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

Mechanisms of Elimination Reactions. III. Rates of Elimination from Some Substituted 2-Phenylethyldimethylsulfonium Bromides in Aqueous Solution[1]

BY WILLIAM H. SAUNDERS, JR., CHARLES B. GIBBONS AND RICHARD A. WILLIAMS[2]

RECEIVED MARCH 6, 1958

Rates of reaction with hydroxide ion in water were determined for the compounds *p*-$XC_6H_4CH_2CH_2S(CH_3)_2Br$, where X = CH_3O, CH_3, H, Cl and CH_3CO. The results are compared with earlier data on the reactions of the same compounds with ethoxide ion in ethanol.[1] Reaction rates in water are about 10^3 less than in ethanol. Enthalpies of activation are nearly the same in the two solvents, but entropies of activation are much lower in water. The data fit the Hammett equation, giving $\rho = +2.64$ in ethanol and $+2.21$ in water at 30.05°. The *p*-acetyl compound reacts normally to give olefin, but the enthalpies and entropies of activation in both solvents are strikingly lower than for the other compounds. The effects of solvent and structure on these eliminations are discussed.

Recent studies of substituent effects in E2 eliminations[1,3] have shown that the Hammett ρ-values vary with the nature of the leaving group. These changes in ρ are believed to result from changes in the balance and timing of bond-making and bond-breaking processes.

Variables other than the leaving group may also influence the nature of the transition state. Among these other variables are the solvent and the base. The behavior of 2-arylethyldimethylsulfonium bromides with hydroxide ion in water was of particular interest, since it was under these conditions that studies of sulfur isotope effects[4] in eliminations were carried out. The present results, therefore, allow a direct connection between the isotope-effect and substituent-effect measures of transition-state structure.

Most of the *p*-substituted 2-phenylethyldimethylsulfonium bromides were prepared in earlier work.[1] Rates of reaction with hydroxide ion in water were determined acidimetrically. Second-order rate constants and olefin yields are recorded in Table I. Enthalpies and entropies of activation were calculated from the temperature dependence of the rate constants and are recorded in Table II. For convenience in discussion Table II contains data on relative rates and on enthalpies and entropies of activation in ethanol[1] as well as in water.

TABLE I

RATE CONSTANTS AND OLEFIN YIELDS IN THE REACTIONS OF *p*-$XC_6H_4CH_2CH_2S(CH_3)_2Br$ WITH SODIUM HYDROXIDE IN WATER

X	*T*, °C.	$k_2 \times 10^5$, l.-mole^{-1} sec.$^{-1}$ [a]	Olefin yield, % [b]
CH_3O	80.70	36.8 ± 1.0	97.2
CH_3O	70.60	12.9 ± 0.17	...
CH_3O	60.55	4.34 ± .10	...
CH_3	80.70	58.0 ± .87	97.6
CH_3	70.60	20.6 ± .43	...
CH_3	60.55	6.70 ± .18	...
H	80.70	121 ± 2.8	100.1
H	70.60	45.3 ± 0.91	...
H	60.55	14.4 ± 0.32	...
Cl	80.70	339 ± 5.8	98.7
Cl	70.60	125 ± 3.1	...
Cl	60.55	44.0 ± 1.0	...
CH_3CO	60.55	1039 ± 21	100.7
CH_3CO	50.00	552 ± 9.4	...
CH_3CO	40.00	288 ± 4.9	...
CH_3CO	10.35	7960 ± 304[c]	99.5[c]
CH_3CO	0.00	3330 ± 201[c]	...

[a] Deviations listed are average deviations. [b] Determined by the procedure of ref. 4; see experimental. [c] These data were obtained with absolute ethanol as solvent and ethoxide ion as base.

TABLE II

EFFECT OF SOLVENT ON ELIMINATIONS FROM *p*-$XC_6H_4CH_2CH_2S(CH_3)_2Br$. RATES AT 30.05°, ENTHALPIES AND ENTROPIES OF ACTIVATION

X	Solvent	$k_2 \times 10^5$, l.-mole^{-1}-sec.$^{-1}$	ΔH^*, [b] kcal./mole	ΔS^*, [c] cal./mole-°C.
H	EtOH	500	23.3	7.7
H	H_2O	0.347[a]	24.0	− 4.2
CH_3	EtOH	232	25.0	12.2
CH_3	H_2O	0.145[a]	24.6	− 4.2
CH_3O	EtOH	111	25.4	11.6
CH_3O	H_2O	0.099[a]	24.2	− 6.2
Cl	EtOH	2440	22.2	7.2
Cl	H_2O	1.19[a]	23.1	− 4.9
CH_3CO	EtOH	34000[a]	12.3	−19.7
CH_3CO	H_2O	146[a]	12.3	−30.9

[a] Extrapolated from the Arrhenius plot of data at other temperatures. [b] Calculated from the slope (method of least squares) of a log *k* *vs.* $1/T$ plot and the equation $\Delta H^* = E_a - RT$. Temperature was taken as the mid-point of the temperature range of the data (see Table I). [c] Calculated from the intercept (method of least squares) of a log *k* *vs.* $1/T$ plot.

The eliminations are slower in water than in ethanol by factors of around 10^3, as would be expected for reactions between oppositely-charged ions.[5] That this rate effect is due almost entirely to a much lower entropy of activation is perhaps less expected. One possible explanation is along lines suggested by Pearson.[6] The destruction of charge which occurs in the transition state should release ethanol, or water, of solvation. The water of solvation is released to a more highly-organized solvent structure than is the ethanol of solvation. Hence, there is a considerable gain in entropy of activation in the ethanol reaction relative to the water reaction.

Rate constants for the *p*-methoxyl-, *p*-methyl-, unsubstituted and *p*-chlorosulfonium salts were

---

(1) Paper II in this series: W. H. Saunders, Jr., and R. A. Williams, THIS JOURNAL, **79**, 3712 (1957).

(2) American Cyanamid Fellow, 1955–1956; Beaunit Mills Fellow, Summer, 1956.

(3) C. H. DePuy and D. H. Froemsdorf, THIS JOURNAL, **79**, 3710 (1957).

(4) W. H. Saunders, Jr., and S. Ašperger, *ibid.*, **79**, 1612 (1957).

(5) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 345–350, 455–460.

(6) R. G. Pearson, *J. Chem. Phys.*, **20**, 1478 (1952).

fitted to the Hammett equation (Table III). If we assume that ρ varies inversely with temperature, a value of 2.236 at 30.05° can be calculated from the data of line 1. This result is in excellent agreement with the value (2.208) given in line 2 for a direct fit to the extrapolated rate constants.

TABLE III

HAMMETT CORRELATION OF RATES OF ELIMINATION FROM p-$XC_6H_4CH_2CH_2S(CH_3)_2Br$[a]

Solvent	T, °C.	ρ	$-\log k_0$[e]
H_2O	60.55	2.032 ± 0.037[d]	3.826
H_2O[b]	30.05	2.208 ± .081	5.440
EtOH[c]	30.05	2.639 ± .157	2.365

[a] Calculations by the least squares procedure of H. H. Jaffé, ref. 8. Substituents (X) were CH_3, CH_3O, H and Cl. [b] Using extrapolated rate constants from Table II. [c] From ref. 1. [d] Standard deviation of ρ. [e] Calculated value of the intercept.

One would expect the stronger base (ethoxide ion) to lead to greater stretching of the β-C–H bond in the transition state. The lower value of ρ with hydroxide ion than with ethoxide ion agrees with this expectation. Unfortunately, not only the base but the solvent as well is varied. Hammett[7] has suggested that ρ should vary inversely with the dielectric constant of the solvent. Our observed change in ρ is in harmony with this prediction, although much other evidence on the effect of solvent on ρ[8] is contradictory and difficult to interpret. Obviously, any definite conclusions about the relative influences of base strength and solvent on ρ must await further study.

Finally, some comment on the enthalpies and entropies of activation is in order. The *p*-chloro-, unsubstituted, *p*-methoxyl- and *p*-methylsulfonium salts show almost constant entropies of activation. The *p*-acetylsulfonium salt, in both water and in ethanol, shows surprisingly lower entropies and enthalpies of activation (Table II). Interestingly, the *p*-acetyl compound fits a Hammett plot nicely at 60.55° (if the phenol–aniline σ is used), but obviously will not at other temperatures because of the abnormally low temperature coefficient in its reaction.

Discontinuities in enthalpies and entropies of activation within a reaction series are usually considered to signal a change in mechanism. A possible variant of the usual E2 mechanism would be one in which an equilibrium preceded the slow step. The observed ΔH^* and ΔS^* would then become composite quantities. This equilibrium might involve a step such as hemiketal (or hydrate) formation at the carbonyl group, which would produce a relatively unreactive species. The equilibrium constant for this "sidetracking" reaction would have to be rather far in favor of the unreactive species, a circumstance which seems to us unlikely. Another possibility would be reversible abstraction of a β-hydrogen by base, followed by slow loss of $(CH_3)_2S$ from the carbanion (or, more correctly, zwitterion) intermediate. We hope to test this hypothesis by means of deuterium-exchange experiments.

The possibility that the peculiar behavior of the *p*-acetylsulfonium salt lies in some trivial factor such as the presence of isomeric impurities was also considered. Oxidation, however, led only to terephthalic acid. The low (28%) yield makes this less conclusive than was hoped, but the experiment does confirm the identity of the salt and strongly suggests that it is free of isomers.

Experimental

Sulfonium Salts.—The compounds used were, for the most part, those prepared in earlier work.[1] Melting points agreed with the previous values.

To check for the possible presence of isomers, a 2.0-g. sample of the *p*-acetylsulfonium salt was refluxed with 2.0 g. of potassium permanganate in 100 ml. of 2% sodium hydroxide. The cooled reaction mixture was filtered and the filtrate acidified. There was obtained 0.32 g. (28%) of terephthalic acid, identified by comparison of its infrared spectrum (KBr pellet) with that of an authentic sample. Further comparison with the spectra of synthetic mixtures showed that no more than 1–2% of the *o*-isomer could be present.

Styrene analyses were performed by the spectrophotometric procedure of Saunders and Ašperger.[4] The extinction coefficients used for styrenes were those of Saunders and Williams.[1] Some runs, particularly with the slower-reacting sulfonium salts, were spoiled by partial or complete polymerization of the styrenes. Since this complication impaired precision, the figures given in Table I are maximum rather than average yields.

Kinetic Measurements.—The sulfonium salt was weighed into a 100-ml. volumetric flask, dissolved in water (*ca.* 50 ml.) and the solution brought to thermal equilibrium. There was then added by pipet 50 ml. of thermally-equilibrated sodium hydroxide solution and the mixture diluted to the mark with water. Initial concentrations were *ca.* 0.05 *M* for the sulfonium salt and *ca.* 0.10 *M* for the sodium hydroxide. Aliquots were withdrawn periodically with a 5-ml. automatic pipet and quenched in excess standard hydrochloric acid. The excess acid was then titrated with standard sodium hydroxide. The thermostat held within ±0.05° of the stated temperature.

ROCHESTER 20, NEW YORK

---

(7) L. P. Hammett, THIS JOURNAL, **59**, 96 (1937).

(8) See p. 219 of H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).