[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Mechanism of Displacement by Hydroxide Ion on Benzylsulfonium Ions in Aqueous Solution[1,2]

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Sodium hydroxide reacts with *p*-methyl-, unsubstituted, or *m*-chlorobenzyldimethylsulfonium *p*-toluenesulfonate in water at 60° to form the corresponding benzyl alcohol in high yield. Although the rate constants (11.0, 6.8 and 10.7 μM^{-1} sec.$^{-1}$) give a Hammett plot with a minimum, the sulfur isotope effects k_{32}/k_{34} (1.0096, 1.0093, and 1.0082) give a linear plot. The mechanism appears to be a one-step process. As the sulfur isotope effect is largest for the *p*-methyl salt, electron supply to the benzylic carbon leads to a *longer* bond between it and sulfur at the transition state.

The products of reaction of sodium hydroxide with *p*-methyl-, unsubstituted, or *m*-chlorobenzyldimethylsulfonium *p*-toluenesulfonate (tosylate) in water at 60° are the corresponding benzyl alcohol and dimethyl sulfide. The yields of recrystallized or distilled alcohol isolated were 78% from the *p*-methyl and 89% from the *m*-chloro salt.

Rate constants are reported in Table I. The reaction is first order in hydroxide ion and first order in sulfonium ion. Both *p*-methyl ($\sigma = -0.17$) and *m*-chloro ($\sigma = +0.37$) substituents increase the rate. Curved Hammett plots have been noted previously and interpreted in terms of changing relative extents of bond breaking and bond making at the transition state, without invoking competition from any two-step or other qualitatively different type of mechanism.[3]

TABLE I

RATE CONSTANTS AND SULFUR ISOTOPE EFFECTS FOR REACTION OF SODIUM HYDROXIDE WITH SUBSTITUTED BENZYLDIMETHYLSULFONIUM TOSYLATES IN WATER AT 60°

Substituent	10^5k_2, M^{-1} Sec.$^{-1}$	k_{32}/k_{34}
p-CH_3	1.10	1.00956 ± 0.00029[a]
H	0.68	1.00934 ± .00177[a]
m-Cl	1.07	1.00818 ± .00072[a]

[a] The ± figures are standard deviations.

Sulfur isotope effects are also recorded in Table I. They are very small, but the best values give a linear Hammett plot with negative slope ρ (an excellent fit with a correlation coefficient of 0.987), again suggesting no discontinuous change to a multistep mechanism. The negative ρ indicates that the carbon-sulfur bond which is breaking is *longer* at the transition state when substituents are present which supply electrons to this carbon. Alternative interpretations, that such substituents increase ground state frequencies or that the remaining bonds on sulfur increase in frequency enough to overcompensate for the bond which is breaking, seem implausible. This effect supports a rule previously given for predicting the effect of structural changes in reactants on the structure of transition states.[4]

EXPERIMENTAL

Benzyldimethylsulfonium tosylate. Benzyl *p*-toluenesulfonate (tosylate), made by reaction of benzyl alcohol and *p*-toluenesulfonyl chloride in ether in the presence of powdered potassium hydroxide,[5] was added to excess dimethyl sulfide. The tosylate dissolved and the sulfonium salt slowly crystallized. After filtration, the salt was recrystallized by adding the salt dissolved in absolute ethanol to excess ethyl acetate followed by cooling, m.p. 124–124.8°. Saponification equivalent by reaction with excess base and back titration indicated 99.8% purity.

Anal. Calcd. for $C_{16}H_{20}O_3S_2$: C, 59.23; H, 6.21; S, 19.76. Found: C, 58.68; H, 6.15; S, 20.02.

p-Methylbenzyldimethylsulfonium tosylate was prepared similarly, m.p. 108–109°. Saponification equivalent by reaction with excess base and back titration indicated 99.3° purity.

Anal. Calcd. for $C_{17}H_{22}O_3S_2$: C, 60.32; H, 6.55; S, 18.94. Found: C, 60.62; H, 6.66; S, 19.48.

p-Methylbenzyl alcohol was prepared by a crossed Cannizzaro reaction of *p*-tolualdehyde and formaldehyde.[6]

m-Chlorobenzyldimethylsulfonium tosylate was prepared similarly, m.p. 114–115°.

Anal. Calcd. for $C_{16}H_{19}ClO_3S_2$: C, 53.54; H, 5.34; Cl, 9.89; S, 17.87. Found: C, 53.83; H, 5.39; Cl, 8.81; S, 18.40.

m-Chlorobenzyl alcohol was prepared by lithium aluminum hydride reduction of *m*-chlorobenzoic acid.[7]

Other reactants. Distilled water redistilled from a trace of potassium permanganate was used as solvent. Carbonate-free sodium hydroxide solution was used for kinetics and titrations.

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(1) Supported by the National Institutes of Health through Research Grant RG-3711 and by a postdoctoral fellowship to E.R.T. from the Division of General Medical Sciences, U. S. Public Health Service.

(2) *Cf.* C. G. Swain and L. E. Kaiser, *J. Am. Chem. Soc.*, **80,** 4089 (1958); C. G. Swain, L. E. Kaiser, and T. E. C. Knee, *J. Am. Chem. Soc.*, **80,** 4092 (1958); C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc., in press.*

(3) C. G. Swain and W. P. Langsdorf, *J. Am. Chem. Soc.*, **73,** 2813 (1951).

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(5) H. Gilman and N. J. Beaber, *J. Am. Chem. Soc.*, **47,** 518 (1925).

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Product identification. p-Methylbenzyl alcohol was isolated from the reaction of $0.2M$ sodium hydroxide with $0.1M$ p-methylbenzyldimethylsulfonium tosylate in water at 100° by extraction of the cooled reaction mixture thrice with ether and evaporation of the ether at room temperature. The crude crystalline product was isolated in 98% yield, m.p. 54–56°. This product was recrystallized from an equal weight of isooctane, the mother liquor being removed by absorption with filter paper. The recrystallized product was isolated in 78.4% yield, m.p. 57–59°. In a blank run in which a known weight of p-methylbenzyl alcohol was suspended in water and extracted as above, an essentially quantitative yield of product, m.p. 58–60°, was obtained.

Likewise, m-chlorobenzyl alcohol was isolated from the reaction of $0.2M$ sodium hydroxide with $0.1M$ m-chlorobenzyldimethylsulfonium tosylate in water at 100° by the above extraction and evaporation procedure. The liquid product was washed into a micro distilling column with a small amount of ether. The ether was distilled at atmospheric pressure after addition of a small amount of ferrous sulfate. The apparatus was then evacuated to below 1 mm., the water present coming over immediately. The product was distilled into a tared receiver, b.p. 67–68° (0.22 mm.) and isolated in 89% yield (the remainder was trapped in the column), b.p. 237° (761.3 mm.).

Anal. Calcd. for C_7H_7ClO: C, 58.96; H, 4.95; Cl, 24.87. Found: C, 58.50; H, 5.41; Cl, 27.82.

The infrared spectrum was in agreement with expectation; an ultraviolet spectrum indicated the absence of the stilbene.[8]

Kinetic measurements. Rough kinetic measurements were made for the reactions of the three sulfonium salts with hydroxide in water at 59.95 ± 05°. The solutions were $0.2M$ in sodium hydroxide and $0.1M$ in sulfonium salt. Aliquots were pipetted into excess standard hydrochloric acid and back-titrated with standard sodium hydroxide to the phenolphthalein end point. The reactions were carried out in sealed ampoules. The infinity points were obtained by heating ampoules in the steam cone. Some inaccuracy was introduced by reaction of base with the glass ampoules.

Sulfur isotope effects. A procedure for isolation of dimethyl sulfide similar to that of Saunders and Asperger[9] was employed. The reaction solution was added through a small glass funnel to bulbous ampoules with standard taper inner joint with a smaller tube extending above the joint, and the tubes were sealed. The ampoules for 99.99% reaction were suspended in a steam cone; the ones for 2% in a bath at 59.95 ± 0.05°. After removal from the bath and cooling to room temperature, each ampoule was scored with a file just above the joint. The joint was greased, the top was cracked off with a hot glass rod, and the ampoule quickly attached to a head equipped with a tube for bubbling in nitrogen dried over Drierite and Ascarite and a small reflux condenser leading through a stopcock to an evacuated U-tube cooled with liquid nitrogen. The stopcock was slowly opened so that nitrogen bubbled slowly through the solution. The condenser helped minimize the amount of water carried along with the dimethyl sulfide. As soon as the nitrogen bubbles stopped, the needle valve on the nitrogen tank was opened so that slow bubbling continued. When the manometer indicated that the nitrogen pressure in the U-tube was slightly greater than atmospheric, a stopcock beyond the U-tube was opened to the air. The dimethyl sulfide was frozen in the U-tube so that no appreciable amount could escape. After 0.5 hr. the nitrogen was shut off, these stopcocks were closed, and a stopcock to the vacuum manifold was opened. A drying tube of phosphorus pentoxide and a glass-jointed tubular ampoule for collection of the dimethyl sulfide were also evacuated. When the pressure was less than 10^{-4} mm., the liquid nitrogen bath was removed from the U-tube and placed around the ampoule. After 20 min. the dimethyl sulfide had nearly all distilled from the U-tube through the drying tube into the ampoule as determined from the low pressure reading on the McLeod gauge. Water was trapped by the phosphorus pentoxide. The drying tube was removed, cleaned, and replaced by a fresh one after distillation of each sample. The ampoule containing the dimethyl sulfide was sealed below its joint and saved for mass spectral analysis.

The isotope effect is given by the equation

$$k_{32}/k_{34} = \frac{(S^{34}/S^{32})_{100\%}}{(S^{34}/S^{32})_{2\%}}$$

where k_{32}/k_{34} is the rate ratio of S^{32} to S^{34}, S^{34}/S^{32} is the ratio of mass 64 peak to mass 62 peak in the isolated dimethyl sulfide, and 100% and 2% subscripts indicate dimethyl sulfide isolated after 2 and >99.99% reaction. The ratio changes so little in the early part of the reaction that samples from 0 to 3% reaction should give practically the same isotope effect.

The mass spectra were taken on a Consolidated electrodynamics Corp. Type 21–103C recording mass spectrometer. The peak heights were read by counting the whole divisions on the record and interpolating fractional divisions with a Bausch and Lomb No. 81–34–35 Measuring Magnifier, which was accurate to about ±0.02 mm. For each sample of dimethyl sulfide at least five separate sets of peaks were measured.

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(8) p-Nitrobenzyldimethylsulfonium tosylate gives a nearly quantitative yield of p,p-dinitrostilbene under similar conditions.

(9) W. H. Saunders, Jr., and S. Asperger, *J. Am. Chem. Soc.*, 79, 1612 (1957).