257. *Isotopic Exchange Reactions of Organic Compounds. Part V. The Kinetics of the Isomerisation and the Deuterium Exchange Reaction of Δ^{α}-Pentenoic Acid.*

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The alkali-catalysed isomerisation of Δ^{α}-pentenoic acid in water has been re-examined. Kinetic data are recorded which establish a reaction mechanism involving Δ^{α}-pentenoic, Δ^{β}-pentenoic, and β-hydroxyvaleric acids in a " triangular " system, each member of which is in direct equilibrium with the other two. The isomerisation proceeds mainly by direct prototropic change, but to a less extent by the addition and fission of water, with the formation of the β-hydroxyvaleric acid as an intermediate stage.

The deuterium exchange reaction which accompanies the isomerisation in a " heavy " medium has also been studied. The results are compatible with the kinetic data and with previous exchange results, and show that the direct isomerisation proceeds by the bimolecular mechanism.

DEUTERIUM has been used as an indicator in the study of three-carbon tautomeric systems in which one isomeride is produced in large predominance (Ingold, de Salas, and Wilson, J., 1936, 1328; Ives, J., 1938, 91). It seemed desirable to extend this work by including a system of which the equilibrium state is less strongly unbalanced and contains both Δ^{α}- and Δ^{β}-isomerides in commensurate amounts. The pentenoic acids satisfy this condition and have accordingly been used in the present work, the first section of which is concerned with a more detailed investigation of the kinetics of the isomeric change, in an isotopically normal system, than has hitherto been made. It has been shown that Δ^{α}-pentenoic acid comes into equilibrium with Δ^{β}-pentenoic and β-hydroxyvaleric acids by reversible, pseudo-unimolecular reactions, giving a " triangular " system in which each member is in direct equilibrium with the other two.

A brief study of the deuterium exchange reaction which accompanies the isomerisation of Δ^{α}-pentenoic acid in a solvent containing deuterium oxide is recorded in the second section. A detailed investigation of this exchange has been found impracticable, but the results are in general conformity with the mechanism of reaction proposed in the first section and indicate that a bimolecular mechanism is involved in the prototropic isomerisation. The research has been unavoidably curtailed, and the experiments are concerned only with the approach to equilibrium from pure Δ^{α}-pentenoic acid: the results, however, are self-contained, and are therefore published at the present stage without the confirmation of experiments starting with the other pure components of the equilibrium system.

The Kinetics of Isomerisation.—A N-solution of sodium Δ^{α}-pentenoate containing 20 equivs. % excess of sodium hydroxide was kept at 100° in pure silver vessels. After determined periods of heating, the acid products were isolated without appreciable loss, and the pentenoic acids separated quantitatively from the hydroxy-acid by methods fully described in the experimental section. The pentenoic acid mixture was analysed by the iodometric method (Linstead and Noble, J., 1934, 616). The results are shown in Table I.

TABLE I.

Time, hrs.	Δ^{β}-Acid: % of pentenoic acid.	Δ^{β}-Acid: % of total acid.	Equiv. of mixed pentenoic acid.	Hydroxy-acid, % of total acid.	Yield of recovered acid, %.
2	1·8	1·7	—	2·9	97·6
22·4	11·6	11·2	100·7	3·3	95·9
46·4	17·5	16·6	100·0	5·0	97·8
70·4	21·8	19·9	100·9	8·5	97·6
94·4	25·4	22·4	100·7	11·8	96·6
166·4	31·7	26·2	100·5	17·4	98·1
600	38·0	26·4	101·4	30·6	97·0

The results of the iodometric analysis are shown in col. 2; comparison with col. 3, where the Δ^{β}-acid is shown as a percentage of the *total* acid (*i.e.*, including the hydroxy-acid), shows that the formation of the hydroxy-acid is far from negligible. The equivalent (by titration) of the mixture of pentenoic acids, freed from hydroxy-acid, is given in col. 4 as some criterion of purity. The smaller amounts of hydroxy-acid were estimated by titration, and are shown, in equivs. %, in col. 5. The total yield of recovered acid is also recorded; the loss of 2—3% in working up has been assigned to the more volatile pentenoic acid fraction, and it has been assumed that this slight loss has not appreciably disturbed the relative proportions of the isomerides.

The first step in the kinetic interpretation has been the setting up of provisional interpolation equations in order to facilitate subsequent calculations and to provide some indication of the random errors in the results. It has been found that the figures in col. 2 of Table I fit closely to a unimolecular velocity law, provided that 15 hours be added to each reaction time. Since these figures do not represent concentrations (or activities), this does not show that the production of the Δ^{β}-acid follows a first-order law, and the uniformity of the values of the " velocity constants " (k_1), which are shown in Table II, is the sole justification for the provisional use of this law for purposes of interpolation.

TABLE II.

Time, hrs.	22·4	46·4	70·4	94·4	166·4	600	
$k_1 \times 10^3$, hr.$^{-1}$	9·74	10·06	10·00	10·09	9·90	—	Mean, 9·96 ± 0·11
$k_2 \times 10^3$, hr.$^{-1}$	4·77	3·59	4·28	4·72	4·56	4·54	Mean, 4·41 ± 0·32

The addition of 15 hours to the time scale corresponds with an initial fast reaction which subsides within 22 hours. This has been confirmed by one short-time experiment (cf. Table I) but no explanation is advanced. It has been shown by suitable experiments that the operations involved in working up the reaction products cause no disturbance in the initial isomeric ratio.

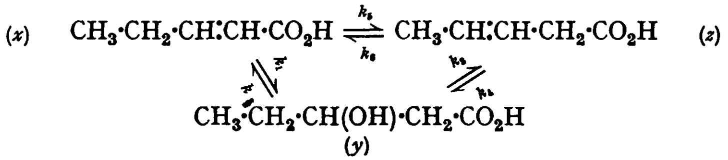
The formation of the β-hydroxyvaleric acid has also been found to follow a first-order law within experimental error, but without any apparent initial fast reaction. Again, no conclusions can be drawn, because it seems likely that the actual law controlling the formation of this acid might be complex, since the reactant which produces it is itself undergoing change. The use of this law is similarly justified by the substantial uniformity of the constants (k_2) shown in Table II. No systematic deviation from linearity can be found in either case from the linear logarithmic plots required by the unimolecular law. Interpolated amounts of the Δ^{α}-acid and its two reaction products (in equivs. % of the total) are shown in Table III, and have been used in subsequent calculations.

TABLE III.

Time, hrs.	30	60	90	120	150	180	∞
Δ^{α}-Acid, %	82·8	73·9	67·3	62·25	58·4	55·4	41·3
Δ^{β}-Acid, %	13·15	18·5	22·0	24·3	25·8	26·7	25·5
Hydroxy-acid, %	4·05	7·6	10·7	13·45	15·8	17·9	32·8

The equilibrium value for the hydroxy-acid was not reached in 600 hours, and was therefore calculated by a short extrapolation. The equilibrium data differ from those previously recorded (Linstead and Noble, *loc. cit.*), *viz.*, 68% of Δ^{α}-acid and 32% of Δ^{β}-acid, the hydroxy-acid being neglected. The corresponding figures now obtained are 62% and 38% respectively; this is attributable to the improved recovery of the reaction products and the consequent avoidance of loss of the more volatile Δ^{β}-pentenoic acid.

The second step in the examination of these results consisted of the application to them of the most general of possible reaction schemes, which is the ternary equilibrium already mentioned. This may be represented diagrammatically as follows:



where x, y, and z are the equivalents % (which are proportional to concentrations) of Δ^{α}-pentenoic, β-hydroxyvaleric, and Δ^{β}-pentenoic acids respectively, and $k_1, k_2, \ldots k_6$ are the pseudo-unimolecular velocity constants of the reactions indicated by the arrows. The rates of change of the concentrations of the three species are given by the equations

$$\mathrm{d}x/\mathrm{d}t = k_6z + k_2y - (k_5 + k_1)x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$\mathrm{d}y/\mathrm{d}t = k_1x + k_4z - (k_2 + k_3)y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$\mathrm{d}z/\mathrm{d}t = k_5x + k_3y - (k_6 + k_4)z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If x_e, y_e, and z_e are the respective equilibrium values of x, y, and z, then, since at equilibrium $\mathrm{d}x/\mathrm{d}t = \mathrm{d}y/\mathrm{d}t = \mathrm{d}z/\mathrm{d}t = 0$,

$$k_6z_e + k_2y_e = (k_5 + k_1)x_e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$
$$k_1x_e + k_4z_e = (k_2 + k_3)y_e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$
$$k_5x_e + k_3y_e = (k_6 + k_4)z_e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Substituting the determined values of x_e, y_e, and z_e in, *e.g.*, equation (6), we have

$$41{\cdot}5k_5 + 32{\cdot}8k_3 = 25{\cdot}5(k_6 + k_4)$$

or

$$k_6 + k_4 = 1{\cdot}635k_5 + 1{\cdot}286k_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

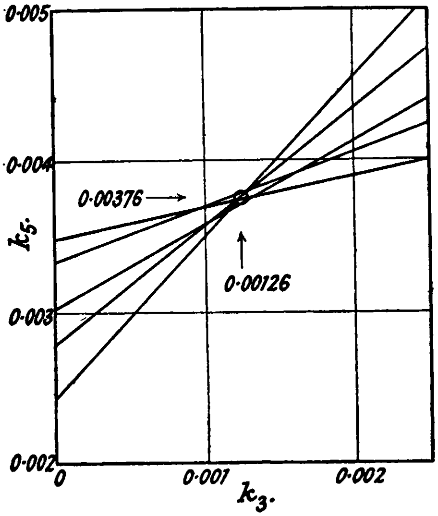
Substitution in equation (3) then gives

$$\mathrm{d}z/\mathrm{d}t = k_5x + k_3y - (1{\cdot}635k_5 + 1{\cdot}286k_3)z \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and, similarly, two other equations for $\mathrm{d}x/\mathrm{d}t$ and $\mathrm{d}y/\mathrm{d}t$ may be obtained, each containing two unknown velocity constants.

These equations have been solved by constructing curves from the data in Table III, measuring gradients graphically to obtain differential coefficients at round times, and reading the corresponding values of x, y, and z. A series of linear simultaneous equations was thus obtained, which were solved graphically in order to check their mutual compatibility and accuracy. The solution of equation (8), the data in Table III between 30 and 150 hours being used, is shown in Fig. 1. It is evident that single values of the constants cover this time range within experimental error. Similar solutions for the other constants gave the following values, in hrs.$^{-1}$:

FIG. 1.



Constant	k_1.	k_2.	k_3.	k_4.	k_5.	k_6.
Value × 10^5	152	145	126	100	376	675

These constants adequately satisfy equations (1), (2), and (3), as shown by comparison of observed and calculated gradients given in the following table.

	Δ^{α}-Acid gradients.		Δ^{β}-Acid gradients.		Hydroxy-acid gradients.	
Time, hrs.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
30	−0·3435	−0·3426	0·2137	0·2145	0·1260	0·1280
60	−0·2548	−0·2548	0·1456	0·1445	0·1169	0·1103
90	−0·1918	−0·1914	0·0951	0·0962	0·0967	0·0952
120	−0·1479	−0·1452	0·0630	0·0627	0·0892	0·0825
150	−0·1119	−0·1111	0·0397	0·0396	0·0731	0·0716

In order to provide a more convincing test of the ternary reaction scheme, the values of the velocity constants have been substituted in equations (2) and (3). This provides a check which is independent of the interpolation equations used in the previous calculation, since solution of these differential equations should reproduce the experimental results at all times until equilibrium is reached. Since

$$x + y + z = 100 \quad \ldots \ldots \quad (9)$$

then

$$dy/dt = 0{\cdot}152 - 0{\cdot}00423y - 0{\cdot}00052z \quad \ldots \quad (10)$$

and

$$dz/dt = 0{\cdot}376 - 0{\cdot}00250y - 0{\cdot}001151z \quad \ldots \quad (11)$$

Values of y and z were calculated by successive approximations in terms of convergent series in powers of t: the general solutions are bulky and are therefore not given, but a comparison of observed and calculated values of y and z is shown on p. 1366 and in Fig. 2 (curves I) and Fig. 3 (where the points are experimental and the curves calculated), and the agreement is well within experimental error.

Time, hrs.	Δ^β-Acid, % of pentenoic acid. Obs.	Calc.	Hydroxy-acid, % of total acid. Obs.	Calc.	Time, hrs.	Δ^β-Acid, % of pentenoic acid. Obs.	Calc.	Hydroxy-acid, % of total acid. Obs.	Calc.
22·4	11·6	11·8	3·3	3·2	94·4	25·4	25·3	11·8	11·2
46·4	17·5	17·3	5·0	6·2	166·4	31·7	31·8	17·4	16·9
70·4	21·8	21·8	8·5	8·8	600	38·0	38·2	30·6	30·1

On the basis of the calculated velocity constants of the three equilibria, it can be shown that the interpolation equations initially used are, in fact, valid: the apparent "velocity constants" of these equations have been calculated and are 0·00989 hr.$^{-1}$ for k_1 (cf. Table II, 0·00996 ± 0·00011) and 0·00481 hr.$^{-1}$ for k_2 (cf. Table II, 0·00441 ± 0·00032). The discrepancy in the latter case affects the equilibrium data, since they depend on a short extrapolation, to the extent of about 0·5%, and this must consequently be regarded as the limit of accuracy of the determinations.

FIG. 2.

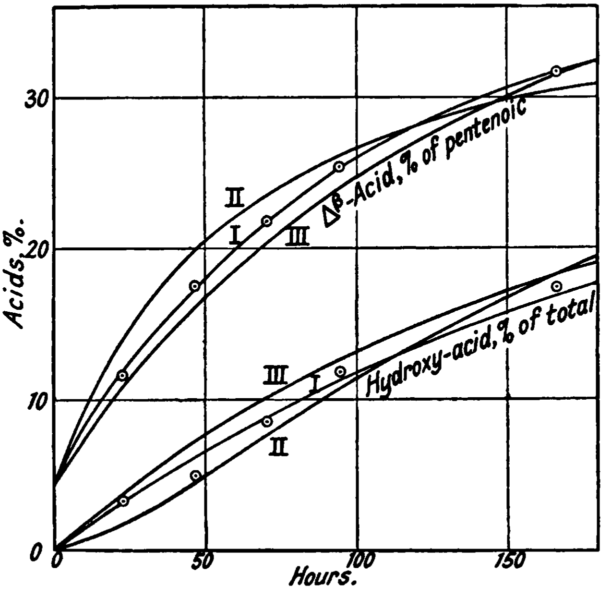
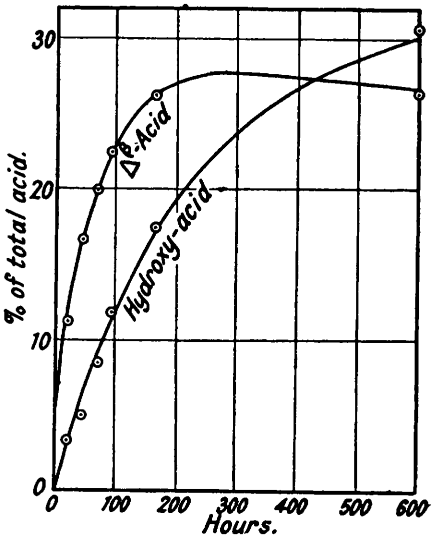


FIG. 3.



Finally, the ternary reaction scheme has been further substantiated by considering, and excluding, the other possible relationships between the three components of the system. There are three such relationships, corresponding with the abolition of each in turn of the three equlibria involved in the general theory; indicated schematically, they are

$\Delta^\alpha \rightleftharpoons \Delta^\beta \rightleftharpoons$ Hydroxy   Hydroxy $\rightleftharpoons \Delta^\alpha \rightleftharpoons \Delta^\beta$ $\Delta^\alpha \rightleftharpoons$ Hydroxy $\rightleftharpoons \Delta^\beta$

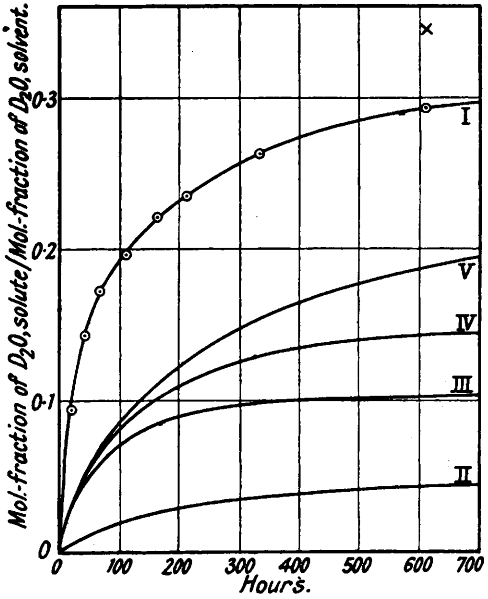
The first two of these are amenable to analysis by the methods already described, and the best possible solutions are shown in curves II and III respectively in Fig. 2. The deviations from the experimental points are systematic and, in the case of the Δ^β-pentenoic acid at least, far outside experimental error. The third scheme cannot be examined quantitatively but may be definitely excluded on the grounds that it necessarily implies a totally different relationship between the concentrations of the reaction products (before equilibrium is reached) from that actually found. The operation of the hydroxy-acid as an essential intermediary in the isomerisation of the components of three-carbon systems has, of course, been previously excluded (cf., *inter alia*, Linstead, J., 1927, 367), but the joint operation of both mechanisms (prototropic, addition and fission) does not seem to have been clearly distinguished previously. It is true that in the pentenoic acids the addition and fission of water accounts for only a small proportion of the conversion (*ca.* 4% at half-change), but the relative predominance of the two modes might be expected to vary from one tautomeric system to another.

The Deuterium Exchange Reaction.—The deuterium exchange experiments were carried out under the same conditions as previously described, except that the solvent contained 7% of deuterium oxide. After being heated, the alkaline solutions were treated with excess of dry carbon dioxide, the solvent removed, and the residue heated to 140° in a high vacuum until all sodium hydrogen carbonate was destroyed. Combustion of the residues gave samples of water which were purified without loss and analysed for deuterium content by the flotation density method. In the longest experiment, however, the reaction products were isolated and analysed separately for deuterium, and the pentenoic acid fraction for the relative proportion of the isomerides. The results of the deuterium analyses are shown below.

Time, hrs.	Mol.-fraction of D_2O in combustn. water, × 10^3.	Effective mol. fractn. of D_2O in solvent, × 10^3.	$\frac{\text{Mol.-fractn. of } D_2O\text{, solute}}{\text{Mol.-fractn. of } D_2O\text{, solvent}}$.
21	6·39	68·0	0·094
44·5	9·69	67·9	0·143
68·7	11·64	67·75	0·172
113·2	13·27	67·6	0·196
165	14·92	67·5	0·221
213	15·89	67·5	0·235
335	17·73	67·35	0·263
610	20·00	68·2	0·293

The last entry in col. 2 is calculated from the data relating to the free acids and is, in effect, the result which would have been obtained by analysis of the mixed sodium salts: it is in good agreement with the previous figures, but this is only the case if it is assumed that the hydroxylic hydrogen of the isolated hydroxy-acid contains deuterium in amount predictable from the known distribution coefficient for such groups (1·09; Hobden, Johnston, Weldon, and Wilson, J., 1939, 61). Since the exchange reaction involves progressive dilution of the solvent owing to the replacement of deuterium by hydrogen, the effective isotopic composition of the solvent must be calculated for each exchange experiment in order to make the results mutually comparable: this has been done with sufficient accuracy by graphical integration, and the results are shown in col. 3. The last column provides the data for showing the increasing deuteration of the solute with time on a common basis: these results are shown graphically in Fig. 4 (curve I). The point indicated by a cross is calculated on the assumption that the hydroxyl group of the hydroxy-acid was normalised during the working up of the acid. The very large divergence shows that this did not occur: satisfactory theoretical reasons for the low acidity of this hydrogen atom can readily be found.

Fig. 4.



It was impracticable to analyse this deuteration curve in detail. The solution may contain 12 different pentenoic acids and 16 different hydroxy-acids of various isotopic constitutions (excluding the possibility of the formation of acids containing deuterium linked to carbon in the β-position), so the multiplicity of equilibria between these species, of which the total deuteration curve is the resultant, is very great indeed. Nevertheless, a partial analysis has led to conclusions which are of some interest.

Considering first the results of the last experiment, of longest heating period, it is found that the ratio of the pentenoic acid isomerides at equilibrium is not affected by the presence of deuterium : this is to be expected on kinetic and thermodynamic grounds. On the other hand, the equilibrium amount of hydroxy-acid appears to be considerably increased by the presence of the heavier isotope (40·6% in 610 hrs., as compared with 30·2% in 600 hrs.). In this case we are concerned with an addition reaction in which the different rates of reaction of the isotopes will be fully apparent. It is surprising that this difference is so great and, without discussing it in detail, it may be suggested that it is connected with the greater basic strength of deuteroxyl than hydroxyl, and with the distribution coefficient which favours the concentration of deuterium in organic hydroxyl groups as compared with water.

The separate deuterium analyses of the hydroxy-acid and pentenoic acid mixture from the last experiment are not informative. Allowance being made for the carboxylic and hydroxylic hydrogen, it is found that the hydroxy-acid, atom for atom, contains less deuterium than the pentenoic acids. It can be shown by a kinetic argument (cf. Ives, J., 1938, 91) that at equilibrium the deuterium content of corresponding positions in these acids must be identical. That this is not found to be the case is almost certainly due to the known fact that equilibrium had not been reached. The alternative explanation that the hydroxy-acid is formed by an irreversible addition process, and is not in reversible equilibrium with the unsaturated acids, is hardly tenable in view of the kinetic evidence.

Next, an attempt has been made to account for as much as possible of the deuterium in the solute in terms of such " partial reactions " as can be distinguished and approximately assessed. For the purposes of this approximate treatment, it is assumed that the rates of isomerisation and hydroxy-acid formation are unaffected by the deuterium in the system. Although the errors involved in this assumption may be considerable, they will be in the direction of over-assessment, and this will not invalidate the argument which is subsequently based on the calculations. Four main contributions to the deuteration can be easily distinguished :

(1) The hydroxylic hydrogen of the hydroxy-acid is assumed to exchange so rapidly under the experimental conditions that it is in continuous equilibrium with the solvent. If we take a distribution coefficient of 1·09, this gives a contribution to the mol.-fraction of deuterium oxide in the combustion water of the solute indicated by curve II in Fig. 4. It is assumed that this acid undergoes no other direct exchange reaction.

(2) The α-hydrogen of the Δ^{β}-pentenoic acid is assumed to undergo rapid exchange, on the grounds of its similarity to vinylacetic and phenylacetic acids, *viz.*, that it possesses a polarisable group attached to the same methylene as the carboxyl (cf. Ives, J., 1938, 81). With a mean distribution coefficient of 0·82 (*cf.* Hobden, Johnston, Weldon and Wilson, *loc. cit.*; Ives, *loc. cit.*; Evans, Rydon, and Briscoe, J., 1939, 1673), this will add to the deuterium content of the solute by an amount which is added to (1) in curve III, Fig. 4.

(3) Since the equilibrium between the various acids in solution is mobile, the postulated rapid exchange of the α-hydrogen of the Δ^{β}-acid will cause a much greater deuterium uptake than is accounted for under the last heading. This acid will form the starting point of an equilibrium system which will contain the Δ^{α}-acid and the hydroxy-acid deuterated to the maximum extent in the α-position. If x' and y' are the respective concentrations of Δ^{α}-acid and hydroxy-acid which have been generated from Δ^{β}-acid and are in equilibrium with each other, then

$$\mathrm{d}x'/\mathrm{d}t = k_6 z + k_2 y' - (k_1 + k_5)x'$$
$$\mathrm{d}y'/\mathrm{d}t = k_4 z + k_1 x' - (k_2 + k_3)y'$$

where z has the same meaning as before. These differential equations have been solved by an approximate graphical method and give curves IV and V in Fig. 4 for these contributions added successively to the previous ones.

Further analysis on these lines becomes more and more approximate, but it is clear that the other partial reactions which can be envisaged are, with one exception, of second order and, at any time, are dependent in rate on the concentrations of either the hydroxy-acid or the Δ^{β}-pentenoic acid. If the deuteration which has not been accounted for is now considered (this is given by the difference between the ordinates of curves I and V in Fig. 4) the figures given below are obtained.

Time, hrs.	Total deuteration.	Deuteration accounted for.	Diff.
30	0·119	0·039	0·080
60	0·161	0·061	0·100
90	0·184	0·079	0·105
150	0·215	0·106	0·109
300	0·256	0·147	0·109
600	0·293	0·186	0·107

It is obvious that the neglected second-order partial reactions cannot possibly account for these differences, because the variation with time is of a totally different order from that required by such a supposition. In the earlier stages of the change, where the Δ^{α}-pentenoic acid is largely preponderant, there is a relatively rapid exchange reaction: the earlier the stage of the reaction which is considered, the less is the proportion of deuterium in the solute which can be accounted for in terms of Δ^{β}-acid or hydroxy-acid. The deduction cannot be avoided that the Δ^{α}-pentenoic acid must itself undergo a direct exchange reaction with the solvent which is independent of isomerisation, and it can hardly be doubted that it is the γ-hydrogen which is concerned. It can be inferred, therefore, that the direct prototropic isomerisation occurs by the bimolecular mechanism and that the intermediate ion becomes kinetically free in solution.

EXPERIMENTAL.

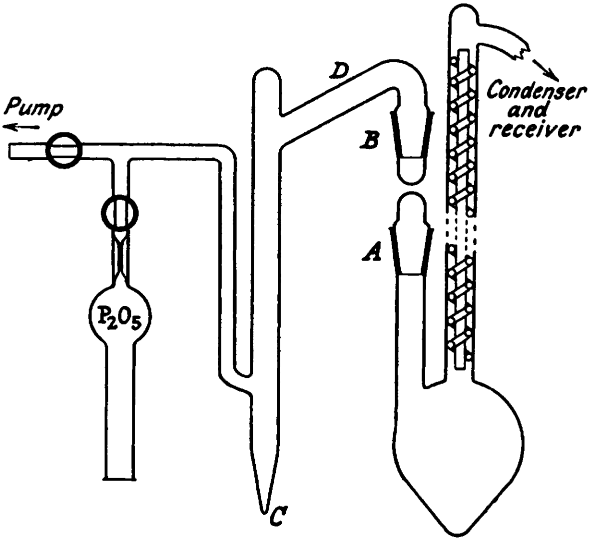
Preparation of Materials.—Δ^{α}-Pentenoic acid was prepared by the condensation of propaldehyde (1 mol.) with malonic acid (1 mol.) in presence of pyridine (1¼ mols.), followed by decarboxylation (cf. Boxer and Linstead, J., 1931, 740; Noble, Thesis, London, 1932). The acid was purified by careful vacuum fractionation; b. p. 62—66°/1·5 mm., m. p. 10·0°, $n_{\mathrm{D}}^{20^\circ}$ 1·4512 (Noble, *loc. cit.*, gives $n_{\mathrm{D}}^{20^\circ}$ 1·4513), iodine addition, 0·8%. All other reagents used were of "AnalaR" purity, and the usual precautions were taken in connexion with the volumetric solutions.

Equilibrations.—Solutions were made up in carefully standardised volumetric apparatus and checked by weighing: a knowledge of the densities was required for the subsequent calculation of yields of recovered products. Freshly distilled Δ^{α}-pentenoic acid was used, and cooled in ice during the addition of the requisite amount of carbonate-free standard sodium hydroxide solution to give a N-solution of the sodium salt containing 20 equivs. % excess of sodium hydroxide. The solutions were heated for determined periods in pure silver capsules sealed into Pyrex boiling-tubes. No distillation of solvent out of the capsules occurred during the heating, and the solutions remained water-white and clear for the longest periods of heating.

Recovery of Acids.—After cooling, the equilibration vessel was opened, and the contents transferred first to a tared flask and weighed, and then, without loss, to an all-glass constant extractor, where they were acidified and extracted with peroxide-free ether for 6 hours. The ethereal solution was dried, first over anhydrous sodium sulphate and then over anhydrous copper sulphate (free from basic salt). The quantitative removal of the ether from this solution without loss or fractionation of the small amount of pentenoic acids which it contained (*ca.* 2 g.) required substantial modification of the methods previously used for this purpose. It was accomplished, together with the separation from hydroxy-acid, in the all-glass apparatus shown in Fig. 5. The solution was filtered into the distillation vessel through a sintered-glass filter stick fitting into *A*. The ground stopper was replaced, and as much ether as possible removed by distillation from the water-bath up the efficient Dufton column shown, into a receiver, protected from moisture with phosphoric oxide, on the right of the apparatus. The distillate was removed, and the last traces of ether eliminated from the residual acid first by gentle suction, and then by pumping out the apparatus for 15 mins. at a controlled pressure of 50 mm. with the water-bath at 100°. Control experiments indicated that *n*-butyric acid (which is considerably more volatile than Δ^{β}-pentenoic acid) could be recovered quantitatively from ethereal solution by this procedure. The right-hand part of the apparatus was then closed, and junction made between the joints *A* and *B*, which were lightly greased with Apiezon L. Distillation was effected in a high vacuum (*ca.* 10^{-3} mm.) between 30° and $-80°$ into the receiver *C*: this gave complete recovery of the pentenoic acids and separation from hydroxy-acid, which is completely non-volatile under these conditions and remained in the distillation vessel for titration or subsequent working up. Dry air was admitted through the phosphoric oxide tube, and the receiver sealed off at *D*: the contents were thus preserved from access of moisture until required for analysis. At every stage ether distillates and washings of vessels and drying agents were titrated with baryta in order to estimate, and ensure, as complete a yield of reaction products as possible.

Examination of the " Hydroxy-acid."—The oily residue remaining in the distillation vessel from the longest-period experiment was redistilled in a suitable apparatus in a high vacuum. The distillate was a water-white syrupy liquid, very hygroscopic, and miscible with water in all proportions. An attempt to determine its molecular weight by a vapour-density method in a spoon gauge gave a value of 98, but was attended with some decomposition. Equiv. (by titration), 120·4 (Calc.: 118·2); iodine addition, 3·2%; H_2O (by combustion), 75·7 (Calc. : 76·2%). A more rigid characterisation of this acid has not been carried out, but there can be little doubt as to its identity; arguments have been put forward which strongly support its convertibility into both pentenoic acids on heating with aqueous alkali.

FIG. 5.



Analysis of Isomerides.—The iodometric method (Linstead and May, J., 1927, 2656) was applied exactly as described by Noble (*loc. cit.*). Solutions were kept at 20·0° ± 0·1° in a water-bath in a large Dewar vessel during the iodine additions. Noble's reference curve was used in interpreting the results : curtailment of the work has prevented this curve being confirmed, but there can be no doubt as to the purity of the materials used, or of the reproducibility of the results under carefully defined conditions. The equivalent (by titration) of the pentenoic acid mixture was determined at the same time as the isomeric ratio.

Recovery of Sodium Salts, Combustions, and Isotopic Analysis.—These operations were carried out by methods similar to those fully described in previous papers in this series, modified in detail to give greater ease and speed of working. The recovery of samples of water from combustions, purifications, and density measurements was quantitative within ordinary analytical accuracy.

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