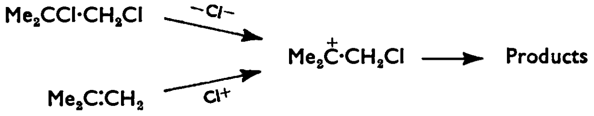
649. *The Kinetics and Mechanisms of Addition to Olefinic Substances. Part III.* The Carbonium Ionic Intermediate involved in Addition of Hypochlorous Acid to* iso*Butene.*

By P. B. D. DE LA MARE and ADIB SALAMA.

Addition of hypochlorous acid to *iso*butene in water gives mainly 1-chloro-2-methylpropan-2-ol; the chief olefinic by-product is 3-chloro-2-methylpropene. The latter olefin is also the predominant by-product in the hydrolysis in water of 1 : 2-dichloro-2-methylpropane. Evidence is presented to support the view that these reactions proceed in substantial part through a common carbonium ionic intermediate. The reaction of *iso*butyraldehyde with phosphorus pentachloride gives a mixture of 1 : 2- and 1 : 1-dichloro-2-methylpropane. The properties of the latter substance are properly established for the first time.

ALTHOUGH the properties and reactions of alkyl carbonium ions have received considerable study, little is established concerning halogen-substituted carbonium ions. These substances are commonly considered to be intermediates both in heterolytic (S_N1) nucleophilic displacements involving 1 : 2-dihalides, and in reactions of olefins with donors of electrophilic halogen. The unimolecular hydrolysis of 1 : 2-dichloro-2-methylpropane and the addition of hypochlorous acid to *iso*butene should both give the same carbonium ion, and therefore the two reactions, if carried out in the same environment, should, on this view, give the same products, provided that the carbonium ion has sufficient life in solution to enable it to attain its equilibrium conformation before reaction is completed :



It is difficult to be sure, by study of the literature, what are the primary products of hydrolysis of 1 : 2-dichloro-2-methylpropane. It is known to be possible to obtain 1-chloro-2-methylpropan-2-ol in up to about 50% yield by direct hydrolysis at 70—80°, the solution being kept neutral or very slightly alkaline during the process.[1] More prolonged hydrolysis, with potassium carbonate, is known to carry the reaction through to 2-methylpropane-1 : 2-diol,[2] and, when sodium hydrogen carbonate is used, the main olefinic by-product is stated to be 1-chloro-2-methylpropene.[3] There have been various reports that, under some conditions, hydrolysis of this dichloride can give *iso*butyraldehyde. The formation [4] of the latter substance during the catalytic hydrolysis of 1 : 2-dichloro-2-methylpropane

---

* Part II, *J.*, 1954, 3990.

[1] Sparks and Nelson, *J. Amer. Chem. Soc.*, 1936, **58**, 1010.

[2] Pogorshelski, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1129 (*Chem. Zentr.*, 1905, **76**, I, 667).

[3] Dobryanski, Gutner, and Shchigelskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1937, **7**, 1315 (*Chem. Abs.*, 1937, **31**, 6189).

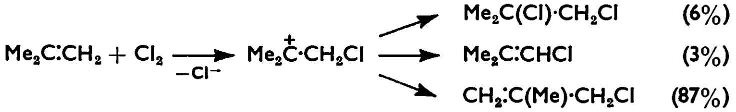
[4] Hersh and Nelson, *J. Amer. Chem. Soc.*, 1936, **58**, 1631.

in the vapour phase at 350° could reasonably be attributed to rearrangement of the chlorohydrin [5] or diol [6] formed initially by direct hydrolysis; and this seems also to be the view adopted [4] in regard to the hydrolysis in the liquid phase at temperatures below 100°, which is reported [4, 7] also to give *iso*butyraldehyde.

A number of workers have recorded [8, 9] that addition of hypochlorous acid, or of chlorine water, to *iso*butene gives, in yields of 50% and upwards, the α-chlorohydrin, 1-chloro-2-methylpropan-2-ol. Michael and Leighton [9] obtained also, as a by-product in this reaction, a dichloro-*tert.*-butyl alcohol, which they considered to be formed by direct chlorination of the chlorohydrin.

Chlorination of gaseous *iso*butene with gaseous chlorine has been the subject of considerable enquiry. The main reaction is a substitution, and the main olefinic product is 3-chloro-2-methylpropene.[10] The reaction, as it is ordinarily carried out, appears to proceed in a liquid film formed by the products of the reaction, or on the surface of a catalyst if one is provided. Under conditions favourable for the minimisation of secondary reactions, the product-composition is as follows: 3-chloro-2-methylpropene, 87%; 1-chloro-2-methylpropene, 3%; 1 : 2-dichloro-2-methylpropane, 6%; and secondary products, 4%. Reeve, Chambers, and Prickett [11] have shown, by labelling $C_{(1)}$ of *iso*butene with ^{14}C, allowing chlorination to take place, and examining the position of labelling in the resulting 3-chloro-2-methylpropene, that most of the entering chlorine is attached, in the latter product, to what was $C_{(1)}$ in the original olefin.

It has generally been considered, therefore,[12] that this type of substitutive chlorination of olefins involves a carbonium ionic intermediate, which can undergo further reaction in a variety of ways, *e.g.*:



This scheme does not, however, appear to provide an adequate explanation of the preponderance of allylic over vinylic chloride in the product. A statistical factor of 3 : 1 should, it is true, favour the former product; but there seems to be no reason why the product ratio should exceed this value. The assumption made by Taft,[12] that the proton will be lost preferentially from the carbon atom which is the most electron-rich, because the double bond will be formed preferentially between the carbonium centre and the most electron-rich carbon atom, seems to the authors as is developed later, to neglect proper consideration of the availability of electrons in the transition state for decomposition of the carbonium ion. Synchronous mechanisms of a cyclic [13] or non-cyclic [14] type have been proposed, and avoid the above difficulty, but the former is of a kind not commonly encountered in reactions of olefinic substances with halogens, even in systems favourable to its operation; [15] and the latter, though a formal possibility, certainly needs further evidence before it could be accepted.

The purpose of the present investigation has been to examine the addition in water of hypochlorous acid to *iso*butene under conditions in which it could reasonably be assumed that a carbonium ionic intermediate is formed, giving particular attention to the products of elimination from the carbonium ion. The kinetics and mechanism of the hydrolysis,

---

[5] Harvey, Riggs, and Stimson, *J.*, 1955, 3267.

[6] Nevole, *Ber.*, 1876, **9**, 448.

[7] Groll and Kautter, U.S.P. 2,042,225; *Chem. Abs.*, 1936, **30**, 4872; Newlin, Thesis, Purdue Univ., 1932, see ref. 4.

[8] Henry, *Compt. rend.*, 1906, **142**, 494; *Rec. Trav. chim.*, 1907, **26**, 142; Krassusky, *J. prakt. Chem.*, 1907, **75**, 238; Moureau and Dode, *Bull. Soc. chim. France*, 1937, **4**, 286.

[9] Michael and Leighton, *Ber.*, 1906, **39**, 2157.

[10] Burgin, Engs, Groll, and Hearne, *Ind. Eng. Chem.*, 1939, **31**, 1413.

[11] Reeve, Chambers, and Prickett, *J. Amer. Chem. Soc.*, 1952, **74**, 5369.

[12] Taft, *ibid.*, 1948, **70**, 3364.

[13] Arnold and Lee, *ibid.*, 1953, **75**, 5396.

[14] Turner and Harris, " Organic Chemistry," Longmans Green & Co., London, 1952, p. 166.

[15] Mislow and Hellman, *J. Amer. Chem. Soc.*, 1951, **73**, 244.

in water, of 1 : 2-dichloro-2-methylpropane, have also been studied in order to establish whether the carbonium ion from this dichloride undergoes elimination to give the same mixture of olefins. To be certain that *iso*butyraldehyde is not a primary product of this reaction, it has proved necessary to establish the properties of 1 : 1-dichloro-2-methylpropane.

EXPERIMENTAL

(a) 1 : 1-*Dichloro-2-methylpropane.*—1 : 1-Dichloro-2-methylpropane is formed, together with other products, in the gas-phase chlorination of *iso*butane or *iso*butyl chloride; [16, 17] but it is difficult to separate this compound from its isomer, 1 : 2-dichloro-2-methylpropane, which is also formed in the same reaction. The only other method which has been used in the preparation of this *gem.*-dichloride is the reaction between *iso*butyraldehyde and phosphorus pentachloride.[18] In the present work, best yields of crude dichloride were obtained in the following way. *iso*Butyraldehyde (100 g.) was added gradually to powdered phosphorus pentachloride (350 g.) with stirring, at $<0°$. The mixture was left overnight at room temperature; it was then added gradually to ice-cold water. Extraction with pentane, followed by fractionation, gave an oil (48 g.), b. p. 102—115°/764 mm., n_D^{25} 1·4323. The following shows the rate of development of acid from this material. Samples (*ca.* 0·04 g.) were weighed into ampoules which were then cooled to $-80°$. Water (50 ml.; sufficient to form a homogeneous solution at the temperature of the reaction) was added, and the ampoules were sealed and placed in a thermostat at 45°; after appropriate times the ampoules were opened, and the contents were titrated with standard alkali to methyl-red.

Time (hours)	2·0	6·0	12·0	24·0	72·0	96·0
Total Cl (%) hydrolysed	1·6	5·1	6·6	15·0	22·0	22·4

It can be seen that reaction had nearly ceased when 22% of chlorine had been liberated from the chloride. The rate of liberation of chloride was such that it was suspected that the reaction mixture contained also 1 : 2-dichloro-2-methylpropane. Hence the mixture of chlorides (95 g., from two such experiments) was mechanically stirred with 3·5 l. of water at 45°. Samples of the clear aqueous layer were removed at intervals for titration with alkali. When the initial hydrolysis was nearly complete (after *ca.* 35 days), the material was cooled and extracted with pentane. The pentane extract was washed with sodium hydrogen carbonate solution, then with water, dried (Na_2SO_4), and carefully fractionated. There were obtained 6 g. of material, b. p. 108—110°/763 mm.,* n_D^{25} 1·4330 (Found: C, 37·9; H, 6·4. Calc. for $C_4H_8Cl_2$: C, 37·8; H, 6·35%). This material hydrolysed negligibly slowly in water at 45° (less than 1% in 45 hr.). At 100°, hydrolysis occurred slowly, and after 100 hr., the aqueous product gave with 2 : 4-dinitrophenylhydrazine a crystalline precipitate, in 30% yield based on the weight of dichloride taken. The precipitate, after crystallisation from aqueous ethanol, had m. p. 179°, and did not depress the m. p. of *iso*butyraldehyde 2 : 4-dinitrophenylhydrazone, m. p. 178—179°.

Reaction of *iso*butyraldehyde with phosphorus pentachloride in *m*-xylene gave smaller yields (*ca.* 15%) of a similar mixture of dichlorides. Reaction in pyridine gave negligible yields. The aqueous layer obtained in the above experiment after partial hydrolysis of the mixture of dichlorides was, after extraction with pentane as described, saturated with sodium chloride and extracted with ether. The ether-extract was washed with water, dried (Na_2SO_4), and fractionally distilled. There were obtained 17 g. of oil, b. p. 126·5°/761 mm., n_D^{25} 1·4368 (Found: C, 44·8; H, 8·4; Cl, 32·4. Calc. for C_4H_9OCl: C, 44·3; H, 8·4; Cl, 32·7%). This was therefore 1-chloro-2-methylpropan-2-ol derived from the 1 : 2-dichloro-2-methylpropane; an authentic specimen prepared by Henry's method [8] from methylmagnesium bromide and ethyl monochloroacetate had b. p. 70—71°/100 mm., 126°/760 mm., n_D^{25} 1·4366.

(b) *Hydrolysis of* 1 : 2-*Dichloro-2-methylpropane.*—(i) *Kinetics of liberation of acid.* 1 : 2-Dichloro-2-methylpropane was prepared as described by Rogers and Nelson [19] by the photochemical chlorination of *tert.*-butyl chloride. Careful fractionation gave a product, b. p. 59—60°/151 mm., 106°/760 mm., n_D^{25} 1·4346. A sample prepared by McBride and Beachell's

---

* Thus this dichloride actually has a b. p. higher than that of the 1 : 2-isomer.

[16] Hass, McBee, and Weber, *Ind. Eng. Chem.*, 1935, **27**, 1190.

[17] Hass and McBee, U.S.P. 2,004,072.

[18] Oeconomides, *Bull. Soc. chim. France*, 1881, **35**, 498.

[19] Rogers and Nelson, *J. Amer. Chem. Soc.*, 1936, **58**, 1028.

method[20] was kindly given to us by Mr. J. B. Ley for comparison, and was found to have identical properties and rate of hydrolysis.

The following results show the rate of hydrolysis of this dichloride in initially neutral solution. The technique has already been described. Values of the first-order velocity coefficients, here and elsewhere except where otherwise stated, have been calculated by using the formula $k_1 = 2{\cdot}303 \log_{10} \{a/(a - x)\}/t$, where a is the initial *molarity* of organic chloride and x is the molarity of chloride released at time t. Initial values, therefore, represent the initial rate of production of the first equivalent of chloride.

Time (min.)	120	240	480	720	960	1200	1680	2160	2400	2640
Total Cl (%) hydrolysed	5·1	9·6	18·9	24·8	31·6	36·4	43·2	48·1	45·1	48·4
10^3k_1 (min.$^{-1}$)†	0·90	0·89	0·99	0·95	1·04	1·08	1·18	1·51	0·97	1·30

The initial rate-coefficient at 45° is, therefore, $0{\cdot}90 \times 10^{-3}$ min.$^{-1}$; it rises gradually through the course of the reaction, since, as will be seen below, the products gradually undergo further reaction, liberating finally rather more than one equivalent of chloride.

The following shows the course taken by the hydrolysis in initially alkaline solution, with 0·0048M-dichloride and 0·0048M-sodium hydroxide. The reaction was followed by titration with standard acid until 50% of the total chlorine in the dichloride had been liberated; then by titration with standard alkali.

Time (min.)	120	240	360	480	840	960	1080	1440	2160	3840	4320
Total Cl (%) hydrolysed	7·7	16·5	24·4	32·1	46·4	48·9	54·5	61·5	66·3	70·9	70·9
10^3k_1 (min.$^{-1}$)†	0·73	0·82	0·86	0·89	0·84	0·79	—	—	—	—	—

The rate-coefficient, at 45°, has the mean value * $k_1 = 0{\cdot}82 \times 10^{-3}$ min.$^{-1}$; reaction proceeds substantially beyond the liberation of one equivalent of chloride.

(ii) *The liberation of olefin.* This was followed in the following way. Ampoules containing 75 ml. of the reaction mixture were removed from the thermostat and cooled. Portions (10 ml.) were removed for titration with standard alkali. To the remainder was added excess of aqueous bromine solution (*ca.* 0·02N in sodium bromide solution). The mixture was shaken and left for 1 hr., and was then treated with excess of potassium iodide and titrated with standard sodium thiosulphate solution to sodium–starch glycollate. Blank experiments showed that under these conditions neither 1 : 2-dichloro-2-methylpropane nor 1-chloro-2-methylpropan-2-ol consumed bromine; and that both 3- and 1-chloro-2-methylpropene reacted rapidly with bromine. The following are the results.

Time (min.)	360	900	1440	2880	4320	4820	12,960
Dichloride (g.) in 75 ml.	0·1164	0·1398	0·1282	0·1168	0·1416	0·1428	0·1459
Titre (ml. of 0·0358N-NaOH = 10 ml. of reactants)	1·00	2·25	2·80	3·65	4·50	4·70	4·95
Titre (ml. of 0·0101N-$Na_2S_2O_3$ = 65 ml. of reactants)	7·15	17·1	20·8	26·8	32·2	32·6	27·2
Total Cl hydrolysed (%)	14·3	26·7	36·3	51·8	52·7	54·6	56·3
Total olefin formed (%)	4·55	9·04	12·0	17·0	16·8	16·8	13·8
Ratio olefin/Cl^-	0·32	0·34	0·33	0·33	0·32	0·31	0·25

The gradual decrease in proportion of olefin towards the end of the reaction is the result, presumably, of slow hydration of this material under the acidic conditions prevailing.

(iii) *Estimation of* 3-*chloro*-2-*methylpropene in the olefinic mixture.* This allylic chloride is hydrolysed in water at a rate similar to that of 1 : 2-dichloro-2-methylpropane, as is shown by the following results, obtained at 45° by a technique similar to that described above.

Time (min.)	60	120	240	480	720	960	1200	1440	1680	1920	2400
Hydrolysis (%)	5·9	12·6	20·6	33·6	47·2	57·2	58·7	69·5	74·5	77·8	83·6
10^4k_1 (min.$^{-1}$)	10·1	11·2	9·6	8·5	8·9	8·8	7·4	8·2	8·1	7·8	7·5

The results are rather less satisfactory than those obtained for the dichloride, probably because the lower boiling point of the former chloride had the result that an appreciable fraction

---

* These values are obtained by assuming that two equivalents of chloride are released for each mole of dichloride which forms chlorohydrin (84%) and one equivalent for the remainder; for the chlorohydrin, but not the other products, will react instantaneously to liberate a further mole of hydrogen chloride. Hence the theoretical infinity value should correspond with the liberation of $(2 \times 84 + 16)/2 = 92\%$ of chloride from the dichloride.

[20] McBride and Beachell, *J. Amer. Chem. Soc.*, 1948, **70**, 2532.

of the material was always in the vapour phase. The initial rate-coefficient ($1{\cdot}0 \times 10^{-3}$ min.$^{-1}$ at 45°) is, however, considered to be correct to within 10%. The product of the reaction must be 2-methylprop-2-en-1-ol, and this is not extracted from aqueous solution by pentane, whereas the vinylic chloride (1-chloro-2-methylpropene), also produced in the hydrolysis of 1 : 2-dichloro-2-methylpropane, is not hydrolysed by water and is extracted quantitatively from water by pentane. The following method was used, therefore, for estimation of the ratio of isomeric olefins produced in the hydrolysis of 1 : 2-dichloro-2-methylpropane. Reaction was allowed to proceed, as described above, for 115 hr., which was sufficiently long to ensure complete hydrolysis of the dichloride, and substantially complete (more than 95%) hydrolysis of the 3-chloro-2-methylprop-1-ene formed in the reaction, and was not too long for any significant destruction of olefin by acid-catalysed hydration. The mixture was then cooled and extracted three times with pentane. The pentane extracts were washed three times with a little water. The residual aqueous solution and the aqueous washings were separately treated with excess of standard bromine solution, and the olefin was determined in them as described above. Blank experiments showed (*a*) that, with 3-chloro-2-methylpropene after this treatment for 72 hr., 95% of olefinic material was in the aqueous fractions; and (*b*) that with 1-chloro-2-methylpropene, no olefinic material remained in the aqueous solution after extraction with pentane. The following are results of a typical experiment. The water-soluble olefinic material in the aqueous residue and washings, after treatment of 0·0810 g. of 1 : 2-dichloro-2-methylpropane with water at 45° for 115 hr., used up bromine equivalent to 12·7 ml. of 0·0102N-sodium thiosulphate. Hence there was produced in the reaction 10·2% of 3-chloro-2-methylpropene. The remainder of the olefinic material, being unhydrolysed by water and extracted from water by pentane, is presumably 1-chloro-2-methylpropene.

A similar technique was used for the estimation of 2-methylprop-2-en-1-ol in the olefinic product obtained in alkaline solution. In this case, reaction with 0·1N-sodium hydroxide was complete in 45 hr., and the percentage of total olefinic material in the aqueous hydrolysate was 34%, calculated on the weight of dichloride taken. This value was reduced to 6·2% when the aqueous solution had first been extracted with pentane to remove 1-chloro-2-methylprop-1-ene.

(iv) *Estimation of* iso*butyraldehyde.* 1 : 2-Dichloro-2-methylpropane (1·7 g.) was dissolved in 3 l. of an aqueous solution of 2 : 4-dinitrophenylhydrazine (0·03% in 0·7N-hydrochloric acid). The solution was kept at 45° for 48 hr. After cooling, filtration gave 0·06 g. of a yellow precipitate, which, after crystallisation from dilute ethanol, had m. p. 175° and did not depress the m. p. of an authentic specimen of *iso*butyraldehyde 2 : 4-dinitrophenylhydrazone, m. p. 178—179°. The maximum amount of *iso*butyraldehyde obtained under these strongly acidic conditions is therefore 1·7%, and this material is probably derived (cf. ref. 4) from the acid-catalysed rearrangement of one of the products of reaction. Under less strongly acidic conditions, *iso*butyraldehyde appears to be absent from the products of hydrolysis. We are indebted to Mr. J. B. Ley for polarographic examination of aqueous solutions obtained by heating 1 : 2-dichloro-2-methylpropane (1 g.) with 1 l. of water at 45° for up to 200 hr. No *iso*butyraldehyde was detected at any stage in the hydrolysis.

(v) *Isolation of 1-chloro-2-methylpropan-2-ol.* In a 100 l. flask provided with a stirrer and a glass-jacketed immersion heater, 50 g. of 1 : 2-dichloro-2-methylpropane were stirred with 90 l. of water for 48 hr., the temperature being maintained at 45° ± 2°. The mixture was cooled to room temperature. Air was bubbled through the solution, dried by passage through calcium chloride, and passed through traps cooled in liquid air; no volatile material was condensed. The solution was saturated with ether and then with sodium sulphate. The ether layer was removed, and the aqueous solution was further extracted with 20 l. of ether. The combined ether extracts were dried (Na_2SO_4) and fractionated, giving 23 g. (*ca.* 56% yield) of crude product, b. p. 63—72°/101 mm., of which a middle fraction (10 g.) had the following properties: b. p. 71—72°/101 mm., n_D^{25} 1·4367 (Found: C, 44·1; H, 8·4; Cl, 32·8. Calc. for C_4H_9OCl: C, 44·3; H, 8·4; Cl, 32·7%).

The rate of hydrolysis of this material was followed in alkaline solution. Known volumes of solutions of the chlorohydrin and of sodium hydroxide were mixed at 0°, and 5 ml. samples were pipetted at intervals into chilled acetone containing excess of standard hydrochloric acid, and were then back-titrated with alcoholic sodium hydroxide to lacmoid. Under these conditions the end-point was stable, and the product (*iso*butene oxide) did not react with the quenching acid. For initial concentrations of chlorohydrin and alkali respectively 0·03186N and 0·07066N, the second-order rate-coefficient (mean, 10·6 l. mole^{-1} min.$^{-1}$) was substantially constant over 80% reaction. The experimental titration at completion of the reaction agreed with that calculated within 5%. This rate-coefficient is almost identical with that (10·7

l. mole^{-1} min.$^{-1}$) obtained independently by Mr. P. Ballinger in these laboratories using a sample of authentic 1-chloro-2-methylpropan-2-ol, b. p. 70—71°/100 mm., 126°/760 mm., n_D^{25} 1·4366, prepared by one of us (A. S.) from the reaction of ethyl monochloroacetate with methylmagnesium bromide as described by Henry.[8]

The fractions of lower b. p. contained olefinic substances, but we did not succeed in isolating a pure material from these.

(c) *Addition of Hypochlorous Acid to* iso*Butene.*—(i) *Isolation of* 1-*chloro*-2-*methylpropan*-2-*ol. iso*Butene was bubbled into *ca.* 80 l. of water maintained at 45° ± 2°. Standardised aqueous hypochlorous acid (2 l.; *ca.* 0·2M) was added at such a rate that the concentration of hypochlorous acid was always below 0·001M. After completion of the reaction, the products were isolated as described above. Fractionation gave an unsaturated fraction (2·4 g.), b. p. 40—122°, n_D^{25} 1·4135, followed by a main fraction (27 g.), b. p. 123—125°/755 mm., n_D^{25} 1·4367. Refractionation of this gave a material, b. p. 125—126°, n_D^{25} 1·4361; there was no sign of the presence of any material of higher b. p.

The mean rate-coefficient for the reaction of this material (0·03089N) with sodium hydroxide (0·07066N) at 0° was 10·6 l. mole^{-1} min.$^{-1}$, in good agreement with that recorded above for material obtained by hydrolysis of 1 : 2-dichloro-2-methylpropane.

(ii) *Estimation of* 3-*chloro*-2-*methylpropene.* Excess of *iso*butene, in a fragile bulb, was placed in a Pyrex tube containing 500 ml. of standardised dilute aqueous hypochlorous acid (*ca.* 0·001M). The tube was sealed, and the bulb was broken by shaking. The tube was placed in a thermostat at 45° for *ca.* 120 hr., to ensure hydrolysis of any 3-chloro-2-methylpropene. The reaction mixture was then cooled to room temperature and extracted three times with pentane, to remove both excess of *iso*butene and any 1-chloro-2-methylpropene. Olefinic material was then estimated in the aqueous residue, by the method described above. The mean of three values for the percentage of 3-chloro-2-methylpropene, based on the amount of hypochlorous acid consumed, was 11·7%.

The above method could not conveniently be used for determination of 1-chloro-2-methylpropene; and it was considered desirable to obtain an independent estimation of 3-chloro-2-methylpropene. The following method, involving isotopic dilution, was adopted. Aqueous hypochlorous acid enriched with radioactive chlorine was prepared by adding N-$H^{36}Cl$ (7 ml.; activity 15 microcuries) to 70 ml. of 0·27M-hypochlorous acid. A portion was retained for reference. It had a specific activity of 2·38 × 10^5 (units : counts per min./concn.); this figure represents the result of determining in a Geiger tube, used for all the measurements recorded in this paper, the number of counts per minute (in this case, 766) corrected for the small background, of a solution of known concentration (in this case, 0·00321M). *iso*Butene was bubbled into water (5 l.) in a flask fitted with a ground-glass precision stirrer and a tap-funnel. It was then warmed to 45°; a sample contained *ca.* 0·003M-olefin, as measured by titration with standard bromine solution. A slow stream of *iso*butene was bubbled through this aqueous solution, to ensure an excess of this material, while 50 ml. of 0·26M-$HO^{36}Cl$ solution were added at such a rate that the concentration of hypochlorous acid did not exceed 0·001M. The reaction mixture was, after completion of the reaction, cooled to 0°. A mixture of 10·38 g. of pure inactive 3-chloro-2-methylpropene and 11·89 g. of 1-chloro-2-methylpropene dissolved in ethanol (150 ml.) was added, and stirred with the aqueous solution of the products for 3 hr. to ensure complete mixing of the materials. It was then extracted with pentane (1·6 l.). The pentane extract was dried (Na_2SO_4) and fractionally distilled, giving a fraction, F_1 (4·3 g.), b. p. 65—73°/764 mm., n_D^{25} 1·4142 (hydrolysable Cl, 38·1%; specific activity, 1511). This was a mixture of the isomeric 1- and 3-chloro-2-methylpropenes, containing also a trace of 1-chloro-2-methylpropan-2-ol, and separate portions were treated in the following ways: (*A*) Fraction F_1 (2·97 g.) was heated at 45° for 17 hr. with 55 ml. of N-sodium ethoxide. Water was then added, and the mixture was extracted with pentane. The sodium chloride recovered from the residue had specific activity 3075; this gives a slightly high estimate of the specific activity of the 3-chloro-2-methylpropene, since it contains a little chloride derived from 1-chloro-2-methylpropan-2-ol. The pentane extract was dried and fractionated; there were recovered 1·03 g., b. p. 68—75°, n_D^{25} 1·4050 (hydrolysable Cl, 5·7; total Cl, 21·4%; specific activity, 386 based on total Cl). (*B*) Fraction F_1 (1·21 g.) was refluxed in 75% ethanol containing 0·1N-sodium hydroxide (5 ml.) for 1 hr., and the mixture was then distilled. The residue of sodium chloride (R_1) had specific activity 9038; this high value results from the presence of a trace of the main product of the reaction, 3-chloro-2-methylpropan-2-ol, which, being undiluted, has very high specific activity. The distillate, from which this material had now been removed completely, was refluxed with alkali, added in 1 ml. portions (sufficient to keep the mixture continually alkaline to lacmoid added as indicator) for *ca.* 6 hr., and the mixture was then again distilled. The residue of sodium chloride, R_2, had specific activity 2863. The distillate was treated again in a similar way, and the residue, R_3, had specific activity 2760. Thus the chloride released on hydrolysis in residues R_2 and R_3 was of uniform specific activity, within the limits of experimental and statistical error, and it is assumed that this represents the specific activity of the diluted 3-chloro-2-methylpropene.

From the given specific activities, the weights of diluting materials added, and the amount of hypochlorous acid used in the reaction, the percentage of 3-chloro-2-methylpropene can be calculated as 11·9%, in good agreement with the value obtained by another method under slightly different conditions of reaction. It is clear that very much less of the isomer, 1-chloro-2-methylpropene, is produced in the reaction, since the specific activity of the organic chloride recovered in experiment (A) is very small. When corrected for the presence of hydrolysable chlorine of specific activity 2800, the amount of vinylic chloride formed in the reaction is not greater than 0·4%.

DISCUSSION

Products of Hydrolysis of 1 : 2-*Dichloro-2-methylpropane.*—The above experiments confirm that *iso*butyraldehyde is not formed in any appreciable extent as a primary product of the hydrolysis of 1 : 2-dichloro-2-methylpropane. It can also be concluded that only the tertiary chlorine atom is concerned in the main reaction; for any hydrolysis of the primary chloride atom would give a chlorohydrin, 2-chloro-2-methylpropan-1-ol, which is known[21] to be hydrolysed very rapidly under the conditions used in the present work. In the present experiments, the course and extent of hydrolysis are quantitatively accounted for, within the experimental error, by the following scheme, in which the rate-coefficient k_1' is estimated by extrapolation, to lower temperatures, of values given by Harvey, Riggs, and Stimson.[5]

$$\mathrm{Me_2CCl{\cdot}CH_2Cl} \xrightarrow{k_1} \left\{\begin{array}{lcl} \mathrm{Me_2C(OH){\cdot}CH_2Cl}\ (84\%) & \xrightarrow{k_1'} & \mathrm{Me_2C(OH){\cdot}CH_2{\cdot}OH} \\ \mathrm{Me_2C{:}CHCl}\ (6\%) & & \\ \mathrm{CH_2Cl{\cdot}CMe{:}CH_2}\ (10\%) & \xrightarrow{k_1''} & \mathrm{CH_2(OH){\cdot}CMe{:}CH_2} \end{array}\right.$$

$$k_1 = 0{\cdot}9 \times 10^{-3}\ \text{min.}^{-1}. \quad k_1' = 0{\cdot}003 \times 10^{-3}\ \text{min.}^{-1}. \quad k_1'' = 1{\cdot}0 \times 10^{-3}\ \text{min.}^{-1}.$$

This scheme requires that the liberation of chlorine from the dichloride (the very slow hydrolysis of the α-chlorohydrin being neglected) should be 55%, and therefore that the values of the first-order rate coefficients, calculated on the liberation of one equivalent of chlorine per mole of dichloride, should rise through the course of the reaction. The very slow[5] hydrolysis of the chlorohydrin accounts for the very slow further increase in the liberation of chloride, and in part for the ultimate formation of 2-methylpropane-1 : 2-diol recorded by Pogorshelski.[2]

Considering first the main product of reaction, 1-chloro-2-methylpropan-2-ol, there is no doubt whatever that this compound is produced in a unimolecular (S_N1) process. The initial rate of hydrolysis is not accelerated by added alkali, so that the main product must be formed in a stage in which the concentration of nucleophilic reagent is not contributing to the rate-equation; this is diagnostic of reaction by the S_N1 mechanism. In any case, so rapid a bimolecular formation of this compound from the dichloride at such moderate temperatures would be extremely improbable in this compound for steric reasons.[22]

Considering now the main olefinic product, 3-chloro-2-methylpropene, the evidence is very strong that this compound is also produced in a unimolecular process, rather than by a bimolecular ($E2$) elimination. For reactions of this compound under conditions favourable to bimolecular processes[23] give the isomeric vinylic halide, 1-chloro-2-methylpropene, which is also, as the present work shows, formed in predominant amount in alkaline solution in water.

It is clear that the vinylic olefin produced in these reactions (1-chloro-2-methylpropene)

---

[21] Nilsson and Smith, *Z. phys. Chem.*, 1933, **166**, *A*, 143.

[22] Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173.

[23] Mouneyrat, *Ann. Chim.* (*France*), 1900, **20**, 533.

is obtained, in alkaline solution, as the result of a bimolecular ($E2$) elimination; as is also, presumably, the case in the experiments recorded by Dobryanski *et al.*,[3] who used aqueous sodium carbonate and sodium hydrogen carbonate solutions. The situation in regard to the mechanism of production of this olefinic chloride by hydrolysis in initially neutral aqueous solution cannot, however, be determined through the experiments so far discussed. It seems possible, from comparison with the orientation observed in the addition of hypochlorous acid to 2-methylpropene, that this vinylic halide, is, in part, produced in neutral or acid conditions by a bimolecular ($E2$) attack of water on the dichloride.

Two subsidary points require discussion. The first refers to the slow fall-off in measured percentage of 3-chloro-2-methylpropene on prolonged heating of the reaction mixture, as shown in the data on p. 3340. This almost certainly results from the slow acid-catalysed hydration of 3-chloro-2-methylpropene. Independent estimations, by Mr. J. B. Ley in these laboratories, of the rate of the latter process at higher temperatures, are consistent with this hypothesis; the effect is not sufficiently great to affect seriously the determination of this olefin in the reaction mixture for the first 100 hours of reaction.

The second point concerns the slight reduction in rate found when the hydrolysis of the dichloride is carried out in the presence of alkali, allowance having been made in the calculation for the instantaneous alkaline hydrolysis of the chlorohydrin. The effect is very near the limit of experimental error, but, if real, may be related to the similar reductions in rate which have been reported in the past for other systems,[24] though no comparative data have been recorded, as far as we are aware, for pure water as solvent.

Addition to iso*Butene.*—The addition of hypochlorous acid to 2-methylpropene is too rapid for kinetic examination; but the aqueous conditions used in the present work are extremely favourable for the formation of a carbonium ion; and it is assumed, by analogy with the situation which is generally accepted [25, 26] for additions to other olefinic compounds, that, in the present case, attack by the hypochlorous acidium ion, H_2OCl^+, or possibly by chlorine when hydrogen chloride was present in the reaction mixture, resulted in the formation of a carbonium ion, $Me_2\overset{+}{C}{\cdot}CH_2Cl$.

No evidence has been found for the occurrence of any 1 : 2-shift in the further reactions of this ion. Thus 1 : 2-shift of hydrogen, giving $Me_2CH{\cdot}\overset{+}{C}HCl$, would result in the formation of *iso*butyraldehyde, which was not detected in the products of addition; 1 : 2-shift of hydrogen giving $^+CH_2{\cdot}CHMe{\cdot}CH_2Cl$ would result in the formation of 3-chloro-2-methylpropan-1-ol, whereas this compound has [27] b. p. 76—78°/21 mm., n_D^{25} 1·4460, both considerably higher than those (b. p. 71°/100 mm., n_D^{25} 1·4367) of the chlorohydrin actually produced in the reaction; and a 1 : 2-shift of chlorine would result in the formation of 2-chloro-2-methylpropan-1-ol, which is known [28] not to be produced in this reaction.

The proportion of 3-chloro-2-methylpropene, relative to the total amount of hypochlorous acid undergoing reaction, has been estimated by two methods; first, from the amount of olefinic material hydrolysable to an olefin not extracted by pentane from water, and, secondly, by isotopic dilution. The results (11·7 and 11·9% respectively) are in concordance which is probably better than the experimental reliability of the methods; they accord fairly well also with the value (10%) obtained in the hydrolysis of 1 : 2-dichloro-2-methylpropane, and this agreement would be improved if allowance were made in the latter case for the extra accompanying alternative elimination. The dichloro-*tert.*-butyl alcohol obtained in small yield by Michael and Leighton [9] is probably, therefore, 1 : 3-dichloro-2-methylpropan-2-ol, formed by addition of hypochlorous acid to 3-chloro-2-methylpropene.

The proportion of 1-chloro-2-methylpropene has been determined by isotopic dilution as being *ca.* 0·4%. This value cannot be considered very reliable, but is a maximum figure. If the determined value is accepted, then the ratio of vinylic to allylic chloride

---

[24] Lucas and Hammett, *J. Amer. Chem. Soc.*, 1942, **64**, 1928; Benfey, Hughes, and Ingold, *J.*, 1952, 2494.

[25] Cf. Gwyn Williams, *Trans. Faraday Soc.*, 1941, **37**, 749.

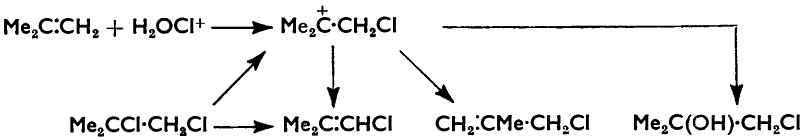
[26] Cf. de la Mare and Pritchard, *J.*, 1954, 3910, 3990.

[27] Waddle and Adkins, *J. Amer. Chem. Soc.*, 1939, **61**, 3361.

[28] Smith and Skyle, *Acta Chim. Scand.*, 1951, **5**, 1415.

formed in the ionising conditions of the present experiments is 1 : 30, in good agreement with that recorded (1 : 29) for the low-temperature chlorination of *iso*butene by chlorine under non-hydrolytic conditions.

The following scheme, therefore, represents, in our view, the reaction in water of *iso*butene with hypochlorous acid, and the hydrolysis of 1 : 2-dichloro-2-methylpropane, at 45° :



In hydrolysis	6·0% ($E_2 + E_1$)	10% ($E1$)	84% (S_N1)
In addition	0·4%	12%	87·6%

If the carbonium ion, $Me_2\overset{+}{C}{\cdot}CH_2Cl$, had the structure implied by this formulation, it seems likely that the direction of elimination would be controlled by factors analogous to those which control orientation in elimination from alkyl carbonium ions. Hughes, Ingold, and their co-workers [29] have established that electromeric effects of substituents control the orientation almost exclusively in such eliminations: the presence of alkyl groups which can hyperconjugate with either end of the developing double bond promotes the elimination.

In the present example, the inductive effect of the chlorine substituent must increase the ease of separation of the proton, other things being equal; and the electromeric effect of the chlorine substituent must increase the ease of double-bond formation between the attached carbon atom and the neighbouring carbonium ionic centre. Both these effects should combine * in making the formation of 1-chloro-2-methylpropene preferred, and, since this result is not found experimentally, it seems that some alternative explanation is called for.

In writing the structure of such a carbonium ion in the simple way so far adopted, one important feature of the structure has been neglected, namely, the possibility of interaction between the carbonium ionic centre and the halogen. Interaction in this way was first proposed by Roberts and Kimball,[30] and the principle has been developed extensively of recent years, particularly by Winstein and his co-workers,[31] to give accounts of stereochemical and kinetic facts observed in reactions which involve carbonium ions of this type. For the present argument, it is irrelevant whether the structures are written in the " chloronium " form,[30, 31] as in formula (I), in which the two carbon atoms are considered to be essentially bonded equivalently to the chlorine, or whether the intermediates are best regarded as having structures in which the interaction between the halogen and one of the carbon atoms is considered to be essentially electrostatic in character, as has been proposed in certain cases [26] (cf. formula II).

Whatever the nature of the interaction, its effect on the relative ease of loss of hydrogen from the two possible positions ought to have the observed effect on the orientation, for the following reasons. The transition state for elimination giving the vinylic halide is shown in (III); the distortion resulting from neighbouring-group interaction tends to maintain the chlorine atom of the CH_2Cl group in a position which is particularly strained relatively

---

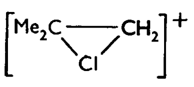
* Taft's theory,[12] referred to on p. 3338, requires that the inductive effect of the chlorine substituent should, despite its acid-promoting power, diminish the relative ease of formation of a double bond with the adjacent carbonium centre, by diminishing the electron density at the carbon atom from which the proton is to be lost. This theory seems to the authors to focus attention on the electron density in the carbonium ion itself, rather than on the electron density in the carbonium ion as it undergoes proton-loss, *i.e.*, in the transition state for elimination. The whole pattern of unimolecular eliminations is one of dominant conjugative and hyperconjugative influences, and Taft's theory does not seem to fit very happily into this pattern.

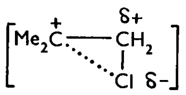
[29] Dhar, Hughes, Ingold, Mandour, Maw, and Woolf, *J.*, 1948, 2093.

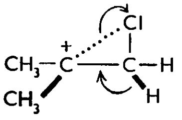
[30] Roberts and Kimball, *J. Amer. Chem. Soc.*, 1937, **59**, 947.

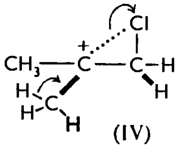
[31] Cf. Winstein, *Bull. Soc. chim. France*, 1951, **18**, C 55.

to the final positions of these atoms in the product. The transition state for the alternative elimination is shown in formula (IV). The unaffected hydrogen atoms of the CH_3 group from which elimination is occurring are able to adopt relatively unstrained positions,


(I)


(II)


(III)

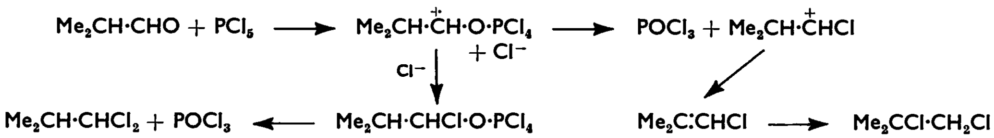

(IV)

and the distortion in the CH_2Cl group does not affect adversely the geometrical requirements of the developing double bond. It is suggested, therefore, that these considerations provide a rationalisation of the orientation observed in these experiments. It is felt, also, that the present experiments, when compared with those involving addition of chlorine to *iso*butene under aprotic conditions, make it more certain that the latter reaction involves a carbonium ionic intermediate, despite the relatively non-ionising conditions.

The Reaction between iso*Butyraldehyde and Phosphorus Pentachloride.*—Little is known concerning the mechanism of this reaction, and, so far as the authors are aware, there have been few discussions of it. Chlorinations, by this reagent, of aliphatic aldehydes and ketones do not usually proceed in good yield, and there have been many reports (cf. refs. 18, 32) that vinylic halides are the most important by-products. Rearrangement during the reaction, to give a 1 : 2-dichloride, has not, so far as we are aware, been noted before the present work. The following route to the vinylic chloride is possible, and in the present case would allow the formation therefrom of the rearranged dichloride :

$$Me_2CH{\cdot}CHO \rightleftharpoons Me_2C{:}CH(OH);\ Me_2C{:}CH(OH) + PCl_5 \longrightarrow Me_2C{:}CHCl + HCl + POCl_3;$$
$$Me_2C{:}CHCl + HCl \longrightarrow Me_2C(Cl){\cdot}CH_2Cl$$

An alternative possibility, which takes into account the specific usefulness of phosphorus pentachloride in these chlorinations, is that shown in the scheme below :



$$\begin{tikzcd}
Me_2CH{\cdot}CHO + PCl_5 \arrow[r] & Me_2CH{\cdot}\overset{+}{C}H{\cdot}O{\cdot}PCl_4 + Cl^- \arrow[r] \arrow[d, "Cl^-"'] & POCl_3 + Me_2CH{\cdot}\overset{+}{C}HCl \arrow[d] & \\
Me_2CH{\cdot}CHCl_2 + POCl_3 & Me_2CH{\cdot}CHCl{\cdot}O{\cdot}PCl_4 \arrow[l] & Me_2C{:}CHCl \arrow[r] & Me_2CCl{\cdot}CH_2Cl
\end{tikzcd}$$

We are greatly indebted to the Shell Group of Companies for a grant (to A. S.) which enabled this work to be completed, and to Professors C. K. Ingold, F.R.S., and E. D. Hughes, F.R.S., for their interest.

William Ramsay & Ralph Forster Laboratories,
University College, Gower St., London, W.C.1.

[*Received, April* 19*th*, 1956.]

---

[32] Henne, Renoll, and Leicester, *J. Amer. Chem. Soc.*, 1939, **61**, 938.