Heat Capacity of Activation for the Hydrolysis of 2,2-Dihalopropanes[1]

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Received December 11, 1965

Abstract: Values of the heat capacity of activation for the hydrolysis of 2,2-dibromo-, 2,2-dichloro-, and 2-bromo-2-chloropropane in water have been determined. These values lie in the more negative range of ΔCp^* which have been shown to characterize other SN1 mechanisms. These observations are related to mechanism and products.

Recent investigations[3,4] indicate that the value of ΔC_p^* for the hydrolysis of several tertiary halides is some 20–30 cal/mole deg more negative than the corresponding term for the hydrolysis of secondary halides. This difference was associated with a change from SN2 to SN1 mechanism and is attributed either to a difference in the extent of breakdown of the initial state solvation shell or to a lack of solvent reorganization associated with nucleophilic interaction. We believe that the first is the major determinant.[5] *gem*-Dihalides, in common with other tertiary halides, are known to be resistant to bimolecular nucleophilic displacement.[6] At the same time the presence of the second halogen is known to facilitate the ionization of the adjacent carbon–halogen bond.[7] A comparison of the relative steric hindrance offered by Br compared to the methyl group toward nucleophilic attack[8] and the dual electronic character of the halogen atoms as substituents[9] support the assumption that the mechanism of hydrolysis of the 2,2-dihalopropanes in water will occur by an SN1 mechanism.

In contrast to results found by Bensley and Kohnstam[7] for the hydrolysis of benzal chloride where the departure of one chloride ion is quickly followed by the elimination of the second and the formation of benzaldehyde, in the case of the 2,2-dihalopropanes for temperatures below 70°, very close to 1 equiv only of halogen is released (Ag titration), the other product being the corresponding 2-halopropene. Vapor phase chromatography shows only a trace of other products. 2-Chloropropene is known to be very stable at the temperatures studied here.[10] Prolonged heating at 140° was required to hydrolyze 2-bromopropene to the acid and acetone (identified as the DNPH derivative). In the case of the 2-bromo-2-chloropropane, 2-chloropropene is the only product in significant amounts.

The question of whether the rate-determining step involved the ionization of one of the halogens or was actually an E2 attack by solvent on a hydrogen would seem settled in favor of the former by a series of parallel experiments with the corresponding deuterated *gem*-dihalides. The values of $\delta_I\Delta F^*$ and $\delta_I\Delta H^*$ found at one temperature are given in Table I and are seen to be about the same as was found in the hydrolysis of tertiary compounds where there is little question that the mechanism is SN1.

Table I. A Comparison of Secondary Deuterium Isotope Effects Associated with the Hydrolysis of Halides from a Tertiary Carbon in Water

Compound	Temp, °C	$\delta_I\Delta F^*/n$, cal/mole	$\delta\Delta H^*/n$, cal/mole	n[a]	Ref
t-Butyl Chloride	20	57	63	9	3
$MeO(CH)_2(CH_3)_2CCl$	25	56	57	6	4
t-BuDiMeS	75	57	56	9	4
2,2-Dichloropropane	40	63	62	6	*b*
2-Br-2-Cl-propane	25	57	43	6	*b*
2,2-Dibromopropane	30	62.5	58	6	*b*

[a] n = number of β-D, approximately. Deuterium analysis varied between 95 and 99% theoretical. [b] A. Queen and R. E. Robertson, unpublished work.

The fact that $\delta_I\Delta F^*$ and $\delta_I\Delta H^*$ are approximately equal throughout this series is further evidence of a common mechanism.[11]

Alternatively, the possibility that hydrogen bromide is formed by the E1-cb mechanism with the formation of a carbanion is unlikely. Only the E1 mechanism is consistent with all the data, and the transition state in that case is identical with that for the SN1 mechanism.

The solvent isotope ratio (k_{D_2O}/k_{H_2O}) was 0.75 at 35° for the dihalides. While this parameter (or the equivalent $\Delta\Delta F^*$) is not sensitive to the mechanism in the hydrolysis of alkyl halides, Robertson and Sugamori[12] have recently shown a grouping of $\Delta\Delta H^*$ values indicating mechanistic differences and an approximate correlation between ΔC_p^* and $\Delta\Delta H^*$. In this correlation, the dihalides fall in with those halides which other evidence suggest react by an SN1 mechanism.

Kinetic rate data for the hydrolysis in water of 2,2-dibromo-, 2,2-dichloro-, and 2-bromo-2-chloropropane for a series of temperatures are given in Tables II, III, and IV. The temperature dependence of the rate of hydrolysis in each case can be fitted within ex-

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[1] Issued as NRC No. 8943.

[2] National Research Council of Canada Postdoctorate Fellow, 1961–1963.

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Table II. Rate Data for the Hydrolysis of 2,2-Dichloropropane

Temp, °C	$k_1 \times 10^5$, sec^{-1}	n^a	Temp, °C	$k_1 \times 10^5$, sec^{-1}	n^a
55.203	55.80 ± 0.07	3	42.328	11.11 ± 0.02	4
52.897	42.41 ± 0.03	3	40.324	8.449 ± 0.014	4
50.267	30.65 ± 0.05	4	37.571	5.823 ± 0.003	3
49.817	29.32 ± 0.05	3	35.012	4.048 ± 0.008	5
47.925	22.95 ± 0.04	4	29.820	1.895 ± 0.002	3
47.606	21.83 ± 0.03	4	27.090	1.257 ± 0.003	3
45.113	15.97 ± 0.04	4			

[a] n = number of replicate runs.

Table III. Rate Data for the Hydrolysis of 2,2-Dibromopropane

Temp, °C	$k_1 \times 10^5$, sec^{-1}	n^a	Temp, °C	$k_1 \times 10^5$, sec^{-1}	n^a
45.007	79.09 ± 0.09	4	30.055	9.93 ± 0.01	4
42.477	56.71 ± 0.12	5	27.460	6.747 ± 0.007	3
40.008	40.72 ± 0.15	6	25.42	4.921 ± 0.002	4
37.788	30.22 ± 0.01	4	22.48	3.124 ± 0.005	4
35.025	20.43 ± 0.04	4	20.095	2.099 ± 0.002	4
32.498	14.26 ± 0.02	4			

[a] n = number of replicate runs.

Table IV. Rate Data for the Hydrolysis of 2-Bromo-2-chloropropane

Temp, °C	$k_1 \times 10^5$, sec^{-1}	n^a	Temp, °C	$k_1 \times 10^5$, sec^{-1}	n^a
34.960	74.09 ± 0.10	4	20.192	8.52 ± 0.02	3
32.824	55.16 ± 0.02	6	18.115	6.11 ± 0.01	4
30.023	37.18 ± 0.06	4	17.480	5.508 ± 0.01	4
27.516	25.90 ± 0.04	3	15.193	3.782 ± 0.011	4
25.171	18.32 ± 0.02	4	15.087	3.723 ± 0.01	3
22.709	12.59 ± 0.03	4	12.646	2.471 ± 0.004	4
			9.844	1.519 ± 0.004	4

[a] n = number of replicate runs.

Table V. Empirical Constants for Rate Eq 1

Halide	A	B	C	n^a	Δ^b
2,2-Dibromopropane	−11,147.6	−39.626	131.105	46	0.0017
2,2-Dichloropropane	−10,789.6	−36.761	122.109	51	0.0017
2-Bromo-2-chloropropane	−11,793.4	−46.288	150.342	53	0.0011

[a] n = number of individual rates in least mean squares calculation. [b] $\Delta = \sqrt{\Sigma(\log k_{\mathrm{calcd}} - \log k_{\mathrm{obsd}})^2/(n - 1)}$. Δ was calculated by computer using 18-digit accuracy. The 12-digit output was arbitrarily rounded to be consistent with experimental error.

perimental error to the three-constant equation

$$\log k = A/T + B \log T + C \qquad (1)$$

the corresponding constants determined by least mean squares on n individual rates being given in Table V. By making the usual assumptions that $\mathrm{d}\Delta C_{\mathrm{p}}^*/\mathrm{d}T$ is small and applying the transition state hypotheses, corresponding values of ΔH^*, ΔS^*, and ΔC_{p}^* are calculated[13] (Table VI).

Discussion

The effect of α halogen bonded to a reacting carbon is known to be complex, combining a negative inductive effect and an electron-releasing resonance effect.[14,15] In the present case, the effect of α-Br as a substituent is to increase the rate 14-fold and for α-Cl about 48-fold for either Br^- or Cl^- as a leaving group. Qualitatively, these effects are consistent with similar data summarized by Streitwieser[15] for other systems.

For reasons cited in the introduction we assume that the mechanism of hydrolysis here is SN1 in common with that for other tertiary halides. This assumption implies that favorable internal structure plus the usual kinetic activation will lead first to the degree of charge separation where

anion–water interaction = water–water interaction

which has been postulated as the equilibrium condition characterizing the transition state for the SN2 mechanism. This is not the critical solvent reorganization required for the SN1 mechanism. Further charge development with some degree of exothermic solvation of the developing anion (electrophilic catalysis[16]) will be required to enhance the charge on the cation to the level where the "solvent shell collapses." [17] Logically, this would seem likely to occur when charge development increases beyond the level where

cation–water interaction = water–water interaction

This assumption emphasizes the essential disruption of solvent about the transition quasi-cation without providing an indication of the number of extent of this disruption, or a quantitative estimate of the charge development required. While this hypothesis is seen to reinforce the qualitative difference in solvation which has been recognized between the SN1 and SN2 mechanisms, it is quite inconsistent with the widely held view that the quasi-cation is stabilized in the transition state by strong cation–solvent interaction. According to the latter hypothesis, Evans[18] and Franklin[19] have estimated the resulting heat of solvation as reducing the activation energy by 40–60 kcal. Our hypothesis implies a negligible contribution to E_{a} from this source. Both cannot be correct, and that one or the other cannot be summarily rejected on the basis of known evidence is significant.

Support for the hypothesis requiring negligible exothermic solvation of the developing cation can be found in the positive entropy of activation which characterizes the hydrolysis of tertiary halides and in the evidence from kinetic solvent isotope effects,[20,21] the apparent temperature independence of ΔC_{p}^*, and

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(13) $A = -\Delta H_0^*/2.3026R$; $\Delta H_{\mathrm{T}}^* = \Delta H_0^* + \Delta C_{\mathrm{p}}^* T$; $B = \Delta C_{\mathrm{p}}^*/R + 1$; $C = (\Delta S_0^* - \Delta C_{\mathrm{p}}^*)/2.3026R + \log k/h$; $\Delta S_{\mathrm{T}}^* = \Delta S_0^* + \Delta C_{\mathrm{p}}^* \log T \times 2.3026$.

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Table VI. Summary of Derived Parameters for the Hydrolysis of Dihalides

Halide	$k \times 10^5$, sec^{-1} (25°)	ΔH^*_{25}, cal/mole	ΔS^*_{25}, cal/mole deg	$\Delta C_p{}^*$, cal/mole deg	Ref
2,2-Dibromopropane	4.618	26,940	12.0	−81	*a*
2,2-Dichloropropane	0.9088	27,000	8.9	−75	*a*
		25,120 (50°)	2.9 (50°)		*a*
2-Bromo-2-chloropropane	17.81	25,950	11.3	−94	*a*
t-Butyl chloride	2975	22,550	10.1	−83	3
2-Bromopropane	0.3816	25,830 (25°)	4	−59	*b*
2-Chloropropane	0.02114	24,940 (50°)	−5.3	−38	*b*

[a] This work. [b] R. L. Heppolette and R. E. Robertson, *Can. J. Chem.*, **44**, 677 (1966).

the changes in $\Delta C_p{}^*$ on the addition of ethanol to water compared to the similar effect where the equilibria of weak acids is concerned.[22] We know that the ΔH^* decreases at about 80–100 cal/deg. This may be achieved with increasing temperature through (1) a destabilization of the initial state solvation shell or (2) through an increase in the solvation energy of the cation formed at the transition state, as a consequence of a decrease in water–water interaction. Our working hypothesis (1) excludes 2, but does not exclude some contribution to $\Delta C_p{}^*$ from the solvation of the anion. We do not believe the latter contribution to be large.

Experimental Detail

2,2-Dibromopropane was synthesized by a modification of the method of Kharasch, Zimmt, and Nudenberg,[23] bp 116–118°, $n^{24.5}\text{D}$ 1.4959. *Anal.* Calcd: C, 17.82; H, 2.97; Br, 79.21. Found: C, 17.98; H, 2.97; Br, 79.12. A sample hydrolyzed in water for 25 min at 60° gave 49.47% of the theoretical amount of bromide, *i.e.*, one bromide is removed. Solvolysis of a larger sample and separation of the product by extraction with CCl_4 showed that 2-bromopropene (vpc and nmr) was the only product in other than trace amounts. When allowed to react with water at 130° under pressure for 36 hr the latter gave acetone as characterized by the DNPH derivative.

2,2-Dichloropropane was synthesized by dropping acetone on PCl_5 by the method of Leitch and Morse[24] and pumping off the *gem*-dihalide at room temperature through a Stock trap. The product was redistilled, bp 68–69°, washed with water, dried, and shown to have a single peak on vpc.

2-Bromo-2-chloropropane was synthesized by a modified Kharasch method and purified by distillation, bp 92°, $n^{23}\text{D}$ 1.4539. Hydrolysis gave 1 equiv of Br^- per mole of the dihalide, and essentially a single vinyl product, 2-chloropropane. Since the latter was very unreactive in the experimental range, the presence of small amounts of this product in the *gem*-dihalide (nmr and vpc) did not influence the rates.

Rate data were determined by a conductance method[25] utilizing the relation

$$\log(1/R_2 - 1/R_1) = kt - C$$

Since our interest is in the temperature dependence of the rate, the effect of this approximation on the derived parameters was assumed to be unimportant. In any case, the differences in the rates between values so determined and checked against calibrations were not judged to be significant.

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Electrochemical Studies of Some Iron–Protoporphyrin Complexes

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Contribution from the Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122. *Received September 23, 1965*

Abstract: The electrochemistry of several complexes of iron-protoporphyrin has been studied by chronopotentiometry, microelectrode voltammetry, and controlled-potential coulometry using platinum electrodes, and by polarography and cyclic voltammetry using mercury electrodes. Complexing agents investigated include cyanide ion, pyridine, picoline (β and γ), water, and hydroxide ion. The electroreduction of these monomeric complexes, corresponding to the reduction of iron(III) to iron(II), proceeds as a reversible, one-electron change. From the data obtained, it is possible to establish the form of the various complexes and the equilibrium constants for the formation of several complexes. Adsorption on the electrode surface of some of the complexes has been measured by both chronopotentiometry and cyclic voltammetry.

In alkaline ethanolic aqueous solution and in the presence of suitable complexing agents, iron–protoporphyrin forms complexes of essentially octahedral symmetry. Four coordination sites of the iron are occupied by the pyrrole nitrogens on the protoporphyrin ring; the ring thus defines the *X–Y* plane of the complex. This feature is drawn schematically in Figure 1. The two remaining coordination positions