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KINETICS OF ELIMINATION REACTIONS OF β-PHENYLETHYL BROMIDES INDUCED BY SODIUM PHENOXIDE AND SODIUM p-NITROPHENOXIDE IN DIMETHYLFORMAMIDE. THE EFFECT OF BASE STRENGTH UPON THE STRUCTURE OF THE TRANSITION STATE.

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In spite of the large amount of work related to the mechanism of E2 elimination reactions, very little information is available about the effect of the basicity of the nucleophile on the structure of the transition state. In most of the studies the change of base was accompanied by a change in solvent and it was impossible to separate the effects of these two factors[1]. Thus a considerable argument still exists on the very important problem of whether a change to a stronger base leads to a greater or to a smaller carbanion character in the transition state[2].

Since significant information in this respect can be obtained by the study of the substituent effects on the rate of elimination reactions induced by nucleophiles of different basicity (but with the same steric requirements) in a solvent which can not interact with them, we have kinetically investigated the reactions of p-substituted 2-phenylethyl bromides (one series which has been studied in great detail in protic solvents) with sodium phenoxide and sodium p-nitrophenoxide in dimethylformamide (DMF). In this solvent the two nucleophiles differ in basicity by a factor of 6 powers of ten[3]. The results of this investigation are reported in the present note.

The reaction were carried out at 0°C and followed by titrating bromide ions with $AgNO_3$. In the case of the very reactive sodium phenoxide kinetics were measured by a batch-wise procedure[4]. The concentration of sodium phenoxide and sodium p-nitrophenoxide was in excess (about 10:1) with respect to that of the substrate[5]. Ion association was a complicating factor[6]. Second order rate constants were found to decrease by increasing the initial concentration of nucleophile. Moreover. when sodium phenoxide was the nucleophile a slight decrease of the rate constants with the progress of the reaction was observed[6]. To overcome these difficulties all the substrates were examined at the same concentration of nucleophile and, for sodium phenoxide, the second order rate constants were evaluated only from data which refer to the first part of the reaction (up to 30%). The results are collected in the Table.

TABLE

Kinetic data for the elimination reactions of 2-(p-Rphenyl)ethyl bromides with sodium phenoxide and sodium p-nitrophenoxide in DMF at 0°C[a].

	Sodium phenoxide		Sodium p-nitrophenoxide	
R	$k_2^E.10$ (l.mole^{-1}sec^{-1})	olefin[b] yield,%	$k_2^E.10^6$ (l.mole^{-1}sec^{-1})	olefin[b] yield,%
H	2.33	98	3.34	57.5
CH_3	0.87	84.5	1.78	47
OCH_3	0.56	84	1.36	38.5
Br	11.5	100	11.1	69.5

(a) The concentration of sodium phenoxide was ~ 0.05M, that of sodium p-nitrophenoxide ~ 0.9M.

(b) Determined according to the procedure described by Hudson and Klopman[7]. Corrections were made for the reaction of Br_2 with DMF. In one case this procedure was checked by v.p.c. analysis.

The rate constants for both the reactions investigated correlate in a satisfactorily fashion with the Hammett equation and ρ values of + 2.64 (r = 0.996 s = 0.059) and + 1.84 (r = 0.992 s = 0.061) were calculated for sodium phenoxide and sodium p-nitrophenoxide, respectively[8]. ρ is therefore significantly more positive with the stronger base and, since a more positive value of ρ implies a larger degree of negative charge on the β-carbon, it may be concluded that the carbanion character of the transition state becomes more pronounced as the basicity of the nucleophile becomes larger.

Interestingly, a decrease of ρ has been observed for the elimination reactions of β-arylethyl bromides and 1-aryl-2-propyl bromides when the base-solvent system has been changed from EtO^--EtOH to t-BuO^--t-BuOH[9]. In the light of the present results it now appears certain that this decrease is due to factors different than the base strength[10].

It must be finally pointed out that an increase in the ρ value does not necessarily imply an increase of carbon-hydrogen stretching in the transition state, since a larger carbanion character can also be determined by a decrease of carbon-bromine stretching, and consequently of double bond formation, whereas the carbon-hydrogen stretching is varied slightly. It is interesting to note that this possibility is clearly predicted by the model proposed by More O' Ferral to interpret the effect of substituents and reaction conditions upon β-eliminations[11].

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References

(1) Sole exception, to our knowledge, is the study of Oae and coworkers, Tetrahedron, 26, 27 (1970), on the elimination reactions of p-substituted phenyl β-chloroethyl sulfones with tertiary amines in acetonitrile. However, this reaction seems to proceed by a two-step process.

(2) For arguments in favor of a larger carbanion character see J.F. Bunnett Surv.Prog.Chem. 5, 53 (1969). For the opposite view see E.R. Thornton, J.Am. Chem.Soc., 89, 2915 (1967) and L.J. Steffa and E.R. Thornton, ibid. 89, 6149 (1967).

(3) C.D. Ritchie in "Solute-solvent interaction", J.F. Coetzee and C.D. Ritchie Eds., M. Dekker, New York and London (1969), p. 224.

(4) E. Baciocchi and L. Mandolini, J.Chem.Soc. B, 1362 (1967).

(5) The excess of nucleophile was also necessary to minimize the effect, on the rate, of the formation of hydrogen-bonded complexes between phenoxide (or nitrophenoxide) ions and phenol (or p-nitrophenol) formed in the elimination reaction. In dipolar aprotic solvents the association constants of these complexes should be very large. See ref. 3, p. 248.

(6) A. Berge and J. Ugelstod, Acta Chem.Scand. 19, 742 (1965).

(7) R.F. Hudson and G. Klopman, J.Chem.Soc., 5 (1964).

(8) The possibility should be considered that the relative sensitivity of each compound in the series to free ion and ion-pair attack is not the same. However, this probably does not occur in our case since the Hammett plots are linear. Moreover when the reactions with sodium phenoxide were carried out in the presence of the crown ether, dicyclohexyl-18-crown-6, the elimination rate increased significantly (~ 5 fold) but the ρ value remained unchanged (+2.62 against +2.64 in the absence of the crown ether).

(9) C.H. De Puy, D.L. Storm, J.T. Frey and C.G. Naylor, J.Org.Chem., 35, 2746 (1970) and references cited therein.

(10) A similar decrease of ρ has been observed for the reactions of 2-arylethyl trimethylammonium bromides (W.H. Saunders, Jr et al. J.Am.Chem.Soc., 90, 1775 (1968) for the same change of base-solvent system. However, in consideration of the striking differences in size and charge type of bromo and trimethylammonio leaving groups, it is not certain that this conclusion can be directly applied also to this series of substrates.

(11) R.A. More O' Ferrall, J.Chem.Soc. (B), 274 (1970).