Kinetic Study of Elimination Reactions Promoted by Crown Ether Complexed Potassium *tert*-Butoxide in *tert*-Butyl Alcohol

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Kinetics of eliminations from 1-bromo-2-arylethanes and 1-chloro-2-phenylethane promoted by 18-crown-6 ether complexed alkali *tert*-butoxides in *tert*-butyl alcohol have been carried out. The reaction rate (ca. 250-fold larger than that of elimination induced by uncomplexed alkali *tert*-butoxides) appears to be influenced by the nature of the cation, complexed *t*-BuOK being 4.5 times more reactive than complexed *t*-BuONa. Moreover, the second-order rate constants appear to increase as the base concentration increases. From kinetic data obtained at the same concentration of complexed *t*-BuOK values of 8, 19, and 2.8 have been calculated for the deuterium kinetic isotope effect, Br/Cl leaving group effect, and the reaction constant ρ, respectively. Since the corresponding data for the same reactions promoted by *t*-BuOK in *t*-BuOH, in the absence of crown ether, are 8.16, 23, and 2.5, it appears that complexation of the base (which should lead to dissociated *tert*-butoxide ions) has little effect on the transition state structure of anti eliminations from 2-phenylethyl derivatives.

Macrocyclic polyethers are known to convert contact ion pairs and ionic aggregates into loose ion pairs or separated ions.[1] Thus, a large number of elimination reactions promoted by crown ether complexed *t*-BuOK in *t*-BuOH (dissociated *t*-BuOK) have been carried out in order to ascertain the role of base association upon stereochemistry and both geometrical and positional orientation of E2 reactions.[2] However, no kinetic information on the eliminations carried out in this base–solvent system is available and even the magnitude of the rate enhancement which occurs when the base is changed from associated to dissociated *t*-BuOK is unknown. Moreover, the sole result concerning the effect of the base association on the transition state structure of elimination reactions refers to a syn elimination and is not derived from a kinetic study.[3]

In order to acquire information on the effect of ion pairing on the kinetic aspects and transition state structure of anti eliminations promoted by *t*-BuOK in *t*-BuOH we have investigated the reactions of 1-bromo-2-arylethanes, 1-bromo-2,2-dideuterio-2-phenylethane, and 1-chloro-2-phenylethane with crown ether complexed *t*-BuOK in *t*-BuOH.

The aim of this work was also that of determining to what extent the effects of base association on the geometrical and positional orientation of elimination reactions can be discussed in terms of effects on the transition state structure.

Results and Discussion

Kinetic experiments were brought about by following spectrophotometrically the formation of styrene or substituted styrene. In each case the optical densities at the infinity time indicated a quantitative yield of olefin. The substrate concentration was ca. 8×10^{-5} M whereas the base concentration was in the range 10^{-3}–10^{-2} M. Measurements at concentrations larger than 10^{-2} M were not possible since complexed *t*-BuOK was found, in these cases, to absorb significantly at the wavelengths used for the kinetic study (see Experimental Section). The reaction of 1-bromo-2-*p*-nitrophenylethane was extremely fast and was kinetically studied by using a stopped-flow spectrophotometer. The macrocyclic polyether was 18-crown-6 ether (henceforth indicated as 18C6) and in one run *t*-BuOK was replaced by *t*-BuONa.

In all experiments the base was always in large excess with respect to the substrate and first-order plots exhibited an excellent linearity, up to 75–80% of reaction. A 1:1 18C6/base molar ratio was not sufficient to assure a complete complexation of the cation in the range of base concentration 1×10^{-3}–5×10^{-3} M. Accordingly, at constant base concentration the derived second-order rate constants (k_2) leveled off only when the 18C6/base molar ratio was at least 2:1 with *t*-BuOK, and 5:1 with *t*-BuONa, in agreement with the fact that potassium is more strongly complexed than sodium by macrocyclic polyethers.[1a] Some representative data for the reaction with *t*-BuOK are reported in Table I.

Table I. Kinetic Data for the Elimination Reactions of 1-Bromo-2-phenylethane in *t*-BuOK–*t*-BuOH in the Presence of Varying Amounts of 18-Crown-6 Ether at 30 °C

[*t*-BuOK], M	[18C6], M	18C6/*t*-BuOK	k_1, s^{-1}	k_2, M^{-1} s^{-1}
2.05×10^{-3}	2.33×10^{-3}	1.14	2.69×10^{-3}	1.31
1.99×10^{-3}	4.48×10^{-3}	2.25	3.24×10^{-3}	1.63
2.09×10^{-3}	6.70×10^{-3}	3.20	3.30×10^{-3}	1.58
2.09×10^{-3}	10.50×10^{-3}	5.02	3.09×10^{-3}	1.48

Interestingly enough, complexed *t*-BuOK is more reactive (4.5-fold) than complexed *t*-BuONa (Table II, note *d*), the difference in reactivity being larger than that exhibited by the uncomplexed bases. This result is surprising since the reactivity of loose or separated ion pairs should be less sensitive to the nature of the cation than that of tight ion pairs and ionic aggregates. Probably even in the presence of a crown ether, ion pairing of alkali *tert*-butoxides in *t*-BuOH plays a significant role with respect to reactivity.

When the concentration of *t*-BuOK was changed significant changes in the k_2 values were observed (Table II), an increase in the base concentration determining a substantial enhancement of the rate. For all of the substrates the k_2 increase is ca. 2.5-fold for a tenfold increase in the base concentration, which corresponds to an apparent order of ca. 1.4 in complexed *t*-BuOK. In contrast, k_2 values for the elimination from 1-bromo-2-phenylethane induced by *t*-BuOK in *t*-BuOH in the absence of crown ether are independent of base concentration,[4,5] as also confirmed by our own results in Table II.

The dependence of the k_2 values on the base concentration for the reactions with complexed *t*-BuOK is difficult to rationalize and, at present, we can only tentatively indicate some possible explanations. Although the addition of KNO_3 does not seem to influence the reaction rate (Table II, note *c*), salt effects could be at the origin of the phenomenon since in a medium of low polarity such as *t*-BuOH, specific ionic effects can be important and solvated *tert*-butoxide anion might exert a positive effect on the rate while other anions are ineffective. Another suggestion could be that the active nucleophile is some multiple negative ion in equilibrium with the ion

Table II. Kinetic Data for the Elimination Reactions of 1-Bromo-2-arylethanes and 1-Chloro-2-phenylethane Promoted by Crown Ether Complexed *t*-BuOK in *t*-BuOH

Registry no.	Substrate[a]	Temp, °C	[*t*-BuOK], M	[18C6], M	k_2, M^{-1} s^{-1}[b]
103-63-9	H	30	0.022		7.26×10^{-3}
	H	30	0.415		7.13×10^{-3}
	H	30	1.03×10^{-3}	2.09×10^{-3}	1.03
23088-37-1	2,2-d_2	30	1.03×10^{-3}	2.09×10^{-3}	0.13
	H	30	3.25×10^{-3}	6.88×10^{-3}	1.74
	2,2-d_2	30	3.25×10^{-3}	6.88×10^{-3}	0.20
14425-64-0	p-OCH_3	30	3.25×10^{-3}	6.88×10^{-3}	0.46
6529-51-7	p-CH_3	30	3.25×10^{-3}	6.88×10^{-3}	0.76
1746-28-7	p-Br	30	3.25×10^{-3}	6.88×10^{-3}	11.72
	H	30	3.45×10^{-3}	6.90×10^{-3}	1.84
	2,2-d_2	30	3.45×10^{-3}	6.90×10^{-3}	0.23
	H	30	3.86×10^{-3}	1.15×10^{-2}	1.92[c]
	H	30	5.15×10^{-3}	1.13×10^{-2}	2.20[d]
	p-OCH_3	30	5.15×10^{-3}	1.13×10^{-2}	0.91
	p-CH_3	30	5.15×10^{-3}	1.13×10^{-2}	0.99
	p-Br	30	5.15×10^{-3}	1.13×10^{-2}	20.68
5339-26-4	p-NO_2	30	5.15×10^{-3}	1.13×10^{-2}	11 650
	H	30	5.40×10^{-3}	1.15×10^{-2}	2.04
	2,2-d_2	30	5.40×10^{-3}	1.15×10^{-2}	0.29
	H	30	1.09×10^{-2}	2.31×10^{-2}	2.56
	2,2-d_2	3		1.09×10^{-2}	2.31×10^{-2}
0.31					
	H	30	1.15×10^{-2}	2.30×10^{-2}	2.66
	2,2-d_2	30	1.15×10^{-2}	2.30×10^{-2}	0.33
	H	39.7	3.25×10^{-3}	6.88×10^{-3}	3.28
	2,2-d_2	39.7	3.25×10^{-3}	6.88×10^{-3}	0.44
	H	39.7	3.45×10^{-3}	6.90×10^{-3}	3.61
	2,2-d_2	39.7	3.45×10^{-3}	6.90×10^{-3}	0.48
	H	48.2	3.45×10^{-3}	6.90×10^{-3}	5.53
	2,2-d_2	48.2	3.45×10^{-3}	6.90×10^{-3}	0.78
622-24-2	$C_6H_5CH_2CH_2Cl$	30	0.492		3.14×10^{-4}
	$C_6H_5CH_2CH_2Cl$	30	1.02×10^{-2}	2.10×10^{-2}	0.14

[a] H refers to 1-bromo-2-phenylethane. [b] Average of at least two determinations. The average error is ±5% using the same batch of solvent. With different batches of *t*-BuOH the error can rise to ±9%. [c] In the presence of 7.92×10^{-3} M KNO_3. This value is compared with that (1.84 M^{-1} s^{-1}) obtained at a concentration of complexed base of 3.45×10^{-3} M. The small difference in k_2 is probably due to the fact that the kinetic experiment in the presence of KNO_3 has been carried out at a slightly larger *t*-BuOK concentration than that in the absence of the salt. [d] This value can be compared with that (0.49 M^{-1} s^{-1}) obtained when the base was complexed *t*-BuONa at a very similar concentration (4.91×10^{-3} M) with a 18C6/*t*-BuONa molar ratio of 5.

pair, thus leading to an order in *t*-BuOK greater than one.[6] Besides, two further possibilities should be considered: an increase in the basicity of the medium that is more rapid than the increase in the base concentration (even at the low concentrations used) and an increase in the elimination rate faster than that in the medium basicity. With respect to the latter possibility it is interesting to note that also in the reaction of 1-bromo-2-phenylethane with *t*-BuOK in Me_2SO-*t*-BuOH the rate was found to rise faster than H_- of the medium as Me_2SO concentration was increased.[4] However, in such a case k_2 was practically insensitive to changes in base concentration at a fixed composition of the mixed solvent.

Complexed *t*-BuOK is also, as expected, much more reactive than the uncomplexed base. At a concentration of 3.45×10^{-3} M, a 250-fold increase in the elimination rate is observed. This increase is due to enthalpic and entropic factors since both the value of $\Delta H^{\ddagger}$ (11.1 ± 1.5 kcal mol^{-1}) and $\Delta S^{\ddagger}$ (−20.7 ± 5 cal mol^{-1} K^{-1}) for the reaction of 1-bromo-2-phenylethane with complexed *t*-BuOK, calculated from data at the same base concentration, are significantly different from those ($\Delta H^{\ddagger}$ = 12.8 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −26 cal mol^{-1} K^{-1}) obtained in the same reaction promoted by *t*-BuOK in the absence of crown ether.[4,7]

From the data of Table II, the Hammett ρ value, the deuterium kinetic isotope effect (k_H/k_D), and the leaving group effect (k_{Br}/k_{Cl}) for the reaction promoted by complexed *t*-BuOK have been calculated using, in each case, kinetic data obtained at the same base concentration. The results are reported in Table III together with the corresponding ones for the reaction induced by uncomplexed *t*-BuOK. It appears immediately clear that in spite of the large effect on the reaction rate, the complexation of *t*-BuOK has not a significant

Table III. Hammett Parameters, Deuterium Isotope Effects, and Leaving Group Effects for the Reactions of 1-Bromo-2-arylethanes with *t*-BuOK–*t*-BuOH in the Absence and Presence of 18C6 at 30 °C

Base–solvent	ρ	k_H/k_D	k_{Br}/k_{Cl}
t-BuOK–*t*-BuOH	2.53[a]	8.16[b]	23[c]
t-BuOK–18C6-*t*-BuOH	2.77[d]	8.05 ± 0.39[e]	19[c]

[a] From ref 4; this value has been confirmed by the recent work of Blackwell et al.[8] Reference 9 reports a value of 2.08. [b] From ref 4; ref 10 reports 7.89. [c] See Table II. [d] Calculated by a least-squares analysis (r = 0.996, S = 0.18) at a base concentration of 5.15×10^{-3} M (substituents: p-OCH_3, p-CH_3, H, p-Br, p-NO_2). The σ^- value was used for the p-NO_2 group.[10] At a base concentration of 3.25×10^{-3} M (substituents: p-OCH_3, p-CH_3, H, p-Br) the ρ value was 2.80 (r = 0.992, S = 0.10). [e] Average of values calculated at different base concentrations (see Table II). From the values of k_H/k_D at 30, 39.7, and 48.2 °C (Table II) an A_H/A_D ratio of 0.84 can be calculated, which would indicate the absence of a tunneling contribution.

effect on the transition state structure of the elimination reactions of 1-bromo-2-phenylethanes. At most, a very small increase in the carbanion character of the transition state could be suggested.

A like situation has been observed in a study of the effect of added Me_2SO on the elimination reactions of 1-bromo-2-phenylethane in *t*-BuOH.[4] Also in that case, in contrast to the effect on rate, the transition state structure did not appear to change appreciably by increasing the basicity of the medium. The finding was explained by considering that in the transition state the base is substantially the same species (partially neutralized *tert*-butoxide anion), differences in rates being due to differences in the solvation of the base and in the tightness of its pairing with cation.

Clearly, also our own results can be rationalized in the same way. However, we feel that data with substrates different from 1-bromo-2-arylethanes are necessary before the above conclusion is definitely assessed. In this respect it is worth noting that in the syn elimination from *trans*-2-arylcyclopentyl tosylate[3] complexed *t*-BuOK was found to bring about a significant increase in the carbanion character of the transition state with respect to associated *t*-BuOK, the ρ value rising from 2.2 (in the absence of crown ether) to 3.1. However, in this case, rather than to a basicity effect, the increase in the carbanion character of the transition state of the reaction in going from associated to dissociated *t*-BuOK could probably be due to the fact that the associated base produces a more synchronous transition state by allowing the simultaneous coordination of the counterion with the base and leaving group,[12] which does not occur with dissociated *t*-BuOK. Of course, it is also possible that the transition state structure for a syn elimination displays a sensitivity to the basicity of the medium different from that of the transition state of an anti elimination.

Finally, the present results allow the conclusion that the significant effects exerted by base association on geometrical and positional orientation of anti eliminations cannot be traced back to effects on the transition state structure. Probably substantial changes in the product composition of an E2 reaction are determined by differences in the energy of the transition states which are too small to produce appreciable variations in the sensitivity of the reaction rate to substituent effects, leaving group effect, and kinetic isotope effect.

Experimental Section

Materials. 1-Bromo- and **1-chlorophenylethane** were commercial products (Fluka) purified by distillation. The other 1-bromo-2-arylethanes were prepared according to a procedure described in the literature.[13] Their properties were as follows.

1-Bromo-2-*p*-methylphenylethane, bp 100–101 °C (9 mm), $n^{24}\mathrm{D}$ 1.5508 [lit.[4] bp 97–99 °C (6 mm), $n^{26}\mathrm{D}$ 1.5472].

1-Bromo-2-*p*-methoxyphenylethane, bp 92–94 °C (1 mm), $n^{24}\mathrm{D}$ 1.5590 [lit.[4] bp 126–128 °C (6 mm), $n^{28}\mathrm{D}$ 1.5571].

1-Bromo-2-*p*-bromophenylethane, bp 97–98.5 °C (1 mm) [lit.[4] bp 127 °C (6 mm)].

1-Bromo-2-*p*-nitrophenylethane, mp 68–70 °C (lit.[4] mp 69 °C).

1-Bromo-2,2-dideuterio-2-phenylethane was prepared as described by Saunders and Edison.[10] The mass spectrum showed that the sample contained 1.92 atoms of D/molecule.

18-Crown-6 ether (18C6), a commercial material (Fluka), was purified by crystallization from *n*-hexane, mp 38.5–39.5 °C (lit.[14] mp 39.5–40.5 °C).

Base-Solvent Solution. *tert*-Butyl alcohol was distilled after treatment with potassium metal. Solutions of alkoxide were obtained by reactions, under nitrogen, of freshly cut potassium and sodium with *tert*-butyl alcohol.

Kinetic Studies. For all compounds, with the exception of 1-bromo-2-*p*-nitrophenylethane, kinetics were carried out in a stoppered two-limb silica cell. In one limb was placed the substrate solution (1 ml) and in the other the base solution (1 ml) obtained mixing identical volumes of alkali *tert*-butoxide in *tert*-butyl alcohol and 18C6 in *tert*-butyl alcohol. The cell was placed in the thermostated compartment of a Beckman DB-GT spectrophotometer. After 20 min, the solutions of the kinetic run were mixed throughly and the cell rapidly placed again in the cell compartment of the spectrophotometer. Absorbances were measured at the following wavelengths (nm): 250 for styrene; 252 for *p*-methylstyrene; 258 for *p*-methoxystyrene; 254 for *p*-bromostyrene. The reference cell contained a solution of alkali *tert*-butoxide and 18C6 in *tert*-butyl alcohol, both at the same concentration used in the kinetic run, to compensate for the significant absorption exhibited by complexed *t*-BuOK at 250–260 nm. The compensation, however, turned out to be not effective when the base concentration was larger than 0.01 M. The eliminations from 1-bromo-2-*p*-nitrophenylethane were followed on a Durrum-Gibson D-110 stopped-flow spectrophotometer. The wavelength used in this case was 300 nm. In some kinetic runs for 1-bromo-2-phenylethane and 1-bromo-2,2-dideuterio-2-phenylethane the mixed kinetic method described by Jones was also used.[15] The values of k_2 obtained with this method were in good agreement with those obtained with the procedure previously described.

The k_2 values at temperatures different from 30 °C were not corrected for the solvent expansion.

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Registry No.—Crown ether, 17455-13-9; *t*-BuOK, 865-47-4; *t*-BuOH, 75-65-0.

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(5) The fact that the k_2 values in *t*-BuOK–*t*-BuOH are independent of the base concentration allows one to conclude that only ion pairs and (or) ionic aggregates (having similar reactivity) are the active nucleophiles in this base–solvent system. On the basis of this conclusion the observed effect of *t*-BuOK concentration on both the geometrical and positional orientation of some elimination reactions[2a] is probably to be attributed to an equilibrium between ion pairs and ionic aggregates (in these cases of different reactivity) rather than to an equilibrium between dissociated and associated *tert*-butoxide ions. Accordingly, whereas the difference in reactivity between associated and dissociated *t*-BuOK must be very large, as shown by the effect of the addition of crown ether, and therefore significant with any substrate, that between ion pairs and ionic aggregates could be much smaller. Thus, it is not unreasonable to suggest that the latter difference may be of importance with some substrates[2a] and insignificant with others (1-bromo-2-phenylethane and 1-phenyl-2-chloropropane[2b]).

(6) An equilibrium of this kind has been suggested to explain the three-halves order dependence of reaction rates on *t*-BuOK concentration found in the reaction of 1-halo-2,2-diphenylethylenes in *t*-BuOK–*t*-BuOH: J. G. Pritchard and A. A. Bothner-By, *J. Phys. Chem.*, **64,** 1271 (1960).

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