obtained, suggesting that the complex had an average composition intermediate between $\underset{*}{C}H{=}\underset{*}{C}H$ and $\underset{*}{C}H_2\underset{*}{C}H_2$, or alternatively $\underset{*}{C}H{=}\underset{*}{C}H_2$. At about 20°, the value of *n* had fallen to 1, in agreement with the result of Jenkins and Rideal[5] whose work on films at this temperature yielded a H/C ratio of unity in the surface residues. On this basis these authors, and also Beeck,[2] suggested the presence of acetylenic residues $\underset{*}{C}H{=}\underset{*}{C}H$ and hence evidence for the dissociative mechanism of ethylene chemisorption. However, as Eischens[7] has pointed out, it is perfectly possible for the surface complex to have an average composition of about (C_1H_1) and still be almost completely saturated if each carbon is bonded to more than one nickel atom. Infrared evidence has added support to the dissociative mechanism on a bare nickel surface, but the present work indicates that the resultant surface complex probably did not have a specific stoichiometric composition, the value of *n* falling continuously with increasing temperature as hydrogen was progressively removed from the surface.

Acknowledgments.—The author is indebted to Drs. E. J. Cairns, J. L. Holman and W. T. Grubb for many helpful discussions during the course of this investigation.

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

The Mechanism of Methyl Hydroperoxide Formation in the Photooxidation of Azomethane at 25°

BY N. R. SUBBARATNAM AND J. G. CALVERT

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Long-path infrared spectrometry has been used to follow the rates of formation of methyl hydroperoxide in the photoöxidation of azomethane in oxygen-rich mixtures at 25°. The rates of formation of CH_3O_2H and/or CD_3O_2D were determined in a series of experiments with varied $[O_2]$, with added C_2F_6, with mixtures of $CD_3N_2CD_3$–O_2, $CH_3N_2CH_3$–$CD_3N_2CD_3$–O_2, and in azomethane–O_2 mixtures with formaldehyde and acetaldehyde. The data prove the unimportance of the H-abstraction reaction, $CH_3O_2 + RH \rightarrow CH_3O_2H + R$, in oxygen-rich atmospheres at 25°; they are consistent with the formation of methyl hydroperoxide in the disproportionation reaction, $CH_3O_2 + CH_3O \rightarrow CH_3O_2H + CH_2O$.

In recent years considerable interest has developed in the mechanism of the room temperature oxidation of alkyl free radicals. The reactions of free radicals in oxygen-rich atmospheres are of special concern to the air pollution area.[1] A number of quantitative studies of the reactions of the simplest alkyl free radical, methyl, with oxygen have been made, and even in this simplest system there is considerable uncertainty as to the mechanism which is operative. Data from many laboratories suggest that the first step in the reaction sequence is the formation of an energy-rich methylperoxyl radical.[2-4] The third-order kinetics

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

of the reaction between the methyl radical and oxygen in the usual pressure region suggests the establishment of an equilibrium between the energy-rich radical, $CH_3O_2^{\ddagger}$, and its dissociation products in 1.

Although most researchers would agree that CH_3O_2 is the initial product of the methyl radical-oxygen interaction at room temperature, there is little agreement as to the fate of this radical.[5-17] Calvert and co-workers contend that the major primary products of the methyl radical reactions in oxygen-rich media at 25° are methanol and formaldehyde, formed in approximately equal amounts.[14] Kutschke and co-workers question this contention; they have recently detected (by mass spectrometry) methyl hydroperoxide among the products of the photoöxidation of azomethane under conditions similar to those used by Calvert and co-workers; they believe that methyl hydroperoxide may be the major primary product under certain conditions.[16] Subbaratnam and Calvert[17] have confirmed the identification of methyl hydroperoxide in these systems using long-path infrared techniques, but under their conditions, oxygen-rich atmosphere at 25°, it is a minor product. They

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(1) P. A. Leighton and W. A. Perkins, *Air Pollution Foundation Rept.* 14, Rept. 15, 1956; Rept. 24, 1958, San Marino, California.

(2) D. E. Hoare and A. D. Walsh, *Trans. Faraday Soc.*, **53**, 1102 (1957).

(3) M. I. Christie, *Proc. Roy. Soc.* (*London*), **A244**, 411 (1958).

(4) W. C. Sleppy and J. G. Calvert, *J. Am. Chem. Soc.*, **81**, 769 (1959).

(5) A. D. Walsh, *Trans. Faraday Soc.*, **43**, 297 (1947); D. Lewis and G. von Elbe, "Combustion, Flames and Explosions," Academic Press, Inc., New York, N. Y., 1951.

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

(7) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold and W. E. Vaughan, *Discussions Faraday Soc.*, **10**, 242 (1951).

(8) F. B. Marcotte and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **74**, 783 (1952).

(9) G. R. Hoey and K. O. Kutschke, *Can. J. Chem.*, **33**, 496 (1955).

(10) By analogy with the mechanism suggested for more complex radicals in solution by G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

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

(12) R. L. Strong and K. O. Kutschke, *Can. J. Chem.*, **37**, 1456 (1959).

(13) F. Wenger and K. O. Kutschke, *ibid.*, 1546 (1959).

(14) D. F. Dever, Ph.D. thesis, Ohio State University, Columbus 10, Department of Chemistry, 1959; to be submitted for publication.

(15) M. Shahin, A. R. Blake and K. O. Kutschke, paper presented at the symposium on air pollution, 138th National Meeting of the Am. Chem. Soc., New York, Sept. 1960.

(16) M. Shahin and K. O. Kutschke, *J. Phys. Chem.*, **65**, 2277 (1961).

(17) N. R. Subbaratnam and J. G. Calvert, in "Chemical Reactions in the Upper and Lower Atmosphere," Interscience Publishers, New York, N. Y., 1961, pp. 109-128.

found that the rate of methyl hydroperoxide formation followed the simple rate law 2 over a wide range of azomethane pressures (all less than 0.44 mm.). The rate was unaffected by the presence of added acetaldehyde up to 1.2 mm. In view

$$R_{CH_3O_2H} = aI_a \qquad (2)$$

of these results Subbaratnam and Calvert concluded that the formation of methyl hydroperoxide in the CH_3–O_2 reaction system for O_2-rich media at 25° does not involve the commonly proposed reaction 3 of thermally equilibrated methylperoxyl radicals. The observed rate data suggested that

$$CH_3O_2 + RH \longrightarrow CH_3O_2H + R \qquad (3)$$

it was formed either in a reaction involving nonthermally equilibrated methylperoxyl radicals and some source of abstractable H-atoms as in 4, or in a reaction of disproportionation between two radicals as in 5 or 6.

$$CH_3O_2^{\ddagger} + RH \longrightarrow CH_3O_2H + R \qquad (4)$$

$$2CH_3O_2 \longrightarrow CH_3O_2H + CH_2O_2 \text{ (or } CH_2O + O) \qquad (5)$$

$$CH_3O_2 + CH_3O \longrightarrow CH_3O_2H + CH_2O \qquad (6)$$

The present work was planned to differentiate between alternative mechanism of methyl hydroperoxide formation. Considerable progress toward this end is reported here.

Experimental

Materials.—Azomethane was prepared and purified by the method described by Renaud and Leitch.[18] A sample of azomethane-d_6 (99% atomic purity) was given to us by Dr. L. C. Leitch of the Pure Chemistry Division of the National Research Council, Ottawa, Canada. Methyl hydroperoxide was prepared by Miss Sue Feil (present address, Department of Chemistry, University of North Carolina) according to the procedures of Eggersglüss.[19] Acetaldehyde was taken as a volatile fraction from the Eastman white label product. C_2F_6 was provided by the Polychemicals Department, E. I. du Pont de N. & Co., Wilmington, Delaware. Formaldehyde monomer was generated from the Eastman white label paraformaldehyde and CD_2O from the $(CD_2O)_n$ polymer (99% atomic purity) of Merck and Co. Limited, Montreal, Que., using the technique of Spence and Wild.[20] Commercial research-grade oxygen and nitrogen gases were used throughout the study without further purification.

Equipment.—The reaction between methyl radicals and oxygen was initiated in a 70-liter Pyrex tank, about 115 cm. in length, which enclosed the multiple-reflection system of a commercial Perkin-Elmer 40-meter long-path infrared spectrophotometer. The original porous flat-black finish provided on the metal parts within the cell housing was found to be quite reactive to ozone, etc., and was removed by buffing all the metal parts; the parts were then painted with a silver-grey commercial auto enamel and then baked. The resulting hard, bright surface was very inert; methyl hydroperoxide and other reactive gases were quite stable in contact with it.[17] Along the top of the glass tank, three 550-watt Hanovia type A burners (S-500) were arranged with equal spacing within a Pyrex, water-cooled condenser. An aluminum reflector was secured above the lamps to concentrate the radiation into the tank volume. A removable, slotted aluminum metal shield surrounded the glass tank and served as a light shutter. The nature of the emission from the lamps coupled with the absorption of the Pyrex condenser and the Pyrex tank limited the effective radiation to the 3660 Å. region near the absorption maximum of azomethane. The glass tank was connected at the top of one end by means of a large stopcock to the vacuum line and introduction system. At the opposite end of the tank and near its bottom there was a second stopcock which allowed flushing of vapors out of the tank into a trap when desired. The open end of the glass tank had a flat, ground surface which made a reasonably good vacuum seal when it was drawn up against a gasket and the metal housing of the instrument by means of a metal collar. The majority of the weight of the tank was supported by a metal frame situated beneath the tank and near its center of gravity.

Experimental Procedure.—Measured pressures of azomethane in the introduction system were expanded into the evacuated glass tank which effected a calculable dilution; the desired atmosphere of oxygen, nitrogen, acetaldehyde, formaldehyde or C_2F_6 was added, and a waiting period of 15 min. was allowed to ensure homogeneity of the mixture and suitable warm-up for the lamps. In the usual experiments in this study a continuous irradiation of the selected mixture was made; the infrared spectrum of the desired region was scanned at measured intervals using a 20-m. path-length setting and the desired scale expansion. In most of the runs herein reported we have followed only CH_3O_2H formation by observation of the characteristic band the Q-branch of which is centered at 12.2μ.[17] Associated with this "spike" of rather large extinction coefficient are P- and R-branches with smaller extinction coefficients, centering at 12.0 and 12.38μ, respectively. There remains some uncertainty in the estimates which we have made in the absolute extinction coefficient of the methyl hydroperoxide because of the highly reactive nature of the peroxide and the difficulties associated with the introduction of known amounts of the standard substance. For this reason we have presented all of the rate data in units of log (I_0/I) measured for the spike length at 12.2μ. CH_3O_2H absorption follows Beer's law within the error of the experimental measurements using this technique. We believe that most reliable estimates of the extinction coefficient for CH_3O_2H were obtained in our experiments carried out in the following fashion. A sample of the standard hydroperoxide was introduced, nitrogen gas was added to make the total pressure equal to that of the atmosphere and the absorption at 12.2μ determined. Nitrogen gas was flushed through the tank containing the hydroperoxide and into two gas scrubbers containing KI solutions. The flushing was continued for a few minutes until the absorption at 12.2μ was lowered an easily measureable amount. The moles of peroxide which were removed and effected the measured lowering in the 12.2-μ absorption were then determined by titration of the liberated iodine in the scrubbing flasks using a standard $Na_2S_2O_3$ solution. These data suggest that about 5% of the methyl radicals formed in our systems reacted to give CH_3O_2H. Other methods based on pressure measurement of standard samples of CH_3O_2H gave results in general agreement with this estimate.

Results and Discussion

Three possible alternative mechanisms of methyl hydroperoxide formation have been suggested by Subbaratnam and Calvert in explanation of azomethane photooxidation at 25° in an oxygen-rich atmospheres.

Possible Mechanism I.

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

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

$$CH_3O_2^{\ddagger} + RH \longrightarrow CH_3O_2H + R \qquad (4)$$

$$CH_3O_2^{\ddagger} + M \longrightarrow CH_3O_2 + M' \qquad (7)$$

$$2CH_3O_2 \longrightarrow 2CH_3O + O_2 \qquad (8)$$

$$2CH_3O \longrightarrow CH_2O + CH_3OH \qquad (9)$$

The theoretically expected rate law for this mechanism choice is 10.

$$R_{CH_3O_2H} = [RH]2I_a\phi_1k_4/([M]k_7 + [RH]k_4) \qquad (10)$$

Possible Mechanism II.—Combine I, 1, 7 above with 11 and 5

$$2CH_3O_2 \longrightarrow CH_3OH + CH_2O + O_2 \qquad (11)$$

$$2CH_3O_2 \longrightarrow CH_3O_2H + CH_2O_2 \text{ (or } CH_2O + O) \qquad (5)$$

The expected rate law for this case is

$$R_{CH_3O_2H} = I_a\phi_1k_5(k_5 + k_{11}) \qquad (12)$$

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(18) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

(19) W. Eggersglüss, *Monograph. Angew. Chem. u. Chem. Ing. Tech.*, No. **61**, 68 (1951).

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

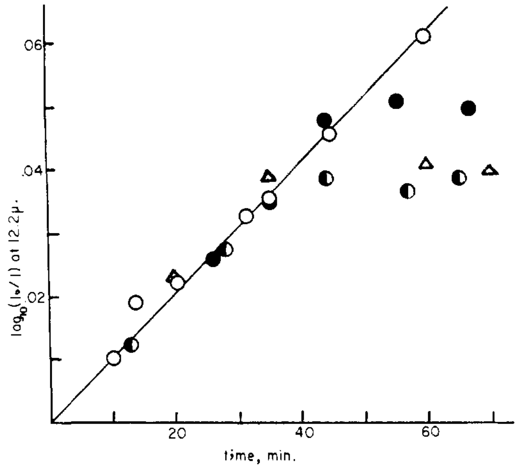

Fig. 1.—Methyl hydroperoxide formation in the photooxidation of $CH_3N_2CH_3$ at 25°: ○ 0.43 mm. $CH_3N_2CH_3$, 740 mm. O_2; △ 0.44 mm. $CH_3N_2CH_3$, 26 mm. O_2, 714 mm. N_2; ◐ 0.44 mm. $CH_3N_2CH_3$, 19 mm. O_2, 720 mm. N_2; ● 0.44 mm. $CH_3N_2CH_3$, 737 mm. O_2, 3.0 mm. C_2F_6; the spike length of the characteristic 12.2μ band was used to determine the ordinate in each experiment.

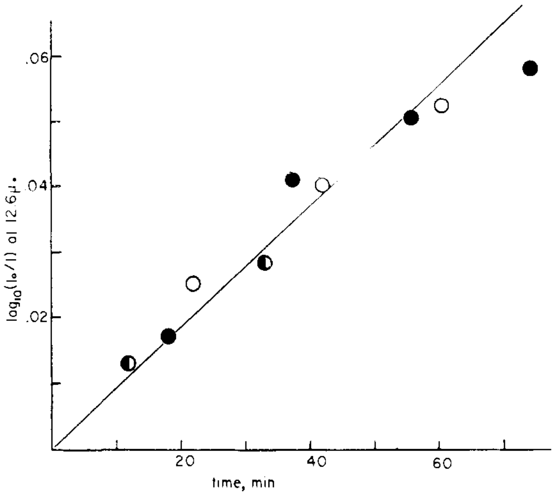

Fig. 2.—CD_3O_2D formation in the photoöxidation of $CD_3N_2CD_3$ and mixtures of $CD_3N_2CD_3$ and CH_3CHO at 25°: ○ 0.44 mm. $CD_3N_2CD_3$, 740 mm. O_2; ◐ 0.44 mm. $CD_3N_2CD_3$, 0.44 mm. CH_3CHO, 740 mm. O_2; ● 0.44 mm. $CD_3N_2CD_3$, 1.66 mm. CH_3CHO, 740 mm. O_2; the characteristic 12.6μ band was used to determine the ordinate in each experiment.

Possible Mechanism III.—Combine I, 1, 7, 8 and 9 above with 6

$$CH_3O + CH_3O_2 \longrightarrow CH_2O + CH_3O_2H \qquad (6)$$

The expected rate law is of the form, $R_{CH_3O_2H} = 2I_a\phi_1F$, where F is a complex function of the rate constants k_8, k_9 and k_6.[17]

The theoretical rate laws for the possible mechanisms II and III are in accord with the experimental law 2; that for mechanism I is also consistent if RH is very much more effective than O_2 as M in reaction 7. Mechanism I would also be consistent with the observed rate law if the methyl hydroperoxide were the major product, *i.e.*, if $k_4[RH] > k_7[O_2] + k_7''[RH]$; this is not the case in our oxygen-rich system. Under these conditions relation 10 reduces to the form, $R_{CH_3O_2H} = 2I_a\phi_1(k_4/k_7)$. The choice of mechanism of conversion of CH_3O_2 to CH_3O is not critical to the form of the rate law for each mechanism. The rather conventional sequence suggested by Rust, *et al.*,[6,7] has been used for mechanisms I and III. The use of the Russell mechanism[10] for direct formation of CH_3OH and CH_2O in reaction 11 of mechanism II is also rather arbitrary but avoids complication of the possible reactions of the CH_3O radical. Until unambiguous evidence of the exact nature of $CH_3O_2 \rightarrow CH_3O$ conversion schemes is had, the choice of the simplest mechanism to explain the results seems advisable.

Test of the Excited Radical Mechanism I.—Our first experiments were designed to test for the variation of rate of methyl hydroperoxide formation with the concentration and nature of the deactivating body M of reaction 7, as demanded by the "excited" radical mechanism I. The effects of varied $[O_2]$ and added C_2F_6 on the rate of formation of methyl hydroperoxide in azomethane photooxidation experiments at 25° are shown in Fig. 1. In runs with exposures up to 40 min. it is seen that there is no significant variation of $R_{CH_3O_2H}$ in experiments with varied $[O_2]$.[21] Only if the conditions, $[O_2]k_7 \cong [N_2]k_7$, and $[O_2]k_7 + [N_2]k_7' << [RH]k_7''$, are met is this observation in accord with the operation of mechanism I. It would be most surprising if azomethane (RH in our experiments) is so much more effective than O_2 and N_2 as M in 7, since $([O_2] + [N_2])/[RH] = 1.7 \times 10^3$ in these runs. The result is in accord with mechanisms II and III, where no effect of $[O_2]$ on $R_{CH_3O_2H}$ is expected.

The experiments with added C_2F_6 gas shown in Fig. 1 compound the evidence against the importance of mechanism I. C_2F_6 should be an effective M for $CH_3O_2^{\ddagger}$ deactivation, and it has no abstractable H-atoms, so it cannot participate in 4. If I were operative the addition of C_2F_6 should lower detectably the rate of hydroperoxide formation; this is not the case.

Evidence of the Mechanism of Methyl Hydroperoxide Formation from Deuterium Labeling Experiments. (a) The Photolysis of $CD_3N_2CD_3$ in Oxygen-rich Media at 25°.—The major products of the reaction are CD_3OD and CD_2O.[22] The characteristic band centered at 12.2μ[17] in the infrared absorption spectrum of CH_3O_2H is missing in the product spectrum from $CD_3N_2CD_3$–O_2 mixture photolyses, and a new band centered at 12.6μ appears. This is not a wave length associated with the major products, CD_2O, CD_3OD or

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(21) After a 40 min. run, 20% of the original azomethane has been photoöxidized; reactions involving the primary products are likely with such extensive conversions. The useful data for our purposes are from the early stages of the reaction. Certainly no realistic attempt can be made to interpret the differences in the fall off of rate at high conversions. The eventual importance of the rate of destruction of CH_3O_2H by the reaction, $CH_3O + CH_3O_2H \rightarrow CH_3OH + CH_3O_2$, with the establishment of a "steady state" concentration of CH_3O_2H, seems likely. Why this concentration would vary with $[O_2]$ and added C_2F_6 remains unexplained.

(22) The characteristic peaks of CD_3OD are present with large absorption (M. Falk and E. Whalley, *J. Chem. Phys.*, **34**, 1554 (1961), but since a standard sample of this compound was not available to us, a mass balance of the products could not be determined.

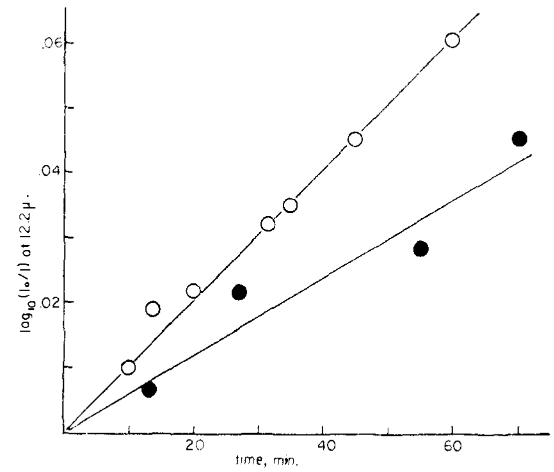

Fig. 3.—CH_3O_2H formation in the photooxidation of $CH_3N_2CH_3$ and in $CH_3N_2CH_3$–$CD_3N_2CD_3$ mixtures at 25°: ○ 0.43 mm. $CH_3N_2CH_3$, 740 mm. O_2; ● 0.44 mm. $CH_3N_2CH_3$, 0.44 mm. $CD_3N_2CD_3$, 740 mm. O_2; the spike length of the 12.2 μ band was used to determine the ordinate in each experiment; the majority of this absorption should be due to CH_3O_2H, with only minor contributions from CH_3O_2D and CD_3O_2H.

the starting material $CD_3N_2CD_3$, and it seems likely in view of the magnitude of the isotopic shift involved that it corresponds to the hydroperoxide, CD_3O_2D. If one considers the 12.2μ band to be associated with the Hooke's law vibration of essentially rigid CH_3O- and -OH groups about the O–O bond, then he would predict that the corresponding vibration in CD_3O_2D would center at about 12.6μ, the observed center of the new band in the $CD_3N_2CD_3$ photoöxidation products. These results confirm that the 12.2μ band in CH_3O_2H is associated with a fundamental stretching vibration about the O–O bond as has been suggested for organic hydroperoxides[23] and peroxyacids.[24]

In Fig. 2 CD_3O_2D rate data are shown for several experiments involving the photooxidation of $CD_3N_2CD_3$. The open circles are data for runs with 0.44 mm. of pure $CD_3N_2CD_3$ in O_2; the half-darkened and darkened circles are data in similar runs but with added amounts (0.44 and 1.66 mm.) of CH_3CHO. The rates of CD_3O_2D formation are the same in all experiments within our experimental error. This is most striking evidence of the mechanism of formation of the hydroperoxide and confirms the unimportance of the possible mechanism I. Either mechanisms II or III would be consistent with these findings.

(b) The Photooxidation of $CH_3N_2CH_3$–$CD_3N_2CD_3$ Mixtures at 25°.—In the photolysis of $CD_3N_2CD_3$–$CH_3N_2CH_3$ mixtures in oxygen at 25°, the major products are CH_3OH, CH_3OD, CD_3OH, CD_3OD, CH_2O and CD_2O. Smaller peaks attributable to the four possible isotopic hydroperoxides are also observed. The absorption at 12.2μ, largely due to CH_3O_2H, is shown as a function of time for the photooxidation of pure $CH_3N_2CH_3$ and a mixture of $CH_3N_2CH_3$ and $CD_3N_2CD_3$ in Fig. 3. The rate is lowered in the mixture photolysis. This result rules out the possible formation of the hydroperoxide product by direct interaction of an excited azomethane molecule and oxygen, but the observations are consistent with the occurrence of possible mechanisms II or III. The absorption coefficients of $CD_3N_2CD_3$ and $CH_3N_2CH_3$ are near equal at 3660 Å., so one expects approximately equal rates of formation of the CH_3O_2 and CD_3O_2 radicals in the experiment with the mixture of azomethanes. Furthermore, the rate of formation of CH_3O_2 in the pure $CH_3N_2CH_3$ experiment and in the mixture experiment should be near equal. Thus if one assumes an equality of rates of 5 and 6 for the different isotopic species and a completely random disproportionation of methylperoxy and methoxy radicals occurs, either by mechanism II or III, we would expect near equal amounts of CH_3O_2H, CH_3O_2D, CD_3O_2H and CD_3O_2D to be formed; since the CH_3O_2 radicals must divide themselves between CH_3O_2H and CH_3O_2D, it follows that we expect that the rate of CH_3O_2H formation in the mixture photolysis will be about one-half the rate of CH_3O_2H formation in the pure $CH_3N_2CH_3$ experiment. At any given time the observed extinction at 12.2μ for the mixture run is somewhat higher than one-half that for the pure $CH_3N_2CH_3$ experiment. This is likely a consequence of small differences in k_5 and k_6 for different isotopic species, and/or some overlap of the weak P-branches of the CH_3O_2D (expected at 12.22μ) and CD_3O_2H (expected at 12.20μ) with the more intense Q-branch of the CH_3O_2H (12.2μ). No quantitative check is possible since standard samples of the deuterated hydroperoxides are not available.

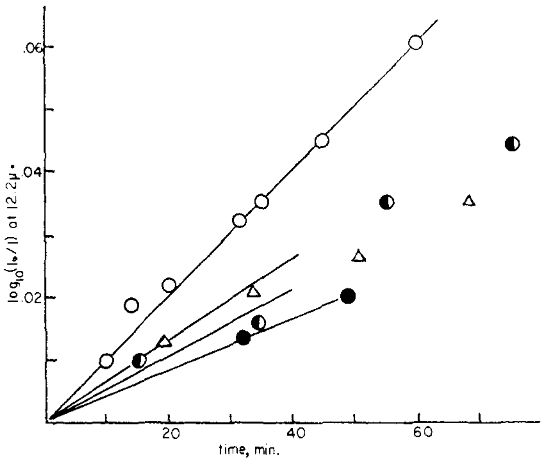

Fig. 4.—CH_3O_2H formation in the photooxidation of $CH_3N_2CH_3$ and in $CH_3N_2CH_3$–CD_2O mixtures at 25°: ○ 0.43 mm. $CH_3N_2CH_3$, 740 mm. O_2; △ 0.44 mm. $CH_3N_2CH_3$, 0.084 mm. CD_2O, 740 mm. O_2; ◐ 0.43 mm. $CH_3N_2CH_3$, 0.13 mm. CD_2O, 740 mm. O_2; ● 0.44 mm. $CH_3N_2CH_3$, 0.32 mm. CD_2O, 739 mm. O_2; the spike length of the 12.2 μ band was used to determine the ordinate in each experiment.

(c) Evidence of the Mechanism of Methyl Hydroperoxide Formation from Experiments with Added Formaldehyde.—An interesting and rather unexpected result was obtained in azomethane photoöxidation experiments with added formalde-

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[23] G. J. Minkoff, *Proc. Roy. Soc. (London)*, **A224**, 176 (1954).

[24] P. A. Giguère, *Can. J. Chem.*, **30**, 821 (1952).

hyde vapor. The data from these experiments are summarized in Fig. 4. It is seen that the addition of increasing amounts of CD_2O to the $CH_3N_2CH_3$–O_2 mixtures decreases the rate of formation of CH_3O_2H, while CH_3O_2D is not observed among the products. The same effect is seen in the data of Fig. 5 which graphs $R_{CH_3O_2H}$ in experiments with $CH_3N_2CH_3$–CH_2O mixtures. The decrease in the rate of formation of the methyl hydroperoxide is not the result of a reaction between formaldehyde and methyl hydroperoxide.[25] The slow, first-order rate of decay of CH_3O_2H in the long-path system is unaffected by the addition of formaldehyde vapor in the amount added in experiments of Figs. 4 and 5.

The results are explained satisfactorily in terms of the suggested mechanism III. It seems likely that the influence of the formaldehyde addition on the rate of CH_3O_2H formation is related to the removal of CH_3O radicals by the reaction 13. If

$$CH_3O + CH_2O \longrightarrow CH_3OH + CHO \quad (13)$$

the $CHOO_2$ radical, the likely major primary product of CHO in O_2, and its subsequent reaction products (possibly CO_2 and OH by analogy with CH_3COO_2)[26] are poorer sources of abstractable H-atoms than the CH_3O radical, then the rate of formation of CH_3O_2H would be lowered in experiments with added formaldehyde. There is no similar simple explanation of the formaldehyde effect which the authors could derive involving the possible mechanism II. The choice of mechanism III is also favored from energy considerations. The energetics of reaction 5 are a matter of speculation, but "reasonable" guesses at these quantities suggest that reaction 5 may have a finite activation energy, and hence it may be expected to be unimportant at room temperature.

The difference between the effects of added acetaldehyde and formaldehyde on the rates of methyl peroxide formation is somewhat surprising. The rate constants for the reaction of H-abstraction from CH_2O and CH_3CHO by CH_3 radicals are near equal at 25°,[27] although the data are not sufficiently accurate to show small differences. One would expect even less selectivity for the more reactive CH_3O radicals than that shown by CH_3 in H-abstraction reactions. However, if $k_{13} \leq 10k_{14}$ at 25° the observed difference in effects of added CH_2O and CH_3CHO can be explained.

$$CH_3O + CH_3CHO \longrightarrow CH_3OH + CH_3CO \quad (14)$$

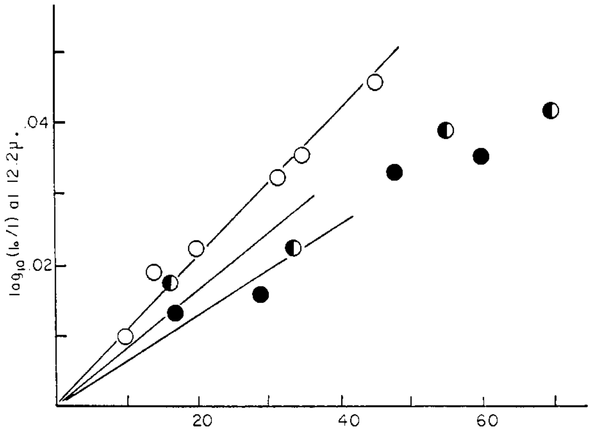

Fig. 5.—CH_3O_2H formation in the photooxidation of $CH_3N_2CH_3$ and in $CH_3N_2CH_3$–CH_2O mixtures at 25°: ○ 0.44 mm. $CH_3N_2CH_3$, 740 mm. O_2; ◐ 0.44 mm. $CH_3N_2CH_3$, 0.19 mm. CH_2O, 740 mm. O_2; ● 0.44 mm. $CH_3N_2CH_3$, 0.38 mm. CH_2O, 740 mm. O_2; the spike length of the 12.2 μ band was used to determine the ordinate in each experiment.

An alternative explanation of the difference lies in the character of the chain carrier for the oxidation of the two aldehydes. Peroxyacetic acid is not an observable product of the runs with added acetaldehyde, however the formation of small amounts of CO_2 in runs with added acetaldehyde may indicate some radical attack on acetaldehyde. At the low pressures of acetaldehyde used here, the major products of the photooxidation of acetaldehyde are CO_2 and CH_3OH.[26] When methoxy radicals react with acetaldehyde, they are likely regenerated in the subsequent rapid chain steps.

$$CH_3O + CH_3CHO \longrightarrow CH_3OH + CH_3CO \quad (14)$$

$$CH_3CO + O_2 \longrightarrow CH_3COO_2 \quad (15)$$

$$CH_3COO_2 \longrightarrow CH_3O + CO_2 \quad (16)$$

One could argue that the steady state of $[CH_3O]$ may not be greatly disturbed in experiments with added small quantities of acetaldehyde. While in the case of formaldehyde addition, the regeneration of CH_3O radicals from the products of 13 is unlikely. However, the occurrence of the reactions 14–16 in the runs with $CD_3N_2CD_3$–CH_3CHO mixtures would lead to the isotopic species CD_3O_2H. Since this is not the case, the first explanation of the difference in acetaldehyde and formaldehyde effects, namely, $k_{13} > k_{14}$, is favored by the results.[28]

Conclusions.—All of the results concerned with the formation of methyl hydroperoxide prove the unimportance of the H-atom abstraction reactions of vibrationally excited or thermally equilibrated CH_3O_2 radicals in O_2-rich media at 25°. The data are consistent with the methyl hydroperoxide formation in the disproportionation reaction 6.

$$CH_3O_2 + CH_3O \longrightarrow CH_3O_2H + CH_2O \quad (6)$$

Sufficient data are not at hand to establish the details of the mechanism of $CH_3O_2 \rightarrow CH_3O$ conversion. The conventional mechanism of Raley, *et al.*,[6,7] has been used in our considerations here, but other mechanisms of transformation with such inovations as the formation of the intermediate ozone[11] would also be in accord with the present findings. Further work concerning this phase of the reaction mechanism is needed to decide among several alternatives.

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[25] The possibility of a gas phase reaction between formaldehyde and methyl hydroperoxide is suggested since the reaction, $t\text{-BuO}_2\text{H} + \text{CH}_2\text{O} \rightarrow t\text{-BuO}_2\text{CH}_2\text{OH}$, has been observed in solution; C. C. Schubert, S. J., and R. N. Pease, *J. Am. Chem. Soc.*, **78**, 5553 (1956).

[26] J. G. Calvert and P. L. Hanst, *Can. J. Chem.*, **37**, 1671 (1959).

[27] S. Toby and K. O. Kutschke, *ibid.*, **37**, 672 (1959); D. H. Volman and R. K. Brinton, *J. Chem. Phys.*, **20**, 1764 (1952); P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **32**, 593 (1954).

[28] The isotopic distribution of the methanols formed in the tracer experiments was determined in a few runs and is consistent with this conclusion. From one $CH_3N_2CH_3$–CD_2O mixture photolysis the characteristic infrared peaks of CH_3OD were seen at 11.30, 11.53 and 11.82 μ. In one run with a $CD_3N_2CD_3$–CH_3CHO mixture bands of CD_3OH at 11.40 and 11.66 μ were below the detection limit of the equipment.

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[Contribution from the Research and Development Division, Humble Oil and Refining Company, Baytown, Texas]

Reactions of Gaseous Ions. XI. Ionic Reactions in Krypton–Methane and Argon–Methane Mixtures

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In a study of the ionic reactions occurring in a mass spectrometer in argon–methane and krypton–methane mixtures, the ion–molecule reaction products ArH^+, ArC^+, $ArCH_2^+$, $ArCH_3^+$, KrH^+, KrC^+, $KrCH_2^+$ and $KrCH_3^+$ were observed. Charge exchange reactions between rare gas ions and methane were observed with Ar^+ producing CH_2^+ and CH_3^+, and Kr^+ producing CH_3^+ and CH_4^+. The ion-molecule reaction rates are in the order of 10^{-12} to 10^{-11} cc. molecule^{-1} sec.$^{-1}$ while the charge exchange reaction rates are in the order of 10^{-10} to 10^{-9} cc. molecule^{-1} sec.$^{-1}$. No reaction products were observed in a neon–methane mixture.

As an extension of the previously reported study of ion–molecule reactions at high pressure in the mass spectrometer in xenon–methane mixtures,[1] studies were made of the ion–molecule reactions in mixtures of other rare gases and methane. This paper is a report on the reactions observed in argon–methane and krypton–methane mixtures at ionization chamber pressures of 45×10^{-3} to 120×10^{-3} mm.

In the previous paper on xenon–methane mixtures the existence of the ions XeH^+ and $XeCH_n^+$, $n = 0$ to 4 was reported. However, in studies of argon–methane and krypton–methane mixtures only the ions ArH^+, KrH^+, $ArCH_n$ and $KrCH_n^+$, $n = 0$, 2 and 3, were observed. It is possible that a small amount of $KrCH_4^+$ was formed, but the large number of krypton isotopes made it impossible to be sure of its existence. In a study of a neon–methane mixture no ion–molecule reaction products were observed. No study was made of helium–methane mixtures as it would be expected that such a mixture would be less reactive than neon–methane.

Experimental

All measurements were made with the Humble chemical physics mass spectrometer which has been described previously.[2] It is a 12 in. radius of curvature 60° magnetic deflection instrument with conventional means of producing, analyzing and collecting the ions.

The ion source used for these studies comprises an ionization chamber 7.0 mm. in length, planar ion repeller electrodes separated by a 3 mm. gap, and a single drawout electrode between the electron gun filament and the entrance to the ionization chamber. This ion source is a compromise between the two different sources used in the xenon–methane studies.

The gas handling system consists of two reservoirs with gold foil leaks allowing the gases to mix and flow into the ionization chamber. Gas pressures in the ionization chamber (P_s) were determined from pressures (P_m) read on a McLeod gage attached to the gas inlet line to the ionization chamber. $P_s - P_m$ correlations were made by independent experiments as described previously.[1] Studies were made holding the P_s of methane constant and varying the rare gas pressure. In general the methane pressure was held at 60×10^{-3} mm. and rare gas pressure was varied at approximately 5×10^{-3} mm. internals between 0 and 60 $\times 10^{-3}$ mm.

The electron current was usually maintained at 1.0 microamp. Nominal electron voltage for all pressure studies was 70 volts. The field strength in the ionization chamber was 12.5 volts/cm. (ion repeller voltage = 5.0 volts), and the distance from the mid-line of the electron beam to the ion-exit electrode was 2.0 mm.

Appearance potential measurements were used to determine the identities of the reactions yelding the observed product ions. For these studies equal volume mixtures of the rare gas and methane components were maintained at a total P_s of 120×10^{-3} mm. The electron voltage scale was calibrated with the $^{36}Ar^+$ and $^{78}Kr^+$ ions.

The methane used in this work was Phillips Research Grade which has a stated purity of 99.9%. The argon (The Matheson Co.) and krypton (Air Reduction Co.) were found by mass spectroscopic analysis in our laboratories to have less than 1% impurities with the major impurity being H_2O. None of the impurities would offer serious interference in these studies.

Results

A. Observed Ion-molecule Reaction Products.—Tables I and II show portions of typical mass spectra for mixtures of equal parts of rare gas and methane at an ionization chamber pressure of 120×10^{-3} mm. The mass 41 peak in Table I is a combination of ArH^+ and $C_3H_5^+$ formed as a tertiary ion from methane. The intensity of ArH^+ can be obtained by subtracting an estimate of the $C_3H_5^+$ intensity from the measured mass 41 intensity.

Analysis of the spectra of krypton–methane mixtures was made complicated by the existence of the six isotopes of Kr. The observed mass spectra were reduced to monoisotopic spectra by application of the known abundances of Kr isotopes. For example, although I_{99} possibly could contain contributions from three different molecular ions, it was found that $^{83}KrCH_4^+$ and $^{86}KrCH^+$ could be taken as negligibly small in comparison with $^{84}KrCH_3^+$. Therefore, the monoisotopic intensity of $KrCH_3^+$ was obtained by dividing the intensity of the mass 99 peak by the relative percentage of ^{84}Kr isotope in pure krypton.

Partial monoisotopic mass spectra of equal volume rare gas and methane mixtures are given

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[1] F. H. Field and J. L. Franklin, *J. Am. Chem. Soc.*, to be published.

[2] F. H. Field, *ibid.*, **83**, 1523 (1961).