The Influence of Crown Ethers on the Activation Parameters of the β-Elimination Reactions of Some *p*-Chlorophenylethanes with Alkoxide Bases

By **Arnold Jarczewski** and **Grzegorz Schroeder**, Institute of Chemistry, Adam Mickiewicz University, 60780 Poznan, Poland
Kenneth T. Leffek,* Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4H6.

The addition of crown ethers 1,4,7,10,13-pentaoxacyclopentadecane and 1,4,7,10,13,16-hexaoxacyclo-octadecane in quantities equimolar to that of the base, to the dehydrochlorination reactions of the *p*-chlorophenylethanes, 2,2-bis-(4-chlorophenyl)-1-chloro-, -1,1-dichloro-, and 1,1,1-trichloro-ethane, promoted by sodium ethoxide and sodium t-butoxide, has been investigated. The crown ethers cause no change in the kinetic order of the reaction, but the second-order rate constants and activation parameters are significantly changed to a greater extent than can be accounted for merely by the assumption that the crown ethers bring about complete dissociation of the alkoxide ion-pairs. The nature of the changes are such that different transition state structures within the *E*2 mechanism must exist in the presence of crown ethers, in addition to different initial state solvation conditions.

SEVERAL studies [1-3] have been made on the effects of crown ethers on the kinetics and mechanism of β-elimination reactions with alkoxide bases. In some reactions, dicyclohexyl-18-crown-6 ether has been found to change the kinetics and, therefore, the mechanism, in that the order in the alkoxide base increased from unity to *ca*. 1.5 in the presence of this crown ether.[2] Zavada *et al.*[1] have studied the changes in the mechanism with respect to the *syn*- and *anti*-elimination pathways when this crown ether is added to a variety of systems.

In the present work, we have attempted to define the general effect, including solvation changes, of crown ethers on β-elimination reactions by studying the addition of 1,4,7,10,13-pentaoxacyclopentadecane (15C5) and 1,4,7,10,13,16-hexaoxacyclo-octadecane (18C6) to the β-elimination reactions of 2,2-bis-(4-chlorophenyl)-1-chloro- (DDM), -1,1-dichloro- (DDD), and -1,1,1-trichloro-ethane (DDT) promoted by sodium ethoxide and t-butoxide in the corresponding alcohol solvents.

In these alkoxide solutions, the base is significantly associated in ion-pairs, or larger aggregates, at the concentrations typically used in elimination reactions. The ion-pair dissociation constant for sodium ethoxide in ethanol [4,5] is *ca*. 0.01—0.02 mol l^{-1} and that for potassium t-butoxide in t-butyl alcohol [6] *ca*. 0.001 6 mol l^{-1}. It has been assumed [1] that the large increase in conductance which is observed when crown ethers are added to salt solutions means that t-butoxide solutions are transformed completely into separated ions, but this may be an over-simplification of the situation. It is known that solutions of partly dissociated salts show a significant increase in conductance when a crown ether is added.[7]

EXPERIMENTAL

Materials.—The alcohols were purified and the sodium alkoxide base solutions were prepared by standard methods as previously described.[8]

DDT and DDD were commercial products (Analabs) with m.p. 108.5 and 109.0 °C, respectively. DDM was prepared by the method of Cristol *et al.*,[9] m.p. 51.0 °C.

The crown ethers were Aldrich products. 15C5 was purified by distillation at reduced pressure and 18C6 was recrystallized from hexane, m.p. 39—40 °C.

Kinetic Measurements.—The reactions were followed spectrophotometrically in the u.v. range and the rate constants were evaluated as previously described.[8,10]

RESULTS AND DISCUSSION

Table 1 shows the pseudo-first-order rate constants for the dehydrochlorination reactions of the three chloroethanes promoted by ethoxide and t-butoxide in which the reacting solutions contain a concentration of crown ether equimolar to that of the alkoxide base. In all cases the plots of pseudo-first-order rate constant against alkoxide concentration are linear, indicating that the order of the reaction in alkoxide base is unity. Thus contrary to the work of Baciocchi *et al.*,[2] who used an excess of crown ether, we find no change in the kinetics of the reaction when either of the crown ethers 15C5 and 18C6 are added. Therefore, at this basic level of the number of alkoxide ions present in the transition state, the mechanism of the reactions is the same in the presence of crown ethers as it is without them.

The second-order rate constants are given in Table 2 for the reactions with the crown ethers, together with a few results from earlier work [10] in the absence of crown ethers, for comparison.

From the ion-pair dissociation constants quoted above, it may be calculated that for the alkoxide solutions used in the rate measurements, there is between 40 and 75% dissociated ethoxide and between 45 and 60% dissociated t-butoxide ion. For the latter calculation, it was assumed that the ion-pair dissociation constant for sodium t-butoxide was equal to that quoted above for potassium t-butoxide. Since the free alkoxide ions are much stronger bases than the ion-pairs, it is assumed that the dehydrochlorination reactions proceed through the ions rather than the ion-pairs.

Crown ethers specifically solvate the sodium ion and lead to a marked increase in the conductivity of a salt solution,[7] which is interpreted as an increase in the concentration of free alkoxide ions in the reaction mixtures. This effect should be qualitatively similar for

TABLE 1

Pseudo-first-order rate constants for the dehydrochlorination reactions of chloroethanes (2.5×10^{-5}M) with equimolar alkoxide–crown ether solutions

Temp. (°C)	[Alkoxide] ≡ [Crown ether]/M	DDM	DDD $10^4k_1/s^{-1}$	DDT
(a) Ethoxide–15-crown-5 in ethanol				
30	0.01	1.00	2.84	9.4
	0.02	1.53	7.34	23.8
	0.03	2.27	11.6	34.1
	0.04	2.65	16.8	46.2
35	0.01	1.63	5.8	19.2
	0.02	2.88	13.3	41.4
	0.03	4.14	19.2	69.6
	0.04	5.30	28.5	95.7
40	0.01	2.54	9.5	29.4
	0.02	4.40	21.4	62.1
	0.03	5.99	33.7	102
	0.04	8.30	46.2	140
45	0.01	3.45	13.8	37.4
	0.02	6.57	33.0	95.1
	0.03	10.0	54.8	157
	0.04	13.4	75.7	219
(b) t-Butoxide–15-crown-5 in t-butyl alcohol				
30	0.002	8.3	68	158
	0.003	11.0	115	251
	0.004	14.3	160	386
	0.005	18.0	207	497
35	0.002	8.9	78	176
	0.003	13.8	154	312
	0.004	17.9	198	450
	0.005	22.5	265	589
40	0.002	12.8	84	224
	0.003	18.2	155	385
	0.004	23.8	227	529
	0.005	29.3	299	691
(c) Ethoxide–18-crown-6 in ethanol				
30	0.01	0.109	0.287	1.95
	0.02	0.268	0.556	3.17
	0.03	0.430	1.01	4.51
	0.04	0.594	1.38	5.82
35	0.01	0.293	0.76	3.45
	0.02	0.483	1.43	5.82
	0.03	0.640	2.10	7.24
	0.04	1.03	2.80	10.0
40	0.01	0.441	1.64	5.31
	0.02	0.779	2.71	8.80
	0.03	1.10	3.84	11.0
	0.04	1.43	4.88	14.3
45	0.01	0.95	2.32	7.60
	0.02	1.38	3.95	11.3
	0.03	1.79	5.19	16.0
	0.04	2.26	6.76	18.6
(d) t-Butoxide–18-crown-6 in t-butyl alcohol				
30	0.002	24.8	81.1	357
	0.0025		106	376
	0.003	43.0	130	403
	0.004	58.9		
	0.005	75.1		
35	0.002	25.6	109	405
	0.0025		137	448
	0.003	46.5	163	494
	0.004	68.5		
	0.005	86.2		
40	0.002	30.0	136	443
	0.0025		179	502
	0.003	52.2	212	582
	0.004	76.4		
	0.005	101		
45	0.002	34.9	142	547
	0.0025		231	632
	0.003	61.0	308	772
	0.004	88.5		
	0.005	114		

TABLE 2

Second-order rate constants for the dehydrochlorination of chloroethanes by equimolar alkoxide–crown ether solutions in alcohol

Temp. (°C)	DDM	DDD $10^3k_2/l\ mol^{-1}\ s^{-1}$ [a]	DDT
(a) Ethoxide in ethanol			
(i) Ethoxide alone			
30	12.9 ± 0.8	180 ± 10	79 ± 9
45	47 ± 1	740 ± 3	334 ± 9
(ii) Ethoxide–15-crown-5			
30	5.7 ± 0.5	46 ± 2	121 ± 6
35	12.3 ± 0.2	74 ± 4	258 ± 8
40	18.9 ± 1.0	122 ± 1	372 ± 11
45	33.3 ± 0.5	208 ± 4	606 ± 7
(iii) Ethoxide–18-crown-6			
30	1.6 ± 0.1	3.7 ± 0.3	13.0 ± 0.2
35	2.4 ± 0.4	6.8 ± 0.1	21.0 ± 2
40	3.3 ± 0.1	10.8 ± 0.1	29.0 ± 2
45	4.3 ± 0.1	14.5 ± 0.5	38.0 ± 3
(b) t-Butoxide in t-butyl alcohol			
(i) t-Butoxide alone			
30	0.0198 ± 0.0004	0.0637 ± 0.0004	0.22 ± 0.05
45	0.026 ± 0.002	0.110 ± 0.007	0.42 ± 0.01
(ii) t-Butoxide–15-crown-5			
30	0.32 ± 0.02	4.64 ± 0.03	11.5 ± 0.5
35	0.45 ± 0.01	6.0 ± 0.4	13.8 ± 0.1
40	0.55 ± 0.01	7.1 ± 0.1	15.4 ± 0.3
45	0.69 ± 0.01	8.1 ± 0.1	17.6 ± 0.6
(iii) t-Butoxide–18-crown-6			
30	1.67 ± 0.04	4.92 ± 0.03	4.6 ± 0.5
35	2.04 ± 0.06	5.4 ± 0.2	8.9 ± 0.1
40	2.37 ± 0.04	7.6 ± 0.6	13.9 ± 1.2
45	2.65 ± 0.03	16.6 ± 0.6	17.5 ± 0.3

[a] The limits quoted are standard deviations.

ethoxide and t-butoxide bases, since the extent of dissociation in the absence of crown ethers is approximately the same. The rate change due to this concentration effect should not exceed a factor of three. Although the sodium ion is a better fit in the ring of 15C5 than in 18C6, both rings are large enough to accommodate this cation, so no major differences can be predicted for the two crown ethers.

The results of Table 2 show in all cases, except one, both crown ethers decrease the rate of the ethoxide promoted dehydrochlorination rather than increase it. On the other hand, for the t-butoxide reactions both crown ethers increase the rate in all cases, by a factor ranging from 16 to 91. Neither of these observations fits the simple concentration of free alkoxide ion factor, so the results must be considered in terms of changes in the solvation states and/or changes in the details of the mechanism.

The activation parameters in Table 3 show that the two crown ethers do have markedly different effects on the two alkoxide reactions. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the three chlorinated ethanes for the ethoxide reaction are quite similar in the absence of crown ethers. The addition of 15C5 increases the $\Delta H^{\ddagger}$ values and adds a positive component to the $\Delta S^{\ddagger}$ values. 18C6 tends to

TABLE 3

Activation parameters for the dehydrochlorination reactions of chloroethanes by alkoxide–crown ether solutions

Substrate	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}$/ kcal mol^{-1}
(a) Ethoxide alone			
DDM	16.7 ± 0.2	−12.2 ± 0.9	20.4
DDD	17.0 ± 0.4	−5.8 ± 1.4	18.4
DDT	16.8 ± 0.9	−8.1 ± 3	19.2
(b) Ethoxide–15-crown-5			
DDM	21.4 ± 1.6	1.7 ± 5.3	20.9
DDD	18.6 ± 0.5	−3.2 ± 1.7	19.5
DDT	19.4 ± 2.0	1.3 ± 6.4	19.0
(c) Ethoxide–18-crown-6			
DDM	12.0 ± 0.5	−31.7 ± 1.7	21.3
DDD	16.8 ± 1.7	−14.1 ± 5.4	21.0
DDT	12.9 ± 1.4	−24.5 ± 4.0	20.1
(d) t-Butoxide alone			
DDM	6.3 ± 0.6	−45.0 ± 2	19.8
DDD	9.4 ± 0.7	−33.0 ± 2	19.3
DDT	11.9 ± 0.7	−21.0 ± 2	18.2
(e) t-Butoxide–15-crown-5			
DDM	9.0 ± 0.8	−31.1 ± 2.4	18.1
DDD	6.5 ± 0.8	−34.1 ± 2.5	16.5
DDT	4.7 ± 0.4	−38.2 ± 1.1	15.9
(f) t-Butoxide–18-crown-6			
DDM	5.3 ± 0.5	−40.1 ± 1.6	17.2
DDD	15.2 ± 4.3	−7.7 ± 14.5	16.8
DDT	16.5 ± 2.5	−0.9 ± 7.9	16.8

lower the $\Delta H^{\ddagger}$ value and add a negative component to $\Delta S^{\ddagger}$.

In the t-butoxide reaction, in the absence of crown ethers, $\Delta H^{\ddagger}$ increases and $\Delta S^{\ddagger}$ becomes less negative as the number of chlorine atoms in the substrate is increased. 15C5 completely reverses both these trends, whereas 18C6 tends to increase $\Delta H^{\ddagger}$ and make $\Delta S^{\ddagger}$ less negative while maintaining the original trend.

The lack of symmetry in these observations makes it unlikely that the results can be accommodated using only solvation arguments, even though the solvation state of the cation (and the anion) is obviously an important factor in the reaction. The changes in the activation parameters in the presence of crown ethers, particularly the effect of 15C5 on the t-butoxide reaction, must, therefore, reflect changes in the structure of the transition states.

In summary, crown ethers do not change the molecularity of the reactions when present in a quantity equimolar to that of the base. However, the rate constants and activation parameters are significantly changed to a greater extent than can be accounted for merely by the assumption that the crown ethers bring about complete dissociation of the alkoxide ion-pairs. Furthermore, the nature of the changes are such that different transition state structures within the *E*2 mechanism must exist in the presence of crown ethers, in addition to different initial state solvation conditions.

[8/1517 *Received*, 17*th August*, 1978]

REFERENCES

[1] J. Závada, M. Pánková, and M. Svoboda, *Coll. Czech. Chem. Comm.*, 1976, **41**, 3778.

[2] S. Alunni, E. Baciocchi, and P. Perucci, *J. Org. Chem.*, 1977, **42**, 2170.

[3] R. A. Bartsch, E. A. Mintz, and R. M. Parlman, *J. Amer. Chem. Soc.*, 1974, **96**, 4249.

[4] J. Barthel, G. Schwitzgebel, and R. Wachter, *Z. Phys. Chem. Neue Folge*, 1967, **55**, 33.

[5] K. T. Leffek and A. Suszka, *Canad. J. Chem.*, 1975, **53**, 1537.

[6] J. R. Jones, *Progr. Reaction Kinetics*, 1973, **7**, 1.

[7] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.

[8] A. Jarczewski and G. Schroeder, *Roczniki Chem.*, 1975, **49**, 2025.

[9] S. J. Cristol, N. L. Hause, A. J. Quant, H. M. Miller, K. R. Eilar, and J. S. Meek, *J. Amer. Chem. Soc.*, 1952, **74**, 3333.

[10] G. Schroeder, A. Jarczewski, and K. T. Leffek, *Roczniki Chem.*, 1977, **51**, 279.