261. *Kinetics and Mechanisms of Addition of Acids to Olefins. Part I. The Addition of Hydrogen Chloride to Isobutene in Nitromethane.*

By Y. Pocker.

Addition of hydrogen chloride to isobutene in nitromethane is of first order in olefin and of second order in hydrogen chloride. Tetraethylammonium chloride suppresses the rate of addition of acid by combining with free hydrogen chloride to produce hydrogen dichloride ions. The observed kinetics require the reaction between the t-butyl cation intermediate and a hydrogen dichloride anion to be slower than elimination of a proton from the cation.

Under acidic conditions the elimination of halogen acid from an alkyl halide is reversible, the equilibrium being generally favourable to addition at low temperatures and to elimination at high temperatures. Information concerning the kinetics and mechanism of addition is therefore pertinent to elimination and symmetrical halogen exchange, by the principle of microscopic reversibility.

For addition of hydrogen chloride to isobutene and of hydrogen bromide to propene in heptane Mayo and his co-workers [1] observed reactions of first order in olefin and of somewhat indefinite order (averaging about three) in hydrogen halide. The kinetics of addition to olefins in aqueous acid are less complex,[2] but the chemical process is hydration, and the reaction orders do not show the degree of involvement of a water molecule in the transition state. An attempt to apply the Zucker–Hammett hypothesis leads to a dilemma:[3] for hydration of 2-methylbut-2-ene this hypothesis would assign to the transition state the composition olefin,H^+, while for dehydration of the corresponding alcohol under identical conditions it would assign the composition olefin,H^+,H_2O. Clearly the same transition state has been assigned different compositions, depending on the direction of approach, and this is contrary to the principle of microscopic reversibility.

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[1] (*a*) Mayo and Katz, *J. Amer. Chem. Soc.*, 1947, **69**, 1339; (*b*) Mayo and Savoy, *ibid.*, p. 1348.

[2] Lucas and his co-workers, *J. Amer. Chem. Soc.*, 1934, **56**, 460, 1230, 2138.

[3] Boyd and Taft, jun., Abs. Amer. Chem. Soc., 132nd Meeting, New York, September, 1957, p. 76; see, however, Melander and Myhre, *Arkiv Kemi*, 1959, **13**, 507.

For more detailed investigation of heterolytic addition of acids to olefins it was advantageous to avoid solvolysis. A solvent had to be employed which was sufficiently ionising to sustain carbonium ions but insufficiently nucleophilic to react with them.[4] This was achieved by studying the addition of hydrogen chloride to isobutene in nitromethane solvent. The conjugate base of hydrogen chloride is more nucleophilic than the nitromethane molecule and enables the essential rate-controlling steps to be studied in greater isolation than is possible in hydration.

1. *Kinetics of Addition of Hydrogen Chloride to Isobutene.*—The kinetics of this reaction were studied in three ways: by following the disappearance of acid, by following the disappearance of chloride ions, and by determining the loss of isobutene. The rates obtained by the three methods are practically identical (see Table 1), indicating that under the conditions employed there is little or no decomposition of the solvent molecules by the hydrogen chloride present or by the carbonium ion intermediate produced during the addition. The stoicheiometry of the addition is one whereby for each molecule of olefin only one molecule of acid disappears, to produce at 25·0° t-butyl chloride in practically quantitative yield. Yet, the kinetics show that at relatively low acidities, *i.e.*, with [HCl] < 0·03M, the rates of addition are first-order with respect to olefin but second-order with respect to hydrogen chloride. This can be seen from the dependence of the second-order rate coefficients calculated as first-order in both olefin and hydrogen chloride on the concentration of the latter. The last column in Table 1 records third-order rate coefficients, k_3, obtained by dividing k_2 by the concentration of hydrogen chloride. These are practically constant, so that, in the range of acidities employed,

$$v(\text{Addition}) = k_3[\text{Olefin}][\text{HCl}]^2$$

Section 2 concerns the condition of the ions when a reaction normally dependent on ions is transferred from a hydroxylic solvent to one which has a high dielectric constant

TABLE 1. *Initial second- and third-order rate coefficients (k_2 in sec.$^{-1}$ l. mole^{-1}; k_3 in sec.$^{-1}$ l.^{2} mole^{-2}) of addition of hydrogen chloride to isobutene in nitromethane at* 25·0°.

[Isobutene] (mole l.$^{-1}$)	[HCl] (mole l.$^{-1}$)	[Method]	10^3k_2 * (sec.$^{-1}$ l. mole^{-1})	k_3 * † (sec.$^{-1}$ l.^{2} mole^{-2})
0·0025	0·0050	$-$dCl$^-$/dt	5·2	1·04
0·0025	0·0050	$-$dOlefin/dt	5·0	1·0
0·0025	0·0050	$-$dH$^+$/dt	5·0	1·0
0·0025	0·0100	,,	11·0	1·1
0·0025	0·0150	,,	14·7	0·98
0·0025	0·0150	$-$dOlefin/dt	15·0	1·0
0·00245	0·0157	,,	16·8	1·07
0·00245	0·0157	$-$dCl$^-$/dt	16·8	1·07
0·00245	0·0157	$-$dH$^+$/dt	16·0	1·02
0·0029	0·0166	,,	17·6	1·06
0·0033	0·0218	,,	23	1·05
0·0050	0·0050	,,	5·0	1·0
0·0050	0·010	,,	9·8	0·98
0·0050	0·015	,,	14·7	0·98
0·010	0·005	,,	5·05	1·01
0·010	0·010	,,	9·9	0·99
0·010	0·015	,,	14·4	0·96
0·011	0·059	,,	6·2	1·05
0·0125	0·0147	,,	14·3	0·97

* For a given run, the possible variation in these values resulting from the uncertainty in determination of initial slopes is about 4%.

† Values of k_3 calculated independently from the equation

$$k_3 = \frac{1}{t(b-a)}\left[\frac{x}{a(a-x)} + \frac{2\cdot303}{(b-a)}\log_{10}\frac{b(a-x)}{a(b-x)}\right]$$

were constant throughout a run within 4% and practically identical with those recorded in the Table.

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[4] de la Mare, Hughes, Ingold, and Pocker, *J.*, 1954, 2930.

but apparently very little capacity for ion solvation. Then a mechanism consistent with the above kinetics is derived in section 3.

2. *The Dissociation of Hydrogen Chloride in Nitromethane.*—Wright, Murray-Rust, and Hartley[5] showed that hydrogen chloride exists largely as undissociated molecules, but that there is present also a certain concentration of ions. In these solutions, therefore, ion-association or recombination is important as a consequence, not of uncommonly strong ionic interaction, but of low solvation energy. This explains the large difference in the degree of dissociation between hydrogen chloride on the one hand and perchloric acid and tetraethylammonium chloride on the other. The undissociated hydrogen chloride is in equilibrium with hydrogen ions and chloride ions:

$$\mathrm{HCl} \rightleftharpoons \mathrm{H^+} + \mathrm{Cl^-};\quad K_1 = [\mathrm{H^+}][\mathrm{Cl^-}]/[\mathrm{HCl}]$$

The concentration of free chloride ions is, however, considerably smaller than that of the hydrogen ions since the former tend to combine in nitromethane with a molecule of hydrogen chloride to produce hydrogen dichloride ions:

$$\mathrm{Cl^-} + \mathrm{HCl} \rightleftharpoons \mathrm{HCl_2^-};\quad K_2 = [\mathrm{HCl_2^-}]/[\mathrm{HCl}][\mathrm{Cl^-}]$$

The HCl_2^- ions are very stable in nitromethane,[6] *i.e.*, $K_2 > K_1$ at 25·0°. Thus, it is now found that adding tetraethylammonium chloride to hydrogen chloride in nitromethane reduces the concentration of free hydrogen chloride, until, at the equivalence point, the concentration of free acid is not higher than 5% of the original (infrared measurements) and possibly as low as 2% of the original (vapour-pressure measurements). Hebrandson, Dickerson, and Weinstein[7] recently isolated tetraethylammonium hydrogen dichloride from nitrobenzene solution, and in the present work we isolated this salt from nitromethane. Conductance measurements[5,6,8] indicate that, in the range of acidities investigated kinetically, the overall ionisation of hydrogen chloride is best described in terms of the equilibrium:

$$2\mathrm{HCl} \rightleftharpoons \mathrm{H^+} + \mathrm{HCl_2^-};\quad K_1K_2 = [\mathrm{H^+}][\mathrm{HCl_2^-}]/[\mathrm{HCl}]^2$$

Added tetraethylammonium perchlorate shows none of the above described effects, so that an HCl molecule does not bond its hydrogen to one of the oxygens of the ClO_4^-, *i.e.*, $[ClHClO_4]^-$ does not exist in nitromethane.

3. *Mechanism of Addition.*—A mechanism consistent * with the kinetics recorded in Section 1 is derived by considering the addition as a two-stage process and remembering that $K_2 > K_1$ (section 2). The first stage involves reversible addition of the proton to isobutene as in (i):

$$\text{(i)}\quad \mathrm{Me_2C{=}CH_2} + \mathrm{H^+} \xrightleftharpoons[v_b]{v_a} \mathrm{Me_3C^+}$$

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* The kinetics presented in Sections 1 and 4 are also consistent with addition through an ion-pair intermediate according to the generalised scheme:

$$\mathrm{Me_2C{=}CH_2} + 2\mathrm{HCl} \xrightleftharpoons[2]{1} \mathrm{Me_3C^+HCl_2^-} \xrightleftharpoons[4]{3} \mathrm{Me_3CCl} + \mathrm{HCl}$$

with reaction 1 or 3 rate-determining. Such a generalised scheme would also accord with Smith and Hammett's measurements of acidity function.[9] In a paper to be published shortly we show that v_d or its variant 4 in the present scheme, is rate-determining for chlorine exchange between t-butyl chloride and hydrogen radiochloride in nitromethane. Therefore, by the principle of microscopic reversibility, step 3 should be rate-determining in the addition. This leads to the same stoicheiometric composition of the transition state by explanations cast in terms of kinetically free ions or in terms of ion-pair intermediates.

[5] Wright, Murray-Rust, and Hartley, *J.*, 1931, 199.

[6] Pocker, *J.*, 1958, 240.

[7] Hebrandson, Dickerson, jun., and Weinstein, *J. Amer. Chem. Soc.*, 1954, **76**, 4046.

[8] Pocker, unpublished observations.

[9] Smith and Hammett, *J. Amer. Chem. Soc.*, 1945, **67**, 23.

This is followed by stage (ii), reaction of the carbonium ion with the hydrogen dichloride ion:

$$\text{(ii)}\quad \mathrm{Me_3C^+ + HCl_2^-} \underset{v_d}{\overset{v_c}{\rightleftharpoons}} \mathrm{Me_3CCl + HCl}$$

The rates of the various steps are given by:

$$v_a = k_a[\mathrm{H^+}][\mathrm{Me_2C{=}CH_2}]$$

$$v_b = k_b[\mathrm{Me_3C^+}]$$

$$v_c = k_c[\mathrm{Me_3C^+}][\mathrm{HCl_2^-}]$$

and

$$v_d = k_d[\mathrm{Me_3CCl}][\mathrm{HCl}]$$

The reverse process v_d is very slow at 25·0° ($k_d = 3{\cdot}9 \times 10^{-6}$ sec.$^{-1}$ l. mole^{-1}), so that the rate of addition at this temperature is governed by the rate at which the t-butyl cation reacts with hydrogen dichloride ion. However, if only a fraction of the carbonium ions produced by v_a combines with a hydrogen dichloride ion, while the majority eliminates a proton and returns to isobutene then, $v_a > v_b > v_c > v_d$, which leads to:

$$v(\text{addition}) = v_c = k_c[\mathrm{Me_3C^+}][\mathrm{HCl_2^-}] = \frac{k_a k_c}{k_b}[\mathrm{Me_2C{=}CH_2}][\mathrm{H^+}][\mathrm{HCl_2^-}]$$

where

$$[\mathrm{H^+}] = K_1K_2[\mathrm{HCl}]^2/[\mathrm{HCl_2^-}]$$

In the absence of added saline chloride

$$[\mathrm{H^+}] \approx [\mathrm{HCl_2^-}] \approx \sqrt{(K_1K_2)}[\mathrm{HCl}]$$

and the equation for the rate of addition reduces to:

$$v_c = (k_a k_c/k_b)K_1K_2[\mathrm{Me_2C{=}CH_2}][\mathrm{HCl}]^2$$

This is in accord with experiment (section 1) where $K_1K_2k_ak_c/k_b$ = Constant = k_3.

4. *Effect of Added Chloride Ions.*—The addition of saline chloride was found to decrease the rate of addition of hydrogen chloride to isobutene, as predicted from the inequality $K_2 > K_1$. When hydrogen chloride is in excess, practically the entire amount of chloride ions initially supplied as tetraethylammonium chloride is transformed into hydrogen dichloride ions, $[\mathrm{HCl_2^-}] \approx [\mathrm{NEt_4Cl}]_0$. The amount of free hydrogen chloride is then no longer practically equal to the total amount of titratable acid but would be reduced accordingly:

$$[\mathrm{HCl}]_{\text{free}} = \{[\mathrm{HCl}]_t - [\mathrm{HCl_2^-}]\} \approx \{[\mathrm{HCl}]_t - [\mathrm{NEt_4Cl}]_0\}.$$

This leads to:

$$[\mathrm{H^+}][\mathrm{HCl_2^-}] \approx K_1K_2\{[\mathrm{HCl}]_t - [\mathrm{NEt_4Cl}]_0\}^2$$

and

$$v(\text{addition}) = v_c = K_1K_2(k_ak_c/k_b)[\mathrm{Me_2C{=}CH_2}]\{[\mathrm{HCl}]_t - [\mathrm{NEt_4Cl}]\}^2$$

Table 2 shows that rate coefficients evaluated in terms of the total amount of titratable hydrogen chloride are not constant. On the other hand, in the region $[\mathrm{HCl}]_t > [\mathrm{NEt_4Cl}]_0$ the rate of addition is fairly well represented by the equation:

$$v(\text{addition}) = k^{f}{}_3[\mathrm{Me_2C{=}CH_2}]\{[\mathrm{HCl}]_t - [\mathrm{NEt_4Cl}]_0\}^2$$

Indeed, $k^{f}{}_3$ is found to be roughly constant even when the ratio $[\mathrm{NEt_4Cl_0}]/[\mathrm{HCl}]_t$ is as high as 0·85. Further, the third-order rate coefficients evaluated in terms of free hydrogen chloride ($k^{f}{}_3$ in Table 2) are practically the same as those obtained in the absence of added saline chloride (k_3 in Table 1), and this supports the theoretical considerations whereby both these coefficients are in fact the product $K_1K_2k_ak_c/k_b$.

TABLE 2. *Initial second- and third-order rate coefficients of addition of hydrogen chloride to isobutene in the presence of tetraethylammonium chloride in nitromethane at 25·0° calculated in terms of both titratable and free acid.*

Titrable hydrogen chloride = $[\mathrm{HCl}]_t = a$.
Free hydrogen chloride = $[\mathrm{HCl}]_f = [\mathrm{HCl}]_t - [\mathrm{NEt_4Cl}]_0 = a_f$. $[\mathrm{Me_2C{=}CH_2}] = b$.

$$k_2 = \frac{2{\cdot}303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)} \qquad k_2{}^{f} = \frac{2{\cdot}303}{t(a_f-b)} \log_{10} \frac{b(a_f-x)}{a_f(b-x)} \qquad k_3 = k_2/a;\ k^f{}_3 = k^f{}_2/a_f.$$

$[\mathrm{Me_2C{=}CH_2}]$	[HCl]	$[\mathrm{NEt_4Cl}]$	10^3k_2 *	k_3 *	$10^3k_2{}^f$ *	$k_3{}^f$ *
0·00373	0·0279	0·00430	19·5	0·69	23·0	0·97
0·0988	0·0267	0·0116	8·4	0·315	14·9	0·987
0·00957	0·0231	0·0058	12·8	0·56	17·2	1·0
0·0109	0·0232	0·0043	14·8	0·64	18·2	0·963
0·0772	0·00985	0·00232	5·6	0·57	7·33	1·04
0·00963	0·01857	0·00215	13·0	0·69	15·4	0·94

* For a given run, the possible variation in these values resulting from the uncertainty in determination of initial slopes is about 6%.

EXPERIMENTAL

Materials.—Nitromethane was dried (P_2O_5), fractionated, and chromatographed as previously described.[5] It was also treated with concentrated sulphuric acid, dried ($CaSO_4$) for long periods, and fractionated through an all-glass, helix-packed column of about 20 theoretical plates, head and tail fractions being rejected; the middle fraction, b. p. 100·3—100·5°, n_D^{25} 1·3797, was used. Nitromethane purified by either of these methods gave practically the same rates of addition of hydrogen chloride (0·010M) to isobutene (0·005M) at 25·0°, k_3 (sec.$^{-1}$ l.^{2} mole^{-2}) being 0·98 and 1·00 with drying by phosphoric oxide and calcium sulphate respectively. Hydrogen chloride was generated by dropping concentrated sulphuric acid on to a paste made of ammonium chloride and concentrated hydrochloric acid, and dried by passage through concentrated sulphuric acid. Fresh solutions in nitromethane were prepared daily, because there is gradual disproportionation [6] (see hydroxylamine dihydrochloride below).

Isobutene was prepared by dehydrating t-butyl alcohol with anhydrous oxalic acid and purified by passage through an ice-cold trap and a calcium chloride tower before dissolution in nitromethane. These solutions were standardised at frequent intervals.

Tetraethylammonium chloride was purified as previously described.[4] Tetraethylammonium hydrogen dichloride was precipitated by concentrating and cooling a solution of tetraethylammonium chloride with an excess of hydrogen chloride in nitromethane. On titration in acetone with sodium methoxide it behaves as a monobasic acid to lacmoid (Found: *M*, 201; Cl^-, 34·8%. Calc. for $C_8H_{21}NCl_2$: *M*, 2023; Cl^-, 35·0%).

Pyridinium hydrogen dichloride was precipitated by concentrating and cooling a nitromethane solution of pyridine and >2 mols. of hydrogen chloride. On titration in acetone with sodium methoxide it behaves as a dibasic acid to lacmoid (pyridinium chloride behaves as a monobasic acid) (Found: *M*, 151; Cl^-, 46·0%. Calc. for $C_5H_7NCl_2$: *M*, 152; Cl^-, 46·6%).

Hydroxylamine dihydrochloride was obtained from concentrated solutions of hydrogen chloride in nitromethane left for one month at room temperature or heated for about 100 hr. in sealed bulbs at 75°. On titration in acetone with sodium methoxide it behaves as a monobasic acid to lacmoid (Found: *M*, 105; Cl^-, 66·0%. Calc. for H_5ONCl_2: *M*, 106; Cl^-, 67·0%).

Infrared Measurements.—The infrared spectrum of HCl_2^- has two important features:[10] the non-occurrence of the HCl frequency at 2840 cm.$^{-1}$, and the occurrence of a strong infrared band * at 1180 cm.$^{-1}$. Adding amounts of tetraethylammonium chloride to a freshly made solution of hydrogen chloride in nitromethane decreases the intensity of the 2840 cm.$^{-1}$ absorption but a strong band appears at 1180 cm.$^{-1}$. At the equivalence point the intensity of the 2840 cm.$^{-1}$ band is less than 5% of its original value, but the band at 1180 cm.$^{-1}$ has almost its full intensity. Addition of tetraethylammonium chloride beyond the equivalence point increases the band at 1180 cm.$^{-1}$ by no more than a few per cent. These measurements

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* The stretching vibration (1565 cm.$^{-1}$) for the hydrogen dichloride ion falls in the region of the broad band associated with the methyl deformation vibrations of the solvent molecule and is partly obscured.

[10] Waddington, *J.*, 1958, 1708; Sharp, *ibid.*, p. 2558.

show that, in a fresh solution in nitromethane, hydrogen chloride is largely in the form of undissociated molecules, so that the concentration of HCl_2^- can be only a few per cent. at the most. They also show that chloride ions remove hydrogen chloride molecules from solution by interacting with them to produce hydrogen dichloride ions.

Comparative measurements at 25·0° indicate that the addition of $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, and 1 equivalent of tetraethylammonium chloride depresses the partial vapour pressure of hydrogen chloride in nitromethane by about 24%, 49%, 73%, and 98% respectively.

Kinetic Measurements.—Aliquot parts (5 ml.) of reaction mixtures, prepared at 0°, were quickly introduced into a series of ampoules, cooled to −80°, sealed, and immersed in a bath at 25·0° ± 0·01°. At kinetic zero three ampoules were withdrawn, cooled to −80°, and used for the estimation of acid, olefin, and chloride ions severally. At intervals thereafter ampoules were withdrawn and acid, olefin, or chloride ions were determined. For the determination of acid the ampoule was broken under dry acetone (30 c.c.) at −80° and titrated with sodium methoxide (lacmoid). For the determination of chloride ions a solution, similarly prepared, was titrated potentiometrically with silver nitrate. For the determination of olefin the frozen ampoule was broken under an excess of bromine in acetic acid, in a stoppered flask. The stopper was held in firmly to prevent escape of gas. After complete reaction an excess of aqueous potassium iodide was added and the liberated iodine titrated with 0·01N-sodium thiosulphate (starch).

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William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1.

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