MECHANISMS OF ELIMINATION

THE E2 REACTION OF SEVERAL *p*-SUBSTITUTED PHENYLTHIAPROPYL BROMIDES AND THE CORRESPONDING OXYGEN ANALOGS IN t-BUTANOL CONTAINING POTASSIUM t-BUTOXIDE

Y. YANO and S. OAE

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan

(Received in Japan 11 August 1969; Received in the UK for publication 22 September 1969)

Abstract—The rates of the base-catalysed elimination of a series of γ -(*p*-substituted-phenylthia)propyl bromides and the corresponding oxygen analogues have been determined in t-butanol containing potassium t-butoxide. Although the oxygen compounds react faster than the sulfur counterparts, the ρ value obtained for the sulfur compounds is larger than that for the oxygen compounds. This difference in reactivity and ρ -values is discussed in terms of the difference between divalent oxygen and sulfur atoms in their ability to transmit electronic effect to a γ -carbon atom.

IN A previous paper,¹ we have shown that β -arylthiaethyl chlorides are $10^2 - 10^3$ times more reactive than the oxygen analogues in the base-catalysed elimination, the ρ -values are 1.98 for sulfur compounds and 1.33 for oxygen compounds. The large difference in reactivity and ρ value was ascribed to the 3d-orbital resonance effect of the S atom, that is called for in the nearly carbanion-like transition state, like in the base-catalysed hydrogen isotopic exchange reactions of mercaptals,² and the basecatalysed decarboxylation of α -polythia acetic acids.³ Meanwhile, it has been suggested that the alkylthia group displays some nonbonding interactions even when the group is located away from the reaction center. For example, the red-shift of UV spectra of allyl and benzyl sulfides has been postulated to be due to the non-bonding interaction between a p π -orbital and a vacant 3d orbital of the S atom,⁴ while the relatively smaller pKa values of α -mercaptoacetic acids than those of the corresponding oxygen acids in 50% aqueous ethanol are also ascribed to the difference of non-bonding interactions of divalent S atom and etheral oxygen with the carboxylate group.⁵ The markedly short distance between non-bonded S atom and an O atom of a nitro group of methyl o-nitrobenzensulfenate,⁶ the very short distance (2.41 Å) of one of the S atoms and CO oxygen of α -(1,2-dithiole-3 ylidene) acetone,⁷ and many similar short distances of non-bonding atoms⁸ are a few examples of such non-bonding interaction between a divalent S atom and a hetero atom bearing lone electron pairs. Such a nonbonding interaction involving 3d orbitals has been postulated to explain the longer wavelength shift of the n- π^* transition of disilyl ketone compared to dialkyl ketone.⁹

Thus, it is interesting to see if such a non-bonding interaction could assist the basepromoted deprotonation reactions. As an extension, we have chosen the base-catalysed E2 reaction of the titled compounds and examined the effects of both arylthia groups and the oxygen counterparts.

RESULTS AND DISCUSSION

The rate constants of the elimination were determined by first titrating the remaining base and then correcting by the yields of olefins. No substitution product was detected by VPC. The details are described in the Experimental. The results are shown in Table 1.

TABLE 1. RATE CONSTANTS OF E2 REACTION OF X ZCH2CH2CH2CH2Br WITH t-BUOK IN t-BUOH

х	Temp" °C	Z = O k _E (M ⁻¹ sec ⁻¹)	Z = S k _E (M ⁻¹ sec ⁻¹)
CH.O-	50	$2.05 \pm 0.03 \times 10^{-3}$	$4.90 \pm 0.20 \times 10^{-4}$
CH ₃ —	50	$2.04 + 0.02 \times 10^{-3}$	$5.24 \pm 0.09 \times 10^{-4}$
	40	$7.25 \pm 0.05 \times 10^{-4}$	$2.25 + 0.03 \times 10^{-4}$
H۴	50	$1.87 \pm 0.05 \times 10^{-3}$	$5.84 \pm 0.11 \times 10^{-4}$
	60	$405 \pm 0.12 \times 10^{-3}$	$1.41 \pm 0.04 \times 10^{-3}$
Cl	50	$1.99 \pm 0.05 \times 10^{-3}$	$7.48 \pm 0.09 \times 10^{-4}$

" Temperature was controlled within $\pm 0.02^{\circ}$.

^b Activation parameters are: $\Delta H^{\ddagger} = 17.4$ Kcal/mol; $\Delta S^{\ddagger} = -17.3$ eu for oxygen, $\Delta H^{\ddagger} = 18.4$ Kcal/mol; $\Delta S^{\ddagger} - 16.5$ eu for sulfur.

The concentrations of the bromides and the base used were 0-1M and 0-15M, respectively.

The faster reactions of the oxygen compounds than the corresponding sulfur analogs is undoubtedly due to the stronger electron-withdrawing inductive effect of the O atom than that of the S atom. Apparently there is no strong non-bonding 3dorbital participation from the S atom to stabilize either the growing negative charge or developing double bond, since any sizeable interaction would have enhanced the rate. Probably the 2p-3d orbital interaction may not come into a synchronous play with the deprotonation from the β -carbon or the double bond formation, because of sterically unfavourable arrangement for 2p-3d interaction at the transition state for E2 reaction, unlike in the equilibrium reaction of α -alkylthiaacetic acids or in the photoexcitation of allyl or benzyl sulfides. The Hammett ρ values,* although very small, were calculated by using σp for both the sulfur compounds, 0.37 (correlation coefficient $\gamma = 0.990$) and the oxygen compounds, (zero). The difference of ρ values for the sulfur and the oxygen compounds is interesting but seems rather strange, since the ability of the O atom to relay inductive effect is considered to be nearly equal to or slightly higher than that of the S atom, according to Miller et al.,¹⁰ who showed that the substituent effects of substituted anisoles and thioanisoles measured from the NMR spectra of these compounds are correlated with Hammett equation with ρ values $(c/s/\sigma)$ of -16 for oxygen compounds and -7 for the sulfur analogues.

As for the transition state of the elimination reactions of these and related compounds, we have shown previously¹¹ that the elimination reactions of 3-chloro-1,1-

^{*} If the leaving group was a Cl atom, the ρ values were 0.81 for sulfur compounds and 0.08 for oxygen compounds at 60°. As the transition state of these chlorides is known to be more carbanionic than that of the bromides, the difference between the oxygen and sulfur compounds must be real. (Unpublished data.)

(bis-ethylmercapto) propane and the corresponding the oxygen analog give hydrogen kinetic isotope effects of β -hydrogen of almost identical values (for sulfur $k_H/k_D = 4.4$, for oxygen, 4.5). Thus it is reasonable to consider that the electronic orientations of the transition states of the present elimination reactions of both oxygen and sulfur compounds are almost identical. The noticeably larger ρ value of the sulfur compounds may be interpreted in terms of a small non-bonding interaction between a vacant 3d-orbital of the S atom and the developing double bond as shown below.



EXPERIMENTAL

p-Substituted phenylmercaptopropyl bromides. Into EtOH (100 ml) containing sodium p-substituted thiophenoxides (0·1 mol), BrCH₂CH₂CH₂Br (0·5 mol) dissolved in EtOH (100 ml) was added. After refluxing 30 min, the mixture was poured into ice-water, and then extracted with CH₂Cl₂ (100 ml). After drying over CaCl₂, it was distilled. The oxygen compounds were synthesized similarly. The yields were usually more than 40%. The purities were checked by VPC and NMR; p-CH₃OPhS; b.p. 134-5°/1 mm, p-CH₃OhS; b.p. 123°/1 mm, PhS; b.p. 120°/1 mm, p-ClPhS; b.p. b.p. 136-7°/1·5 mm, p-CH₃OPhO; b.p. 107-109°/1 mm, p-CH₃PhO; b.p. 102-103°/1 mm, PhO; b.p. 91-92°/1 mm, p-ClPhO; b.p. 103-104°/0·5 mm.

Preparation of elimination products

p-Substituted phenyl allyl sulfides. These compounds were prepared according to the procedure used by Tarbell et al.¹² The yields were usually more than 80%; p-CH₃O b.p. 155°/23 mm, p-CH₃ b.p. 120°/30 mm, H; b.p. 116°/26 mm p-Cl b.p. 140°/33 mm

p-Substituted phenyl allyl ethers. These compounds were synthesized by the method of White et al.¹³ A mixture of p-substituted phenol (0-1 mol), allyl bromide (0-15 mol) and dry K_2CO_3 (0-1 mol) in 50 ml of dry acetone was refluxed for 8 hr with stirring. The mixture was diluted with 200 ml water and extracted with ether. After distilling off the ether, the residue was distilled under reduced press. The yields were always more than 70%. The purity was checked with VPC and NMR; p-CH₃O b.p. 115°/10 mm (lit.¹³ 116·5–117·5°/11·5 mm), p-CH₃. b.p. 89°·10 mm (lit.¹³ 97·5–98·5°/17·2 mm), p-H b.p. 76–78°/14 mm (lit.¹³ 93–93·7°/29 mm), p-Cl b.p. 108–109°/10 mm (lit.¹³ 109–110°/15 mm).

Kinetic measurements. The preparations of the base and the solvent used were as reported previously.¹ The observed rate constants were determined by the titration of the remaining base and the rate constants of the elimination were calculated by correcting the observed rate constants with the yields of the olefins.

Olefin determination. Product analysis was performed by gas chromatography as follows: 5 ml of the infinity sample of the kinetic run was poured into 200 ml ice-water containing an inner standard (diphenyl ether), and extracted with 100 ml ether. After drying over CaCl₂, the ether was distilled off *in vacuo*. The residue was analyzed by VPC. From the calibration which was made beforehand in a similar procedure described above, the yields of the olefins of all the compounds were found to be $100 \pm 5\%$ (the average of two runs).

For the sulfur compounds, the olefins produced were not allyl aryl sulfides, but mixtures of cis- and trans-propenyl aryl sulfides. As isomerization of allylic sulfides under these conditions has been well studied, $1^{2, 14}$ we have not examined it in detail.

REFERENCES

- ¹ S. Oae and Y. Yano, Tetrahedron 24, 5721 (1968).
- ² S. Oae, W. Tagaki and A. Ohno, Ibid. 20, 417 (1964).
- ³ K. Uneyama, W. Tagaki, I. Minamida and S. Oae, Ibid. 24, 5271 (1968).

- ⁴ C. C. Price and S. Oae, Sulfur Bonding p. 54. Ronald Press, N.Y. (1962).
- ⁵ I. Minamida, Y. Ikeda, K. Uneyama, W. Tagaki and S. Oae, Tetrahedron 24, 5293 (1968).
- ⁶ W. C. Hamilton and S. J. Le Placa, J. Am. Chem. Soc. 86, 2289 (1964).
- ⁷ A. Hordvik, 3rd Organosulfur Chemistry Symposium Caen, France (1968).
- ⁸ S. Bezzi, M. Mammi and C. Garbuglis, Nature, Lond. 182, 247 (1958).
- ⁹ H. Bock, H. Alt and H. Seide, J. Am. Chem. Soc. 91, 355 (1969).
- ¹⁰ S. H. Marcus, W. F. Reynolds and S. I. Miller, J. Org. Chem. 30, 1872 (1966).
- ¹¹ S. Oae, A. Ohno and W. Tagaki, Tetrahedron 20, 443, (1964).
- ¹² D. S. Tarbell and M. A. McCall, J. Am. Chem Soc. 74, 48 (1952).
- ¹³ W. N. White, D. Gwynn, R. Schlitt, C. Girard and W. Fife, *Ibid.* 80, 3271 (1958).
- ¹⁴ D. E. O'Connor and W. I. Lyness, *Ibid.* 86, 3840 (1964).