582. *Reactions Related to the Pinacol–Pinacone Rearrangement. Part I. The Acid-catalysed Rearrangement of* 2-*Methylpropane*-1 : 2-*diol and its Ethers.*

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Rearrangement of 2-methylpropane-1 : 2-diol has been shown to give *iso*butyraldehyde and to depend on the acidity function of the medium. The reaction thus proceeds through a carbonium ion. The analogous rearrangement of 1 : 2-dimethoxy-2-methylpropane in anhydrous methanol has also been studied, and has been shown to involve an internal hydrogen migration.

THE mechanism of the acid-catalysed rearrangement of pinacol and related compounds is thought to involve the reversible formation of the conjugate acid of the substrate followed by the annexed steps, step (2) being rate-determining. The evidence on which this view is based has been reviewed by Ingold.[1]

$$\underset{\text{(I)}}{{}^{+}H_2O\cdot CR^1R^2\cdot CR^3R^4\cdot OH} \xrightarrow{(2)} \underset{\text{(II)}}{{}^{+}CR^1R^2\cdot CR^3R^4\cdot OH} \longrightarrow \underset{\text{(III)}}{CR^1R^2R^3\cdot C^{+}R^4\cdot OH} \longrightarrow \text{Product}$$

In the present paper the rearrangements of 2-methylpropane-1 : 2-diol and its ethers to *iso*butyraldehyde and its derivatives have been studied in relation to the above mechanism by kinetic and isotopic techniques which have been but little used in rearrangements of this type. In a subsequent paper the fate of the intermediate carbonium ion (II) will be considered in greater detail. A preliminary account of some of our work in this field has been published.[2]

It has been found convenient to discuss the relevant results of other workers together with our own results in the discussion section.

RESULTS

Kinetic Results.—2-Methylpropane-1 : 2-diol, 1 : 2-dimethoxy-2-methylpropane, and 1-methoxy-2-methylpropan-2-ol rearranged in aqueous acid to *iso*butyraldehyde which was characterised by direct isolation, as its 2 : 4-dinitrophenylhydrazone, and by its polarographic half-wave potential. No ethyl methyl ketone was detected.

The kinetics of the rearrangement were followed, for the glycol, by the rate of its disappearance as determined by periodate titration, and by the rate of appearance of *iso*butyraldehyde determined polarographically. For the two ethers only the second method was used, the first being inapplicable. The polarographic method of analysis of *iso*butyraldehyde was developed specially for this work since methods depending on the formation of the oxime [3, 4, 5] or the 2 : 4-dinitrophenylhydrazone [6] gave poor results.

The reactions were studied at different acidities, with different acid catalysts, and in every case the first-order rate coefficients were sensibly constant throughout a run, and the observed infinity values agreed, within the experimental error, with the calculated values. Collected results obtained at 72·9° are in the annexed Table.

The results from the two analytical methods for the rearrangement of the glycol show no significant differences. For the rearrangements of both the glycol and the dimethyl ether, the first-order rate coefficients rise much more rapidly than stoicheiometric acidity, and, with the glycol, where different acids have been used, are not independent of the nature of the acid at

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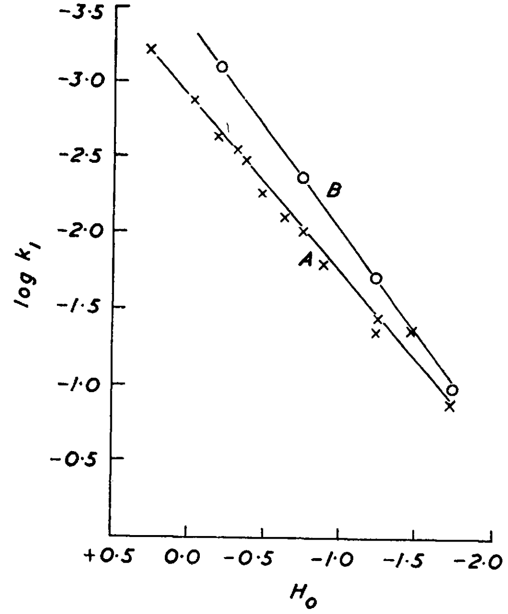
[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, p. 474.
[2] Ley and Vernon, *Chem. and Ind.*, 1956, 146.
[3] Bryant and Smith, *J. Amer. Chem. Soc.*, 1935, **57**, 57.
[4] Mitchell and Smith, *Analyt. Chem.*, 1950, **22**, 750.
[5] Buchanan, *Austral. J. Appl. Sci.*, 1951, **2**, 276.
[6] Jackson, *Ind. Eng. Chem. Analyt.*, 1941, **13**, 449.

some fixed value of stoicheiometric acidity. The logarithms of the first-order rate coefficients when plotted against values of Hammett's acidity function H_0, however, give straight lines of slope $-1{\cdot}16$ and $-1{\cdot}33$ respectively (see Figure), the points for all three acids used in the rearrangement of the glycol lying on or near the same straight line.

The effect of change of solvent from water to deuterium oxide on the rate of rearrangement of the glycol was investigated. The rate coefficients obtained with 0·93M-sulphuric acid at 72·9° were 1·33 and $3{\cdot}04 \times 10^{-3}$ min.$^{-1}$ in water and 95% deuterium oxide respectively. Hence the reaction, under these conditions, is faster in 95% deuterium oxide by a factor of 2·28.



A, *2-Methylpropane-*1 : 2*-diol.* *B*, 1 : 2*-Dimethoxy-*2*-methylpropane.*

Isotope Results.—Rearrangement of 1 : 2-dimethoxy-2-methylpropane was carried out with 2M-perchloric acid at 72·9° in water containing an enriched abundance of the isotope ^{18}O. At the end of the reaction methanol was isolated and found to contain a normal abundance of ^{18}O. Consequently, the oxygen–methyl bonds must remain intact throughout the reaction.

Acid	Concn. of acid (M)	Method of analysis	10^3k_1 (min.$^{-1}$)
*2-Methylpropane-*1 : 2*-diol*			
$HClO_4$ ...	0·481	G	0·60
$HClO_4$ ...	1·08	A	2·18
$HClO_4$ ...	1·23	G	2·74
$HClO_4$ ...	1·35	A	3·48
$HClO_4$ ...	1·61	A	5·24
$HClO_4$ ...	2·16	A	9·86
$HClO_4$ ...	2·47	G	14·9
$HClO_4$ ...	3·24	G	40·7
$HClO_4$ ...	3·24	A	42·9
$HClO_4$ ...	4·32	A	123
H_2SO_4 ...	0·93	G	1·33
HCl	2·22	G	7·55
HCl	4·44	G	42·3

Acid	Concn. of acid (M)	Method of analysis	10^3k_1 (min.$^{-1}$)
1 : 2*-Dimethoxy-*2*-methylpropane*			
$HClO_4$ ...	1·08	A	0·79
$HClO_4$ ...	2·16	A	4·36
$HClO_4$ ...	3·24	A	19·7
$HClO_4$ ...	4·32	A	104
1*-Methoxy-*2*-methylpropan-*2*-ol.*			
$HClO_4$ ...	1·08	A	1·36

The rearrangement of 1 : 2-dimethoxy-2-methylpropane was also carried out at 72·9° in anhydrous methanol containing 46% of DOMe in the presence of *ca.* M-methanesulphonic acid. At the end of the reaction 1 : 1-dimethoxy-2-methylpropane was isolated and its deuterium content found mass-spectrographically to 2·34—2·14 atoms % of D. A control experiment in which an initially isotopically normal sample of the acetal was subjected to the same experimental conditions for the same time was also carried out: this gave 1·20—1·18 atoms % of D, probably due to presence of traces of water which would be involved in the equilibrium $Me_2CH{\cdot}CH(OMe)_2 + H_2O \rightleftharpoons Me_2CH{\cdot}CHO + 2MeOH$. *iso*Butyraldehyde so formed could exchange its β-hydrogen atom for a deuterium atom present in the solvent by keto–enol tautomerism. Although all the reagents were thoroughly dried and precautions were taken to exclude moisture, the experiments cannot be carried out under completely anhydrous conditions since esterification of the solvent by methanesulphonic acid necessarily produces some water. After subtraction of the control value, the enrichment due to the rearrangement is 1·05 compared with 3·26 atoms % of deuterium for full equilibrium. Hence, on the basis of these figures, *ca.* 67% of the hydrogen shift is internal.

DISCUSSION

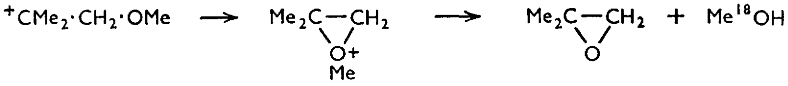
Rearrangement of 2-methylpropane-1 : 2-diol could lead, by migration of a hydrogen atom, to *iso*butyraldehyde, or, by migration of a methyl group, to ethyl methyl ketone. The formation of *iso*butyraldehyde, which has been previously observed in the presence of acids, involves separation of the hydroxyl group from the tertiary rather than the primary centre and this reaction would be expected, on the basis of previous studies of rearrangements of the pinacol–pinacolone type, to predominate. The present results show that 94% of the reaction can be accounted for as giving *iso*butyraldehyde; the remaining 6% is probably due to the known reaction between the glycol and the aldehyde.[8] Rearrangement of the dimethyl ether, which gives *iso*butyraldehyde quantitatively, is exactly analogous (similar rearrangements of glycol ethers have been previously reported);[9] in methanol, *iso*butyraldehyde dimethyl acetal is formed, $MeO{\cdot}CMe_2{\cdot}CH_2{\cdot}OMe \longrightarrow CHMe_2{\cdot}CH(OMe)_2$, and this reaction, although not explicitly studied, has been observed by Teuscher.[10]

The rate of rearrangement of the glycol in water is increased (*ca.* 2·3 times) by change of solvent to 95% deuterium oxide, and this shows that the conjugate acid of the glycol, through which reaction proceeds, is present in equilibrium amounts,[11] $HO{\cdot}CMe_2{\cdot}CH_2{\cdot}OH + H_3O^+ \longrightarrow {}^+H_2O{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$. It has also been found that the rate is dependent on acidity function rather than on stoicheiometric acidity, and, on the basis of the well-established Zucker–Hammett hypothesis,[12] the rate-determining step does not, therefore, involve a water molecule, and may be represented as ${}^+H_2O{\cdot}CMe_2{\cdot}CH_2{\cdot}OH \longrightarrow {}^+CMe_2{\cdot}CH_2{\cdot}OH$. This result, which is consistent with the modern formulation [1] of this type of rearrangement, is no doubt a general one; other examples are the previously reported dependence of rate on acidity function for the rearrangement of benzopinacol in slightly aqueous acetic acid [13] and for the rearrangement of pinacol in water.[14, 15] Similarly the reaction of the dimethyl ether is dependent on acidity function; the rate-determining step is therefore analogously, ${}^+HO(Me){\cdot}CMe_2{\cdot}CH_2{\cdot}OMe \longrightarrow {}^+CMe_2{\cdot}CH_2{\cdot}OMe$. We had hoped to show by the use of the Zucker–Hammett criterion that the analogous reaction in methanol, giving 1 : 1-dimethoxy-2-methylpropane, is also unimolecular. However, indicator measurements [16] have shown that the criterion is inapplicable in methanol since H_0 values calculated by use of three amine indicators increase with acidity at much the same rate as the stoicheiometric acidity. However, there is no reason to doubt that the rearrangements of the diether in water and in methanol are mechanistically similar, although no formal demonstration of this has been given.

[7] Groll and Hearne, U.S.P. 2,042,224/1936.
[8] Dolgorokova-Dobryanska, *J. Russ. Phys. Chem. Soc.*, 1925, **57**, 283.
[9] Linder, *Monatsh.*, 1911, **32**, 409.
[10] Teuscher, *J. Amer. Chem. Soc.*, 1950, **72**, 4316.
[11] Bonhoeffer, *Trans. Faraday Soc.*, 1938, **34**, 252.
[12] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.
[13] Gebhart and Adams, *J. Amer. Chem. Soc.*, 1954, **76**, 3925.
[14] Bunton, Hadwick, Llewellyn, and Pocker, *Chem. and Ind.*, 1956, 547.
[15] Bunton, Ley, Rhind-Tutt, and Vernon, *J.*, 1957, 2327.
[16] Duncan and Lynn, *J.*, 1956, 3512.

The relative rates of rearrangement of the glycol, the dimethyl ether, and the 1-monomethyl ether in water at 72·9° at a fixed concentration of perchloric acid (1·08M) can be seen from the Table to be 1, 0·36, and 0·62 respectively. Although it is difficult to interpret rate differences in acid-catalysed reactions, the similarity in rate for all three compounds is consistent with the common mechanism proposed.

The fate of the carbonium ion $^{+}CMe_2{\cdot}CH_2{\cdot}OH$ is of great interest. The following possibilities exist : (*a*) recombination with a solvent molecule regenerating the original substrate; (*b*) loss of proton to give 2-methylallyl alcohol; (*c*) formation of the oxide; and (*d*) loss or migration of proton, giving ultimately *iso*butyraldehyde. A similar set of possibilities exist for the carbonium ion $^{+}CMe_2{\cdot}CH_2{\cdot}OMe$. Recombination with a solvent molecule has been shown,[14] by use of ^{18}O tracer methods, to occur in the rearrangement of pinacol, and in a subsequent paper indirect evidence will be produced supporting the view that recombination with a solvent molecule occurs, with the ion $^{+}CMe_2{\cdot}CH_2{\cdot}OH$, about three times more frequently than reaction leading to the formation of *iso*butyraldehyde. Formation of 2-methylallyl alcohol could not be detected in this system since the rate of formation of the glycol from this substance is, under the experimental conditions, much too rapid. However it will be shown in a subsequent paper that this process is probably unimportant. For similar reasons the formation of the oxide could not be detected. In some pinacol-type rearrangements, notably that of benzopinacol,[13] the oxide is relatively stable and may be detected as a product. In the present case, although its formation is formally possible in the reaction of the glycol, it cannot be formed in the rearrangement of the diether since this would require, contrary to what was found, that methanol isolated from a reaction carried out in water enriched with the isotope ^{18}O should be partially enriched :

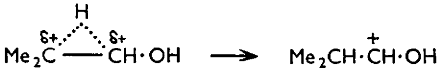


The formation of *iso*butyraldehyde can take place either by external hydrogen shift :

$$^{+}CMe_2{\cdot}CH_2{\cdot}OH \xrightarrow{-H+} CMe_2{:}CH{\cdot}OH \xrightarrow{+H+} CHMe_2{\cdot}{}^{+}CH{\cdot}OH \xrightarrow{-H+} CHMe_2{\cdot}CHO$$

or by an internal hydrogen shift through an intermediate ion of structure (IV) :

(IV)



The second route is the one followed in all pinacol-type rearrangements where the migrating group is not hydrogen, but when the migrating group is hydrogen the first route becomes a possibility especially since ions similar in structure to $^{+}CMe_2{\cdot}CH_2{\cdot}OH$ are known to undergo elimination.[17] In principle, the matter might be settled by running the reaction in deuterium oxide and determining whether the product contains a hydrogen or a deuterium atom attached to the β-carbon atom. In practice this criterion is inapplicable in aqueous solutions since the relatively rapid enolisation of the product causes exchange of the β-hydrogen atom irrespective of the mechanism of rearrangement. For the rearrangement of the diether in anhydrous methanol, however, the test is applicable since the product, 1 : 1-dimethoxy-2-methylpropane, will not exchange its β-hydrogen atom with the solvent providing all traces of water are excluded. It was found, by control experiments, that some exchange does in fact occur, no doubt because water, which is slowly formed by esterification of the solvent, cannot be completely excluded from the system. By allowing for the enrichment in the control experiments, the rearrangement was found to give a product whose deuterium enrichment, calculated on the basis of one

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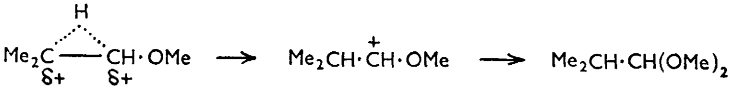
[17] de la Mare and Salama, *J.*, 1956, 3337.

hydrogen being involved in the exchange, was *ca.* 33% of that theoretically possible. This result means that at least 67% of the reaction proceeds by the route :



$$\mathrm{Me_2\overset{\delta+}{C}\overset{H}{—}\overset{\delta+}{C}H\cdot OMe \longrightarrow Me_2CH\cdot\overset{+}{C}H\cdot OMe \longrightarrow Me_2CH\cdot CH(OMe)_2}$$

The significance of the 33% enrichment actually observed is doubtful. The errors inherent in the experiment, *i.e.*, adventitious exchange produced by small quantities of water and failure to remove all traces of methanol from the product, are such as to produce enrichment figures which are spuriously high. On the other hand, it is possible that the two processes, proton loss and proton migration, are so energetically similar that both may occur under suitable conditions. What the experiment does show is that a substantial proportion of the reaction in methanol occurs by internal proton migration.

EXPERIMENTAL

Materials.—2-Methylpropane-1 : 2-diol was prepared by the following modification of the procedure described by Miles and Sussman.[18] Anhydrous sodium sulphate was added in small portions to a mixture of *tert.*-butyl alcohol (1200 c.c.) and 100-volume hydrogen peroxide (300 c.c.). Separation into two layers was complete in about 6 hr. The alcohol layer, which now contained *ca.* 6% of *tert.*-butyl hydroperoxide, was dried (Na_2SO_4), cooled to −8°, and saturated with *iso*butene. Osmium tetroxide (0·1 g.) was added, and after gentle shaking for a few minutes, the solution, which was deep red, was kept at 0° overnight. By then it was colourless and reaction was complete. Preliminary distillation gave the product (52 g.), b. p. 170—180°. Fractionation gave the pure material, b. p. 74°/10 mm., n_D^{25} 1·4309.

1-Methoxy-2-methylpropan-2-ol was made by dropwise addition of dimethyl sulphate (90 g.) to a cooled, stirred mixture of 2-methylpropane-1 : 2-diol (20 g.) and sodium hydroxide solution (40 g. in 200 c.c. of solution). The mixture was refluxed for 2 hr., then saturated with potassium chloride and extracted with ether. Fractionation yielded 1-methoxy-2-methylpropan-2-ol (10 g.), b. p. 115—116°/760 mm., n_D^{25} 1·4022 (cf. Sparks and Nelson,[19] b. p. 115—115·6°/734 mm., n_D^{20} 1·4047.

1 : 2-Dimethoxy-2-methylpropane was prepared by adding, dropwise, methyl iodide (1300 g.) to a cooled mixture of 2-methylpropane-1 : 2-diol (130 g.) and silver oxide (1 kg.). The mixture was refluxed for 2 hr., more methyl iodide (300 g.) was then added, and refluxing continued for a further 6 hr. The mixture was filtered and the filtrate, after combination with pentane washings of the silver residues, was poured into saturated salt solution. The pentane layer was separated, dried ($CaCl_2$), and distilled, giving a liquid with a camphor-like odour, b. p. 109—112°/760 mm. Refractionation from clean sodium gave the pure diether, b. p. 110·5—111·0°/759 mm., n_D^{25} 1·3935 (Found : C, 60·5; H, 11·9. Calc. for $C_6H_{14}O_2$: C, 61·0; H, 11·9%).

1 : 1-Dimethoxy-2-methylpropane was prepared by refluxing *iso*butyraldehyde (250 g.) and toluene-*p*-sulphonic acid (20 g.) in dry methanol (280 c.c.) for 7 hr. The mixture was washed with sodium carbonate solution until no longer acid, then with a warm dilute solution of hydrogen peroxide, and with sodium carbonate solution again, and dried (Na_2SO_4, followed by K_2CO_3). Fractionation gave the product (250 g.), b. p. 101·5—102°/760 mm., n_D^{25} 1·3850 (Found : C, 60·5; H, 11·2. Calc. for $C_6H_{14}O_2$: C, 61·0; H, 11·9%).

Anhydrous methanesulphonic acid was prepared from a commercial sample by distillation at *ca.* 1 mm., head and tail fractions being rejected.

Solvents.—Anhydrous methanol was prepared as described by Vogel.[20] Deuteromethanol (MeOD) was obtained by fractionating a mixture of methanol (80 g., 2·5 moles) and 99·8% deuterium oxide (50 g., 2·5 moles). The fraction boiling between 64° and 65° was dried as for ordinary methanol. It contained 11·9 atoms % of D, *i.e.*, 47·6% of MeOD.

Analytical Methods.—Rearrangement of the glycol was conveniently followed by periodate titration (cf. Buist and Bunton [21]). Rearrangements of the ethers, however, could not be so

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[18] Miles and Sussman, *J. Amer. Chem. Soc.*, 1936, **58**, 1302.
[19] Sparks and Nelson, *ibid.*, p. 671.
[20] "Practical Organic Chemistry," Longmans, Green and Co. Ltd., London, 1951, p. 168.
[21] Buist and Bunton, *J.*, 1954, 1407.

followed, and a method of estimation of *iso*butyraldehyde (the common product) was sought which would be suitable in all cases.

Estimation[3,4,5] by treatment with hydroxylamine hydrochloride followed by titration of the liberated acid with standard alkali was found to be accurate to within *ca.* 5% for initially neutral solutions of *iso*butyraldehyde of concentration greater than 10^{-1}M. It was unsuitable for smaller concentrations and for the estimation of *iso*butyraldehyde formed by rearrangement of 2-methylpropane-1 : 2-diol or its ethers, since in these reactions the solutions contained considerable concentrations of acid, and the small additional amount formed in the estimation could not be accurately determined.

Gravimetric procedures based on the formation of the 2 : 4-dinitrophenylhydrazone have been described, but there is apparently no record of their use with *iso*butyraldehyde. Various conditions of precipitation and of washing and drying the precipitate were tried, but results were inconsistent, and the method was abandoned.

Polarography has been found entirely suitable as a method for estimation of *iso*butyraldehyde over wide ranges of concentration and acidity. Estimation of some other aldehydes by this method has been previously described.[21] A Cambridge photographic recording instrument was used. The capillary was made from drawn-out standard thermometer tubing, and with a mercury reservoir of height 54·3 cm. gave a drop time of 3 sec. The procedure was as follows: 5 c.c. of lithium hydroxide solution (1·186M) were pipetted into the polarographic cell and enough mercury added to provide an anode of surface area *ca.* 3 $cm.^2$. The cell was immersed in ice-water and swept out with pure nitrogen. The sample to be analysed was adjusted, by dilution with water or by addition of stronger acid, so that it contained 1·08M-perchloric acid; 5 c.c. of the resultant solution were then added to the cell, and after a few minutes readings were started. Eight consecutive recordings over the range 1·2—2·2 v were made for each sample. The recordings were developed and the height of each polarogram measured in the usual way. The height divided by the sensitivity used was found to be accurately proportional to the aldehyde concentration over the range 0·5—8·0 × 10^{-3}M. A calibration curve was constructed by using standard samples, and reference was made to it in all subsequent determinations. Any given determination was accurate to within ±2%. Good resolution between the waves for *iso*butyraldehyde and the lithium ion were obtained with the supporting electrolyte used (0·54M-$LiClO_4$, 0·05M-LiOH). Higher concentrations of supporting electrolyte rendered the method less sensitive by reducing the diffusion current, and with sodium or potassium ions the resolution was poorer. At 0°, under the conditions given, the half-wave potential for *iso*butyraldehyde against a saturated calomel electrode was −1·91 v.

Products.—The three compounds studied all gave *iso*butyraldehyde when heated with aqueous acid at 72·9°. From the reaction products of each, the 2 : 4-dinitrophenylhydrazone of *iso*butyraldehyde was isolated, m. p. and mixed m. p. 184°.

Polarographic analysis indicated that *iso*butyraldehyde was produced quantitively from 1 : 2-dimethoxy-2-methylpropane and, in kinetic runs, the calculated infinity values agreed, within the experimental error, with those observed. To eliminate the possibility that the polarograph did not distinguish between *iso*butyraldehyde and ethyl methyl ketone (a possible reaction product) it was shown that the latter substance produces no polarographic wave under the conditions used in the analysis and does not affect the estimation of *iso*butyraldehyde.

With the glycol, rather less than the theoretical amount of *iso*butyraldehyde was produced at complete reaction, namely, 94% at 72·9° in 3N-perchloric acid. This discrepancy appeared to be due to a reaction between the aldehyde formed and residual glycol and was not further investigated.

Kinetic Methods.—Kinetic experiments depending on the estimation of *iso*butyraldehyde were carried out as follows: 5·5 c.c. portions of reaction mixture, containing *ca.* 2 × 10^{-2}M-substrate in aqueous perchloric acid of known concentration, were sealed in ampoules and placed in a thermostat at 72·9°. Ampoules were withdrawn at appropriate intervals and immersed in alcohol–carbon dioxide. Samples (5 c.c.) were pipetted from the ampoules and adjusted to a perchloric acid concentration of 1·08M: 5 c.c. of the resultant solution were then pipetted into the polarographic cell for estimation of *iso*butyraldehyde, as already described.

First-order rate coefficients were calculated in the usual way, infinity values being calculated from the initial concentrations of substrate. These coefficients were sensibly constant through a run.

The following results obtained with 1 : 2-dimethoxy-2-methylpropane (1·66 × 10^{-2}M) in aqueous perchloric acid (2·16M) at 72·9° are typical (x, in arbitrary units, represents polarogram heights divided by the sensitivity used; the expected infinity value is 58·43 units):

Time (min.)	x	10^3k_1 (min.$^{-1}$)	Time (min.)	x	10^3k_1 (min.$^{-1}$)	Time (min.)	x	10^3k (min.$^{-1}$)
0	0	—	150	29·0	4·29	285	42·6	4·58
30	6·83	4·14	188	32·3	4·27	375	48·0	4·59
60	12·74	4·10	210	34·2	4·20	420	50·0	4·61
90	19·3	4·45	240	36·0	3·99	∞	58·5	—
120	24·45	4·51						

In kinetic experiments depending on the analysis of 2-methylpropane-1 : 2-diol, portions (5 c.c.) of reaction mixture were neutralised with saturated sodium hydrogen carbonate solution, standard periodate solution (*ca.* 2 × 10^{-2}N; 25 c.c.) was added, and the whole set aside for 1 hr. Potassium iodide (*ca.* 1 g.) was then added and the liberated iodine titrated with standard sodium arsenite (*ca.* 4 × 10^{-3}N). The following results for 2-methylpropane-1 : 2-diol (1·446 × 10^{-2}M) in perchloric acid (1·23M) at 72·9° are typical (titres refer to c.c. of sodium arsenite solution, 2·78 × 10^{-2}N):

Time (min.)	Titre	10^3k (min.$^{-1}$)	Time (min.)	Titre	10^3k_1 (min.$^{-1}$)	Time (min.)	Titre	10^3k_1 (min.$^{-1}$)
0	19·02	—	120	25·86	2·62	240	31·11	2·69
30	21·10	2·85	150	27·55	2·73	270	32·40	2·71
60	22·90	2·84	180	29·00	2·79	300	32·49	2·60
100	25·10	2·74	210	30·36	2·79	∞	44·34	—

Isotope Experiments.—The following details are typical: (*a*) 1 : 2-Dimethoxy-2-methylpropane (1·2 g.) was dissolved in water (40 c.c.) containing 1·0 atom % enrichment in the isotope ^{18}O, and 10M-perchloric acid (10 c.c.) was added. The solution was sealed up in a tube and heated to 72·9° for 24 hr. The tube was then opened, and the solution saturated with solid 2 : 4-dinitrophenylhydrazine, set aside for 24 hr., and centrifuged. The supernatant liquid was again treated with 2 : 4-dinitrophenylhydrazine, and after removal of any further precipitate by centrifugation, was fractionated in a semimicro-column with metallic spiral packing. The first c.c. of distillate was collected and refractionated from isotopically normal water. Methanol, b. p. 65°, was obtained as the first few drops of distillate. It was "cracked" and its ^{18}O content determined mass-spectrometrically.[23] For two samples the excess abundance of ^{18}O was 0·018% and 0·003%.

(*b*) 1 : 2-Dimethoxy-2-methylpropane (2 g.), anhydrous methanesulphonic acid (1 c.c.) and anhydrous deuterated methanol (10 c.c.; 48% of MeOD) were sealed in a tube, heated to 72·9° for 24 hr., then poured into an equal volume of methanol containing enough sodium methoxide to make the final mixture alkaline. Saturated sodium chloride solution (2 c.c.) was added and the mixture extracted five times with pentane. The combined pentane extracts were washed with saturated sodium chloride solution and dried ($CaCl_2$; $CaSO_4$). After removal of the pentane the residue was fractionated in a spiral-packed micro-column. 1 : 1-Dimethoxy-2-methylpropane (1·0 g.), b. p., 101—102°, n_D^{20} 1·3865, was identified by its physical constants and by its immediate hydrolysis to *iso*butyraldehyde in acid solution. It was oxidised to water and this was reduced to hydrogen by zinc dust. The hydrogen was analysed for its deuterium content mass-spectrometrically.

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[22] Boyde and Bambach, *Ind. Eng. Chem. Analyt.*, 1941, **13**, 149.

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