Assuming that ΔH^0 is independent of temperature over this range and from the ΔF^0 of 8,610 cal. given by the solubility product at 25°, the ΔS^0 for reaction 6 is -21.2 e.u. Using -19.1 e.u. as the standard entropy[8] of Mn^{++} and $+28.0$ e.u. for IO_3^-,[9] the standard entropy of solid manganese(II) iodate was calculated to be 58.1 e.u. This value may be compared with 54 e.u. which would be obtained by the use of the tables given by Latimer[10] for the entropies of ions in solids.

[8] A. F. Kapustinskii, *J. Phys. Chem.* (*U. S. S. R.*), **15**, 220 (1941).

[9] W. M. Latimer, K. S. Pitzer and W. V. Smith, THIS JOURNAL, **60**, 1829 (1938).

[10] W. M. Latimer, *ibid.*, **73**, 1480 (1951).

AMES, IOWA RECEIVED MAY 4, 1951

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, POLYMER CORPORATION LIMITED]

The Persulfate–Iron(II) Initiator System for Free Radical Polymerizations[1]

BY J. W. L. FORDHAM AND H. LEVERNE WILLIAMS

In dilute aqueous solutions of acrylonitrile and under a nitrogen atmosphere the oxidation of iron(II) by persulfate is a second order reaction, probably the bimolecular reaction: $Fe^{++} + S_2O_8^{--} \rightarrow Fe^{+++} + SO_4\cdot^- + SO_4^{--}$. The rate constant of the second order reaction at weak ionic strengths of the solution is expressed by the Brønsted–Debye–Hückel equation for a reaction between two oppositely charged divalent ions. The calculated product of the ionic charges of the reactants has a value of -4.15 at 0° and -3.80 at 10°. In the temperature range from 0 to 10° the rate constant at infinite dilution is given by $k_0 = 1.0 \times 10^{11} e^{-12,100/RT}$ l. mole^{-1} sec.$^{-1}$.

In the presence of 2,2′-bipyridine the addition of the first two molecules of complexing agent to the ferrous ion does not destroy the reactivity of the complex with persulfate. However, with the formation of the tribipyridine complex its reactivity is destroyed. The rate constant of the second order reaction is unchanged in the presence of the emulsifiers Agent 140 BK and Daxad 11 but is increased in the presence of Nacconol NRSF.

Introduction

The persulfate–iron(II) reaction has not yet been studied extensively as a source of free radicals although this system will initiate acrylonitrile polymerization.[2] However it has been postulated that the reaction produces sulfate radical ions which are able to initiate the oxidation chain for alcohols.[3] Saal[4] studied the rate of the reaction in the presence of different concentrations of the electrolytes potassium chloride, magnesium chloride and magnesium sulfate but he neglected the bimolecular terminating step between the iron(II) and the sulfate radical ions and "his method of expressing concentrations is obscure and apparently burdened with typographical errors".[5]

In view of the lack of reliable data on the rate constant of the oxidation of iron(II) by persulfate this study was undertaken. Determinations of the rate constant at various ionic strengths of the solution were made in order to determine the rate constant at infinite dilution. The effect of adding the iron(II) complexing agent 2,2′-bipyridine and various emulsifiers was investigated.[5a]

Theoretical

If the $SO_4\cdot^-$ radical ion formed by the reaction

$$Fe^{++} + S_2O_8^{--} \xrightarrow[k]{} Fe^{+++} + SO_4^{--} + SO_4\cdot^-$$

reacts solely with a monomer molecule to initiate polymerization, then in the absence of interfering side reactions the iron(II) should disappear by a second order reaction and eq. 1 should be valid.

$$\ln(1 - (b - a)/[Fe^{++}]) = -(b - a)kt + \ln a/b \qquad (1)$$

where $a = [S_2O_8^{--}]_0$ and $b = [Fe^{++}]_0$.

Preliminary experimental data indicated that the initial reaction involving traces of atmospheric oxygen, very difficult to remove experimentally, results in an increase in the initial rate of iron(II) disappearance and a decrease in the value of $(b - a)$ for the subsequent oxygen-free reaction. Consequently the difference between the initial concentrations of iron(II) and persulfate cannot be used to determine the value of $(b - a)$ for the oxygen-free reaction. But when $a < b$ and $t \rightarrow \infty$

$$b - a = [Fe^{++}]_\infty \qquad (2)$$

Hence under these conditions eq. 1 becomes

$$\ln(1 - [Fe^{++}]_\infty/[Fe^{++}]) = [Fe^{++}]_\infty kt + C \qquad (3)$$

where C = a constant.

Since the reaction is ionic, the observed rate constant will be dependent on the activity coefficients of the reactants and the activated complex. In dilute solutions the equation of the observed rate constant should be given by

$$\log k = \log k_0 - 4\frac{A\mu^{1/2}}{(DT)^{3/2}} \qquad (4)$$

where k_0 = rate constant at infinite dilution; A = a constant; D = dielectric constant of the medium; T = temperature; and μ = ionic strength of the solution.

When 2,2′-bipyridine (bip) is added to the system the following equilibria are assumed to be valid.

$$Fe^{++} + (bip) \rightleftharpoons Fe(bip)^{++} \qquad K_1$$

$$Fe(bip)^{++} + (bip) \rightleftharpoons Fe(bip)_2^{++} \qquad K_2$$

$$Fe(bip)_2^{++} + (bip) \rightleftharpoons Fe(bip)_3^{++} \qquad K_3$$

$$(bip)H^+ \rightleftharpoons (bip) + H^+ \qquad K_a$$

When the total bipyridine concentration and the pH of the solution are adjusted so that practically

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[1] Presented before the Division of Inorganic and Physical Chemistry, American Chemical Society, Cleveland, Ohio, April, 1951.

[2] R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946).

[3] J. H. Merz and W. A. Waters, *Faraday Soc. Discussions*, **2**, 179 (1947).

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

[5] C. V. King and O. F. Steinbach, THIS JOURNAL, **52**, 4779 (1930).

[5a] Subsequent to the preparation of this paper the work by Kolthoff, Medalia and Raaen has been published (*ibid.*, **73**, 1733 (1951)) extending considerably the knowledge of the persulfate-iron(II) reaction under various conditions. Their data do not alter any of the considerations in this paper.

all the iron(II) is present as the tribipyridine complex, then

$$[\mathrm{Fe(bip)}^{++}]_0/[\mathrm{Fe}^{++}]_0 = K_1\,([\mathrm{bip_T}]_0 - 3[\mathrm{Fe(bip)_3}^{++}]_0)\left(\frac{K_a}{K_a + [\mathrm{H}^+]}\right) \quad (5)$$

$$[\mathrm{Fe(bip)_2}^{++}]_0/[\mathrm{Fe}^{++}]_0 = K_1K_2\,([\mathrm{bip_T}]_0 - 3[\mathrm{Fe(bip)_3}^{++}]_0)^2\left(\frac{K_a}{K_a + [\mathrm{H}^+]}\right)^2 \quad (6)$$

$$[\mathrm{Fe(bip)_3}^{++}]_0/[\mathrm{Fe}^{++}]_0 = K_1K_2K_3([\mathrm{bip_T}]_0 - 3[\mathrm{Fe(bip)_3}^{++}]_0)^3\left(\frac{K_a}{K_a + [\mathrm{H}^+]}\right) \quad (7)$$

where $[\mathrm{bip_T}]$ = total bipyridine concentration.

Values of K_a, K_1 and $K_1K_2K_3$ have been determined by Baxendale and George[6] at various temperatures and hence the first and the last ratios can be determined easily.

Results

The linearity of the semilogarithmic plots of $1 - [\mathrm{Fe}^{++}]_\infty/[\mathrm{Fe}^{++}]$ *versus* time in Figs. 1 to 4 suggests that in an unbuffered, dilute, aqueous solution of acrylonitrile with a *p*H value of about 4 and under a nitrogen atmosphere the oxidation of iron(II) by persulfate proceeds by a second order reaction, which is probably the bimolecular reaction previously postulated. Furthermore the linearity of the semilogarithmic plots of *k versus* $\mu^{1/2}$ in Fig. 5 and the calculated values of −4.15 at 0° and −3.80 at 10° for the product of the ionic charges of the reactants indicates that the Brønsted–Debye–Hückel theory is valid for this reaction and the reaction is between two oppositely charged divalent ions. Values of μ were calculated based on the assumption that the ionic strength of the solution remained practically constant throughout the experiment. This assumption would appear to be valid in view of the linearity of the semilogarithmic plots of $1 - [\mathrm{Fe}^{++}]_\infty/[\mathrm{Fe}^{++}]$ *versus* time. The values

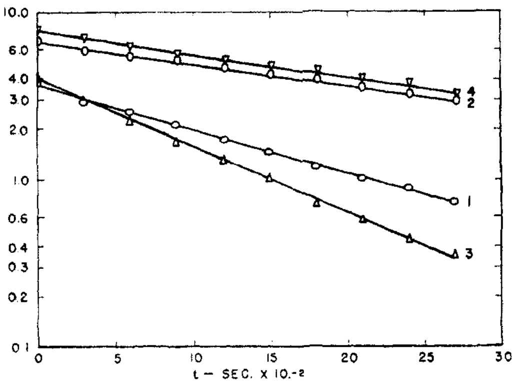

Fig. 1.—The persulfate–iron(II) reaction in the absence of added electrolytes at 0.0°. Initial persulfate, initial iron(II), and final iron(II) concentrations are, respectively: curve 1, 2.00, 6.00 and 3.75 × 10^{-5} molar; curve 2, 4.00, 6.00 and 1.90 × 10^{-5} molar; curve 3, 4.00, 10.00 and 5.75 × 10^{-5} molar; and curve 4, 8.00, 10.00 and 2.00 × 10^{-5} molar.

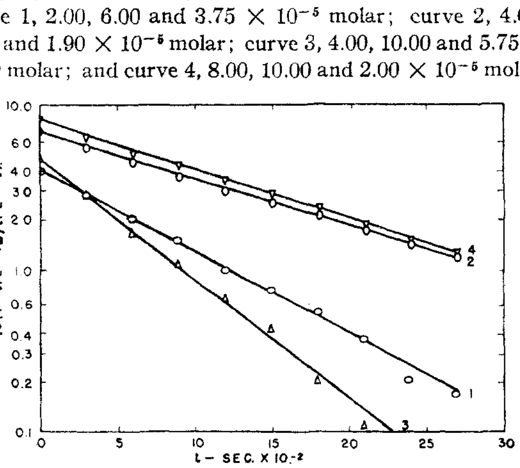

Fig. 2.—The persulfate–iron(II) reaction in the absence of added electrolytes at 10.0°. Initial persulfate, initial iron (II) and final iron(II) concentrations are, respectively: curve 1, 2.00, 6.00 and 3.60 × 10^{-5} molar; curve 2, 4.00, 6.00 and 1.90 × 10^{-5} molar; curve 3, 4.00, 10.00 and 5.25 × 10^{-5} molar; and curve 4, 8.00, 10.00 and 1.90 × 10^{-5} molar.

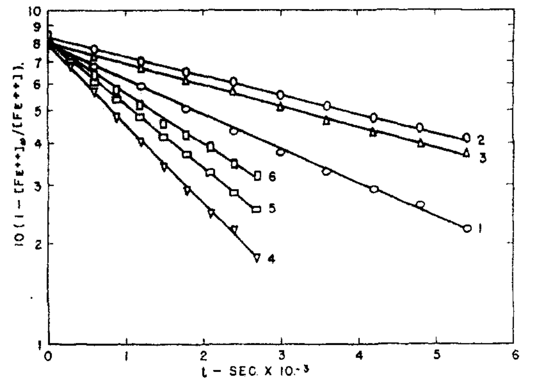

Fig. 3.—The persulfate–iron(II) reaction in presence of potassium chloride. Initial persulfate and iron(II) concentrations are 8.00 and 10.00 × 10^{-5} molar, respectively. The potassium chloride and the final iron(II) concentrations at 0.0° are, respectively: curve 1, 2.00 × 10^{-3} and 2.00 × 10^{-5} molar; curve 2, 6.00 × 10^{-3} and 1.55 × 10^{-5} molar; and curve 3, 10.00 × 10^{-3} and 1.95 × 10^{-5} molar. Similarly at 10.0°: curve 4, 2.00 × 10^{-3} and 2.05 × 10^{-5} molar; curve 5, 6.00 × 10^{-3} and 2.00 × 10^{-5} molar; and curve 6, 10.00 × 10^{-3} and 1.95 × 10^{-5} molar.

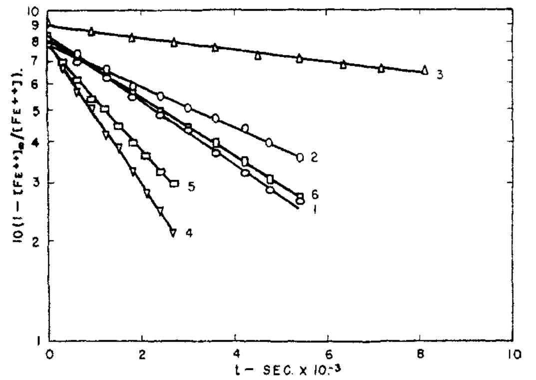

Fig. 4.—The persulfate–iron(II) reaction in the presence of potassium chloride (curves 1, 2, 4 and 5) and calcium sulfate (curves 3 and 6). Initial persulfate and iron(II) concentrations are, respectively, 8.00 and 10.00 × 10^{-5} molar. Initial concentration of electrolyte and final concentration of iron(II) at 0.0° are, respectively: curve 1, 4.00 × 10^{-3} and 2.05 × 10^{-5} molar; curve 2, 8.00 × 10^{-3} and 1.90 × 10^{-5} molar; and curve 3, 5.00 × 10^{-3} and 0.90 × 10^{-5} molar. Similarly at 10.0°: curve 4, 4.00 × 10^{-3} and 1.95 × 10^{-5} molar; curve 5, 8.00 × 10^{-3} and 2.05 × 10^{-5} molar; and curve 6, 5.00 × 10^{-3} and 1.60 × 10^{-5} molar.

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[6] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 55 (1950).

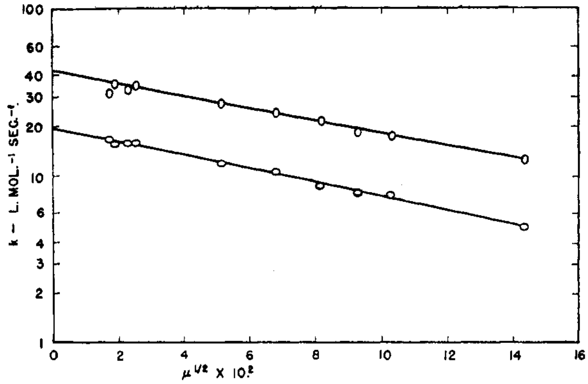

Fig. 5.—Plot of *k versus* $\mu^{1/2}$ at 0.0° (lower) and at 10.0° (upper).

for the product were calculated with the assumption that the dielectric constant of the medium was the same as that of water, namely, 88 at 0° and 84 at 10°.

Extrapolation to zero ionic strength gave values of 19.3 and 42.6 l. mole^{-1} sec.$^{-1}$ at 0 and 10°, respectively, for the rate constant at infinite dilution (k_0). These values yield the following equation in the temperature range 0 to 10°

$$k_0 = 1.0 \times 10^{11} e^{-12,100/RT}$$

In an acetate buffered solution with a *p*H of 3.90 in the presence of 2,2′-bipyridine the variation of the initial rate of total iron(II) disappearance with a change of bipyridine concentration is illustrated by the plots of [Fe_T^{++}] (total iron(II) concentration) *versus* time in Fig. 6 and by the data in Table I. Only initial rates were measured because the formation of the product, iron(III), which is also complexed by bipyridine introduces a complicating factor that cannot be treated until quantitative data are available for the iron(III)–bipyridine system.

TABLE I

EFFECT OF TOTAL BIPYRIDINE CONCENTRATION ON INITIAL RATE OF TOTAL IRON(II) DISAPPEARANCE

Temp., °C.	[bip_T]$_0$, $M \times 10^4$	$-d[Fe_T^{++}]/dt_0$, mole l.$^{-1}$ sec.$^{-1}$ $\times 10^{10}$
0.0	4.00	8.9
0.0	10.00	1.3
10.0	4.00	23.5
10.0	10.00	3.6

The data in Table I indicate that the persulfate–$Fe(bip)_3^{++}$ reaction is not the principal reaction because in all these experiments the initial concentration of tribipyridine complex is practically unchanged and the large variation in the initial rate of total iron(II) disappearance should not occur at a given temperature if that reaction were predominant. The insignificance of this reaction is further substantiated by the very small initial rate ($< 5 \times 10^{-11}$ mole l.$^{-1}$ sec.$^{-1}$) in the presence of 10^{-2} *M* bipyridine. Also the concentration of uncomplexed iron(II) calculated from eq. 7 is so minute in each case that the contributions made by the persulfate–uncomplexed iron(II) reaction is negligible. Hence it would appear that the major contribution to the initial rate is made by the reaction or reactions between persulfate and the $Fe(bip)^{++}$ complex and/or the $Fe(bip)_2^{++}$ complex.

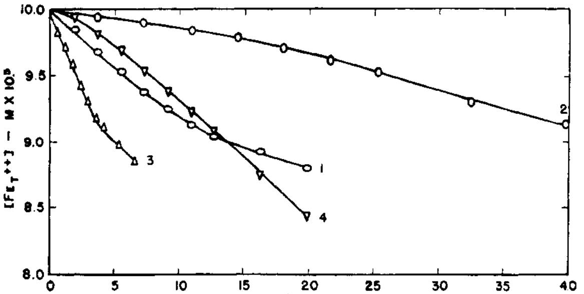

Fig. 6.—The disappearance of total iron(II) in the presence of 2,2′-bipyridine. Persulfate and iron(II) concentrations initially are 8.00 and 10.00 × 10^{-5} molar. The initial bipyridine concentration is 4.00 × 10^{-4} molar for curves 1 and 3 and 10.00 × 10^{-4} molar for curves 2 and 4. Curves 1 and 2 are at 0.0° and curves 3 and 4 at 10.0°.

If the only iron(II) reactant is the monobipyridine complex, a value of k_1, the rate constant of the persulfate–$Fe(bip)^{++}$ reaction, can be easily calculated in each case with the use of eq. 5 to determine the initial concentration of the complex. However if the sole contributor to the total iron(II) disappearance is the persulfate–$Fe(bip)_2^{++}$ reaction then the product k_2K_2, where k_2 is the rate constant of that reaction, can be calculated with the aid of eq. 6 to determine the initial $Fe(bip)_2^{++}$ complex concentration. The values of k_1 and k_2K_2 at 0 and 10° are given in Table II.

TABLE II

VALUES OF k_1 AND k_2K_2

Temp., °C.	[bip_T]$_0$, $M \times 10^4$	k_1, l. mole^{-1} sec.$^{-1}$ $\times 10^3$	$k_2K_2 \times 10^{-8}$
0.0	4.00	3	1.55
0.0	10.00	25	1.60
10.0	4.00	4	1.60
10.0	10.00	25	1.70

In Table II the lack of agreement between the two values of k_1 at each temperature, the high values of k_1, and the low activation energy of the persulfate–monobipyridine complex reaction indicate that this reaction probably does not occur to a significant extent under the conditions of the experiments. Conversely the good agreement between the values of k_2K_2 at each temperature suggest that the principal reaction under these conditions is the persulfate –$Fe(bip)_2^{++}$ reaction. Consequently it would seem that the addition of two bipyridine molecules to the ferrous ion does not destroy the reactivity of the complex with persulfate, but with the addition of the third molecule its reactivity is destroyed.

A study of the effect of adding various emulsifiers to the system yielded the plots shown in Fig. 7 and the data given in Table III. Obviously these emulsifiers do not change the order of the reaction. The non-ionic emulsifier Agent 140 *BK* and Daxad 11 have no significant effect on the rate constant of the second order reaction but the Nacconol NRSF causes an increase in the rate constant.

In addition to these results it was found that there was practically no disappearance of iron(II)

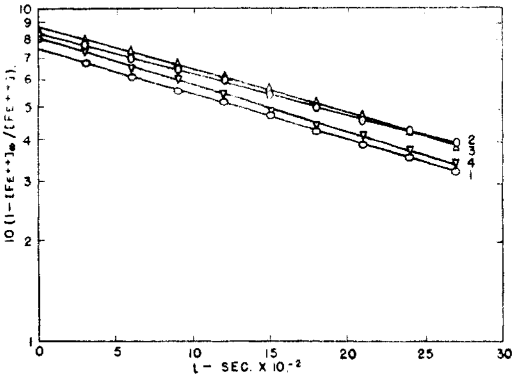

Fig. 7.—The persulfate-iron(II) reaction in the presence of emulsifiers at 0.0°. Initial persulfate and iron(II) concentrations are, respectively, 8.00 and 10.00 × 10^{-5} molar. The initial concentration of emulsifier and the final concentration of iron(II) are: curve 1, Agent 140 *BK* 0.100 g./l. and 2.00 × 10^{-5} molar; curve 2, Daxad 11 0.100 g./l. and 1.80 × 10^{-5} molar; curve 3, Nacconol NRSF 0.100 g./l. and 1.40 × 10^{-5} molar; and curve 4, Nacconol NRSF 0.010 g./l. and 1.85 × 10^{-5} molar.

TABLE III

EFFECT OF VARIOUS EMULSIFIERS ON THE RATE CONSTANT AT 0°

Emulsifier, 0.100 g./l.	Final *p*H	*k*, l. mole^{-1} sec.$^{-1}$
Agent 140 BK	7.7	15.6
Daxad 11	7.1	15.6
Nacconol NRSF	3.5	21.0
Nacconol NRSF[a]	4.0	17.4

[a] Initial concentration 1.00 × 10^{-2} g./l.

after 20 hours with cetylpyridinium chloride or cetyltrimethylammonium bromide as emulsifier. Presumably these emulsifiers promote the reaction of persulfate with acrylonitrile at this *p*H (about 6). The effect on the rate constant of adding potassium fatty acid soap could not be followed because the addition of the soap elevates the *p*H of the solution to a point where the persulfate is rapidly destroyed by the acrylonitrile.

Discussion

The persulfate–iron(II) reaction provides a very rapid means of generating free radicals. The rate constant at infinite dilution is about seven-fold that of the cumene hydroperoxide–iron(II) reaction[7] in the temperature range 0 to 10°. However, in actual practice the former rate constant is decreased by an increase in the ionic strength of the solution or by a decrease in the dielectric constant of the medium according to the Brønsted–Debye–Hückel theory, which has also been found to be valid for the reaction of persulfate with other ions such as the silver ion[8] and the iodide ion.[9,10] Nevertheless the activation energy of the persulfate–iron(II) reaction, 12 kcal. per mole, is lower than the value of 26 kcal. per mole for that of the unimolecular decomposition of persulfate[11] and consequently the persulfate–iron(II) initiating system will be effective over a wider temperature range than will the persulfate alone.

The lack of reaction between the tribipyridine complex of iron(II) and persulfate is quite similar to that noted when the oxidant is cumene hydroperoxide.[7] The present work suggests that the assumption made in that work that the initial concentration of $Fe(bip)_2^{++}$ is negligible relative to the concentration of $Fe(bip)^{++}$, is not strictly valid unless the value of k_2 is unusually large. If the assumption is not true, then the calculated concentrations of uncomplexed iron(II) and the monobipyridine complex were too great. However if the presence of $Fe(bip)_2^{++}$ is taken into consideration in the calculations, there is a marked similarity between the results of this series and the results of the earlier series with the exception of those of the experiment conducted at *p*H 2.21. The results of this experiment should be discarded because equilibrium was not established at the time of measureurement of the concentration of $Fe(bip)_3^{++}$ or, probably, during the initial stages of the reaction. The loss of reducing power of the bipyridine complex of iron(II) with the addition of the third molecule of bipyridine would appear to be general.

Calculations based on the results obtained in the experiments with cumene hydroperoxide as the oxidant yielded an estimate of 1 × 10^6 for the value of K_2 at 25.1°. From the temperature independence of the product k_2K_2 it is evident that the heat of the reaction between $Fe(bip)^{++}$ and bipyridine is equal to the negative activation energy of the persulfate $Fe(bip)_2^{++}$ reaction which may be estimated to be that of the persulfate–iron(II) reaction. With these estimates the calculated values of k_2 are of the same order of magnitude as those of the persulfate–iron(II) reaction (27 and 55 l. mole^{-1} sec.$^{-1}$ at 0 and 10°, respectively). The high values might be explained by increased initial rates of total iron(II) disappearance in the presence of traces of oxygen.

The observation that the presence of the emulsifiers Agent 140 BK, an aromatic polyglycol ether, and Daxad 11, a sodium salt of polymerized alkyl naphthalenesulfonic acid does not bring about a significant change in the rate constant of the second order reaction is in agreement with the lack of effect of the emulsifier cetyltrimethylammonium bromide on the rate constant of the hydrogen peroxide–iron(II) reaction at 25° with methyl methacrylate as monomer.[12] The difference noted between the effect of cetyltrimethylammonium bromide on the disappearance of iron(II) in the latter reaction and that in the persulfate–iron(II) reaction indicates presumably that acrylonitrile is much more reactive with persulfate in a neutral solution than methyl methacrylate is with hydrogen peroxide in a slightly acidified solution. This result would be expected from the reactivities of the acrylonitrile and the methyl methacrylate monomers and the persulfate and hydrogen peroxide oxidants. With Nacconol NRSF, a sodium alkyl aryl sulfonate, the increase in the rate constant and

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[7] J. W. L. Fordham and H. L. Williams, THIS JOURNAL, **73**, 1634 (1951).

[8] E. Bekier and S. W. Kijowski, *Roczniki Chem.*, **15**, 136 (1935).

[9] E. S. Amis and J. E. Potts, Jr., THIS JOURNAL, **63**, 2883 (1941).

[10] C. V. King and M. B. Jacobs, *ibid.*, **53**, 1704 (1931).

[11] R. L. Eager and C. A. Winkler, *Can. J. Research*, **26B**, 527 (1948).

[12] J. H. Baxendale, M. G. Evans and J. K. Kilham, *Trans. Faraday Soc.*, **42**, 668 (1946).

the decrease of the residual iron(II) at the end of the reaction suggest that the iron(II) is disappearing by some additional method. This disappearance may be related to the emulsifier itself or some accompanying impurity.

Experimental

The source and purity of the ferrous sulfate 2,2′-bipyridine, acrylonitrile, water, acetate buffer and nitrogen have been described previously.[7,13] The potassium persulfate was Baker and Adamson reagent grade used without further purification and the potassium chloride and calcium sulfate Baker Analyzed reagents. The emulsifiers were the commercial products: General Aniline Agent 140 BK, Dewey and Almy Daxad 11, National Aniline Nacconol NRSF, Merrell cetylpyridinium chloride, Fine Organic cetyltrimethylammonium bromide, and Swift potassium fatty acid soap flakes.

The same apparatus procedure as described in a previous publication[7] was used with the exception that the bipyridine was added to the flask before the contents were deoxygenated. Calculations based on the value of the rate constant of the reaction

$$Fe^{++} + 3bip \longrightarrow Fe(bip)_3^{++}$$

determined by Baxendale and George[14] indicated that the establishment of equilibrium under the actual experimental conditions is practically instantaneous. All reactions took place in tenth molar solutions of acrylonitrile in water under an atmosphere of oxygen-free nitrogen. Samples were removed at various intervals, centrifuged to remove any polyacrylonitrile and analyzed for residual iron(II) by a colorimetric bipyridine procedure.

Acknowledgments.—The authors appreciate the courtesy of Polymer Corporation Limited in extending permission to publish this paper. The assistance of Mr. W. L. McPhee is acknowledged.

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[13] J. W. L. Fordham and H. L. Williams, THIS JOURNAL, **72**, 4465 (1950).

[14] J. H. Baxendale and P. George, *Nature*, **162**, 777 (1948).

SARNIA, CANADA RECEIVED MARCH 29, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The System Methyl Ethyl Ketone–Water below 0°[1]

BY MERLE RANDALL AND F. E. MCKENNA[2]

The freezing curves for the system, methyl ethyl ketone–water, have been determined in both the water-rich and the ketone-rich one-phase solutions. Mutual solubilities of the two liquid phases have been measured between −2 and −19°

The temperature–composition relations for solutions of methyl ethyl ketone and water were studied below 0° because of the non-ideality of the system. Rothmund,[3] Marshall[4] and the Shell Chemical Company[5] have reported solubility measurements in this system, and Marshall has also measured vapor pressures of the system. No determinations of the freezing curve have been reported.

Freezing Points of Aqueous Solutions of Methyl Ethyl Ketone. Apparatus.—In Fig. 1 the cryostat for binary solutions is shown at A; B is a dewar for an ice–water mixture for the reference junction of the thermo-element. These are suspended from a Bakelite panel, CC, by brass rods, DD, a circular brass disc, EE, and wing nuts, F. The copper thermo-element tube, G, terminates in the distributor head, H, with clear amber Bakelite cap, I, and six copper terminals, J; the distributor is supported by a Bakelite strip, KK. The stirrers, LL, are driven at 90 r.p.m. by a 0.03 H.P., 60-cycle continuous-duty motor, M, with a 20:1 gear ratio, mounted on a panel, NN. Brass rods, CN, connect CC with NN. Gears, OO, on the stirrers are connected by the chain, P, which also passes over an idler, Q. The stirrer shaft bearings, v, are packed with mica-impregnated asbestos twine; triangular plates, RR, prevent sidewise motion of the stirrers. Samples are removed through the tube, S. Heat losses along the stirrer are minimized by the rubber coupling disc, T.

Dry, CO_2-free air from an air liquefier system entered the system at 20 p.s.i. through brass tubing, U, W and X. Refrigeration was obtained by cooling the air stream in the copper coil, y, which was immersed in liquid air in the dewar, Y. Tubing, XX, was insulated with cotton bound with linen tape. The air flow was controlled by the solenoid valve, V5, operated by a switch at the potentiometer, so that the cryostat temperature could be held constant to 0.0001°. To warm the cryostat, valve V4 was closed, and V2 was opened to allow room temperature air to enter the system.

Samples were removed through S by application of air pressure to the cryostat through V1 and UU. Excess air pressure could be released through V6.

The outer brass jacket, aa, of the cryostat is fastened to the panel, CC, by rubber washers and knurled nuts, bb. The dewar, ee, is held in place by a balsa wood block, c, a spring bronze support, dd, and a balsa wood ring, ff. Within the dewar is a copper tube, h, of 5-cm. diameter, to which is soldered the cooling coil XX, with exit at Z. The copper thermocouple tube, gg, which is coiled inside the tube h, has a junction at i to German silver tubing to lessen the heat-leak. The German silver sample tube, S, terminates in a fan-shaped stainless steel gauze, k (200-mesh). The stainless steel stirrer tube, m, has three sets of blades, n. The outer jacket is sealed to the Bakelite panel by a cork ring, oo. Glands, p and q, were packed with beeswax-impregnated cotton string. A liquid drain, r, is provided in the bottom of the outer jacket.

Construction and Calibration of the Multiple Thermo-element.—The No. 30 double silk-covered constantan wire which was used by Randall and Vanselow[6] and No. 36 double silk-covered copper wire were arc-welded (1 amp., 110 v., d.c.) to form a 6-junction thermo-element. The constantan wire was tested for homogeneity by the method of White,[7] while the copper wire was assumed to be of sufficient uniformity. The entire thermo-element was doubly coated with Bakelite varnish and wrapped with silk lingerie binding tape, which was also coated with the varnish. The annealed copper tubes were filled with molten naphthalene before insertion of the couple. The thermo-element leads were soldered to copper binding posts in the Bakelite cap before the tubing was coiled and mounted in the apparatus. The resistance of the thermo-element was checked at each stage of its construction. Joints between the copper tubes and the compression T-fitting, t, were moisture-proofed with "Vinyl-Seal."

The thermo-element was calibrated against melting ice, subliming carbon dioxide, and boiling oxygen as suggested by Wiebe and Brevoort.[8] The solid CO_2 which was ob-

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[1] Presented at Pittsburgh, Pennsylvania, Meeting of the American Chemical Society, September 6, 1943, by the late Dr. Randall.

[2] Air Reduction Co., Inc., Research Laboratories, Murray Hill, New Jersey.

[3] V. Rothmund, *Z. physik. Chem.*, **26**, 433 (1898).

[4] A. Marshall, *J. Chem. Soc.*, **89**, 1350 (1906).

[5] Shell Chemical Co., "Methyl Ethyl Ketone," 1938.

[6] M. Randall and A. P. Vanselow, THIS JOURNAL, **46**, 2425 (1924).

[7] W. P. White, *ibid.*, **36**, 2292 (1914).

[8] R. Wiebe and M. J. Brevoort, "U. S. Dept. Commerce, Bur. Mines Rept. Investigations," No. 3077 (1931).