138. *The Brönsted Relation in the Hydrolysis of the Halogenoacetates and the Theory of Acids and Bases.*

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The hydrolysis of the chloroacetate ion is subject to general basic catalysis, and the Brönsted catalysis relation is found to hold for a series of basic catalysts, although important exceptions are noted.

The bearing of these results on the theory of acids and bases is discussed.

The hydrolysis of the group $CH_2X{\cdot}C\bar{O}_2$ ($X = Cl$ or Br) is represented by the stoicheiometric equation $CH_2X{\cdot}C\bar{O}_2 + H_2O \longrightarrow CH_2(OH){\cdot}CO_2H + \bar{X}$, but the actual mechanism by which the reaction products are formed is complex and consists primarily of a series of simultaneous bimolecular reactions involving the $CH_2X{\cdot}C\bar{O}_2$ ion and each basic species present. Except in the direct reaction in which water molecules participate, these simultaneous reactions can be written as

$$CH_2X{\cdot}C\bar{O}_2 + \bar{B} \longrightarrow CH_2B{\cdot}C\bar{O}_2 + \bar{X} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

where B is a base which may thus be the hydroxyl ion, the chloroacetate ion, or any basic anion present in the solution. Except when $\bar{B}$ is the hydroxyl ion, the product formed in (1) is then hydrolysed by the solvent in accord with the equation

$$CH_2B{\cdot}C\bar{O}_2 + H_2O \longrightarrow CH_2(OH){\cdot}CO_2H + \bar{B} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

Although the rate of reaction (2) is not known, it is clear that the base catalyses the hydrolytic reaction, since it brings about an alteration in the speed of the reaction and is itself eventually re-formed. Moreover, since a variety of bases are effective (Dawson, Pycock, and Smith, preceding paper) the reaction is subject to general basic catalysis and it therefore becomes of interest to enquire whether this reaction, like other base-catalysed reactions, conforms to the Brönsted catalysis relation. For basic catalysis this relation may be written in the form $\log (k/q) = \log G + \beta \log (K_b p/q)$, where k is the velocity coefficient of reaction (1), K_b is the basic dissociation constant of $\bar{B}$, G and β are constants for a given temperature, and p and q are statistical factors. The relevant data are recorded in Tables I and II, which refer respectively to the hydrolysis of the chloro- and the bromo-acetate group. In the former case, since the velocity coefficients refer to 45°, values for K_b are used at or near this temperature when these data are available, but otherwise those at 25°. Except with the very strong bases, however, the exact temperature to which K_b refers (col. 3) is not of great significance. All the velocity coefficients, except that for the sulphite ion, relate to solutions in which the ionic strength was unity, whereas the dissociation constants refer to dilute, and in some cases to infinitely dilute, solutions; but no difficulty arises in respect of this, since it is probable (Dawson and Lowson, J., 1929, 1217) that the dissociation constants of different acids vary with the ionic strength of the solution in a precisely similar manner.

Inspection of the numbers in the body of Table I shows that the equation at the head of the table accounts satisfactorily for the experimental values of k, except in the case of water, where the reaction is somewhat different. The data in Table II show that for the hydrolysis of the bromoacetate group a relation of the same type probably exists, with a very similar value for β. At the foot of the tables are also given the velocity coefficients for the sulphite and the thiosulphate ion (Krapavin, *J. Chim. physique*, 1912, **10**, 289; La Mer, *Chem. Rev.*, 1932, **10**, 179). It is obvious that the relation breaks down completely for these ions, and that here specific effects have a preponderating influence. Although specific effects of these very large magnitudes have not previously been observed, it is well established that they do occur in lesser degree in other base-catalysed reactions, *e.g.*, in the nitroamide reaction and the mutarotation of glucose (see Hammet, " Physical Organic Chemistry," McGraw-Hill Book Co., 1940, p. 225; Bell, " Acid–Base Catalysis," Clarendon Press, 1941, p. 88), so the difference between the two classes of reaction would appear to be one of degree rather than of kind.

The results given above lead unquestionably to the conclusion that the basic catalysis of the hydrolysis of the group $CH_2X{\cdot}C\bar{O}_2$ exhibits, in the main, the characteristics usually associated with general acid–base catalysis. On the basis of present views this is surprising, since there appears to be an important difference in reaction type. It is generally accepted that acid–base catalysed reactions are protolytic processes. For instance, in the conversion of the species SH into products X under the catalytic influence of a base $\bar{B}$, the rate-determining step can be formulated as $SH + \bar{B} \longrightarrow \bar{S} + HB$, and this is followed by rapid reactions involving the conversion of $\bar{S}$ into X and the regeneration of $\bar{B}$. In the present case, no proton transfer can be involved, the primary reaction being the displacement of $\bar{X}$ by $\bar{B}$ from the group $CH_2X{\cdot}C\bar{O}_2$, in accord with equation (1). It can only be concluded, therefore, that the transfer of a proton is not, as usually supposed, an essential process in basic or acid catalysis. If this is accepted, then, since acid–base catalysis must involve the acid and basic functions of the species concerned, it follows that in acid–base equilibria the proton is not, of necessity, involved.

TABLE I.

The Brönsted relation in the reaction $\mathrm{CH_2Cl{\cdot}C\bar{O}_2} + \bar{\mathrm{B}} \longrightarrow \mathrm{CH_2B{\cdot}C\bar{O}_2} + \bar{\mathrm{Cl}}$ (45°).

$\log (k/q) = -6{\cdot}090 + 0{\cdot}203 \log (K_b p/q)$.

No.	Base.	log K_b.	Temp.	p.	q.	10^6k, calc.	10^6k, obs.
1	Water	−1·74	45°	1	1	(0·36)	0·030
2	*o*-Nitrobenzoate	2·17	25	1	2	3·9	4·4
3	*o*-Hydroxybenzoate	2·98	25	1	2	5·7	4·5
4	Chloroacetate	2·91	45	1	2	5·5	5·7
5	*o*-Chlorobenzoate	2·94	25	1	2	5·6	6·1
6	*m*-Nitrobenzoate	3·46	50	1	2	7·1	6·5
7	*p*-Nitrobenzoate	3·42	25	1	2	6·9	7·3
8	Mandelate	4·37	25	1	2	10·9	8·2
9	*m*-Chlorobenzoate	3·83	25	1	2	8·5	8·2
10	*p*-Chlorobenzoate	3·98	25	1	2	9·1	8·7
11	*p*-Bromobenzoate	3·97	25	1	2	9·1	9·3
12	Benzoate	4·18	45	1	2	10·0	9·5
13	*p*-Nitrophenylacetate	4·85	25	1	2	13·7	9·8
14	*m*-Toluate	4·17	25	1	2	9·9	9·8
15	*p*-Toluate	4·62	25	1	2	12·2	10·6
16	Glycollate	3·84	45	1	2	8·5	10·8
17	*m*-Hydroxybenzoate	4·08	25	1	2	9·5	11·1
18	Phenylacetate	4·29	35	1	2	10·5	11·6
19	*o*-Toluate	3·91	25	1	2	10·1	12·3
20	*p*-Hydroxybenzoate	4·54	25	1	2	11·8	12·6
21	*n*-Butyrate	4·87	45	1	2	13·8	13·8
22	Propionate	4·90	45	1	2	14·0	15·0
23	Acetate	4·78	45	1	2	10·3	15·5
24	Formate	3·77	45	1	2	8·3	20·3
25	Tartrate	4·54	25	1	4	20·5	21·3
26	Malate	5·13	25	1	4	27·7	26·3
27	Oxalate	4·39	45	1	4	24·0	26·4
28	Succinate	5·7	37—50	1	4	34·9	29·9
29	Malonate	5·36	25	1	4	30·1	31·1
30	Phthalate	5·41	25	1	4	30·8	31·8
31	Carbonate	10·22	38	1	3	230	140
32	Hydroxyl	15·14	45	1	1	960	1040
33	Sulphite	5·3	25	—	—	—	4610 (25°) ($\mu = 0$)
34	Thiosulphate	2	25	—	—	—	10,700 (25°)

TABLE II.

The Brönsted relation in the reaction $\mathrm{CH_2Br{\cdot}C\bar{O}_2} + \bar{\mathrm{B}} \longrightarrow \mathrm{CH_2B{\cdot}C\bar{O}_2} + \bar{\mathrm{Br}}$ *at* 25°.

$\log (k/q) = -5{\cdot}500 + 0{\cdot}198 \log (K_b p/q)$.

No.	Base.	log K_b (25°).	p.	q.	10^6k, calc.	10^6k, obs.
1	Water	−1·74	1	1	(1·43)	0·059
4	Chloroacetate	2·86	1	2	23·3	14·0
35	Bromoacetate	2·86	1	2	23·3	19·3
16	Glycollate	3·83	1	2	31·6	35
24	Formate	3·75	1	2	30·5	50
23	Acetate	4·76	1	2	48·3	50
32	Hydroxyl	15·74	1	1	4140	4150
34	Thiosulphate	2	—	—	—	$1{\cdot}065 \times 10^6$

References to dissociation constants : (4) Wright, *J. Amer. Chem. Soc.*, 1934, **56**, 314 (extrapolated); (16) Nims, *ibid.*, 1936, **58**, 987 (interpolated); (21) Harned and Sutherland, *ibid.*, 1934, **56**, 2039; (22) Harned and Ehlers, *ibid.*, 1933, **55**, 2379; (23) *Idem*, *ibid.*, p. 652; (24) Harned and Embree, *ibid.*, 1934, **56**, 1042; (27) Harned and Fallon, *ibid.*, 1939, **61**, 3111; (32) Harned and Hamen, *ibid.*, 1933, **55**, 2194; (2), (3), (5), (7), (9), (10), (11), (13), (14), (15), (17), (19), (20) Watson, "Modern Theories of Organic Chemistry," 1937, pp. 36, 207; (6), (8), (12), (18), (25), (26), (28), (29), (30), (31), (33), (34), (35) Landolt–Börnstein, "Tabellen," 1923 and 1931.

References to velocity coefficients : Dawson and Pycock, J., 1934, 778; 1936, 153; Dawson, Pycock, and Smith, *loc. cit.*; Dawson and Dyson, J., 1933, 49; Brook and Dawson, J., 1936, 497.

This is in sharp disagreement with the Lowry–Brönsted definition of acids and bases, which, as summarised by the relation $\mathrm{B} + \mathrm{H}^+ \rightleftarrows \mathrm{BH}^+$, insists that the proton plays a necessary and vital part. Since this is not the case, it becomes necessary to take a broader view, as suggested by Lewis (*J. Franklin Inst.*, 1938, **226**, 293). A base may then be defined as a species possessing a free electron pair which can enter the shell of another atom, and an acid as a species which can receive such an electron pair. These definitions may conveniently be expressed by the scheme $\mathrm{B)} + \mathrm{)A} \rightleftarrows \mathrm{BA}$, where) after the letter represents a free electron pair and) before the letter represents the corresponding deficiency. This concept introduces no new bases, since every base defined in this manner will also be a base on the Lowry–Brönsted view, but it displaces the proton from its unique position in that it recognises the fact that the proton is one only amongst many species, each of which, in virtue of its ability to accept an electron pair, may therefore combine with a base.

Such an extension of our present views is permissible only if it can be demonstrated that acids and bases as defined above conform closely to the generally recognised criteria of acids and bases. In this connection it is noted that Lewis (*loc. cit.*) has recorded a number of experiments involving substances of the type $B)$ and $)A$, both these and the solvent media being chosen so as to exclude the possibility of protolytic reactions. In these circumstances, he demonstrated that, qualitatively at least, these substances simulate in a very remarkable manner some of the salient properties normally associated with acids and bases. The experiments referred to in the present paper, although of a very different nature, lead to the same conclusion, and receive a ready explanation in terms of the views expressed above. The group $CH_2X{\cdot}C\overset{-}{O}_2$ may be regarded as a compound formed from the base $\overset{-}{X})$ and the acid $)\overset{+}{C}H_2{\cdot}C\overset{-}{O}_2$.* On addition of the stronger base $\overset{-}{B})$, the weak base $\overset{-}{X})$ is displaced from its compound with the acid. This, then, becomes a normal acid–base reaction. Furthermore, on comparing the reactions (3) and (4), a parallelism between them is understandable only if both are recognised as reactions of essentially the same type, *i.e.*, acid–base reactions.

$$CH_2X{\cdot}C\overset{-}{O}_2 + \overset{-}{B}) \longrightarrow CH_2B{\cdot}CO_2 + \overset{-}{X}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$H_3\overset{+}{O} + \overset{-}{B}) \rightleftarrows HB + H_2O) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It should be pointed out that the parallelism between (3) and (4) would be expected to be less pronounced than in those cases where both the reacting systems involve protolytic reactions. For in the processes $SH + \overset{-}{B}) \longrightarrow \overset{-}{S}) + HB$ and $H_3\overset{+}{O} + \overset{-}{B}) \rightleftarrows H_2O) + HB$ the acid $)H^+$ and the base $\overset{-}{B})$ are involved in both, while in (3) and (4) the only common factor is the base $\overset{-}{B})$, and hence specific effects are likely to be of much greater importance in the latter case. Indeed, since, in general, the ability of an acid and base to react is essentially specific in character, it may be regarded as the exception that a relation should exist between the abilities of two acids $)H^+$ and $)\overset{+}{C}H_2{\cdot}\overset{-}{C}O_2$ to react with a series of bases, and it is in no way surprising that in other cases this parallelism should no longer be found.

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