408. *Isotopic Exchange Reactions of Organic Compounds. Part I. The Intermolecular Nature of Three-carbon Tautomerism.*

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An important application of deuterium in organic chemistry is its use as an " indicator " in the study of tautomeric changes involving the migration of a hydrogen atom : results stated to have some bearing on keto-enol tautomerism have already been obtained by this means (cf. Bonhoeffer and Klar, *Naturwiss.*, 1934, **22**, 45; Schwartz and Stenier, *Z. physikal. Chem.*, 1934, **25**, *B*, 153; Klar, *ibid.*, 1934, **26**, *B*, 335; Halford, Anderson, and Bates, *J. Amer. Chem. Soc.*, 1934, **56**, 491). The present evidence on the mechanism of three-carbon tautomerism is compatible with a number of different theories, and application of the new method is, therefore, of particular interest.

With this object we have studied the partition of deuterium and hydrogen between the butenoic acids and the solvent under conditions known to produce substantially complete tautomeric equilibrium, *viz.*, treatment with 1·05 mols. of *N*-sodium hydroxide in aqueous solution at 100° for 2 hours. As a check, the behaviour of butyric acid under the same conditions has been examined. The isotopic ratios of deuterium to hydrogen in all components of the systems, both before and after the " equilibration," have been taken into consideration. That of the organic materials used initially has been assumed to be normal, and those of the initial and the final solvent, and of the residual equilibrated solutes have been determined.

At every stage, particular attention has been paid to minimising loss, and consequent possibility of isotopic fractionation. The results have been expressed in the form of " deuterium oxide balance sheets " (p. 1742), calculated from observed isotopic ratios and theoretical yields; this allows the validity of the results to be assessed in each case by the degree of agreement between the initial and final amounts of deuterium oxide. Since *N*-solutions were used, the molar proportion of solvent to solute in the systems was approximately 50 : 1. It is therefore evident that any effect of isotopic interchange on the solvent will be very small compared with that on the solute, so only the latter results can be regarded as decisive.

The properties of the waters produced by combustion of the final solutes are shown in the following table of the increases of density and of mol.-fraction of deuterium oxide brought about by equilibration. Butyric and crotonic acids show no appreciable isotopic interchange with the solvent, whereas vinylacetic acid shows substantial interchange. The very slight " heaviness " of the first two waters is attributed to experimental error (see p. 1742).

Deuterium Content of Combustion Waters.

	Butyric acid.	Crotonic acid.	Vinylacetic acid.
$\Delta d_{4^\circ} \times 10^6$	1·4	1·7	71·4
Mol.-fraction of $D_2O \times 10^3$	0·013	0·015	0·670

The result with butyric acid is of interest as indicating that no appreciable enolisation occurs under our experimental conditions : a similar result has been obtained for sodium acetate, but in the absence of excess alkali (Bonhoeffer, *Z. Elektrochem.*, 1934, **40**, 469; Hall, Bowden, and Jones, *J. Amer. Chem. Soc.*, 1934, **56**, 750; the latter authors, however, report interchange on prolonged treatment). Enolisation in the sense $CH_2R\cdot CO\cdot OH \rightleftharpoons CHR{:}C(OH)_2$ has been extensively and successfully invoked to explain, *inter alia*, bromination on the α-carbon atom (Lapworth, J., 1904, **85**, 30; Aschan, *Annalen*, 1912, **387**, 9; Ward, J., 1922, **121**, 1161; Shaw, J., 1923, **123**, 2233; but contrast Watson, J., 1925, **127**, 2067), racemisation (Lowry, *B.A. Report*, 1904, p. 211; Frankland, J., 1913, **103**, 725; Rothe, *Ber.*, 1914, **47**, 843; McKenzie and Widdows, J., 1915, **107**, 702; Wren, J., 1918, **113**, 210), and the interconversion of *cis–trans*-isomerides (Aschan, *loc. cit.*; Mohr, *J. pr. Chem.*, 1912, **85**, 334; Wren, *loc. cit.*; Hückel and Goth, *Ber.*, 1925, **58**, 447).

In the case of the butenoic acids, there is a parallelism between isotopic interchange and tautomerism. Crotonic acid tautomerises at most to the extent of 2% (Linstead and Noble, J., 1934, 614) and shows very little, if any, interchange. Vinylacetic acid, on the other hand, tautomerises readily to the extent of at least 98% (Linstead and Noble, *loc. cit.*) and undergoes considerable interchange; quantitative interpretation of this result involves assumptions which, pending further investigation, are only tentative. It has been shown that interchange reactions of deuterium and hydrogen involve an equilibrium, the constant of which may differ from unity (cf. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, 1935, p. 200), and definite quantitative conclusions with regard to the reaction cannot be reached unless the value of this constant is known. Since, however, vinylacetic acid shows isotopic interchange, but, during the process, is being continuously transformed into crotonic acid which does not show interchange, it seems likely that the interchange reaction is not strictly reversible and is thus not an interchange equilibrium in the ordinary sense. As a preliminary working hypothesis, we assume that a proton is removed from the α-position in the molecule at the demand of the protophilic solvent. Following internal electronic rearrangement of the molecule, a proton or a deuteron re-enters the molecule in the γ-position, in a statistical ratio which is mainly determined by the isotopic composition of the solvent but may be modified by isotopic discrimination. It is probable, however, that the addition of a proton or a deuteron to the "activated" tautomeric residue of the acid is a reaction of high free energy, and that any such isotopic discrimination will consequently be small.

Subject to the two assumptions that isotopic interchange is a function of tautomerism and that no appreciable isotopic discrimination occurs, the reaction may be examined on the following lines. It is clear that, on the above basis, the isotopic composition of the solvent is continuously changing during the course of the isomerisation. Let M be the total number of mols. of solvent, a constant; x the mol.-fraction of D_2O in the solvent; and m the number of mols. of water equivalent to the hydrogen concerned in the interchange. For an infinitesimal interchange, $x \,.\, dm = M \,.\, dx$; therefore $dm = M \,.\, dx/x$. Integration for a total interchange of m mols. of water gives

$$m = M \,.\, \log x_0/x$$

where x_0 and x are the mol.-fractions of D_2O in the initial and the final solvent, respectively. Therefore $x = x_0 \,.\, e^{-m/M}$, and, since m/M is small, $x = x_0(1 - m/M)$ as a close approximation. Further, let there be r mols. of vinylacetic acid present, and let n of the 5 hydrogen atoms per mol. undergo interchange. Then the mol.-fraction of deuterium in the final acid, or of deuterium oxide in the combustion water, will be

$$y = (x_0 - x)M/5r = mx_0/5r = nx_0/5 \text{ or } n = 5y/x_0.$$

Substituting the experimental values for y and x_0, we obtain $n = 0{\cdot}92$. It thus seems probable that one of the propene hydrogen atoms of the vinylacetic acid molecule undergoes isotopic interchange with the solvent during isomerisation. It must be emphasised, however, that the only result which is beyond doubt at present is that interchange does occur. It is thus clear that the solvent plays an important part in the isomerisation process; the change must, therefore, be intermolecular, any intramolecular mechanism being unacceptable.

EXPERIMENTAL.

Preparation of Materials.—Butyric acid. Pure *n*-butyric acid (B.D.H.) was redistilled, b. p. 161—163° (Found: equiv., by titration, 88·2. Calc.: 88·06).

Crotonic acid. The pure acid (L. Light & Co.) was twice recrystallised from water and dried over calcium chloride in vacuum; m. p. 70—71° (Found: equiv., by titration, 86·16. Calc.: 86·05).

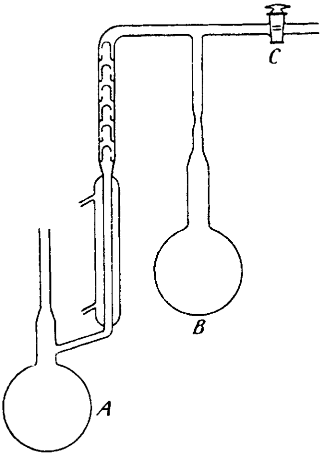
Vinylacetic acid. This was prepared by Linstead, Noble, and Boorman's method (J., **1933**, 560) and twice redistilled shortly before use; b. p. 74°/16 mm. (Found: equiv., by titration, 86·0. Calc.: 86·05).

Deuterium oxide. 0·4% Deuterium oxide (Norsk Hydro-Elektrisk Kvaelstofaktieselskab) was refluxed from alkaline potassium permanganate and twice redistilled, a sample being stored in a sealed tube for subsequent isotopic analysis.

Volumetric solutions. Approximately 1·05*N*-sodium hydroxide solution was prepared from B.D.H. " AnalaR " sodium hydroxide and 0·4% deuterium oxide; hydrochloric acid solution of comparable strength was made by absorption of a measured volume of the dry gas in a further portion of the same solvent. These solutions were stored in closed vessels, protected from contamination and change, standardised independently, and checked by titration against each other. Microvolumetric methods were employed, all apparatus being carefully calibrated against weights of boiled-out distilled water.

Equilibration Experiments.—The apparatus (Fig. 1) consisted of a 500 c.c. Pyrex flask, *A*, connected by means of a side tube to a reflux condenser, an efficient splash-head, and a receiver, *B*, for the solvent distilled during the recovery process; the whole could be exhausted when desired through the tap, *C*. Preliminary cleaning was effected by treatment with nitric–chromic acid, thorough washing with distilled water, and baking under vacuum. A small quantity of silver oxide was introduced into *B* prior to the experiment and dried in vacuum.

FIG. 1.



Slightly less than the required quantity of acid (0·15 mol. of butyric acid or 0·2 mol. of the butenoic acids) was weighed into *A*, a weight pipette being used for the liquid acids. Adjustment to the required quantity, within 1 mg., was then effected by adding the balance in a small glass capsule. After the sodium hydroxide solution (150 c.c. or 200 c.c. respectively) had been added from a pipette, the vessel was sealed, and heated under reflux in a boiling water-bath for 2 hours. After cooling, the flask was opened, and the contents exactly neutralised by addition of the calculated volume of the standard hydrochloric acid from a microburette; this neutralisation eliminated the difficulty of removing water completely from material containing free sodium hydroxide and fixed a standard time for the equilibration.

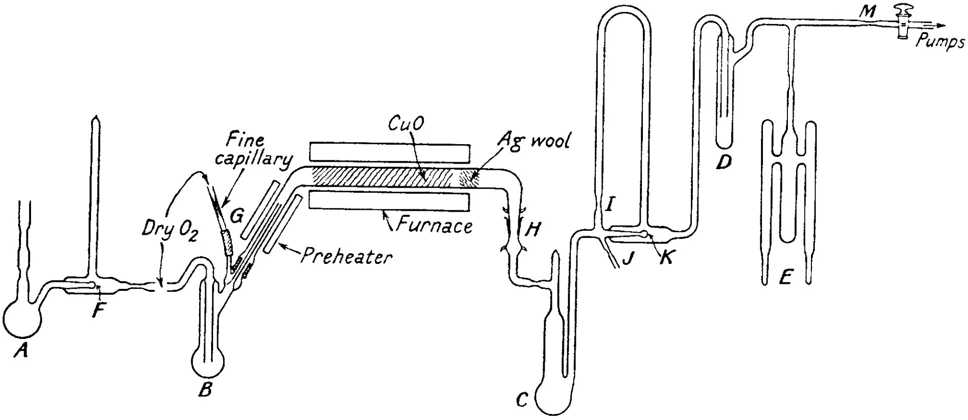
Recovery of Water.—Solvent. Following neutralisation of the contents, flask *A* was sealed, the water drained from the condenser jacket, the whole apparatus rapidly evacuated, and tap *C* closed. Distillation from *A* to *B* was effected by cooling *B* in ice and warming *A* on the water-bath, and was completed by heating *A* in a boiling water-bath and keeping *B* at 0° for some hours. *B* was then sealed off and stored; *A* was detached, and the hard dry residue scraped out as completely as possible.

Residue. After being ground to a fine powder and stored over-night in a vacuum desiccator containing phosphoric oxide, the residue was rapidly mixed with ignited copper oxide and introduced into a large combustion tube (125 × 2 cm.), packed in the usual way and previously burned out for some hours. The combustion was carried out in a slow stream of dried air, water being collected in a weighed trap maintained at — 20° in ice–salt mixture. To check the efficient recovery of the combustion water, the absorption train included a second similarly cooled trap and a weighed calcium chloride tube; the latter gained 10—20 mg. in weight during the course of the combustion (12 hours). The over-all yield of water in each case was approximately 93% of the theoretical.

Isotopic Analysis.—The isotopic ratio in the water samples was estimated by the " flotation " method of density determination (see, *e.g.*, Farkas, *op. cit.*). A vacuum technique of purification and measurement in an all-Pyrex glass apparatus was employed; the sample (7—8 c.c.) was completely recovered (at least 99% yield) and the entire process could thus be carried out repeatedly. It was found, however, that constancy of density was reached after the first treatment, indicating the effectiveness of, and the absence of isotopic fractionation in, the purification process. It was also possible to redetermine the density of a sample stored in a sealed tube over a period of time, and the measurements showed that, within the limits of accuracy (*ca.* 1 part per million in density), there was no disturbing change in the measuring apparatus during the experiments.

Summary of Purification Method.—Since the initial materials were " chemically pure," the purification process did not have to be so rigorous as that of Emeléus, James, King, Pearson, Purcell, and Briscoe (J., **1934**, **1207**), which was designed for natural waters. Briefly, it consisted of five main operations: (*a*) preliminary treatment with silver oxide, (*b*) distillation in a stream of oxygen over heated copper oxide, (*c*) further treatment with silver oxide, (*d*) removal of dissolved gas, and (*e*) vacuum distillation. None of these stages could be omitted without disturbing the density results, except that stage (*a*) was unnecessary for samples already treated. In earlier work an attempt was made to use a stock of substantially pure water as a " sub-standard " (tap-water, completely purified according to the above scheme, being taken as the primary standard), in order to carry out repeated checks on the stability of the measuring apparatus. This water was subjected to stages (*d*) and (*e*) only, and gave erratic density results; it would seem that only freshly and rigidly purified samples of water can provide results of the required accuracy.

FIG. 2.



Apparatus.—The components are illustrated in Fig. 2. Stage (*a*) was carried out in vessel *A* and followed by transfer of the sample to the trap *B*. During Stage (*b*), the sample was passed through the combustion tube into the trap *C*, where Stages (*c*) and (*d*) were effected. Trap *D* served as a receiver in the vacuum distillation prior to the final transfer to the flotation vessel *E*.

The object of the " septa " *F* and *K* (*i.e.*, thin-walled bulbs, broken by the usual electromagnetic device when desired) attached to vessels *A* and *C* was (i) to ensure complete interaction of the sample with silver oxide in a confined space, and (ii) to avoid the introduction of foreign water into the sample as a result of the glass-blowing operations required during the actual purification process. The " loop-way " tube surrounding the septum *K* was used only during preliminary steaming and pumping, and was sealed at *I* at the conclusion of these operations; during the combustion, oxygen issued at the outlet *J*.

The method of introducing the oxygen–steam mixture into the combustion tube by means of a preheater and an oxygen by-pass *G* is self-evident from the figure, and was very efficient in preventing condensation or back-distillation of the sample. The rubber stopper attaching trap *B* to the combustion tube was also kept cool and well away from the sample by this device. The combustion tube was packed with copper oxide and with a plug of silver wool at the receiver end; it was connected to the remainder of the apparatus by means of the unlubricated ground joint *H*, which did not have to withstand any pressure difference. Tap *L*, used to isolate the apparatus from the pump when necessary, was lubricated with ordinary vaselin; as it was far removed from the sample throughout the experiments, there was no danger of contamination.

The apparatus was exhausted by means of a single-stage mercury diffusion pump, backed by a Cenco "Hyvac" pump, the usual type of discharge tube providing a rough vacuum gauge.

The flotation vessel, *E*, consisted of three compartments, a receiver, used in the final vacuum distillation, and two side-limbs into which the silica floats were introduced at the appropriate stage. The floats, together with the other apparatus associated with the physical measurements, are described on p. 1740.

Cleaning of the Apparatus.—Since the ratio of surface of apparatus to volume of sample was relatively large, rigorous cleaning methods were essential. During the purification process, the sample was transferred successively through the vessels *A*, *B*, *C*, *D*, and *E*, and the cleaning of these vessels thus became increasingly significant in the same order. Previous to use, all vessels were kept over-night filled with fuming nitric acid; the use of cleaning mixtures containing non-volatile material was found to be undesirable. Vessels *A* and *B* were then washed thoroughly with distilled water, dried by "pumping out," and finally baked under vacuum. The remainder of the apparatus, with the exception of the vessel *E*, consisted of a single glass piece between *H* and *L*, and was steamed for 3 hours after the nitric acid treatment. Steam was generated from "conductivity water," prepared in a still of the Stuart and Wormwell type (J., **1930**, 85), in an all-Pyrex boiler, the necessary connexion being made by means of tin-foil. The flotation vessel was cleaned similarly, steam being generated from a separate boiler. After steaming, the vessels were drained, sealed together, dried by pumping out, and finally thoroughly baked under high vacuum.

The absence of "pin-holes" in the apparatus was ensured by the maintenance of a high vacuum for 1 hour with the tap *L* closed. This precaution was essential because the floats were less compressible than water and therefore sensitive to pressure during flotation; a minute leak in the apparatus would cause a considerable discrepancy in the flotation temperatures.

The floats were cleaned by standing in fuming nitric acid over-night and washing with freshly distilled conductivity water immediately before being introduced into the flotation vessel.

Procedure.—About 0·2 g. of silver oxide, freshly precipitated and dried in a vacuum at 100°, was placed in flask *A*, and further pumped, with gentle baking, until a high vacuum was maintained. The vessel was then opened, the sample introduced from a pipette, and frozen at −20°. The flask was next rapidly exhausted, sealed, and immersed in a boiling water-bath for 2 hours. Meanwhile, a similar quantity of the same silver oxide was introduced into the trap *C* and further exhausted by pumping at *J*, the by-pass tube having been sealed at *I*. Subsequently, *C* was sealed to the ground joint *H*, and a stream of dry oxygen passed, with continual baking of the trap, to remove traces of moisture introduced by the sealing operation; the combustion tube had previously been burned out for at least 3 hours in dry oxygen.

On removal from the water-bath, flask *A* was sealed, *via* the side tube containing the septum *F*, to trap *B*, and traces of moisture were removed from the latter by pumping and baking. After introduction of the breaker into the fall tube, re-evacuation, and sealing of the apparatus from the pump, the septum was broken, and the sample evaporated completely from *A* to *B*, without boiling, by cooling *B* in ice-water and warming *A* at or below 35°. At the conclusion of the distillation *B* was sealed off from *A*.

The stream of oxygen passing through the combustion tube was stopped, and trap *C* cooled in an ice–salt mixture to − 20°. The entry and delivery tubes of *B* were opened (thereby admitting about 150 c.c. of moist air, containing not more than 3 mg. of moisture), and *B* was rapidly fitted to the combustion tube as shown in Fig. 2. Distillation of the sample in a slow stream of dry oxygen was then carried out, trap *B* being heated in a glycerol-bath to such a temperature that boiling of the sample was just avoided. At the conclusion of the distillation, the oxygen stream was continued for at least ½ hour, the joint *H* and the adjacent part of the combustion tube being gently warmed to transfer the last traces of water to *C*, which was then sealed from the joint *H*, rapidly evacuated, and sealed at *J*. After melting, the sample was heated in a water-bath for 1 hour to ensure complete interaction with the silver oxide. Meanwhile, the flotation vessel was removed, the floats introduced, and the vessel resealed to the apparatus; the breaker was introduced into the fall tube above the septum *K*, and the whole apparatus pumped out to a high vacuum. After cooling, the sample was refrozen at − 20°, and the septum broken, with the tap *L* closed. Dissolved gas was then removed by successively freezing, pumping for not more than 2 minutes, and melting with the tap closed. Distillation from *C* to *D* was carried out over-night by leaving *D* cooled in ice-water in a Dewar vessel, the apparatus being sealed at *M* to avoid possible leakage of air through the tap over a long period. Similar distillation from *D* to *E* was effected immediately before the sealing and removal of *E*, and the determination of the density of the sample. In none of the distillations was boiling allowed to occur; transfer by surface evaporation over a temperature gradient of 30° was rapid, and very efficient in removing dissolved non-volatile impurities, thus making the use of splash-heads unnecessary.

Density Measurements.—The accuracy required in the density measurements demanded the control and comparative measurement of temperature within about 0·001°, and this was achieved by the following apparatus. The thermostat consisted of a 30-litre glass tank, heated by means of a cylindrical lamp, arranged co-axially with a helical toluene regulator of large capacity, and so designed as to allow fine temperature regulation, the mercury contact being kept clean by a shunting capacity of 16μF to avoid " drifting " of temperature. The associated electrical equipment was of the usual type, the relay current, supplied by a potentiometer connexion at about 10 volts, operating an " Isenthal " mercury switch in the heater circuit. A rheostat was also included, in series with the heater, in order to adjust the periods of heating and cooling to approximate equality at about 10 seconds. A cooling coil was used when necessary, and was supplied with water at a constant head in order to maintain a steady rate of cooling. The disposition of the various components in the bath was of the greatest importance. A symmetrical arrangement was adopted: the regulator and heater in one corner, the stirrer, propelling upwards, in the centre, and the thermometer and flotation vessel in the opposite corner. The cooling coil was placed as near the regulator as possible.

A Sutton bomb-calorimeter thermometer, 65 cm. long and graduated in 0·01° from 21° to 34°, was used, and found to be remarkably free from secular change and capable of giving reproducible readings over a long period. The scale was standardised initially by means of the transition point of sodium sulphate decahydrate. During the measurements a further check on the temperature scale was kept by the use of two arbitrary " fixed points," supplied by the equilibrium temperatures of two large silica floats, permanently sealed in evacuated vessels containing samples of pure water. This device eliminated the very considerable corrections for changes in barometric pressure and for the alteration of the stem exposure effect with room temperature; subject to these variations, the fixed points remained reproducible within 0·001° over the whole period of the recorded measurements. Appreciable secular change was, therefore, absent but, in any event, would not have been of any significance. The thermometer and motion of the floats were observed by means of a reading microscope, parallax errors being negligible.

The floats were cylindrical and drawn from " Vitreosil " tubing, the " experimental " and the " fixed point " float being 30 × 2 mm. and 60 × 3 mm. respectively. Small hooks at the top facilitated manipulation by means of a platinum wire. The object of duplication was to minimise danger due to possible damage or secular change; none was observed after the first month or two following manufacture. During the experiments, centring and depression or elevation of the float within the sample was accomplished by means of suitably varied swirling motions of the containing vessel; very rigid mounting of the latter was essential in the course of the observations to avoid the disturbing effect of vibration on the motion of the float.

The exact equilibrium temperature was found by interpolation from a plot of the rate of motion of the float against the temperature (Emeléus, James, King, Pearson, Purcell, and Briscoe, *loc. cit.*). The rate of motion was observed for 2 minutes, temperature readings being taken immediately before and after this period. The difference between these two readings was seldom more than 0·001°, and the range of a single determination of equilibrium temperature, 0·01°; the latter could thus be interpolated within 0·001°. The determination of the density of a given sample consisted of about ten measurements of flotation temperature, observations of each " experimental " float and of the fixed points being taken successively on rising and falling temperature scales. The first measurement on a given sample was consistently lower than the succeeding measurements by *ca.* 0·01°; this is attributed to solution of impurities from the glass vessel by the freshly distilled sample. At present, the difficulty of cleaning the apparatus to a degree of purity commensurate with that of the sample seems to place a limit on the accuracy of the method (see above). The effect seemed to be quite constant, however, and the results are probably comparable, and certainly reproducible, to limits much less than this error would indicate at first sight; in effect, the results are really comparative densities of samples of water containing the same small limiting amount of impurity. It is hoped to eliminate this difficulty in the further development of the method.

Two typical series of readings are shown in the following table, where bracketed figures represent a single determination of flotation temperature.

Sample.			Fixed points.			Difference.
Tap-water.						
1.	2.	Mean.	1.	2.	Mean.	
27·417°	27·449°	27·433°	27·645°	28·333°	27·989°	− 0·556°
27·423	27·450	27·4365	27·645	28·333	27·989	− 0·5525
27·423	27·453	27·438	27·645	28·332	27·9885	− 0·5505
27·424	27·452	27·438	27·645	28·332	27·9885	− 0·5505
					Mean	− 0·552
Crotonic acid solvent.						
28·797	28·830	28·8135	27·648	28·335	27·9915	0·822
28·805	28·830	28·8175	27·648	28·336	27·992	0·8255
28·804	28·832	28·818	27·648	28·336	27·992	0·826
28·805	28·832	28·8185	27·649	28·336	27·9925	0·826
					Mean	0·825

The results of the flotation-temperature measurements are summarised below; the tap-water and original solvent measurements were interspersed with the other determinations and therefore serve as a check on the relative accuracy of the results. The figures in parentheses indicate the number of times the relevant samples had been subjected to the purification process. Results marked with an asterisk relate to samples in which stage (*c*) (see p. 1738) had been omitted in the purification immediately prior to measurement; these results are substantially higher than the others and are not included in the final mean values. ΔT indicates flotation temperatures relative to London tap-water, which is taken as the standard of normal isotopic composition, and T represents the temperatures corrected relative to the sodium sulphate transition point.

Sample	Tap-water.	Original solvent.	Butyric acid. Solvent.	Butyric acid. Combustion water.
Mean flotation temps. relative to mean fixed points.	(1) − 0·552°	(1) 0·858°	(1) 0·835°	(1) − 0·548°
	(1) − 0·554	(2) 0·863	(2) 0·837	(2) − 0·546
	(2) − 0·552	(3) 0·858		
	(4) − 0·550	(4) 0·858		
	(3) − 0·546*	(1) 0·871*		
	(1) − 0·534*			
Mean	− 0·552	0·859	0·836	− 0·547
ΔT	0	1·411	1·388	0·005
T	27·056	28·467	28·444	27·061

Sample.	Crotonic acid. Solvent.	Crotonic acid. Combustion water.	Vinylacetic acid. Solvent.	Vinylacetic acid. Combustion water.
Mean flotation temps. relative to mean fixed points	(1) 0·826°	(1) − 0·546°	(1) 0·821°	(1) −0·293°
	(1) 0·825		(1) 0·819	
	(1) 0·830		(2) 0·820	
Mean	0·827	− 0·546	0·820	− 0·293
ΔT	1·379	0·006	1·372	0·259
T	28·435	27·062	28·428	27·315

It is evident that the results are reproducible to within ± 0·003°, corresponding to an accuracy in the density values of less than $\pm 1 \times 10^{-6}$. For this reason it has been considered unnecessary to duplicate measurements on a single sample in the case of the last two "combustion waters."

Calculation of Densities and Mol.-fractions of Deuterium Oxide.—In calculating the so-called "mol.-fractions" of deuterium oxide, it must be remembered that the quantities considered are mols. of pure deuterium oxide (or atoms of deuterium) and mols. of water (or atoms of hydrogen) of normal isotopic composition. Any other treatment is not possible in the absence of the necessary physical data on pure "light water," and it is evident that this approximation cannot have any appreciable significance.

The various interpolation equations which have been used in the calculations are as follows :

(*a*) Densities of normal water (in g. per ml.) at various temperatures were taken from the International Critical Tables. Over the temperature range 26—30°, the equation $d_{4^\circ}^{T^\circ} = 0{\cdot}9968128 - 0{\cdot}0002662\Delta T - 0{\cdot}0000452(\Delta T)^2$, where $\Delta T = T - 26^\circ$, was found to apply within 1×10^{-7}.

(*b*) Densities of deuterium oxide : Lewis and Macdonald's values of Δd_{4° (*J. Amer. Chem. Soc.*, 1933, **55**, 3057) approximate to a parabolic curve when plotted against temperature, between 10° and 40°. Over the experimental range of temperature (27—28·5°) the equation $\Delta d_{4^\circ} = 0{\cdot}105256 + 0{\cdot}000199T - 0{\cdot}0000039T^2$ was used and probably represents the difference in the densities of light and heavy water with sufficient accuracy.

(*c*) Mol.-fractions of deuterium oxide: it has been shown that the density–composition relationship of deuterium oxide and water is not strictly linear. Luten (*Physical Rev.*, **1934**, **45**, 161) gives $d_{4^\circ}^{25^\circ} = 0{\cdot}9970 + 0{\cdot}1078x - 0{\cdot}0012(1 - x)$ or $\Delta d_{4^\circ}^{25^\circ} = 0{\cdot}1078x - 0{\cdot}0012(1 - x)$, where x = mol.-fraction of deuterium oxide. For temperatures other than 25°, Δd_{4° for pure deuterium oxide has been obtained from equation (*b*), and the factor 0·0012, giving the departure from linearity, has been assumed constant.

Allowance has been made for the alteration in the density of the floats over the temperature range of the determinations, the coefficient of cubical expansion of "Vitreosil" being taken as 162×10^{-8} per degree.

Densities of the volumetric solutions used in the equilibration experiments were interpolated from data given in the International Critical Tables, allowance being made for the heavy water content, and were used in calculating the theoretical results.

The final results are expressed below in the form of balance sheets of deuterium oxide (see p. 1735); theoretical and experimental mol.-fractions of deuterium oxide and density differences are also shown.

	Original solvent.	Final solvent.	Combustion water.	Total D_2O.	Error, %.
Butyric acid.					
$\Delta d_{4^\circ} \times 10^6$	395·8	389·3	1·4		
Mol.-fraction $D_2O \times 10^3$	3·714	3·653	0·013		
D_2O, g.	0·6533	0·6542	0·0001	0·6543	+ 0·15
Crotonic acid.					
$\Delta d_{4^\circ} \times 10^6$	395·8	386·7	1·7		
Mol.-fraction $D_2O \times 10^3$	3·714	3·629	0·015		
D_2O, g.	0·8704	0·8658	0·0002	0·8660	– 0·51
Vinylacetic acid.					
$\Delta d_{4^\circ} \times 10^6$	395·8	384·7	71·4		
Mol.-fraction $D_2O \times 10^3$	3·714	3·610	0·670		
D_2O, g.	0·8704	0·8613	0·0068	0·8681	– 0·26

It is evident that in further work attention should be paid to the quantitative separation of, and recovery of water from, the components of the final equilibrated system, rather than to the density determinations. The slight "heaviness" of the butyric and crotonic acid "combustion waters" may be due to the original acids not being of normal isotopic composition, but is more probably connected either with firmly adsorbed solvent or with the incomplete yield in the large-scale combustion experiments. The hydrolysis of the sodium salts may also have some bearing on this point. The similarity of the two cases makes it unlikely that the effect in the case of crotonic acid is due to incipient interchange, but a definite decision on this point must await more accurate treatment. The decrease in the densities and mol.-fractions of deuterium oxide shown by the solvents from butyric and crotonic acids is, of course, due to the normal water produced by neutralisation.

SUMMARY.

The "equilibration" of vinylacetic and crotonic acids in the presence of 1·05 mols. of sodium hydroxide in dilute "heavy water" at 100° has been studied; as a check, the behaviour of butyric acid under the same conditions has also been examined. A method of isotopic analysis depending on density determinations accurate to one part per million, applicable to small samples of water and involving no loss, is described.

The experimental results show that, although there is no detectable interchange with butyric and crotonic acids, substantial interchange occurs in the case of vinylacetic acid; on the basis of the necessarily tentative assumption that no isotopic discrimination occurs, the results indicate that one of the propene hydrogen atoms of vinylacetic acid undergoes isotopic interchange with the solvent. It is concluded that purely intramolecular mechanisms for this type of three-carbon tautomerism are unacceptable.

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