The Disproportionation of Trityl Benzyl Ethers. Kinetic Analysis of the Trityl Salt Catalyzed Reaction. Evidence for the Involvement of Ion Pairs in the Hydrogen Transfer Step

Michael P. Doyle*[1] and Bernard Siegfried

Contribution from the Department of Chemistry, Hope College, Holland, Michigan 49423. *Received April 25, 1975*

Abstract: Trityl benzyl ethers disproportionate to triphenylmethane and benzaldehydes in reactions catalyzed by trityl salts. The rate of reaction is dependent on the concentrations of the ether and the trityl salt. At 25° in methylene chloride, the enthalpy of activation for the disproportionation of trityl benzyl ether, catalyzed by triphenylmethyl hexafluoroarsenate, is 9.8 kcal/mol; the corresponding entropy of activation is −34.8 eu. The rate constants for the triphenylmethyl hexafluoroarsenate catalyzed disproportionation of substituted benzyl trityl ethers in methylene chloride correlate with Hammett σ values yielding a ρ value of −4.0. These results are discussed in relationship to the mechanism of the hydrogen transfer process. The kinetic isotope effect, determined with benzyl and α,α-dideuteriobenzyl trityl ethers and triphenylmethyl hexafluoroarsenate, is 9.74. The corresponding isotope effect observed with triphenylmethyl tetrafluoroborate is 3.56. This result is interpreted as demonstrating that the extent of hydrogen transfer in the rate-limiting step for ether disproportionation is dependent on the trityl salt ion pair rather than solely on the trityl cation. Conductometric measurements on both triphenylmethyl hexafluoroarsenate and tetrafluoroborate salts were made in methylene chloride. Triphenylmethyl hexafluoroarsenate behaves as a weak electrolyte; the tetrafluoroborate salt exhibits abnormal behavior.

The formal transfer of hydrogen with its pair of electrons from carbon to an electrophilic center is of fundamental importance in numerous reaction processes.[2] However, many of these processes are not amenable to kinetic studies and, consequently, their detailed mechanisms, particularly of those reactions involving intermolecular hydrogen transfer, have not been investigated.

Carbocation reductions by alcohols and ethers have received considerable attention.[2-6] In a majority of these investigations, strongly acidic media supported the carbenium ion. Kinetic parameters for intermolecular reactions involving the triphenyl and related carbenium ions have been obtained.[3,4] However, due to the nature of the reacting systems, the kinetic data reflected the energetics of hydrogen transfer from the alcohol or ether to the carbocation as well as the relative stabilities of the reacting cation and the cation being formed (eq 1).

$$(C_6H_5)_3C^+ + R_2CH{-}O{-}A \rightarrow (C_6H_5)_3CH + R_2C{=}O + A^+ \qquad (1)$$

We have recently reported that trityl alkyl ethers disproportionate to triphenylmethane and a carbonyl compound in a reaction catalyzed by stable triphenylmethyl salts (eq 2).[7]

$$(C_6H_5)_3C{-}O{-}CHR_2 \xrightarrow[(Z^- = AsF_6^-,\ BF_4^-)]{(C_6H_5)_3C^+Z^-} (C_6H_5)_3CH + R_2C{=}O \qquad (2)$$

This disproportionation process occurs readily in nonacidic solvents, such as methylene chloride, and is well suited to kinetic investigations. Solvation effects are minimized in methylene chloride, and the reacting cation and the cation being formed are identical. In addition, since the solvent is nonnucleophilic, the effect, if any, of variation in the anion associated with the carbocation catalyst can be established. We report the results of our investigations of the process represented by eq 2.

Results and Discussion

Trityl benzyl ethers disproportionate to triphenylmethane and substituted benzaldehydes quantitatively in methylene chloride or acetonitrile solutions. The rate of disproportionation is proportional to the concentration of the ether and to the trityl salt catalyst concentration.[7] With trityl benzyl ether and triphenylmethyl hexafluoroarsenate in methylene chloride, the second-order rate constant at 23.5° is $3.43 \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$.[8] Activation parameters for trityl benzyl ether disproportionation were obtained from kinetic determinations at seven different temperatures over the range 0.2-32.7°. A plot of ln k_2 vs. $1/T$ gave a straight line (correlation coefficient = 0.991). For the reaction at 25°, the enthalpy of activation was calculated to be a relatively low 9.8 ± 0.2 kcal/mol, and the entropy of activation was −34.8 ± 0.8 eu. Comparative values from the reaction of the triphenylmethyl cation with ethyl ether in aqueous sulfuric acid at the same temperature were $\Delta H^\ddagger = 18.9$ kcal/mol and $\Delta S^\ddagger = -15$ eu.[3,9] The comparatively low $\Delta H^\ddagger$ value for the trityl ether disproportionation appears to reflect the stabilization imparted to the reacting system by the ether triphenylmethyl group compared with the ethyl group in the corresponding ethyl ether oxidation (or to a proton in alcohol oxidations[3]). The highly negative $\Delta S^\ddagger$ value for trityl benzyl ether disproportionation reflects the severe steric requirements in this hydrogen transfer process.

Hydrogen transfer can occur to the central tertiary electrophilic carbon of the triphenylmethyl cation or to the less hindered ortho or para positions of the phenyl rings of this ambident electrophile. This latter process has recently been observed in hydrogen transfer reactions from metal hydrides and from cycloheptatriene but does not occur in hydrogen abstraction by the trityl cation from simple ethers.[10] The hydrogen transfer step in the disproportionation of trityl benzyl ethers might be expected to differ from that with simple ethers, however, because of steric crowding around the ether oxygen of trityl benzyl ether. To determine the actual site of the transferred hydrogen, α,α-dideuteriobenzyl trityl ether was prepared and reacted with both triphenylmethyl hexafluoroarsenate and tetrafluoroborate in separate experiments. Only triphenylmethane possessing deuterium at the tertiary carbon was observed in each of these reactions within the limits of our detection. If hydrogen transfer to the phenyl ring had occurred, the triphenylmethane

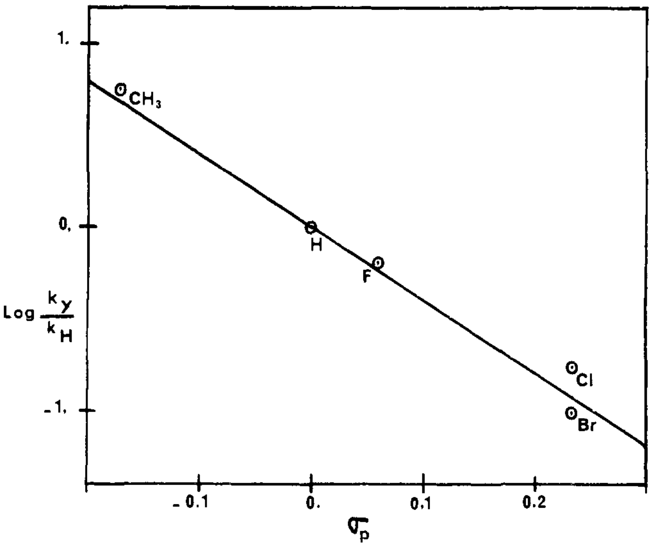
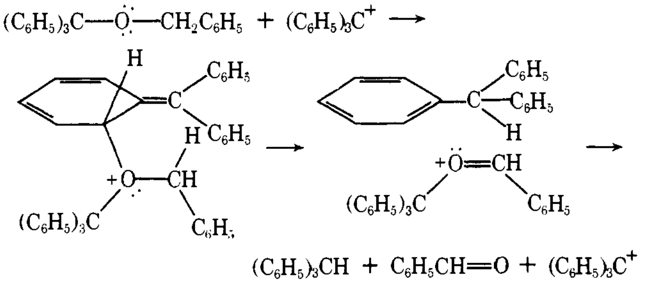


Figure 1. Hammett plot for triphenylmethyl hexafluoroarsenate catalyzed disproportionation of trityl benzyl ethers in methylene chloride at 23.5°.

product would have retained a portion of the deuterium in the aromatic ring.

The present results are consistent with the reaction process proposed by Olah and Svoboda (Scheme I) in which interaction of the ether oxygen with electrophilic sites of the trityl cation phenyl rings precedes hydrogen transfer.[10] This preliminary interaction may not lead to a stable intermediate but does serve to bring together the reactive sites of the hydrogen donor and the hydrogen acceptor.

Scheme I

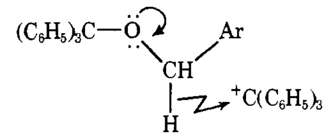


The second-order rate constants at 23.5° for a series of para-substituted benzyl trityl ethers are reported in Table I. Attempts were made to include *p*-methoxybenzyl trityl ether in this kinetic analysis. However, competing hydride transfer involving the methoxy group prevented kinetic comparison of this very reactive substrate with those in Table I. A surprisingly good correlation between log (k_Y/k_H) was observed with the Hammett σ values[11] (correlation coefficient = 0.990), yielding a ρ value of -4.0 ± 0.1 (Figure 1). Similar correlations with the Brown-Okamoto σ^+ constants[12] ($\rho = -3.6 \pm 0.3$, correlation coefficient = 0.961) or with the calculated σ^+ constants of Swain and Lupton[13] ($\rho = -3.4 \pm 0.8$, correlation coefficient = 0.737) were much less satisfactory. The application of σ rather than σ^+ constants to this system is in accordance with Scheme I and suggests that primary resonance stabilization of the developing sp^2-hybridized carbon is due to *n*-bonding electrons on the adjacent oxygen rather than from the substituted phenyl ring. The sign and magnitude of the ρ value for trityl benzyl ether disproportionation indicate a substantial degree of positive charge development at the benzyl carbon.

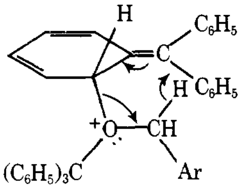
Table I. Second-Order Rate Constants for the Disproportionation of Trityl Benzyl Ethers in Methylene Chloride at 23.5°[a]

p-Y-$C_6H_4CH_2$-$OC(C_6H_5)_3$ Y =	[Ether], *M*	$[(C_6H_5)_3C^+$-$AsF_6^-]$, *M*	10^3k,[b] M^{-1}, sec^{-1}
CH$_3$	0.321	0.101	19.10
H	0.295	0.101	3.43
F	0.384	0.107	2.22
Cl	0.306	0.212	0.611
Br	0.326	0.107	0.329

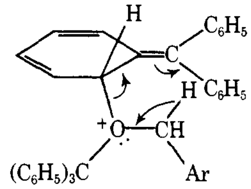
[a] Temperature control was within ±0.1°. [b] The maximum standard deviation from duplicate or triplicate runs with each ether was ±2.5% of the reported value.



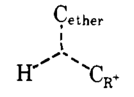
1



2a



2b



3

In the mechanism for trityl benzyl ether disproportionation, hydrogen transfer can be assumed to occur directly to the tertiary carbon of the triphenylmethyl cation (**1**) or occur subsequent to formation of an oxonium ion (**2**) as indicated by Scheme I. If hydrogen transfer is a direct process, a hydrogen with its pair of electrons is abstracted by the trityl cation. If, however, interaction of the ether oxygen with the triphenylmethyl cation occurs at the ortho position to produce a stable intermediate, two representations may be employed to describe the transfer of hydrogen. That shown by **2b** essentially involves a proton transfer, whereas the alternate representation in which the flow of electrons is reversed describes a "hydride" transfer. "Hydride" transfer is appropriately described by a three-center, two-electron transition state or intermediate (**3**), rather than by a linear movement of hydrogen with its pair of electrons from the benzyl carbon to the tertiary carbon of the triphenylmethyl cation. In each of these structures (**1**, **2a**, and **2b**), a high entropy of activation would be expected to characterize the hydrogen transfer process. However, due to the nature of the three-center, two-electron transition state, steric crowding during the hydrogen transfer process, particularly in the trityl ether disproportionation reaction, should conceivably be especially restrictive. Kinetic data for hydrogen transfer from secondary and tertiary positions on alkanes by *tert*-alkyl cations have been reported. The $\Delta S^\ddagger$ values for hydrogen abstraction reactions of *tert*-hexyl hexafluoroantimonate at the secondary positions of either *n*-hexane or 2,2-dimethylbutane in HF were determined to be −17 and −18 eu, respectively;[14] for the corresponding reaction between isobutane and the *tert*-butyl cation in SO_2-CH_2Cl_2 containing AsF_5, the $\Delta S^\ddagger$ value was −27 eu.[15] Both reactions are reported to involve a three-center, two-electron transition state for hydrogen transfer and suggest that a similar process is not unreasonable in the trityl ether disproportionation reaction. Yet in view of the paucity of data concerning the steric requirements of hydrogen transfer through a three-center, two-electron transition state,[16] no definite conclusion can be drawn concerning the appropriateness of proton or hydride transfer mechanisms solely on the basis of activation parameters.

Among the processes representing hydrogen transfer, both "hydride" abstraction without prior oxonium ion formation (**1**) and that involving prior oxonium ion formation (**2a**) should produce the same effect on the benzyl carbon during hydride transfer, namely positive charge development. On the other hand, in the transition state for the proton transfer reaction (**2b**), electron-donating substituents on the substituted phenyl group would not be expected to facilitate proton transfer to the extent that has been observed. Although no clear-cut distinction can be made here regarding the exact nature of the hydrogen transfer process, the present results do point to "hydride" abstraction as being involved in the reactions of ethers with the triphenylmethyl cation.

The isotope effect for the triphenylmethyl hexafluoroarsenate catalyzed disproportionation of trityl benzyl ether was obtained from the rate constants for reactions of the benzyl and α,α-dideuteriobenzyl trityl ethers in methylene chloride. The high value of 9.74 determined for k_H/k_D at 23.5° reflects both primary and secondary kinetic isotope contributions and is near the theoretical maximum expected for the isotope effect in a linear transfer of hydrogen.[17] However, since the maximum primary kinetic isotope effect in hydrogen transfer reactions proceeding through a three-center, two-electron transition state has not yet been estimated, no conclusion can be made from this data regarding the nature of the hydrogen transfer process. Indeed, the actual difference between a linear and a three-center transition state in trityl ether disproportionation reactions may be diminished due to distortions caused by steric crowding.

The triphenylmethyl tetrafluoroborate catalyzed disproportionation reaction was investigated to determine the effect of different trityl salts on the extent of hydrogen transfer. Previous studies have assumed that the counterion played no important role in the actual hydrogen transfer step. For the disproportionation of trityl benzyl ether, the second-order rate constant for the triphenylmethyl tetrafluoroborate catalyzed reaction was 3.68×10^{-2} M^{-1} sec^{-1}, more than ten times greater than that for the triphenylmethyl hexafluoroarsenate catalyzed reaction ($k_{BF_4^-}/k_{AsF_6^-} = 10.7$). In itself this rate increase by the tetrafluoroborate salt may reflect either differences in equilibrium steps prior to the rate-limiting step or an actual difference in the hydrogen-transfer step. However, the deuterium isotope effect for the trityl tetrafluoroborate catalyzed reaction, obtained in the same manner as that for the trityl hexafluoroarsenate catalyzed reaction, was found to be 3.56. This result can only be interpreted as demonstrating that the extent of carbon-hydrogen bond cleavage in the rate-limiting step is greater when the tetrafluoroborate salt is used than when the hexafluoroarsenate salt is employed.[18]

Differences in the reactivities of trityl ether disproportionation reactions with triphenylmethyl tetrafluoroborate and hexafluoroarsenate salts can be attributed to corresponding differences in the "effective" concentration of the trityl cation in the reaction medium. The effective concentration of the trityl cation is related to the degree of ion pairing of trityl salts.[19] However, this same explanation does not account for the observed change in the kinetic isotope effect with a change in the catalyst. These results are explained if the ion pair itself is involved in the hydrogen-transfer step.

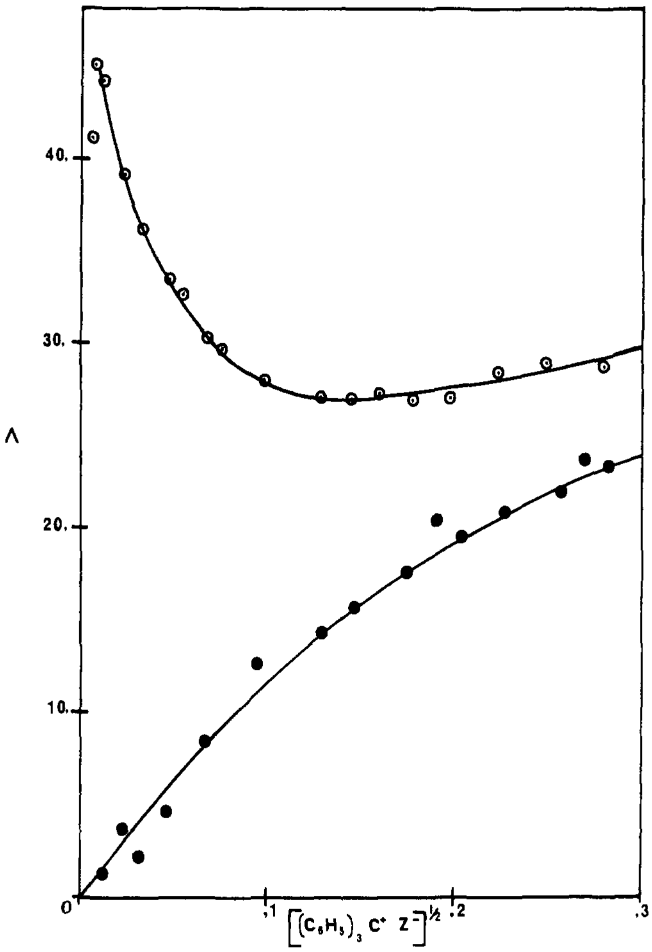


Figure 2. Molar conductivity (Λ, ohm^{-1}, cm^2, eq^{-1}) for triphenylmethyl hexafluoroarsenate (⊙) and tetrafluoroborate (●) salts in methylene chloride at 23.5°.

To determine the nature of the trityl salts in methylene chloride, conductometric measurements were made on both triphenylmethyl hexafluoroarsenate and triphenylmethyl tetrafluoroborate in methylene chloride at 23.5°. The results from this study are presented in Figure 2. Surprisingly, the tetrafluoroborate salt does not exhibit the behavior expected of a weak electrolyte (e.g., the AsF_6^- salt)[20] over the entire range of concentrations used. At low concentrations, the plot of Λ vs. $[Ph_3C^+BF_4^-]^{1/2}$ is reminiscent of the titration curve of a very weak acid.[21] The continual decrease in conductance with decreasing concentration suggests that a chemical reaction between the triphenylmethyl cation and the tetrafluoroborate anion, such as that described in eq 3,[22] is occurring.

$$(C_6H_5)_3C^+ + BF_4^- \rightleftharpoons (C_6H_5)_3C{-}F + BF_3 \qquad (3)$$

This same behavior is observed in spectral measurements of the triphenylmethyl tetrafluoroborate salt in the low concentration range; the molar absorptivity decreased with decreasing concentration.[23]

Although it is not possible to provide meaningful ion-pair dissociation constants for the two trityl salts using the data from Figure 2, the two salts do appear to be similar in the concentration range employed for the kinetic measurements. However, the abnormal behavior of the tetrafluoroborate salt does suggest that care be used in interpretations of results from studies employing this reagent.

Experimental Section

Instrumentation. Proton magnetic resonance spectra were obtained with a Varian Model A-60A spectrometer; chemical shifts are reported in δ units using tetramethylsilane as the internal reference. Analytical GLC analyses were performed on a Varian Aerograph Model 2720 gas chromatograph using thermal conductivity detectors. Use was made of 5-ft columns of 20% Carbowax 20M on Chromosorb P. Mass spectra were obtained using a Finnigan Model 1015 gas chromatograph-mass spectrometer operated at 70 eV. A Cary 14 recording spectrophotometer was used to obtain uv-visible spectra. Calculations were performed on the CDC 3800 computer of the University of Geneva. Melting points were obtained on a Thomas-Hoover apparatus and were not corrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Materials. Triphenylmethyl tetrafluoroborate and hexafluoroarsenate salts (Ozark-Mahoning Co.) were dried at 10 Torr for several hours prior to use. Anhydrous dichloromethane was distilled from calcium hydride through a 30-cm Vigreux column at atmospheric pressure; a center fraction was collected, redistilled from calcium hydride, and stored over molecular sieves 4A.

Syntheses of Trityl Benzyl Ethers. Trityl ethers were prepared from the reaction of trityl chloride with the appropriate alcohol in pyridine. A typical synthesis for *p*-chlorobenzyl triphenylmethyl ether involved the addition of 13.9 g (0.050 mol) of trityl chloride to 7.13 g (0.050 mol) of *p*-chlorobenzyl alcohol in 25 ml of anhydrous pyridine. The resulting solution was stirred at 70-80° for 3 hr and cooled, and the pyridine was removed by distillation under reduced pressure. Methylene chloride (300 ml) and water (300 ml) were subsequently added, the solution was thoroughly mixed, and the aqueous and organic layers were separated. The aqueous solution was washed twice with 150-ml portions of methylene chloride and the combined methylene chloride solution washed once with 300 ml of water. The organic solution was passed through anhydrous magnesium sulfate and the methylene chloride removed under reduced pressure. The resulting solid was recrystallized from ether-acetone to give 16.8 g (0.040 mol, 80% yield) of *p*-chlorobenzyl triphenylmethyl ether, mp 137-138° (lit.[24] mp 136-137°). No attempt was made to maximize the yields of trityl ethers. Physical constants of the trityl benzyl ethers corresponded to those reported in the literature.[24] *p*-Bromobenzyl trityl ether, mp 150.5-152.5°, and *p*-fluorobenzyl trityl ether, mp 130.0-131.0°, had not been prepared earlier.

Anal. Calcd for $C_{26}H_{21}BrO$: C, 72.73; H, 4.93; Br, 18.61. Found: C, 72.56; H, 4.96; Br, 18.42.

Anal. Calcd for $C_{26}H_{21}FO$: C, 84.76; H, 5.74; F, 5.16. Found: C, 84.83; H, 5.60; F, 5.10.

Trityl α,α-dideuteriobenzyl ether was prepared from trityl chloride and α,α-dideuteriobenzyl alcohol by the above procedure, mp 102-103°. The ^1H NMR spectrum of this ether exhibited no detectable methylene absorption; mass spectral analysis showed the molecular ion at *m/e* 352 and no peak at *m/e* 350.

Kinetic Measurements. In a typical experiment, a 25.0-ml stock solution of between 0.6 and 0.8 *M* trityl benzyl ether and 0.20 *M* in the ^1H NMR or GLC standard (diphenylmethane or toluene) was prepared using anhydrous methylene chloride. A 25.0-ml stock solution of methylene chloride containing 0.2 to 0.4 *M* trityl salt was also prepared. The ether-standard stock solution (5.00 ml) was pipetted into a three-necked flask set in a thermostated water bath at the reaction temperature. After 20 min of temperature equilibration, 5.00 ml of the stock trityl salt, also thermostated, was added to the three-necked flask. At regular intervals, 0.2-0.5 ml aliquots were removed from the reaction solution and transferred to NMR tubes wetted with 1 drop of D_2O. The reaction was quenched by capping the tube and shaking until the light brown reaction solution became clear. All reactions were performed under nitrogen with suitable precautions to ensure the absence of water. Each aliquot was analyzed by ^1H NMR spectroscopy through comparison of the aldehydic proton signal of benzaldehyde with the methylene proton signal of diphenylmethane or the methyl proton signal of toluene. The average of between five and seven integrations was determined for each aliquot. Reactions were followed over at least 2 half-lives. Deuteriobenzaldehyde was quantitatively analyzed by GLC methods through comparison with the toluene internal standard. Duplicate runs of each kinetic determination were made. Least-squares analysis of each set of data was used to determine the rate constant for the first-order rate equation.

Conductivity measurements were made with a Methrom Conductoscope E365B using a cell having a constant of 0.790 cm^{-1} at 23.5°. The cell constant was verified by the semiempirical equation of Chiu and Fuoss[25] for the molar conductivity of potassium chloride at 23.5°. All solution transfers were made in a drybox under a nitrogen atmosphere. The cell was washed with water, acetone, and dichloromethane, dried in an oven at 110°, cooled in the drybox, and finally dried with a stream of nitrogen. A stock solution of the trityl salts (0.10-0.15 *M*) was prepared under nitrogen; dilutions were made in the drybox. A 3-ml aliquot of the stock solution was transferred to the cell thermostated at 23.50 ± 0.02° and the conductivity measured after 15 min. No variation was observed in the conductivity after the first measurement. Dilutions for the trityl salts were made in the range $0.15-3 \times 10^{-5}$ *M*. The solvent conductivity was negligible. Two runs were made for each salt using two different stock solutions. Substantial agreement between the two runs was observed.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation for this work. We thank Mr. Jared Thomas for the synthesis of the substituted benzyl trityl ethers used in this study.

References and Notes

(1) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee, 1973-1978.

(2) Detailed reviews of intermolecular processes are provided by (a) C. D. Nenitzescu in "Carbonium Ions", Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, Chapter 13; (b) N. C. Deno, H. J. Peterson, and G. S. Saines, *Chem. Rev.*, **60**, 7 (1960).

(3) P. D. Bartlett and J. D. McCollum, *J. Am. Chem. Soc.*, **78**, 1441 (1956).

(4) N. C. Deno, G. Saines, and M. Spangler, *J. Am. Chem. Soc.*, **84**, 3295 (1962), and references therein.

(5) D. H. R. Barton, P. D. Mangus, G. Smith, G. Streckert, and D. Zurr, *J. Chem. Soc. C*, 542 (1972).

(6) G. Baddeley and P. G. Nield, *J. Chem. Soc.*, 4684 (1954); H. Burton and G. W. H. Chesseman, *ibid.*, 986 (1953); A. Reiche and E. Schmitz, *Chem. Ber.*, **90**, 531 (1957); F. G. Kny-Jones and A. M. Ward, *J. Chem. Soc.*, 535 (1930); M. P. Balfe, J. Kenyon, and E. M. Thain, *ibid.*, 790 (1952).

(7) M. P. Doyle, D. J. DeBruyn, and D. J. Scholten, *J. Org. Chem.*, **38**, 625 (1973).

(8) This value is higher than that previously reported[7] by a factor of 2.6, due primarily to water contamination of the methylene chloride used earlier for kinetic determinations. A repeat of the experiments to determine the rate law, however, showed the same dependence of the rate on the cation salt and ether concentration.

(9) Both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were observed to change with alcohol and ether structure.[3] However, the variation in these parameters was relatively small ($\Delta H^\ddagger$ = 16.8 kcal/mol and $\Delta S^\ddagger = -21$ eu for isopropyl ether oxidation, for example).

(10) G. A. Olah and J. J. Svoboda, *J. Am. Chem. Soc.*, **95**, 3794 (1973).

(11) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(12) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4980 (1958).

(13) C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.*, **90**, 4328 (1968).

(14) D. M. Brouwer and J. M. Oelderik, *Recl. Trav. Chim. Pays-Bas*, **87**, 721 (1968).

(15) S. Brownstein and J. Bornais, *Can. J. Chem.*, **49**, 7 (1971).

(16) (a) G. A. Olah, Y. K. Mo, and J. A. Olah, *J. Am. Chem. Soc.*, **95**, 4939 (1973); (b) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *ibid.*, **95**, 4960 (1973); (c) D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, **9**, 179 (1972), and references therein.

(17) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(18) A. J. Kresge, D. S. Sagatys, and H. L. Chen, *J. Am. Chem. Soc.*, **90**, 4174 (1968); R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 194 (1970).

(19) (a) J. W. Bayles, A. G. Evans, and J. R. Ross, *J. Chem. Soc.*, 206 (1955); (b) F. Fairbrother and B. Wright, *ibid.*, 1058 (1949).

(20) N. N. Lichtin, *Prog. Phys. Org. Chem.*, **1**, 75 (1963); T. Shedlovsky in "Physical Methods of Organic Chemistry", Vol. 1, Part 4, 3rd ed, A. Weissberger, Ed., Wiley-Interscience, New York, N.Y., 1960, Chapter 45.

(21) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", 2nd ed, Butterworths, London, 1959, Chapter 12.

(22) Similar processes are observed spectrometrically from trityl bromide and stannic bromide[19b] and from trityl chloride and mercuric chloride.[19a]

(23) Since two independent analytical methods, conductometric and spectrometric, describe the same anomalous behavior of triphenylmethyl tetrafluoroborate, it appears unlikely that these observations could be interpreted as being due to fortuitous impurities in the trityl salt. Also, the absence of impurities in the solvent is amply demonstrated by the differences in and reproducibility of the conductance data for the trityl salts in methylene chloride.

(24) M. F. Hawthorne and D. J. Cram, *J. Am. Chem. Soc.*, **76**, 3451 (1954).

(25) Y. C. Chiu and R. M. Fuoss, *J. Phys. Chem.*, **72**, 4123 (1968).