

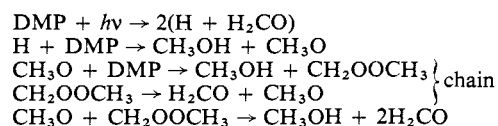
The Photolysis of Dimethyl Peroxide

L. M. Toth and H. S. Johnston

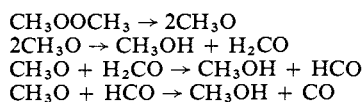
Contribution from the Department of Chemistry, University of California, Berkeley, California. Received October 17, 1968

Abstract: The gas-phase photolysis of dimethyl peroxide (DMP) has been studied with ultraviolet radiation in the range 2400–3400 Å. Quantum yields establish the presence of a chain reaction for the initial process, presumably by way of $\text{CH}_3\text{O} + \text{CH}_3\text{OOCH}_3 \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{OOCH}_3$ (e) and $\text{CH}_2\text{OOCH}_3 \rightarrow \text{H}_2\text{CO} + \text{CH}_3\text{O}$ (f). As formaldehyde builds up or if it is added initially, the chain reaction is suppressed by competition from $\text{CH}_3\text{O} + \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH} + \text{HCO}$ (g). The ratio, g/e , was found to be 151 at 25°. Formaldehyde also undergoes a sensitized decomposition upon collision with photoexcited DMP: $\text{DMP}^* \rightarrow 2\text{CH}_3\text{O}$ (b) and $\text{DMP}^* + \text{H}_2\text{CO} \rightarrow \text{DMP} + \text{H} + \text{HCO}$. The rate constant b was found to be about 10^8 sec^{-1} for DMP excited by 2537-Å radiation. A third effect of added formaldehyde is that it undergoes a chain polymerization as a troublesome, minor side reaction.

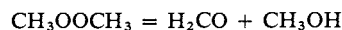
The photolysis of dimethyl peroxide (DMP) was studied by Takezaki, *et al.*,¹ who proposed an initial split to give hydrogen atoms and a chain reaction carried by the methoxyl radical.



The thermal decomposition of DMP was studied by Hanst and Calvert,² who found a 3:1 ratio between the products CH_3OH and CO and no formaldehyde. They proposed the decomposition of DMP to methoxyl radicals, which then disproportionate and consume any formaldehyde temporarily formed.



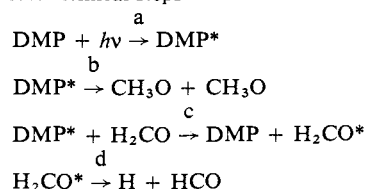
These authors did not accept a chain mechanism. However, Takezaki's chain reaction and the disproportionation reaction have the same over-all stoichiometry between reactant and products.



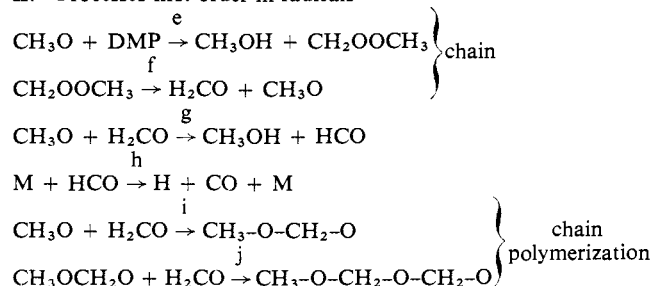
Product analysis alone is incapable of deciding between these two mechanisms, but quantum yield measurements in the case of the photodecomposition could identify the presence of a chain reaction.

This study was designed to give quantum yields for the products CH_3OH , H_2CO , CO , and H_2 at very early stages of the reaction, 0.02–4%. The primary purpose was to make an unambiguous finding as to whether there was a chain reaction in the system, and the general purpose was to identify the elementary chemical reactions occurring in the process. For the sake of future discussion we summarize here all elementary reactions that will be referred to later.

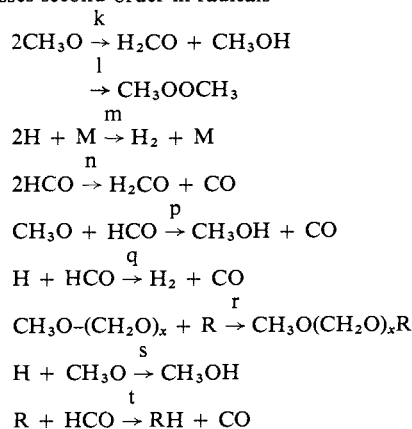
I. Primary photochemical steps



II. Processes first order in radicals



III. Processes second order in radicals



Experimental Section

The DMP was prepared in a manner similar to the one described by Hanst and Calvert.² Only the deviations from this procedure are reported here. DMP was regarded as a highly explosive material.^{3,4} The reaction vessels and traps were assembled prior to the reaction, and the peroxide was prepared while the apparatus was

(1) Y. Takezaki, T. Miyazaki, and N. Nakahara, *J. Chem. Phys.*, **25**, 536 (1956); Y. Takezaki and C. Takeuchi, *ibid.*, **22**, 1527 (1954).
(2) P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, **63**, 104 (1959).

(3) (a) A. Rieche, *Ber.*, **61**, 951 (1928); (b) *ibid.*, **62**, 218 (1929).
(4) G. Baker, R. Pape, and R. Shaw, *Chem. Ind. (London)*, **48**, 1988 (1964).

Table I. Quantum Yields for Various Times of Photolysis at Approximately Equal DMP Pressure

<i>t</i> , min	DMP, torr	Photons absorbed, 10 ⁻¹⁶ cc ⁻¹	Quantum yield (0 to <i>t</i>)			
			H ₂	CO	CH ₃ OH	H ₂ CO
A. 25°, 2537-Å Radiation						
3.0	26.1	0.036	0.00	0.50	6.6	...
7.5	29.2	0.092	0.07	0.67	4.9	...
15.0	28.9	0.194	0.05	0.78	3.6	2.50
30	27.2	0.395	0.07	0.84	3.2	1.05
120	30.2	1.46	0.06	0.93	2.9	0.50
182	30.5	2.48	0.07	0.99	2.7	0.23
38	35.8	1.11	2.9	0.88
60	25.0	0.84	...	0.80	2.8	0.52
540	36.8	19.5	0.06	0.99	3.0	0.04
B. 60°, 2537-Å Radiation						
2.5	29.3	0.032		0.56	10.0	...
5.0	30.0	0.064	0.05	0.57	4.9	...
10.0	30.6	0.132	0.06	0.82	4.2	...
20.0	30.1	0.28	0.08	0.78	4.0	1.2
40.0	28.5	0.55	0.14	1.00	3.9	1.0
80.0	29.4	1.00	0.13	1.00	3.8	0.58
120.0	28.2	2.40	0.10	0.97	3.3	0.38

thoroughly shielded. A CaCl₂ drying tube between the generator and the trap was used for removing most of the water carried over in the distilling DMP, and purification of the peroxide was carried out by gas chromatography. A 20 ft × 3/8 in. Pyrex column of 20% Carbowax 400 on Chromosorb W was used at room temperature. By merely changing the dewar on the collection trap (mentioned in the preparation²) from liquid nitrogen to ice water, the trap served as the supply for the gas chromatograph. The DMP peak, which eluted from the preparative chromatograph, was caught in a similar trap which in turn served as the supply during the photolysis experiments. These two traps containing liquid DMP were shielded by open-ended steel sleeves and, as a matter of strict practice, never handled.

Formaldehyde was prepared according to the method of Spence and Wild.⁵ The monomer was stored in an evacuated glass trap attached to the vacuum system and maintained in liquid nitrogen. Under these conditions, it was possible to maintain the monomer for up to a month with little sign of polymerization.

The DMP was photolyzed in a 125-cc, 10-cm path-length quartz cylinder. The ultraviolet radiation from a Hanovia 1000-W Hg-Xe dc arc was passed through a Bausch and Lomb 33-86-25 monochromator using either a 1200- or a 2700-line/mm grating. The radiation issuing from the monochromator was collimated through the ends of the cylindrical cell and fell on a RCA 935 phototube which had been calibrated with potassium ferrioxalate actinometry.⁶ Corrections for losses at all surfaces were made. With this system, it was found that the light intensity in the cell was of the order of 1.6 × 10¹⁵ photons cm⁻² sec⁻¹.

The quartz cell was fitted with two tubes, one for filling with DMP vapor and the other for extracting a sample by gas expansion into the analysis system. Also connected in parallel to the latter tube was the gas manifold, which was used to handle the gas chromatograph calibration gases. The system was constructed of continuous glass tubing and fitted with "Westeff" high-vacuum greaseless stopcocks (West Glass Corp., S. El Monte, Calif.). Gas pressures were measured with a "Kel-F" oil monometer of 1.98 density (supplied by Minnesota Mining and Manufacture Co.). Although the vapor pressure of this oil was low (1 μ), this portion of the system was always closed off from the rest of the system to prevent any contamination. Gases exposed to the oil were pumped away so that there was little chance of back diffusion into the very clean regions of the vacuum system.

All analyses were made with gas chromatography. A Varian "Hy-Fi" Aerograph Model A-600 B flame ionization detector was used to measure DMP and MeOH. With the addition of a 5-in. nickel reducer column following in series behind the separation

column (described by Porter and Volman⁷), it was possible to measure CO and H₂CO quantitatively by converting them to CH₄ and MeOH, respectively. A 10 ft × 1/8 in. column of Ethofat 60/25 on Columapak T, 40-60 mesh having a 760 theoretical plate number was used at room temperature to separate CO, DMP, and MeOH. Then the column was heated to 140° and the H₂CO eluted.

The hydrogen analysis was accomplished by means of the thermoconductivity detector in an "Autoprep" Aerograph by Varian, a 4 ft × 0.25 in. stainless steel column packed with 10% Carbowax 400 on Chromosorb P, HMDS 60-80 mesh. Nitrogen was used as the carrier gas to provide the necessary contrast in thermoconductivity for measuring trace amounts of hydrogen. By changing to a helium carrier gas, CO could be measured and the results compared with those of the flame ionization detector. The difference in these two measurements was always found to be less than 5%.

The chromatographs were calibrated by injecting measured pressures of the gases in question through the sampling valves. Hence a direct relation between area (and/or peak height) and pressure of the gas was obtained.

The absorption spectrum of DMP was taken on a Cary Model 14 recording spectrometer and is shown in Figure 1. It was found to agree with the previously reported spectrum of Takezaki, *et al.*,¹ from the visible to 2150 Å. However, below 2150 Å, it was found that the spectrum continues to increase whereas the previously reported one shows a peak and then a sharp decrease. It is suspected that the spectrum of Takezaki, *et al.*, was extended beyond the reliable range of their spectrometer.

The H₂CO spectrum was also taken and found to agree with previously reported spectra.^{8,9}

Results

A series of runs was made at approximately constant DMP (26-36 torr), at approximately constant radiation (2537 Å) intensity, and for various times of photolysis. By means of chemical actinometry, the radiation intensity was periodically monitored, and its relative value was continuously followed by a phototube during the period of photolysis. At the end of the exposure time, the contents of the reaction cell were consumed in the analysis of products. The ratio of number of molecules formed to number of photons absorbed by DMP gives the quantum yield from zero time to the time of photolysis. Such data

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

(6) (a) C. A. Parker, *Proc. Roy. Soc. (London)*, **A220**, 104 (1953); (b) C. G. Hatchard and C. A. Parker, *ibid.*, **A235**, 518 (1956); (c) J. Lee and H. H. Seliger, *J. Chem. Phys.*, **40**, 519 (1964).

(7) K. Porter and D. H. Volman, *Anal. Chem.*, **34**, 748 (1962).

(8) G. Herzberg, *Trans. Faraday Soc.*, **27**, 378 (1931).

(9) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N.Y., 1966, pp 651-659.

Table II. Quantum Yield as a Function of Temperature^a

Temp, °C	Absorbed light, photons cc ⁻¹ × 10 ⁻¹⁶	DMP, torr	Quantum yield (0 to <i>t</i>)				
			H ₂	CO	CH ₃ OH	H ₂ CO	¹ / ₂ ΣC
25	0.574	30.2	0.07	0.90	3.05	0.70	2.33
40	0.621	30.8	...	0.94	3.16	0.70	2.40
60	0.553	28.5	0.14	1.00	3.90	1.0	2.50
60	0.460	31.0	...	1.01	4.10	1.4	3.25

^a 2537-Å radiation; *t* = 40 min.**Table III.** Quantum Yields for Various Amounts of Added Formaldehyde

Initial additive, torr	Initial DMP, torr	<i>t</i> , min	Photons absorbed cc ⁻¹ × 10 ⁻¹⁶	Quantum yield (0 to <i>t</i>)				
				H ₂	CO	CH ₃ OH	H ₂ CO	¹ / ₂ ΣC
A. 25°, 2537 Å								
H ₂ CO								
0	21.7	60	0.80	0.08	0.90	2.80	0.49	2.10
0.60	21.3	60	0.81	0.14	0.96	1.81	-0.62	1.08
1.54	23.0	60	0.91	0.13	1.00	1.36	-0.31	1.03
2.15	21.6	60	0.84	...	1.03	1.22	-1.44	0.41
2.96	17.5	60	0.54	0.17	1.00	1.08	-2.0	0.04
4.20	19.3	60	0.76	0.17	1.01	1.05	-2.5	-0.23
11.5	15.7	60	0.59	0.20	0.98	0.42	-3.0	-0.80
14.5	7.5	64	0.38	0.27	1.00	0.21	-3.5	-1.14
12.1	1.5	64	0.14	0.46	1.02	0	-3.0	-0.99
16.4	0	214	0.23	0.98	0.99	0
0	36.8	540	19.6	0.06	0.99	3.01	0.04	2.02
5.5	22.1	665	11.6	0.17	0.78	1.50	-0.77	0.75
B. 60°, 2537 Å								
0.0	22.5	60	0.81	0.11	1.00	3.10	+0.20	2.15
0.64	23.3	60	0.83	0.18	1.04	2.78	-0.06	1.88
1.70	22.9	60	0.82	0.20	1.01	1.82	-0.60	1.11
2.65	21.2	60	0.76	0.20	1.00	1.55	-0.66	0.94
C. 25°, 2537 Å, added CO or CH ₃ OH								
CO								
4.4	19.1	40		3.0	1.1	...
CH ₃ OH								
3.7	15.4	62		...	0.90	3.6	0.7	2.6

for 25° are given in Table IA, and for 60° in Table IB. A portion of these data is illustrated by Figure 2. At a constant time of photolysis and constant DMP, a series of runs was made at different temperatures, Table II.

The principal products are methanol, formaldehyde, and carbon monoxide, with hydrogen as a minor product. The effect of each of the major products was tested, and results are presented in Table III. Initially added carbon monoxide and methanol have a negligible effect on the quantum yields, but formaldehyde has a major effect, Table IIIA. With large pressures of added H₂CO, a solid material slowly built up on the walls of the photolysis cell. The negative quantum yields for formaldehyde indicate that this solid material is a polymer incorporating formaldehyde.

Miscellaneous effects of DMP pressure, absorbed light intensity, and wavelength are given in Table IV.

The effect of an inert gas on the photolysis was checked from 0 to 760 torr by adding helium. No change of pattern of quantum yields was observed. The effect of oxygen contamination was investigated by photolyzing DMP in the presence of 3% O₂. No significant change was seen here either, although some formation of formic

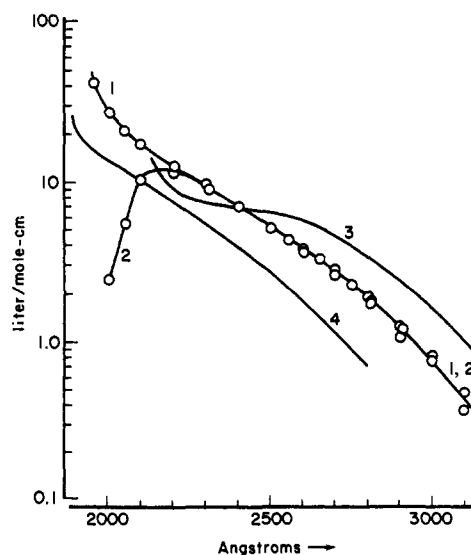


Figure 1. Ultraviolet absorption spectrum of dimethyl peroxide compared to other similar spectra and to observations by ref 1: (1) this study, (2) ref 1, (3) *t*-butyl peroxide, and (4) hydrogen peroxide, reduced by factor of 10 ($\epsilon = (\log I_0/I)C^{-1}L^{-1}$ 1. mole⁻¹ cm⁻¹).

Table IV. Quantum Yield as a Function of DMP Pressure, Absorbed Light Intensity, and Wavelength at 25°

t , min	Absorbed intensities, photons $\text{cc}^{-1} \text{sec}^{-1} \times 10^{-12}$	DMP, torr	Wavelength, Å	Quantum yield (0 to t)			
				H ₂	CO	CH ₃ OH	H ₂ CO
A. 62	1.88	28.4	2537	...	0.88	3.3	1.0
60	2.08	33.1	2537	...	0.89	3.4	1.0
60	0.52	3.8	2537	...	0.48	1.6	0.4
66	0.52	3.7	2537	0.06	0.60	1.8	0.3
B. 200	0.40	33.0	2537	0.09	0.76	3.4	1.1
38	4.9	35.8	2537	3.0	0.9
220	0.58	30.8	2537	0.10	0.91	3.6	1.1
40	0.43	34.8	2537	0.08	0.86	3.0	1.0
C. 60	2.47	33.2	3130	...	0.87	3.5	1.0
40	3.48	29.8	2537	...	0.93	3.4	1.0
60	2.32	30.6	3130	...	0.87	3.6	1.1
20	1.88	28.4	2537	...	0.88	3.3	0.8

Table V. Differential Quantum Yield between Successive Times^a

Photons absorbed/ molecules of reactant		Quantum yield (t to $t + \Delta t$)				
		H ₂	CO	CH ₃ OH	H ₂ CO	$1/2 \Sigma C$
0	-0.00025		0.50	6.6	(6.1)	(6.6)
0.00025	-0.00050	0.07	0.76	3.6	(2.8)	(3.6)
0.0050	-0.0010	0.07	0.78	3.2	2.4	3.2
0.0010	-0.0025	0.07	0.88	2.9	1.2	2.5
0.0025	-0.0050	0.07	0.92	2.9	0.32	2.1
0.0050	-0.0100	0.07	0.96	2.8	0.12	1.9
0.010	-0.020	0.07	1.00	2.5	~0	1.8
0.020	-0.040	0.07	1.00	2.4	~0	1.7

^a Smoothed data, 25°, 2537-Å radiation.

acid might have been expected. Since olefins exhibit chain-inhibiting properties which are attributed to free-radical additions to the C=C bond, a photolysis in their presence was carried out. Twenty torr of DMP was photolyzed in the presence of 31.5 torr of propylene. The quantum yield of CH₃OH was reduced by 35%, and within the system's limits the quantum yield of H₂CO was zero. There is an effect due to the added propylene similar to the one found by Danby and Hinshelwood in the photolysis of acetaldehyde.¹⁰

All data at 25°, 2537 Å, and initial DMP of 31 ± 5 torr (with no added formaldehyde) were pooled and plotted in terms of products per cubic centimeter vs. photons absorbed per cubic centimeter (Figure 3). Product molecules per cubic centimeter were normalized by division by the initial concentration of reactant. In this way successive quantum yields were evaluated for different degrees of photolysis. Such differential quantum yields up to 4% photolysis are listed in Table V.

Discussion

Initial Photolysis. From the tables and figures one readily sees that the photolysis of DMP is quite a complicated reaction. Quantum yields for the initial products (0.03–3%) of photolysis at 60° are displayed in Figure 2. Unfortunately, the gas chromatographic method could not measure formaldehyde until the degree of conversion

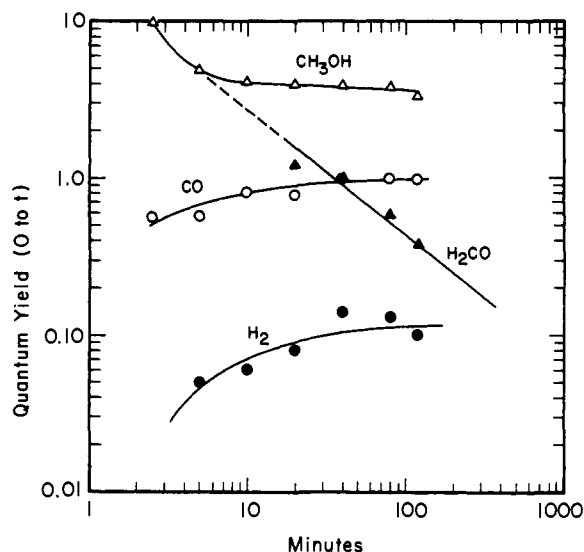


Figure 2. Integrated quantum yields for different products in the photolysis of DMP: 60°, 2537-Å radiation, 30 torr of DMP.

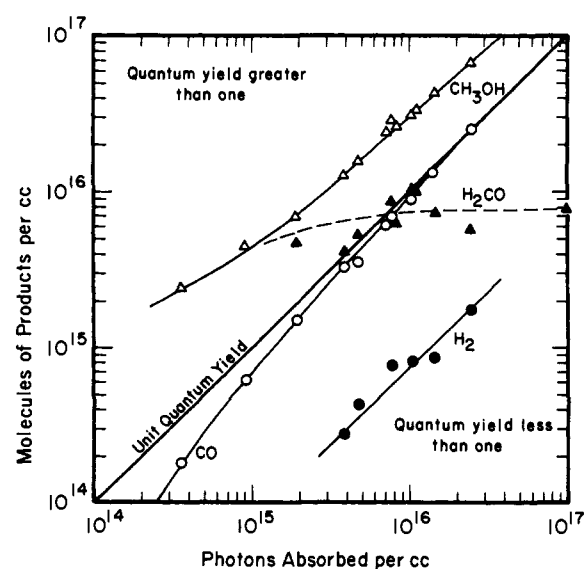


Figure 3. Products formed as a function of photons absorbed: approximately 30 torr of DMP, 25°, 2537-Å radiation. Finite differences on this graph give the differential quantum yields of Table V.

(10) C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A129**, 169 (1942).

reached about 0.3%, but its earlier history is indicated by extrapolation in Figure 2. As can be seen in Figure 2 (and other examples at 25° are shown in Table I), the initial quantum yield of CH₃OH is at least 10, and thus it is certainly formed by some chain reaction. In a number of systems¹¹ it is apparent that the principal reaction of the methoxyl radical is to abstract a hydrogen atom from other molecules to form CH₃OH. Formaldehyde is an initial product (Figure 2 or Figure 3), but its quantum yield drops rapidly to zero as it builds up to a steady state (Figure 3). Extrapolation of Figure 2 suggests that the initial quantum yield of H₂CO is about the same as that of CH₃OH. The quantum yield of carbon monoxide rises rapidly from 0 to 1. The quantum yield of total carbon-containing compounds drops from about 13 to 3.5 (Table V) over the course of the first 4% of reaction. These facts indicate the following mechanism for the dominant features of the reaction

Primary steps: a, b
 Chain reaction: e, f
 Competition with chain as H₂CO builds up: g
 Chain termination: at first, k, l; later, p
 Side reaction to produce H₂: m, q, etc.

This mechanism gives a primary split to methoxyl radicals, similar to the thermal decomposition mechanism.⁴ The CH₃O radicals attack DMP to give a chain reaction,³ with equal amounts of CH₃OH and H₂CO as products. The chain-termination process is disproportionation (and recombination) of CH₃O radicals, further to give equal amounts of CH₃OH and H₂CO. However, the accumulation of the product H₂CO rapidly leads to competition for CH₃O between the reactant DMP and H₂CO. After 120 min of photolysis time (Table I), H₂CO reaches a steady state where, to a first approximation, the rate of reaction e (e) is equal to the rate of reaction g (g).

$$g[\text{CH}_3\text{O}][\text{H}_2\text{CO}]_s = e[\text{CH}_3\text{O}][\text{DMP}] \quad (1)$$

At 25° the steady-state pressure of H₂CO is 0.20 torr and that of DMP is 30 torr; at 60° these figures respectively are 0.27 and 28. Thus at 25° we can write

$$\frac{g}{e} = 151 = \frac{A_g}{A_e} \exp(E_e - E_g)/RT \quad (2)$$

Since DMP has six equivalent reaction sites (hydrogen atoms) and H₂CO has two, the ratios of A factors should incorporate a factor of $\frac{2}{6}$ or $\frac{1}{3}$

$$\frac{g}{e} = 151 = \frac{1}{3} \exp(E_e - E_g)/RT \quad (3)$$

On this basis the activation energy for reaction e is about 3.6 kcal/mole greater than that for reaction g.

$$E_e - E_g = 3.6 \quad (4)$$

Added Formaldehyde. According to the mechanism deduced from the initial photolysis, the addition of excess formaldehyde should enhance the rates of g and p and

(11) (a) F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, *J. Am. Chem. Soc.*, **72**, 338 (1950); (b) M. H. J. Wijnen, *J. Chem. Phys.*, **28**, 271, 939 (1958).

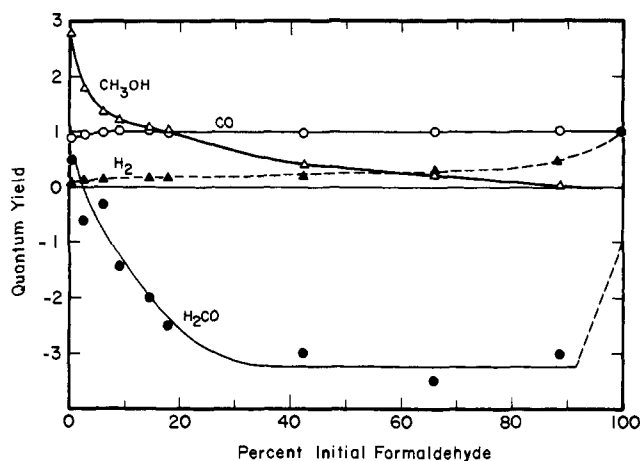


Figure 4. Quantum yields in photolysis of DMP in presence of added formaldehyde: 25°, 2537-Å radiation, DMP + H₂CO ≈ 20 torr, photolysis time 60 min (except for point at 100% H₂CO, 214 min).

thereby suppress the chain, e and f. The expected, limiting quantum yields with added H₂CO are: CH₃OH, 2; CO, 1; and H₂CO, -1. A series of runs was made where the initial pressure of DMP plus H₂CO was 20 torr, DMP varied from 100 to 0%, exposure time was 60 min at 2537 Å, and the temperature was 25°. The full results are given in Table III, and a portion of the results are demonstrated in Figure 4. The results are quite contrary to expectations of the mechanism that accounts for the initial photolysis. The quantum yield of CH₃OH drops (with initially added H₂CO) from 3 to 1 to 0.35 at 50% H₂CO. The quantum yield of H₂CO goes below -3. The quantum yield of CO is constant at the value 1. Hydrogen is a minor product in the photolysis of DMP alone, but it becomes important in the mixed system, H₂CO + DMP; the quantum yield is about 0.07 in pure DMP, 0.25 in 50% H₂CO, and 1.0 in pure H₂CO.

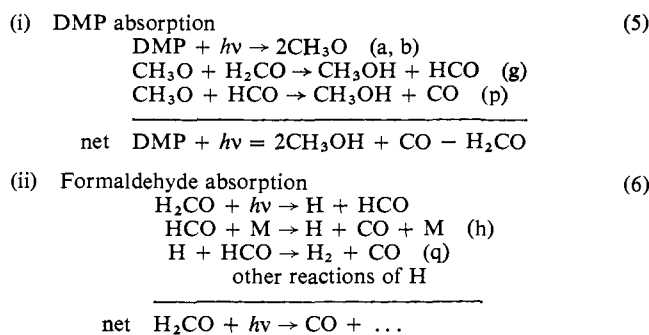
In systems with large percentages of H₂CO, a troublesome side reaction occurred during photolysis, the slow formation of a nonvolatile white solid (presumably radical-polymerized formaldehyde) on the walls of the photolysis vessel. This solid material absorbs 2537-Å radiation, and thus it was necessary to dismantle the system and clean the cell with chromic acid cleaning solution after a few runs with large additions of H₂CO. The occurrence of polymerization is represented by eq i and j. The photolysis experiments at 60° showed much less polymerization and coating of the reaction vessel than did experiments at 25°.

The absorption coefficient for DMP for our photolysis radiation centered on 2537 Å was ten times greater than that for H₂CO. Even so, at large partial pressures of formaldehyde a considerable amount of absorption of radiation by H₂CO occurred, and the observed quantum yields are a composite effect of absorption by DMP and by H₂CO. The magnitude of this effect is seen by Table VI, interpolated from Figure 4.

One notable fact in Table VI is that in DMP and H₂CO mixtures the quantum yield of CO is 1, regardless of whether radiation is absorbed by DMP or H₂CO. This fact can be explained by previously proposed steps.

Table VI. Relative Rates of Absorption of 2537-Å Radiation by DMP and H₂CO

Composition, %		Light absorbed, %		Quantum yields			
DMP	H ₂ CO	DMP	H ₂ CO	H ₂	CO	CH ₃ OH	H ₂ CO
100	0	100	0	0.07	0.90	2.8	0.5
90	10	99	1	0.15	1.0	1.2	-1.3
80	20	98	2	0.20	1.0	0.90	-2.6
50	50	91	9	0.25	1.0	0.35	-3.3
20	80	71	29	0.35	1.0	0.10	-3.3
10	90	50	50	0.50	1.0	0.05	-3.0
0	100	0	100	1.0	1.0	0	-1



Whereas this mechanism explains the remarkably constant quantum yield for formation of CO, it requires the quantum yield of CH₃OH to be twice the rate of light absorption by DMP, but actually the quantum yield of CH₃OH is reduced to 0.05 even when DMP absorbs 50% of the photolyzing radiation. The reduction of quantum yield of CH₃OH could be explained by consumption of radicals by the polymerization reaction, but then the quantum yield for CO would not exceed the fraction of light absorbed by H₂CO. (The polymerization reaction is thus shown to be unimportant in radical removal, but by virtue of long chain length it is important in removal of H₂CO, whose quantum yield goes as low as -3.5.)

Considering the facts in Table VI and all known reactions of methoxyl radicals, we can only explain the situation by assuming the DMP absorbs 2537-Å radiation and H₂CO decomposes. DMP absorbs radiation to produce an excited electronic state, reaction a. The excited DMP has a finite lifetime with decomposition rate constant *b*. Upon collision of H₂CO with excited DMP, there is a finite rate constant *c* for transfer of the electronic excitation from DMP to H₂CO. The excited formaldehyde promptly dissociates, reaction d, to H and HCO (or possibly to CO + 2H). This energy-transfer mechanism accounts for all the major trends found upon addition of H₂CO to DMP.

(i) Constant quantum yield of CO. When DMP absorbs radiation it either dissociates to 2CH₃O which by way of reactions g and p gives CO, or it transfers its energy to dissociate H₂CO to give one CO by way of reactions h, q, etc.

(ii) Reduction of quantum yield of CH₃OH to a value far below the absorption of light by DMP. The DMP absorbs 2537-Å radiation and passes it to H₂CO, without dissociation to CH₃O radicals. Thus the usual products expected from CH₃O radicals are not found.

(iii) The quantum yield of H₂CO going as low as -3.5. This effect is explained only by consideration of the long-

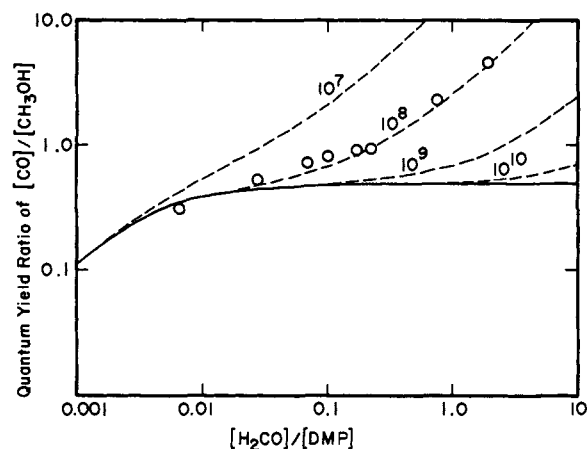


Figure 5. Ratio of quantum yield of carbon monoxide to methanol in the photolysis of DMP (Table III). The estimation of the rate constant *b* (DMP* → 2CH₃O (b)) by means of eq 10, where *g/e* = 151 and *c* was assumed to be 4.3 × 10⁻¹⁰ cc/sec.

chain polymerization of H₂CO by radicals, reactions i and j.

The mechanism involves at least five intermediate free radicals, CH₃O, CH₂OOCH₃, HCO, H, and CH₃O-(CH₂O)_x. In this study observations were made only of the products, H₂, CO, H₂CO, and CH₃OH. In such a situation it is impossible to deduce an unambiguous mechanism or to evaluate reliable rate constants.¹² However, it appears that the major products, CO and CH₃OH, and the major intermediate CH₃O may be primarily determined by a relatively small part of the full mechanism, especially after a small amount of H₂CO is present. The constancy of quantum yield for carbon monoxide suggests that its rate of formation is essentially

$$\frac{d[\text{CO}]}{dt} = d[\text{H}_2\text{CO}^*] + g[\text{CH}_3\text{O}][\text{H}_2\text{CO}] \quad (7)$$

After a measurable amount of H₂CO has formed, reactions k and l are replaced by processes g and p, s, etc. Thus, as a good approximation, one may assign as the rate of formation of methanol

$$\frac{d[\text{CH}_3\text{OH}]}{dt} = 2b[\text{DMP}^*] + e[\text{CH}_3\text{O}][\text{DMP}] \quad (8)$$

and, as an approximation, it is assumed that the steady-

(12) H. S. Johnston and F. Cramarossa, *Advan. Photochem.*, **4**, 1 (1966).

state of methoxyl radicals is largely determined by reactions b and g

$$\frac{d[\text{CH}_3\text{O}]}{dt} = 2b[\text{DMP}^*] - 2g[\text{CH}_3\text{O}][\text{H}_2\text{CO}] \approx 0 \quad (9)$$

With these three relations and the usual steady-state treatment of the excited molecules DMP^* and H_2CO^* , one obtains the following relation for the ratio of quantum yield of carbon monoxide to methanol.

$$\frac{\text{QY}(\text{CO})}{\text{QY}(\text{CH}_3\text{OH})} = \frac{1 + (c/b)[\text{H}_2\text{CO}]}{2 + (e/g)[\text{DMP}]/[\text{H}_2\text{CO}]} \quad (10)$$

As was noted in eq 2, the ratio g/e is 151 at room temperature. Thus the ratio c/b can be estimated from experimental data. Alternately, the constant c was assigned the value of 4.3×10^{-10} cc/sec (hard-sphere constant with molecular diameter of 5 Å), and the function $\text{QY}(\text{CO})/\text{QY}(\text{CH}_3\text{OH})$ was plotted against the ratio of H_2CO to DMP for various assumed values of the rate constant b , the unimolecular decomposition of excited DMP (Figure 5). The data indicate a value of about 10^8 sec^{-1} for b . This value of b , inferred from the experimental data, can be compared as to order-of-magnitude with the simplest form of Rice-Ramsperger-Kassel theory.¹³ Whereas the simple, classical form of this theory is quite inadequate at energies just above the

(13) H. S. Johnston, "Gas Phase Reaction Rate Theory," The Ronald Press Co., New York, N.Y., 1966, pp 266-297.

critical energy, it agrees fairly well with much more elaborate theories at high excitation energy, such as that involved in excitation of DMP by 2537-Å radiation. The relation is

$$b = D \left(\frac{\epsilon - \epsilon_c}{\epsilon} \right)^{s-1}$$

Here D is an empirical constant, which usually¹⁴ falls within the range of $10^{13 \pm 1} \text{ sec}$; ϵ is the vibrational energy of the molecule; ϵ_c is the "critical energy" for unimolecular decomposition; and s is the number of oscillators or normal modes of vibration of the molecule. The total energy corresponding to 2537-Å radiation is 113 kcal/mole, and this value is ascribed to ϵ . The oxygen-oxygen bond dissociation energy of DMP is about 36 kcal/mole, and this value is ascribed to ϵ_c . Thus the order-of-magnitude estimate of b is

$$b = 10^{13 \pm 1} \left(\frac{113 - 36}{113} \right)^{23} = 10^{9 \pm 1} \text{ sec}^{-1}$$

The value inferred from experiments, 10^8 sec^{-1} , is then not unreasonable.

Acknowledgment. This work was supported by the National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control, Public Health Service under Grant AP-104.

(14) S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N.Y., 1960, Tables X1.4 and X1.5.