[CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

Rate Studies of the Oxidation of Methyl Radicals in Oxygen-rich Media at 25°

BY DAVID F. DEVER[1] AND JACK G. CALVERT

RECEIVED OCTOBER 13, 1961

A rate study of the photoöxidation of azomethane has been made using long-path infrared spectrometry. The nature of the primary products and their initial rates of formation were determined in experiments at 25° and in oxygen-rich media. The major products, methanol and formaldehyde were formed in approximately equal amounts. The minor products were identified as formic acid and methyl hydroperoxide. In all runs a reasonably good mass balance was obtained: $R_{CH_3OH} + R_{CH_3O_2H} = R_{CH_2O} + R_{HCO_2H} = -R_{Me_2N_2}$, within the experimental error. In runs with added formaldehyde, the rate of methanol formation increased with the amount of formaldehyde added up to a limiting rate which was approximately equal to the rate of methyl radical formation in the system. The data were used to evaluate several alternative reaction mechanisms.

Studies of the reactions of simple alkyl free radicals with oxygen at room temperature have been stimulated in recent years by the need of air pollution workers, and others concerned with oxidation studies, for quantitative rate data related to these systems.[2] The great complexity of the products of the oxidation of alkyl free radicals and the instability and high reactivity of many of these complicate the quantitative study of these systems. In recent years the development of long-path infrared spectrometry has made possible accurate and definitive analysis of products without the condensation, distillation, or other separation procedures which are usually employed: the loss or transformation of many reactive substances is thus minimized. The many diverse observations and conclusions of the previous studies of methyl radical oxidation at 25° require that we obtain a better knowledge of the rates of formation of the initial products of the reaction.[2] In this study the initial rates of formation of the products of the methyl radical-oxygen reaction have been determined using long-path infrared analysis. The rate data presented here suggest several new and interesting details of the mechanism of the methyl radical oxidation in oxygen-rich media at 25°.

Experimental

Long-path Infrared Studies.—The reaction between methyl radicals and oxygen was initiated through the photolysis of azomethane in oxygen mixtures contained within the optical path of a modified Perkin–Elmer 40-meter long-path infrared spectrometer which has been described previously.[2,3]

The instrument was equipped with an ordinate scale-expander allowing 5-, 10- and 20-fold signal amplification. Most of the procedures employed have been described elsewhere [2,3] and need not be given in detail here. There are some differences which should be pointed out. In the present work the relatively weak absorption of the reactant azomethane was blanked by charging the reference cell as well as the reaction cell with a given pressure of azomethane: this made possible much simplification in the treatment of spectra. In a typical experiment a reaction was started and allowed to proceed for about three minutes, the shutter was interposed and the entire spectrum scanned: then the shutter was removed again and the cycle repeated until the reactant had been photolyzed for a total of 10 min. At this time about 6% of the original reactant had decomposed. The entire infrared product spectrum gave indication of only three products: methanol, formaldehyde and formic acid. Subbaratnam and Calvert[2,3] have shown in runs of longer duration that methyl hydroperoxide is also a product[3]; however, its absorption coefficient at 12.2 μ was too weak to allow initial rates of formation to be determined in this work. Rate data of Subbaratnam and Calvert[2,3] can be used to estimate the methyl hydroperoxide product, and these will be coupled with the present rate data to obtain checks of the mass balance, etc. Methanol was determined through the use of the spike length at 9.67μ, formic acid at 9.06μ, formaldehyde at 3.61 and 5.75 μ, azomethane loss (negative peak in these azomethane blanked experiments) at 7.00μ and methyl hydroperoxide at 12.2μ. A typical set of analytical data for different irradiation times is shown in Fig. 1. There is no induction period observed for methanol and formaldehyde products, and the formation of each is very nearly a linear function of time for these short exposures. The situation is not as clear with formic acid. Some acceleration of the rate of formic acid formation may occur as the run progresses. From these and similar data for many runs under different conditions, an extrapolation to zero time has been made and initial rates of product formation determined. These results are summarized in Table I. Experiments with varied azomethane and oxygen pressures and with added nitrogen, neopentane, tetramethylethylene and formaldehyde are shown. In the runs with added formaldehyde only rate data for the products methanol and methyl hydroperoxide could be obtained: characteristic spectral regions of other products were sufficiently obscured to prevent accurate analysis. Thus information on the reactions of the HCO radical (product of reaction 7) can not be derived from this study.

Product Analysis through Ultraviolet Spectroscopy.—In several experiments an attempt was made to determine the nature of the products of the photoöxidation of azomethane through the use of ultraviolet spectroscopy. These were carried out largely to test the mechanism of methyl radical oxidation favored by Hanst and Calvert[4] which incorporates the intermediate formation of ozone. A Pyrex tube of 1.0-m. length was enclosed on each end with a quartz window. Along the center tube, enclosed in a water-jacket, were three Hanovia 550 w. medium pressure mercury lamps. At one end of the tube was placed a hydrogen-lamp from a Beckman *DU* spectrophotometer. A lens following the cell focused the beam from the hydrogen-lamp onto the slit of a Hilger Medium Quartz Spectrograph. In a series of experiments, azomethane was introduced into the 1 m.-cell at its Dry-Ice vapor pressure (about 6 mm.) and 734 mm. of oxygen added. The photodecomposition of azomethane in the oxygen-rich mixtures was stopped or started as desired by withdrawing or replacing a shutter between the lights and the reaction tube. During the photoöxidation, exposures of the photographic plate of the spectrograph were made at intervals of five minutes. After development of the plate, the transmissions of the different exposures were measured with a Leeds and Northrup Electronic Densitometer. In addition to the typical spectra of the expected products CH_2O and CHO_2H (CH_3OH is transparent), an additional absorption in the 2450–2600 Å. region was always present.

---

[1] Chemistry Department, University of Miami, Coral Gables 46, Florida.

[2] For a review of much of the pertinent literature related to the mechanism of methyl radical oxidation, see: N. R. Subbaratnam and J. G. Calvert, chapter in "Chemical Reactions in the Upper and Lower Atmosphere," Interscience Publishers, (1962); proceedings of a symposium held in San Francisco, April, 1961.

[3] N. R. Subbaratnam and J. G. Calvert, *J. Am. Chem. Soc.*, submitted for publication.

[4] P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, **63**, 71 (1959).

TABLE I

INITIAL RATES OF PRODUCT FORMATION IN THE PHOTOOXIDATION OF AZOMETHANE AT 25°

Run no.	Pressure, mm. (1) Me_2N_2	(2) O_2	(3) Other gases	Initial rates, mm./min. × 10^3 (4) CH_3OH	(5) CH_2O	(6) HCO_2H	(7) CH_3O_2H[a]	(8) $-Me_2N_2$	(9) 4/1 × 10^3	(10) 6/1 × 10^3	(11) (5 + 6)/1 × 10^3	(12) (4 + 7)/1 × 10^3	(13) (11/12)
1	0.0853	740	....	0.47	0.48	0.038	0.051	..	5.5	0.45	6.1	6.1	1.0
2	.164	740	....	0.96	1.1	.11	.099	1.0	5.9	.67	7.4	6.5	1.1
3	.242	740	....	1.5	1.6	.18	.14	1.8	6.2	.74	7.4	6.8	1.1
4	.316	740	....	2.2	2.1	.26	.19	..	7.0	.82	7.5	7.6	1.0
5	.480	740	....	3.1	3.2	.51	.29	..	6.5	1.1	7.7	7.1	1.1
6	.650	740	....	3.9	4.0	.65	.39	..	6.0	1.0	7.2	6.6	1.1
7	.163	151	N_2. 589	1.1	1.1	.10	.098	1.1	6.7	0.61	7.4	7.3	1.0
8	.164	46	N_2. 694	0.96	1.1	.13	.098	..	5.9	0.79	7.5	6.5	1.1
9	.154	13	N_2. 727	.94	0.92	.17	.092	..	6.1	1.1	7.1	6.7	1.1
10	.158	6	N_2. 734	.96	0.96	.13	.095	..	6.1	0.82	6.9	6.7	1.0
11	.647	1	N_2. 739	4.8	4.4	.44	.39	..	7.4	.68	7.5	8.0	0.9
12	.155	740	Me_4C. 0.14	0.92	0.90	.084	...	..	5.9	.54	6.3	..	..
13[b]	.161	740	$Me_2C{=}CMe_2$, 0.15	(.75)	(0.97)	(.11)	...	..	(4.7)	.68	(6.7)	..	..
14[b]	.161	739	$Me_2C{=}CMe_2$. 0.64	(.85)	(1.1)	(.10)	...	..	(5.3)	.62	(7.5)	..	..
15	.160	11	CH_2O. 0.64 N_2. 729	2.33	....	...	...	..	14.6	..	...	..	..
16	.0852	11	CH_2O. 0.66 N_2. 729	1.14	....	...	...	..	13.4	..	...	..	..
17	.165	740	CH_2O. 0.07	0.99	....	...	0.091	..	6.0	..	...	..	..
18	.145	740	CH_2O. .28	1.08	....	...	.069	..	7.4	..	...	..	..
19	.142	740	CH_2O. .40	1.21	....	...	.060	..	8.5	..	...	..	..
20	.165	740	CH_2O. .52	1.49	....	...	.053	..	9.0	..	...	..	..
21	.165	13	CH_2O, .58 N_2. 727	2.03	....	...	.046	..	12.3	..	...	..	..
22	.000	740	CH_2O, 0.74	....	....	2.4	...	..	...	...	...	..	..

[a] Rate data for CH_3O_2H are from Subbaratnam and Calvert data obtained in similar experiments of longer duration; there was no induction period in the formation of CH_3O_2H. however. and these should be good approximations to initial rates. [b] In runs 13 and 14 an attempt was made to measure the rate of acetone formation through its characteristic peak at 8.3 μ. The rate was not measurable in 13. but with the increased tetramethylethylene used in 14 a value of $R_{CH_3COCH_3}$ = 0.000095 mm./min. was derived.

A large part of this absorption was due to methyl hydroperoxide, but a small unexplained absorption remained after correction for this compound. However. it was not possible to get truly quantitative results with the equipment used, and the correction of absorption due to CH_3O_2H was difficult to assess. The results although qualitative in nature are consistent with the presence of 10^{-4} to 10^{-5} mm. of ozone. The absorption of ozone in the ultraviolet near 2550 is very intense but rather structureless. so the identification from absorption in these experiments is impossible. Since the results of these experiments were not definitive. they were not continued further.

Discussion of Results

The present work should provide some resolution of the many conflicting observations and conclusions concerning the mechanism of oxidation of methyl free radicals at 25°. Long-path infrared spectrometry has been used to establish the nature of the initial products of the reaction. The rate data of Table I derived in the photoöxidation of azomethane–oxygen mixtures show that the major initial products of the reactions of methyl radicals in oxygen-rich media at 25° are methanol and formaldehyde. Smaller amounts of formic acid and methyl hydroperoxide are also formed. Analyses could not be made for the infrared inactive nitrogen product in these experiments. Much indirect evidence has been presented which suggests that a small steady state concentration of ozone (about 10^{-5} mm.) is established when azomethane is irradiated in an oxygen-rich system.[2,4] We have obtained new indirect evidence which is consistent with this notion (see the following section on ozone formation), but a truly unambiguous proof of its presence is still not at hand. Other possible products, carbon monoxide, carbon dioxide, water, nitrous oxide, dimethylperoxide and peroxyformic acid could not be detected among the products. In consideration of the observed product distribution and the initial rates of formation of the products summarized in Table I, it will be instructive to utilize the mechanism suggested by Subbaratnam and Calvert[2,3] in explanation of methyl hydroperoxide formation in these systems.[3]

$$CH_3N_2CH_3 + h\nu \longrightarrow 2CH_3 + N_2 \qquad (I)$$

$$CH_3 + O_2 \rightleftarrows CH_3O_2^{\ddagger} \qquad (1)$$

$$CH_3O_2^{\ddagger} + M \longrightarrow CH_3O_2 + M' \qquad (2)$$

$$2CH_3O_2 \longrightarrow 2CH_3O + O_2 \qquad (3)$$

$$2CH_3O \longrightarrow CH_3OH + CH_2O \qquad (4)$$

$$CH_3O + CH_3O_2 \longrightarrow CH_3O_2H + CH_2O \qquad (5)$$

$CH_2O^{\ddagger}$ represents an energy-rich methylperoxyl radical which dissociates rapidly into CH_3 and O_2 unless stabilized through loss of energy by collision in 2.

Rate Data from Experiments with Varied Pressures of Azomethane and Oxygen.—In runs 1–6 of Table I the pressure of azomethane has been varied from 0.085 to 0.65 mm. in 740 mm. of oxygen. In runs 7–11 the oxygen pressure has been changed from 740 to 1 mm. at selected azomethane pressures. An observation of columns 4,5,6,7 and 13 of Table I shows that within the experimental error there is a good mass balance between the observed products

$$R_{CH_3OH} + R_{CH_3O_2H} = R_{CH_2O} + R_{HCO_2H} \qquad (6)$$

If the formic acid is derived from a portion of the primary product formaldehyde, in a fashion which we will consider later, then the relation 6 is expected on operation of the above mechanism. Furthermore the rate of loss of azomethane (column 8 of Table I) is equal to the rate summation on either side of the equality 6 within our error of measurements in the three experiments in which this was determined. Thus a good account is made of all the methyl radicals formed in the experiments. When the rate functions, $R_{CH_3OH} + R_{CH_3O_2H}$ and $R_{CH_2O} + R_{HCO_2H}$, are divided by the pressure of azomethane (columns 11 and 12 of Table I), a near constant value, independent of the pressures of azomethane and oxygen, is found. Under our conditions in which the pressure of azomethane is always less than 0.65 mm., the light absorption is simply proportional to the pressure of azomethane. Then the constancy of the functions of columns 12 and 13 implies that the quantum yields of the products are independent of the pressures of azomethane and oxygen used in our experiments. This observation is also in accord with the mechanism I-5 above.

The Rate of Methanol Formation in the Photolysis of Azomethane-Oxygen Mixtures with Added Formaldehyde.—Compare the rates of methanol formation divided by the azomethane pressure (column 9 of Table I) for the pure azomethane–oxygen mixture runs with those in which formaldehyde was added. It can be seen that in the runs with the highest pressures of formaldehyde used (0.66 mm.), $R_{CH_3OH}/P_{CH_3N_2CH_3}$ has climbed to a value near equal to the rate of production of methyl radicals/$P_{CH_3N_2CH_3}$ (the sums of columns 11 and 12 of Table I). Concurrent with the increase in the rate of methanol formation on formaldehyde addition, the rate of formation of methyl hydroperoxide is decreased. Both of these observations suggest the removal of methoxyl radicals by reaction with formaldehyde in the experiments with added formaldehyde; they are consistent with the mechanism I-5 above plus the additional reaction

$$CH_3O + CH_2O \longrightarrow CH_3OH + HCO \qquad (7)$$

When the formaldehyde was added in sufficient quantity the sequence I, 1, 2, 3 is followed primarily by (7), so that effectively all methyl radicals formed in I lead to methanol. In experiments without added formaldehyde the disproportionation reactions 4 and 5 dominate and $R_{CH_3OH} + R_{CH_3O_2H}$ is only one-half of the rate of methyl radical formation in I. If one assumes the operation of the above mechanism then the theoretical rate law 8 is expected to hold. I_a is the absorbed

$$(2R_{CH_3OH} + 2R_{CH_3O_2H} - 2I_a\phi_1)(2I_a\phi_1 - R_{CH_3O_2H})^{1/2}/R_{CH_3O_2H} = (k_7(2k_3)^{1/2}/k_5)[CH_2O] \qquad (8)$$

light intensity; ϕ_1 is the primary quantum yield of azomethane decomposition in process I. $2I_a\phi_1$ can be estimated from the mass balance of the products, that is, the sum of columns 4, 5, 6 and 7 of Table I, for experiments of equal azomethane pressure but without added formaldehyde. The accuracy of the present data is not great, and inaccuracies are accentuated in that the difference between quantities which are near equal in size must be taken in the evaluation of function 8. However, the data of runs 17, 18, 19 and 20 have been used to obtain a best estimate of the theoretical rate constant expression; the function 8 in the units (mm. min.)$^{-1/2}$ is plotted *versus* [CH$_2$O] in Fig. 2.

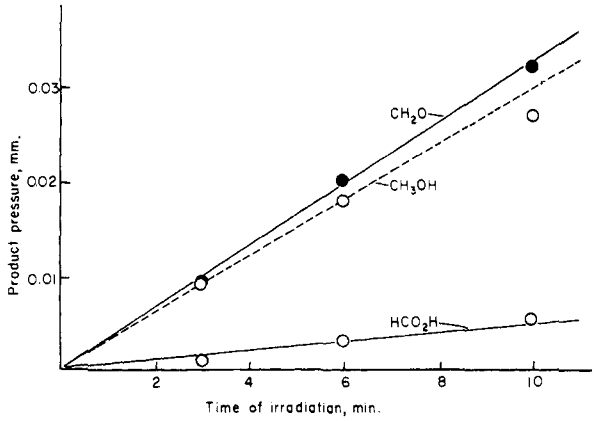

Fig. 1.—Product pressures as a function of irradiation time: from the photoöxidation of azomethane (0.480 mm.) in oxygen (740 mm.) at 25° (run 5 of Table I): from these and similar data initial rates of formation of the products were determined as summarized in Table I.

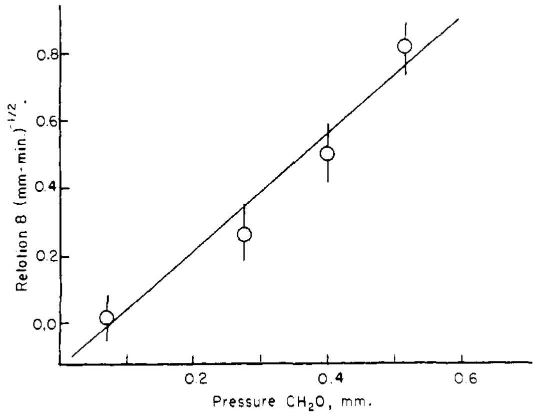

Fig. 2.—The rate equation 8. theoretically equal to $[k_7(2k_3)^{1/2}/k_5][CH_2O]$, as a function of the pressure of added formaldehyde: data from photooxidations of azomethane–oxygen mixtures with added formaldehyde at 25°: the vertical lines indicate the probable error in the determination of the points.

Within the large error of the determinations the function has the linear dependence on [CH$_2$O] predicted by 8. The slope of the line through the experimental points leads to the estimate, $k_7 \cdot (2k_3)^{1/2}/k_5 = 5 \times 10^{-5}$ (cc./mole sec.)$^{1/2}$. There are no previous estimates of these rate constants of which the authors are aware. Toby and Kutschke[5] report that the rate constant ratio, $k_9/k_{10}^{1/2} = 7.2 \times 10^{-4}$ (cc./mole sec.)$^{1/2}$ at 25°. If the rate constants k_{10}, k_3 and k_5 were of the same mag-

---

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

nitude, then the present data would require that $k_9 < k_7$ at 25°. The results of Wijnen[6] and Berces

$$CH_3 + CH_2O \longrightarrow CH_4 + HCO \qquad (9)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (10)$$

and Trotman-Dickenson[7] indicate that the rate constants for H-abstraction by CH_3O are larger than those of CH_3 for the same conditions, so some inequality between k_{10}, k_3 and k_5 is indicated. In view of the very polar character of the CH_3O and CH_3O_2 radicals and the extremely exothermic character of the reaction 5 (about 65 kcal./mole of CH_3O_2H formed[17]), it is likely that k_5 is the order of magnitude of k_{10}. Reaction 3 is only slightly exothermic, so it may have a finite activation energy such that k_3 may be considerably less than k_5. If this condition holds, then our present results can be rationalized satisfactorily in terms of the mechanism given. If $k_3 < k_5$ and CH_3O_2 radicals react primarily by 3, as seems likely, it follows that the lifetime of CH_3O_2 radicals is greater than that of the CH_3O radicals in this system. The failure of CH_3O_2 radicals to react by H-atom abstraction from molecular species even in experiments with added CH_2O[2,3] probably reflects the weakness of the CH_3O_2–H bond in methyl hydroperoxide. ($D_{CH_3O_2-H} \cong 90$, $D_{CH_3O-H} \cong 100$ kcal./mole.)

The Mechanism of Formic Acid Formation.—In Table I it may be noted that formic acid is formed at a rate which is about 10–16% that of formaldehyde. There are several alternative schemes of formation of formic acid which might be considered. Hanst and Calvert[4] found that formic acid and methanol were the dominant products of azomethane photoöxidation in their runs at higher azomethane pressures and more extensive decompositions. They assumed that some reactive species (presumably CH_3O, O_3 or O) started a chain oxidation of formaldehyde to formic acid. Peroxyformic acid could not be detected by Hanst and Calvert.[4] In this work a standard sample of peroxyformic acid was prepared by the method of Eggersglüss[8]; its infrared spectrum at 3.04μ showed absorption characteristic of the higher aliphatic peroxyacids.[9] During the azomethane photoöxidations and the experiment in which we photoöxidized formaldehyde (run 22 of Table I), the 3.04μ region was scanned with the highest signal amplification; no absorption attributable to peroxyformic acid was observed. Whatever the mechanism of formic acid formation, peroxyformic acid can have only a transient existence. if it is involved at all. It is unlikely that chain reactions involving formaldehyde contribute significantly in the present initial rate studies; where much more extensive conversions are allowed, as in the work of Hanst and Calvert,[4] chain reactions may be important.

The majority of the formic acid product in this study is not formed as a result of direct light absorption by an initial formaldehyde product. In run 22 of Table I the rate of formaldehyde photoöxidation was determined; if one extrapolates this rate to the small formaldehyde product pressures present in the usual experiments, the rate of formic acid formation due to direct light absorption by formaldehyde product is about 40-times smaller than the observed rate of formic acid formation.

There are several interesting alternative sources of formic acid in this study which seem more likely than those considered above. If the formaldehyde is formed in reaction 4, as we suggest, then the immediate products of this reaction, CH_3OH and CH_2O, are energy-rich to the extent of about 75 kcal./mole of CH_2O formed.[17] It is attractive to speculate that a fraction of the formaldehyde (10–16% here) is sufficiently excited, vibrationally or otherwise, to oxidize readily to formic acid in the oxygen-rich media of these experiments. In run 12 a small quantity of neopentane was added to test this "hot" molecule mechanism of formic acid formation. Neopentane should be an effective moderating gas. The results are not striking, but, consistent with the "hot" formaldehyde mechanism, there is some lowering of the R_{HCO_2H} in this run compared to that of a similar run without neopentane (compare 12 with 2). The addition of further neopentane to provide a more critical test of the theory caused the formic acid region of the infrared spectrum to become so highly absorbing that accurate analysis for formic acid was impossible. However this "hot" formaldehyde mechanism for formic acid formation seems inconsistent with the variation of R_{HCO_2H} in runs with varied pressures of azomethane and oxygen. Note in column 10 of Table I that $R_{HCO_2H}/P_{Me_2N_2}$ increases as the azomethane pressure increases (runs 1–6). Furthermore this ratio increases to a maximum as the oxygen is replaced by nitrogen in runs 7–9 and then decreases as further oxygen reduction is made (runs 9–11). If the "hot" formaldehyde mechanism were operative one would expect the opposite trend, an equilibration of "hot" formaldehyde and a lowered formic acid formation, with azomethane pressure increase. As the oxygen is replaced by nitrogen, one would expect the rate of formic acid formation to lower continually, not rise at first and then decrease as is observed.

An alternative scheme of formic acid formation which is consistent with the observations involves the possible reaction 11. "Reasonable" thermal

$$CH_3O + CH_3O_2 \longrightarrow CH_3OH + CH_2O_2 \qquad (11)$$

data[17] suggest that reaction 11 should be exothermic to the extent of at least 48 kcal. and more exothermic if CH_2O_2 is not a diradical but a paired electron species. Hence the reaction may be of low activation energy. Conceivably the species, CH_2O_2, could either isomerize to formic acid by 12 or dissociate according to 13. Reaction 12

$$CH_2O_2\,(+M) \longrightarrow HCO_2H\,(+M) \qquad (12)$$

$$CH_2O_2\,(+M) \longrightarrow CH_2O + O\,(+M) \qquad (13)$$

would be strongly exothermic (140 kcal./mole HCO_2H) and 13 exothermic by about 20 kcal.

---

(6) M. H. J. Wijnen, *J. Chem. Phys.*, **27**, 712 (1957).

(7) T. Berces and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 348 (1961).

(8) W. Eggersglüss, Monograph, *Angew. Chem. u. Chem. Ing. Tech.*, No. 61 (1951).

(9) P. Giguere and W. A. Olmes, *Can. J. Chem.*, **30**, 821 (1952).

if CH_2O_2 is in the diradical form. If this mechanism is operative in our systems then the variation of HCO_2H rates with $[Me_2N_2]$, $[O_2]$, $[Me_4C]$ and $[N_2]$ demands that the fraction of CH_2O_2 radicals which react by paths 12 or 13 depends, at least in part, on energy transfer processes involving collisions with some body or wall, *M*. Furthermore the effectiveness of N_2, O_2, CH_3N_2-CH_3, etc., as M must be different. From the evidence at hand it is impossible to establish the mechanism of formic acid formation, although there are some unusual and interesting mechanisms consistent with the present data which warrant further testing.

The Disproportionation and Combination Reactions of Methoxyl Radicals.—Our results suggest that the major portion of the methanol and formaldehyde formed in the photoöxidation of azomethane in oxygen-rich media at 25° is derived from the disproportionation reaction 4 involving

$$2CH_3O \longrightarrow CH_3OH + CH_2O \qquad (4)$$

methoxyl radicals.[10] By analogy with the reactions of the alkyl free radicals, one expects that dimethylperoxide would also be formed in an association reaction which would compete with 4.

$$2CH_3O \longrightarrow CH_3OOCH_3 \qquad (14)$$

Dimethyl peroxide was not a detectable product in any of the runs of this work, although the characteristic peaks at 6.8 and 8.7μ were scanned closely during each run. In order to obviate the possibility that dimethylperoxide might be formed and then decomposed thermally or photochemically as the run progressed, a standard sample of dimethylperoxide was prepared by the Eggersglüss method,[8] combined with azomethane and oxygen in their usual quantities, and a photochemical run made. The characteristic peaks of dimethylperoxide did not change during the normal run period. Thus dimethylperoxide seems to be an unimportant product here. This result is not so surprising when one considers the following related experimental observations. Many investigators have shown that the ratio of disproportionation to combination rate constants for the ethyl radical, $k_{15}/k_{16} = 0.12 \pm 0.01$.[11] The rate constant ratio for the similar reactions between methyl and ethyl radicals is $k_{17}/k_{18} = 0.05 \pm 0.01$.[12]

$$2C_2H_5 \longrightarrow C_2H_4 + C_2H_6 \qquad (15)$$

$$2C_2H_5 \longrightarrow C_4H_{10} \qquad (16)$$

$$CH_3 + C_2H_5 \longrightarrow CH_4 + C_2H_4 \qquad (17)$$

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \qquad (18)$$

If $k_{16} \cong k_{18}$, as seems likely, then the difference between the two ratios is approximately that which is expected from statistical reasoning; the abstraction of any one of six H-atoms in the transition state for reaction 15 will lead to ethylene and ethane formation, while the abstraction of one of only three H-atoms will be effective in leading to reaction 17. Contrast this result with that of Wijnen[13] who studied the disproportionation reactions of the methyl and methoxyl radicals. He found that $k_{19}/k_{20} = 1.8$. On the basis of the methyl–ethyl data and their statistical nature, one would expect that $k_{19}/k_{20} \cong 0.05$, whereas it is

$$CD_3 + CD_3O \longrightarrow CD_4 + CD_2O \qquad (19)$$

$$CD_3 + CD_3O \longrightarrow CD_3OCD_3 \qquad (20)$$

a factor of 30 higher than this value. From the detection limits of our instrument we can estimate from this work that $k_4/k_{14} \geq 60$. If 4 and 14 were analogous to 15 and 16 we would expect a ratio of $k_4/k_{14} \cong 0.12$ from statistical reasoning alone. The trend in size of the ratios, k_{17}/k_{18}, k_{19}/k_{20}, k_4/k_{14} suggests that the very polar character of the methoxyl radical leads to an appreciable dipole-dipole interaction which effectively orients approaching methoxyl radicals to favor 4 and oppose 14.

"Ozone" and Possible Mechanisms for Its Formation.—Several independent observations of our research group suggest that a small steady state concentration of ozone is built up during the photoöxidation of azomethane:

(1) Using long path infrared spectrometry Hanst and Calvert[4] observed an infrared absorption band at 9.5μ which is consistent with that for ozone. A large absorption due to the R-branch of the 9.68μ band of CH_3OH had to blanked in the reference cell in these experiments.

(2) Ozone reacts with tetramethylethylene to form acetone. Hanst and Calvert[4] found that acetone becomes a major product when tetramethylethylene is added to an irradiated azomethane oxygen system. We have confirmed this finding in initial rate studies (runs 13 and 14 of Table I). If one assumes that the acetone has its origin in the ozone–tetramethylethylene reaction, then the rate of acetone formation in run 14, coupled with the rate data of Verbaski and Cvetanovic,[14] leads to an estimate of $[O_3] \cong 0.4 \times 10^{-5}$ mm. This is in good agreement with that derived by Hanst and Calvert[4] from similar experiments involving more extensive photolysis. This evidence for ozone formation is not unambiguous however, since methyl peroxyl or other unknown peroxidic radicals or highly reactive intermediates also could conceivably lead to acetone on interaction with tetramethylethylene.

(3) Subbaratnam and Calvert found some unexplained "oxidant" in addition to methyl hydroperoxide in the products of the photoöxidation of pure azomethane and azomethane with added acetaldehyde, through the use of a sensitive "ozone" meter.[2] This instrument which depends on the rapid oxidation of iodide in buffered neutral solution was not specific in the response to ozone but also recorded the methyl hydroperoxide for which correction had to be made. Subbaratnam and Calvert suggested that the unexplained oxidant was possibly peroxyacetic acid or ozone. In subsequent experiments, they have been unable to detect peroxyacetic acid in the products,[3]

---

[10] J. H. Raley, L. M. Porter, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **73**, 15 (1951).

[11] For example see: M. H. J. Wijnen and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1092 (1951); R. K. Brinton and E. W. R. Steacie, *ibid.*, **33**, 1840 (1955).

[12] C. A. Heller, *J. Chem. Phys.*, **28**, 1255 (1958); P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1062 (1955).

[13] M. H. J. Wijnen, *J. Chem. Phys.*, **28**, 271 (1958).

[14] T. Verbaski and R. J. Cvetanovic, *Can. J. Chem.*, **38**, 1063 (1960).

so the presence of ozone or some other unidentified strong oxidizing agent is implicated.

(4) In one phase of this study (see the Experimental section) an unexplained structureless ultraviolet absorption was found in the 2500–2600 Å. region of the irradiated azomethane–oxygen mixtures which was consistent with the presence of $10^{-4} - 10^{-5}$ mm. of ozone. A correction for the absorption of methyl hydroperoxide had to be made in arriving at this estimate. Every experiment which we have designed specifically to determine the ozone level in irradiated azomethane–oxygen mixtures has been consistent with its presence, but each of these experiments has been rather indirect and inconclusive for one reason or another. However, we feel that the evidence is best explained by ozone formation in these systems.

Hanst and Calvert[4] favored the reaction 21 to explain "ozone" formation; they concluded that O_3 would be maintained at a low steady state concentration by reactions such as 22. Reaction 21

$$CH_3O_2 + O_2 \longrightarrow CH_3O + O_3 \qquad (21)$$

$$O_3 + CH_3 \longrightarrow CH_3O + O_2 \qquad (22)$$

has been considered by a number of workers in the oxidation and air pollution areas.[4,15] Hanst and Calvert[4] argued that unless CH_3O_2 radicals were removed rapidly by some reaction such as 21, some peroxidic products should be formed and give evidence of their presence; they could detect no such products in their experiments. The identification of methyl hydroperoxide in the products of azomethane photoöxidations by the Kutschke group,[16] the subsequent verification of this by our group and the methyl hydroperoxide mechanism studies of Subbaratnam and Calvert[2,3] prove that CH_3O_2 radicals have a considerable lifetime in irradiated oxygen-rich azomethane systems at 25°. Above we have given reasoning which indicates the steady state concentration of CH_3O_2 may be much greater than that for CH_3O in these systems. In view of these findings a major argument for the importance of 21 given by Hanst and Calvert[4] is weakened considerably. Of course, reaction 21 is not unique in the explanation of ozone formation in these systems. It is evident that the formation of oxygen atoms in the possible reaction sequence 11 and 13 would be followed in oxygen rich media largely by 23.

$$O + O_2 + M \longrightarrow O_3 + M \qquad (23)$$

A consideration of the energy relations between methyl radicals and oxygen, and the oxygenated radicals and molecules derived from them, is of interest in the consideration of the possible mechanisms of ozone formation. "Reasonable" thermal data related to the various oxidation intermediates have been derived from the published data of Gray and others,[17] and these are summarized in Fig. 3. It is seen from these enthalpy data that

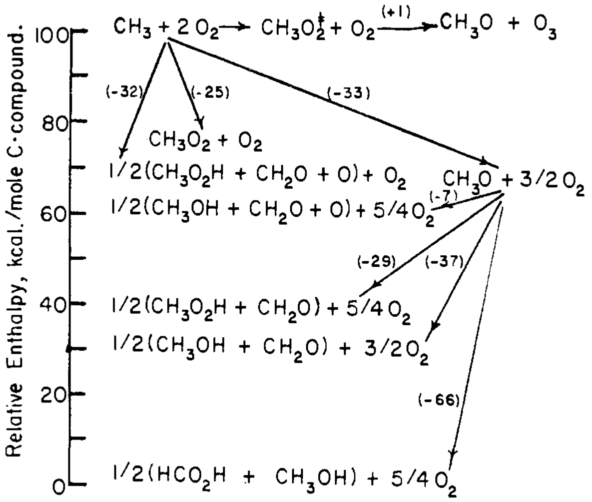

Fig. 3.—Relative enthalpy of various products of the CH_3–O_2 reactions at 25°: $CH_3O_2^{\ddagger}$ represents an energy-rich methylperoxyl radical which dissociates rapidly into CH_3 and O_2 unless deactivated by collision in reaction 2; all other species shown are assumed to be thermally equilibrated; the sources of data used in deriving this figure are listed in ref. 17.

reaction 21 can only be important if the non-thermally equilibrated $CH_3O_2^{\ddagger}$ radicals formed in the equilibrium 1 react in an early collision with O_2. If the energy released as CH_3 and O_2 react remains available in the CH_3O_2 radical, then the reaction of this radical with O_2 to form O_3 and CH_3O is about thermoneutral; thus it may have a small activation energy associated with it. In oxygen-rich systems this reaction may be important, although theoretically it appears unlikely even in this most favorable case.[18] In dealing with the reactions of oxygen with the ethyl, propyl and the more complex radicals, the possible ozone forming reactions, generalized by 24, are less likely to be important than in the case of the methyl radical. As the complexity of the radical increases

$$RO_2 + O_2 \longrightarrow RO + O_3 \qquad (24)$$

there is an increased likelihood of energy transfer within the molecule, so that the probability is lowered that the energy which is released as the reaction, $R + O_2 \rightarrow RO_2$, occurs will be available to contribute in an effective manner to the formation of the transition state leading to the ozone forming reaction. In gas or liquid phase studies of oxygen-poor systems at 25°, reaction 24 should

---

(15) P. George and A. Robertson, *Trans. Faraday Soc.*, **42**, 217 (1946); F. S. Dainton, *ibid.*, 223 (1946); C. C. Schubert, S. J., and R. N. Pease, *J. Chem. Phys.*, **24**, 919 (1956); C. C. Schubert, S. J., and R. N. Pease, *J. Am. Chem. Soc.*, **78**, 2044 (1956); E. R. Stephens, P. L. Hanst, R. C. Doerr and W. E. Scott, *Ind. Eng. Chem.*, **48**, 1498 (1956); R. P. Taylor and F. E. Blacet, *ibid.*, **48**, 1505 (1956).

(16) M. Shahin, A. R. Blake and K. O. Kutschke, paper presented at the symposium on air pollution, 138th National Meeting of the American Chemical Society, New York, September, 1960; M. Shahin and K. O. Kutschke, *J. Phys. Chem.*, **65**, 189 (1961).

(17) P. Gray, *Trans. Faraday Soc.*, **55**, 408 (1959); P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959); W. M. D. Bryant, *J. Polymer Sci.*, **6**, 359 (1951); "Selected Values of Chemical Thermodynamic Properties," Circular of National Bureau of Standards, 500; W. Pritzkow and K. A. Müller, *Chem. Ber.*, **89**, 2318 (1956); the approximate enthalpies of formation (kcal./mole) for the gaseous molecules or radicals at 25° which are used in deriving Fig. 3 and throughout this paper are: CH_3OH, −48.1; CH_2O, −27.7; CH_3O_2H, −31 ± 4; HCO_2H, −86.7; O_3, 34; H, 52.1; O, 59.2; OH, 8.9; CH_3, 32 ± 1; CH_3O, −0.5 ± 3; CH_3O_2, 7 ± 5; CH_2O_2 (diradical), 53 ± 6; CH_2-OH, −2 ± 4.

(18) Discussions of one of the authors with Professors S. A. Benson (Univ. Southern Calif.) and H. S. Johnston (Univ. Calif.), Air Pollution Foundation meeting, San Marino, California, 1959.

be unimportant. Under these conditions it is likely that the $CH_3O_2^{\neq}$ or $RO_2^{\neq}$ will react either to abstract an H-atom in an early collision after formation or it will be thermallized by collisions before a suitable encounter with O_2 can occur. Once the CH_3O_2 or RO_2 radical has been thermallized, an activation energy greater than 25 kcal. would be required to form ozone by reactions 21 or 24; this is so large an energy as to make the reactions unimportant at room temperature. On the other hand the reverse of reactions 21 and 24, that is the reaction of ozone with an alkoxyl radical to form an alkylperoxyl radical and oxygen, is about 25 kcal. exothermic; if ozone is formed in the system by any path whatsoever, it should be rapidly removed, not only by reaction with alkyl free radidals (analogs to 22), but by reaction with alkoxyl radicals as well. Thus a very low stationary concentration of ozone would be quickly established.

There seems to be substantial evidence which supports the disproportionation reaction 5 in the photoöxidation of azomethane at room temperature.[2,3] The rather analogous disproportionation reaction 11 may also occur, and 11 may be followed by 13 and 23. Some evidence in this regard has been cited in the formic acid mechanism discussion above. The high exothermicity of these reactions suggests a low activation energy and their possible importance. Obviously some reliable estimates of the ozone concentrations in these systems under different conditions must be determined before a realistic evaluation of mechanisms can be made. A suitable method for such measurements has not yet been devised by these authors.

Acknowledgments.—The authors gratefully acknowledge the support of this work by the United States Public Health Service, National Institutes of Health, Bethesda, Maryland. We also wish to thank Drs. K. O. Kutschke and R. J. Cvetanovic (National Research Council, Ottawa), Dr. M. H. J. Wijnen (Mellon Institute), Professor S. A. Benson (Univ. Southern California) and Professor H. S. Johnston (Univ. California) for their helpful discussions related to various aspects of this work.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UTAH STATE UNIVERSITY, LOGAN, UTAH]

The Quenching Effect of Naphthalene on the Photoreduction of Benzophenone

BY WILLIAM M. MOORE AND MARSHALL KETCHUM

RECEIVED OCTOBER 18, 1961

Quantum yield determinations on the photoreduction of benzophenone have been used as a method of evaluating the efficiency of the triplet to triplet energy transfer between benzophenone and naphthalene. The ratio of the quenching rate constant to the reaction rate constant has been determined by two methods: benzhydrol concentration as a variable; naphthalene concentration as a variable. Naphthalene quenches photo-excited benzophenone as efficiently as oxygen and other paramagnetic molecules. The evidence indicates that the triplet to triplet energy transfer process must be diffusion controlled and gives additional support to the postulate that the triplet state is the chemically reactive state of benzophenone. A novel method of actinometry involving the limiting quantum yield of benzophenone is demonstrated.

The photochemistry of benzophenone in solution has been studied extensively.[1-3] Evidence has been accumulated to show that the triplet is the chemically reactive excited state[1] and that the limiting quantum yield for the disappearance of benzophenone is unity. Certain paramagnetic substances quench the triplet state of benzophenone and lower the quantum yield.[1] Oxygen and ferric dipivaloylmethide were found to be efficient quenchers, but aluminum dipivaloylmethide did not alter the photochemical activity. No appreciable quenching of the excited state by benzene, toluene, cumene, isopropanol or benzhydrol has been observed.[1,2]

Terenin and Ermolaev[4] demonstrated that benzophenone could photosensitize the phosphorescence of naphthalene in EPA glass at 77°K. The energy transfer process was such that the sensitized phosphorescence was more efficient than the normally induced phosphorescence. Simultaneously, the benzophenone phosphorescence was quenched. These workers suggested that a triplet to triplet energy transfer (with total spin conservation) was the mechanism for the process. The excited singlet state of naphthalene lies at a higher energy level than that of the excited singlet of benzophenone, but the triplet of naphthalene lies at a lower energy level than that of benzophenone. They postulated that energetically favorable triplet to triplet transfers might be of a general nature, and they illustrated several cases. Using biacetyl and benzil, which show phosphorescence under these conditions, Bäckström and Sandros[5] have found the same effect in solution at room temperature.

Recently, Farmer, Gardner and McDowell,[6] using electron spin resonance, demonstrated that the triplet state of naphthalene could be induced with photo-excited benzophenone. This work was done in EPA glass at 77°K. Porter[7] has mentioned studies involving flash photolysis techniques in which the triplet state of naphthalene was produced by benzophenone photosensitization.

---

[1] W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

[2] G. S. Hammond, W. P. Baker and W. M. Moore, *ibid.*, **83**, 2795 (1961).

[3] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, *ibid.*, **81**, 1068 (1959).

[4] A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, **52**, 1042 (1956).

[5] H. L. J. Bäckström and K. Sandros, *Acta. Chem. Scand.*, **14**, 48 (1960).

[6] J. B. Farmer, C. L. Gardner and C. A. McDowell, *J. Chem. Phys.*, **34**, 1058 (1961).

[7] G. Porter, *Proc. Chem. Soc.*, 291 (1959).