[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Reaction between Potassium Ferrocyanide and Iodine in Aqueous Solutions

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The reaction between potassium ferrocyanide and molecular iodine in an aqueous solution has an initial rate which is first order with respect to the concentrations of both reagents. At *p*H values of 7.1 and 9.2 the rate constant for this reaction was $(1.3 \pm 0.3) \times 10^3$ liter mole^{-1} sec.$^{-1}$. The equilibrium constant for the reaction $2\text{FeoCy} + I_3^- = 2\text{FeiCy} + 3I^-$ calculated from values of rate constants does not agree with the equilibrium constant determined potentiometrically.

The reaction between potassium ferrocyanide and iodine appears to have been first reported by Preusz[1] in 1839. Since that time a number of studies have been made on the rate of the reverse reaction between potassium ferricyanide and iodide ion,[2] on the equilibrium attained between ferrocyanide, iodine (or triiodide), ferricyanide and iodide[3] and on the rate of the forward reaction.[4] Despite this work the mechanisms involved in these reactions are incompletely understood. The experiments reported below were undertaken to determine the kinetic behavior of the forward reaction in particular.

Experimental

Reagents.—The chemicals employed in the preparation of stock solutions of potassium ferrocyanide, potassium ferricyanide, iodine and potassium iodide and in the preparation of the various buffer solutions and reaction media were all reagent grade chemicals and were used without further purification. The potassium ferrocyanide stock solution was deaerated and kept under a nitrogen atmosphere when stored for short periods of time; the results obtained with these solutions of ferrocyanide were identical to results obtained with freshly prepared air-free solutions of ferrocyanide.

Hypoiodous acid was prepared by precipitating the iodide ion from a slightly basic solution of iodine with the theoretical quantity of silver nitrate. The precipitate first formed was somewhat brown in color but upon making the solution slightly acid the color of the precipitate became pale yellow, the color of silver iodide. A portion of the hypoiodous acid solution thus prepared did not give an iodine color when acidified strongly showing that iodide ion was virtually absent. When iodide ion was added to a portion of the hypoiodous acid solution and the latter acidified, the brown color of I_3^- appeared immediately.

Conductivity water was used in the preparation of all solutions and was prepared by distillation from alkaline permanganate and then from dilute sulfuric acid.

Apparatus.—The reaction vessel was a 100-cc. Pyrex bottle fitted with a perforated metal screw cap and self-sealing gasket. Above the middle of the bottle on one side was fitted an absorption cell of square Pyrex tubing. The reaction vessel could be removed from the constant temperature bath, tipped to fill the absorption cell and the absorbance of the reaction mixture determined without removing a sample.

A Beckman DU spectrophotometer was employed for all the optical density measurements.[5]

A Beckman model H *p*H meter was used for the cell potential measurements, with a saturated calomel electrode as reference electrode.

Procedures.—The reaction was followed spectrophotometrically by measuring, at various times, the absorbance of the triiodide ion, I_3^-, at 350 mμ when excess iodide was present or by measuring, at various times, the absorbance at 470 mμ when no added iodide ion was present. The molar extinction coefficients of ferrocyanide, ferricyanide, triiodide and iodine were determined at 350 and 470 mμ so that absorption resulting from the presence of each species could be accounted for when necessary.

Since the presence of air seemed to decrease the rate of reaction somewhat all solutions, with the exception of the iodine stock solutions, were deaerated by flushing the solutions with purified nitrogen. Because approximately 1 ml. of iodine stock solution was used in a total volume of 25 ml., the amount of oxygen introduced in this way was very small and did not appear to cause any irreproducibility.

Electrode potentials of solutions containing I_3^- and I^- and of solutions containing ferro- and ferricyanide were measured with a Beckman model H *p*H meter employing a saturated calomel electrode as reference electrode and a gold wire electrode as indicator electrode.

Results and Discussion

The Reactive Iodine Species.—It is known that when I_2 is added to an aqueous solution the following equilibria are rapidly established. The values given for the equilibrium constants are for 25°. It

$$I_2 + H_2O \overset{K_1}{\rightleftarrows} I^- + HOI + H^+;$$
$$K_1 = 5.4 \times 10^{-13}\ (\text{mole/l.})^2 \quad (1)$$

[6]

$$I_2 + I^- \overset{K_2}{\rightleftarrows} I_3^-;\ K_2 = 770\ (\text{mole/l.})^{-1} \quad (2)$$

[7]

$$HOI \overset{K_3}{\rightleftarrows} H^+ + OI^-;\ K_3 = 2 \times 10^{-10}\ (\text{mole/l.}) \quad (3)$$

[8]

$$H_2OI^+ \overset{K_4}{\rightleftarrows} H^+ + HOI;$$
$$K_4 > 5.4 \times 10^{-3}\ (\text{mole/l.}) \quad (4)$$

[5]

is also known that IO^- will undergo a self oxidation–reduction reaction to yield IO_3^- and I^-.[9] Therefore, in order to postulate a mechanism for the reaction between iodine and ferrocyanide, it was necessary to know which of the iodine species, I_3^-, I_2, HOI, H_2OI^+, OI^- and IO_3^- reacted with ferrocyanide. After standing 24 hr. at room temperature a solution containing 1.0 *M* NaOH, 0.01 *M* IO_3^- and 0.005 *M* ferrocyanide (FeoCy) remained clear and colorless indicating that no oxidation of FeoCy had occurred. A solution containing 0.001 *M* FeoCy and 0.0005 *M* added iodine in 0.5 *M* NaOH remained clear and colorless for several hours but became very slightly yellow overnight at room temperature showing that a very small amount of FeoCy was oxidized by IO^- before the latter was converted to IO_3^- and I^-. It

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(1) J. Preusz, *Ann.*, **29**, 323 (1839).

(2) (a) F. G. Donnan and R. LeRossignol, *J. Chem. Soc.*, 703 (1903); b) G. Just, *Z. physik. Chem.*, **63**, 513 (1908); (c) C. Wagner, *ibid.*, **113**, 261 (1924); A. von Kiss, *Rec. trav. chim.*, **52**, 289 (1933); H. B. Friedman and B. E. Anderson, THIS JOURNAL, **61**, 116 (1939).

(3) (a) V. K. LaMer and K. Sandved, *ibid.*, **50**, 2656 (1928); (b) V. K. LaMer and H. B. Friedman, *ibid.*, **52**, 876 (1930); (c) R. G. Dickinson and S. F. Ravitz, *ibid.*, **52**, 4770 (1930).

(4) R. N. J. Saal, *Rec. trav. chim.*, **47**, 385 (1928).

(5) The author wishes to thank Professor Rufus Lumry for his kind permission to use this instrument.

(6) T. L. Allen and R. M. Keefer, THIS JOURNAL, **77**, 2957 (1955).

(7) M. Davies and E. Gwynne, *ibid.*, **74**, 2748 (1952).

(8) M. L. Josien and G. Sourisseau, *Bull. soc. chim. France*, 225 (1950).

(9) C. H. Li and C. F. White, THIS JOURNAL, **65**, 335 (1943).

is readily calculated from equations 1 and 3 that in 0.5 *M* NaOH the hydrolysis of I_2 to IO^- and I^- is virtually complete and hence the added iodine was present chiefly as IO^- and I^-. Ferricyanide, FeiCy, was stable for at least 24 hr. in the presence of IO^- and I^- in 0.5 *M* NaOH. Hence it may be concluded that the oxidation of FeoCy to FeiCy by IO^- is a slow reaction.

From equations 3 and 4 it may be calculated that when IO^- solution (containing no I^-) is added to an acetate–acetic acid buffer of *p*H 4.78, the IO^- ion is converted mainly to HOI with negligible amounts of IO^- and H_2OI^+ present. A solution containing 0.001 *M* FeoCy and 0.0005 *M* HOI in the above acetate–acetic acid buffer showed no apparent oxidation of FeoCy to FeiCy overnight at room temperature. However, when the IO^- solution is added to a sulfate–bisulfate buffer of *p*H 1.48, appreciable quantities of H_2OI^+ should be formed. A solution containing 0.001 *M* FeoCy and 0.0005 *M* total hypoiodite in the above sulfate–bisulfate buffer showed an autocatalytic oxidation of FeoCy to FeiCy. This observation could be explained as the result of a slow reaction between H_2OI^+ and FeoCy to form I^- and FeiCy followed by a rapid reaction between H_2OI^+ (or HOI) and I^- to form I_2 which in turn reacts rapidly with FeoCy to produce more I^- and FeiCy.

In most of the experiments on the rate of reaction between FeoCy and iodine, an excess of I^- was used so that the iodine was present largely as I_3^-. It was observed that increasing the excess of I^- decreased the rate of reaction approximately inversely as the I^- concentration. Thus it appeared that I_3^- did not react directly with FeoCy. On the other hand, the reaction between I_2 and FeoCy in the absence of added I^- was too rapid to follow at most of the *p*H values employed even at very low concentrations of the reactants.

From the experiments described above it may be concluded that in aqueous iodine solutions the hydrated iodine molecule is the main oxidizing agent for FeoCy.

Products of the Reaction.—The products formed in the reaction between iodine and ferrocyanide are difficult to define. The equilibrium which is said to obtain[3] in the system ferrocyanide, ferricyanide, iodine and iodide is not a stable equilibrium since, in acid solution, ferro- and ferricyanide hydrolyze to form HCN and slightly soluble Prussian Blue whereas in neutral and alkaline solutions iodine hydrolyzes to give hypoiodite ion which in turn undergoes further reaction to form the iodate ion.

The exchange of free CN^- with bound CN^- in ferrocyanide ions in aqueous solutions has been shown to be very slow.[10] Thus the rapid disappearance of I_2 (or I_3^-) in the presence of FeoCy could not have resulted from the dissociation of ferrocyanide ion to a pentacyanoferrate (II) complex and free CN^- followed by reaction of I_2 with either of the dissociation products.

Hypoiodites or higher oxidation states of iodine were not formed as products during the first several hours of a reaction because acidification of a reaction mixture containing a large excess of I^- did not produce the characteristic I_3^- color at the end of this time.

It was assumed, therefore, that I_2 was reduced to I^- and that FeoCy was oxidized to FeiCy and that the over-all reaction could be written as

$$2\text{FeoCy} + I_2 = 2\text{FeiCy} + 2I^-$$

or as

$$2\text{FeoCy} + I_3^- = 2\text{FeiCy} + 3I^-$$

Mechanism of Reaction.—Wagner[2] postulated reactions 6, 7 and 8 of the mechanism written below as a result of his study of the reaction between FeiCy and I^- in the presence of thiosulfate. In view of the facts that the system FeoCy, FeiCy, I_2 and I^- has been reported[3] as coming to equilibrium and that only the reaction between FeoCy and molecular iodine of the possible iodine containing species need be considered, equation 5 was added to the mechanism of Wagner.

$$\text{FeoCy} + I_2 \xrightarrow{k_1} \text{FeiCy} + I_2^- \qquad (5)$$

$$\text{FeiCy} + I_2^- \xrightarrow{k_2} \text{FeoCy} + I_2 \qquad (6)$$

$$\text{FeoCy} + I_2^- \xrightarrow{k_3} \text{FeiCy} + 2I^- \qquad (7)$$

$$\text{FeiCy} + 2I^- \xrightarrow{k_4} \text{FeoCy} + I_2^- \qquad (8)$$

Assuming a steady-state concentration for the intermediate I_2^- and assuming that the equilibrium expressed in (2) was always maintained, one may readily derive the following expression for the rate of disappearance of FeoCy. When I^- was used in large excess $[I^-]$ was

$$\frac{-d[\text{FeoCy}]}{dt} = \frac{2}{K_2[I^-]} \left\{\frac{k_1k_3[\text{FeoCy}]^2[I_3^-] - k_2k_4K_2[\text{FeiCy}]^2[I^-]^3}{k_3[\text{FeoCy}] + k_2[\text{FeiCy}]}\right\} \qquad (9)$$

constant throughout a given rate experiment and the reaction was followed by means of the variation of the triiodide absorbance with time. The absorbances of FeoCy, FeiCy and I_2 at 350 mμ were small and so the observed absorbance could be corrected readily to give the absorbance *E* of I_3^-. Thus, when an excess of I^- was employed, one may write

$$\frac{-d[\text{FeoCy}]}{dt} = \frac{-2d[I_3^-]}{dt} = \frac{-2}{el} \times \frac{dE}{dt} = \frac{-2}{el} \times S \qquad (10)$$

where *e* is the molar extinction coefficient of I_3^- at 350 mμ, *l* is the length of the cell used for the absorbance measurements and *S* is the slope of the absorbance–time plot at time *t*.

Equation 9 was tested by utilizing equation 10 and rearranging to give

$$k_1x - by - cz = \frac{K_2[I^-]}{el} \qquad (11)$$

where

$$x = \frac{[\text{FeoCy}][I_3^-]}{(-S)},\ y = \frac{[\text{FeiCy}]^2}{[\text{FeoCy}](-S)},\ z = \frac{[\text{FeiCy}]}{[\text{FeoCy}]}$$

$$b = \frac{k_2k_4K_2[I^-]^3}{k_3} \text{ and } c = \frac{k_2K_2[I^-]}{k_3el}$$

The quantities *x*, *y* and *z* were known because $[I_3^-]$ was determined from the measured absorbance at 350 mμ, [FeoCy], and [FeiCy] were calculated from the stoichiometry of the reaction, the

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[10] A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

amount of I_3^- consumed, and the initial concentrations of FeoCy and FeiCy, and because S at time t was measured with a mechanical slope-finding device. The data obtained at various times throughout the reaction were divided into three sets. The method of averages was applied to the data in each set to give the three equations which were solved simultaneously for k_1, b and c.

Typical experimentally determined absorbance–time curves are shown in Fig. 1. The data presented in Tables I and II are typical of the data obtained from the absorbance–time curves.

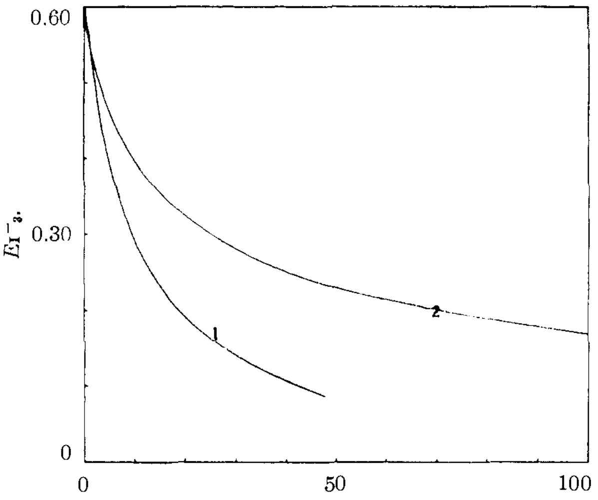

Fig. 1.—Absorbance-time curves for ferrocyanide-iodine reactions at pH 7.13 and $\mu = 0.20$. Curve 1, $[FeoCy]_0 = 12.5 \times 10^{-4}$ M, $[I_3^-]_0 = 3.55 \times 10^{-5}$ M, $[I^-]_0 = 0.0938$ M. Curve 2, $[FeoCy]_0 = 6.24 \times 10^{-5}$ M, $[I_3^-]_0 = 3.15 \times 10^{-5}$ M, $[I^-] = 0.0970$ M.

TABLE I

$[FeOCy]_0 = 12.5 \times 10^{-5}$ M; $[I_3^-]_0 = 3.55 \times 10^{-5}$ M; $[I^-] = 0.0938$ M; $[FeiCy]_0 = 0$; $e = 2.39 \times 10^4$ M^{-1} cm.$^{-1}$; $l = 0.78$ cm.; 24.0 ± 0.1°; pH 7.13; $\mu = 0.20$.

Time (min.)	E	$-S \times 10^2$, min.$^{-1}$	$x \times 10^8$	$y \times 10^3$	z
3.00	0.458	4.33	5.82	0.109	0.214
6.00	.366	2.41	7.60	0.450	.340
9.00	.308	1.61	8.93	1.03	.436
12.0	.266	1.27	9.32	1.72	.513
15.0	.232	1.03	9.58	2.60	.582
18.0	.205	0.800	10.5	3.95	.645
21.0	.184	.648	11.4	5.42	.689
24.0	.167	.552	11.7	7.07	.737
33.0	.129	.370	12.7	13.1	.844

TABLE II

$[FeOCy]_0 = 6.24 \times 10^{-5}$ M; $[I_3^-]_0 = 3.15 \times 10^{-5}$ M; $[I^-] = 0.0970$ M; $[FeiCy]_0 = 0$; $e = 2.39 \times 10^4$ M^{-1} cm.$^{-1}$; $l = 0.78$ cm.; 24.0 ± 0.1°; pH 7.13; $\mu = 0.20$

Time (min.)	E	$-S \times 10^4$, sec.$^{-1}$	$x \times 10^6$	y	z
3.00	0.500	3.59	3.95	4.65×10^{-3}	0.177
6.00	.446	2.46	4.60	1.99×10^{-2}	.322
9.00	.409	1.85	5.11	4.61×10^{-2}	.444
12.0	.378	1.43	5.70	8.80×10^{-2}	.560
15.0	.356	1.14	6.30	0.144	.660
18.0	.336	0.942	6.84	0.214	.752

When FeoCy was used in excess (Table I), the average values of k_1, b and c were found to be 8.40×10^4 liter mole^{-1} min.$^{-1}$ (1.40×10^3 liter mole^{-1} sec.$^{-1}$), 8.82×10^{-2} min.$^{-1}$ and 7.10×10^{-3} mole/liter, respectively. The value of c when combined with the values of the other quantities in c gave a value of 1.8 for the ratio k_2/k_3. This value of k_2/k_3 is in agreement with the work of Donnan and Le Rossignol and of Wagner[2] who studied the reaction between FeiCy and I^- at constant I^- concentration by reducing I_2 with thiosulfate as rapidly as it was formed and concluded that the observed rate constant was inversely proportional to the total initial iron concentration, $[FeoCy]_0 + [FeiCy]_0$. This result can be obtained from equation 9 by multiplication by -1 to convert the equation to one for the rate of disappearance of FeiCy and by setting $[I_3^-] = 0$. Thus

$$\frac{-d[FeiCy]}{dt} = \frac{2}{K_2[I^-]} \frac{k_2k_4K_2[FeiCy]^2[I^-]^3}{k_3[FeoCy] + k_2[FeiCy]} = \left\{\frac{2k_4[I^-]^2}{[FeoCy] + [FeiCy]}\right\} [FeiCy]^2 \text{ if } k_3 = k_2$$

Since FeoCy and FeiCy are converted into one another their total concentration remains constant. Wagner obtained a value of 4 for k_2/k_3 at 15°.[2]

From b a value of k_4 can be obtained because $[I^-]$, K_2 and k_2/k_3 are known. Thus k_4 was calculated to be 1.27×10^{-3} liter^2 mole^{-2} sec.$^{-1}$. Unfortunately, the value of k_4 obtained here cannot be compared directly with other values which have been obtained[2] because the other values have been derived at temperatures other than 24° and activation energies have not been determined and because the ionic strengths employed differ considerably. However, the order of magnitude of k_4 compares favorably with 1.22×10^{-3} liter^2 mole^{-2} sec.$^{-1}$, the value obtained by Wagner[2] at 15° but at much higher ionic strengths than used here. Since increase in ionic strength increases the rate of reaction between similarly charged ions, the effect of decrease of temperature on k_4 is at least partly compensated for by the increased ionic strength.

When approximately equivalent quantities of FeoCy and iodine were used (Table II) the values calculated for k_1, k_2/k_3 and k_4 were 1.20×10^3 liter mole^{-1} sec.$^{-1}$, 1.1, and 6.1×10^{-3} liter^2 mole^{-2} sec.$^{-1}$, respectively. However, the data of Table II cover only the first 50% of the reaction. Thereafter the derived equation 11 does not fit the data well and, although essentially the same values of k_1 and k_2/k_3 are obtained throughout the reaction, the value of k_4 became negative. Similar observations were made when FeiCy was added initially. Addition of FeiCy retarded the reaction. Use of equation 11 as outlined above gave values of k_1 and k_2/k_3 which were in agreement with values reported above, but a negative value was again obtained for k_4. Other reasons given below lead one to conclude that the postulated mechanism is inadequate, especially equation 8.

Initial Rates of Reaction in Presence of Excess Iodide.—When FeiCy is absent initially the initial rate of reaction should be controlled by reactions 5 and 7 and the rate of disappearance of FeoCy given by

$$\frac{-\mathrm{d}[\mathrm{FeoCy}]}{\mathrm{d}t} = \frac{2k_1[\mathrm{FeoCy}][\mathrm{I_3^-}]}{K_2[\mathrm{I^-}]} = \frac{-2}{el}\frac{\mathrm{d}E}{\mathrm{d}t} \quad (12)$$

when I^- is present in excess. When integrated, equation 12 becomes

$$\frac{1}{E} = \frac{1}{E_0} + \frac{2k_1t}{elK_2[\mathrm{I^-}]} \quad (13a)$$

or

$$\log\left(2 + \frac{A}{E}\right) = \log\left(\frac{2E_0 + A}{E_0}\right) + \frac{([\mathrm{FeoCy}]_0 - 2[\mathrm{I_3^-}]_0)}{2.30K_2[\mathrm{I^-}]}k_1t \quad (13b)$$

depending on whether equivalent or non-equivalent concentrations of ferrocyanide and iodine were used. In (13b), $A = el([\mathrm{FeoCy}]_0 - 2[\mathrm{I_3^-}]_0)$. The subscript zero indicates the value of the quantity at zero time.

Equation 13 was applied for the first 20–25% of the reaction at different concentrations of I_3^-, I^- and FeoCy and at two *p*H values. The results are given in Table III. The average value of k_1 was found to be 1.3×10^3 liter mole^{-1} sec.$^{-1}$ with a standard deviation of $\pm 0.3 \times 10^3$. The error was large because of inaccuracies in determining the initial part of the absorbance–time curve. This was especially true at the lower iodide concentrations because the reaction was so rapid there. However, k_1 does not show any tendency to drift with decreasing iodide concentration. The rate constant k_1 did not show any dependency on ionic strength μ, when μ was decreased from 0.2 to 0.11. However, unless k_1 was very sensitive to changes in μ the effect would be masked by the error in k_1. Therefore in the remaining experiments where iodide concentration was varied μ was not maintained constant.

TABLE III

THE RATE CONSTANT FOR THE REACTION BETWEEN IODINE AND FERROCYANIDE BY THE INITIAL RATE METHOD

24.0 ± 0.1°

*p*H	μ	$[\mathrm{FeoCy}]_0 \times 10^5$, *M*	$[\mathrm{I_3^-}]_0 \times 10^5$, *M*	$[\mathrm{I^-}]$, *M*	$k_1 \times 10^{-3}$, l. mole^{-1} sec.$^{-1}$
9.2	0.20	6.24	3.23	0.097	1.1
	.20	6.24	3.12	.097	1.2
	.20	12.5	3.18	.097	1.1
	.20	6.24	6.24	.097	1.5
	.20	6.24	6.24	.097	1.2
7.13	.20	6.24	3.15	.097	1.0
	.20	6.00	3.13	.097	1.8
	.20	12.5	3.19	.097	1.3
	.20	12.5	3.55	.097	1.2
	.20[a]	12.8	3.14	.097	0.92
	.20	6.24	6.38	.097	0.84
	.20	6.24	6.40	.097	1.0
	.20[b]	6.08	3.11	.012	1.0
	.20[b]	6.08	3.11	.012	1.1
	.11	6.08	3.11	.012	1.3
	.13	5.20	3.22	.025	1.8
	.13	6.24	3.26	.025	1.6
	.13	6.24	3.26	.025	1.3
	.13	5.02	3.13	.031	1.5
	.15	6.08	3.11	.050	1.4

[a] 0.100 *M* NaI in place of 0.100 *M* KI. [b] $NaClO_4$ was added to bring ionic strength up to this value.

Specific effects by K^+ and by Na^+ have been reported on the rate of the FeiCy + I^- reaction,[2] but these have not been systematically investigated. One experiment with 0.100 *M* NaI in place of 0.100 *M* KI showed a tendency for k_1 to decrease but since the effect was hardly outside the experimental error, specific effects of K^+ and Na^+ were not investigated further.

Attempts to study the reaction in the presence of excess I^- in acetate–acetic acid and in sulfate–bisulfate buffers were unsuccessful. At these *p*H values solutions became turbid shortly after addition of the ferrocyanide to the buffer containing KI even when 0.01 *M* KI was used. The turbidity appeared to be a result of the presence of I^- since it did not appear when salts such as KNO_3 or KCl were used in place of KI.

Reaction in Absence of Added Iodide.—One rate measurement was carried out in sulfate–bisulfate buffer of *p*H 1.48 in the absence of added iodide. The reaction was followed by the change in absorbance at 470 mμ in 10 cm. cells. The amount of triiodide at any time was too small to measure accurately at 350 mμ. At 470 mμ I_3^-, I_2 and FeiCy absorb and the total absorbance E is given by

$$E = e_{\mathrm{FeiCy}}\, l[\mathrm{FeiCy}] + e_{\mathrm{I_3^-}} l[\mathrm{I_3^-}] + e_{\mathrm{I_2}}\, l[\mathrm{I_2}] \quad (14)$$

where the e's are the molar extinction coefficients of the indicated species and E is the measured absorbance corrected for the absorbance of the solvent. Thus the equation for the rate of change of absorbance may be written

$$\frac{\mathrm{d}E}{\mathrm{d}t} = l\left\{e_{\mathrm{FeiCy}}\frac{\mathrm{d}[\mathrm{FeiCy}]}{\mathrm{d}t} + e_{\mathrm{I_3^-}}\frac{\mathrm{d}[\mathrm{I_3^-}]}{\mathrm{d}t} + e_{\mathrm{I_2}}\frac{\mathrm{d}[\mathrm{I_2}]}{\mathrm{d}t}\right\} \quad (15)$$

Expressions for the rate terms inside the parentheses may be found from the postulated reaction mechanism. The material balance and stoichiometry equation may be employed along with

$$[\mathrm{FeoCy}] + [\mathrm{FeiCy}] = [\mathrm{FeoCy}]_0 \quad (16a)$$

$$[\mathrm{I_2}]_0 - [\mathrm{I_2}] - [\mathrm{I_3^-}] = \frac{1}{2}[\mathrm{FeiCy}] \simeq [\mathrm{I_2}]_0 - [\mathrm{I_2}] \quad (16b)$$

$$[\mathrm{I^-}] + [\mathrm{I_3^-}] = [\mathrm{FeiCy}] \simeq [\mathrm{I^-}] \quad (16c)$$

equations 2 and 14 to give the concentration of each species in terms of E. Thus an equation giving $\mathrm{d}E/\mathrm{d}t$ in terms of E can be derived. The numerical values of e_{FeiCy}, $e_{\mathrm{I_3^-}}$ and $e_{\mathrm{I_2}}$ at 470 mμ were determined to be 18, 623 and 530 l. mole^{-1} cm.$^{-1}$, respectively. For $[\mathrm{I_2}]_0 = 1.92 \times 10^{-5}$ *M* the equation was obtained

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{5.00}{k_3(E - 0.007) + k_2(0.102 - E)}\{k_2k_4f(E) + k_1k_3g(E)\}$$

where

$$f(E) = -5.16 \times 10^{-8}E^5 + 8.9 \times 10^{-8}E^4 - 3.09 \times 10^{-8}E^3 + 4.46 \times 10^{-9}E^2 - 2.92 \times 10^{-10}E + 7.30 \times 10^{-12}$$

and

$$g(E) = 6.35 \times 10^{-5}E^4 - 8.50 \times 10^{-5}E^3 + 1.76 \times 10^{-6}E^2 - 1.21 \times 10^{-8}E + 2.79 \times 10^{-11}$$

The function $f(E)$ was approximately equal to zero throughout the reaction. Hence the equation for $(\mathrm{d}E/\mathrm{d}t)$ may be written

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{5.00k_1k_3g(E)}{k_3(E - 0.007) + k_2(0.102 - E)} = \frac{5.00k_1g(E)}{(E - 0.007) + (k_2/k_3)(0.102 - E)}$$

Two measured values of the slope will thus give k_1 and k_2/k_3. Results are presented in Table IV. The value of k_1 remained constant over most of the reaction, and the ratio k_2/k_3 was of the order of unity as found when I^- was used in excess. The value of k_1 was much less at pH 1.48 than at 7.13 and 9.2, however. Had this not been so, the direct reaction between FeoCy and I_2 could not have been measured in this way at pH 1.48. At pH 7.13 and 9.2 the ionization

$$HFe(CN)_6^{-3} \rightleftharpoons H^+ + Fe(CN)_6^{-4}; \; K_a = 5.8 \times 10^{-5} \text{ mole/liter}^{11}$$

where K_a is the acid dissociation constant in terms of activities, was complete and k_1 was independent of pH. At pH 1.48 the ionization was not complete. If the assumption that only $Fe(CN)_6^{-4}$ reacts with I_2 was made, the correct $[H^+]$ dependence was not obtained. Apparently species other than $Fe(CN)_6^{-4}$ react with I_2. The pH effect was not studied further.

TABLE IV

REACTION BETWEEN FERROCYANIDE AND IODINE IN ABSENCE OF ADDED IODIDE

$[\mathrm{FeoCy}]_0 = 3.85 \times 10^{-5}$ M; $[I_2]_0 = 1.92 \times 10^{-5}$ M; 24.0 ± 0.1°; pH 1.48; $\mu = 0.10$.

Time (sec.)	E	$g(E) \times 10^8$	$(dE/dt) \times 10^4$, sec.$^{-1}$	k_2/k_3	k_1, mole^{-1} sec.$^{-1}$
0	0.118	...	...	..	..
10	.110	−8.5	−7.0	1.0	156
20	.104	−7.1	−5.8	0.7	157
30	.099	−6.0	−5.0	4.8	155
60	.086	−3.8	−3.6		
(10 min.)	0.66	...			

The Equilibrium Constant.—From equation 9 it is seen that the rate of reaction is zero whenever

$$k_1k_3[\mathrm{FeoCy}]^2[I_3^-] = k_2k_4K_2[\mathrm{FeiCy}]^2[I^-]^3$$

The concentration equilibrium constant is therefore given by

$$K_c = \frac{[\mathrm{FeoCy}]^2[I_3^-]}{[\mathrm{FeiCy}]^2[I^-]^3} = \frac{k_2k_4K_2}{k_1k_3} = \frac{K_a}{K_f} \qquad (17)$$

where K_a is the activity equilibrium constant and K_f is the activity coefficient part of K_a. LaMer and Sandved[3] reported values of K_c in the range $0.3 \times 10^{-3} < K_c < 2 \times 10^{-2}$ liter^2 mole^{-2} at considerably higher ionic strengths than were used in the present work. From the values of k_1, k_2/k_3, k_4 and K_2 given in previous sections the values of 1.3×10^{-3} and 4.3×10^{-3} liter^2 mole^{-2} can be calculated for K_c. Thus there is agreement at least as to the order of magnitude of K_c with the results of LaMer and Sandved. From the activity coefficients listed by Kielland[12] it may be calculated that K_f should be approximately $1/16$ at $\mu = 0.2$ and hence the corresponding activity equilibrium constants are 8×10^{-5} and 2.7×10^{-4} liter^2 mole^{-2}, respectively. The value of K_a calculated, using the free energies of formation of $I_3^-{}_{aq}$, $I^-{}_{aq}$ and FeoCy_{aq} and the standard potential of the FeoCy/FeiCy couple from Latimer,[13] was 1.2×10^{-6} liter^2 mole^{-2}. Thus the kinetic value was 60–220 times too large.

TABLE V

MEASUREMENT OF E.M.F.'S IN $H_2PO_4^-$–HPO_4^{-2} BUFFER

pH 7.13; 25°; $\mu = 0.10$

$[I_3^-]$, M	$[I^-]$, M	[FeOCy], $\times 10^3$, M	[FeiCy], $\times 10^3$, M	E, v. $vs.$ S.C.E.	E^{01}
1.00×10^{-3}	0.100	..	..	0.300	0.300
5.00×10^{-4}	.0500	..	..	.318	.300
2.50×10^{-4}	.0250	..	..	.334	.298
....	....	1.00	1.00	.140	.140
....	....	1.00	0.50	.120	.138
....	....	0.50	1.00	.158	.140

As a result of the disagreement between the kinetic and predicted values of K_a at pH 7.13, it was decided to measure the e.m.f.'s of the I_3^-/I^- and FeoCy/FeiCy couples in the reaction medium employed, namely, $H_2PO_4^-$–HPO_4^{-2} buffer of $\mu = 0.100$. The results are given in Table V. The e.m.f. E^{01} is defined by the equations

$$E = E^0 + \frac{RT}{nF}\ln\left[\frac{a_{I_3^-}}{a^3_{I^-}}\right] = E^{01} + \frac{RT}{nF}\ln\left[\frac{[I_3^-]}{[I^-]^3}\right]$$

for the iodine couple and by

$$E = E^0 + \frac{RT}{nF}\ln\left[\frac{a_{\mathrm{FeiCy}}}{a_{\mathrm{FeoCy}}}\right] = E^{01} + \frac{RT}{nF}\ln\left[\frac{[\mathrm{FeiCy}]}{[\mathrm{FeoCy}]}\right]$$

for the iron couple. At 25° the equilibrium constant (17) was calculated from these e.m.f. measurements to be 4×10^{-6} liter^2 mole^{-2}. Thus the value of K_c determined from kinetic measurements was approximately 1000-fold greater than the value of K_c determined potentiometrically. It would seem that the equilibrium was not between FeoCy, FeiCy, I_3^- (or I_2) and I^- as has been previously assumed but that some other species were involved. One possibility may be the species which caused the turbidity when FeoCy was added to acidic I^- containing systems.

Because of the disagreement between kinetic and potentiometric values of K, an attempt was made to determine the equilibrium constant in the kinetic system by measuring the various concentrations spectrophotometrically in the absence of added I^-. It will be noticed from the infinite time reading in Table IV that the measured absorbance at 470 mμ shows that considerable I_2 was left in the system and hence the concentrations of the various reactants should be determinable. For this reason equilibrium measurements were made in acid media at pH 4.78 and 1.48. The absorbances at 350, 420 and 470 mμ were measured. The stoichiometry of the reaction was assumed to be 2:1 and the concentrations of I_2, I^-, FeoCy and FeiCy were calculated from the measured absorbances. The molar extinction coefficients used at the various wave lengths are given in Table IV. The results of the calculation of K's from the concentrations of the four species are presented in Table VII. K_c and K_a are the concentration and activity equilibrium constants, respectively. In the calculation of the unprimed K's the concentration of the ferrocyanide ion was taken to be equal to the total ferrocyanide concentration present at equilibrium; allowance was not made for the incomplete ionization of $HFe(CN)_6^{-3}$.[11]

When the concentration of ferrocyanide ion was calculated from the dissociation of $HFe(CN)_6^{-3}$ in

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(11) I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 955 (1935).

(12) J. Kielland, THIS JOURNAL, **59**, 1675 (1937).

(13) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

TABLE VI

MOLAR EXTINCTION COEFFICIENTS IN LITER MOLE^{-1} CM.$^{-1}$

λ, mμ	ε(FeiCy)	ε(FeoCy)	ε(I_2)	ε(I_3^-)	ε(I^-)
470	18	0	530	623	0
420	1010	0	390	2.90 × 10^3	0
350	318	184	170	2.43 × 10^4	0

TABLE VII

THE EQUILIBRIUM CONSTANT FOR $2Fe(CN)_6^{-4} + I_2 = 2Fe(CN)_6^{-3} + 2I^-$; 24°, $\mu = 0.10$

pH	[FeOCy]$_0$ × 10^5, M	[I_2]$_0$ × 10^5, M	K_c × 10^3	K_a × 10^3	K_c'	K_a'
4.78	10.5	5.22	11	1.3	9100	1000
	10.5	5.22	10	1.2	8300	950
	19.8	4.96	0.91	0.10	760	86
	44.4	22.2	2.1	0.24	1700	200
	88.9	22.2	0	0	0	0
1.48	11.8	5.86	8.4	0.95	0.75	0.085
	3.85	1.92	22.6	2.6	2.0	0.23

the acid media used and this concentration value for $Fe(CN)_6^{-4}$ employed in the calculation of K, the primed constants were obtained. The value of K_a was most nearly constant in the range $1 \times 10^2 \leqslant K_a \leqslant 2.6 \times 10^3$ liter/mole except for one experiment. However, K_a appeared to increase with decreasing initial concentrations of FeoCy and I_2 at a constant value of $[FeoCy]_0/[I_2]_0$ and to decrease with decrease in the ratio $[FeoCy]_0/[I_2]_0$. K_a' varied greatly with conditions. It should be noted that if the equilibrium involved some ferrocyanide species (*e.g.*, $HFe(CN)_6^{-3}$) other than $Fe(CN)_6^{-4}$ then K_a would not be equal to the true equilibrium constant but would be proportional to it at a given pH; the proportionality constant would be independent of the initial concentrations of the reactants but would vary with the pH of the medium.

Since considerable I_2 remained when "equilibrium" was attained (within a few minutes) in systems containing initially equivalent concentrations of FeoCy and I_2, then considerable I_2 should be formed when excess I^- is added to a solution of FeiCy. In one experiment with $[FeiCy]_0 = 2.38 \times 10^{-4}$ M and $[I^-]_0 = 4.76 \times 10^{-4}$ M the amounts of I_3^- and I_2 formed were so small as to make their determination unreliable even after 1 hr. Thus it is clear that the same positions of "equilibrium" were not attained from FeiCy + I^- and from FeoCy + I_2 unless much longer times were allowed. Hydrolysis of the complex cyanides obscures the events which may happen when longer times are allowed, however.

From the reported facts it was concluded that equilibrium was not obtained between $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$, I_2 (or I_3^-) and I^- in the various systems described and that this could account for the negative values obtained for k_4 in many experiments.

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[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Temperature Dependence of the Carbon Isotope Effect in the Acid Hydrolysis of Urea

BY PETER E. YANKWICH AND AUDREY E. VEAZIE

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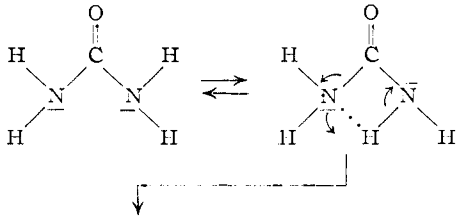
The carbon isotope effect in the hydrolysis of urea has been measured over the temperature range 60–96°. While theoretical calculations based on a number of models reproduce the temperature dependence observed, no model up to three centers with internally consistent properties was found to yield the experimentally observed temperature-independent factor in the isotopic rate constant ratio.

Introduction

In two recent papers, Shaw and his co-workers have presented the results of studies on the effects of salt and hydrogen-ion concentration on the rates of decomposition of aqueous urea[1] and thiourea.[2] The absence of a large primary salt effect, the activation energy of nearly 33 kcal. per mole, the modest entropy of activation (*ca.* 6 e.u.), and the absence of hydrogen-ion catalysis are compatible with the scheme



$$NH_3 + HNCO \rightleftharpoons NH_4^+ + NCO^- \quad (1)$$

In acidic solutions cyanate is hydrolyzed rapidly[3]

$$2H^+ + NCO^- + H_2O = NH_4^+ + CO_2 \quad (2)$$

Schmitt and Daniels[4] have recorded only two experiments on the carbon isotope effects; the hydrolyses were carried out at 100° in a phosphate buffer system at pH 5.0. With C^{13} their result for k_1/k_2 (*vide infra*) was 1.055 ± 0.003, somewhat larger than the figure calculated from the exact Eyring equation[5] on the assumption of simple C–N bond rupture.

In this paper we report a study of the C^{13} isotope effect in the decomposition of urea in dilute aqueous acid over the temperature range 60–96° and comparison of the results with the predictions of theoretical models of various degrees of complexity.

Experimental

Materials.—J. T. Baker "Analyzed" reagent urea was used without further purification. The solvent was 0.05 M sulfuric acid prepared by dilution of the du Pont 96% C.P. re-

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[1] W. H. R. Shaw and J. J. Bordeaux, THIS JOURNAL, **77**, 4729 (1955). This paper contains a convenient summary of earlier investigations of the mechanism of urea hydrolysis.

[2] W. H. R. Shaw and D. G. Walker, *ibid.*, **78**, 5769 (1956).

[3] A. R. Amell, *ibid.*, **78**, 6234 (1956).

[4] J. A. Schmitt and F. Daniels, *ibid.*, **75**, 3564 (1953).

[5] H. Eyring and F. W. Cagle, *J. Phys. Chem.*, **56**, 889 (1952).