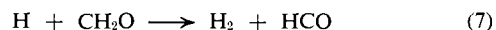
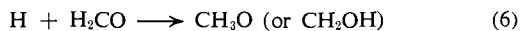
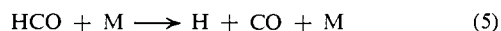


Figure 5. A plot of the carbon monoxide excess function, $\Phi_{CO} - \Phi_{H_2}$, vs. the variables of function 13 of the text; data are from 3130-A photolysis of formaldehyde and formaldehyde-neopentane mixtures at 129°.

examined the photolysis of formaldehyde using the full arc in one series of runs. The incident intensity was approximately 10^4 times greater than that used for the routine experimental work. Formaldehyde pressures were varied over the range 24–120 mm, with up to 266 mm of added neopentane; the ratio of H_2 to CO was 1.03 ± 0.03 for all runs, confirming McQuigg's observations from the photolyses at the very high intensities. Thus it appears that the mechanism which leads to carbon monoxide and hydrogen changes as a function of the light intensity.

The carbon monoxide excess is not the result of direct mechanical loss of hydrogen, nor is it formed in these experiments from a dark reaction such as has been observed previously for other conditions.^{3d,24} Some process which produces carbon monoxide and not hydrogen or that consumes H_2 or H atoms must be involved. An H-atom addition to the formaldehyde molecule with the ultimate formation of methanol seems an attractive possibility.²⁵ Consider the following simplified mechanism to occur following primary process I.²⁶



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(25) An extensive effort was made to detect unambiguously the photochemical generation of methanol in the products. Methanol is present after a condensation and work-up of the products for analysis, but it is difficult to evaluate the extent to which it is formed in the photochemical runs. This results from the fact that polymerization of pure formaldehyde induces the thermal formation of small amounts of methanol as identified by infrared and mass spectrometric analyses. Thus the prior removal of formaldehyde to facilitate identification of methanol in the photochemical products is impossible. Furthermore, when small amounts of methanol are added to pure formaldehyde and a polymerization is effected, both formaldehyde and much of the methanol are removed. No quantitative method could be found to determine the methanol unambiguously, but its presence seems highly probable from the qualitative results which were obtained.

(26) At the lowest intensities employed in this work, a first-order chain termination step should be included in the mechanism, since Φ_{H_2} is nearly independent of I_a for these conditions. However, the accuracy of the $\Phi_{CO} - \Phi_{H_2}$ data does not warrant the sophistication and complication of this added reaction.

One can show from the assumption of this mechanism that relation 10 will define the carbon monoxide excess

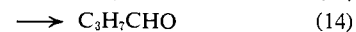
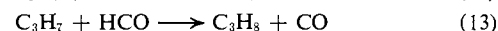
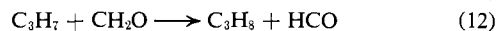
$$\Phi_{CO} - \Phi_{H_2} = \left[\frac{[CH_2O][M]\phi_1 k_5}{I_a(k_6 + k_7)k_8} \right]^{1/2} k_6 \quad (10)$$

The data from the 3130-A experiments are in accord with this mechanism and relation 10 as seen in Figure 5. From a thermochemical standpoint, reaction 6 is favored over 7 since the heats of reaction are -25 and -16 kcal/mole, respectively. Radical addition to the carbonyl bond in acetone has not been observed in acetone photolysis, but in this case the addition of the methyl radical would occur with the liberation of only 5 kcal/mole. Radical attack on the carbonyl bond has been observed previously for hexafluoroacetone.²⁷

A number of experimental observations are explicable on the basis of the above mechanism. At lower temperatures, reaction 5 will be slow, and chains, if any, will be quite short. Thus $\Phi_{CO} - \Phi_{H_2}$ will be small. However, at higher temperatures and pressures, the chain sequence 5, 6, 9, 5, . . . , may repeat many cycles before chain termination occurs. As the data of Kutschke and Venugopalan show, $\Phi_{CO} - \Phi_{H_2}$ may become quite large. However, the thermal stability of CH_3O (or CH_2OH) and the effect of the higher temperatures on the ratio k_6/k_7 may tend to lessen the importance of the aldehyde reduction relative to chain decomposition. At high intensities and lower temperatures, such as used by McQuigg, and in the high-intensity experiments used in the one phase of this work, radical-radical reactions should predominate. Thus reaction 8 is favored as the usual fate of H and HCO radicals, and a hydrogen-carbon monoxide balance is observed at high intensities.

A possible alternative in the mechanism given is the inclusion of the primary process III as a contributor to the carbon monoxide excess observed. Such a primary process alone cannot lead to $\Phi_{CO} - \Phi_{H_2}$ values greater than unity. Since the data of Kutschke and Venugopalan show that this difference can be greater than unity, this reaction cannot account for all of the effect, but its possible small contribution cannot be excluded from the facts at hand. Indeed, in view of the evidence for energy limitations on process I at 3660 Å, postulation of its occurrence at 3660 Å is attractive.

The quantitative mechanistic treatment of the carbon monoxide over hydrogen excess data for the propylene inhibition studies is impossible with the limited data at hand. However, some interesting observations can be made. In addition to the reaction sequence I, II, 5–9, reactions 11–14 are probably important. The



addition of the propyl radical to propylene, and subsequent addition steps, may also occur, and these would be followed by H-abstraction or chain-termination reactions analogous to eq 12 and 13–14, respectively.

It can be seen from the data of Tables I–III that propylene addition increases the quantum yield of carbon monoxide, although that for hydrogen is

(27) A. S. Gordon, *J. Chem. Phys.*, **36**, 1330 (1962).

suppressed to a limiting value. This probably results in part from the increased rate of reaction 5 with increasing gas concentration, but in addition the rate constant ratio $k_{12}/(k_{13} + k_{14})$ may be greater than $(k_6 + k_7)/k_8$; that is, the propyl radical may be more effective in propagating the chain decomposition of formaldehyde than is the hydrogen atom.

It is evident from the results described here that the photolysis of formaldehyde is a much more complex system than has been expected previously. Some of the details are clear from this work, but obviously further definitive experiments will be necessary to determine the extent of the process III in the creation of the carbon monoxide excess in the products.

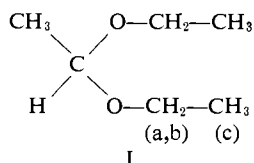
The ^{13}C -H Satellite Nuclear Magnetic Resonance Spectrum of Nonequivalent Protons in Acetal

Lana S. Rattet, L. Mandell, and J. H. Goldstein

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322. Received December 22, 1966

Abstract: The nuclear magnetic resonance spectrum of the ethoxy protons in acetaldehyde diethyl acetal (acetal) has been investigated. By using, in addition to the normal proton spectrum, the data provided by the ^{13}C -H satellite spectrum, a unique set of spectral parameters has been obtained, eliminating the previously reported ambiguity in the solution of this problem. The ^{13}C -H coupling parameters of the two methylene protons are different, providing a new criterion of nonequivalence in structures of low symmetry.

The proton magnetic resonance spectrum of acetaldehyde diethyl acetal, or simply acetal (I), exhibits a much more complex structure in the methylene region



than is to be expected from a simple A_2B_3 spin system. Since there is no evidence of coupling through the oxygen atom, this complexity has been attributed to magnetic nonequivalence of the methylene protons.¹⁻³ Three analyses of the spectrum of acetal have been described, all of which treat the ethoxy group as an ABC_3 system, but leading to two markedly different sets of values of the proton-proton couplings. In the first approach Shafer, *et al.*,¹ and Waugh and Cotton² assumed J_{gem} to be of the same sign as the vicinal couplings (taken to be positive). Two different values of the vicinal couplings were then required to match the observed spectrum. The coupling values reported in these studies were: $J_{gem} = 9.4$ cps, $J_{vic} = 7.35, 6.68$ cps;¹ and $J_{gem} = 9.2$ cps, $J_{vic} = 7.2, 6.7$ cps.² Subsequently, however, Kaplan and Roberts reexamined the problem and reported an acceptable fit using $J_{gem} = -9.30$ cps, in which case the vicinal couplings are identical, $J_{ac} = J_{bc} = +7.03$ cps.³ Since both sets of values led to acceptable agreement with experiment, the outcome was described as indecisive, following the pattern of some other reported nonunique iterative analyses.⁴

In similar situations we have previously demonstrated that the requirement of simultaneously matching ^{13}C -H satellite patterns and normal proton spectra can yield unique sets of parameters.⁵ Several factors suggested the desirability of attempting to resolve the existing ambiguous situation in the case of acetal. Obviously, the occurrence of multiple solutions of the spectroscopic problem is, in general, a deterrent to efforts directed toward the interpretation of nmr parameters. There is, in addition, considerable intrinsic importance and interest in the origin and magnitude of the effects produced by nonequivalent environments such as those existing in acetal. Finally, successful analysis of the satellite patterns would provide still another and different kind of criterion of nonequivalence.

This communication describes the results obtained from such a simultaneous study of the proton and ^{13}C -H satellite spectra of the ethoxy region of acetal. The proton-proton couplings so obtained are in close agreement with the results of the last analysis cited above (J_{gem} and J_{vic} of opposite sign), and the alternative solution was found to be unacceptable. A small (~ 1.4 cps) but real difference in the ^{13}C -H couplings was observed for the two geminal protons. These results are discussed in relation to the other relevant nmr data and to the structural situation in acetal.

Experimental Section

The acetal used was the commercially available material, purified by fractional distillation over a range of $\sim 0.5^\circ$. All spectra were observed with a Varian Associates A-60-A spectrometer operating at 60 Mc/sec. Calibrations were performed by the side-band technique using a Hewlett-Packard Model 200J oscillator monitored with a Hewlett-Packard Model 5512A counter. All reported frequencies represent the average of at least four forward and four reverse sweeps. The neat liquid acetal was used throughout with

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