

(5)

Hydrogen Atom Abstraction by Methyl Radicals in Methanol Glasses at 67-77°K¹

Alan Campion² and Ffrancon Williams*

Contribution from the Department of Chemistry, University of Tennessee,
Knoxville, Tennessee 37916

Received

Abstract: It has been shown by esr studies that the thermal decay of $\text{CH}_3\cdot$ radicals in a methanol-d glass at 77°K proceeds with the concomitant formation of the $\cdot\text{CH}_2\text{OD}$ radical. The reaction obeys first-order kinetics over 75 percent of its course and there is reasonably good agreement between the rate constants as determined from $\text{CH}_3\cdot$ decay and $\cdot\text{CH}_2\text{OD}$ growth. At 77°K, the rates of H-atom abstraction by $\text{CH}_3\cdot$ from CH_3OD and CH_3OH are comparable but the rate of $\text{CH}_3\cdot$ decay in CD_3OD is slower by at least a thousandfold. This primary deuterium isotope effect confirms that abstraction occurs almost exclusively from the hydrogens of the methyl group. The apparent activation energy of $0.9 \text{ kcal mol}^{-1}$ for the abstraction reaction in the glassy state at 67-77°K is much lower than the value of $8.2 \pm 0.2 \text{ kcal mol}^{-1}$ previously reported for essentially the same reaction in the gas phase above 376°K. These findings are remarkably similar to those reported for H-atom abstraction by $\text{CH}_3\cdot$ radicals from acetonitrile and methyl isocyanide, and are consistent with the proposal that these reactions proceed mainly by quantum-mechanical tunneling at low temperatures. When $\text{CH}_3\cdot$ radicals are produced by the

photolysis of CH_3I and ~~of~~ of TMPD (N,N,N',N'-tetramethyl-p-phenylenediamine)- CH_3Cl with uv light in methanol, the contribution of hot radical processes to the abstraction reaction appears to be negligibly small in comparison with the rate of the thermal reaction.

Recent work in this laboratory has provided definitive evidence for hydrogen atom abstraction by thermal methyl radicals in crystalline acetonitrile³ and methyl isocyanide⁴ at 77°K and higher temperatures. These reactions in the solid state are characterized by apparent activation energies (ca. 1.4 kcal mol⁻¹ at 77°K³) which are much lower than the value of 10.0 kcal mol⁻¹ obtained for the corresponding reaction of methyl radicals with acetonitrile above 373°K in the gas phase.⁵ However, it has been shown that these unusually low activation energies are consistent with a very large contribution from quantum mechanical tunneling at low temperatures.⁶

In contrast to the above findings, the importance of hydrogen atom abstraction as a process responsible for the decay of alkyl radicals in glassy matrices at low temperatures has not been clearly established. Although abstraction reactions have been postulated in some systems,^{7,8} no evidence for product radical formation has been obtained despite extensive kinetic studies⁹ of alkyl radical decay in organic glasses, and this latter work⁹ has led to the conclusion that abstraction by thermal radicals is unlikely to be significant at temperatures as low as 77°K.

To obtain unequivocal evidence for hydrogen atom abstraction, it is necessary to establish a kinetic coincidence between the decay of the

reactant radicals and the formation of the product radicals. In principle, esr studies provide an ideal method for observing such a reaction, but there are serious practical difficulties when these studies are attempted in the solid state. Although the esr spectra of the reactant radicals are frequently well resolved in the case of simple alkyl radicals such as methyl and ethyl, the resulting product radicals would be expected to have broad ill-defined spectra in many of the glassy matrices usually employed. This basic difficulty has been overcome in the present investigation by using methanol-d as the glassy matrix since the esr spectrum of the $\cdot\text{CH}_2\text{OD}$ radical shows two fairly sharp lines which do not overlap significantly with the quartet spectrum of the $\text{CH}_3\cdot$ radicals.

Experimental Section

Materials and Preparation of Samples. Methanol (Fisher Certified A.C.S. grade) was dried in vacuo over powdered barium oxide, degassed, and distilled into breakseals for storage. Methanol-d (CH_3OD) was supplied by Diaprep Inc. and by E. Merck AG., Darmstadt. Methanol-d₄ (CD_3OD) was obtained from Stohler Isotope Chemicals and E. Merck AG. Both of these deuterium-containing compounds were guaranteed by their manufacturers to be not less than 99% deuterated in the labeled positions. These materials were degassed and distilled into breakseals before use. Methyl chloride (The Matheson Co. Inc.) was used as received. Methyl iodide (Fisher Certified A.C.S. grade) was degassed, dried over magnesium sulfate, and

then distilled into breakseals which were stored in the dark. N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) was received as the dihydrochloride from Eastman Organic Chemicals (White Label grade). The free base was released by adding excess alkali to an aqueous solution of the salt. The solid TMPD was filtered and sublimed prior to use.

Samples of methanol, CH₃Cl, and TMPD were prepared as follows: a methanolic solution of TMPD was syringed into an esr tube which was then connected to the vacuum line with a ground glass joint. The methanol was distilled off leaving the TMPD in the esr tube. Methyl chloride was admitted into the vacuum from a cylinder and the required amount condensed in a graduated tube. The needed amount of the appropriate isotopic methanol was then added by distillation from the breakseal storage ampoule. This mixture was subsequently distilled into the esr tube which was then sealed under vacuum. The standard concentrations used in this work were 0.2 mole % TMPD and 2 mole % CH₃Cl. On quenching the sample to 77°K, a transparent glass was readily formed. The methanol samples containing 2 mole % CH₃I as the only solute were prepared in a similar fashion.

Ultraviolet Irradiation. Irradiations were carried out in the cavity of the esr spectrometer with light from a B-H6 high-pressure mercury arc lamp. The lamp was mounted in an Oriel Optics Corp. C-60-53 Universal Lamp Housing equipped with a 2 inch condenser lens (uv-grade fused silica) and a spherical rear-mirror reflector. A water filter reduced the intensity

of the unwanted ir radiation and a Pyrex (Corning 0-53) glass filter eliminated most of the light below 290 nm. A secondary lens (fused silica) was used to focus the beam on the irradiation slots of the cavity. Exposure times could be controlled and reproduced fairly accurately through the use of a shutter.

Esr Measurements. The esr spectrometer (Varian Model V-4502) and associated equipment have been described.¹⁰ Measurements were made with the samples in a liquid nitrogen dewar which had an unsilvered tail section extending through the sensitive region of the cavity. Temperatures lower than 77.3°K were obtained by bubbling dry helium gas through the liquid nitrogen,¹¹ and a constant temperature of 67±1°K could easily be maintained. During the experiments involving this technique, the temperature was monitored continuously with a copper-constantan thermocouple placed in the esr dewar next to the sample tube. The thermocouple leads were connected to the Digitec Thermocouple Thermometer (United Systems Corp. Model 564) which had been calibrated at 77.3°K.

Standard esr tubes of 2 or 3 mm i.d. made out of Spectrosil or Suprasil quartz were employed, the smaller size being especially convenient for use in the 67°K experiments. For long term experiments entailing storage at 77°K for several days, it was necessary to use a different design of sample tube¹² which could accommodate an internal standard so that relative measurements were independent of day-to-day fluctuations

in instrument sensitivity. The tubes designed¹² for this purpose were constructed from ca. 2 mm and 5 mm o.d. Suprasil tubing. The capillary was inserted into the larger tube and sealed to it at both ends. This provides an annular space to contain the sample material while the standard may be placed inside the capillary. Ultramarine (Reckitts Blue) in chalk was used as the standard in this work because its resonance occurs at much lower field than that of the methyl radical and there is negligible overlap between the spectra of sample and standard.

Results

~~~~~  
Two methods<sup>13</sup> were employed to generate methyl radicals in the various methanol glasses: the first depends on the photoionization of TMPD and subsequent dissociative electron capture by methyl chloride, and the second involves the photodissociation of methyl iodide. Both of these techniques allowed the rapid in situ generation of  $\text{CH}_3\cdot$  radicals within the spectrometer cavity, an important requirement in view of the fast decay at the temperatures of interest. Although  $\text{CH}_3\cdot$  radicals are also formed efficiently by  $\gamma$ -irradiation of glasses containing methyl halides,<sup>9</sup> this method was found to be much less useful for the present purpose due to the significant decay which occurred during  $\gamma$ -irradiation and transfer, even when the sample temperature was reduced to 67°K. Most of the kinetic work to be described here was carried out with  $\text{CH}_3\text{OD}$  rather than  $\text{CH}_3\text{OH}$  because the prominent low-field and center lines in the triplet spectrum of  $\cdot\text{CH}_2\text{OD}$  are considerably sharper than the corres-

ponding lines from  $\cdot\text{CH}_2\text{OH}$ <sup>14</sup> which are broadened by hyperfine interaction with the hydroxyl proton.

Recordings of esr spectra taken from a typical kinetic experiment are presented in Figure 1. Comparison of Spectrum A with Spectrum B shows that the decay of the  $\text{CH}_3\cdot$  quartet signal is accompanied by the appearance of new spectral features. These are more clearly revealed as the sharp lines in the residual Spectrum C which can be definitely assigned to  $\cdot\text{CH}_2\text{OD}$ .<sup>14</sup> Since these lines are not present in Spectrum A, it can be inferred that the spectrum of  $\cdot\text{CH}_2\text{OD}$  grows in during the decay of the  $\text{CH}_3\cdot$  quartet. However, this conclusion rests on the assumption that the prominent lines of the  $\cdot\text{CH}_2\text{OD}$  spectrum are not obscured by the more intense lines of the  $\text{CH}_3\cdot$  quartet in the original spectrum. To verify this point, an experiment was carried out in which the sample was re-irradiated briefly after the lines from  $\cdot\text{CH}_2\text{OD}$  became clearly recognizable in the spectra recorded after the first photolysis. The results in Figure 2 show that the sudden large increase in the intensity of the  $\text{CH}_3\cdot$  quartet has very little effect on the signal heights of the two sharp lines assigned to  $\cdot\text{CH}_2\text{OD}$  and, as expected, the subsequent decay of  $\text{CH}_3\cdot$  leads to a further growth of  $\cdot\text{CH}_2\text{OD}$ . Thus, it can be confidently asserted that the appearance of  $\cdot\text{CH}_2\text{OD}$  during the thermal decay of  $\text{CH}_3\cdot$  is real and not an experimental artifact.

The thermal reaction was followed by repetitive scanning at 1 min intervals. Kinetic measurements were made using lines 1 and 3 (from low

field) of the  $\text{CH}_3\cdot$  quartet and the two sharp components of the  $\cdot\text{CH}_2\text{OD}$  spectrum. For the analysis of several kinetic runs, a computer program was used to subtract out the contribution of the  $\text{CH}_3\cdot$  radical spectrum from the composite spectrum. The original  $\text{CH}_3\cdot$  spectrum was employed for this purpose after normalization to the observed intensity. This procedure did not yield signal heights for  $\cdot\text{CH}_2\text{OD}$  significantly different from those obtained by direct measurement, providing further confirmation that there is negligible overlap between the pertinent components in the spectra of these two species. Accordingly, the actual signal heights were taken as proportional to the radical concentrations. It would have been valuable to obtain the stoichiometric relationship between  $\text{CH}_3\cdot$  decay and  $\cdot\text{CH}_2\text{OD}$  growth but accurate estimates were precluded by the overall anisotropy of the  $\cdot\text{CH}_2\text{OD}$  spectrum.

The decay of  $\text{CH}_3\cdot$  radicals in  $\text{CH}_3\text{OD}$  is described fairly well by first-order kinetics over the first 75 percent of the reaction. Actually, for a typical set of data derived from a single kinetic run, the fit to standard first-order and second-order plots was about equally good. However, the first-order rate constant was found to be independent of the initial  $\text{CH}_3\cdot$  radical concentration when this was varied by a factor of four, and this criterion led to the adoption of first-order kinetics for the reaction. In the later stages of  $\text{CH}_3\cdot$  decay, the concentration declined at a slower rate than that represented by an extension of the first order plot. Previous workers<sup>15,16</sup> have also observed deviations from linear first-order plots for the decay of alkyl radicals in organic glasses.

/=/



As indicated by the parallel plots in Figure 3 and by the comparison of data in Table I, there is satisfactory agreement between the rate constants calculated independently from  $\text{CH}_3\cdot$  decay and  $\cdot\text{CH}_2\text{OD}$  formation. For the system (TMPD- $\text{CH}_3\text{Cl}$ - $\text{CH}_3\text{OD}$ ) which has been studied most thoroughly, the agreement is particularly good and well within the reproducibility ( $\pm 20$  percent) of these data. This demonstration of kinetic coincidence clearly establishes the abstraction reaction in the  $\text{CH}_3\text{OD}$  glass.

Reference to Table I shows that similar kinetic results were obtained when the methyl radicals were generated by the photolysis of  $\text{CH}_3\text{I}$  in  $\text{CH}_3\text{OD}$ . Incidentally, it was noticed that the increase in the  $\cdot\text{CH}_2\text{OD}$  signal height relative to the initial  $\text{CH}_3\cdot$  signal was less after  $\text{CH}_3\text{I}$  photolysis than after TMPD- $\text{CH}_3\text{Cl}$  photolysis, suggesting that the  $\cdot\text{CH}_2\text{OD}$  components are selectively broadened in the  $\text{CH}_3\text{I}$  system.

The temperature dependence of the abstraction rate constant (Table I) corresponds to an apparent activation energy of ca.  $0.9 \text{ kcal mol}^{-1}$  between 67 and 77°K. In view of this very small temperature coefficient, it should be possible to extend the kinetic measurements to even lower temperatures in future work with additional cryogenic facilities.

Additional studies with  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  glasses provide evidence for a specific deuterium isotope effect. Although the measurements in  $\text{CH}_3\text{OH}$  are subject to a greater uncertainty because the  $\cdot\text{CH}_2\text{OH}$  spectral components are not as well resolved, the rate constants for the abstraction reactions in the  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  glasses (Table I) are comparable.

In contrast, the decay of  $\text{CH}_3^\bullet$  in  $\text{CD}_3\text{OD}$  was found to be slower than in  $\text{CH}_3\text{OH}$  or  $\text{CH}_3\text{OD}$  by more than three orders of magnitude under corresponding conditions. This large deuterium isotope effect is consistent with the previous demonstration that abstraction occurs from the hydrogens of the methyl group.

In view of the many observations in the literature regarding the prevalence of hot radical reactions in photolytic processes,<sup>17</sup> an investigation of this possibility in the present systems seemed to be desirable. Since a hot radical reaction would be expected to show little selectivity between H and D atom abstraction, the photolysis (with Pyrex filter) of  $\text{TMPD-CH}_3\text{Cl}$  and of  $\text{CH}_3\text{I}$  was studied in  $\text{CD}_3\text{OD}$ . In each case, photolysis for 10 min (as compared to 5 sec employed in the  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  studies) produced a high concentration of  $\text{CH}_3^\bullet$  radicals but failed to result in the growth of a signal attributable to either  $\cdot\text{CD}_2\text{OD}$  or  $\text{D}\dot{\text{C}}\text{O}$ , the latter being a possible photolysis product of  $\cdot\text{CD}_2\text{OD}$ . Even when the photolysis of  $\text{CH}_3\text{I}$  was carried out with unfiltered uv-light having considerable intensity at 2500 Å, only  $\text{CH}_3^\bullet$  and a much smaller yield of  $\text{CD}_3^\bullet$  radicals (the latter were produced by the photolysis of the  $\text{CD}_3\text{OD}$  matrix) were observed and there was no significant production of radicals resulting from deuterium atom abstraction.

In an effort to observe deuterium atom abstraction by thermal  $\text{CH}_3^\bullet$  radicals from  $\text{CD}_3\text{OD}$  at higher temperatures than those used in the preceding studies with  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$ , the  $\text{CD}_3\text{OD}$  matrix was warmed to ca. 108°K

at which point the  $\text{CH}_3^\bullet$  radicals decayed out very rapidly without the observation of any product radical.

### Discussion

This work provides what appears to be the first convincing demonstration of a thermal H-atom abstraction reaction in a glass at low temperature. The primary evidence consists of the unambiguous identification of the product radical together with the good agreement between the rate constants as determined from  $\text{CH}_3^\bullet$  decay and  $\cdot\text{CH}_2\text{OD}$  (or  $\cdot\text{CH}_2\text{OH}$ ) growth. Supporting evidence is provided by a comparison of the decay rates in  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OD}$ , and  $\text{CD}_3\text{OD}$  which establishes that abstraction occurs almost exclusively from the methyl hydrogens and shows the expected large primary deuterium isotope effect.

In the absence of information about the stoichiometry of the reaction, the kinetic results obtained here do not exclude other paths of  $\text{CH}_3^\bullet$  decay in parallel with abstraction. The possibility of a competition between abstraction and recombination processes should therefore be considered, especially since a similar reaction scheme has been definitely established in the crystalline acetonitrile systems.<sup>3,12,18</sup> For the  $\text{TMPD-CH}_3\text{Cl}$  systems investigated here, the recombination reactions could in principle involve both a reaction between two  $\text{CH}_3^\bullet$  radicals as well as geminate recombination of the  $\text{CH}_3^\bullet$  radical with the chloride ion. Indeed, the latter reaction has been postulated<sup>9,16</sup> to account for the decay of  $\text{CH}_3^\bullet$  radicals which

S/

were similarly generated in hydrocarbon and 2-methyltetrahydrofuran glasses, but no supporting esr evidence was obtained.<sup>13,15,16</sup>

If a significant fraction of the  $\text{CH}_3\cdot$  decay in  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  were to occur by combination of two separated  $\text{CH}_3\cdot$  radicals, diffusion would be involved. However, the extremely slow decay of  $\text{CH}_3\cdot$  radicals in  $\text{CD}_3\text{OD}$  as compared to that in  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  would then correspond to a solvent isotope effect of more than  $10^3$ . This is entirely unreasonable considering that no isotope effect is observed for  $\text{CH}_3\text{OD}$ , and consequently it is thought that the combination reaction is unlikely to contribute to  $\text{CH}_3\cdot$  decay in this system. Turning to the possibility of the geminate recombination process, no evidence was obtained in the present work for a recombination product, although esr spectra attributable to weakly interacting methyl radical-halide ion pairs have been observed in a crystalline matrix.<sup>19</sup>

The apparent activation energy of ca.  $0.9 \text{ kcal mol}^{-1}$  for the H-atom abstraction reaction by  $\text{CH}_3\cdot$  from  $\text{CH}_3\text{OD}$  in solid methanol at 67-77°K is very much lower than the value of  $8.2 \pm 0.2 \text{ kcal mol}^{-1}$  reported for essentially the same reaction ( $\text{CH}_3\cdot$  with  $\text{CH}_3\text{OH}$ ) at 376-492°K in the gas phase.<sup>20</sup> Calculation of the Arrhenius pre-exponential factor from the low temperature data gives a value of  $1.1 \text{ sec}^{-1}$  which is much lower than the vibration frequency of ca.  $9 \times 10^{13} \text{ sec}^{-1}$  assumed in some recent calculations<sup>6</sup> for a non-tunneling reaction. The general similarity of these results to those for the corresponding abstraction reaction from acetonitrile is striking and suggests a common explanation for the anomalously low activation energy and pre-exponential factor in the low temperature region. Quantum mechanical

tunneling has been proposed to account for this behavior,<sup>6</sup> and the present results lend further credence to this hypothesis. On the other hand, if the correct explanation for the low activation energies were to reside in "cage effects" by which the potential energy surfaces become modified for reactions in the solid state, it might be expected that such effects would be very sensitive to the difference between crystalline and glassy solids. From the results for acetonitrile and methanol considered here, this does not appear to be the case. However, a more definitive test of the importance of "cage effects" would result from a comparison of results for the same reaction in a crystalline and glassy matrix. Further work is planned on the methanol system with this idea in mind.

This work demonstrates that hydrogen atom abstraction can occur by a thermal reaction at low temperatures on a timescale which is short compared to the irradiation times commonly employed in many photochemical and radiation chemical experiments with solid matrices. Hence, under these conditions, caution should be exercised in attributing all the trapped intermediates present after photolysis or radiolysis at low temperatures to the results of primary processes and hot radical reactions. Also, since the present results in  $\text{CD}_3\text{OD}$  provide no evidence for abstraction by hot radical reactions in the photolysis of  $\text{CH}_3\text{I}$  and  $\text{TMPD-CH}_3\text{Cl}$  in methanol, it would seem that the importance of such processes<sup>9,17</sup> may be critically dependent on the nature of the matrix.

Acknowledgment. We thank Dr. C. M. L. Kerr for computational help  
~~~~~  
and useful discussions during the course of this work.

REFERENCES

- (1) This research was supported by the U.S. Atomic Energy Commission under Contract No. AT-(40-1)-2968, and this is AEC Document No. ORO-2968-74.
- (2) Undergraduate on leave from New College, Sarasota, Fl. 33578.
- (3) E. D. Sprague and F. Williams, J. Amer. Chem. Soc., 93, 787 (1971).
- (4) J.-T. Wang and F. Williams, ibid., in press.
- (5) M. H. J. Wijnen, J. Chem. Phys., 22, 1074 (1954).
- (6) R. J. Le Roy, E. D. Sprague, and F. Williams, J. Phys. Chem., 76, 546 (1972).
- (7) H. S. Judeikis and S. Siegel, J. Chem. Phys., 43, 3625 (1965).
- (8) C. U. Morgan, J. Amer. Chem. Soc., 91, 1599 (1969).
- (9) J. E. Willard in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience-Wiley, New York, N.Y., 1968, p 599.
- (10) J. Lin, K. Tsuji, and F. Williams, J. Amer. Chem. Soc., 90, 2766 (1968).
- (11) F. W. Lytle and J. T. Stoner, Science, 148, 1721 (1965).
- (12) E. D. Sprague, Ph.D. Dissertation, The University of Tennessee, 1971.
- (13) R. F. C. Claridge and J. E. Willard, J. Amer. Chem. Soc., 87, 4992 (1965).
- (14) P. J. Sullivan and W. S. Koski, ibid., 85, 384 (1965).
- (15) M. Shirom and J. E. Willard, J. Phys. Chem., 72, 1702 (1968).
- (16) W. G. French and J. E. Willard, ibid., 72, 4604 (1968).
- (17) C. D. Bass and G. C. Pimentel, J. Amer. Chem. Soc., 83, 3754 (1961).
- (18) K. Takeda and F. Williams, J. Phys. Chem., 74, 4007 (1970).
- (19) E. D. Sprague and F. Williams, J. Chem. Phys., 54, 5425 (1971).
- (20) A. F. Trotman-Dickenson and E. W. R. Steacie, ibid., 19, 329 (1951).

Table I. Experimental Rate Constants for Hydrogen Atom Abstraction by Methyl Radicals from Methanol-h and Methanol-d in the Glassy State

| Temperature °K | Source of CH ₃ • Radicals | Glass | No. of Runs | Rate Constant ^a | |
|-------------------|-----------------------------------------|--------------------|-------------------|-------------------------------|-------------------------------|
| | | | | $\frac{k^b}{\text{min}^{-1}}$ | $\frac{k^c}{\text{min}^{-1}}$ |
| 77 | TMPD-CH ₃ Cl | CH ₃ OH | 2 | 0.14 | 0.20 |
| 77 | TMPD-CH ₃ Cl | CH ₃ OD | 9 ^d | 0.19(0.20) ^e | 0.21(0.23) ^f |
| 77 | CH ₃ I | CH ₃ OD | 2 | 0.20 | 0.30 |
| 67 | TMPD-CH ₃ Cl | CH ₃ OD | 4 | 0.07 | 0.10 |

^aBased on first-order plot of measurements over the first 75 percent of reaction. ^bFrom decay of line 3 of CH₃• quartet. ^cFrom growth of •CH₂OD or •CH₂OH center line. ^dThe standard deviation for the rate constants obtained in this group of runs is 20 percent of the mean value. ^eValue in parentheses determined from decay of line 1 of CH₃• quartet. ^fValue in parentheses determined from growth of low-field line from •CH₂OD.

CAPTIONS TO FIGURES

Figure 1. ESR spectra of TMPD-CH₃Cl-CH₃OD system at 77°K recorded immediately after 5 sec photolysis (A), after 6 min (B), and after 90 min (C). Spectrum C was recorded at a gain of 2.5 times that used to record the other two spectra.

Figure 2. ESR spectra of TMPD-CH₃Cl-CH₃OD system at 77°K recorded under the same conditions (A) 9 min after an initial photolysis for 5 sec, (B) 1 min later and immediately after a second photolysis for 10 sec, and (C) 3 min after the second photolysis.

Figure 3. First-order kinetic plots derived from measurements on ESR spectra after photolysis of TMPD-CH₃Cl-CH₃OD at 77°K: (O), CH₃ decay; (), CH₂OD growth; the corresponding λ_t values represent the signal heights for the low-field outer line of the CH₃• quartet and the center line of the •CH₂OD spectrum recorded at the same gain.





