was evaporated *in vacuo*. A colorless oil was obtained which crystallized on cooling in ice but melted at room temperature. It was treated with 20 ml. of water and the white crystalline solid was filtered, washed with ice–water, and air dried yielding 9.5 g. (64%), m.p. 34–36°. Two recrystallizations from ether raised the m.p. to 38–39°.

Anal. Calcd. for $C_{14}H_{22}N_2O_3S$: C, 56.35; H, 7.43; N, 9.39. Found: C, 56.52; H, 7.34; N, 9.20.

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Solvent Effects on the Reaction of Sodium Azide with Substituted Benzyldimethylsulfonium *p*-Toluenesulfonates[1]

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In a reaction involving the destruction of ions, the effect of solvent changes on the reaction rate may be used as a criterion of the extent of charge destruction at the transition state. Since a recently proposed rule[2] suggests a relation between the electronic nature of substituents and the structure of the transition state, it is of interest to examine the influence of substituents on such a solvent effect.

Rate constants for the reactions of sodium azide with substituted benzyldimethylsulfonium *p*-toluenesulfonates (tosylates) at 60° in both water and 80% dioxane–20% water are listed in Table I.

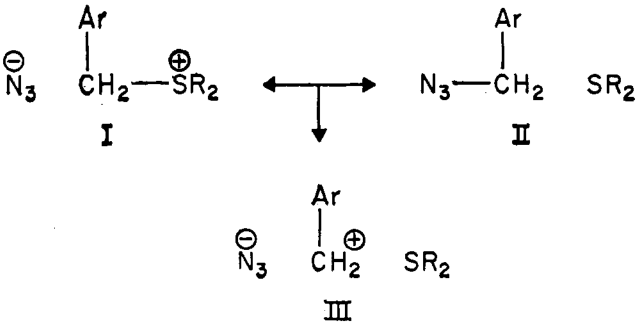
Table I

Reactions of Sodium Azide with Substituted Benzyldimethylsulfonium Tosylates at 60.1°

Substituent	k_2 in water, M^{-1} sec.$^{-1}$	k_2' in 80% dioxane, M^{-1} sec.$^{-1}$	k_2'/k_2
p-CH_3	10.45×10^{-5}	11.99×10^{-3}	115
H	4.78×10^{-5}	9.65×10^{-3}	202
m-Cl	3.50×10^{-5}	8.43×10^{-3}	241

The data indicate that the effect of electron-supplying substituents is to make the transition state more polar. It is convenient to discuss this result by considering the transition state as a resonance hybrid of structures I, II, and III.

Structure III is probably not quite so polar as I, but much more polar than II. The observed increase of the transition-state polarity with increasing electron supply indicates that the contribution of I or of III is increased at the expense of II. Since II is the only structure having a C–N bond, we may conclude that electron supply leads to a weaker C–N bond at the transition state. This is in agreement with the rule.[2]



It is more difficult to determine the substituent effect on the length of the C–S bond, since the bond will become stronger if the contribution of I is increased but weaker if the contribution of III is increased. However, an electron-supplying substituent would be better able to stabilize the positive charge in III than in I; therefore it is probable that the principal effect is to increase the contribution of III and lengthen the C–S bond at the transition state, as the rule predicts. This accords with the conclusion from the increasing sulfur isotope effect in the closely related reaction of hydroxide ion with the same benzylidimethylsulfonium tosylates in water at 60°.[3]

Experimental

Materials.—Water used in kinetic studies was distilled from sodium hydroxide–potassium permanganate and boiled prior to use to remove carbon dioxide. Dioxane was Fisher reagent grade. Eastman grade sodium tosylate was recrystallized from water–ethanol. Technical sodium azide was purified by recrystallization from an aqueous ethanolic solution which had been acidified with hydrazoic acid.[4] The sulfonium salts were prepared previously.[3]

Kinetics in Aqueous Solution.—A volumetric flask containing 100 ml. of a solution 0.05 *M* sulfonium salt, 0.10 *M* in sodium azide, and 0.35 *M* in sodium tosylate was placed in a constant temperature bath operating at 60.08 ± 0.04°. At intervals 5-ml. aliquots were removed from the flask and added to a measured excess of 0.20 *M* silver nitrate. The silver azide was filtered at 0° and washed with water. The excess silver ion was determined by adding a measured excess of 0.20 *M* potassium iodide and back-titrating with the 0.20 *M* silver nitrate with eosin Y as indicator.

During this investigation a somewhat simpler analytical method[5] was found to give rate constants agreeing with the first method. A 4-ml. aliquot of the reaction mixture was placed in a glass-stoppered erlenmeyer flask. Ten milliliters of a 10% ferric chloride indicator solution 1 *M* in sulfuric acid was added. The resulting hydrazoic acid was titrated with 0.25 *M* sodium nitrite. The flask was stoppered and shaken vigorously just before the end point was reached. The end point was determined by comparison with a standard solution prepared by mixing appropriate amounts of the indicator and sodium nitrite solutions.

Kinetics in Aqueous Dioxane.—A reaction mixture 0.0125 *M* in the sulfonium salt, 0.025 *M* in sodium azide, and 0.0875 *M* in sodium tosylate was prepared by weighing appropriate quantities of the three salts into a 250-ml. volumetric flask, dissolving in 50 ml. of water, and adding 200 ml. dioxane. Both water and dioxane had been preheated to 60° and volumes were measured at that temperature. The volumetric flask was placed in a bath at 60.08 ± 0.04°. At intervals 5-ml. aliquots were removed from the flask and added to a measured excess of 0.05 *M* silver nitrate. Filtration of the silver azide was followed by addition of an excess of 0.05 *M* potassium iodide and back-titration with 0.05 *M* silver nitrate with eosin Y as indicator.

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(2) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 817 (1962).

(3) C. G. Swain and E. R. Thornton, *J. Org. Chem.*, **26**, 4808 (1961).

(4) A. W. Browne, *Inorg. Syn.*, **1**, 79 (1939).

(5) J. F. Reith and J. H. A. Bouwman, *Pharm. Weekblad.*, **67**, 475 (1930); *Chem. Abstr.*, **24**, 3968 (1930).