Elimination and Substitution Reactions of 1-Bromodecane with Alkoxide Ions in Dimethyl Sulfoxide/Alcohol Mixtures

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The rates of elimination and substitution reactions of 1-bromodecane have been studied using potassium hydroxide, methoxide, ethoxide, isopropoxide, and t-butoxide in the corresponding dimethyl sulfoxide/alcohol mixtures. Parallel studies have also been performed in the presence of 0.1 M 18-crown-6 in the same reaction mixtures. From estimation of the H_--function of the alkoxide mixtures it is found that the elimination and substitution reactions follow a Brønsted relation ($\ln k = A + \beta\, H_-$), where the β-coefficient of elimination is always greater than the β-coefficient of substitution towards the same alkoxide. Linear extrapolation of the Brønsted relation ($\ln k$ vs. H_-) in DMSO/alcohol mixtures shows that: (a) elimination totally dominates at very high H_- and (b) MeO^- is a stronger base than EtO^- and $t\text{-}BuO^-$ when the ions become strongly desolvated. The results accord with the finding that the basicity of completely desolvated alkoxide ions in the gas phase decreases in the following series: $MeO^- > EtO^- > i\text{-}PrO^- > t\text{-}BuO^-$, and that 1-bromopropane and methoxide ions in the gas phase give exclusively propene.

Recently it was shown that the gas-phase reaction of 1-bromopropane and methoxide ions gives the elimination product, propene, and no traces of the substitution product, 1-methoxypropane.[1] It is well known that high basicity of the nucleophile favours elimination in preference to substitution in alkyl halides.[2] Comparing the Brønsted relation: $\ln k = A + \beta pK$, of elimination and substitution, it is found that the β_E-coefficient of elimination is higher than the β_S coefficient of substitution. In alcoholic solution, β_E and β_S of the secondary bromide Pr_2CHBr are reported to be 0.39 and 0.27, respectively.[3] Primary alkyl halides usually give such small amounts of alkene in protic solvents that it is difficult to study the elimination/substitution ratio quantitatively. However, when dipolar solvents, as dimethyl sulfoxide (DMSO), and N,N-dimethylformamide (DMF) are used, or when crown ethers are added to the reaction mixture, a much greater proportion of alkene is obtained.[4–8] This observation indicates that the intrinsic basicity of alkoxide ions is increased by the use of a large proportion of dipolar aprotic solvents, and by crown ethers.

This study is directed toward a quantitative evaluation of elimination and substitution reactions of 1-bromodecane and alkoxide ions in DMSO/alcohol mixtures, with and without the addition of 18-crown-6.

Experimental

Materials. 1-Bromodecane, p.a., from Fluka A/G, was used without further purification.

Potassium alkoxides. The alkoxides were made from alcohols of highest possible purity by treatment with pure po-

tassium under a stream of dry nitrogen. The solutions were titrated with standard 0.1 M HCl, and diluted with DMSO to the appropriate concentrations. The DMSO was purified by being boiled under reduced pressure over calcium hydride for 1 h before being fractionated at reduced pressure. Only freshly prepared alkoxide solutions were used. If the solutions were stored for some days, they were kept in a refrigerator, and the base content was checked immediately before use.

Kinetic measurements. A 100 ml portion of the reaction solution containing an equivalent amount of 1-bromodecane and potassium alkoxide (approximately 0.1 M), was used. The total rate of reaction (elimination + substitution), was followed by titration of the alkoxide after fixed time intervals from the start of reaction. Samples of 5 ml were withdrawn from the reaction solution, and rapidly transferred to an excess of standard acid, and back-titrated with standard base. In each sample the 1-decene content was quantitatively determined by the bromide/bromate/thiosulfate method.[9]

Results and discussion

Since the rates of elimination and substitution of primary alkyl halides are both second-order reactions, the overall second-order rate constant, k_o, is the sum of the rate constants of elimination and substitution. The ratio between the amount of elimination and substitution at any time will thus be equal to the ratio between the corresponding rate constants: k_E/k_S.

In Table 1 are recorded the rate constants, k_o, k_E, k_S, and the percentage 1-decene formed by potassium hydroxide

Table 1. Rate constants for elimination and substitution reactions of 1-bromodecane with potassium hydroxide, and respective alkoxides, in 83.7 mol % DMSO/alcohol mixtures, with and without 0.1 M 18-crown-6. Equimolar concentrations of reactants, approximately 0.1 M. Temp. = 20 °C.

K⁺ salt solution	0.1 M 18-crown-6	Rate constant / M⁻¹ s⁻¹		k_E/k_S	Decene / %
		k_S	k_E		
DMSO/MeOH/HO⁻	–	4.3×10^{-2}	5.5×10^{-3}	0.13	11.3
DMSO/MeOH/MeO⁻	–	4.3×10^{-2}	5.9×10^{-3}	0.14	12.0
DMSO/EtOH/EtO⁻	–	1.3×10^{-1}	3.0×10^{-2}	0.23	18.8
DMSO/iPrOH/iPrO⁻	–	3.5×10^{-1}	1.1×10^{-1}	0.31	23.9
DMSO/tBuOH/tBuO⁻	–	3.6×10^{-1}	6.5×10^{-1}	1.80	64.4
DMSO/MeOH/HO⁻	+	5.2×10^{-2}	7.4×10^{-3}	0.14	12.4
DMSO/MeOH/MeO⁻	+	5.7×10^{-2}	8.5×10^{-3}	0.15	13.0
DMSO/EtOH/EtO⁻	+	1.5×10^{-1}	3.5×10^{-2}	0.23	18.9
DMSO/iPrOH/iPrO⁻	+	6.2×10^{-1}	1.8×10^{-1}	0.29	22.5
DMSO/tBuOH/tBuO⁻	+	1.26	2.34	1.86	65.0

and the different alkoxides in 83.7 mol % DMSO/alcohol mixtures. The reaction with KOH was performed in DMSO/methanol, instead of DMSO/water, due to the problem of obtaining a homogeneous solution in the latter mixture. As expected, the rate of elimination increased with the basicity of the nucleophile. The effect of addition of 0.1 M 18-crown-6 was small for hydroxide, methoxide, and ethoxide, but quite considerable for isopropoxide and t-butoxide.

Since the basicity of the methoxide ion has been measured in a series of DMSO/methanol mixtures, the H_--function can be calculated up to 95 mol % DMSO.[10] This enabled us to determined the elimination/substitution ratio of 1-bromodecane as a function of the H_--function of DMSO/methanol mixtures. The data are listed in Table 2. When 18-crown-6 was added, slightly higher rate constants were the general picture of a linear dependence between ln k and the H_--function persists (Fig. 1). The slopes of the
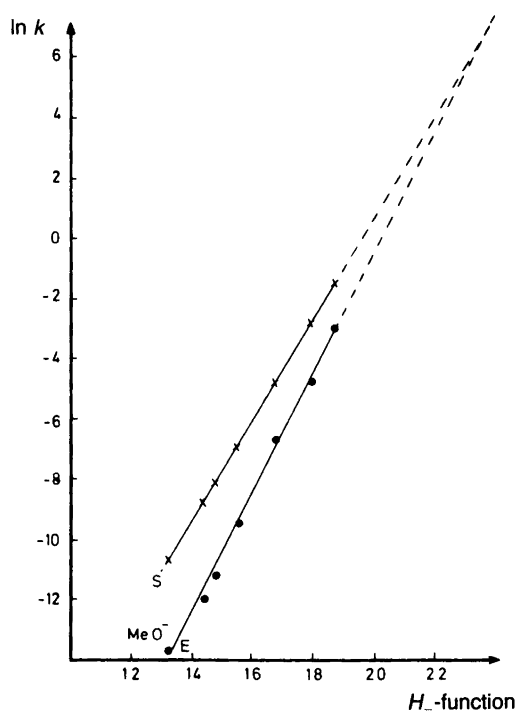

Fig. 1. The Brønsted relation of the rate of elimination and substitution of 1-bromodecane by potassium methoxide (ln k vs. H_-) in various mixtures of DMSO/MeOH/MeO⁻. S = substitution, E = elimination. Temp. = 20 °C.
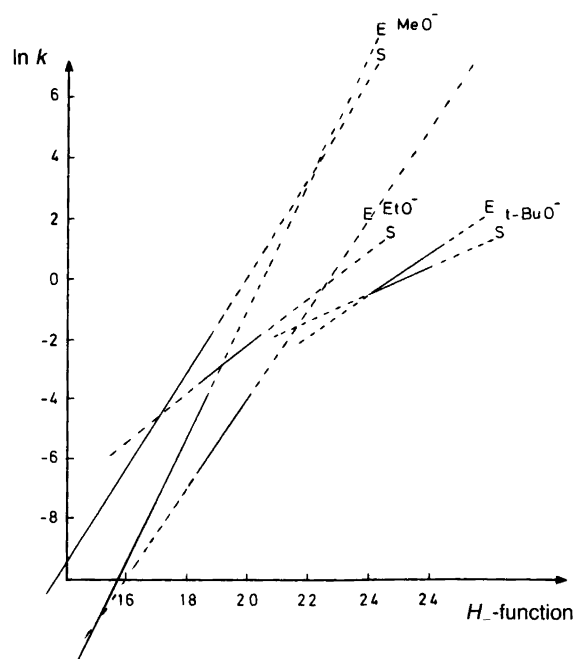

Fig. 2. Fully drawn lines: experimental curves of the linear Brønsted relation of the elimination and substitution of 1-bromodecane by MeO⁻, EtO⁻ and t-BuO in their respective DMSO/ROH/RO⁻ mixtures. Broken lines: the same Brønsted function extended to lower and higher H_- values. S = substitution, E = elimination. Temp. = 20 °C.

Table 2. Overall, elimination and substitution rate constants, k_o, k_E, k_S, respectively, of 1-bromodecane and potassium methoxide in various DMSO/methanol mixtures. Initial concentrations: 0.1 M 1-bromodecane and 0.1 M potassium methoxide. Temp. = 20 °C.

DMSO/mol %	Rate constant/M⁻¹ s⁻¹			Decene/%	Estimated H_--function
	k_o	k_E	k_S		
12.5	1.97×10^{-5}	7.0×10^{-7}	1.9×10^{-5}	3.5	13.2
31.8	1.45×10^{-4}	5.2×10^{-6}	1.4×10^{-4}	3.7	14.4
41.1	3.04×10^{-4}	1.4×10^{-5}	2.9×10^{-4}	4.6	14.8
51.4	7.80×10^{-4}	4.0×10^{-5}	7.4×10^{-4}	5.1	15.6
69.5	8.72×10^{-3}	7.2×10^{-4}	8.0×10^{-3}	8.3	16.8
83.7	4.90×10^{-2}	5.9×10^{-3}	4.3×10^{-2}	12.0	18.0
91.6	1.34×10^{-1}	2.4×10^{-2}	1.1×10^{-1}	18.6	18.7

straight lines of elimination and substitution, the β-values, are approximately 0.9 and 0.7, respectively. When the lines are extrapolated to still higher H_--values, they cross at about $H_- = 22.5$, and at very high H_-, which is typical for methoxide in the gas phase, the elimination reaction predominates totally.

The effect of DMSO is to desolvate the alkoxide ions through formation of strong hydrogen bonds with the alcohol. As a result the alkoxide ion will be increasingly 'naked' and more effective as a base and as a nucleophile. Complete desolvation is only obtainable in the gas phase, where, accordingly, the alkoxide ions must be characterized as having very high H_--values. The recently published study of Jones and Ellison,[1] showing that 1-bromopropane and methoxide ions in the gas phase give exclusively propene, is therefore a consequence of the extremely high basicity of the alkoxide ions.

Studies of the basicity of alkoxide ions in the gas phase have shown that the basicity order is reversed in comparison with the basicity in solution.[11] The following basicity series: methoxide > ethoxide > isopropoxide > t-butoxide, then arises.[12] If the rate of elimination, which is initiated by proton abstraction, is taken as a measure of basicity, the same basicity series can be deduced from extrapolation of the elimination curve of ln k vs. the H_--function of the different alkoxides in the corresponding DMSO/alcohol mixtures (Fig. 2). Although literature data of the H-data of ethoxide and t-butoxide in DMSO are fewer than

the corresponding H_--data of methoxide,[10] it is still safe to conclude that the $β_E$ values of elimination decrease from methoxide to t-butoxide, and that extrapolation to very high H_--values, typical for desolvated ions, appears to give the same basicity order as in the gas phase.

References

1. Jones, M. E. and Ellison, G. B. *J. Am. Chem. Soc. 111* (1989) 1645.
2. Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed., Cornell University Press, New York 1969.
3. Hudson, R. F. and Klopman, G. J. *J. Chem. Soc. B* (1964) 5.
4. Buncel, E. and Wilson, J. *Adv. Phys. Org. Chem. 14* (1977) 133.
5. Schlosser, M. In: Houben-Weyl, *Methoden der Organischen Chemie*, Band V/1b, Thieme, Stuttgart 1772, p. 138.
6. Veeravagu, P., Arnold, R. T. and Eigemann, G. W. *J. Am. Chem. Soc. 86* (1964) 3072.
7. Fraser, G. M. and Hoffmann, H. M. R. *J. Chem. Soc. B* (1978) 425.
8. Zavada, J. and Pankova, M. *Collect. Czech. Chem. Commun. 43* (1978) 1080.
9. Veibel, S. *The Identification of Organic Compounds*, 7th ed., G. E. Gads Forlag, København 1956.
10. Coetzee, J. F. and Ritchie, C. D. *Solute–Solvent Interactions*, Marcel Dekker, New York 1969, p. 195.
11. Brauman, J. I. and Blair, L. K. *J. Am. Chem. Soc. 92* (1970) 5986.
12. Bohme, D. K., Lee-Ruff, E. and Young, L. B. *J. Am. Chem. Soc. 91* (1971) 4608.