various time intervals. The color was developed directly in the colorimeter tube and was read in a Coleman Junior Spectrophotometer at 660 mμ. The *p*H values given in the figures are those determined at room temperature with a Beckman Model G *p*H meter.

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

Solvent Effects in the Reaction of *p*-Substituted-α-chlorotoluenes with Thiosulfate. The Relationship of Rho and Dielectric Constant

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The rates of reaction of α-chloro-*p*-nitro-, α,*p*-dichloro-, α-chloro-, and α-chloro-*p*-isopropyltoluenes with thiosulfate have been measured in eleven partially aqueous solvents of dielectric constant (*D*) 25 to 101. For reactions in seven of the solvents the Hammett rho value is a linear function of $1/D$. The conditions under which this relationship can be expected to hold are discussed. Although the rate for a given compound is not a simple function of the dielectric constant of the solvent, the activation energies show a decided tendency to rise with increasing *D*.

The observation[1] that the rates of reaction of four variously substituted α-chlorotoluenes with thiosulfate are unequally affected by a change of solvent evoked an interest in a more general study of solvent effects in these reactions. Extensive studies of solvent effects in solvolyses have been reported,[2-5] and attempts have been made to correlate the rates or entropies and enthalpies of activation with solvent composition or solvent properties such as dielectric constant. Ideally, one might prefer a relationship between rates and independently determined properties of the solvent or solution, but attempts in this direction[4] have met with limited success.[6] To date more useful results have been obtained with empirical relationships such as those of Swain[7] and of Winstein,[8] which employ parameters derived from kinetic data.

Non-solvolytic displacement reactions by anions on neutral molecules, although an extremely important mechanistic type, have received relatively little attention in solvent studies. This has resulted in part from the limited effect of solvent variation, due to the rather indirect participation of solvent in these reactions. To a considerable extent, however, the limited data available[2,9] have followed the generalization[10] that (with the degree of ion-pair dissociation taken into account) anion–neutral molecule reactions proceed faster in solvents of low dielectric constant. The present work presents evidence (Table I) in apparent disagreement with such a statement. Second-order rate constants are presented for the reactions of α-chloro-*p*-nitro-, α,*p*-dichloro-, α-chloro- and α-chloro-*p*-isopropyltoluenes with sodium thiosulfate taking place in nine mixtures of 40% water–60% organic solvent and in two 50–50 mixtures. Energies of activation (Table III) have been calculated for the reaction of one or more of the α-chlorotoluenes in each of seven solvents, making use of rate measurements at 10, 20, and 30°, or 20, 30 and 40° (Table II).

TABLE I

RATES OF REACTION[a] OF *p*-SUBSTITUTED-α-CHLOROTOLUENES WITH THIOSULFATE AT 30°

Solvent[b]	*D*[c]	*p*-NO$_2$	*p*-Cl	*p*-H	*p*-*i*-Pr
Dioxane	25	9.95	5.20	3.48	3.84
Dioxane[d]		17.2	...	5.29	6.12
Dioxane[e]	34.5	14.5	8.54	6.35	7.24
1,2-Dimethoxyethane	37.4	13.8	6.57	4.12	4.07
Diglyme[f,g]	38	26.0	11.9	7.10	7.95
2-Ethoxyethanol	41	13.7	8.19	5.38	6.87
Ethanol[g]	45	9.62	7.32	5.35	8.35[h]
Acetone	45.5	11.9	6.59	4.82	5.64
Acetone[d]		18.3	...	6.47	8.94
Acetone[e]	71.2	13.7	9.35	6.99	8.22
Acetonitrile	52.3	4.12	3.17	2.88	3.24
Butyrolactone	58.5	16.0	11.4	8.69	11.3
N-Methylacetamide	101	...	...	39.3	...

[a] Second-order rate constants (l. mole^{-1} sec.$^{-1}$) × 10^3. All values are averages of two to four determinations. At time of mixing, $(\mathrm{S_2O_3^{=}})$ = 0.04 *M*, (RCl) = 0.0 25 *M*; stated temperature regulated to ± 0.02°. [b] 40% water + sufficient solvent as indicated to make up the total volume. [c] Dielectric constant measured with a Sargent Oscillometer at 23 ± 1°. [d] At time of mixing $(\mathrm{S_2O_3^{=}})$ = 0.008 *M*. (RCl) = 0.005 *M*. [e] 50% water + sufficient solvent to make up the total volume. [f] Bis-(2-methoxyethyl) ether. [g] Ref. **1**. [h] 9.55 with initial $(\mathrm{S_2O_3^{=}})$ = 0.02 *M*, (RCl) = 0.013 *M*.

Discussion

The following statements can be made on the basis of the above data: (1) The Hammett ρ-value is a linear function of $1/D$ [or $(D - 1)/(2D + 1)$] for the majority of the solvents (Fig. 1). (2) There is no simple relationship between absolute reaction rates and *D*, nor is there any particular tendency for the reaction to proceed faster in solvents of relatively low dielectric constant or of low water content. (3) The rate constant for the

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[1] R. Fuchs, THIS JOURNAL, **79**, 6531 (1957).

[2] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

[3] S. Winstein and A. H. Fainberg, THIS JOURNAL, **79**, 5937 (1957).

[4] G. S. Hammond, C. E. Reeder, F. T. Fang and J. K. Kochi, *ibid.*, **80**, 568 (1958).

[5] J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **34**, 863 (1956); **34**, 931 (1956).

[6] However, for a correlation of solvolysis rates with spectral data see E. M. Kosower, THIS JOURNAL, **80**, 3267 (1958).

[7] C. G. Swain, R. B. Mosely and D. E. Bown, *ibid.*, **77**, 3731 (1955); C. G. Swain, D. C. Dittmer and L. E. Kaiser, *ibid.*, **77**, 3737 (1955).

[8] See, for example, E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

[9] Reference 1, footnote 6.

[10] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 347.

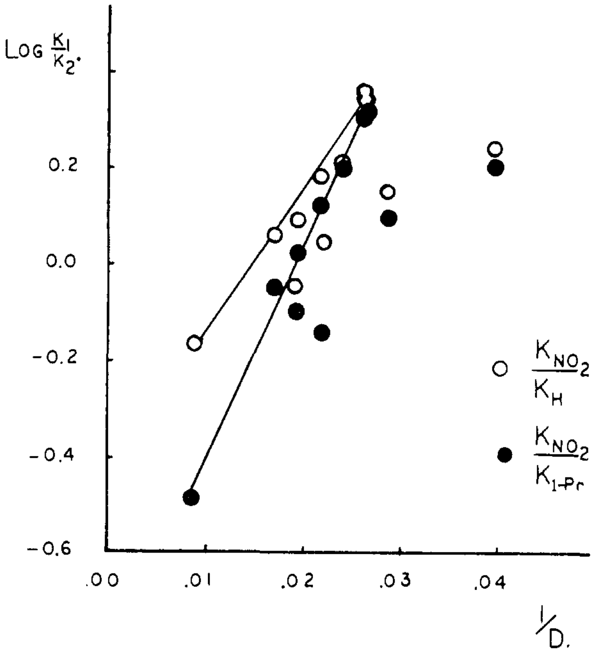

Fig. 1.—Relative rates of reaction of *p*-substituted-α-chlorotoluenes with thiosulfate as a function of the dielectric constant of the solvent.

reaction in aqueous dimethyl sulfoxide is at least an order of magnitude larger than in other solvents when temperature differences are taken into account. (4) Activation energies tend to increase with increasing *D*. Only in the case of acetonitrile does an exception fall considerably outside of experimental error.

TABLE II

RATES OF REACTION OF *p*-SUBSTITUTED-α-CHLOROTOLUENES WITH THIOSULFATE AT VARIOUS TEMPERATURES[a]

Solvent[b]	Temp., °C.	*p*-NO_2	*p*-Cl	*p*-H	*p*-*i*-Pr
1,2-Dimethoxy-ethane	20	. . .	. . .	1.88	. . .
	10	. . .	. . .	0.764	. . .
Diglyme	20	13.6	5.80	3.42	3.97
	10	5.79	2.64	1.51	1.78
Acetone	20	5.09	2.74	1.99	2.55
	10	2.02	1.13	0.772	1.02
Acetone[c]	20	5.64	. . .	2.79	3.70
	10	2.32	. . .	1.24	1.61
Ethanol	40	23.0	16.3	12.6	19.2
	20	3.92	2.85	2.17	3.35
Acetonitrile	40	12.0	9.96	7.96	10.3
	20	1.19	1.00	0.882	1.02
Butyrolactone	20	6.54	4.67	3.54	4.45
	10	2.40	1.64	1.24	1.68
Dimethyl sulfoxide[d]	0	. . .	. . .	13.3[e,f]	. . .
N-Methylacetamide	20	16.9[f]	17.7[f]	15.4[f]	33.5[f,g]
	10	. . .	. . .	5.40	. . .
	0	. . .	. . .	1.72	. . .

[a] Footnote *a*, Table I. [b] Footnote *b*, Table I. [c] Footnote *e*, Table I. [d] Dielectric constant, 72. [e] 14.7 at initial ($S_2O_3^=$) = 0.02 *M*. [f] Initial (RCl) = 0.013 *M*. [g] 35.6 at initial ($S_2O_3^=$) = 0.02 *M*.

Hammett equation plots (of log *k* *vs.* σ) give U-shaped curves typical of reactions between anions and benzyl compounds.[11] Because of the large deviations from linearity for such a system, the log of the ratio of rates[12] of two α-chlorotoluenes is used instead of the necessarily arbitrary value of rho.[13] Various ratios ($k_{NO_2}/k_{i\text{-Pr}}$, k_{NO_2}/k_H or k_{Cl}/k_H) are logarithmic functions of $1/D$; however, the fit is best for the first two ratios, in which the σ-values and rates are considerably different for the two compounds involved in each ratio. Regardless of which ratio is used, points representing the same four "anomalous" solvents (60% dioxane, 50% dioxane, 60% ethanol and 60% acetonitrile) fall off the straight line, and the same seven "regular" solvents are on or near the line (60% 1,2-dimethoxyethane, 60% diglyme, 60% 2-ethoxyethanol, 60% acetone, 50% acetone, 60% butyrolactone and 60% N-methylacetamide).

TABLE III

ACTIVATION ENERGIES[a] OF THE REACTIONS OF *p*-SUBSTITUTED-α-CHLOROTOLUENES WITH THIOSULFATE

Solvent[b]	*p*-NO_2	*p*-Cl	*p*-H	*p*-*i*-Pr
1,2-Dimethoxyethane	. .	. .	14.2	. .
Diglyme	12.8	12.9	13.2	12.8
Ethanol	16.1	16.0	15.9	15.9
Acetone	15.2	15.1	15.6	14.7
Acetone[c]	15.1	. .	14.8	13.9
Acetonitrile	21.2	20.9	20.1	21.1
Butyrolactone	16.2	16.2	16.7	16.6
N-Methylacetamide	. .	. .	17.4	. .

[a] Kcal. mole^{-1}; obtained graphically from the slope of the Arrhenius plot of log *k* *vs.* $1/T$. [b] Footnote *b*, Table I. [c] Footnote *e*, Table I.

Undoubtedly at least several experimental factors affect ρ. One of these certainly is the dielectric constant of the solvent. Other factors which might be postulated are: (1) the concentration of specifically solvating solvents (ethanol, acetonitrile and, possibly, water. However, a change from 60% acetone to 50% acetone produces a change in ρ close to that predicted for an uncomplicated change of $1/D$), and (2) a relatively low concentration of dissociated ions compared with the concentration of ion-pairs.

In the present study the concentration of solvating solvent has been kept constant except in 50% dioxane, 50% acetone, and in the cases in which a solvating solvent other than water is present.[14]

A solvent of high, specific solvating ability (such as water or ethanol) may participate in the reaction in the following ways: (1) the attacking thiosulfate ion may be rendered somewhat less reactive because of the difficulty in removing surrounding solvent molecules during reaction; however, this large, diffusely charged ion is probably not strongly solvated in the solvents used. (2) The departure of the chloride ion will be

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(11) Reference 1, footnotes 9–14.

(12) Rho is directly proportional to log (k/k_0): $\rho = (1/\sigma)\log(k/k_0)$, or, in general, where neither substituent need be H, $\rho = (1/(\sigma_1 - \sigma_2))\log(k_1/k_2)$.

(13) The slope of the best straight line which can be drawn through a plot of log *k* *vs.* σ can vary positive to negative depending on the choice of substituents.

(14) Many salts dissolve and are strong electrolytes in acetonitrile, but solvation energies of cations, and especially of anions, are lower in this solvent than in water; L. F. Coetzee and I. M. Kolthoff, THIS JOURNAL, **79**, 6110 (1957).

aided; and, (3) the transition state may be stabilized through the organic portion by solvation to a degree dependent on the amount of positive charge developed (*i.e.*, the amount of "S_N1" character). Factor 1 will be more important in the formation of the "tight" transition state from α-chloro-*p*-nitrotoluene than for any other case, whereas 2 and 3 will be least important in this case. The other extreme is represented by the transition state for the *p*-isopropyl compound, wherein 1 is less significant and 2 and 3 are more significant than in any of the other transition states.

Solvents of high dielectric constant may participate in the reaction in much the same ways as do specifically-solvating solvents. It is postulated that the relationship of ρ with $1/D$ holds true for all solvents for which the over-all solvating ability is a linear function of D. Since factor 1 decreases rates and 2 and 3 increase rates, it is apparent that in solvents of high over-all solvating ability α-chloro-*p*-nitrotoluene will tend to be slow, while the *p*-isopropyl compound for which the transition-state stability is dependent largely on 2 and 3 will tend to react rapidly.

The reactions of the α-chlorotoluenes are suggestive of "borderline" mechanisms, all second-order kinetically, but with different amounts of carbonium ion character. They lie in the mechanistic spectrum between the perfectly synchronized bimolecular (or termolecular) nucleophilic displacement reaction (in which factors 1 and 2 only are involved) and the unimolecular or carbonium ion mechanism (in which factors 2 and 3 only are significant, since the nucleophile is not involved in the rate-determining step).

Strong, specific solvating ability cannot reasonably be attributed to dioxane. It is preferable to suppose that the "anomalous" behavior of 60% dioxane (and, probably, of 50% dioxane) is related to the very low concentration of free ions[15] in this medium of low D. In the light of recent information[16] that ion-pairs as well as ions may be active in displacement, it is not unreasonable to expect different relative efficacies toward the various α-chlorotoluenes, and, therefore, "anomalous" rate ratios, whenever ion-pairs account for an appreciable fraction of the total reaction.[17] Consistent with this are the rate determinations in 60% dioxane and in 60% acetone run at one-fifth of the usual concentrations. All of the rate constants are higher for the reactions in dilute solution, following the expected ionic strength effect,[18] but the percentage of increase is greater for dioxane than for acetone, especially in the case of α-chloro-*p*-nitrotoluene. The fraction of sodium thiosulfate present as dissociated ions increases on dilution, and the rate constant of the nitro compound becomes larger.[17]

The reactions in 60% dimethyl sulfoxide could not be studied extensively under similar conditions because of the limited solubility of the substituted α-chlorotoluenes. The reaction of α-chlorotoluene is much more rapid in this solvent than in others, and probably proceeds by a different mechanism involving an intermediate which contains dimethyl sulfoxide.[19]

Energies of activation in the various solvents (Table III) tend to rise with increasing D. In acetonitrile E_a is about 4 kcal./mole higher than would be expected from D; E_a in diglyme is slightly low, but as in the reversal of acetone and ethanol, the discrepancy probably does not lie outside of the experimental error. An increase in water from 40 to 50% in aqueous acetone lowers E_a slightly. It is apparent that, for the most part, the rates do not parallel the activation energies, nor is there any obvious relationship between ΔS_a and solvent properties.

Experimental

Purification of the four α-chlorotoluenes, ethanol and diglyme (b.p. 161.6–161.7°), and the kinetic procedure and calculations have been described previously.[1] A number of the iodine–thiosulfate titrations were performed using a Sargent–Malmstadt automatic titrator. The results were quite close to those obtained by hand titration to the starch end-point. Dioxane was purified by the method used for diglyme, b.p. 100.7°. N-Methylacetamide, m.p. 29–30°, was used as received from Distillation Products Ind. Acetone was distilled from permanganate, b.p. 55.7°. Other solvents were dried with Drierite and fractionally distilled: 1,2-dimethoxyethane, b.p. 84.0–84.2°; 2-ethoxyethanol, b.p. 134.3–134.8°; acetonitrile, b.p. 80.6–80.8°; γ-butyrolactone, b.p. 83.8° at 12 mm.; and dimethyl-sulfoxide, which was first purified by fractional crystallization, b.p. 75.6–75.8° at 12 mm.

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[15] For example, a solution of lead chloride in 60% dioxane (ionic strength = 0.1) has a mean activity coefficient of 0.035, and about three times this value at ionic strength = 0.02; M. V. Noble and A. B. Garrett, *ibid.*, **66**, 231 (1944).

[16] The rate of radioactive bromine exchange with α-bromo-*p*-nitrotoluene was found to be 8.19×10^{-5} l. mole^{-1} sec.$^{-1}$ for the free ion, and 5.0×10^{-6} l. mole^{-1} sec.$^{-1}$ for the KBr ion pair; N. N. Lichtin and K. Narayana Rao, Abst. 134th Meeting A.C.S., September, 1958, p. 12-S; see, also, A. Brandstrom, *Arkiv Kemi*, **11**, 567 (1957); **13**, 51 (1958).

[17] It is assumed that α-chloro-*p*-nitrotoluene is relatively unreactive toward ion-pairs and relatively reactive toward anions.

[18] On the other hand, assuming that ion-pairs are unreactive, the rate of reaction of 1-bromopropane with thiosulfate in aqueous methanol has been found to be directly proportional to the fraction of sodium thiosulfate present as ions, and independent of ionic strength; J. R. Bevan and C. B. Monk, *J. Chem. Soc.*, 1392 (1956).

[19] S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).