SOLVENT EFFECTS ON HBr-CYCLANOL REACTIONS

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Influence of solvents on the reactions of cyclanols with HBr is reported. Hydrocarbons and some dipolar aprotic solvents were used as binary mixtures with acetic acid. The order of reactivity in various solvent mixtures tried is:

Acetic acid—Dimethylsulphoxide > Acetic acid—Toluene
> Acetic acid—Nitromethane > Acetic acid—Benzene
> Acetic acid—Sulpholane > Pure Acetic acid

There was no appreciable reaction with Dimethylformamide and Dimethylacetamide. The reactions are in general dependent upon the dielectric constant of the solvent mixture. The reactions are found to be of positive ion-dipole type as the Amis equation is valid for these reactions.

INTRODUCTION

RADHAKRISHNAMURTHI and Visvanathan (1969) have made a preliminary report of the reaction of HBr with cyclanols in pure acetic acid to correlate conformation and reactivity. The present work is an extension of this to study the effect of dielectric constant of the media on these reactions, using cyclopentanol, cycloheptanol and cyclooctanol. A possible mechanism is also suggested for the reaction. Amis treatment has been utilised to confirm ion-dipole nature of the reactions.

EXPERIMENTAL PROCEDURE

The solvents used are either purified by the usual procedure and redistilled just before use or are of AnalaR quality from Fluka. The substrates are of guaranteed quality from Fluka. Hydrobromic acid is a freshly distilled azeotropic mixture (b.p.126°C). The kinetics has been followed by the usual Volhard's argentimetric procedure.

RESULTS AND DISCUSSION

It has been noticed that the reaction is a positive ion-dipole reaction as the reaction rate decreases generally with increase in dielectric constant of the medium. Good second order rate constants are obtained, first order with respect to HBr and first order with respect to the alcohol (Table I and II). The effect of binary solvent mixtures on the reaction is in the order :

AcOH-DMSO > AcOH-Toluene > AcOH-CH_3NO_2 > AcOH-benzene

Since the reactions are of positive ion-dipole type, the solvating power of a solvent can also give correct prediction, of a qualitative nature, about the rate of a

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TABLE I

Second order rate constants for cyclohexanol

(Temperature—80°C; mixed solvents)

Solvent mixture (% v/v)		Dielectric constant	k (l.mole^{-1} min^{-1}) × 10^2
Acetic acid	Toluene		
100	—	6.15	0.2944
90	10	5.77	1.800
80	20	5.39	4.030
75	25	5.21	7.030
	CH_3NO_2		
99	1	6.45	1.43
97.5	2.5	6.89	2.77
	Sulpholane		
99	1	—	0.3400
	DMSO		
99	1	6.58	16.57
	Benzene		
90	10	5.76	0.3663

TABLE II

Second order rate constant for cyclanols

(Temperature 80°C; mixed solvents)

Solvent mixture (% v/v)		Dielectric constant	k (l.mole^{-1} min^{-1}) × 10^2			
			1	2	3	4
Acetic acid	Toluene					
100	—	6.15	1.6	0.2944	3.202	8.86
90	10	5.77	5.193	1.80	5.334	15.12
80	20	5.39	8.09	4.03	8.88	18.97
75	25	5.21	12.60	7.03	13.51	21.57
	DMSO					
99	1	6.58	46.83	16.57	129.2	279.0

1-Cyclopentanol; 2-Cyclclohexanol; 3-Cycloheptanol; 4-Cyclooctanol

reaction in different solvents. An increase in the dielectric constant should result in a decrease in the rate, as is observed, except in the case of nitromethane AcOH mixture. The deviation in the case of binary mixture of nitromethane and acetic acid can be attributed to specific solvent influences, such as selective solvation by the higher dielectric constant component of the mixed solvent, in this case nitromethane.

According to Amis the specific rate constant is related to the dielectric constant for an ion-dipole reaction by the equation:

$$\ln k_D' = \ln k'_{\infty} + \frac{Ze\mu}{k\,Tr^2 D}$$

In the present investigations, the plots of $\log_{10}k$ vs. $1/D$ are all linear and the slopes obtained are positive indicating the reactions are of positive ion-dipole type.

MECHANISM

The reactions under investigation are S_N2 processes bordering on S_N1—in as much as the rate determining step is the formation of a conjugate acid, at the hydroxylic oxygen, which tends to produce an incipient and transient carbonium ion. The transition state can be depicted as follows taking the example of cyclohexanol;—

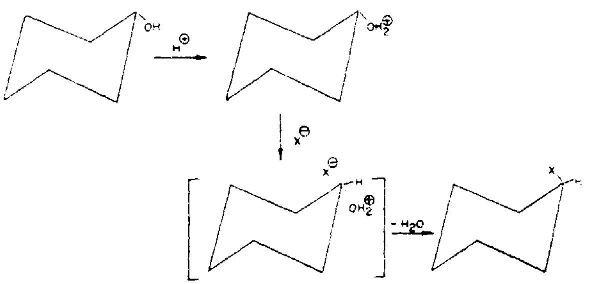

FIG. 1

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