927. *Hydrolysis of* 3,4-*Dibromo- and* 3,4-*Dichloro*-2,2-*dimethylchroman*

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Rates and activation parameters have been obtained for the hydrolysis of *trans*-3(*eq*),4(*eq*)-dihalogeno-2,2-dimethylchroman in acetone–water and in dioxan–water. The structures of the dihalogeno-compounds have been determined by nuclear magnetic resonance measurements. The reactions involve a carbonium-ion intermediate, the mechanism being dependent on steric and neighbouring-group effects.

Empirical equations have been obtained expressing the experimental rate constant as a function of (i) temperature, (ii) water concentration at 298·2°K, (iii) anion concentration of the added salt, and (iv) the Y values for acetone–water and dioxan–water.

For both dihalogeno-compounds the activation energy was larger in dioxan–water than in acetone–water and did not vary significantly in either solvent over a range of water concentrations; the entropy of activation increased with increasing water content and remained constant for the same water concentration in both solvents.

It has been demonstrated[1] that the hydrolysis of 3,4-dichloro- and 3,4-dibromo-2,2-dimethylchroman involved the replacement of the chlorine or bromine atom in the 4-position and that substitution of the second bromine atom required much more forcing conditions, which did not remove the analogous chlorine atom. A study has been made of the mechanism of the hydrolysis of the *trans*-3(*eq*),4(*eq*)-dihalogeno-2,2-dimethylchroman.

Experimental

Materials.—Commercial acetone was purified[2] and stored over calcium sulphate. Before use, it was refluxed for 24 hr. over the drying agent and fractionated (b. p. 56·5—57°).[3] AnalaR dioxan was purified conventionally[3] (b. p. 101—102°). The solvents used were prepared by volume, acetone–water at 20° and dioxan–water at 25°. Solutions of lithium bromide and chloride were prepared by dissolving weighed amounts of the salt (dried over P_2O_5) in definite volumes of the solvents and standardised with silver nitrate solution. Acetone was added to an aqueous solution of lithium nitrate giving a solution containing $(100 - x)\%$ acetone. The strength of this solution was determined[4] with Nitron reagent.

3,4-Dibromo-2,2-dimethylchroman[1] was recrystallised from light petroleum (b. p. 40—60°), m. p. 81—82°. 3,4-Dichloro-2,2-dimethylchroman[5] was recrystallised from light petroleum (b. p. below 40°), m. p. 59—60°.

Product Analysis.—3,4-Dichloro-2,2-dimethylchroman (2·360 g., 0·1013 mole) and 50% aqueous acetone (150 ml.) were refluxed for 20 hr. Isolation with ether gave 3-chloro-2,2-dimethylchroman-4-ol (2·160 g., 0·1009 mole), m. p. and mixed m. p. 71—74°. 3,4-Dibromo-2,2-dimethylchroman (2·060 g., 0·0640 mole) were treated as above and gave 3-bromo-2,2-dimethylchroman-4-ol (1·630 g., 0·0632 mole), m. p. and mixed m. p. 104—107°. It was concluded that only one product was formed from the hydrolysis of each dihalogeno-compound with water.

Kinetic Measurements.—Rates of liberation of protons and halide ions were measured at temperatures controlled to ±0·05°. A sampling procedure was used below 25° and a sealed-tube technique at higher temperatures. Aliquot portions (5·0 ml.) were quenched in ice-cold acetone (150 ml.) and titrated for acid (lacmoid indicator); or quenched in ice-cold ether (150 ml.), the solution extracted with water (3 × 10 ml.) and the halide in the aqueous layer

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[1] R. Livingstone, *J.*, 1962, 76.

[2] A. I. Vogel, " A Text-Book of Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p. 171.

[3] " Organic Solvents," ed. A. Weissberger, Interscience, New York, 1955.

[4] A. I. Vogel, " A Text-Book of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1953, p. 505.

[5] J. Cottam, R. Livingstone, and S. Morris, *J.*, 1965, in the press.

determined potentiometrically.[6] Blank experiments showed that the quenching was efficient, that the reaction was irreversible, and that only one halogen was displaced in the reaction. First-order rate coefficients were calculated (Table 1). Calculated and experimental "infinity" values agreed to within experimental error.

Initial concentrations of organic halide were usually ~0·06M, though a series of experiments showed that the rate constant did not vary significantly over the range 0·02—0·08M. The rate coefficient was not affected by the volume of space above the solution and, in the absence of salts, had the same value whether obtained by acid or halide estimation.

All runs were performed in duplicate and the rate constants tested for significance by the "*t*" test.[7] Reactions were followed to 70% completion in most cases except for the slower runs.

Spectra.—The 60 Mc./sec. proton magnetic resonance spectra were recorded on a Varian

TABLE 1

Reaction of 3,4-dichloro-2,2-dimethylchroman in 76% acetone at 328·4°K, in the presence and absence of salts (k_1 in sec.$^{-1}$)

10^2[Chloro-cpd.]	Electrolyte	[Anion]	$10^4 k_1$ (Obs.)	$10^4 k_1$ (Calc.) *
6·58	—	0·0062 †	1·82 ± 0·03	1·81
6·50	LiCl	0·0561	1·66 ± 0·05	1·62
6·27	,,	0·109	1·43 ± 0·03	1·46
6·02	,,	0·158	1·33 ± 0·02	1·32
6·20	$LiNO_3$	0·0537	1·97 ± 0·08	1·95
6·29	,,	0·110	2·08 ± 0·03	2·09
6·37	,,	0·145	2·17 ± 0·03	2·19

* Calculated from equations (1) and (2) in Table 5. † Due to hydrolysis before the first reading.

TABLE 2

Reaction of 3,4-dibromo-2,2-dimethylchroman in 84% acetone at 298·2°K, in the presence and absence of salts (k_1 in sec.$^{-1}$)

10^2[Bromo-cpd.]	Electrolyte	[Anion]	$10^4 k_1$ (Obs.)	$10^4 k_1$ (Calc.) *
6·08	—	0·0036 †	3·25 ± 0·05	3·29
6·08	LiBr	0·0544	3·18 ± 0·03	3·12
6·21	,,	0·107	2·93 ± 0·02	2·94
6·03	,,	0·157	2·72 ± 0·02	2·77
6·15	$LiNO_3$	0·0510	3·40 ± 0·07	3·40
6·31	,,	0·100	3·53 ± 0·08	3·54
6·15	,,	0·148	3·62 ± 0·12	3·65

* Calculated from equations (3) and (4) in Table 5. † Due to hydrolysis before the first reading.

TABLE 3

Rate constants for the hydrolysis of 3,4-dichloro- and 3,4-dibromo-2,2-dimethylchroman

Halide	Solvent	xH_2O	$10^5 k_1$ (sec.$^{-1}$); temperatures in parenthesis (°K)			
Chloro	Acetone	0·311	0·0426(298·2)	0·131(307·2)	0·257(313·2)	0·470(318·6)
,,	,,	0·400	0·141(298·3)	0·493(308·5)	0·849(313·2)	1·51(318·3)
,,	,,	0·500	0·490(298·3)	1·73(308·5)	3·03(313·2)	4·85(317·3)
,,	,,	0·600	1·80(298·2)	6·92(308·7)	11·8(313·3),	21·0(318·3)
Bromo	,,	0·250	0·792(293·7)	4·78(288·4)	8·27(293·3)	14·3(298·3)
,,	,,	0·311	1·78(273·3)	10·2(288·2)	17·5(293·2)	29·8(298·2)
,,	,,	0·350	2·45(273·2)	14·9(287·9)	26·5(293·2)	45·7(298·3)
,,	,,	0·400	4·17(273·2)	25·5(287·9)	46·8(293·2)	83·0(298·3)
Chloro	Dioxan	0·344	0·00875(297·3)	0·140(320·1)	0·744(335·0)	3·52(350·0)
,,	,,	0·407	0·0273(298·2)	0·0960(307·9)	0·182(313·2)	0·343(318·6)
,,	,,	0·500	0·0850(298·3)	0·332(308·5)	0·580(313·0)	1·10(318·3)
,,	,,	0·600	0·333(298·3)	1·20(308·4)	2·20(313·2)	4·00(318·4)
Bromo	,,	0·250	0·480(288·6)	0·935(293·9)	1·62(298·4)	2·63(302·6)
,,	,,	0·300	0·952(288·2)	1·78(293·3)	3·27(298·6)	5·32(302·9)
,,	,,	0·344	1·65(288·0)	5·10(297·5)	17·8(308·4)	
,,	,,	0·407	3·53(288·2)	6·68(293·3)	12·0(298·4)	20·7(303·2)

xH_2O represents molar fraction of water; all rate constants have coefficients of variation of less than 3%.

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[6] C. R N. Strouts, L. Parry-Jones, and N. Wilson, "Chemical Analysis," vol. II, Oxford University Press, London, 1962, p. 371.

[7] M. Moroney, "Facts from Figures," Penguin Books, London, 1960, p. 371.

A60 spectrometer for ~10% solutions in deuterochloroform. Chemical shifts (δ) were measured in p.p.m. as displacements downfield from tetramethylsilane, used as internal reference.

Tables 1 and 2 show variations in rate constants with added salts. Four equations specify the behaviour of the rate coefficients, each possessing the form $\log k_1 = 1/(A + B[\mathrm{An}^-])$ where $[\mathrm{An}^-]$ represents the anion concentration. Table 5 gives values of A and B corresponding to each halide and salt.

The rate coefficients for the hydrolyses in aqueous acetone and aqueous dioxan are shown in Table 3.

The apparent activation energy and the entropy of activation were calculated by the method of least squares and are shown in Table 4 together with the least-squares coefficients a and b.

Plots of $\log k_1$ against $\log [H_2O]$ at 298·2°K gave good straight lines for each of the solvents, $[H_2O]$ representing the molarity of water estimated from density data (k_1 at 298·2°K was measured directly or estimated from the data given in Table 4). Table 6 shows least-squares values for c and d, in the equation $\log k_1 = c \log [H_2O] + d$.

TABLE 4

Values of a and b in $\log k_1 = a + b/T$ and of E and ΔS^* for the hydrolysis of 3,4-dichloro- and 3,4-dibromo-2,2-dimethylchroman

Halide	Solvent	$x\mathrm{H_2O}$	E (kcal. mole^{-1})	ΔS^* (e.u.)	a	$-b$
Chloro	Acetone	0·311	22·2 ± 0·6	15·3 ± 2·1	9·9	4878·5
,,	,,	0·400	22·4 ± 0·1	12·3 ± 0·3	10·5	4888·1
,,	,,	0·500	22·7 ± 0·2	8·8 ± 0·2	11·3	4960·6
,,	,,	0·600	23·1 ± 0·6	4·9 ± 1·9	12·2	5038·9
Bromo	,,	0·250	19·1 ± 0·2	14·1 ± 0·4	10·1	4171·4
,,	,,	0·311	18·3 ± 0·2	15·2 ± 0·6	9·9	4003·0
,,	,,	0·350	18·9 ± 0·5	12·4 ± 1·7	10·5	4130·7
,,	,,	0·400	19·3 ± 0·2	9·9 ± 0·5	11·0	4214·0
Chloro	Dioxan	0·344	23·5 ± 0·6	13·7 ± 1·8	10·2	5139·0
,,	,,	0·407	23·4 ± 0·3	12·0 ± 0·9	10·6	5118·6
,,	,,	0·500	24·2 ± 0·3	7·3 ± 1·1	11·6	5281·1
,,	,,	0·600	23·4 ± 0·8	7·2 ± 2·4	11·7	5113·2
Bromo	,,	0·250	21·1 ± 0·3	11·7 ± 1·1	10·7	4613·6
,,	,,	0·300	20·3 ± 0·3	13·2 ± 1·2	10·4	4430·1
,,	,,	0·344	20·6 ± 0·5	10·9 ± 1·6	10·8	4498·1
,,	,,	0·407	20·4 ± 0·5	10·0 ± 1·8	11·0	4464·7

TABLE 5

Dependence of $\log k_1$ on anion concentration

Halide Anion	Chloro Chloride	Chloro Nitrate	Bromo Bromide	Bromo Nitrate
$-A$	0·2672 ± 0·0016	0·2674 ± 0·0006	0·2874 ± 0·0015	0·2868 ± 0·0006
B	0·06 ± 0·01	−0·04 ± 0·01	0·04 ± 0·01	−0·03 ± 0·01
Equation	(1)	(2)	(3)	(4)

TABLE 6

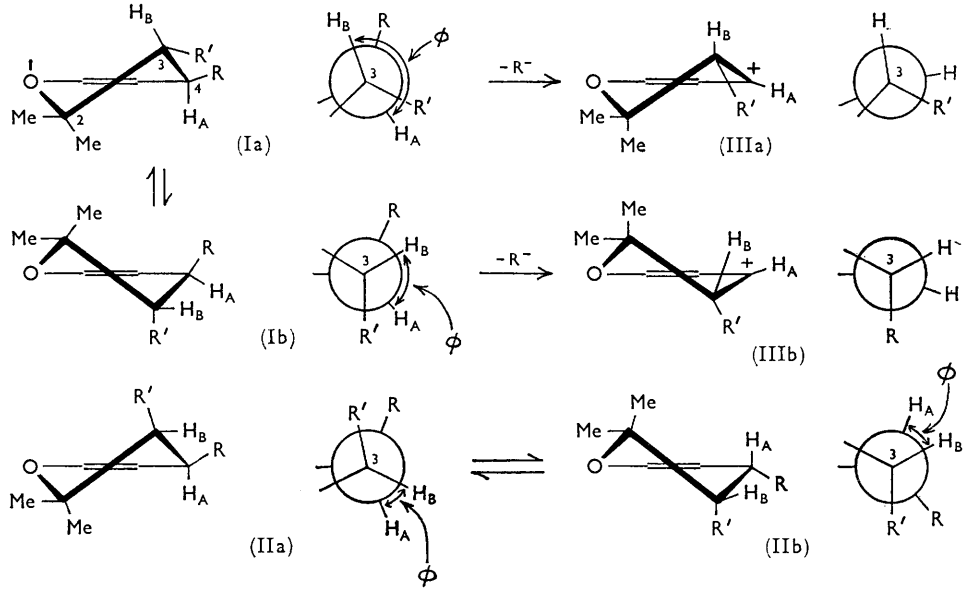
Dependence of $\log k_1$ on water molarity at 298·2°K

Halide Solvent	Chloro Acetone	Chloro Dioxan	Bromo Acetone	Bromo Dioxan
c	3·7 ± 0·4	4·0 ± 0·4	2·8 ± 0·2	3·2 ± 0·5
$-d$	9·2 ± 0·4	10·0 ± 0·3	5·6 ± 0·2	6·6 ± 0·5
Equation	(5)	(6)	(7)	(8)

DISCUSSION

The results show a decrease in rate coefficients for both halides on the addition of common ion and an increase on the addition of non-common ion. This indicates an S_N1 (or S_N1-like) mechanism. No decrease in the rate constant throughout any one run was observed; apparently the ionic strength and mass-law effect here balance. The near equivalence of the ratios of the coefficients of the chloride and bromide ion-concentration to that of the nitrate (in Table 5), indicates similar mechanism for the solvolyses of the chloride and bromide.

Dreiding models of 3,4-dihalogeno-2,2-dimethylchromans show that the heterocyclic ring is distorted from the half-chair cyclohexene analogue; although there is no eclipsing strain along the C(2)–C(3) bond, strain is present along the C(3)–C(4) bond. The models show that there are four possible structures, two conformations (Ia and Ib) of the *trans*- and two of the *cis*-dihalogeno-compound (IIa and IIb). The nuclear magnetic resonance (n.m.r.) spectra of the 3,4-disubstituted-2,2-dimethylchromans were used to determine the configurations of the substituents at C-3 and C-4 by comparing the observed vicinal coupling constants with those predicted by the Karplus $\cos^2 \phi$ equation[8] for the measured dihedral angles (ϕ) between H_A and H_B. (The variation of coupling constants with the electronegativity of substituents was neglected.[9]) The values 155, 85, 35, and 35° of the dihedral angle between H_A and H_B in (Ia), (Ib), (IIa), and (IIb), respectively, are those for the structures which are estimated to have the least combined angle and eclipsing strain in the pyran ring. (Because of the flexibility of this ring the C(3)–C(4) dihedral angle may be varied without undue ring strain.) These angles give theoretical coupling constants of 7·4 (Ia), ∼0 (Ib), and 5·3 c./sec. (IIa and IIb). These values, when compared with those obtained experimentally (Table 7), show that, in all of the 3,4-dihalogeno-2,2-dimethylchromans and 3-halogeno-2,2-dimethylchroman-4-ols studied, the most probable configuration is that with the 3- and 4-substituents *trans* and equatorial (Ia).



Conformations of the heterocyclic ring of *cis*- (II) and *trans*-3,4-disubstituted-2,2-dimethylchromans (I), with Newman projection formulae of the C(3)–C(4) bonds

It is likely that in the samples of *trans*-3,4-dihalogeno-2,2-dimethylchromans there would be present the 3(*ax*),4(*ax*)-dihalogeno-conformer (Ib) in amounts which would be undetected by n.m.r. This conformation (Ib) is not favoured because of the strong repulsion between the 2(*ax*)-methyl and the 4(*ax*)-halogen. In solution this repulsion energy would be increased [solvation increases the effective size of the 4(*ax*)-halogen] making it difficult to predict the equilibrium point in the conformational mixture. The amount of the *trans*-3(*ax*),4(*ax*)-dihalogeno-conformer (Ib) will be small at equilibrium, but it may hydrolyse more rapidly than the *trans*-3(*eq*),4(*eq*)-conformer (Ia) (equilibrium would be maintained by the rapid inversion of the heterocyclic ring) in which case it would play an important part in the mechanism.

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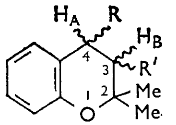
[8] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

[9] K. L. Williamson, *J. Amer. Chem. Soc.*, 1963, **85**, 576.

TABLE 7



(IV)

Reactants R = R′ = Br or Cl
Products R = OH; R′ = Br or Cl

Chemical shifts and coupling constants for the 3- and 4-hydrogen atoms in 3,4-disubstituted 2,2-dimethylchromans (IV)

Substituents		Chemical shifts (δ p.p.m.)		Coupling constants (c./sec.)
R	R′	H_A	H_B	J_{AB}
Cl	Cl	5·2	4·2	8·5
OH	Cl	4·7	3·9	7·6
Br	Br	5·5	4·5	9·7
OH	Br	4·9	4·1	10·8

Effect of the Various Groups on the Mechanism of the Hydrolysis.—(a) *Neighbouring phenylene group.* This group will stablise a positive charge at C-4 in the cationic transition state. The magnitude of the effect is expected to be the same for different dihalogeno-compounds and independent of conformation.

(b) *Neighbouring halogen.* This 3-substituent will have an electron-withdrawing influence tending to hinder the formation of the carbonium ion and slow the rate.

In the trans-3(*ax*),4(*ax*)-dihalogeno-conformer (Ib) the rate could be enhanced by anchimeric assistance;[10] 4-halogeno-2,2-dimethylchroman-3-ols, which would be expected if this effect were present, were never isolated from the hydrolysis products.

(c) 2-*Methyl groups.* These groups lie two carbon atoms away from the reaction centre so that their inductive effect on this position has been neglected.

In the *trans*-3(*ax*),4(*ax*)-dihalogeno-conformation (Ib) there is a strong repulsion between the 2(*ax*)-methyl and 4(*ax*)-halogen, which would increase the rate of ionisation. The carbonium ion (IIIb) which formed would be shielded from attack on one side, and the major product would be the *cis*-halogenohydrin (treatment of the halogenohydrins with base yielded epoxide and no ketone). Since only *trans*-halogenohydrins have been isolated, to obtain these from the *trans*-3(*ax*),4(*ax*)-dihalogeno-compounds there would have to be strong neighbouring-group participation with both bromine and chlorine. Chlorine generally is a weakly anchimeric-assisting [11] group and so, if the *trans*-3(*ax*),4(*ax*)-dichloro-conformer is mechanistically important, then the *cis*-chlorohydrin should be isolated. On this evidence it is considered that the 3(*ax*),4(*ax*)-dihalogeno-conformation is not important in the hydrolysis of *trans*-3,4-dihalogeno-2,2-dimethylchroman.

In the *trans*-3(*eq*),4(*eq*)-dihalogeno-conformation (Ia) the repulsion between the 2(*ax*)-methyl and the 4(*ax*)-hydrogen would increase the rate of ionisation equally for both dihalogeno-compounds. However, the 2(*ax*)-methyl group would shield one side of the carbonium ion, making attack from the same side as the leaving group more favourable. This agrees with the isolation of *trans*-3(*eq*)-halogeno-2,2-dimethylchroman-4(*eq*)-ols (~98%) from the hydrolyses.

(d) *Oxygen atom.* This hetero-atom distorts the pyran ring from the cyclohexene analogue so that there will be considerable eclipsing strain along the C(3)–C(4) bond in the solvated compounds. Formation of the transition state (III) relieves this strain, and the increased tendency to form the carbonium ion is accompanied by rate enhancement.

Comparison of the rate coefficients for the hydrolyses of the dihalogeno-compounds in acetone–water shows that the ratio k_1(dibromo)/k_1(dichloro) is approximately seven times

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[10] S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 828.

[11] See Table 50 in A. Streitwieser, *Chem. Rev.*, 1956, **56**, 571, from results by S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 1948, **70**, 821.

greater than the ratio k_1(bromo)/k_1(chloro) for the hydrolyses of some monohalogeno-compounds.[12] This can be explained for *trans*-3(*eq*),4(*eq*)-dihalogeno-2,2-dimethlychroman as a differential effect between bromine and chlorine. Chlorine is more electronegative than bromine and when present at C-3 would, by its inductive effect, tend to slow the rate as compared with the bromo-analogue. The formation of the transition-state carbonium ion leads to a relief of eclipsing strain along the C(3)–C(4) bond which would be greater for the dibromo- than for the dichloro-compound. Neither of these effects would play any part in the hydrolyses of monohalogeno-compounds and, when combined, afford an explanation for the ratio of the rate constants for the dihalogeno-compounds being greater than that for the monohalogeno-compounds.

The salt effects and variations of energy and entropy of activation indicate a similar mechanism for the solvolyses of the dibromo- and dichloro-compounds, but the results do not distinguish between the chemical S_N1 scheme,[13] and schemes involving "internal" and "external" ion-pairs.[14]

A non-linear relationship was observed between log k_1 and $(D - 1)/(2D + 1)$, for the reaction in aqueous acetone and aqueous dioxan. The failure to follow a linear relationship [15] may be attributed to one or more of the following: (i) the dielectric constant is not a good guide to interactions in solutions since it is a macroscopic property,[16] (ii) solvation effects are completely ignored,[17] (iii) the non-electrostatic terms are neglected.[18]

The relationships between log k_1† and the Y values of the acetone–water and dioxan–water solvents [19] for the dichloro- and dibromo-compounds are adequately (± 2% for log k_1) represented by equations (9)—(12), which are of the form log $k_1 = mY + f$.

TABLE 8

Halide	Chloro	Chloro	Bromo	Bromo
Solvent	Acetone	Dioxan	Acetone	Dioxan
m	0·92 ± 0·04	0·99 ± 0·08	0·74 ± 0·08	0·79 ± 0·02
$-f$	4·67 ± 0·04	4·96 ± 0·20	2·17 ± 0·15	2·64 ± 0·05
Equation	(9)	(10)	(11)	(12)

The slopes, m, in equations (9) and (10), obtained for the line relating log k_1 to Y for the chloro-compound, compare favourably with the value of 0·9—1·0 observed for unimolecular (S_N1) reactions;[20] m in equations (11) and (12) is midway between 0·4 and 1·0 ($m \sim 0{\cdot}4$ is the value observed in typical S_N2 reactions [20]), suggesting that some intermediate type of mechanism may be operating.

Plots of log k_1 against log [H_2O] gave excellent linearity. The slopes, c, in Table 6, show the order with respect to the water involved in the reaction. The values of c are lower for the dibromo- than for the dichloro-compound in similar solvents, owing to the relative size of the halogens. For the same halides the values are larger in dioxan than in acetone. The observed values of c (approximately 3) are lower than those for other reactions.[21]

Variation of E and ΔS^*.—Values of E and ΔS^* are presented in Table 4. The majority of the rate constants are subject to errors of 1—3% with none >5%. Under these conditions the errors involved in the calculation of E are of the order of 400 cal./mole [with the

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† k_1 at 298·2°K is estimated from Table 4.

[12] See, for example, C. R. Cowie, H. J. M. Fitches, and G. Kohnstan, *J.*, 1963, 1585, for various pairs in acetone solvents.

[13] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J.*, 1940, 979.

[14] S. Winstein *et al.*, *J. Amer. Chem. Soc.*, 1958, **80**, 169, 459, and earlier Papers.

[15] J. G. Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351; S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill, New York, 1941, p. 419.

[16] V. V. Zelinskii and V. P. Kolobobkov, *Doklady Akad. Nauk S.S.S.R.*, 1959, **142**, 1272.

[17] J. B. Hyne, *J. Amer. Chem. Soc.*, 1960, **82**, 5129.

[18] N. C. Deno, *J. Phys. Chem.*, 1961, **65**, 179.

[19] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2773.

[20] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 1597, 1602; S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, p. 4146.

[21] G. Kohnstam in "The Transition State," *Chem. Soc. Special Publ.*, no. 16, London, 1962, p. 186.

least accurate 800 cal./mole (one value) and 500 cal./mole (six values)]. The errors in ΔS^* average 1·5 e.u. with none $>2{\cdot}4$ e.u. In view of these errors, discussion of the variation of these parameters must be made with some caution.

For the dibromo- and dichloro-compounds, E is larger in dioxan than in acetone ($\Delta E_{\text{dibromo}} \sim 0{\cdot}7$ kcal./mole and $\Delta E_{\text{dichloro}} \sim 1{\cdot}0$ kcal./mole) and for each compound ΔS^* remains the same in both solvents (within experimental error). The differences in the value of E may be attributed [22] to be the more polar character of acetone.

For each halide, the variation of activation energy with change of water concentration was not significant, but the entropy of activation was found to increase with increase of water molar fraction, thus being responsible for the increase in rate. The difference between activation parameters for the hydrolysis of the dihalogeno-compounds were comparable with those observed for other halides [12] under similar water concentrations (*i.e.*, $E_{\text{dichloro}} - E_{\text{dibromo}} \sim E_{\text{chloro}} - E_{\text{bromo}}$ and, similarly, $\Delta S^*_{\text{dichloro}} - \Delta S^*_{\text{dibromo}} \sim \Delta S^*_{\text{chloro}} - \Delta S^*_{\text{bromo}}$).

The values of the thermodynamic parameters are of the usual order found for unimolecular reactions [15,23] and the relationships found for the variation of E with ΔS^* are not unusual for reactions in mixed solvents.[24]

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College of Technology, Huddersfield.
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[22] C. K. Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 345.

[23] See, *e.g.*, G. Kohnstam, ref. 21.

[24] See, *e.g.*, J. E. Leffler and E. Grunwald, " Rates and Equilibria of Organic Reactions," Wiley, New York, 1963, p. 389 *et seq.*