CHEMISTRY LETTERS, pp. 129-130, 1979. Published by the Chemical Society of Japan

THE REACTION OF ARYL METHYL SULFIDES WITH ALKYL METHANESULFONATES. A KINETIC STUDY FOR THE SULFONIUM SALT FORMATION

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A kinetic study has been carried out for the reaction of aryl methyl sulfides with alkyl methanesulfonates giving sulfonium salts. Activation parameters, substituent and steric effects were examined.

Although some reactions involving sulfonium intermediates have been studied kinetically,[1-3] the kinetic behavior of the reaction giving sulfonium salt as the final product has not been known yet. The most typical reaction giving sulfonium salt is the reaction of sulfide with haloalkane. The kinetic study of this reaction, however, is difficult due to the existence of the reverse reaction.[4] We have tried a kinetic study for the reaction of alkyl methanesulfonates with aryl methyl sulfides and wish to report some kinetic aspects of the sulfonium salt formation.

$$\text{R-S-R'} + \text{R''-X} \rightleftharpoons \text{RR'R''S}^+ \text{X}^- \rightleftharpoons \text{R-S-R''} + \text{R'-X} \rightleftharpoons \text{etc.}$$

Methyl phenyl sulfide was heated with slight excess of methyl methanesulfonate and the product was converted to perchlorate salt for identification (mp 157-158°C). Dimethylphenylsulfonium benzenesulfonate (mp 120°C, from acetone) was isolated in 79% yield by the reaction of methyl phenyl sulfide with methyl benzenesulfonate. Found: C, 56.4; H, 5.2%. Calcd for $C_{14}H_{16}O_3S_2$: C, 56.7; H, 5.4%.

Methyl phenyl sulfide in methyl methanesulfonate (0.41 mol/l) was heated in a NMR sample tube and the conversion was measured by following decrease of sulfide methyl (δ 2.47 ppm) and increase of sulfonium methyl (δ 3.19 ppm) signals at time intervals. A good pseudo-first-order rate constant was obtained with a fair reproducibility (less than 10% error). Under the conditions, the reverse reaction was found to be neglegible. Kinetics of the other reactions were carried out similarly.

Table Kinetic Aspects of the Reaction of Aryl Methyl Sulfides with Alkyl Methanesulfonates.

Sulfide[a)]	Sulfonate	Temp.°C	k_{obs}X $10^4 s^{-1}$	Remarks
$C_6H_5SCH_3$	$CH_3O_3SCH_3$	70	1.04	
$C_6H_5SCH_3$	$CH_3O_3SCH_3$	80	2.03	$\Delta H^{\ddagger}$=15.0Kcal/mol, $\Delta S^{\ddagger}$=-33e.u.
$C_6H_5SCH_3$	$CH_3O_3SCH_3$	90	3.69	
$C_6H_5SCH_3$	$CH_3O_3SCH_3$	100	7.25[b)]	
p-$NO_2C_6H_4SCH_3$	$CH_3O_3SCH_3$	80	0.21	$\rho_{(\sigma)}=-1.2$, (γ=0.994)
p-$ClC_6H_4SCH_3$	$CH_3O_3SCH_3$	80	0.90	
p-$CH_3C_6H_4SCH_3$	$CH_3O_3SCH_3$	80	2.96	
p-$CH_3OC_6H_4SCH_3$	$CH_3O_3SCH_3$	80	3.14	
$C_6H_5SCH_3$	$C_2H_5O_3SCH_3$	100	0.54	k_{Et}/k_{Me} = 0.07

a), 0.41 mol/l as the initial concentration. b), Extraporated value.

As shown in the Table, the observed activation parameters and the substituent effect are in consistent with a bimolecular nucleophilic reaction and pretty close to those observed for the reaction involving rate determining formation of sulfonium salt intermediate.[1)] The steric effect (k_{Et}/k_{Me}) is somewhat larger than that in the other reactions of sulfur compounds[1,5)] but still in the range of S_N2 reactions.[6)] Although the reaction of 2-propyl methanesulfonate was tried in order to obtain more results about the steric effect, the substrate was decomposed under the reaction conditions.

These results might be helpfull to elucidate the mechanism of reaction of sulfur compounds whether it involves sulfonium intermediate or not.

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(Received August 21, 1978)