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Abstract

Full Text

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KINETICS OF THE REACTIONS OF SODIUM WITH WATER AND WITH THE SYSTEMS: WATER–DIOXANE, WATER–BUTYRIC ACID

(Presented by Academician P. A. Rehbinder, 22 VI 1957)

In studying the kinetics of dissolution of metallic sodium in benzene solutions of butyric acid, it seemed of interest to investigate the influence of water on the course of this process. However, before studying the reaction of sodium with the systems benzene—butyric acid—water, it was necessary to determine how sodium reacts with water alone, and then with the systems water—butyric acid. The present article is devoted to the results of these investigations.

Water, owing to the very high rate of its interaction with sodium, was diluted with dioxane, which, as preliminary experiments showed, does not react with sodium at room temperature, at least with evolution of hydrogen. In systems consisting of water and butyric acid, the acid played the role of a peculiar "diluent" for the water.

Fig. 1. Curves of sodium dissolution in water-dioxane systems. Q is the volume of evolved hydrogen in milliliters (reduced to normal conditions) from 1 cm^2 of sodium surface. The numbers beside the curves refer to the system numbers.

The experimental procedure remained as before (¹), with the only difference that, in studying the reactions of sodium with water and with water-dioxane systems, the tubes in which the sodium was enclosed were taken of smaller diameter (~ 1 mm), in order to reduce still further the surface of contact of the metal with the solution. At the same time we made sure beforehand that such a narrowing of the tube opening did not interfere with the uniform course of the reaction, as is shown by Fig. 1.

The experiments were carried out at 20°. The sodium sample weighed ~ 3 mg; the eudiometer was a microburette. The water was bidistillate. The dioxane-1,4 of Kahlbaum, repeatedly frozen out, had b.p. 100.8; m.p. 11°; p_4^{20} 1.035; judging from the values of these constants, it was practically anhydrous. *n*-Butyric acid (¹) was a chemically pure preparation with b.p. 162° and d_4^{20} 0.9640. The sodium (¹), also chemically pure, contained no potassium impurity.

We give the composition of the systems studied.

Water–dioxane

System No.	1	2	3	4	5
Water conc. in mole fractions × 10^3	330	500	700	750	830

Water–butyric acid

System No.	1	2	3	4	5	6	7	8
Water conc. in mole fractions × 10^3	0	1.0	2.0	4.0	8.0	16	31	62

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

System No.	9	10	11	12	13	14	15	16	17	18	19	20	21
Water conc. in mole fractions × 10^3	111	204	333	500	667	750	800	833	875	900	909	923	1000

The reaction with pure water was completed within a few seconds (1 sec at 20° and 3 sec at 4°), which made visual observation of the course of the reaction very difficult. Therefore most of the experiments were carried out with water-dioxane systems. The data characterizing the dependence of the reaction rate on the concentration of water in such systems are shown in Fig. 2.

Fig. 2

Fig. 3

Fig. 2. Dependence of the rate of dissolution of sodium on the concentration of water in water-dioxane systems

Fig. 3. Dependence of the rate of dissolution of sodium in butyric acid—water systems on the concentration of water in them

From these data it follows that the reaction rate in systems Nos. 1–4 is a linear function of the concentration of water in them and, thus, obeys the equation of a first-order reaction $dC/dt = kC$, with a constant equal to $4.7 \cdot 10^{-5}$. On passing from system 4 to system 5, however, the reaction rate increases sharply, reaching values close to the rate in pure water. The order of the reaction also changes, approaching zero, which is characteristic of the reaction of sodium with pure water and with water-dioxane systems containing an ever decreasing amount of dioxane.

In all probability, dioxane forms with water, by means of hydrogen bonds, a series of oxonium compounds (?) and thereby to a certain extent inactivates the water. The sharp acceleration of the reaction observed on passing from system 4 to system 5 may in this case be due to a corresponding sharp increase in the concentration of "free" water, with its fraction predominating over the fraction of "bound" water. In favor of such an assumption, apparently—

apparently, is indicated by the increase in the activation-energy value on going from pure water to water-dioxane systems.

As measurements of the rate of the reaction of water with sodium at 4, 14, and 24° have shown, its apparent activation energy is 6 kcal/mole*, whereas for the reaction of water-dioxane system No. 1 (from rate measurements at 20, 30, and 40°) it is 14.5 kcal/mole. As is known, the energy of a hydrogen bond lies in the range 6–8 kcal/mole.

The dependence of the rate of dissolution of sodium in butyric acid-water systems on the water content is shown in Fig. 3; it is striking in its peculiar "stepwise" character. The graph consists of a series of "steps," parallel to the abscissa axis, corresponding to a certain range of molar ratios of water and butyric acid within which the rate of dissolution of sodium remains constant, obeying the equation for a zero-order reaction. Moreover, the "steps" differ from one another both in length and in height, i.e., in the "jumps" of the rate upon passing from one "step" to another. No less strange is also the (repeatedly verified) drop in rate that is observed after the third step and precedes the last abrupt acceleration of the reaction, when the values of its rate approach the value characteristic of the reaction with pure water.

A natural question arises concerning the nature of so strange a kinetic regularity, concerning the mechanism of the "stepwise" effect. Judging from the fact that this effect is not observed when metallic sodium is acted upon by water alone or by butyric acid alone, it must be concluded that it is a consequence of the joint action of both these reagents on the metal. If we now assume that water and butyric acid do not enter into any interaction with one another, then it is probable that water reacts with sodium first, since the "apparent" activation energy of this reaction is 6 kcal/mole, whereas for the reaction with butyric acid (dissolved in benzene) it is 13.5 kcal/mole**. However, the supposition suggests itself that butyric acid forms with water, by means of hydrogen bonds, a series of molecular compounds. It is precisely in the formation of such compounds, which play the predominant role in the kinetics of the reaction with sodium, that, as it seems to us, the key to the explanation of the kinetic regularities discovered should be sought.

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* According to the data of Deal and Svec (³), the *E* of the reaction between metallic lithium and water vapor was, depending on the vapor pressure, from 6.2 to 5.5 kcal/mole.

** The amount of water in the system corresponding to the first point of the first step is already sufficient to convert the entire weighed portion of metallic sodium into its hydrate.

Note: Figure translations are in progress. See original paper for figures.

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