The Exchange Reaction of Oxygen Atoms between Inorganic Anions and Water

By Toshizo TITANI, Kaoru DATE and Mitsuko AMBE

(Received November 26, 1964)

About 25 years ago Titani and Goto[1] investigated the exchange reaction of O-atoms between some inorganic oxyanions and water, and found that the oxyanions of strong acids, such as SO_4^{2-}, NO_3^-, and ClO_3^-, exchanged their O-atoms with those of water in acid solutions, but not in neutral solutions. They found, further, that the same exchange reaction took place in the solutions of the neutral salts of such weak acids as potassium carbonate without any catalytic additives, although in this case the solutions turned alkaline as a result of the hydrolytic dissociation of the salts. The same result was obtained by Blumenthal and Herbert[2] with potassium phosphate. At almost the same time, it was reported by Ingold and his collaborators[3] that sodium sulfate rapidly exchanged its O-atoms with those of water in the presence of alkali. Since all these results suggested that

---

[1] T. Titani and K. Goto, This Bulletin, **14**, 77 (1939).

[2] E. Blumenthal and J. B. M. Herbert, *Trans. Faraday Soc.*, **33**, 849 (1937).

[3] S. C. Datta, J. N. E. Day and C. K. Ingold, *J. Chem. Soc.*, **1937**. 1968,

the reaction was catalyzed by both acid and alkali, we assumed the conventional acid-base catalysis as a primary mechanism of the reaction. At the same time, however, we proposed as an alternative mechanism a reversible dissociation of the neutral acid molecules, such as:

$$H_2SO_4 \rightleftarrows H_2O + SO_3 \qquad (1)$$

Neutral acid molecules can be formed either by the addition of hydrogen ions to the oxyanions:

$$2H^+ + SO_4^{2-} \leftrightarrows H_2SO_4 \qquad (2)$$

as in the case of the acid solutions of strong acid salts, or by hydrolytic dissociation:

$$CO_3^{2-} + 2H_2O \rightleftarrows H_2CO_3 + 2OH^- \qquad (3)$$

as in the case of weak acid salts. With this alternative mechanism, we can explain the results of Titani and Goto as well as those of Blumenthal and Herbert. The only exceptions were the results of the experiment of Ingold and his collaborators, who found the exchange of O-atoms between the oxyanions of such strong acids as SO_4^{2-} and water in an alkaline solution, as has been described above. Therefore, we attempted first to repeat the experiment of Ingold and his collaborators. Unfortunately, however, it was very difficult to carry out such an experiment because the glass surface of the reaction vessel was seriously attacked by the aqueous alkaline solutions at elevated temperatures.

Since the publication of the papers mentioned above, several similar studies have appeared,[4-9] and the reversible anhydride formation has also been assumed by several workers[6,8,9] as the mechanism of the reaction. Furthermore, Winter, Carlton and Briscoe[4] could not observe the catalytic action of the hydroxyl ion on the exchange reaction of the sulfate ion and they suggested that, in view of the rapid exchange of sodium metasilicate, the reaction between the glass wall of the reaction vessel and the strongly alkaline solution might account for the observed exchange in such cases. The same finding and opinion were presented by Hall and Alexander.[7] Mill[6] observed, however, no exchange reaction between Pyrex glass and a strongly alkaline solution at a high temperature, even though the glass was markedly etched, and suggested that different kinds of glass react differently.

Such problems can now easily be solved by the use of a stainless steel vessel. In this way we have studied the reaction in a strongly alkaline solutions. As a result we have come to the conclusion that no exchange reactions take place betwen SO_4^{2-} and water in an alkaline solution; the decrease in the heavy oxygen content of the water which is observed in the case of alkaline solutions in glass reaction vessels must be ascribed to the exchange of O-atoms between the water and the surface of the glass reaction vessel.

Experimental and Results

The experiments were carried out using both ordinary glass ampoules and a stainless steel reaction vessel which will be described below. The stainless steel vessel consists of four parts, A, B, C and D, which are shown on the left hand side of Fig. 1. A is a stainless steel guard ring. B is a strainless steel plate, at the center of which a short Kovar tube K is welded. This Kovar tube is then welded to an ordinary glass tube, G, by means of Kovar glass, KG. C is a packing ring made of Teflon. D is a stainless steel cylinder which is 3 cm. in inner diameter and 20 cm. long. This lower end of the cylinder is sealed by welding, while the upper end of the cylinder is welded to a guard ring which has the same form and size as the guard ring A mentioned above. These four parts are tightly screwed together by six sets of bolts and nuts, as is shown on the

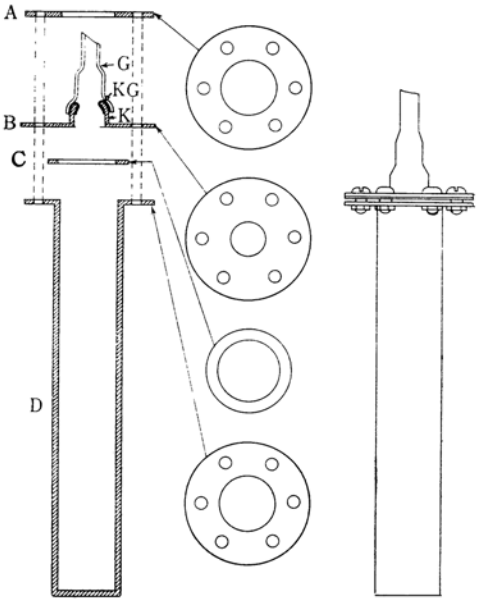

Fig. 1. Stainless steel reaction vessel.

---

[4] E. R. S. Winter, M. Carlton and H. V. A. Briscoe, ibid., **1940**, 131.

[5] G. A. Mills and H. C. Urey, *J. Am. Chem. Soc.*, **62**, 1019 (1940).

[6] G. A. Mills, ibid., **62**, 2833 (1940)·

[7] N. F. Hall and O. R. Alexander, ibid., **62**, 3455 (1940).

[8] E. R. S. Winter and H. V. A. Briscoe, *J. Chem. Soc.*, **1942**, 631.

[9] T. C. Hoering and J. W. Kennedy, *J. Am. Chem. Soc.*, **79**, 56 (1957).

TABLE I. EXPERIMENTS WITH GLASS AMPOULES

No.	$H_2{}^{18}O$ g.	Na_2SO_4 g.	Na g.	Time hr.	^{18}O %	
					C_B	C_A
1	3.424	6.804	0	24	0.302	0.301
2	3.940	1.776	conc. HCl 0.051*	24	0.332	0.317
3	3.970	1.843	0.03	24	0.332	0.329
4	3.789	1.510	0.10	26	0.329	0.326
5	2.861	4.204	0.08	24	0.315	0.302
6	3.235	4.901	0.09	70	0.332	0.315
7	2.538	0	0.13	24	0.291	0.280
8	3.130	0	0.08	70	0.284	0.280

* Instead of sodium, 0.051 g. of concentrated hydrochloric acid was added.

TABLE II. EXPERIMENTS WITH A STAINLESS STEEL VESSEL

No.	$H_2{}^{18}O$ g.	Na_2SO_4 g.	Na g.	Time hr.	^{18}O %	
					C_B	C_A
9	3.535	1.359	0.10	70	0.332	0.333
10	3.560	5.150	0.09	70	0.292	0.288

right hand side of Fig. 1. In this way this stainless steel vessel can be welded to a glass vacuum line just as an ordinary glass ampoule.

All the experiments were carried out in the same way, either with glass ampoules or with the stainless steel vessel. First, a weighed amount of purified anhydrous sodium sulfate and metallic sodium were placed in the reaction vessel. After this vessel had been welded to a vacuum line, a weighed amount of ^{18}O-enriched water was distilled into the vessel. Then the vessel was evacuated, sealed off from the vacuum line, and heated at 100°C for more than 24 hr. in an air thermostat. After the heating, the vessel was again connected to the vacuum line and the water was distilled off into the other glass ampoule. The concentration of ^{18}O in the separated water was measured by the conventional method; the water was brought into equilibrium with the CO_2, and the ^{18}O content of the latter was measured by a mass spectrometer.

The experimental results are shown in Tables I and II, where C_B and C_A represent the atomic percentage of ^{18}O in the water before and after the experiment respectively.

Among the results of the experiments with glass ampoules which are shown in Table I, the results of Nos. 1 and 2 are in accord with the previous results of Titani and Goto; the exchange reaction of O-atoms does not take place between $SO_4{}^{2-}$ and water in neutral solutions, but it does in acid solution. On the contrary, the results of the experiments from Nos. 3 to 6, which were carried out with the addition of sodium, i. e., alkali, conflict somewhat with one other. Although a small decrease in the ^{18}O-content of the water was observed in all experiments, as was expected from the experimental results of Ingold and his collaborators, the amount of the decrease is very irregular; it is not always proportional to the amount of sodium sulfate and sodium and to the time of the reaction, as may be seen, for example, by a comparison of the results of Nos. 4 and 5 and Nos. 5 and 6. These results suggest that the cause or the mechanism of the decrease in the ^{18}O-content in water is too complicated to be explained solely by the exchange reaction between $SO_4{}^{2-}$ and water. From this point of view, we carried out experiments Nos. 7 and 8, where only sodium, but no sulfate, was added to the solutions. Here we have found also the same degree of decrease in the ^{18}O-content of the water as in those experiments with the addition of sulfate, i. e., experiments from No. 3 to 6. We, therefore, assumed that the decrease in the ^{18}O-content of the alkaline solution might be entirely due to the exchange reaction of O-atoms between the water and the surface of the glass reaction vessels.

This assumption was actually confirmed by the experiments with the stainless steel reaction vessel, the results of which are shown in Table II. From Table II, we can safely conclude that no exchange of O-atoms take place within the limits of experimental error when there is no glass surface in the reaction system; the decreases in the ^{18}O-content of the water which is observed with alkaline solutions in glass reaction vessels are entirely due to the exchange reaction of O-atoms between water and the glass surface of the reaction vessels.

Discussion

From the present experiments it can be concluded that the exchange reaction of O-atoms between oxyanions of strong acids and water takes place only in acid solutions, but in neither neutral nor alkaline solutions. This result excludes the acid-base catalyzed mechanism, at least in its general form,[10] from the two alternative mechanisms which we have previously presented; the exchange reaction must be explained either by the reversible anhydride formation or by some other appropriate mechanism. The decreas in ^{18}O-content in the alkaline solutions of oxyanions of strong acids is entirely due to the exchange of O-atoms between water and the glass surface of the reaction vessels. Recently it has been repoted by Maass[11] that the exchange of O-atoms between water vapor and the glass surface takes place above 100°C without the addition of alkali. If this result is taken into account, the exchange of the O-atoms observed in the present experiments at 100°C between alkaline solutions and the glass surface may be said to be due to the corrosion of the glass surface by alkali. At any rate, we must be very careful of the exchange reaction between water and the glass surface in the experiments with ^{18}O-enriched water using glass reation vessels, as has already been pointed out by Maass.

Department of Chemistry
Faculty of Science
Tokyo Metropolitan University
Setagaya-ku, Tokyo

---

[10] The reaction proceeds by the ternary collison between the reactant molecule, Brönsted's acid and base.

[11] I. Maass, *Kernenergie*, 3, 843 (1960).