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

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

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

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

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

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

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

Experimental Section

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

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[1] P. J. Sullivan and W. S. Koski, *J. Am. Chem. Soc.*, **85**, 384 (1963).

[2] D. W. Skelly, R. G. Hayes, and W. H. Hamill, *J. Chem. Phys.*, **43**, 2795 (1965).

[3] J. Turkevich and Y. Fujita, *Science*, **152**, 1619 (1966).

[4] H. D. Gesser, B. Garbutt, and A. Cohen, *ibid.*, **154**, 381 (1966).

[5] S. B. Milliken and R. H. Johnsen, *J. Phys. Chem.*, **71**, 2116 (1967).

[6] M. Rogers and L. Kispert, *J. Chem. Phys.*, **46**, 221 (1967).

[7] E. A. Gere, Bell Laboratories, Inc., Murray Hill, N. J., personal communication, 1966.

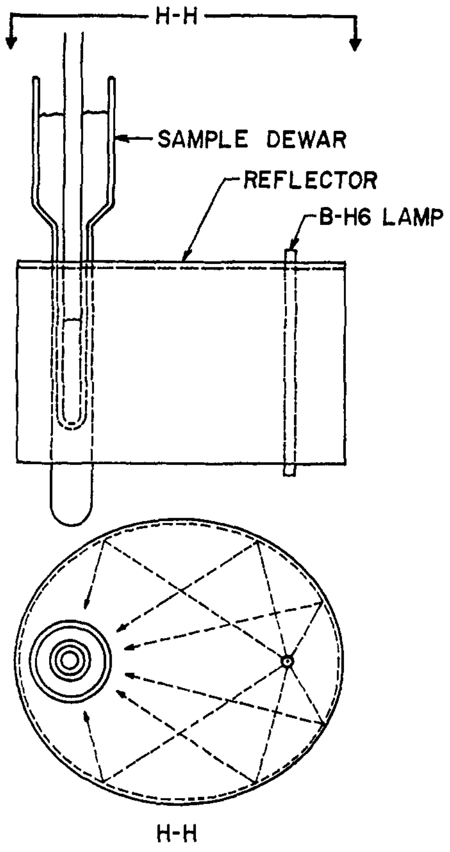

Figure 1. Experimental arrangement for ultraviolet irradiation of samples.

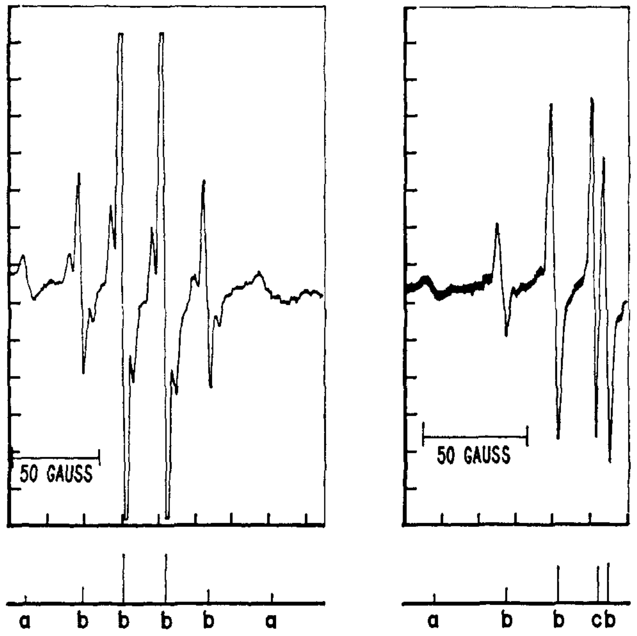

Figure 2. Left trace shows spectrum of 50% methanol sample at a power setting of 3 db below maximum microwave power. Right trace shows spectrum of a 50% methanol sample at a power setting of 8 db below maximum power. In the stick diagram, a represents formyl lines, b the methyl lines, and c the line from the Bell Laboratories standard.

In order to see if the quartz–methanol interface in the sample tube influenced the decay characteristics of the $\cdot CH_3$ radical, a run was made with 80% methanol clear glassy balls.

One 100% methanol sample was degassed by pumping on the sample during successive freezing and melting cycles. This sample was then run in the normal manner.

Results

The kinetic scheme used for the decay of the $\cdot CH_3$ radicals in the methanol–water matrices was

first order $A \xrightarrow{k_1} D$

first order $B \xrightarrow{k_2} B' \xrightarrow{k_1} D$

first order $G \xrightarrow{k_3} G' \xrightarrow{k_1} D$

where D = resultant products.

$$A = A_0e^{-k_1t} \text{ (concentration of } \cdot CH_3 \text{ in state A)}$$

$$B = B_0e^{-k_2t} \text{ (concentration of } \cdot CH_3 \text{ in trap } T_2)$$

$$B' = \frac{B_0k_2}{k_1 - k_2}(e^{-k_2t} - e^{-k_1t}) \text{ (concentration of } \cdot CH_3 \text{ in state A from trap } T_2)$$

$$G = G_0e^{-k_3t} \text{ (concentration of } \cdot CH_3 \text{ in trap } T_3)$$

$$G' = \frac{G_0k_3}{k_1 - k_2}(e^{-k_3t} - e^{-k_1t}) \text{ (concentration of } \cdot CH_3 \text{ in state A from trap } T_3)$$

$A + B' + G'$ = total concentration of $\cdot CH_3$ in state A at any time. Since in all these runs k_1 is from three to four orders of magnitude greater than k_3, G' is negligibly small for all values of t. G is essentially constant over a 24-hr period. The total concentration of $\cdot CH_3$ in A, T_2, and T_3 at any time less than 8 hr can be represented by the term

$$S = A + B + B' + G_0$$

The decay rate constant k_3 was estimated from the decay of the $\cdot CH_3$ in the 50 and 40% CH_3OH-H_2O matrices over a 2-week period. The concentration of $\cdot CH_3$ in T_3 was estimated in the various matrices by monitoring the decay of $\cdot CH_3$ in a 30 and 80% matrix over a 2-day period.

A least-squares fit to the experimental curve for the decay of $\cdot CH_3$ in the various matrices was obtained by using the above equation. Initial values of k_1, k_2, A_0, and B_0 were assumed, and an iterative program[8] was carried out on the BRL BRLESC computer. All runs for a given CH_3OH-H_2O matrix converted to the same values of k_1, k_2, A_0, and B_0 to within the experimental error. The decay in the 60, 50, and 40% matrices was extremely slow and was not carried out on the computer. Two illustrations of the decay of $\cdot CH_3$ concentrations *vs.* time for the various matrices are given in Figures 3 and 4. The solid curves in these illustrations with the exception of the 40 and 60% matrices represent computer calculated curves for particular runs. The dots and × marks represent the experimental points for these same runs.

For each of the 100, 80, and 30% matrices several runs were made with different initial concentrations of $\cdot CH_3$ which varied by as much as a factor of 5. These data were normalized and when plotted yielded the

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(8) M. J. D. Powell, *Computer J.*, 7, 155 (1964).

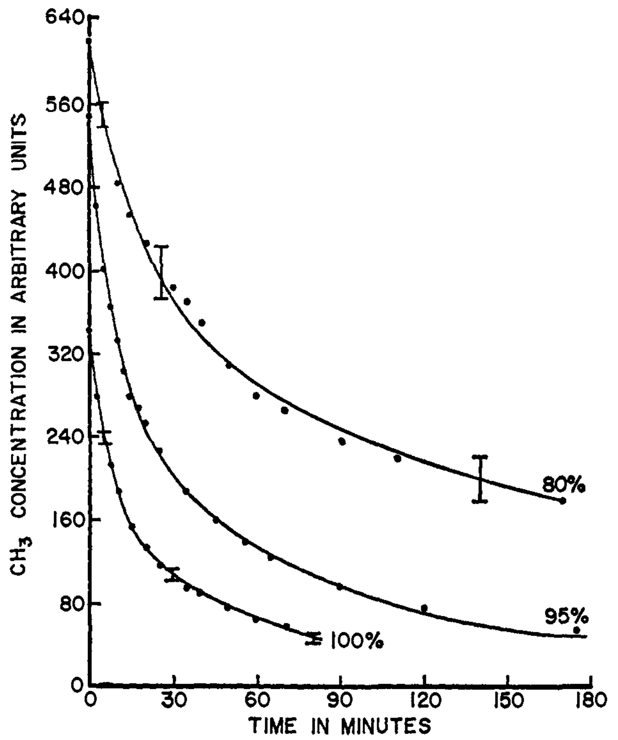

Figure 3. Decay of methyl radical concentration *vs.* time in 80, 95, and 100% methanol samples.

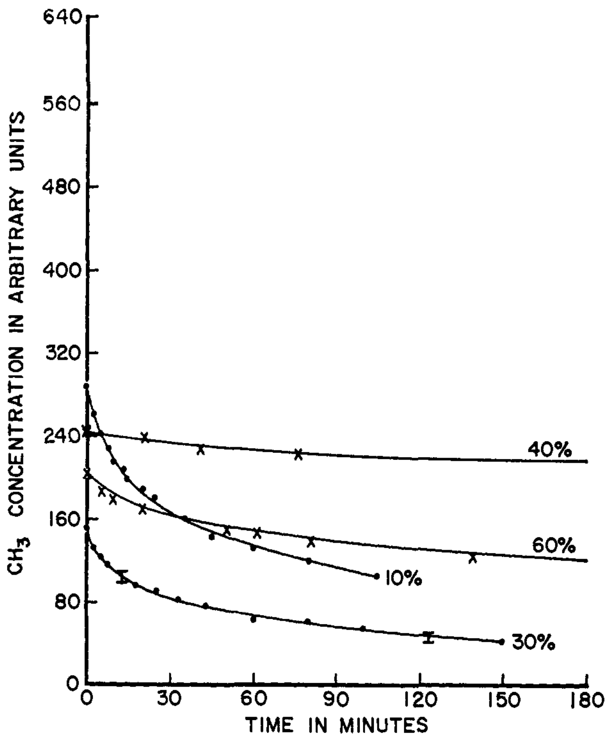

Figure 4. Decay of methyl radical *vs.* time in 10, 30, 40, and 60% methanol samples.

Table I. Decay Rate Constants and Related Data of Methanol-Water Matrices[a]

% CH_3OH	$k_1 \times 10^3$ sec^{-1}	$k_2 \times 10^4$ sec^{-1}	$k_3 \times 10^7$ sec^{-1}	% A_0	% B_0	% G_0	Half-life, hr	Physical appearance
100	2.48	2.83	1.7	53.1	46.7	<0.5	0.2	Glassy
95	2.23	2.79	1.7	49.2	44.8	6.0	0.3	Glassy
80	0.93	0.73	1.7	50.3	39.5	10.2	0.8	Glassy
60	0.92	0.63	1.7	16.6	51.2	32.2	5.0	Glassy
50	0.80	0.63	1.7	0.0	48.5	51.5	183.0	Glassy
40	0.80	0.75	1.7	0.0	37.7	62.3	>258.0	Glassy
30	1.62	1.47	1.7	37.4	45.6	16.7	0.8	Polycryst
10	1.67	1.15	1.7	35.5	57.8	6.7	0.8	Polycryst

[a] Estimates of error are shown in Figures 3 and 4.

error bars indicated in Figures 3 and 4. The concentration of $\cdot CH_3$ in all the matrices varied from 10^{16} to 10^{17} spins/cc. The matrix curves illustrated in Figures 3 and 4 are plotted as the logarithm of the $\cdot CH_3$ concentration *vs.* time in Figure 5. The concavity of these curves is typical of that for all the matrices. The pertinent data for the various runs are tabulated in Table I.

The decay of $\cdot CH_3$ in the 80% irradiated balls did not vary substantially from the other 80% samples which indicates that surface effects are unimportant. It was therefore included with the other samples in determining the standard deviations for the various quantities. With the degassed 100% methanol run no change in the decay characteristics occurred, indicating the oxygen does not play an important role in the reaction.

Only in the 40, 50, and 60% methanol-water matrices was a doublet observed with a splitting of 505 G. This is approximately the same spectrum as the free hydrogen atom in the gaseous state or in other solid matrices.[9] The trapping of hydrogen atoms as well as the long half-lives of the $\cdot CH_3$ radicals in these matrices illustrate the efficiency of these matrices as trapping media (Table I).

Discussion

From the results of these experiments it is postulated that the primary rate-determining mechanism in the decay of $\cdot CH_3$ in these matrices is the escape of the radicals from their trapping sites. Simple first-order parallel reactions were considered for the disappearance of $\cdot CH_3$ from state A and the escape of $\cdot CH_3$ from trap T_2, but the resulting curve fell outside the experimental error. A much better fit was obtained by using a parallel-series scheme in which the $\cdot CH_3$ passed from T_2 through state A by a first-order mechanism before decaying to the resultant products. In the case of T_3, the rate of escape of $\cdot CH_3$ is so slow that either method

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(9) R. Livingston, H. Zeldes, and E. H. Taylor, *Discussions Faraday Soc.*, **19**, 166 (1955).

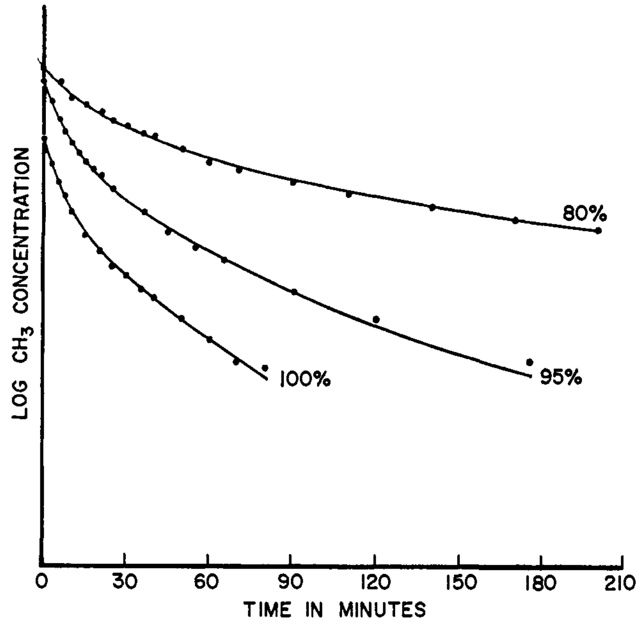

Figure 5. Logarithm of decay of methyl radical *vs.* time in 80, 95, and 100% methanol samples.

could have been used without a noticeable change in the results.

An attempt was made to explain the half-lives of these reactions with a second-order radical–radical reaction. Using the rate constant[10] determined at 455°K, it was found that half-lives for such reactions should be on the order of a few milliseconds at 77°K. This result is in substantial agreement with the half-life of the ethyl radical (5.93 msec) determined by Fessenden[11] for a second-order radical–radical recombination reaction. Such lifetimes are much too short to account for our results, and hence radical–radical recombination alone can be ruled out as a possibility for the reaction represented by rate constant k_1. It is quite possible that k_1 represents an untrapping of the $\cdot CH_3$ radical with subsequent diffusion and reaction with another trapped radical. Although there is some indication[5] that the reaction represented by the decay rate constant k_1 is too fast to be attributed to a hydrogen atom abstraction mechanism, this process cannot be eliminated as a possibility. If, in fact, it is an abstraction, the decay kinetics would still be the same since this process would proceed by a first-order mechanism.

In the case of the rate constants k_2 and k_3, three factors point to the conclusion that these represent physical rather than chemical mechanisms.

(1) Only a slight change in chemical environment is involved when progressing from a 40 to 30% CH_3OH–H_2O matrix, yet the observed change in the stability of the $\cdot CH_3$ radical in these matrices is quite large. The half-life of the $\cdot CH_3$ radical changes by more than two orders of magnitude (Table I).

(2) The large change in the stability of the $\cdot CH_3$ radical when progressing from a 40 to a 30% matrix is accompanied by a change in the physical appearance of the sample from a glassy matrix to a polycrystalline solid.

(3) Hydrogen atoms were stabilized only in the 40, 50, and 60% matrices.

Conclusion

Although there are indications that the reaction represented by decay rate constant k_1 is physical, the possibility of the reaction being a chemical abstraction cannot be ruled out. Nevertheless, the chemical or physical nature of this reaction would not change the first-order kinetic decay scheme. The experimental evidence makes the assignment of the reactions represented by decay rate constants k_2 and k_3 to a physical mechanism considerably more probable.

Acknowledgments. I wish to thank Dr. Kevin White and Mr. Webster Kendrick for their many useful suggestions and discussions in the progress and completion of this report.

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(10) T. W. Shannon and A. G. Harrison, *Can. J. Chem.*, **41**, 2455 (1963).

(11) R. W. Fessenden, *J. Phys. Chem.*, **68**, 1508 (1964).