PHYSICAL CHEMISTRY

==========

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

I. G. Ryss and V. B. Tulchinskii

KINETICS OF THE AQUATION OF THE MONOFLUOROPHOSPHATE ION

(Presented by Academician A. A. Grinberg, 24 VII 1961)

The aquation (hydrolysis) of the monofluorophosphate ion in a neutral or alkaline medium is a very slow process. According to Lange ([1]), for the complete decomposition of 0.05 M K_2PO_3F in an excess of 1 M KOH it is necessary to heat the solution on a water bath for 50 hours; in a strongly acidic medium the decomposition of PO_3F^{2-} is completed in several minutes. However, it has been recommended ([2]) that, before the colorimetric determination of fluorine in monofluorophosphates, the acidic solution be allowed to stand for not less than one hour. In ([3]) it was found that the hydrolysis of $CaPO_3F \cdot 2H_2O$ in an initially neutral medium proceeds extremely slowly; the pH of the solution continues to change for more than three months at 25°.

In the present work the kinetics of the aquation of dissolved PO_3F^{2-} has been quantitatively investigated for the first time. The same sample of sodium monofluorophosphate was used in the investigation as in the previous work ([4]). During the intervening time the salt had become somewhat enriched with phosphate (owing to interaction with the moisture contained in the salt), the impurity of which did not affect the kinetics of the process; the initial phosphate content (4.2% PO_4^{3-}) was taken into account in the calculations. Analyses of periodically withdrawn samples of solutions undergoing aquation showed that the argentometrically determined change in phosphate content ([5]) was equivalent to the change in their content as determined alkalimetrically (by titration in the presence of thymolphthalein to HPO_4^{2-} ([5]); it was found that the presence of PO_3F^{2-} or F^- does not affect the results of this titration). By this method it was established that, in both alkaline and neutral or acidic media, the aquation (hydrolysis) of the monofluorophosphate ion proceeds according to the stoichiometric equation

$$PO_3F^{2-} + H_2O \rightarrow H_2PO_4^- + F^-;$$

it is self-evident that $H_2PO_4^-$ is in equilibrium, dependent on the pH of the solution, with the other forms of orthophosphate. In none of the experiments was the formation of metaphosphates detected.

Owing to the extreme slowness of the aquation of PO_3F^{2-} in neutral and alkaline media, the rate of this process was investigated at 120–140°. Cylindrical reaction vessels, of about 20 ml capacity, closed hermetically with screw-on lids, were made of stainless steel. It was found that introducing ~2 g of shavings of the same steel into the vessel did not affect the determined rate of aquation; the vessel walls did not catalyze the reaction and did not react with the products of aquation. Throughout the entire work the walls of the vessels showed no noticeable corrosion.

For thermostating, a heat-insulated aluminum block was used (height 170, diameter 190 mm) with 6 symmetrically arranged sockets for the vessels and channels for contact and standard thermometers. The temperature of the block was regulated automatically with an accuracy of $±$0.02°. The thermometer was carefully checked. To compensate for cooling of the block when cold reaction vessels with solutions were introduced, the block was overheated by several degrees before the start of the experiment. Constancy of tempera-

Table 1

Aquation of PO_3F^{2-} at ionic strength $\mu = 1.15$ and an initial fluorophosphate concentration of $\sim 0.0486\ M$

Temp., °C	Initial alkali molarity	Duration of experiment, min	Degree of aquation attained	$10^3 \cdot 0.4343\,k$, $\min^{-1}$	$\lg x_0$	$10^3 \cdot \frac{\Sigma\lvert\Delta\rvert}{n}$
120.23	0.1000	540	0.6725	0.885	−0.0082	2.3
120.23	0.4000	540	0.7953	1.26	−0.0047	3.3
120.23	0.7000	360	0.7310	1.56	−0.0097	2.5
120.23	1.000	510	0.9056	1.98	−0.0018	5.7
130.42	0.4000	240	0.8222	3.25	+0.0287	3.9
130.42	0.7000	230	0.8774	3.97	+0.0093	7.5
130.42	1.000	180	0.8609	+4.95	+0.0374	6.1
140.34	0.1000	135	0.8328	5.96	+0.0345	3.0
140.34	0.4000	120	0.8659	7.49	+0.0268	2.6
140.34	0.7063	100	0.8668	8.18	+0.0408	4.6
140.34	1.000	95	0.8973	10.90	+0.0538	9.7

The block temperatures were restored 7–10 min after the start of the experiment. To accelerate heat transfer from the block to the solutions, paraffin was placed in the wells. The dependence of the temperature difference between the block and the solution on time was well described by the equation $\lg(T^0 - T) = \lg(T^0 - T_1) - av$, readily derived from Newton's law of heat transfer when the dependence of heat capacity and thermal conductivity on temperature is neglected. In this equation T^0 and T_1 denote the initial temperatures of the block and of the solution, and T is the temperature of the solution at time v, counted from

the moment the vessel was introduced into the block. Extrapolation of the experimentally found dependence showed that, for $T^0 - T_1 = 120$, the values of $T^0 - T$ after 6, 9, and 12 min were equal to 1, 0.1, and 0.01°; in the absence of paraffin in the wells the coefficient a was approximately three times smaller.

The first reaction vessel was removed from the block 20 min after the start of the experiment at 140°; at 130 and 120° this time interval was 40 min. Then, at specified time intervals, the subsequent vessels were removed. The vessel taken from the block was immediately cooled in ice water; the solution was quantitatively transferred to a flask and analyzed. For the argentometric determination of phosphate, a variant of the method described in ([5]) was developed, in which a minimal excess of Ag^+, titrated from an aliquot portion of the filtrate after separation of the silver phosphate precipitate, was titrated with 0.05 N KCNS solution from a microburette.

The dependence, calculated from the results of the analyses, of the degree of aquation of PO_3F^{2-} on the duration of aquation (v, in minutes) in each experiment, i.e., each series of six samples, corresponded well to the equation expected for first-order reactions,

$$\lg x = \lg x_0 - 0.4343kv, \tag{1}$$

where x is the fraction of monofluorophosphate undecomposed at time v, and k is the rate constant (in min^{-1}); x_0, i.e., the value of x extrapolated to $v = 0$, differed only slightly from unity because in the first minutes the rate of aquation was lower owing to the lower temperature of the solution. The mean values of $\lg x_0$ and k for each experiment were calculated by the method of averages ([7]). The differences (Δ) between the values of $\lg x$ calculated from the coefficients found in equation (1) and the experimental values were random rather than systematic in character and did not exceed the limits of possible analytical errors. To characterize the mean error of each experiment, Table 1 gives the values of

$$\frac{\Sigma|\Delta|}{n},$$

where n is the number of samples.

Since preliminary experiments showed that the rate of aquation increases with increasing ionic strength of the solution, in the main experiments the ionic···

the strength of the solutions was kept constant by introducing sodium nitrate. In the basic experiments, solutions with an almost constant initial concentration of PO_3F^{2-} were used; since equation (1) described the results of the experiments well even at high degrees of aquation, there is no doubt that the aquation of PO_3F^{2-} is a first-order process with respect to PO_3F^{2-}.

The conditions of the experiments on the aquation of PO_3F^{2-} in alkaline solutions and their principal results are given in Table 1.

The values of the rate constants at constant temperature increase in proportion to the alkali concentration

$$k = k_1 + k_2[OH^-]. \tag{2}$$

Table 2

Temp., °C	$10^3 \cdot 0.4343\, k_1$, min^{-1}	$10^3 \cdot 0.4343\, k_2$, $l \cdot mol^{-1} \cdot min^{-1}$	$10^3 \cdot 0.4343\,(k_{calc} - k_{found})$ at initial alkali conc. 0.100	$10^3 \cdot 0.4343\,(k_{calc} - k_{found})$ at initial alkali conc. 0.400	$10^3 \cdot 0.4343\,(k_{calc} - k_{found})$ at initial alkali conc. 0.700	$10^3 \cdot 0.4343\,(k_{calc} - k_{found})$ at initial alkali conc. 1.00
120.23	0.764	1.195	0.00	−0.02	+0.04	−0.02
130.42	2.07	2.833	–	−0.05	+0.09	−0.04
140.34	5.35	5.49	−0.06	+0.06	+0.05	−0.06

This is confirmed by the data of Table 2, which gives the values of k_1 and k_2 calculated by the least-squares method and, at $\mu = 1.15$, the differences between the values of k calculated from equation (2) and those found experimentally.

The value of k proved to be practically constant in each of the experiments, since an appreciable change in the OH^- concentration during the experiment occurred only at an initial alkali concentration of 0.1 M, but in these experiments the term $k_2[OH^-]$ was small in comparison with k_1.

The form of equation (2) shows that the decomposition of PO_3F^{2-} in an alkaline medium proceeds by two parallel processes with rates

$$v_1 = k_1[PO_3F^{2-}],$$

$$v_2 = k_2[PO_3F^{2-}][OH^-].$$

The temperature dependence of k_1 and k_2 is satisfactorily represented by the Arrhenius equations with the following coefficients (calculated from the data of Table 2 by the least-squares method):

$$\lg(0.4343k_1) = 14.267 - \frac{6839.4}{T},$$

Fig. 1

Figure 1: Fig. 1

$$\lg(0.4343k_2) = 10.72 - \frac{5363}{T}.$$

The differences between the logarithms of the constants calculated from these equations and those found are given below:

Temp., °C	$\Lambda(\lg k_1)$	$\Lambda(\lg k_2)$
120.23	−0.002	+0.010
130.42	+0.004	−0.020
140.34	−0.002	+0.010

Naturally, for $\lg k_2$ these differences are greater than for $\lg k_1$; the maximum deviations of k_1 and k_2 from the calculated values are respectively equal to 1 and 5%.

The calculated activation energies of the first and second reactions are $E_1 = 31.2_8$ and $E_2 = 24.5_3$ kcal, and the activation entropies at 25° are $\Delta S_1^{\ddagger} = -1.7_5$ and $\Delta S_2^{\ddagger} = -17.9$ entropy units.

In attempts at direct determination of k_1 by studying the rate of aquation of monofluorophosphate in water, values were obtained that were smaller than those derived by extrapolating the dependence of k on the initial alkali concentration. This is caused by partial conversion of PO_3F^{2-} into HPO_3F^-, the aquation of which is slower. Since extrapolation of the measured dissociation constants of HPO_3F^- and $H_2PO_4^-$ only up to 60–65° to 120–140° is very unreliable, it is impossible to take quantitatively into account the degree of conversion of PO_3F^{2-} into HPO_3F^- in these experiments.

The approximate value of the dissociation constant of HPO_3F^- at 140.3° and $\mu = 1$, obtained by extrapolation of measurement results between 0 and 65° (4), is $4 \cdot 10^{-6}$, i.e., under these conditions HPO_3F^- is a weak acid.

Fig. 1

Consequently, in mixtures of Na_2PO_3F and HNO_3, the degree of conversion of PO_3F^{2-} into HPO_3F^- is determined by stoichiometric ratios. Figure 1 presents the results of determining the rate constants for aquation of PO_3F^{2-} in water and in mixtures with a deficiency of HNO_3 at 140.34° and $\mu = 1.15$. In water, $0.4343\,k = 5.22 \cdot 10^{-3}$, i.e., 2.4% less than $0.4343\,k_1$ under the same conditions; upon adding 50% of the equivalent amount of HNO_3, the value of k decreases almost by half; with a further increase in the amount of HNO_3, the decrease

in k slows, probably in connection with the acid catalysis of aquation that progresses as the pH of the solution falls. In a strongly acidic medium, aquation of monofluorophosphate proceeds very rapidly. The rate of this process in solutions 0.05 M in Na_2PO_3F and 1.06 M in HNO_3 ($\mu = 1.21$) was studied at 0–25° by the method of periodic determination of phosphate in samples of solutions kept in thermostatted polyethylene vessels; the reaction in the sample taken was stopped by introducing the sample into a slight excess of cold alkali.

Aquation of monofluorophosphate under these conditions was a reaction of first order with respect to monofluorophosphate; the rate constants $0.4343\,k$ at 0, 15.00, and 25.00°, respectively, were $0.975 \cdot 10^{-3}$, $4.92 \cdot 10^{-3}$, and $13.3 \cdot 10^{-3}$ min^{-1}. Their dependence on temperature corresponds to the equation

$$\lg(0.4343\,k\,) = 10.513 - \frac{3694}{T}.$$

The values of k calculated from this equation differ from the experimental values by no more than 0.3%. The calculated energy and entropy of activation are $E = 16.9$ kcal and $\Delta S^{\ddagger} = -18.9$ entropy units.

The probable mechanism of the monofluorophosphate aquation reactions will be considered in another article, after study of the kinetics of aquation of other fluorophosphates.

Dnepropetrovsk Institute of Engineers
of Railway Transport

Received
19 VI 1961

CITED LITERATURE

6. W. Lange, *Ber. Deutsch. Chem. Ges.*, **62**, 793 (1929).

7. H. Hill, C. Reynolds, *Anal. Chem.*, **22**, 448 (1950).

8. V. Kinh, G. Montel, *C. R.*, **250**, 131 (1960).

9. I. G. Ryss, V. B. Tulchinskii, *ZhNKh*, **6**, 1856 (1961).

10. I. M. Kolthoff, V. A. Stenger, *Volumetric Analysis*, 2, 1952, pp. 354, 170.

11. K. P. Yakovlev, *Mathematical Processing of Measurement Results*, Moscow, 1953.

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