Dehalogenation Reactions of Vicinal Dihalides. Part IV.[1] Kinetics of Amine-promoted Eliminations of 1-Chloro-2-iodo-1,2-diphenylethane in Aqueous Dioxan

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The rate constants for the dehalogenation of 1-chloro-2-iodo-1,2-diphenylethane promoted by a series of amines have been determined in 60% dioxan. Pyridine reactivity follows a Brönsted relation with a slope β 0·29, which suggests little bond formation between the incoming nucleophile and iodine. Dehalogenation rates also correlate the stability constants of charge-transfer complexes between amines and iodine. The slope of this correlation is close to unity and this indicates that the charge distribution in the transition state of the dehalogenation reaction should be very similar to that of the charge-transfer complex.

THE dehalogenation of 1-chloro-2-iodo-1,2-diphenylethane(I) occurs by nucleophilic attack on the iodine atom and therefore represents a very useful tool to obtain data for nucleophilic reactivity towards iodine. In a previous paper [1] we reported kinetic data for the dehalogenation of (I) by different classes of nucleophiles and showed that they may follow a general correlation of nucleophilic reactivity such as the Edwards equation. Now we report kinetic data for the reaction of (I) with a number of amines in 60% dioxan solution. The aim of this work is that of acquiring, through the determination of the Brönsted β constant and the comparison of the reactivity data with the stability constants of charge-transfer complexes between amines and iodine, more detailed information on the nature of the interaction between iodine and the nucleophile in the transition state.

RESULTS AND DISCUSSION

Dehalogenation reactions of (I) [equation (1)] were studied in 60% dioxan at 25°. The progress of the reaction was followed spectrophotometrically by measuring the absorption of *trans*-stilbene at 320 nm. In all cases the final spectrum of solution closely resembled that of *trans*-stilbene. The yields were >90%.

$$erythro\text{-PhCHI-CHClPh} \xrightarrow[\text{H}_2\text{O-dioxan}]{\text{amine}} trans\text{-PhCH=CHPh} + \text{ICl} \quad (1)$$

The concentration of (I) was in the range 3·8—5·5 × 10^{-5}M, whereas that of the amines varied from 0·03 to 5M, depending on the reactivity, and was such as to minimize competition by the reaction of (I) with the solvent which gives *ca.* 70% of *trans*-stilbene. An excess of nucleophile was thus used in each case and the first-order plots exhibited excellent linearity up to 70—80% of reaction; an exception was the reaction with hydrazine where a marked downward drift was observed after 40—50% of reaction. Experiments in the presence of hydroquinone, *p*-cresol, and ICl gave the same result. Therefore, the rate constant for hydrazine was calculated from the first portion of the plot.

Second-order rate constants (k_2), obtained by dividing the first-order rate constant by the concentration of nucleophile, are reported in the Table and cover a reactivity range of *ca.* 400 for a pK_a interval of *ca.* 6. The concentration of nucleophile did not influence the k_2 values with the exception of pyridine and 4-methylpyridine, for which a decrease of k_2 on increasing the concentration of amine was found. A similar phenomenon was observed in reactions of pyridines with *p*-nitrophenyl phosphate dianon [2] and *p*-nitrophenyl methylphosphonate ion [3] and attributed to self association by the pyridines, which leads to an unreactive dimer. Since it was found that by plotting k_2 against initial base concentration a straight line was obtained for

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[1] Part III, E. Baciocchi and C. Lillocci, *J.C.S. Perkin II*, 1973, 38.

[2] A. J. Kirby and W. P. Jencks, *J. Amer. Chem. Soc.*, 1965, **87**, 3209.

[3] H. J. Brass, J. O. Edwards, and M. J. Biallas, *J. Amer. Chem. Soc.*, 1970, **92**, 4675.

both pyridine and 4-methylpyridine, the rate constants for these two bases were calculated by extrapolating to zero base concentration.

Kinetic data for the dehalogenation of 1-chloro-2-iodo-1,2-diphenylethane induced by amines in 60% dioxan at 25°

Amine	k_2 / l mol^{-1} s^{-1}	pK_a [a]
Piperidine	0·220	10·35
Dimethylamine	0·104	10·28
n-Butylamine	0·0297	10·00
Ethylamine	0·0233	10·25
Morpholine	0·0225	8·08
Methylamine	0·0218	10·24
Hydrazine	0·00276 [b]	7·85
Ammonia	0·00095	8·96
4-Aminopyridine	0·0148 [c]	8·27
4-Methylpyridine	0·00122 [c]	4·55
Pyridine	0·000742 [c]	3·90

[a] Determined in 60% dioxan (see Experimental section). [b] Corrected for the statistical factor. [c] Value extrapolated at zero concentration of amine (see text).

In Figure 1, log k_2 is plotted against the pK_a of amines measured in the same solvent. The reactivities of primary, secondary, and aromatic amines fall into distinct groups and three lines are obtained. Using data for the group of pyridines, which give the best correlation, a Brönsted β constant of 0·29 is obtained. Ammonia does not fit any of these lines, whereas hydrazine does not seem to display any α effect. The observed separation of reactivity is similar to that noticed in other nucleophilic reactions of amines [2,4] and is probably the consequence of the fact that different classes of amines represent separated sets of substrates with respect to acid–base properties rather than of a different response of the reactivity of (I) to different classes of amines. It is well known that the pK_a values of amines are sensitive to the structure due to the varying ability of ammonium ions to form hydrogen bonds with the aqueous solvent, through the N$^+$–H bonds.[5] This factor, which tends to increase the pK_a of ammonia and primary amines, should be less important when nucleophilicity is considered. Accordingly, the separation between primary and secondary amines disappears when log k_2 is plotted against $\Sigma\sigma^*$.[6] A fairly good linear relationship is obtained (Figure 2; r 0·978, s 0·137). The value of ρ^*, $-1{\cdot}41$, is indicative of considerable influence by the polar effects of the alkyl groups in the transition state. Steric effects, in contrast, appear relatively less important since secondary amines are more reactive than primary amines and n-butylamine is the most reactive among the primary amines.

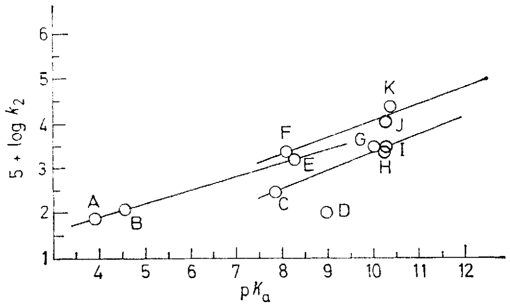

FIGURE 1 Plot of rates of dehalogenation against pK_a: A, pyridine; B, 4-methylpyridine; C, NH_2NH_2; D, NH_3; E, 4-aminopyridine; F, morpholine; G, $BuNH_2$; H, $MeNH_2$; I, $EtNH_2$; J, Me_2NH; K, piperidine

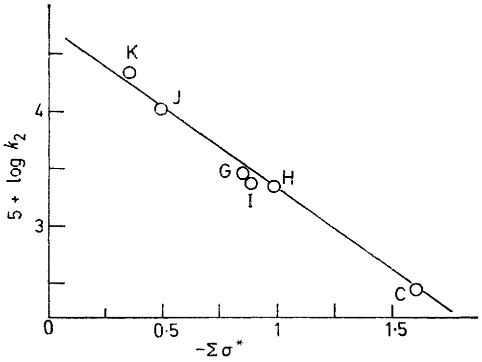

FIGURE 2 Plot of rates of dehalogenation against $\Sigma\sigma^*$ (for key see Figure 1)

The value of the Brönsted slope is rather small and would suggest a transition state involving little bond formation between the incoming nucleophile and iodine. Further information in this respect may be obtained by comparing dehalogenation rates with the stability constants of charge-transfer complexes (K_{CT}) between amines and iodine.[7] Such a comparison is shown in Figure 3, where log k_2 for the dehalogenation reaction is plotted against log K_{CT} in n-heptane. The plot is reasonably linear (r 0·972, s 0·212) for ammonia and primary and secondary amines. The slope is 1·037. An analogous plot, with a very similar slope, may also be obtained for the aromatic amines whose K_{CT} values have

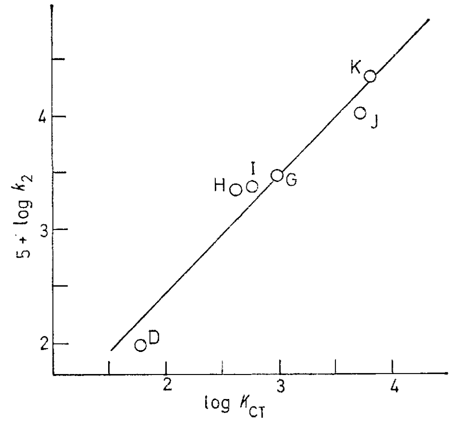

FIGURE 3 Plot of rates of dehalogenation against the stability constants of the charge-transfer complexes between amines and iodine (for key see Figure 1)

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[4] S. J. Benkovic and P. A. Benkovic, *J. Amer. Chem. Soc.*, 1966, **88**, 5504.

[5] F. E. Condon, *J. Amer. Chem. Soc.*, 1965, **87**, 4481, 4485, 4491.

[6] H. K. Hall, jun., *J. Amer. Chem. Soc.*, 1957, **79**, 5441.

[7] H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, 1960, **33**, 1660.

been determined in the different solvent, dichloromethane.[8] The slope of close to unity shows clearly that in the transition state the charge distribution of the dehalogenation reaction should be very similar to that of the charge-transfer complex. It may be also observed that, since K_{CT} refers to a non-polar solvent, the linear correlation of Figure 3 indicates that in the dehalogenation in aqueous dioxan the energetic factors associated with the solvation of the amines and of the transition states are not very important or, more likely, are nearly independent of the structure of the base.

EXPERIMENTAL

Materials.—1-Chloro-2-iodo-1,2-diphenylethane was prepared as previously described.[1] 1,4-Dioxan was purified according to ref. 9. Piperidine, n-butylamine, morpholine, 4-methylpyridine, and pyridine were commercial products (Erba, RP) purified by refluxing over KOH and distillation. 4-Aminopyridine (Fluka, purum) was recrystallized from dry benzene and dried, m.p. 158—160°. Dimethylamine (Erba, RP), Ethylamine (Erba, RP), methylamine (Erba, RP), ammonia (SIO), and hydrazine hydrate (BDH, 99%) were used without further purification. The solutions of hydrazine were shown, by iodometric titration, to be stable for at least 12 h.

Kinetic Experiments.—The mixed solvent for the kinetic work was prepared by adding purified dioxan (600 ml) to redistilled water (400 ml). The appearance of *trans*-stilbene was followed spectrophotometrically at 320 nm. The solutions of the reactants were directly mixed in the absorption cell at 25°, which was then placed in the thermostatted compartment of a Beckmann DU spectrophotometer.

Measurements of pK_a Values in 60% Dioxan.—The pK_a values of amines were determined by the half-neutralization method with a glass electrode.

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[9] L. S. Fieser and M. Fieser, ' Reagents for Organic Synthesis,' Wiley, New York, 1967, p. 333, method a.