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Kinetic Studies of Bimolecular Nucleophilic Substitution. V.*[1] Rates of S_N2 and E2 Reactions of 1, 2-Dichloroethane with Various Nucleophiles in Aqueous Solutions

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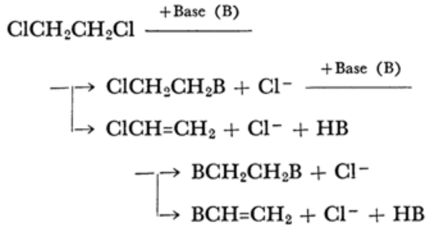
The rates of the reactions of 1, 2-dichloroethane with sodium hydroxide, sodium phenoxide, trimethylamine, pyridine, and sodium acetate have been measured in aqueous solutions at 110 and 120°C. On the assumption that the substitution reaction of 1, 2-dichloroethane produces two equivalents of the chloride ion because of the greater reactivity of the mono-substitution products (β-substituted ethyl chlorides) than that of the starting substrate, while the elimination product from 1, 2-dichloroethane, *i. e.*, vinyl chloride, does not react with the bases under the reaction conditions employed, the k_{S_N2} and k_{E2} have been calculated from the rate of the chloride-ion liberation and from the number of moles of the base required to react with one mole of the substrate. For a series of k_{S_N2} values there is no linear relation between the rates and the pK_a's of the conjugate acids, whereas a parallelism exists between the k_{E2} and the pK_a. The stronger the base, the more the elimination is promoted.

Although there have been several articles[1] dealing with the effects of the base strength on the partition between the bimolecular elimination and the bimolecular substitution in the reaction of alkyl halide with various bases, or nucleophiles, there appear to have been few investigations making possible a systematic scrutiny of this problem. We have, therefore, measured the rates of the S_N2 and E2 reactions of 1, 2-dichloroethane with various nucleophiles in order to obtain such data. The titled compound was chosen as a substrate, for it offers the advantage of simplicity in the estimation of the rates of the two possible paths, *i. e.*, the S_N2 and E2 reactions.

Results and Discussion

The reactions of 1, 2-dichloroethane with a series of nucleophiles, *i. e.*, NaOH, NaOPh, Me_3N, pyridine, and NaOAc, were conducted in aqueous solutions at 110 and 120°C. The reaction may follow either one or both of two possible paths, substitution (S_N2) or elimination (E2), and the substitution product (β-substituted ethyl chloride) may also then follow either one or both of two paths:



$$ClCH_2CH_2Cl \xrightarrow{+\text{Base (B)}} \begin{cases} ClCH_2CH_2B + Cl^- \xrightarrow{+\text{Base (B)}} \begin{cases} BCH_2CH_2B + Cl^- \\ BCH{=}CH_2 + Cl^- + HB \end{cases} \\ ClCH{=}CH_2 + Cl^- + HB \end{cases}$$

The substitution products with hydroxide ions and acetate ions, *i. e.*, ethylene chlorohydrin[2] and β-acetoxyethyl chloride[3] respectively, are much more reactive than is the starting 1, 2-dichloroethane toward the respective nucleophile, while the elimination product (vinyl chloride) is much less reactive. In fact, at 120°C in an aqueous solution β-acetoxyethyl chloride is about 10^3 times as reactive as 1, 2-dichloroethane toward sodium acetate.[3] The substitution product with phenoxide ions, *i. e.*, β-phenoxyethyl chloride, is as reactive toward sodium acetate as is 1, 2-dichloroethane.[4] Although we have no pertinent information about the reactivity of β-chloroethyltrimethylammonium chloride and of β-chloroethylpyridinium chloride, it is conceivable that these chlorides are more reactive than 1, 2-dichloroethane because of the large inductive effect of the β-substituents with a positive charge.[5]

The over-all reaction rate may be expressed as:

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*[1] Part IV: K. Okamoto, T. Kita, K. Araki and H. Shingu, This Bulletin, **40**, 1913 (1967).

[1] For a summary, see a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca (1953), pp. 451—453; b) D. V. Banthorpe, "Elimination Reactions," Elseveir, Amsterdam (1963), pp. 27—37.

[2] J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **78**, 5002 (1956).

[3] K. Okamoto and T. Kita, unpublished results.

[4] K. Okamoto, T. Kita, K. Araki and H. Shingu, This Bulletin, **40**, 1913 (1967).

[5] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley, New York (1956), Chap. 13.

$$\frac{d(ClCH_2CH_2Cl)}{dt} = k_{S_N2}(ClCH_2CH_2Cl)(B) + k_{E2}(ClCH_2CH_2Cl)(B)$$

or when α is expressed as $(k_{E2}+k_{S_N2})/(k_{E2}+2k_{S_N2})$:

$$\frac{d(Cl^-)}{dt} = \frac{dx}{dt} = (k_{E2}+2k_{S_N2})(a-\alpha x)(b-x) \tag{1}$$

where $a=(ClCH_2CH_2Cl)_0$, $b=(B)_0$, and $x=(Cl)=x_{E2}+2x_{S_N2}$. The integration of Eq. (1) gives:

$$k = (k_{E2} + 2k_{S_N2}) = \frac{2.303}{t(a-\alpha x)} \log \frac{b(a-\alpha x)}{a(b-x)} \tag{2}$$

The derivation of Eq. (2) is based on the principle which Hine and Langford[2)] presented for the reactions of β-haloethyl bromides with sodium hydroxide; however, we used $k_{E2}+2k_{S_N2}$ as the apparent second-order rate constant instead of $k_{E2}+k_{S_N2}$.[2)]

The value of α may be determined by permitting the reaction with an excess of nucleophiles to proceed to completion, because the vinyl chloride is not reactive toward the respective bases under the reaction conditions employed. In fact, infinity titers determined at seventy-five and ninety half-lives of the chloride-ion liberation were invariant within the range of experimental error in each reaction. From k and α, k_{E2} and k_{S_N2} may be calculated. Table 1 lists all of the rate constants and activation parameters obtained. The reaction with sodium hydroxide proceeded so largely through the E2 path that the value of k_{S_N2} could not be determined.

In Fig. 1 the values of $\log k_{S_N2}$ for a series of nucleophiles (or bases) are plotted against the pK_a

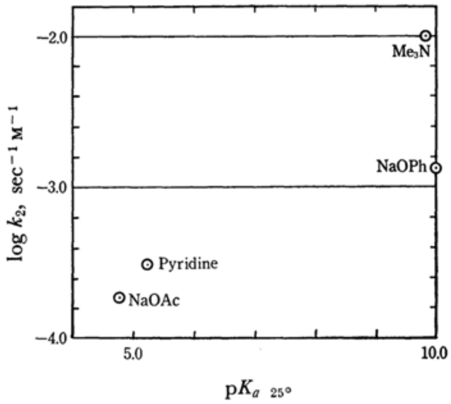

Fig. 1. Rate constants of S_N2 reactions of 1,2-dichloroethane with various bases in aqueous solution at 120°C.

TABLE 1. THE RATE CONSTANTS AND ACTIVATION PARAMETERS FOR S_N2 AND E2 REACTION OF 0.05 M 1,2-DICHLOROETHANE WITH 0.100 N NUCLEOPHILES IN AQUEOUS SOLUTION

Nucleophile		10^4k_2 (sec^{-1} M^{-1})[a)]		$\Delta H^{\ne}_{120°}$ kcal/mol	$\Delta S^{\ne}_{120°}$ e. u.	$pK_{a\ 25°}$[c)] for HB
	Temp.	100°C	120°C			
NaOH	S_N2	—	—	—	—	15.7
	E2	77.2	152	19.7	−16.9	
	E2%	100	100			
NaOPh	S_N2	5.19	13.0	26.7	−4.34	9.98
	E2	8.44	17.4	20.9	−20.8	
	E2%	61.8	57.3			
Me_3N	S_N2	64.3	101	12.8	−35.7	9.80
	E2	14.8	26.0	16.1	−29.9	
	E2%	18.7	20.4			
Pyridine	S_N2	1.64	3.11	18.4	−28.4	5.23 (20°C)
	E2	0.93	1.48	13.1	−43.2	
	E2%	36.1	32.3			
NaOAc	S_N2	—	1.87 1.96[b)]	— 20.0[b)]	— −26.5[b)]	4.76
	E2	—	0.43 0.46[b)]	— 19.7[b)]	— −25.8[b)]	
	E2%	—	18.7 19.0[b)]			

a) The rate constants obtained have not been devided by a statistical factor of two.
b) The figures, previously reported,[4)] are multiplied by two.
c) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co., London (1962).

values of the respective bases. The variations in $\log k_{S_N2}$ with the pK_a appear to be random; this is not an unexpected result since, as has previously been discussed,⁶⁾ the linear correlation between $\log k_{S_N2}$ and pK_a has been observed only in a narrow range of structural variation for various nucleophiles. The non-linearity may be explained in theory by a separation of a polar factor and a steric factor. In practice, however, this goal is unattainable at the present state of our knowledge of the S_N2 reactivity.

In sharp contrast to the case of k_{S_N2}, in the plot of $\log k_{E2}$ against pK_a a linear relation is observed, although it is not entirely satisfactory. This is illustrated in Fig. 2. This observation reconfirms the previous generalization¹ᵃ,²⁾ that the acidity of the β-hydrogen of alkyl halides is indeed an important factor with respect to the E2 reactivity. However, as has previously been observed in the E2 reaction of 1,2-dichloroethane with sodium acetate,⁴⁾ the steric retardation by a β-chloro-substituent is also important in the E2 reactions of this substrate; it seems to us that these steric factors bring about approximately the same amount of retardation for each nucleophile, resulting in a parallelism between $\log k_{E2}$ and pK_a for the respective nucleophiles.

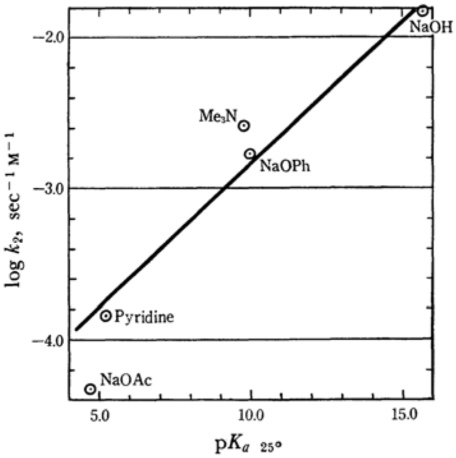

Fig. 2. Rates constants of E2 reactions of 1,2-dichloroethane with various bases in aqueous solution at 120°C.

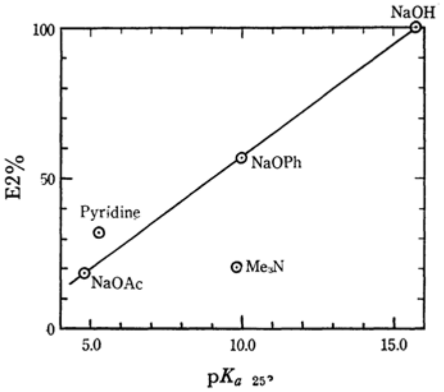

Fig. 3. E2% in the reactions of 1,2-dichloroethane with various bases in aqueous solution at 120°C.

With respect to the partition between elimination and substitution, it is shown in Fig. 3 that the stronger bases, such as the hydroxide ion, favor the E2 reaction path more, although this generalization is not necessarily applicable to all the bases examined, as is indicated in the case of trimethylamine. This partition is controlled by the balance of the carbon basicity and the hydrogen basicity of these nucleophiles; these two sorts of basicities are not always parallel to each other.⁷⁾ This may be the cause of the partial failure of parallelism between E2% and pK_a.

Experimental

Materials. Pyridine, bp 114.0—115°C, and 1,2-dichloroethane, bp 83.0°C, were purified by the fractional distillation of reagent-grade chemicals. A stock solution of trimethylamine was prepared by leading gaseous trimethylamine, prepared from trimethylammonium chloride and aqueous sodium hydroxide, into water; after appropriate dilution with water, it was used for kinetic runs. Sodium acetate of a reagent grade was dried *in vacuo* at 110°C to a constant weight. Sodium hydroxide of reagent-grade quality was used as received. Sodium phenoxide was prepared from phenol and sodium in ethanol, and dried *in vacuo* at 50°C to a constant weight.

Kinetic Measurements. A sealed-ampoule technique was employed; each ampoule contained 5 cc

TABLE 2. KINETICS OF THE REACTIN OF 1,2-DICHLOROETHANE WITH SODIUM PHENOXIDE IN AQUEOUS SOLUTION AT 120.0±0.05°C
$(NaOPh)=0.112$ N; $(ClCH_2CH_2Cl)=0.0488$ N
$\alpha=0.702$

Time min	cc 0.09053 N $AgNO_3$/5 cc	10^4k sec⁻¹ M⁻¹
0	0.000	—
20	1.225	45.3
40	1.977	47.3
60	2.337	43.3
90	2.808	44.4
120	3.065	42.7
180	3.356	40.1
3000	3.915	
3600	3.907	(43.4) Graphically obtained

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[6] K. Okamoto, H. Kushiro, I. Nitta and H. Shingu, This Bulletin, **40**, 1900 (1967).

[7] For a summary, see J. F. Bunnett, "Nucleophilicity," in Annual Reviews of Physical Chemistry, Annual Reviews Inc., Palo Alto, California, Vol. 14 (1963), pp. 271—290.

of aliquots. The thermostat was maintained at an appropriate temperature with ±0.05°C. The liberated chloride ion was titrated by the Mohr method. The rate data were treated graphically by a plot of $\log\{b(a-\alpha x)/a(b-x)\}$ against the time (see Eq. (2)). The values calculated for the k_{SN2} and the k_{E2} have been tabulated in Table 1. Data for a typical run, along with the integrated rate constants, are listed in Table 2; the values of α were determined from the mean value of the titers at seventy-five and ninety half-lives.