Hydrogen Atom Abstraction by Methyl Radicals in Methanol Glasses at 67–77°K[1]

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Abstract: It has been shown by esr studies that the thermal decay of $CH_3\cdot$ radicals in a methanol-*d* glass at 77°K proceeds with the concomitant formation of the $\cdot CH_2OD$ radical. The reaction obeys first-order kinetics over 75% of its course, and there is reasonably good agreement between the rate constants as determined from $CH_3\cdot$ decay and $\cdot CH_2OD$ growth. At 77°K, the rates of H-atom abstraction by $CH_3\cdot$ from CH_3OD and CH_3OH are comparable, but the rate of $CH_3\cdot$ decay in CD_3OD is slower by at least 1000-fold. 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 kcal mol^{-1} for the abstraction reaction in the glassy state at 67–77°K is much lower than the value of 8.2 ± 0.2 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 $CH_3\cdot$ 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 $CH_3\cdot$ radicals are produced by the photolysis of CH_3I and 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 acetonitrile[3] and methyl isocyanide[4] 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°K[3]) 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 studies[9] of alkyl radical decay in organic glasses, and this latter work[9] 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 $\cdot CH_2OD$ radical shows two fairly sharp lines which do not overlap significantly with the quartet spectrum of the $CH_3\cdot$ radicals.

Experimental Section

Materials and Preparation of Samples. Methanol (Fisher Certified ACS grade) was dried *in vacuo* over powdered barium oxide, degassed, and distilled into break-seals for storage. Methanol-*d* (CH_3OD) was supplied by Diaprep Inc. and by E. Merck A.G., Darmstadt. Methanol-d_4 (CD_3OD) was obtained from Stohler Isotope Chemicals and E. Merck A.G. 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 break-seals before use. Methyl chloride (Matheson Co.) was used as received. Methyl iodide (Fisher Certified ACS grade) was degassed, dried over magnesium sulfate, and then distilled into break-seals 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, CH_3Cl, 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 behind the TMPD in the esr tube. Methyl chloride was admitted into the vacuum line 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 break-seal 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 mol % TMPD and 2 mol % CH_3Cl. On quenching the sample to 77°K, a transparent glass was readily formed. The methanol samples containing 2 mol % CH_3I as the only solute were prepared in a similar fashion.

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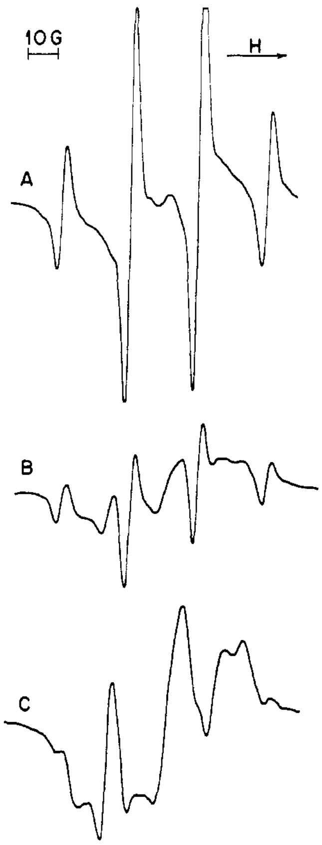

Figure 1. Esr spectra of TMPD-CH_3Cl-CH_3OD system at 77°K recorded immediately after 5-sec photolysis (A), after 6 min (B), and after 90 min (C). Spectrum C was recorded at a gain of 2.5 times that used to record the other two spectra.

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-in. 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 tube[12] which could accommodate an internal standard so that relative measurements were independent of day-to-day fluctuations in instrument sensitivity. The tubes designed[12] for this purpose were constructed from *ca.* 2- 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[13] 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 $CH_3\cdot$ radicals within the spectrometer cavity, an important requirement in view of the fast decay at the temperatures of interest. Although $CH_3\cdot$ radicals are also formed efficiently by γ irradiation of glasses containing methyl halides,[9] this method was found to be much less useful for the present purpose owing to the significant decay which occurred during γ 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 CH_3OD rather than CH_3OH because the prominent low-field and center lines in the triplet spectrum of $\cdot CH_2OD$ are considerably sharper than the corresponding lines from $\cdot CH_2OH$[14] 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 $CH_3\cdot$ 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 $\cdot CH_2OD$.[14] Since these lines are not present in spectrum A, it can be inferred that the spectrum of $\cdot CH_2OD$ grows in during the decay of the $CH_3\cdot$ quartet. However, this conclusion rests on the assumption that the prominent lines of the $\cdot CH_2OD$ spectrum are not obscured by the more intense lines of the $CH_3\cdot$ quartet in the original spectrum. To verify this point, an experiment was carried out in which the sample was reirradiated briefly after the lines from $\cdot CH_2OD$ 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 $CH_3\cdot$ quartet has very little effect on the signal heights of the two sharp lines assigned to $\cdot CH_2OD$ and, as expected, the subsequent decay of $CH_3\cdot$ leads to a further growth of $\cdot CH_2OD$. Thus, it can be confidently asserted that the appearance of $\cdot CH_2OD$ during the thermal decay of $CH_3\cdot$ 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 $CH_3\cdot$ quartet and the two sharp components of the CH_2OD spectrum. For the analysis of several kinetic runs, a computer program was used to subtract out the contribution of the $CH_3\cdot$ radical spectrum from the composite spectrum. The original $CH_3\cdot$ spectrum was employed for this purpose after normalization to the observed intensity. This procedure did not yield

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

Temp, °K	Source of $CH_3\cdot$ radicals	Glass	No. of runs	Rate constant,[a] min^{-1}	
				k^b	k^c
77	TMPD–CH_3Cl	CH_3OH	2	0.14	0.20
77	TMPD–CH_3Cl	CH_3OD	9[d]	0.19 (0.20)[e]	0.21 (0.23)[f]
77	CH_3I	CH_3OD	2	0.20	0.30
67	TMPD–CH_3Cl	CH_3OD	4	0.07	0.10

[a] Based on first-order plot of measurements over the first 75% of reaction. [b] From decay of line 3 of $CH_3\cdot$ quartet. [c] From growth of $\cdot CH_2OD$ or $\cdot CH_2OH$ center line. [d] The standard deviation for the rate constants obtained in this group of runs is 20% of the mean value. [e] Value in parentheses determined from decay of line 1 of $CH_3\cdot$ quartet. [f] Value in parentheses determined from growth of low-field line from $\cdot CH_2OD$.

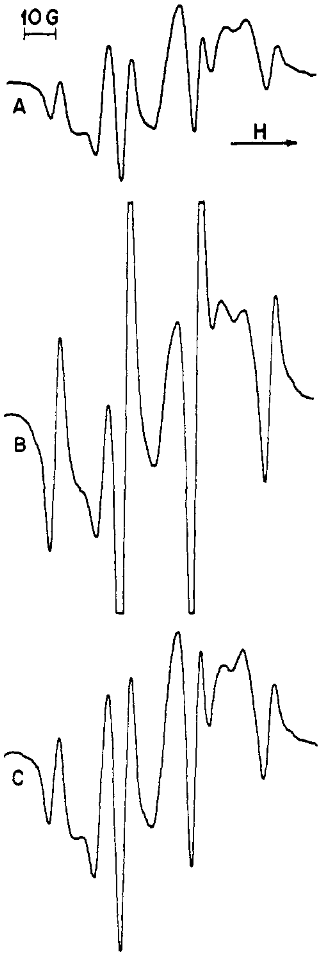

Figure 2. Esr spectra of TMPD–CH_3Cl–CH_3OD system at 77°K recorded under the same conditions: (A) 9 min after an initial photolysis for 5 sec, (B) 1 min later and immediately after a second photolysis for 10 sec, and (C) 3 min after the second photolysis.

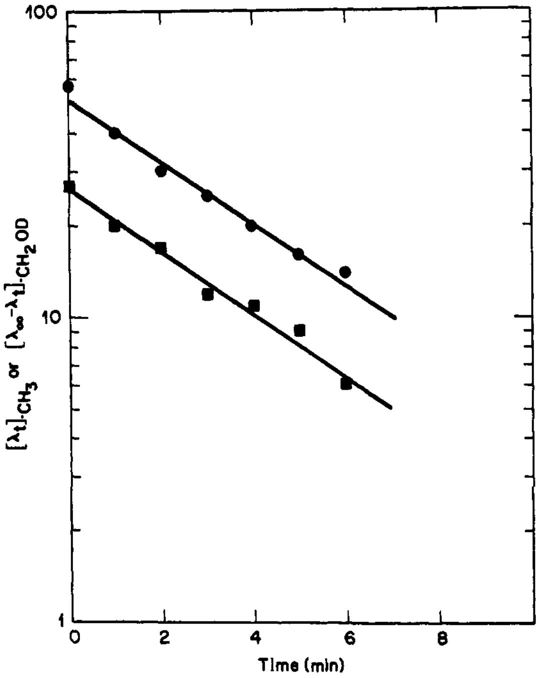

Figure 3. First-order kinetic plots derived from measurements on esr spectra after photolysis of TMPD–CH_3Cl–CH_3OD at 77°K: (●) $CH_3\cdot$ decay, (■) $\cdot CH_2OD$ growth; the corresponding λ_t values represent the signal heights for the low-field outer line of the $CH_3\cdot$ quartet and the center line of the $\cdot CH_2OD$ spectrum recorded at the same gain.

signal heights for $\cdot CH_2OD$ 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 $CH_3\cdot$ decay and $\cdot CH_2OD$ growth, but accurate estimates were precluded by the overall anisotropy of the $\cdot CH_2OD$ spectrum.

The decay of $CH_3\cdot$ radicals in CH_3OD is described fairly well by first-order kinetics over the first 75% of the reaction. Actually, for a typical set of data derived from a single kinetic run, the fits to standard first-order and second-order plots were about equally good. However, the first-order rate constant was found to be independent of the initial $CH_3\cdot$ radical concentration when this was varied by a factor of 4, and this criterion led to the adoption of first-order kinetics for the reaction. In the later stages of $CH_3\cdot$ decay, the concentration declined at a slower rate than that represented by an extension of the first-order plot. Previous workers[15,16] 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 $CH_3\cdot$ decay and $\cdot CH_2OD$ formation. For the system TMPD–CH_3Cl–CH_3OD which has been studied most thoroughly, the agreement is particularly good and well within the reproducibility (±20%) of these data. This demonstration of kinetic

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coincidence clearly establishes the abstraction reaction in the CH_3OD glass.

Reference to Table I shows that similar kinetic results were obtained when the methyl radicals were generated by the photolysis of CH_3I in CH_3OD. Incidentally, it was noticed that the increase in the $\cdot CH_2OD$ signal height relative to the initial $CH_3\cdot$ signal was less after CH_3I photolysis than after TMPD–CH_3Cl photolysis, suggesting that the $\cdot CH_2OD$ components are selectively broadened in the CH_3I system.

The temperature dependence of the abstraction rate constant (Table I) corresponds to an apparent activation energy of *ca.* 0.9 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 CH_3OH and CD_3OD glasses provide evidence for a specific deuterium isotope effect. Although the measurements in CH_3OH are subject to a greater uncertainty because the $\cdot CH_2OH$ spectral components are not as well resolved, the rate constants for the abstraction reactions in the CH_3OH and CH_3OD glasses (Table I) are comparable. In contrast, the decay of $CH_3\cdot$ in CD_3OD was found to be slower than in CH_3OH or CH_3OD 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,[17] 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 TMPD-CH_3Cl and of CH_3I was studied in CD_3OD. In each case, photolysis for 10 min (as compared to 5 sec employed in the CH_3OH and CH_3OD studies) produced a high concentration of $CH_3\cdot$ radicals but failed to result in the growth of a signal attributable to either $\cdot CD_2OD$ or $D\dot{C}O$, the latter being a possible photolysis product of $\cdot CD_2$-OD. Even when the photolysis of CH_3I was carried out with unfiltered uv light having considerable intensity at 2500 Å, only $CH_3\cdot$ and a much smaller yield of $CD_3\cdot$ radicals (the latter were produced by the photolysis of the CD_3OD 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 $CH_3\cdot$ radicals from CD_3OD at higher temperatures than those used in the preceding studies with CH_3OH and CH_3OD, the CD_3OD matrix was warmed to *ca.* 108°K at which point the $CH_3\cdot$ 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 $CH_3\cdot$ decay and $\cdot CH_2OD$ (or $\cdot CH_2OH$) growth. Supporting evidence is provided by a comparison of the decay rates in CH_3OH, CH_3OD, and CD_3OD 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 $CH_3\cdot$ 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.[3,12,18] For the TMPD–CH_3Cl systems investigated here, the recombination reactions could in principle involve both a reaction between two $CH_3\cdot$ radicals as well as geminate recombination of the $CH_3\cdot$ radical with the chloride ion. Indeed, the latter reaction has been postulated[9,16] to account for the decay of $CH_3\cdot$ radicals which were similarly generated in hydrocarbon and 2-methyltetrahydrofuran glasses, but no supporting esr evidence was obtained.[13,15,16]

If a significant fraction of the $CH_3\cdot$ decay in CH_3OH and CH_3OD were to occur by combination of two separated $CH_3\cdot$ radicals, diffusion would be involved. However, the extremely slow decay of $CH_3\cdot$ radicals in CD_3OD as compared to that in CH_3OH and CH_3OD 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 CH_3OD, and consequently it is thought that the combination reaction is unlikely to contribute to $CH_3\cdot$ 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.[19]

The apparent activation energy of *ca.* 0.9 kcal mol^{-1} for the H-atom abstraction reaction by $CH_3\cdot$ from CH_3OD in solid methanol at 67–77°K is very much lower than the value of 8.2 ± 0.2 kcal mol^{-1} reported for essentially the same reaction ($CH_3\cdot$ with CH_3OH) at 376–492°K in the gas phase.[20] Calculation of the Arrhenius preexponential factor from the low-temperature data gives a value of 1.1 sec^{-1} which is much lower than the vibration frequency of *ca.* 9×10^{13} sec^{-1} assumed in some recent calculations[6] for a nontunneling 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 preexponential factor in the low-temperature region. Quantum mechanical tunneling has been proposed to account for this behavior,[6] 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

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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 time scale 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 CD_3OD provide no evidence for abstraction by hot radical reactions in the photolysis of CH_3I and TMPD–CH_3Cl in methanol, it would seem that the importance of such processes[9,17] may be critically dependent on the nature of the matrix.

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Detritiation of Malononitriles in Mixed Aqueous Solvents and in Salt Solutions. A Kinetic Probe for Solvent Basicity[1,2]

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Abstract: The water-catalyzed detritiations of malononitrile and its *tert*-butyl derivative represent an interesting new probe for solvent basicity. The rates of detritiation have been measured in mixed solvents of water with dioxane, ethanol, and dimethyl sulfoxide. Replacement of water by the nonaqueous component leads to a rate maximum at about 0.2 mol fraction replacement, implying an initial increase in solvent basicity. The magnitudes of the maxima (dimethyl sulfoxide > ethanol > dioxane) and the solvent compositions at which they occur vary with the particular nonaqueous additive. In largely nonaqueous solution, the rate is reduced below its value in water; *i.e.*, the basicities decrease. The overall variation of the rate of detritiation with solvent composition in water–ethanol roughly follows the H_- indicator acidity function, but this correlation breaks down for water–dioxane solutions. In the presence of tetraalkylammonium halides the rate of the water-catalyzed detritiation of *tert*-butylmalononitrile is increased; the magnitude of the effect increases with the cationic radius of the salt. Alkali metal halides reduce the rate. These salt effects and the influences of mixed solvents on the rate of detritiation can be understood in terms of medium effects on the activity of the ion-pair transition state. The kinetic results also correlate closely with effects on the structure of water.

The detritiation of malononitriles in aqueous solution is a slow proton (triton) transfer reaction.[4]

$$\begin{array}{ll} RCT + B \xrightarrow{k} RC^- + BT^+ & \text{slow} \\ RC^- + \text{proton species} \longrightarrow RCH & \text{fast} \end{array} \qquad (1)$$

The rate coefficient k of the base-catalyzed detritiation is directly proportional to the strength of the general base catalyst as measured by the dissociation constant of its conjugate acid (K_{HB}). In other words

$$k = \text{constant} \times (1/K_{HB})^\beta \qquad (2)$$

where the Brønsted coefficient β is practically unity, 0.98 ± 0.02. Calculation of the reverse rates of recombination of the general acids with malononitrile anions showed these reactions to be virtually diffusion controlled (*e.g.*, $k_{H_3O^+} = 4 \times 10^9\ M^{-1}\ sec^{-1}$ at 25°). Other properties of the reverse reaction confirm this conclusion. The transition state for proton transfer (eq 1) therefore resembles an ion pair in which the proton is almost completely transferred from the carbon acid.

In aqueous hydrochloric acid a "spontaneous" detritiation is observed. This has been identified as a simple base-catalyzed slow triton transfer in which the solvent, water, acts as the base catalyst.[4,5] For malononitrile ($pK^0 = 11.19$) and *tert*-butylmalononitrile ($pK^0 = 13.10$) the rate of this reaction can conveniently be measured. The existence of the water-catalyzed detritiation suggests the possibility of a new probe for solvent basicity. By studying the variation of the rate of detritiation with composition in a two-component aqueous solvent mixture, information about the basicity of the mixture is obtained. This type of study has been applied to three mixed aqueous solvents, water with dimethyl sulfoxide, ethanol, and dioxane, as well as to a number of aqueous salt solutions.

Previous information about the basicity of aqueous two-component solvent mixtures has been obtained

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(2) A preliminary report of this work has been published: F. Hibbert, F. A. Long, and E. A. Walters, *J. Amer. Chem. Soc.*, **91**, 2381 (1969).

(3) To whom requests for reprints should be sent.

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