414. Exchange between Light and Heavy Oxygen. Part I. Oxygen Interchange between Sulphate Ions and Water.

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By the use of heavy-oxygen water and ordinary sodium sulphate or heavy-oxygen sodium sulphate and ordinary water, it is proved that water and sulphate ions interchange their oxygen, the reaction being catalysed by hydroxide ions. It is suggested that the exchange depends on the partial or complete temporary inclusion of a pair of electrons belonging to a foreign oxygen atom in the central valency shell of the sulphate ion. The main evidence for this idea (from which both the exchange and its characteristic catalysis were predicted) is that the highly nucleophilic hydroxide ion is a much more effective reagent for exchange than the feebly nucleophilic water molecule.

Many mechanisms are possible by which the anions of oxy-acids might exchange their oxygen with that of solvent water, either in neutral solution, or in the presence of an enhanced concentration of hydroxonium or hydroxide ions. The more apparent possibilities may be divided into three groups:

(1) *Dehydration followed by Hydration.*—We may expect to realise this type of mechanism with anions such as orthosilicate, orthophosphate, or sulphite, since the corresponding acids undergo facile reversible dehydration. It is unnecessary to discuss here whether these dehydrations are intramolecular decompositions of the undissociated acids, proceed by a specialised interaction of the cation and anion, or take any other of the conceivable routes. For the subsequent hydration there are likewise various possibilities which need not separately be considered. We have envisaged the whole group of mechanisms collectively, and may illustrate it by reference to the orthophosphate ion:

$$2PO_4^{---} + 2H^+ \rightleftharpoons 2HPO_4^{--} \rightleftharpoons P_2O_7^{----} + H_2O$$

(2) *Hydration followed by Dehydration.*—Mechanisms of this type become possible with unsaturated ions such as carbonate and nitrate, which, though mesomeric, possess a total unsaturation equivalent to one double bond. Here again there are many possible variations: the water may add either to the acid or to its anion, and may do so either as a molecule, or as a pair of ions, which may attack the unsaturated centre in either order. There are likewise various possible routes for the subsequent dehydration. However, we group all these mechanisms together, and may exemplify them by means of the carbonate ion, employing one canonical structure as a reaction formula in accordance with the usual convention:

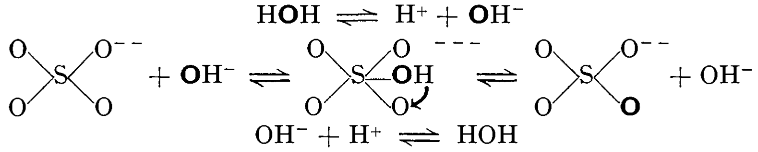
$$O_2C{:}O^{--} + H_2O \rightleftharpoons O_2C(OH)_2^{--}$$

(3) *Temporary Covalency Increase.*—Mechanisms of this type become possible (*a*) when the central atom of the oxy-acid is capable of covalency increase, *e.g.*, when it is 4-covalent and is not a first-row element; (*b*) when an adequate concentration of a sufficiently nucleophilic reagent is provided by the aqueous solvent; and (*c*) when no interference arises through the incursion of mechanisms of types (1) and (2). The sulphate and perchlorate ions might be hoped to satisfy conditions (*a*) and (*c*); whilst, as to (*b*), the water molecule itself is feebly nucleophilic, and the hydroxide ion very strongly so. According to the most elementary conception of this reaction, the nucleophilic reagent would include a pair of its electrons in the valency shell of the central atom of the anion, which, after a proton-migration (Lewis, 1923), would eject a hydroxide ion containing a different oxygen atom. For example, in the hypothetical equation

$$ClO_4^- + OH^- \rightleftharpoons ClO_5H^{--}$$

the chlorine atom temporarily becomes 5-covalent. It may, of course, be suggested that the addition, proton-migration and elimination are less sharply separated in time than this equation implies, and, indeed, one may envisage all the possibilities which lie between a complete separation of the stages and their complete synchronisation; nevertheless, should it be found that the exchange depends fundamentally on the nucleophilic potency of the reagent, we might justifiably conclude that exchange involves at least partial covalency increase.

Interested especially in the third group of mechanisms, we chose the sulphate ion as the starting point of the present enquiry, since the ability of sulphur to increase its covalency is well established. The technique involved the use of " heavy-oxygen water," *i.e.*, water containing more than the normal proportion of ^{18}O. It is assumed that no appreciable separation of the oxygen isotopes occurs in the course of the experiments, *i.e.*, that " heaviness " conferred on the oxygen of one of the interacting species constitutes a well-fixed label for that particular oxygen. Using heavy type to denote isotopic " heaviness," one possible variant of the reaction we have sought to investigate may be formulated thus :



The forward reaction is between ordinary sulphate ion and heavy water, but naturally one may also study the back-reaction, *i.e.*, that between heavy sulphate ion and ordinary water.

Of the methods available for the preparation of heavy-oxygen water, *viz.*, diffusion (Hertz), distillation (Lewis), and exchange (Urey), the second was used. A relatively simple laboratory still having delivered in quantity water heavier than normal water by 30 p.p.m., we were encouraged to enlist the co-operation of Professor H. E. Watson, who built a much larger and more efficient still, which has already given water heavier than normal water by more than 700 p.p.m. This work will be separately published. The present experiments were carried out with the aid of a sample of water given by the large still in the earlier stages of a distillation. This water had an excess density of 132 p.p.m. Its oxygen was separated by electrolysis and combined with normal hydrogen.* The water thus produced had an excess density of 86 p.p.m., due entirely to the increased proportion of the heavier isotopes of oxygen. The error in a single measurement of density being only 1 p.p.m., the material was quite dense enough for the experiments contemplated.

The materials used were well-dried sodium sulphate and water, and in some experiments an enhanced concentration of hydroxide ions was provided by previously dissolving a small amount of sodium in the water. The neutral or alkaline aqueous solutions of sodium sulphate were heated at 100° for 18—26 hours, after which the water was recovered and examined for changes of density.

The data are contained in the following table. Expts. 1 and 2 show that oxygen exchange between sodium sulphate and neutral water is at most very slow. By contrast, the remaining experiments prove that in the presence of an approximately normal con-

Distribution of Heavy Oxygen between Sulphate Ions and Water.

Expt. No.	Time at 100° (hrs.).	Materials (wt. in g.).	H_2O wt. (g.).	Excess density (p.p.m.).			Density change (p.p.m.).	
				Original H_2O.	Recovered H_2O.	Calc. for equilm.	Found.	Calc. for equilm.
1.	18	Na_2SO_4 2·894	6·20	86	86	70	± 0	− 16
2.	26	Na_2SO_4 4·667	9·92	71	68	57	− 3	− 14
3.	22	Na_2SO_4 4·163 Na 0·24	9·15	79	66	64	− 13	− 15
4.	26	Na_2SO_4 4·528 Na 0·25	10·26	71	60	58	− 11	− 13
5.	26	Residue from 4, vacuum-dried at 220°	7·23	0	9	12	+ 9	+ 12

* Actually the hydrogen was " light " by about 2 p.p.m. in terms of water-density.

centration of hydroxide ions rapid interchange of oxygen occurs between the sulphate ion and the solvent water. In expts. 3 and 4 we find that, when the alkaline heavy water is treated with ordinary sodium sulphate, the water undergoes reduction of density to an extent approximately corresponding to a pooling of its oxygen with that of the sulphate. Expt. 5 proves that the " heaviness," which in the previous experiment had disappeared from the water, is really present in the sulphate, since it could be partly recovered therefrom : when this heavy sulphate was treated with alkaline ordinary water the solvent gained in density to an extent once more corresponding approximately to a uniform distribution of oxygen isotopes between the sulphate and the water.

These experiments show that the active agent in the demonstrated exchange of oxygen with the sulphate ion is, not the water molecule, but the hydroxide ion. It will be appreciated that, independently of whether or not the concentration of the hydroxide ions is artificially augmented, the oxygen of the hydroxide ions will at all times be a true sample of the oxygen of the solvent water. This follows from the fact that the hydroxide ion is an ion of water and contains the whole of its oxygen :

$$\mathrm{HOH} + \mathrm{OH}^- \rightleftharpoons \mathrm{HO}^- + \mathrm{HOH}$$

The same consideration shows, furthermore, that the hydroxide ion will not merely carry its own oxygen into the exchange reaction with the sulphate ion, but will also act as a vehicle in this sense for the whole of the oxygen of the solvent water. Thus the hydroxide ion could be described as a catalyst for the exchange, but there can be no doubt that the reason why it is a catalyst is because it is the real reagent. The much greater reactivity of the hydroxide ion than of the water molecule in the exchange of oxygen with the sulphate ion is in agreement with our view that this reaction involves a fractional or integral covalency increase of the sulphur atom, and thus depends in an essential manner on the nucleophilic activity of the reagent. A similar mechanism may be suggested to account for the oxygen exchange, very recently reported by Blumenthal and Herbert (*Trans. Faraday Soc.*, 1937, **33**, 849), between the orthophosphate ion and water containing carbonate and hydroxide, but the difficulty of demonstration is greater in this example. Another related observation is that of Anderson (*Z. physikal. Chem.*, 1936, *B*, **32**, 237), who prepared thiosulphate from sulphite and radioactive sulphur, and showed that the latter became free on acidification. Here the isotopic label distinguishes the peripheral from the central sulphur atom of the thiosulphate ion, and we would expect the former to be the more readily eliminated.

EXPERIMENTAL.

Heavy-oxygen Water.—The crude sample from the still (p. 1969) was digested with potassium permanganate and potassium hydroxide for 24 hours at room temperature and then for 32 hours at the b. p. It was distilled from these reagents, redistilled with a little sulphuric acid in order to remove traces of ammonia, and again distilled from potassium hydroxide to remove acid products. It was then given an ordinary distillation at atmospheric pressure, and finally a non-ebullient distillation between 25° and 0° in a sealed, air-free apparatus. Its density at 25° was 132 p.p.m. above that of similarly purified tap-water.

The heavy water was then electrolysed in a divided cell, designed to minimise the usual troubles attending the use of moderate currents, *viz.*, heating, spraying, and mixing of the gases. An outer tube, of 5 cm. internal diameter and 20 cm. long, closed at the bottom, and bearing a small gas-delivery tube at the top, was fitted with a concentric inner tube, of 2·2 cm. internal diameter, and open at its bottom which was about 3 cm. above the bottom of the outer tube. The inner tube also carried a gas-delivery tube near the top, and it contained the anode, an open cylinder of sheet nickel, about 1·5 cm. in diameter and 5 cm. high. The cathode, which was always at earth potential, consisted of a closely wound spiral of copper tubing surrounding the inner glass tube for a height of about 5 cm.* Both electrodes were arranged so that their bottoms were about 2 cm. above the bottom of the inner glass tube. When the cell was being operated a rapid stream of tap-water was passed through the tubular catnode ; also the outer glass tube was surrounded with ice-water. With this arrangement a current of 5 amps. could

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* The copper tubing had to be first bent double and then wound, in order to get the spiral into the available space with both ends of the tubing projecting from the top of the cell.

be used without appreciable heating of the electrolyte. The gas-space at the top was sufficient for the subsidence of the froth and most of the spray; and the vertical clearance between the electrodes and the bottom of the inner tube was enough to prevent more than a very slight mixing of the gases through the swirling of the electrolyte in the neighbourhood of the electrodes. The evolved oxygen was dried by passage through an empty U-tube cooled by means of solid carbon dioxide. The requisite conductivity was provided by adding 0·8 g. of sodium hydroxide to each 100 c.c. of the water.

The hot copper which was used to catch the oxygen from the cell was prepared in a Pyrex combustion tube by the reduction of copper oxide by means of hydrogen, previously freed from traces of oxygen by passage over red-hot copper in another tube and subsequently dried. When the reduction was complete, *i.e.*, when water ceased to be formed, the excess of hydrogen was swept away by a stream of nitrogen, previously freed from oxygen and moisture in the same manner as the hydrogen. Before being connected to the tube, thus prepared, of hot copper in nitrogen, the electrolytic cell was operated for 10 minutes in order to sweep out any contained air; and, after the connection was made, the stream of nitrogen was continued, primarily in order to prevent the creation of a partial vacuum owing to the absorption of the oxygen, and partly also to reduce the local heating due to the absorption. It was necessary completely to prevent the access of air to the exit end of the tube of hot copper, and with this object an extension of the tube was caused to dip under water, and the nitrogen supply was so regulated that the pressure in the tube was never less than atmospheric. The gases entering the hot tube contained, besides nitrogen and oxygen, a trace of hydrogen arising from the slight mixing of the cell gases; and this hydrogen was, of course, converted into water. Any residual moisture arising in this way was swept out of the tube by continuing the nitrogen stream after the cessation of electrolysis.

After disconnection of the electrolytic cell, the caught oxygen was reconverted into water by means of a stream of hydrogen drawn from a cylinder, and freed from oxygen and moisture by methods similar to those already described. The approximately normal isotopic composition of this hydrogen (p. 1969, footnote) had previously been established by combining it with the oxygen of electrolysed tap-water, and comparing the density of resultant water with that of the original water. The water from this normal hydrogen and the heavy oxygen, collected at the temperature of ice-water and purified as described for the original water, had, at 25°, a density 86 p.p.m. greater than that of similarly purified tap-water.

Interchange Experiments.—The sodium sulphate was first dried at 225° and atmospheric pressure for 24 hours; it was then heated strongly in a vacuum to constant weight, although the loss of weight in this second stage of drying was found in practice to be negligible.

The reagents, in the quantities given in the table, were enclosed in 50-c.c. bulbs, which were heated in boiling water for the stated times. Each bulb, after being cooled, was opened, and the water was distilled out, the residue being strongly heated. The distillate was then purified as usual, except that sodium was added instead of sodium hydroxide in the distillation to remove acids. The apparatus used for the purification was similar to that described by Day, Hughes, Ingold, and Wilson (J., 1934, 1598), and the procedure was essentially the same except that no oxygen was passed. All purified samples of water were tested for, and found to be free from, sulphate ion and ammonia.

The determinations of density were made with a 3-c.c. pyknometer as described on p. 1599 of the paper referred to. Individual measurements are believed to be reliable to ±1 p.p.m., and differences to ±2 p.p.m.

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