was added dropwise 43.5 mmoles of *n*-butyllithium in pentane. After the mixture had been stirred at −30° for 30 min., 9.6 g. (40 mmoles) of triethyltin chloride was added. The reaction mixture was filtered; the solvent was distilled from the organic phase, and the residue was diluted to 100 ml. with diethyl ether. This solution was treated with dry ammonia gas for 3 hr. in order to precipitate triethyltin chloride as its ammonia adduct. This solution was filtered and distilled to give 0.5 g. of crude triethylperfluorovinyltin (4.4%), b.p. 56–59° at 9 mm., $n^{25}D$ 1.4406 (lit.[7] $n^{25}D$ 1.4396), confirmed by infrared, 8.3 g. of crude *n*-butyltriethyltin, b.p. 71–77° at 4 mm., and 11.1 g. (75% recovery) of tri-*n*-butylperfluorovinyltin, b.p. 78–80° at 0.3 mm.

Reaction of Triethyltin Chloride with Di-*n*-butylbisperfluorovinyltin.—A mixture of 13 g. (33 mmoles) of di-*n*-butylbisperfluorovinyltin[7] and 5 g. (20 mmoles) of triethyltin chloride was distilled slowly between 80–100° at 12 mm. The distillate was treated with KF solution to remove triethyltin chloride, any di-*n*-butylperfluorovinyltin chloride which might have formed, and di-*n*-butylbisperfluorovinyltin (for the reaction of the latter two with KF solution, see ref. 7). Only 0.5 g. of crude triethylperfluorovinyltin could be isolated by distillation from the filtrate.

Decomposition of Perfluorovinyllithium in the Presence of Excess of Phenyllithium.—The reagent solution was prepared by adding 101 ml. of 1.02 *M* ethereal phenyllithium (103 mmoles) over 90 min. to 5 g. (11.4 mmoles) of phenyltrisperfluorovinyltin in 85 ml. of ether at −40°. The mixture was stirred at −40° for 30 min., warmed slowly to 0°, kept at this temperature for 30 min., and finally warmed to room temperature. After 3 hr. at room temperature, the mixture was filtered to give 4.6 g. (95%) of tetraphenyltin, m.p. 224–227°. The filtrate was shaken with 50 ml. of water, and the ether layer was dried. Removal of ether at reduced pressure left a deep red oil which crystallized on standing. The latter (2.75 g.) was dissolved in 8.17 g. of reagent grade xylene and analyzed by gas chromatography using Dow Corning 710 Silicon Oil on Chromosorb W (jacket at 240°, preheater at 210°, 14.3 psi. helium). Diphenylacetylene (43%) and minor amounts of biphenyl were present. The xylene solution was treated with Norite until colorless. Removal of xylene at reduced pressure gave 2.36 g. of diphenylacetylene (38%), m.p. and mixed m.p. 56°, whose infrared spectrum was identical with that of an authentic sample.

Preparation of Authentic Trimethylperfluorovinylsilane.—Freshly distilled trimethylchlorosilane (71 g., 0.65 mole) and 145 g. (0.9 mole) of bromotrifluoroethylene in 800 ml. of tetrahydrofuran were added dropwise over 5 hr. to 20.8 g. (0.85 g. atom) of magnesium turnings in 75 ml. of tetrahydrofuran at −15°. Upon completion of the reaction, all volatiles were distilled at reduced pressure into a receiver cooled to −78°. The colorless solution (at 0°) was treated with 62 g. (0.39 mole) of bromine during a 96 hr. period. The solvent and other low boiling compounds were removed at 27°(5 mm.), leaving 39.7 g. of pale yellow oil, $n^{25}D$ 1.4532, $(CH_3)_3SiCFBrCF_2Br$.

Anal. Calcd. for $C_5H_9Br_2F_3Si$: C, 19.10; H, 2.86; Br, 50.80. Found: C, 19.24; H, 2.90; Br, 51.03.

Thirty grams of this dibromide (0.0954 mole) in 50 ml. of diglyme was added dropwise to 7 g. (0.107 g. atom) of zinc dust in diglyme. The mixture was stirred for 1 hr., filtered, and the filtrate distilled to give 13.0 g. (89%) of trimethylperfluorovinylsilane, b.p. 65°, $n^{25}D$ 1.3569.

Anal. Calcd. for $C_5H_9F_3Si$: C, 38.94; H, 5.88; Si, 18.22. Found: C, 38.76; H, 5.73; Si, 18.31.

Its infrared spectrum (carbon tetrachloride solution) showed major absorption at 2950, 1715, 1285, 1260, 1130, 1040 and 850 cm.$^{-1}$.

Acknowledgments.—The early stages of this investigation were supported by the United States Air Force under Contract No. AF 33(616)-7124, monitored by the Materials Central, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.[16] The authors are grateful to the National Science Foundation for support of the later stages of this work under Grants NSF G-7325 and G-21051 and to the Metal & Thermit Corporation for gifts of organotin chemicals.

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(16) D. Seyferth, W. Freyer and G. Raab, ASD Technical Report 61-1, Part I, July 1961; ASTIA Document No. AD-268334 (Div. 4).

[Contribution from the Department of Chemistry, Washington University, St. Louis 30, Mo.]

Electron Transfer between Tris-*p*-nitrophenylmethyl Radical and Tris-*p*-nitrophenylmethide Ion Studied by Electron Spin Resonance Techniques[1]

By M. Thomas Jones[2] and S. I. Weissman

Received April 18, 1962

The rate constants and the activation energies for the electron transfer between tris-*p*-nitrophenylmethyl radical and tris-*p*-nitrophenylmethide ion for all combinations of the sodium or potassium salts in 1,2-dimethoxyethane, tetrahydrofuran, pyridine, and acetonitrile have been measured by electron spin resonance (e.s.r.) methods. The rates lie in the range 10^7 to 10^9 liter mole^{-1} sec.$^{-1}$. The activation energies lie in the range 0.9 to 2.3 kcal. mole^{-1}. The analysis of the rate constants and the activation energies is straightforward except for the case of the sodium tris-*p*-nitrophenylmethide in THF, where the dependence of rate on total methide concentration is not linear. In a particular solvent the sodium salt yields a slower rate than the potassium salt except in acetonitrile.

In this paper we report measurements of the rates of electron transfer reactions between tris-*p*-nitrophenylmethyl and the sodium and potassium salts of the corresponding methide ion. Although the reaction rates lie close to the limit for diffusion controlled processes, heroic techniques are not required for their measurement. The e.s.r. spectrum of dilute solutions of tris-*p*-nitrophenylmethyl consists of about 100 lines in a span of 26 gauss.[3] Addition of the methide ion produces a broadening of the lines from which the mean time between electron transfer events may be determined. The principles of the method have been so thoroughly discussed[4] that we shall not take them up here.

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(1) This work was supported in part by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract and by an equipment loan contract with O.N.R. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.

(2) E. I. du Pont de Nemours and Co., Central Research Department, Experimental Station, Wilmington 98, Delaware.

(3) M. T. Jones, *J. Chem. Phys.*, **35**, 1146 (1961).

(4) A recent review is given by S. I. Weissman, *Z. Elektrochem.*, **64**, 47 (1960).

Experimental

Solvents.—The solvents used were 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), acetonitrile, and pyridine. They were purified to remove traces of water and acidic materials. The DME and THF were refluxed over sodium hydride for 6–8 hours, a center fraction of the distillate collected and stored over sodium-potassium alloy in vacuum storage bottles. The acetonitrile was allowed to stand over sodium hydroxide, distilled and then stored over Molecular Sieves which were prepared by evacuating until they no longer gave off gas at a detectable rate. The pyridine was dried over barium oxide for several days, distilled and stored over Molecular Sieves prepared as described above.

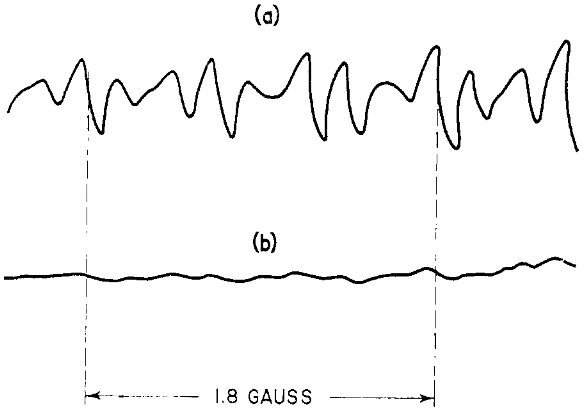

Fig. 1.—(a) Portion of spectrum of saturated solution of tris-*p*-nitrophenylmethyl; (b) with added methide.

Tris-*p*-nitrophenylmethane and Tris-*p*-nitrophenylmethyl Bromide.—Although there are several recipes for preparing tris-*p*-nitrophenylmethane by nitration of triphenylmethane, the one used was that given by Lewis, Lipkin and Magel.[5] The tris-*p*-nitrophenylmethyl bromide was made by refluxing a mixture of bromine and tris-*p*-nitrophenylmethane.[5]

Tris-*p*-nitrophenylmethide Ion.—Methide solutions were prepared by reactions between solution of the methane in DME or THF and alkali metals. All operations were carried out on the vacuum line. The sodium or potassium were deposited as mirrors by vacuum distillation and the excess removed by sealing off after the reaction was complete. When the negative ion was allowed to stand in contact with the alkali metal for extended periods of time a paramagnetic purple solid was formed which remained attached to the surface of the metal mirror. This solid was insoluble in the solvents used in these experiments. This solid was also produced from the reaction of potassium ethoxide and tris-*p*-nitrophenylmethane. Sodium ethoxide did not react to produce this material over a period of several days. This difference was probably due to the solubility difference between sodium and potassium ethoxide in the solvents used. Although the solid was not identified, we suspect it to be a salt of the dinegative ion of tris-*p*-nitrophenylmethyl.

The procedure used for obtaining the extinction coefficients of the sodium and potassium tris-*p*-nitrophenylmethide in DME, THF, and pyridine is given below. An aliquot containing a known amount ($\sim 10^{-6}$ mole) of tris-*p*-nitrophenylmethane in DME was placed in the reaction vessel after an excess of the desired metal ($\sim 10^{-3}$ mole) was placed in a side arm provided on the reaction vessel. The vessel was connected to the vacuum line, the DME solution degassed and the solvent distilled out. The metal was distilled to form a mirror and a small amount of dry ethanol was then allowed to react with it to form the ethoxide. After the metal had completely reacted with the ethanol, the vessel was again evacuated to a "stick vacuum." The desired solvent was then distilled into the vessel, frozen, and the vessel sealed from the line. The tris-*p*-nitrophenylmethane was allowed to react with the ethoxide.[6] The equation of the reaction is written

$$(p\text{-NO}_2C_6H_4)_3CH + CH_3CH_2O^- = (p\text{-NO}_2C_6H_4)_3C^- + CH_3CH_2OH$$

Because of the reactivity of sodium and potassium ethoxide with acetonitrile the above procedure could not be used to determine the extinction coefficients in that solvent. Instead, the negative ion was prepared in DME by the procedure described earlier from the methane and metal. When the desired concentration of negative ion was obtained the reaction was stopped by removal of the metal mirror. An accurate determination of the volume and concentration of the negative ion was then made. The vessel was connected to the vacuum line and the DME removed. When the vacuum reached a "stick vacuum," the acetonitrile was distilled into the vessel. Removal of the acetonitrile and return of the DME restored the original optical absorption.

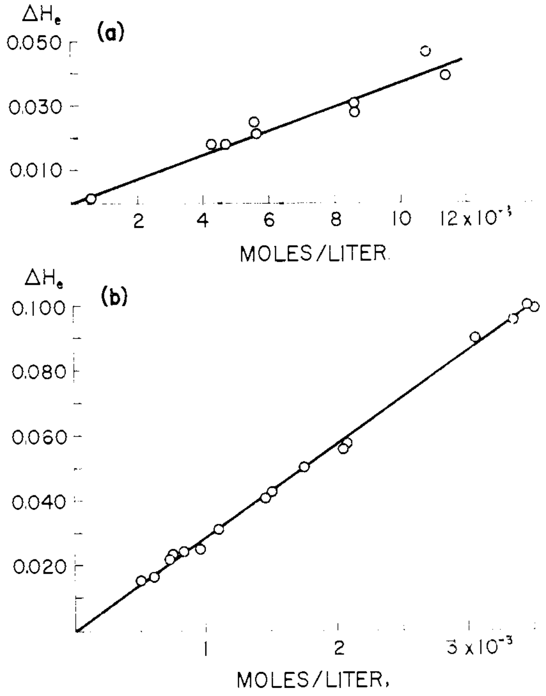

Fig. 2.—Broadening *vs.* concentration of methide in DME: (a) potassium salt; (b) sodium salt.

The reaction of the methane with sodium ethoxide in DME, THF, and pyridine proceeded rapidly and was finished within 15 to 30 minutes. At this point the optical density remained constant for at least several days. On the other hand, the reaction of the methane with potassium ethoxide in DME, THF, and pyridine proceeded more rapidly and was complete in a few minutes. The reaction did not stop at the negative ion and further reaction with the potassium ethoxide produced the insoluble purple solid described above. Therefore, the optical spectrum of the potassium tris-*p*-nitro-phenylmethide had to be taken immediately after it was prepared.

Tris-*p*-nitrophenylmethyl Radical.—The radical, which forms a saturated solution at approximately 5×10^{-4} molar, was produced in two different ways.

To prepare the mixture of radical and negative ion, tris-*p*-nitrophenylmethyl bromide was introduced into a reaction vessel in which the negative ion had been prepared. The reaction between the tris-*p*-nitrophenylmethide ion and the tris-*p*-nitrophenylmethyl bromide is written as

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(5) G. N. Lewis, D. Lipkin and T. T. Magel, *J. Am. Chem. Soc.*, **66**, 1579 (1944).

(6) R. S. Stearns and G. W. Wheland, *ibid.*, **69**, 2025 (1947).

$$(p\text{-}NO_2C_6H_4)_3C^- + (p\text{-}NO_2C_6H_4)_3CBr = 2(p\text{-}NO_2C_6H_4)_3C\cdot + Br^-$$

Obviously, the procedure, as described above, which was used to prepare the mixture of negative ion and radical was satisfactory for solvents such as DME and THF which are stable in the presence of sodium and potassium. However, the procedure had to be modified so that mixtures of the negative ion radical could be made in acetonitrile and pyridine. The whole procedure as described above was used for making a mixture of negative ion and radical in DME. DME was used because the reaction which forms the negative ion proceeds more rapidly in DME than in THF. By means of a breakseal, which was provided for this purpose, the reaction vessel was connected to the vacuum line where the DME was removed and replaced by the desired solvent.

The second procedure used for the preparation of the tris-*p*-nitrophenylmethyl radical was the reaction between mercury and tris-*p*-nitrophenylmethyl bromide. The reaction is written

$$(p\text{-}NO_2C_6H_4)_3CBr + Hg = (p\text{-}NO_2C_6H_4)_3C\cdot + (^1/_2)Hg_2Br_2$$

This procedure was used to prepare a saturated solution of the radical in order to determine the line breadth of the radical solution in the absence of the negative ion. Furthermore, this procedure could be used in all four solvents without any modification and simply consisted of placing mercury and 1–2 mg. of tris-*p*-nitrophenylmethyl bromide in a reaction vessel, evacuating, distilling in the proper solvent, and sealing from the vacuum line.

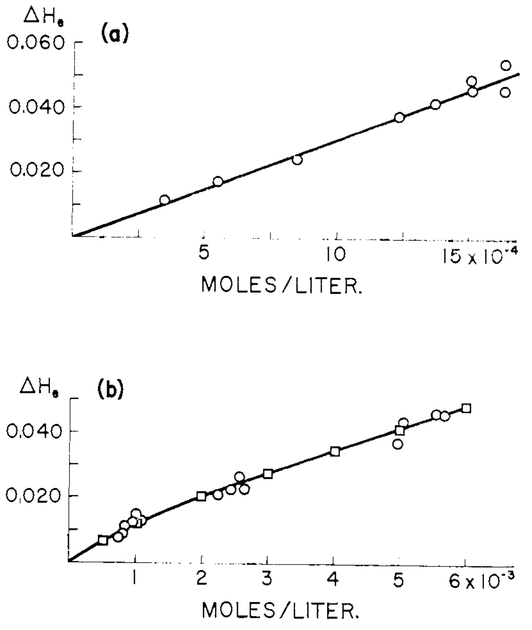

Fig. 3.—Broadening *vs.* concentration of methide in THF: (a) potassium salt, (b) sodium salt.

Optical Measurements.—All of the optical measurements were made on the Cary Recording Spectrophotometer Model 11M, except for the negative ion in pyridine which had to be measured on a Beckman DU Spectrophotometer because the absorption maximum occurs beyond the long wave length limit of the former. The concentration of the negative ion was determined by measuring the optical density at the wave length which yielded the maximum absorption. As few determinations of the extinction coefficients[7,8] of the tris-*p*-nitrophenylmethide ion had been made, it was found necessary to measure them in order to obtain the concentration of the negative ion in the various solvents.

The extinction coefficients of the sodium and potassium tris-*p*-nitrophenylmethide in the four solvents used in these experiments are listed in Table I. The uncertainties listed are measures of precision and are the root mean square deviations.

For each pair of sodium and potassium salts in a particular solvent (with the exception of acetonitrile) the maximum absorption peak of the sodium salt was shifted to shorter wave lengths relative to the potassium salt. Such phenomenon have also been observed in other systems such as the ketyls by Carter, McClelland and Warhurst.[9] This is generally considered to be a symptom of ion pairing, *i.e.*, the member of the series which is shifted to the shortest wave length is the member which forms the most tightly bound ion pair.

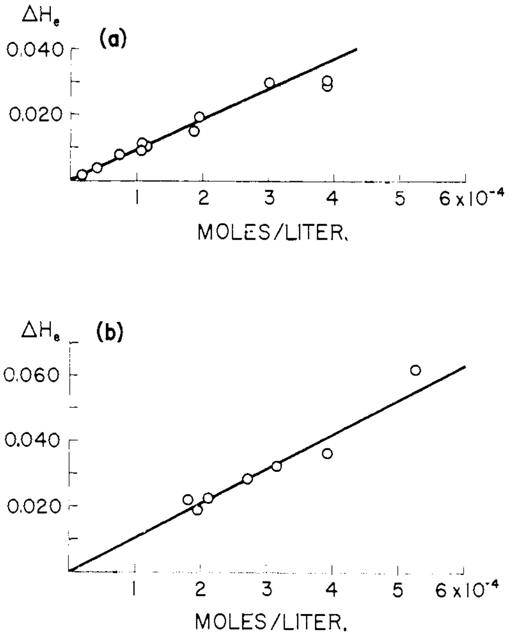

Fig. 4.—Broadening *vs.* concentration of methide in acetonitrile: (a) potassium salt, (b) sodium salt.

TABLE I

EXTINCTION COEFFICIENTS OF TRIS-*p*-NITROPHENYLMETHIDE ION IN VARIOUS SOLVENTS

Positive ion	Solvent	Wave length of max. abs., Å.	Extinction coefficient × 10^{-4}
Sodium	DME	6850	3.40(±0.10)
Potassium	DME	7700	4.77(± .17)
Sodium	THF	6680	3.17(± .11)
Potassium	THF	7800	4.19(± .04)
Sodium	Pyridine	8200	5.95(± .01)
Potassium	Pyridine	8250	6.79(± .08)
Sodium	Acetonitrile	8000	5.88(± .31)
Potassium	Acetonitrile	8000	6.05(± .27)

E.s.r. Measurements.—All of the e.s.r. measurements recorded in this work were obtained by means of a spectrometer which was designed and constructed by Professor J. Townsend of the Department of Physics at Washington

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[7] N. C. Deno, *J. Am. Chem. Soc.*, **74**, 2039 (1952).

[8] K. Ziegler and E. Boyle, *Ann.*, **458**, 252 (1927).

[9] H. V. Carter, B. J. McClelland and E. Warhurst, *J. Chem. Soc.*, 455 (1960).

University. The klystron was operated at a frequency near 9000 Mc. and the applied field was near 3200 gauss. The magnetic field was modulated at 100 kc. In all experiments reported here the modulation amplitude was set at 0.02 gauss.

Low Temperature Measurements.—In order to obtain values for the activation energies for each of the reactions, it was necessary to make measurements of the electron transfer rates at several temperatures below room temperature. The low temperatures were obtained by boiling liquid nitrogen and streaming the cold gas past the samples which were surrounded by a vacuum-jacketed quartz tube in the microwave cavity. The temperature was measured with a copper-constantan thermocouple connected to a Leeds and Northrup continuous indicator. The temperature could be controlled very easily to within 1°.

Results

Because of the complexity of the hyperfine structure exhibited by the radical and the fact that some of the lines overlap slightly, the question arises as to which of the lines should be considered in determining the amount of broadening which has occurred. The lines which were chosen are shown on the spectrum of the tris-*p*-nitrophenylmethyl radical displayed in Fig. 1. These lines were chosen because of their intensity relative to their neighbors and because their broadening is directly measurable. The spectra were recorded two or three times each for a saturated solution of the tris-*p*-nitrophenylmethyl radical and the solution containing the mixture of radical and the tris-*p*-nitrophenylmethide ion. The breadths of each of the six lines chosen were measured between points of extreme slope and averaged.

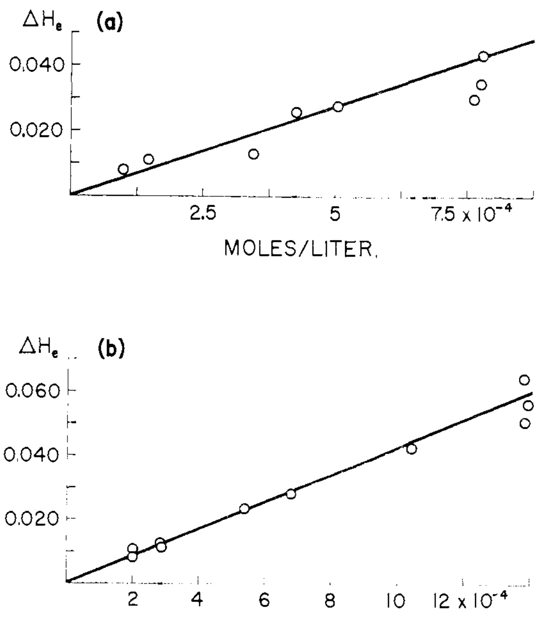

Fig. 5.—Broadening *vs.* concentration of methide in pyridine: (a) potassium salt, (b) sodium salt.

The primary quantity obtained from the increase of line breadth on addition of the methide is the reciprocal of the mean lifetime of a radical molecule. In each case except that of the sodium salt in THF, the reciprocal of the mean lifetime is a linear function of concentration of the methide. Hence the electron transfer reaction is first order with respect to the methide. Although a direct determination of the order with respect to radical concentration was not possible because of limited solubility of the radical, it is most likely that the reaction is first order. The rate constants calculated on the assumption of first order dependence on radical concentration lie within the limits for diffusion controlled reactions, while the assumption of any higher order leads to unreasonably large rate constants. Thus the assumption of second order dependence on radical concentration leads to rate constants greater than 10^{12} M^{-2} sec.$^{-1}$. We shall tabulate all the data on the assumption that the reactions are first order with respect to radical concentration.

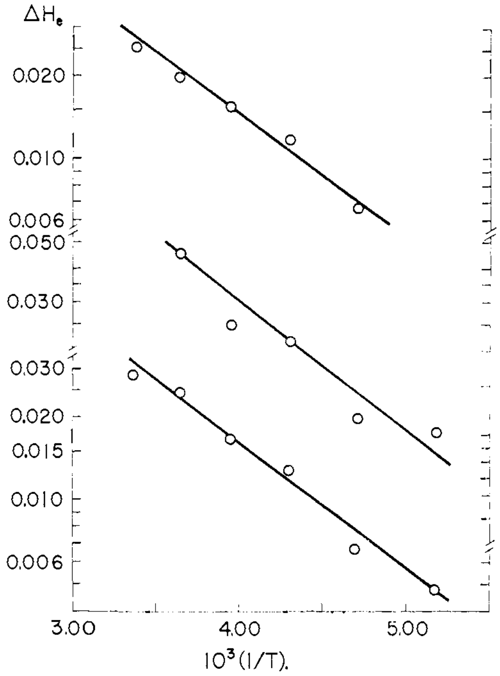

Fig. 6.—Logarithm of broadening *vs.* $1/T$ at several concentrations of potassium methide in DME.

Representative plots of line broadening *versus* concentration of methide are given in Figs. 2 to 5. Only in the case of the sodium salt in THF is there a significant deviation from linearity.

Rate constants are listed in Table II. The two numbers given for the reaction with the sodium salt in THF represent slopes at high and low concentrations.

The activation energies were determined from the temperature dependence of the contribution to the line breadth due to the electron transfer process. The line breadth of the saturated radical solution also displayed a temperature dependence which had to be taken into consideration.

Representative plots of log ΔH_e at fixed methide concentration *versus* $1/T$ are given in Figs. 6 to 9. The corresponding activation energies are listed in Table II. The slopes were obtained from a least squares fit and the uncertainties given are the root mean square deviations of the values from their respective means.

Significant deviations from linearity appear only for the reaction of the sodium salt in THF. The two listed activation energies for the latter reaction correspond to slopes at 300° and 220° K., respectively.

The dependence of the optical spectrum of the methide on cation in all the solvents except acetonitrile suggests that the methide and cation are predominantly associated. Since the rate constants relative to the total methide concentration are very high, the reactions probably do not proceed through species such as dissociated ions present in low concentration. The reaction, except in acetonitrile, should probably be represented as $R\cdot + M^+R^- \rightleftarrows R^-M^+ + R\cdot$. An argument based on detailed balancing excludes the reaction $R\cdot + M^+R^- \rightarrow R^- + M^+ + R\cdot$.

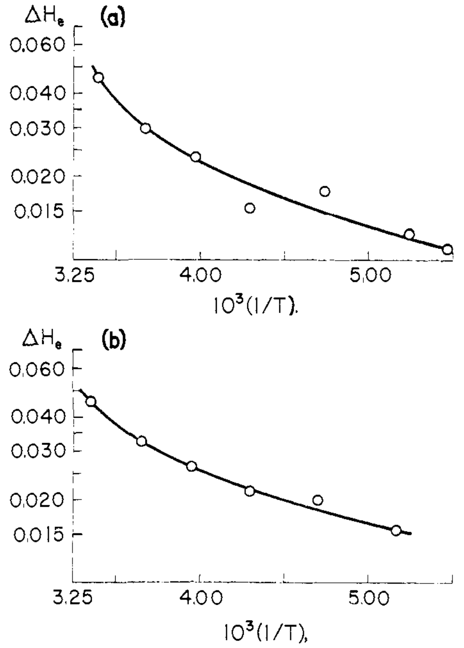

Fig. 7.—Logarithm of broadening *vs.* $1/T$ at two concentrations of sodium methide in THF.

TABLE II

RATE CONSTANTS AND ACTIVATION ENERGIES

Positive ion	Solvent	$k \times 10^{-8}$ at 25°, M^{-1} sec.$^{-1}$	Activation energy, kcal.
Sodium	DME	4.35 ± 0.15	2.04 ± 0.24
Potassium	DME	5.99 ± 0.81	1.99 ± .07
Sodium	THF	0.76 ± 4.56	0.86 ± .05– 2.63 ± .42
Potassium	THF	4.70 ± 0.23	2.25 ± .06
Sodium	Pyridine	6.79 ± 0.59	2.03 ± .33
Potassium	Pyridine	8.7 ± 2.5	1.95 ± .29
Sodium	Acetonitrile	16.3 ± 1.5	1.04 ± .08
Potassium	Acetonitrile	13.8 ± 1.6	1.12 ± .23

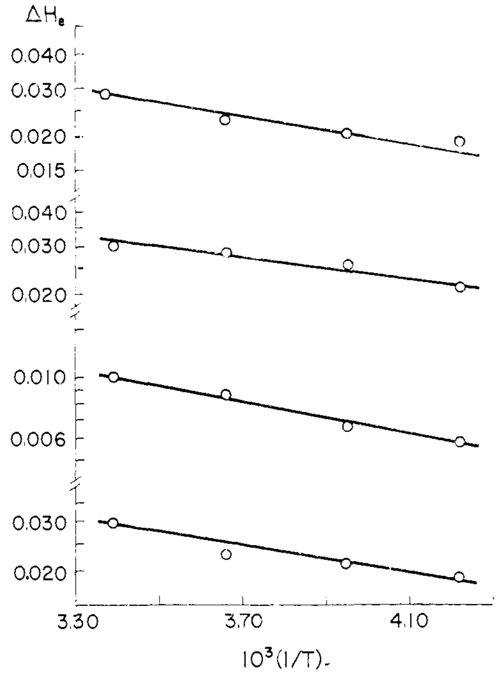

Fig. 8.—Logarithm of broadening *vs.* $1/T$ for several concentrations of potassium methide in acetonitrile.

It is interesting that such a reaction proceeds with very low activation energy. In acetonitrile where the reaction may proceed through dissociated ions the rates and activation energies are not greatly different from the other cases.

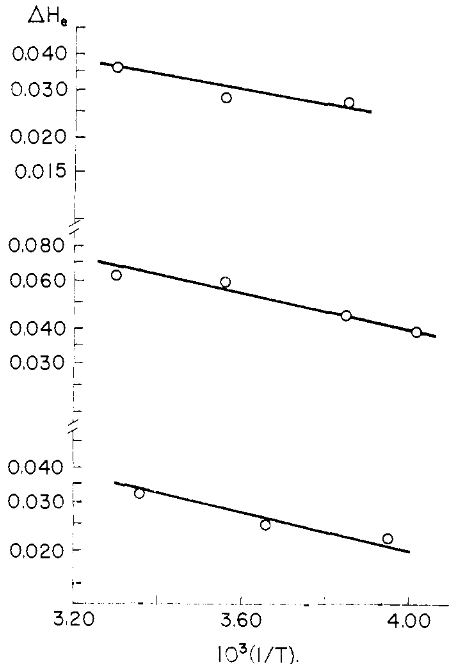

Fig. 9.—Logarithm of broadening *vs.* $1/T$ for several concentrations of sodium methide in acetonitrile.

In the reaction with the sodium salt in THF, where departures from first order dependence of reciprocal lifetime or methide concentration are observed, the reaction probably proceeds by two or more paths, the relative contribution of the paths being both concentration and temperature dependent. Examination of the ketyls in THF[10] reveals an equilibrium between single ion pairs and clusters with the clusters yielding low transfer rates. Such phenomena are probably responsible for the anomalies reported here.

(10) Work of N. Hirota, this Laboratory.