415. *Hydrolysis of the Uranyl Ion.*

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The pH of uranyl perchlorate solutions has been measured over a wide concentration range at various temperatures and ionic strengths. The results can be explained in terms of two hydrolytic reactions, leading respectively to the formation of the monomeric $UO_2{\cdot}OH^+$ and the dimeric $UO_2{\cdot}UO_3^{2+}$ ion, ΔH for formation of the former being considerably larger than for the latter. The effect of complex formation with anions is discussed and a new method of detecting perchlorate-complex formation is suggested.

THE hydrolysis of uranyl salts has been investigated several times (for a survey see Kraus [1]). The problem is complex and the work of Sutton [2] and of Ahrland [3] leaves little doubt that in solutions containing added alkali or an excess of uranium trioxide polymeric species containing three or more uranium atoms occur. The species existing in stoicheiometric uranyl salt solutions however are less certain. The work of Singh and Ahmad [4] on the pH of uranyl nitrate, sulphate, and acetate solutions does not permit a detailed analysis as no attempt was made to control the ionic strength. The same criticism also applies to the much-quoted work of Longsworth and MacInnes,[5] although they attempted to interpret their results in terms of various possible hydrolytic equilibria and obtained a fair agreement with experiment over a moderate concentration range by means of the single reaction :

$$2UO_2^{2+} + H_2O \rightleftharpoons UO_2{\cdot}UO_3^{2+} + 2H^+ \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Guiter's measurements [6] on uranyl nitrate solutions purported to show the existence of species such as $UO_2{\cdot}OH,NO_3$, and $UO_2{\cdot}OH(NO_3^-)_2$, in addition to $UO_2{\cdot}UO_3^{2+}$. The pH measurements however were made colorimetrically, neither temperature nor ionic strength was controlled, and the analysis given involves some doubtful assumptions. In Faucherre's very careful work,[7] however, both ionic strength and temperature were controlled and the conclusion reached was that the hydrolysis could in fact be explained entirely on the basis of reaction (1); this investigation was carried out on uranyl nitrate in barium nitrate solution and as it has been demonstrated that the nitrate ion forms a complex with the uranyl ion [8, 9] it is clear that the hydrolytic constants given by Faucherre [7] may contain a factor dependent on this effect.

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[1] Kraus, Proc. Internat. Conference on the Peaceful Uses of Atomic Energy, Vol. VII,, p. 245, United Nations, N.Y., 1956.

[2] Sutton, Nat. Res. Council, Canada Atomic Energy Project, Report CRC 325 (1947); *J.*, 1949, S 275.

[3] Ahrland, *Acta. Chem. Scand.*, 1949, **3**, 374; 1954, **8**, 1907.

[4] Singh and Ahmad, *J. Chim. phys.*, 1937, **34**, 351.

[5] Longsworth and MacInnes, U.S.A.E.C. Report MDDC 911 (1947).

[6] Guiter, *Bull. Soc. chim. France*, 1947, 64.

[7] Faucherre, *Compt. rend.*, 1948, **227**, 1367.

[8] Betts and Michels, *J.*, 1949, S 186.

[9] Ahrland, *Acta Chem. Scand.*, 1951, **5**, 1271.

So it seemed worth while to carry out measurements similar to those described by Faucherre [7] but with uranyl perchlorate in a perchlorate medium and, as all previous work has been carried out at one temperature only, to extend them to at least two temperatures.

EXPERIMENTAL AND RESULTS

Solutions were made up with doubly distilled water freed from carbon dioxide by the passage of nitrogen. The pH of this water was 6·95.

Uranyl perchlorate stock solutions were made by dissolving high-purity uranium trioxide, the water content of which was determined by analysis just before use, in the stoicheiometric quantity of 2M-perchloric acid and diluting the product to the required volume with water. Dissolution of the oxide required 24—48 hr. at 40—50°. Other solutions were prepared by dilution of the uranyl perchlorate stock with water and/or barium perchlorate solution. The pH of the barium perchlorate solution used for the dilutions was 7·13.

Two specimens of uranium trioxide were used, one supplied by Mr. P. C. Davidge of this Division, the other prepared by the peroxide precipitation process.[5] Results obtained with them were identical.

Pyrex glassware was used and all pH's, save those of the stock solutions, were measured as soon after making up of a given solution as possible. A check on the uranyl perchlorate stock solution revealed no change in pH during many days.

pH was measured with a Cambridge glass electrode and a Cambridge pH meter used as a valve potentiometer. The reference electrode was a calomel element containing saturated sodium chloride with a saturated sodium chloride salt bridge. This procedure was adopted to avoid the difficulties which would arise at the liquid junction, owing to precipitation, if a potassium chloride element were used.

The cell was that described by Coates,[10] modified by use of a bulb, of approx. 100 ml. capacity, as the glass electrode compartment, provision of a tap in the side arm for introduction of the solution, and addition of inlet and outlet tubes for the passage of nitrogen through the solution in the glass electrode compartment. A standard cone and socket joint was used to hold the glass electrode which was cemented in place with Apiezon W wax.

TABLE 1. pH *of uranyl perchlorate solutions at* 25·0°.

$UO_2(ClO_4)_2$ (10^{-2} M)	9·4	5·0	0·94	0·188	0·0376	0·0188	0·00752	0·0047	0·00188
pH	2·61	2·75	3·25	3·71	4·15	4·38	4·69	4·81	5·18

TABLE 2. pH *of uranyl perchlorate solutions at* 25·0°.

Stoicheiometric uranyl perchlorate.

10^{-3}M ...	94	11·58	9·4	1·88	0·94	0·47	0·188	0·094	0·047	0·0235
pH	2·55	3·25	3·34	3·86	4·10	4·36	4·72	4·95	5·21	5·45

Ionic strength 0·347.

10^{-3}M ...	115·8	11·58	2·315	0·479	0·1158	0·02315	0·0158
pH	2·45	3·15	3·61	4·09	4·49	4·98	5·22

Ionic strength 0·0347.

10^{-3}M ...	11·58	2·315	0·279	0·1158	0·02315
pH	3·25	3·73	4·21	4·61	5·10

TABLE 3. pH *of uranyl perchlorate solutions at* 40·0°.

Stoicheiometric uranyl perchlorate.

10^{-3}M ...	115·8	11·58	1·88	0·94	0·47	0·188	0·094	0·047	0·0188	0·0094
pH	2·38	3·19	3·79	3·97	4·27	4·58	4·87	5·07	5·45	5·73

Ionic strength 0·0347.

10^{-3}M ...	11·58	2·315	0·479	0·158	0·02315
pH	3·19	3·57	4·07	4·47	4·96

The entire cell assembly was immersed in a thermostatically controlled (±0·02°) oil-bath. When the bath-temperature was changed the cell was left for 24 hr. before further measurements.

The glass-electrode response was checked frequently during the measurements with 0·05M-potassium hydrogen phthalate and with 0·01M-hydrochloric acid.

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[10] Coates, *J.*, 1945, 489.

After introduction of a solution into the cell ¾—1 hr. was allowed to elapse in order to attain temperature equilibrium before the liquid junction was made and the potential measured. During this time nitrogen, saturated with water vapour at the bath-temperature, passed continuously in a rapid stream through the solution in the cell.

The only previous measurements of the pH of stoicheiometric uranyl perchlorate are those of Sutton,[2] but it is not clear whether the author took precautions to exclude carbon dioxide. To check this, measurements were carried out of the pH of stoicheiometric uranyl perchlorate solutions which had been made from ordinary distilled water and in which no nitrogen was passed through the cell. The results are given in Table 1, and when plotted are in good agreement with Sutton's results, suggesting that the latter were obtained in the presence of carbon dioxide. Further measurements were then made by the method described above, in which carbon dioxide was excluded, both of the pH of stoicheiometric uranyl perchlorate solutions and of solutions kept at constant ionic strength by the addition of barium perchlorate. The results are reported in Tables 2 and 3. A plot of the results of Table 1 together with the comparable figures from Table 2, in the form of pH against log c, reveals that failure to take adequate precautions to remove carbon dioxide has a pronounced effect which is of particular importance since in the interpretation much depends upon the slope of similar plots. It therefore appears to be a fortunate cancellation of errors that gave Longsworth and MacInnes[5] and Sutton[2] a pH—log c plot of the slope required by reaction (1) and not one indicating a quite different mechanism.

DISCUSSION

As a starting point for the analysis of the results obtained in this investigation the method proposed by Geloso and Faucherre[11] and slightly modified by Faucherre[7] was used. These authors show that for the general hydrolytic reaction

$$n\mathrm{A}^{z+} + p\mathrm{H_2O} \rightleftharpoons \alpha_n^{\,y+} + q\mathrm{H}^+$$

where $\alpha_n^{\,y+}$ is the n-meric hydrolysis product, the hydrogen-ion concentration and the total metal concentration $[\mathrm{A}]_T$ are related by the expression:

$$\log\,[\mathrm{H}^+] = \frac{n}{q+1}\log\,([\mathrm{A}]_T - [\mathrm{H}^+]) + \frac{1}{q+1}\log Kq \quad . \quad . \quad . \quad (2)$$

[It should be noted that the original authors replaced Kq in the final term of eqn. (2) with a combined constant k.] The slope of a plot of pH against log $([\mathrm{A}]_T - [\mathrm{H}^+])$, thus provides, n and q being assumed equal, a measure of the number of metal ions taking part in the reaction, while the intercept yields a value for the hydrolysis constant K.

Our results, for the series carried out at constant ionic strength, plotted in this way, lie on straight lines, as required by eqn. (2), while those for the stoicheiometric solutions give curves. Change of ionic strength markedly affects K, as expected, and it is presumably this effect which produces the curvature in the plots for stoicheiometric solutions. It is important to note that the plots for the stoicheiometric solutions are rather misleading as, over more limited concentration ranges, they are approximately linear. In the present case, for example, a line of slope 0·8 could be drawn through many of the points apparently indicating a value of 4 for n, *i.e.*, the formation of a tetrameric hydrolysis product. When attention is confined to the results at constant ionic strength the slopes of the best straight lines, determined by the method of least squares, are: at 25°, 0·646 for ionic strength $\mu = 0{\cdot}347$, and 0·646 for $\mu = 0{\cdot}0347$; at 40°, 0·607 for $\mu = 0{\cdot}0347$; this indicates a very different state of affairs.

The difference in the slope from the value of 0·67 found by Faucherre,[7] and expected if reaction (1) is the sole hydrolytic process, is susceptible of two explanations: one, the least probable, is that n and q differ; the other that in addition to reaction (1) the equilibrium,

$$\mathrm{UO_2}^{++} + \mathrm{H_2O} \rightleftharpoons \mathrm{UO_2{\cdot}OH^+} + \mathrm{H^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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[11] Geloso and Faucherre, *Compt. rend.*, 1948, **227**, 200.

also occurs to a small extent. Komar and Tretyak [12] claim to have demonstrated that (3) is the sole hydrolytic reaction in slightly acidified solutions of uranyl nitrate; however, only a very narrow concentration range was covered and no attempt was made to work at constant ionic strength; their claim cannot, without further evidence, be regarded as valid. Neither can Harris and Kolthoff [13] be considered to have proved the existence of $UO_2{\cdot}OH^+$; their pH measurements, on uranyl chloride, were made with the quinhydrone electrode and are all very much lower than those of Longsworth and MacInnes,[5] suggesting that the solutions contained excess of acid. The hydrolysis "constant" which they calculated is based on a number of very dubious assumptions concerning activity coefficients.

If we assume that the hydrolytic processes occurring under the conditions of the present work are represented by reactions (1) and (3) and write

$$K_1 = [UO_2{\cdot}OH^+][H^+]/[UO_2^{2+}] \text{ and } K_2 = [UO_2{\cdot}UO_3^{2+}][H^+]^2/[UO_2^{2+}]^2$$

then, by combination with the conditions that

$$[U_T] = [UO_2^{2+}] + [UO_2{\cdot}OH^+] + 2[UO_2{\cdot}UO_3^{2+}]$$

and

$$[U]_T = [UO_2^{2+}] + [H^+]$$

where $[U_T]$ is the total analytical uranium concentration, it follows that

$$[U_T] = ([U_T] - [H^+])\left\{1 + \frac{K_1}{[H^+]} + \frac{2K_2([U_T] - [H^+])}{[H^+]^2}\right\} \quad . \quad . \quad . \quad (4)$$

For testing the experimental data rearrangement of eqn. (4) to the form (5) is more

$$\left\{\frac{[U_T]}{[U_T] - [H^+]} - 1\right\}[H^+] = K_1 + 2K_2\left(\frac{[U_T]}{[H^+]} - 1\right) \quad . \quad . \quad . \quad . \quad (5)$$

satisfactory. In the attached Figure the function on the left-hand side of eqn. (5) has been plotted against $([U_T]/[H^+] - 1)$ for the three sets of measurements made at constant ionic strength, and in each case there is a linear relation and a non-zero intercept, as is required if eqn. (5) and the assumptions upon which it rests represent the processes essentially correctly. From the slopes and intercepts of these plots values have been calculated for K_1 and K_2 which are given in Table 4.

TABLE 4.

Temp.	25·0°		40·0°
μ	0·347	0·0347	0·0347
10^6K_1	4	·1·5	8
10^6K_2	1·5	0·7	1·2

Before considering these values it is necessary to examine the various assumptions which are implicit in their calculation. The most important is that in a medium of constant ionic strength all activity coefficients may be regarded as constant and included in the measured values of K_1 and K_2, so that:

$$K_1 = K_{01} \cdot \gamma_{UO_2^{2+}}/\gamma_{UO_2\cdot OH^+}\gamma_{H^+} \text{ and } K_2 = K_{02} \cdot \gamma^2_{UO_2^{2+}}/\gamma_{UO_2\cdot UO_3^{2+}}\gamma^2_{H^+}$$

where K_{01} and K_{02} are the true thermodynamic hydrolysis constants. For the hydrogen ion the concentration of which is always very low and which is present in only small quantities relatively to the total ion concentration, this is probably nearly true, but it is speculative whether this is also the case for the uranyl ion and its hydrolysis products in a medium varying from pure uranyl perchlorate to barium perchlorate containing a

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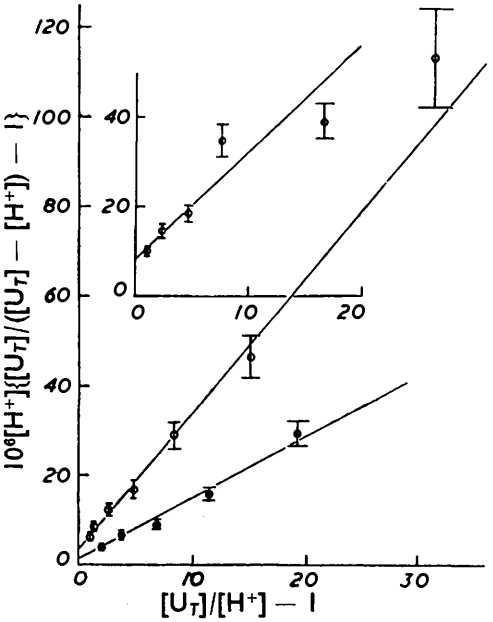
[12] Komar and Tretyak, *Zhur. analit. Khim.*, 1955, **10**, 236.

[13] Harris and Kolthoff, *J. Amer. Chem. Soc.*, 1947, **69**, 446.

small amount of the uranyl salt. If the activity coefficients of the uranium species should vary with the barium : uranium ratio of the medium, then possibly K_1 and certainly K_2 would also vary with this ratio, making eqn. (5) non-linear. The experimental results show that eqn. (5) is approximately linear, so that the effect, if it occurs, cannot be large. However, a satisfactory resolution of this point cannot be achieved without either results of much higher precision or, preferably, an independent determination of the requisite activity coefficients. The other important assumption is that in view of the very low concentrations involved the value of γ_{H^+} can be set equal to unity, permitting the use of the simplification $pH = -\log_{10} [H^+]$.

The derivation of eqn. (5) also assumes (*a*) that there is no complex formation between the uranyl ion and perchlorate ion or (*b*) that, if such complex formation occurs, the uranyl ions possess identical hydrolysis constants whether engaged in complexes or not. Attempts to detect such complex-ion formation have so far failed (cf., *e.g.*, Betts and Michels [8]), but it cannot be ruled out. The alternative supposition (*b*) is most unlikely to be valid, as may be seen by comparison of the present results with those of Faucherre.[7] Faucherre, working with nitrate solutions, found the value of K_2 to increase with a decrease in ionic strength, whereas the results given above show that in perchlorate solutions K_2 decreases with a decrease in ionic strength. If the changes in activity coefficients with concentration are comparable in nitrate and perchlorate solution this difference can be explained in terms of the formation of $UO_2{\cdot}NO_3^+$ complex ions, which is known to occur [8, 9] in nitrate solutions, only if these ions either are not hydrolysed or have a very much smaller hydrolysis constant than the uranyl ion has. In Faucherre's work a decrease in ionic strength implies also a decrease in the total nitrate concentration and hence a decrease in the extent of complex formation by the nitrate ion, thus leaving more uranyl ion free for hydrolysis, *i.e.*, apparently increasing the hydrolysis constant.



Plot of data according to eqn. (5).

○, $\mu = 0{\cdot}347$. ●, $\mu = 0{\cdot}0347$. Temp. = 25·0°.

Inset: ○, $\mu = 0{\cdot}0347$. Temp. = 40·0° Vertical and horizontal lines indicate the effects of errors of 0·02 unit of pH.

The problem of competition between complex-ion formation and hydrolysis is worth examining in more detail. Consider the case of the perchlorate and assume that in addition to the two reactions (1) and (3) the equilibrium (6) also occurs :

$$UO_2^{2+} + ClO_4^- \rightleftharpoons UO_2{\cdot}ClO_4^+ \quad . \; . \; . \; . \; . \; . \; . \quad (6)$$

with $K_c = [\mathrm{UO_2{\cdot}ClO_4^+}]/[\mathrm{UO_2^{2+}}][\mathrm{ClO_4^-}]$. Combination with K_1 and K_2 and the new conditions that

$$[\mathrm{U}_T] = [\mathrm{UO_2^{2+}}] + [\mathrm{UO_2{\cdot}OH^+}] + 2[\mathrm{UO_2{\cdot}UO_3^{2+}}] + [\mathrm{UO_2{\cdot}ClO_4^+}]$$

and

$$[\mathrm{U}_T] = [\mathrm{UO_2^{2+}}] + [\mathrm{UO_2{\cdot}ClO_4^+}] + [\mathrm{H^+}]$$

leads, for conditions under which it is permissible to write $[\mathrm{ClO_4^-}] = [\mathrm{ClO_4}]_T$, the latter being the total perchlorate concentration, tȯ the expression (7) :

$$\left\{\frac{[\mathrm{U}_T]}{[\mathrm{U}_T] - [\mathrm{H^+}]} - 1\right\}[\mathrm{H^+}] = \frac{K_1}{(1 + K_c[\mathrm{ClO_4}]_T)} + \frac{2K_2}{(1 + K_c[\mathrm{ClO_4}]_T)^2}\left(\frac{[\mathrm{U}_T]}{[\mathrm{H^+}]} - 1\right) \quad (7)$$

Comparison of eqns. (5) and (7) reveals that complex-ion formation will not modify the conclusions regarding the mechanism of hydrolysis but that the constants will differ from the true hydrolysis constants K_1 and K_2.

Equation (7) is not restricted solely to the perchlorate ion as the derivation is valid for any complex ion of the type $\mathrm{UO_2X^+}$. Hence by combination of hydrolysis constants derived in perchlorate solutions with those obtained in different media the relative extent of complex formation in these media may be compared, or if, in the case of perchlorate, $K_c = 0$, the actual values of the complexity constants may be calculated.

The apparent hydrolysis constants determined in perchlorate solutions K_1^{P} and K_2^{P} and those determined in solutions of $\mathrm{X^-}$ of the same ionic strength, K_1^{X} and K_2^{X}, are related to the true hydrolysis constants K_1 and K_2 by the expressions

$$K_1^{\mathrm{P}} = \frac{K_1}{(1 + K_c[\mathrm{ClO_4}]_T)}\ ; \qquad K_1^{\mathrm{X}} = \frac{K_1}{(1 + K_{\mathrm{X}}[\mathrm{X}]_T)}$$

and

$$K_2^{\mathrm{P}} = \frac{K_2}{(1 + K_c[\mathrm{ClO_4}]_T)^2}\ ; \qquad K_2^{\mathrm{X}} = \frac{K_2}{(1 + K_{\mathrm{X}}[\mathrm{X}]_T)^2}$$

from which it follows that

$$K_{\mathrm{X}} = \frac{1}{[\mathrm{X}]_T}\left\{\left(\frac{K_1^{\mathrm{P}}}{K_1^{\mathrm{X}}} - 1\right) + K_c[\mathrm{ClO_4}]_T\,\frac{K_1^{\mathrm{P}}}{K_1^{\mathrm{X}}}\right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and also that

$$K_{\mathrm{X}} = \frac{1}{[\mathrm{X}]_T}\left\{\left(\sqrt{\frac{K_2^{\mathrm{P}}}{K_2^{\mathrm{X}}}} - 1\right) + K_c[\mathrm{ClO_4}]_T\sqrt{\frac{K_2^{\mathrm{P}}}{K_2^{\mathrm{X}}}}\right\} \quad . \quad . \quad . \quad . \quad (9)$$

If K_c is assumed to be zero, then K_{X}, the formation constant for the ion $\mathrm{UO_2X^+}$, may be readily calculated from the measured hydrolysis constants in the two media. Eqns. (8) and (9) may be used to detect complex formation by perchlorate ions. If it is known that K_{X} is not zero, and if $K_1^{\mathrm{P}}/K_1^{\mathrm{X}}$ and $K_2^{\mathrm{P}}/K_2^{\mathrm{X}}$ are <1, then $K_c > 0$, *i.e.*, formation of perchlorate complexes occurs. Implicit in this argument is the assumption that K_1 and K_2 (as defined above) remain unchanged when the medium is changed from one of perchlorate to one of $\mathrm{X^-}$, *i.e.*, that all activity coefficients remain unchanged. This condition is unlikely to be fulfilled, as is shown, for example, by Robinson and Lim's work [14] on the activity coefficients of uranyl nitrate, chloride, and perchlorate; it is therefore preferable to rewrite eqns. (8) and (9) so as to include all the appropriate activity coefficient terms; they then become :

$$K_{\mathrm{X}} = \frac{1}{\Pi_{\mathrm{X}}^{\mathrm{X}}[\mathrm{X}]_T}\left\{\left(\frac{K_1^{\mathrm{P}}\Pi_1^{\mathrm{X}}}{K_1^{\mathrm{X}}\Pi_1^{\mathrm{P}}} - 1\right) + K_c\Pi_c^{\mathrm{P}}[\mathrm{ClO_4}]_T\,\frac{K_1^{\mathrm{P}}\Pi_1^{\mathrm{X}}}{K_1^{\mathrm{X}}\Pi_1^{\mathrm{P}}}\right\} \quad . \quad . \quad (8a)$$

and

$$K_{\mathrm{X}} = \frac{1}{\Pi_{\mathrm{X}}^{\mathrm{X}}[\mathrm{X}]_T}\left\{\left(\sqrt{\frac{K_2^{\mathrm{P}}\Pi_2^{\mathrm{X}}}{K_2^{\mathrm{X}}\Pi_2^{\mathrm{P}}}} - 1\right) + K_c\Pi_c^{\mathrm{P}}[\mathrm{ClO_4}]_T\sqrt{\frac{K_2^{\mathrm{P}}\Pi_2^{\mathrm{X}}}{K_2^{\mathrm{X}}\Pi_1^{\mathrm{P}}}}\right\} \quad . \quad (9a)$$

where the Π symbols represent the appropriate activity coefficient terms, the subscript denoting the constant concerned and the superscipt the nature of the medium. Note that

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[14] Robinson and Lim, *J.*, 1951, 1840.

$\Pi_1{}^X$ and $\Pi_1{}^P$ apply to K_1 in the two media and not to the experimental quantities $K_1{}^X$ and $K_1{}^P$; similarly $\Pi_2{}^X$ and $\Pi_2{}^P$ apply to K_2. Unfortunately data at present available are insufficient to provide a valid test of these relations.

The quantities K_1 and K_2 given in Table 4 (in the nomenclature of the last section these would be $K_1{}^P$ and $K_2{}^P$) may be used to calculate the heat content, free energy, and entropy changes associated with reactions (1) and (3). The values obtained are given in Table 5.

TABLE 5.

Temp. = 25·0°. μ = 0·0347.

	ΔH (kcal./mole)	ΔF (kcal./mole)	ΔS (cal./°c)
K_1	20·8	8·0	43
K_2	6·7	8·4	−6

The large value of ΔH for reaction (2) compared with reaction (1) makes it easy to see why evidence for its occurrence is not readily obtained at room temperature and leads to the conclusion that it would become the dominant process at sufficiently high temperatures. This possibility was, in fact, predicted by Kraus [1] who also calculated a value of ΔS for reaction (3) of 16 cal./°c. Detailed calculations based on the values in Table 5 would be of little value owing to the obvious crudity of the measurements of K_1 and K_2.

We are greatly indebted to Dr. J. Faucherre of the Université de Paris for much valuable correspondence and in particular for his kindness in making available to us a copy of his doctoral thesis and for access to his original experimental results.

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