[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. IV. Effect of Solvent Composition on the Kinetics of Dehydrochlorination of Benzene Hexachloride Isomers in Aqueous Ethanol[1,2]

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A study has been made of the effects of temperature and solvent composition on the rate of alkaline dehydrochlorination of α-, β- and ε-benzene hexachloride in aqueous ethanol. The effects of solvent composition on the energies of activation were found not to be in accord with those predicted from a simple electrostatic theory.

Previous work[3,4,5] has shown the general preference for elimination (second-order) of the elements of hydrogen halides from systems in which these elements are *trans* over those in which they are *cis* to each other. It has been suggested that this preference is due to a steric requirement in the *trans* concerted process, involving the simultaneous removal of hydrogen by base, formation of the carbon–carbon double bond and loss of halide ion, this situation being energetically more favorable than the *cis* process presumably involving only removal of the proton, yielding a carbanion in the rate-determining step.

As the *trans* process involves a transition state with the negative charge spread over five atoms, *viz.*

$$[\text{HO---H---C}{=\!=\!=}\text{C---X}] \qquad (1)$$

and the carbanion process one in which the charge is spread over only three atoms, *viz.*

$$[\text{HO----H----C}-] \qquad (2)$$

we attempted to characterize the two mechanisms by studying the variation of rates with solvating power of solvent, *i.e.*, by variation in solvent composition. Although we failed in this attempt, which was based upon a current concept of solvent effects,[6,7] our results, as well as the results and discussions of others, suggest the necessity of revising this concept.

For this work, we used three isomers of benzene hexachloride (BHC): alpha (1, *cis*-2, *trans*-3, *trans*-4, *cis*-5, *trans*-6-hexachlorocyclohexane), beta (1, *trans*-2, *cis*-3, *trans*-4, *cis*-5, *trans*-6-hexachlorocyclohexane), and epsilon (1, *cis*-2, *cis*-3, *trans*-4, *trans*-5, *trans*-6-hexachlorocyclohexane).[8,9] With these three isomers and aqueous ethanolic alkali, the reactions are all first order in halide and first order in hydroxide ion and the loss of the first molecule of hydrogen chloride is rate-determining, as found previously[4,10] and in this work. The β-isomer requires *cis* elimination and the others permit *trans* elimination.

The materials and procedures used to obtain and calculate the kinetic data were substantially as described previously.[4] The reaction-rate data are collected in Tables I, III and V and are summarized in Tables II, IV and VI. Error analyses indicate that the rate constants are accurate to within 2–3%, and the activation energies to within 0.5–1.0 kcal./mole.

According to electrostatic theory, an ion-neutral molecule reaction would be expected to exhibit both a lowered rate and a higher activation energy in changing from less to more aqueous solvents—that is, in better solvating solvents—because of the greater dispersal of charge in the transition state compared with that in the reactants.[6,7] This argument has been used by Hughes and Ingold and their co-workers to explain the relative rates of elimination and substitution in the reactions of alkyl halides with alkali, normally giving more olefin in the less aqueous solvents. An extension of their arguments would suggest, assuming transition states (1) and (2), that the effect of solvent composition upon activation energy and rate would be greater for *trans* elimination than for *cis* elimination; in each case it would be predicted that the rate would increase with increasing amount of ethanol and the activation energy decrease with increasing ethanol. (The rate behavior prediction was based upon the assumption that the entropy of activation would be affected only slightly or not at all by variation in solvent composition and that the major change would reflect the effect on activation energy.)

Hughes and Ingold's own results on the second-order substitution reactions of isopropyl bromide,[7] as well as Fairclough and Hinshelwood's data on the alkaline hydrolysis of ethyl benzoate[11] and Rylander and Tarbell's work with other esters and thiolesters[12]—all reactions of the ion-neutral molecule type—show that the general trend of the change of activation energy with solvent composition may be opposite to that predicted from the simple theory, although in some cases the relative rates were in the direction predicted.

The non-validity of the use of relative rate constants in comparing structural or solvent effects is particularly demonstrated by our data. It is often assumed that in comparable reactions there is a parallelism between reaction-rate constant and activation energy—that is, that higher rate constants are associated with lower activation energies. Fig-

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[1] Previous paper in series: S. J. Cristol, N. L. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951).

[2] The work was supported by the Office of Naval Research.

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[7] (a) K. A. Cooper, M. L. Dhar, E. D. Hughes, C. K. Ingold, B. J. MacNulty and L. I. Woolf, *J. Chem. Soc.*, 2043 (1948); (b) K. A. Cooper, E. D. Hughes, C. K. Ingold, G. A. Maw and B. J. MacNulty, *ibid.*, 2049 (1948).

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TABLE I

DATA AND REACTION-RATE CONSTANTS FOR DEHYDROCHLORINATION OF β-BENZENE HEXACHLORIDE WITH SODIUM HYDROXIDE IN AQUEOUS ETHANOL

Ethanol, wt. %	Temp., °C.	[Halide] M	[NaOH] M	10^5k l./sec./mole	Av.	Av. dev. %
76.1	29.69				2.00	1.7[a]
	30.59	0.00100	0.0457	2.30	2.30	...
	40.12				10.9	0.9[a]
	48.81				42.5	0.9[a]
	50.00	.00100	.0226	47.1	47.1	...
81.5	30.59	.00200	.0457	2.37	2.38	0.4
		.00200	.0366	2.39		
	43.10	.00200	.0495	18.6	18.4	1.2
		.00200	.0396	18.1		
	50.00	.00200	.0362	50.0	49.8	0.4
		.00197	.0445	49.6		
89.0	30.59	.00333	.0464	2.38	2.40	0.8
		.00333	.0342	2.42		
	43.10	.00200	.0186	19.2	19.0	2.0
		.00200	.0371	18.8		
	50.00	.00300	.0697	56.2	56.0	0.3
		.00300	.0558	55.9		
91.2	30.58	.00234	.0286	2.52	2.55	1.2
		.00333	.0175	2.58		
	43.10	.00333	.0437	20.6	20.5	0.5
		.00333	.0291	20.4		
	50.00	.00300	.0583	54.4	55.7	2.3
		.00312	.0874	57.0		
92.6	30.58	.00333	.0291	2.26	2.23	0.8
		.00334	.0583	2.21		
		.00200	.0466	2.23		
	37.64	.00200	.0432	7.38	7.12	3.6
		.00200	.0516	6.87		
	43.10	.00200	.0495	17.6	18.3	4.2
		.00200	.0297	17.8		
		.00333	.0437	19.5		
	50.00	.00300	.0583	62.2	61.6	0.9
		.00300	.0583	61.1		
	52.90	.00199	.0346	96.5	94.4	2.1
		.00200	.0432	92.4		
94.1	30.58	.00334	.0291	2.12	2.19	3.2
		.00334	.0175	2.26		
	43.10	.00333	.0437	20.2	20.4	0.8
		.00330	.0289	20.5		
	50.00	.00300	.0583	54.4	54.0	2.0
		.00300	.0874	52.3		
		.00333	.0583	55.1		
97.6	30.59	.00300	.0495	1.96	1.97	1.0
		.00300	.0743	1.95		
		.00300	.0248	2.00		
	43.10	.00200	.0495	14.8	15.5	2.8
		.00200	.0396	15.6		
		.00200	.0297	16.0		
	50.00	.00300	.0485	46.7	46.7	0.1
		.00400	.0720	46.8		
		.00400	.0396	46.6		

[a] Data from ref. 4.

ure 1 illustrates the general fact that if two reactions have activation energies and entropies differing in the same sense, their rate–temperature curves cross; it is obvious that in such a case, the mentioned relationship of rate constants to activation energies is valid only at temperatures below that at which the two rate–temperature curves

TABLE II

QUANTITIES OF ACTIVATION FOR THE ALKALINE DEHYDROCHLORINATION OF β-BENZENE HEXACHLORIDE

Ethanol %	$E_{\text{act.}}$ kcal./mole	log PZ	$\Delta S^{\ddagger}$, e. u.	10^5k at 30° l./sec./mole	10^5k at 50° l./sec./mole
76.1	30.9	17.57	20.0	2.1	47.1
81.5	30.6	17.36	18.9	2.2	49.8
89.0	31.4	17.98	21.7	2.2	56.0
91.2	31.1	17.76	20.8	2.4	55.7
92.6	33.1	19.12	27.0	2.0	61.6
94.1	32.1	18.42	23.8	2.1	54.0
97.6	31.7	18.07	22.1	1.8	46.7

TABLE III

DATA AND REACTION-RATE CONSTANTS FOR DEHYDROCHLORINATION OF α-BENZENE HEXACHLORIDE WITH SODIUM HYDROXIDE IN AQUEOUS ETHANOL

Ethanol, wt. %	Temp., °C.	[Halide] M	[NaOH] M	k l./sec./mole	Av.	Av. deviation, %
92.6	−0.34	0.00100	0.00866	0.0242	0.0243	0.4
		.00100	.00433	.0244		
	10.30	.00100	.00437	.0905	.0880	2.2
		.00100	.00437	.0901		
		.00070	.00437	.0866		
		.00070	.00874	.0850		
	16.20	.00100	.00433	.175	.177	1.1
		.00100	.00649	.179		
97.6	7.14	.00300	.00990	.0782	.0770	1.6
		.00250	.00990	.0758		
	14.42	.00100	.00396	.169	.167	1.2
		.00150	.00495	.165		
	22.50	.00100	.00396	.497	.495	0.7
		.00070	.00396	.492		

TABLE IV

QUANTITIES OF ACTIVATION FOR THE ALKALINE DEHYDROCHLORINATION OF α-BENZENE HEXACHLORIDE

Ethanol, wt. %	$E_{\text{act.}}$ kcal./mole	log PZ	$\Delta S^{\ddagger}$, e.u.	k at 10°
76.1[a]	18.5	13.03	−0.85	0.059
92.6	18.6	13.23	0.12	.080
97.6	20.0	14.47	5.79	.105

[a] Data of reference 4.

TABLE V

DATA AND REACTION-RATE CONSTANTS FOR DEHYDROCHLORINATION OF ϵ-BENZENE HEXACHLORIDE WITH SODIUM HYDROXIDE IN AQUEOUS ETHANOL

Ethanol, wt. %	Temp., °C.	[Halide] M	[NaOH] M	k, l./sec./mole	Av.	Av. deviation, %
92.6	10.41	0.00147	0.01830	0.0146	0.0147	1.0
		.00100	.00457	.0149		
	22.49	.00070	.00457	.0805	.0807	0.2
		.00200	.01830	.0809		
	30.59	.00111	.00457	.206	.203	1.5
		.00070	.00457	.200		

TABLE VI

QUANTITIES OF ACTIVATION FOR THE ALKALINE DEHYDROCHLORINATION OF ϵ-BENZENE HEXACHLORIDE

Ethanol, wt. %	$E_{\text{act.}}$, kcal./mole	log PZ	$\Delta S^{\ddagger}$, e.u.	k at 30°
76.1[a]	21.4	14.63	6.5	0.182
92.6	22.3	15.36	9.7	.195

[a] Data from reference 4.

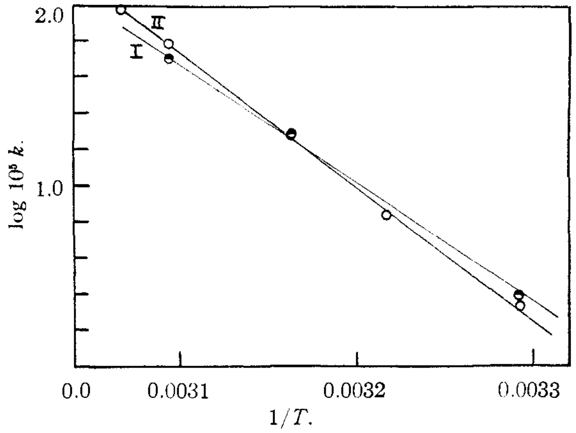

Fig. 1.—Plots for calculation of activation energies for the alkaline dehydrochlorination of β-benzene hexachloride in 81.5 (I) and 92.6 (II) weight % ethanol.

cross. This has been pointed out previously,[13,14] but seems to be frequently overlooked.

Our data (Tables II, IV and VI) indicate that, in the limited systems studied, increasing ethanol does increase the rate constants at 10° for α-BHC and at 30° for ϵ-BHC, but that this rate increase is caused by favorable entropy effects at these temperatures, whereas the energy of activation is apparently increased by increasing ethanol. The β-isomer actually gives a maximum in rate constant, which again is an entropy effect and is opposed by the effect of activation energy, which also shows a maximum. The direct or inverse relationships between rate constants and Arrhenius activation energies, are, as mentioned above, functions of the temperatures at which the data were obtained and thus have no simple theoretical significance.

We are unable to account for the appearance of the maxima for the β-isomer and the lack of such maxima with the α-isomer. Similar maxima have been observed previously in water–organic solvent mixtures.[15–19]

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The Use of the Gradient Tube for the Determination of Crystal Densities[1a]

BY BARBARA W. LOW AND F. M. RICHARDS[1b]

A study has been made of the applicability of the Gradient Column Technique to the determination of the densities of crystalline solids. The usable density range has been extended to provide coverage for a wide variety of crystalline preparations. The use of the column has led to a modification which appears better suited to the determination of solid densities. Gradient columns may be set up in 10-cc. centrifuge tubes and spun in a centrifuge without seriously affecting the gradient. This modified procedure greatly increases the speed of the density measurement. The modified gradient column is the basis of a new method for the detection and separation of impurities in crystalline preparations. The method has also been used to demonstrate the formation of mixed crystals between components of known and different densities. The use of the Gradient Column for the determination of "wet" and "dry" protein crystal densities has been investigated. Density measurements have been made on the two protein crystal preparations—β-lactoglobulin and insulin—both of which have been previously studied by other methods.

Introduction

The gradient tube was originally devised by Linderstrøm-Lang[2,3] for the determination of the specific gravity of aqueous solutions in the dilatometric micro-estimation of enzyme activity. It was later extended[4] to the determination of the densities of D_2O–H_2O mixtures in the range of density 0.99–1.01. The apparatus is capable of a sensitivity of 0.000001 g./ml. A description of the apparatus, its calibration and some modification in the procedure is given by Anfinsen.[5] The use of a simplified gradient tube prepared in a vertical measuring cylinder without thermostating was described by Jacobsen and Linderstrøm-Lang[6] for rapid though less accurate (0.1%) laboratory measurements.

Boyer, Spencer and Wiley[7] have applied the gradient tube to the study of high polymers in the three fields—crystallization rate/data, inhomogeneities in the composition of copolymers, and rates of polymerization. The density gradient column has also been used to determine the densities of natural and synthetic fibers in the study of their textural inhomogeneities.[8]

The possibility of employing the gradient tube for the determination of crystal density was suggested to us by Professor Stig Claesson.[9] We have

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