[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Solvent Effects in the Reaction of *p*-Substituted α-Chlorotoluenes with Thiosulfate

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The rates of reaction of α-chloro-, α-chloro-*p*-nitro-, α-chloro-*p*-isopropyl- and α,*p*-dichlorotoluenes with sodium thiosulfate have been measured at 30° in 60% bis-(2-methoxyethyl) ether–40% water and in 60% ethanol–40% water mixtures. The ratio of the rates in the two solvents (k_D/k_E) varies from 2.71 for the nitro compound to 0.95 for the isopropyl compound, and appears to be a linear function of the σ-values of the substituents.

Extensive studies of solvent effects in solvolysis reactions have been reported.[1] Correlative equations[2–4] are available which often permit the prediction of solvolysis rates for a variety of compounds and solvents. Solvent effects in nonsolvolytic nucleophilic substitution reactions have received relatively little attention, even in the common case of direct displacement by anions on neutral molecules, although an equation has been proposed[5] which deals with both the nucleophilic and electrophilic species attacking a substrate molecule.

In general, rates of solvolysis are enhanced by solvents of high ion-solvating ability. By contrast, second-order reactions between anions and molecules are usually faster in solvents of low dielectric constant and poor ion-solvating ability,[6] unless the ion pairs are incompletely dissociated under these conditions.[6] In the latter case the addition of a limited amount of a solvating solvent causes an increase in dissociation and rate, but further addition decreases the rate because of the relatively large loss of solvation energy in attaining the diffusely charged and weakly solvated transition state from the strongly solvated, ionic initial state.

In the present study the rates of reaction of three of four *p*-substituted-α-chlorotoluenes with sodium thiosulfate were found to be faster in a mixture of 60% bis-(2-methoxyethyl) ether (diglyme) and 40% water (dielectric constant at 20°, 36.4[7]) than in a more strongly solvating mixture of 60% ethanol and 40% water (dielectric constant 44.7[4]) (Table I). By contrast, α-chloro-*p*-isopropyltoluene reacted more rapidly in ethanolic solution than in aqueous diglyme, although the small difference does not greatly exceed the experimental error. The ratio $k_{\text{diglyme}}/k_{\text{ethanol}}$ varies from 2.71 for α-chloro-*p*-nitrotoluene to 0.95 for α-chloro-*p*-isopropyltoluene, and appears to approach a linear function of the σ-values[8] for the *p*-substituents (Fig. 1), or possibly a logarithmic function with a considerable deviation by the *p*-isopropyl compound.

TABLE I

RATES OF REACTION OF α-CHLORO-*p*-SUBSTITUTED TOLUENES WITH SODIUM THIOSULFATE AT 30°

$Y-C_6H_4-CH_2Cl$, Y =		$k_D \times 10^3$, l. mole^{-1} sec.$^{-1}$ 60% diglyme	$k_E \times 10^3$ 60% ethanol	k_D/k_E
NO_2		26.5	9.55	
		25.5	9.67	
	Av.	26.0	9.61[a]	2.71 ± 0.07[b]
Cl		12.0	7.26	
		11.9	7.36	
	Av.	12.0	7.31	1.64 ± 0.02
H		7.01	5.45	
		7.18	5.25	
	Av.	7.10	5.35[c]	1.33 ± 0.04
$(CH_3)_2CH$		7.95	8.23	
		7.95	8.27	
			8.54	
	Av.	7.95	8.35	0.95 ± 0.02

[a] Slater[6] reported k^{35} 5.0 × 10^{-3} in 62% ethanol using a rate expression which omits the factor 2.303. Inclusion of this gives k^{35} 11.5 × 10^{-3}, which appears somewhat low when compared with the above data at 30°. Slater's rate for iodoethane was lower than that of E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1576 (1933). [b] Maximum deviation based on the extremes of individual runs in the two solvents. [c] Reported[6] k^{35} 2.8 × 10^{-3}. Inclusion of the factor 2.303 gives k^{35} 6.5 × 10^{-3}; k_{nitro}/k_H is virtually identical in the two studies.

In each solvent α-chlorotoluene represents the rate minimum, and the electron-withdrawing nitro and chloro groups and the electron-donating isopropyl group all increase the rate. The rate enhancement is relatively large for the nitro and chloro compounds in diglyme, but much less in ethanol, whereas the rate enhancement of the isopropyl compound is greater in alcohol.

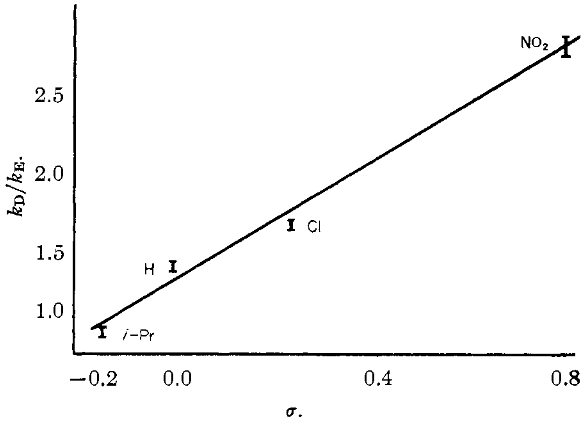

Fig. 1.—Reaction rates of *p*-substituted-α-chlorotoluenes in aqueous diglyme and in aqueous ethanol at 30°.

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(1) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

(2) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).

(3) C. G. Swain, R. B. Mosely and D. E. Bown, *ibid.*, **77**, 3731 (1955).

(4) C. G. Swain, D. C. Dittmer and L. E. Kaiser, *ibid.*, **77**, 3737 (1955).

(5) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

(6) K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940); L. J. le Roux and S. Sugden, *J. Chem. Soc.*, 1279 (1939); A. Slater and D. F. Twiss, *ibid.*, **95**, 93 (1909); D. Segaller, *ibid.*, **105**, 113 (1914); R. D. Heyding and C. A. Winkler, *Can. J. Chem.*, **29**, 790 (1951); J. W. Hackett and H. C. Thomas, THIS JOURNAL, **72**, 4962 (1950); O. R. Quayle and E. E. Royals, *ibid.*, **64**, 226 (1942).

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(8) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

Benzyl halides and nitrates commonly show a rate minimum for the unsubstituted compound in second-order substitution reactions with anions including iodide in acetone,[9] bromide in glycol diacetate,[10] alkoxides,[11,12] and hydroxide in aqueous ethanol.[11] The rate minimum, the cause of which has been discussed by Swain,[13] may occur at other values of sigma.[14]

The reactions in this work all followed second-order kinetics even in the case most favorable for solvolysis, α-chloro-*p*-isopropyltoluene in aqueous alcohol. The specific rate of the latter was found to be dependent on thiosulfate concentration.

Discussion

α-Chloro-*p*-nitrotoluene, and to lesser extents, α,*p*-dichlorotoluene and α-chlorotoluene, react more rapidly in aqueous diglyme than in aqueous alcohol, as expected, whereas α-chloro-*p*-isopropyltoluene reacts more rapidly in alcohol. A useful viewpoint of the results is the following. While the gross mechanism is the same for all of these compounds, the nature of the transition state varies considerably. The transition state for the nitro compound is relatively tight, with considerable S–C and C–Cl covalent bonding, a diffuse charge, and little solvation. At the other extreme, the transition state involving the isopropyl compound has relatively weak S–C and C–Cl bonding, rather long bond distances, large fractional charges on the thiosulfate, carbon and chloride, and strong solvation.

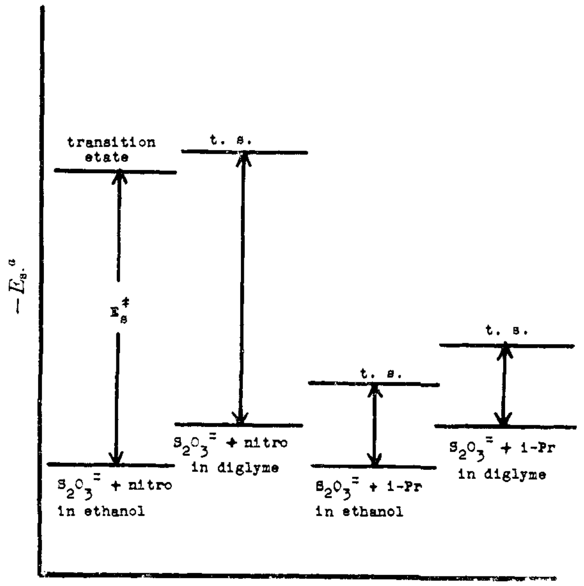


Fig. 2.—Solvation energies (E_s) in the reactions of $O_2N-C_6H_4-CH_2Cl$ and $(CH_3)_2CH-C_6H_4-CH_2Cl$ with thiosulfate.

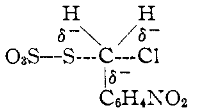
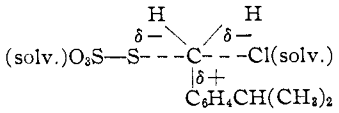
[a] It is probable that entropy differences exist between the solvation processes in the two solvents, and that it is the free-energy of solvation that should be considered. In the absence of definitive data, the term "energy of solvation" has been used without prejudice.

TABLE II

REACTION OF α-CHLORO-*p*-ISOPROPYLTOLUENE WITH THIOSULFATE IN 60% ETHANOL-40% WATER AT 30°

t, sec.	(RCl)[a]	$k^{30} \times 10^3$, l. mole^{-1} sec.$^{-1}$
0[b]	0.0204	
600	.0173	8.50
1320	.0144	8.64
2280	.0155	8.74
3300	.0095	8.45
5520	.0064	8.39[c]
	Av.	8.54 ± 0.12[d]

[a] At time of mixing ($S_2O_3^{=}$) = 0.038, (RCl) = 0.024; at t = 0 ($S_2O_3^{=}$) = 0.0340. All concentrations in mole l.$^{-1}$. [b] 600 sec. after mixing. [c] k showed no downward trend in duplicate runs. [d] Average deviation. k calculated from the expression $k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$.

In the latter case there is relatively little loss of solvation energy accompanying the formation of the transition state.

In terms of Swain's four parameter rate equation,[6] log $(k/k^0) = sn + s'e$, s should be large and s' small for α-chloro-*p*-nitrotoluene, and s small and s' large for α-chloro-*p*-isopropyltoluene. The value of e should be greater for ethanol–water than for diglyme–water. The nucleophile is thiosulfate in both solvents, but differences in solvation may cause a difference in the value of n.

Because of the large deviations from ρ-values calculated for anion–benzyl halide reactions, it may well be that a comparison of reaction rates in two solvents gives a better picture of the transition state for a particular reaction than is given by the (average) ρ-value for the reactions of a series of substituted benzyl compounds.

Experimental

Materials.—Commercial α-chlorotoluenes were fractionally distilled and either used within two days or redistilled before use. Rates were measured on samples which boiled over a range of 1° or less. α-Chloro-*p*-nitrotoluene was recrystallized from heptane; m.p. 71.8–72.4°. α,*p*-Dichlorotoluene was recrystallized from heptane after distillation; m.p. 28°. Diglyme was refluxed with dilute hydrochloric acid, refluxed with calcium hydride, and distilled from the hydride. The material boiling at 162.5° was used to make up solvent mixtures; lower boiling material interferes with the subsequent titration with iodine. Commercial absolute alcohol was used directly. Because of the volume contraction during mixing of the solvents, the organic components make up slightly more than 60% by volume.

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[9] G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935); J. W. Baker and W. S. Nathan, *ibid.*, 236 (1936); A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, **47**, 25 (1951).

[10] S. Sugden and J. B. Willis, *J. Chem. Soc.*, 1360 (1951).

[11] W. T. Miller, Jr., and J. Bernstein, THIS JOURNAL, **70**, 3600 (1948).

[12] H. Franzen and I. Rosenberg, *J. prakt. Chem.*, [2] **101**, 333 (1921).

[13] C. G. Swain and W. P. Langsdorf, THIS JOURNAL, **73**, 2813 (1951).

[14] The solvolyses of benzoyl chlorides show a rate minimum for the *p*-methoxy, *p*-methyl, *p*-chloro or *p*-nitro compound depending on the solvating ability of the solvent: D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, 883 (1953); E. W. Crunden and R. F. Hudson, *ibid.*, 501 (1956). These cases differ from the present work in that solvent changes alter considerably both the nucleophilic and electrophilic properties of the medium. From the non-kinetic data it has been inferred that the 3,4-dichloro compound represents the rate minimum in the reaction of 3- and 4-substituted styrene oxides with lithium borohydride; R. Fuchs, THIS JOURNAL, **78**, 5612 (1956).

Measurements.—Aqueous 0.1 *N* thiosulfate solution (20 ml.) at 30° was pipetted into a stoppered volumetric flask. About 29 ml. of diglyme was added, and the mixture was allowed to attain thermal equilibrium in a bath at 30.00 ± 0.01°. To the mixture was added 1 ml. of a freshly prepared solution of the halogen compound in diglyme, and diglyme was added to bring the total volume to 50 ml. The first 5-ml. sample was transferred 10 minutes later ($t = 0$) into cold water and titrated with 0.02 *N* iodine solution. The reaction was followed to 60–80% completion. Infinite time titrations were made 24 hours later, and were unchanged at the end of 48 hours. The reactions between many organic halides and thiosulfate are known to be nearly quantitative.[6,15] An acetate buffer at a concentration 20% of the initial thiosulfate concentration was used to prevent decomposition of the latter by any acid formed by (slow) solvolysis.[16]

Acknowledgment.—This work was aided by grants from the Research Corporation and The University of Texas Research Institute.

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[16] P. M. Dunbar and L. P. Hammett, *ibid.*, **72**, 109 (1950).

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The Preparation and Properties of Some Vinyl and Glycidyl Fluoroethers

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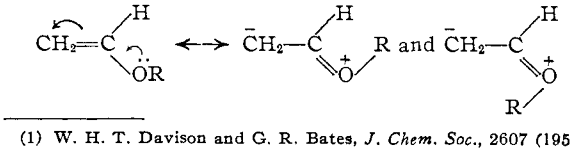
A series of vinyl fluoroalkyl and glycidyl fluoroalkyl ethers have been synthesized. A study of the infrared spectra of vinyl ethers was made and an explanation is offered for the presence of two bands in the carbon–carbon double bond stretching regions in non-fluorine-containing ethers. The spectra of the glycidyl ethers containing fluorine are similar to their unhalogenated analogs.

The chemical reactivity of vinyl and glycidyl ethers makes them useful in organic synthesis. Their ease of polymerization also makes them valuable for industrial purposes. In the present study, the preparation of vinyl and glycidyl ethers containing fluorine and a study of the effect of the fluorine substitution on their infrared spectra were undertaken.

Vinyl ethers exhibit a reactivity which is too great to be attributed solely to the separate functional groups which are present. Their vibration spectra also have characteristics which are different from those of either functional group alone. Instead of the usual single band for the carbon–carbon double bond stretch near 6.00 μ, two bands occur in their infrared spectra,[1,2] and a third has been reported for vinyl *n*-butyl ether.[3] Triplet lines are present in the Raman spectra of vinyl ethers in this region.[4] Also, a band probably associated with the carbon–oxygen stretch, usually found at about 9.0 μ in the infrared spectra of saturated ethers,[5] occurs at about 8.3 μ in the spectra of vinyl ethers and is very intense.

Batuev, *et al.*,[4] have proposed that the triplet carbon–carbon double bond stretching vibration in the Raman spectra is due to the existence of vinyl ethers as rotational isomers. The isomerism is explained as resulting from restricted rotation of the alkyl group about the carbon–oxygen bond because of conjugation of the unshared pair of electrons of the oxygen atom with the double bond



The low wave length for the carbon–oxygen stretch in the infrared spectra, occurring at 8.3 μ, is consistent with the conjugation effect, which would result in a shorter, higher-energy carbon–oxygen bond. Shostakovskii[6] has postulated such a resonance effect to explain the unusual chemical reactivity of vinyl ethers. Heat of hydrogenation measurements[7] indicate that vinyl ethyl ether has a resonance energy of about 3.6 kcal. per mole. However, no direct proof of the nature of the resonance has been reported.

In the present study, two methods for testing the existence of the proposed resonance effect and resulting isomerism were undertaken. First, it was desired to ascertain whether the conjugation could be overcome by the presence of a strongly electronegative substituent in the alkyl group of the vinyl ether. Because no infrared spectra of vinyl ethers substituted in this manner could be found in the literature, the synthesis of a series of vinyl fluoroethers was attempted, and infrared spectra were obtained for those ethers which were successfully prepared. Secondly, a study of the effect of a change in temperature on the relative intensities of the double-bond bands of an unfluorinated vinyl ether, in this case vinyl 2-ethylhexyl ether, was made in order to determine whether or not the split in the stretching frequency was due to the existence of rotational isomers. If the bands were due to rotational isomers, an increase in temperature would cause an increase in the concentration of higher energy isomer, shown by an increase in intensity of its band, and corresponding decrease in concentration of isomer of lower energy, with decrease in intensity of its band. This method has been used effectively by Mizushima and coworkers[8] to prove the existence of rotational isomerism in other types of compounds.

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[1] W. H. T. Davison and G. R. Bates, *J. Chem. Soc.*, 2607 (1953).

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