Cu(I)) is affected by ammonia and sulfite concentration. The polarographic analysis of these titrations indicates that all the cysteine is completely converted into cysteine sulfonate at the second end-point. The low consumption of cupric copper in these titrations is due to the oxygen oxidation of the cuprous cysteinate after the first end-point. This oxidation is catalyzed by the cuprous copper formed in the reaction between cuprous cysteinate and cupric copper. The air oxidation of RSCu is almost negligible when the reaction between cuprous cysteinate, cupric copper and sulfite is fast, but it becomes pronounced when this reaction is slow. The reaction is rapid at low ammonia (0.05 *M*) and high sulfite (0.15 *M*) concentrations and under those conditions, stoichiometrically correct results with air-saturated cupric copper solutions are obtained (see Fig. 7).

In a subsequent paper it is shown that the reaction between cysteine and cupric copper in the presence of sulfite can be made the basis of an accurate and rapid amperometric titration of traces of cysteine and cystine, using the rotating platinum wire electrode as indicator electrode.

Acknowledgment.—This investigation was supported by a research grant from the National Cancer Institute, United States Public Health Service.

MINNEAPOLIS, MINN. RECEIVED OCTOBER 9, 1950

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

The Reaction between Ferrous Iron and Peroxides. IV. Reaction with Potassium Persulfate[1a]

BY I. M. KOLTHOFF, A. I. MEDALIA[1b] AND HELEN PARKS RAAEN

Upon very slow addition of ferrous iron to an acid (0.5 *M* sulfuric acid), neutral or alkaline (0.1 *M* pyrophosphate) persulfate solution, the molar reaction ratio of ferrous iron to persulfate is found less than 2. Upon rapid mixing of the reactants, the stoichiometric reaction ratio of 2 is found in the absence of organic substances. Upon rapid mixing or slow addition of ferrous iron to ethanol containing persulfate solution in the absence of oxygen, Fenton reaction occurs, in which alcohol is oxidized to aldehyde. The reaction ratio is less than 2. Chloride and especially bromide suppress the induced alcohol oxidation, but acetic acid and acetone have no effect. Acrylonitrile suppresses the induced alcohol oxidation; the reaction ratio in the presence of acrylonitrile is close to 1, because the $SO_4^{\overline{\cdot}}$ radical-ions formed in the reaction between ferrous iron and persulfate are effectively consumed in the initiation of the acrylonitrile polymerization. In the presence of oxygen and organic compounds like ethanol, acetone, acetic acid, reaction ratios greater than 2 are found. The induced oxygen oxidation of ferrous iron is explained. Bromide is an effective suppressor of this induced reaction.

The peroxidisulfate ion, $S_2O_8^{=}$ (hereinafter referred to simply as the persulfate ion), is a symmetrically substituted derivative of hydrogen peroxide. The present study was carried out in order to establish whether and to what extent the phenomena which are characteristic of the reaction of ferrous iron with hydrogen peroxide[2,3] also occur with persulfate; *viz.*, the decomposition of the peroxide induced by the peroxide–ferrous iron reaction, the induced reaction between the peroxide and alcohols, the induced oxidation of ferrous iron by molecular oxygen in the presence of the peroxide and various organic substrata, and the effect of chloride ion and other compounds in suppressing these induced reactions.

Since the start of the present work, valuable papers by Merz and Waters[4,5] have been published. These authors have made a thorough quantitative study of the reaction ratios obtained in the oxidation of various organic compounds by hydrogen peroxide in the presence of ferrous iron (Fenton reaction), a few experiments also having been carried out with sodium persulfate.[4] By extrapolation of a series of experiments with increasing ratios of organic substratum to ferrous iron, values have been found for the relative reaction rates of the hydroxyl radical (formed in the hydrogen peroxide–ferrous iron reaction) with the substratum and with ferrous iron, respectively. Unfortunately, Merz and Waters were evidently unaware of the induced oxygen oxidation accompanying these reactions,[2] and although they worked in relatively concentrated solutions, our work indicates that this induced oxidation may have led to a very considerable error in the observed reaction ratios. This is particularly true in experiments with an initial large excess of organic substratum, since under these conditions the direct oxidation of ferrous iron by peroxide becomes so small as to be of comparable magnitude with the induced oxidation by dissolved air. On the other hand, at *low* initial concentrations of the organic substratum, considerable error may result from competition or suppression by the primary products, as recognized by Merz and Waters. For these reasons some uncertainty must be attached to the ratios reported by these authors (*cf.* Table II). The work of Merz and Waters has shown definitely, however, that the primary active intermediate in the persulfate–ferrous iron reaction is not the same as that formed in the hydrogen peroxide–ferrous iron reaction (contrary to the suggestion of Morgan[6] that the hydroxyl radical might be the active species in both reactions). Polymerization

---

(1a) This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation in connection with the synthetic rubber program of the United States Government.

(1b) Brookhaven National Laboratory, Upton, Long Island, New York.

(2) I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, **71**, 3777, 3784 (1949).

(3) A. I. Medalia and I. M. Kolthoff, *J. Polymer Sci.*, **4**, 377 (1949).

(4) J. H. Merz and W. A. Waters, *Faraday Soc. Discussion*, **2**, 179 (1947).

(5) J. H. Merz and W. A. Waters, *J. Chem. Soc.*, S-15 (1949).

(6) L. B. Morgan, *Trans. Faraday Soc.*, **42**, 169 (1946).

studies by several authors[7,8,9] have also afforded evidence that a sulfur-containing fragment derived from persulfate is capable of reacting directly with monomers. All these studies indicate that the active species is the sulfate radical-ion, $SO_4^{\dot{-}}$. Nothing is known about the reactivity of this free radical with water to form the hydroxyl free radical, although there is little doubt that such a reaction can take place.

Several groups of reactions which are of importance in the interpretation of the experimental results of this paper are presented below. The stoichiometric reaction between persulfate and ferrous iron

$$2Fe^{++} + S_2O_8^{=} = 2Fe^{+3} + 2SO_4^{=} \qquad (I)$$

presumably takes place through the steps

$$Fe^{++} + S_2O_8^{=} = Fe^{+3} + SO_4^{=} + SO_4^{\dot{-}} \qquad (1)$$

$$Fe^{++} + SO_4^{\dot{-}} = Fe^{+3} + SO_4^{=} \qquad (2)$$

From the data of Saal,[10] King and Steinbach[11] have calculated the rate constant of the over-all reaction (I), for which step (1) is rate-determining, as approximately 5000 l./mole/min. at 25°.

The following steps account for the induced reaction between persulfate and organic compounds, of which ethanol may be taken as typical

$$SO_4^{\dot{-}} + CH_3CH_2OH = HSO_4^{-} + CH_3CHOH \qquad (3)$$

followed by either

$$CH_3\underset{\cdot}{C}HOH + S_2O_8^{=} = CH_3CHO + HSO_4^{-} + SO_4^{\dot{-}} \qquad (4)$$

or

$$CH_3\underset{\cdot}{C}HOH + Fe^{+3} = CH_3CHO + Fe^{++} + H^{+} \qquad (5)$$

The objection of Merz and Waters to step (5) on the ground that the consumption ratio is not significantly altered by addition of ferric iron to a mixture of hydrogen peroxide, ferrous iron, and ethanol[4] is valid only if step (3) (or the corresponding step with hydroxyl radical) is considered to be reversible, or if we consider that the hydroxyethyl radical can react with ferrous as well as with ferric iron. However, if each hydroxyethyl radical formed reacts with ferric iron according to (5), then the consumption ratio will depend only on the relative extent of steps (2) and (3) and not at all on the velocity of step (5), so that we cannot then decide between steps (4) and (5). The sum of steps (3) and (4), or of (3), (5) and (1) is the net reaction

$$CH_3CH_2OH + S_2O_8^{=} = CH_3CHO + 2HSO_4^{-} \qquad (II)$$

The mechanism of the induced oxidation of ferrous iron in the presence of organic compounds and of air has been discussed elsewhere[2]; the initial step appears to be addition of oxygen to the organic radical, R·, formed as in (3), to form a peroxide radical, ROO·; subsequent chain autoxidation of the organic substratum, followed by reaction between the peroxidic compounds and ferrous iron, leads to an extensive induced oxidation of the latter.

Slow Addition of Ferrous Iron to Persulfate in the Absence of "Promoters"

It has been known for some time that the decomposition of hydrogen peroxide to water and oxygen is induced by the hydrogen peroxide–ferrous iron reaction; however, the corresponding effect with persulfate does not appear to have been observed previously. A quantitative study of the ferrous iron–persulfate reaction has now been carried out under conditions designed to permit detection of this induced reaction; namely, with very slow addition of ferrous iron to persulfate, using the apparatus and technique described in the Experimental section. The slow addition of ferrous iron to hydrogen peroxide has also been investigated with this apparatus, and the data obtained are in satisfactory agreement with the results of Haber and Weiss.[12] It was first established that upon pipetting a 50% excess of standard ferrous iron solution into persulfate solutions of concentrations between 2.5×10^{-4} and 5×10^{-1} *M*, and back-titrating the excess of iron, the stoichiometric reaction ratio was found. When the initial concentration of persulfate was 2.5×10^{-4} *M*, the reaction mixture was allowed to stand for 2 hours before back titration in order to allow the reaction to go to completion. With an initial persulfate concentration of 2.5×10^{-3} *M* or greater, a period of half an hour was sufficient for the reaction to go to completion. These reaction times were employed in all the following experiments. All experiments were carried out at room temperature.

The experiments reported in Table I were carried out with nitrogen saturation, in vacuum, and with air saturation. The nitrogen was purified by washing through alkaline permanganate and 0.5 *M* sulfuric acid. In all instances the reaction ratio found was less than 2. Special precautions were taken to guard against the presence of organic impurities, because organic substances in the absence of oxygen give rise to reaction ratios less than the stoichiometric ratio of 2 (v.i.). The greatest deviations from reaction ratio 2 were found with the smallest concentrations of persulfate. Under these circumstances the inadvertent presence of traces of organic substances has relatively the greatest effect. Both in the presence and absence of oxygen molar reaction ratios of less than 2 were found, indicating that decomposition of persulfate takes place through some mechanism other than by reaction with trace organic impurities; since, as shown in Table VII, the presence of organic compounds would lead to reaction ratios greater than 2 in the presence of oxygen. Experiments have been carried out with various types of apparatus to determine whether the decomposition of persulfate under the present conditions leads to the formation of oxygen. However, in none of the experiments was it possible to detect the formation of oxygen. The nature of the decomposition therefore remains uncertain. Possibly reaction with inorganic impurities, dissolved or suspended glass, etc., may take place; or it may be that the techniques employed for the detection of oxygen were not sufficiently

---

[7] W. V. Smith and H. N. Campbell, *J. Chem. Phys.*, **15**, 338 (1947); W. V. Smith, THIS JOURNAL, **71**, 4077 (1949).

[8] P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

[9] W. E. Mochel and J. H. Peterson, THIS JOURNAL, **71**, 1426 (1949).

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

[11] C. V. King and O. F. Steinbach, THIS JOURNAL, **52**, 4793 (1930).

[12] F. Haber and J. Weiss, *Proc. Roy. Soc.* (*London*), **A147**, 332 (1934).

TABLE I

SLOW ADDITION OF FERROUS IRON TO PERSULFATE, IN THE ABSENCE OF ORGANIC COMPOUNDS

Stirring apparatus	Gas present	$(S_2O_8^=)_0$ (M)	Fe^{++} added slowly[c] (M)	Delivery time (hours)	Molar reaction ratio, R: $\Delta Fe^{++}/\Delta S_2O_8^=$				
			A. In 0.5 M sulfuric acid						
Paddle	N_2	2.5×10^{-4}	0.50×10^{-4}	2.5–2.75	1.63	1.68	1.72	1.73	1.76
Paddle	N_2	2.5×10^{-3}	0.50×10^{-3}	2.75–3	1.87	1.79			
Magnetic	Vacuum	2.5×10^{-3}	5.5×10^{-3}	24	1.66	1.59			
Paddle	Air	2.5×10^{-3}	5.5×10^{-3}	22–24	1.77	1.80	1.86	1.91	1.94
Magnetic	Air	2.5×10^{-3}	5.5×10^{-3}	23–24	1.80	1.86			
Paddle	Air	2.5×10^{-2}	5.5×10^{-2}	22–24	1.91	1.93	1.98	2.02	
Magnetic	Air	2.5×10^{-2}	5.5×10^{-2}	22	1.87	1.88			
			B. In nearly neutral medium[a]						
Paddle	N_2	2.5×10^{-4}	0.50×10^{-4}	2.75	1.71				
Paddle	N_2	2.5×10^{-3}	0.50×10^{-3}	2.5	1.37	1.37			
Paddle	N_2	2.5×10^{-3}	2.75×10^{-3}	2.5	1.78	1.78			
Paddle	N_2	2.5×10^{-3}	5.5×10^{-3}	3.5	1.78	1.82			
Paddle	N_2	2.5×10^{-3}	5.5×10^{-3}	21	1.60				
			C. In pyrophosphate[b]						
Paddle	N_2	2.5×10^{-3}	0.50×10^{-3}	3.5	1.11	1.15	1.45	1.64	
Paddle	N_2	2.5×10^{-3}	5.5×10^{-3}	3	1.74	1.88			
Paddle	N_2	2.5×10^{-2}	2.75×10^{-2}	3	1.54	1.55	1.55		

[a] The ferrous solution of both concentrations was prepared in 5×10^{-4} M sulfuric acid; the persulfate solution was initially neutral and unbuffered. [b] The experiments with 2.5×10^{-3} M persulfate were carried out in 0.10 M $Na_4P_2O_7$; those with 2.5×10^{-2} M persulfate, in 0.13 M $Na_4P_2O_7$. [c] Concentration in this column corresponds to the molarity in the mixture after addition of all the ferrous iron if no reaction took place with persulfate.

sensitive. In any case the extent of the induced decomposition is very much less than was found on the slow addition of ferrous iron to hydrogen peroxide, under comparable conditions.

In many of the experiments of Table I it was attempted to magnify the induced decomposition of persulfate by maintaining a high ratio of persulfate to ferrous iron; thus, the amount of persulfate used in each such experiment was ten times that required stoichiometrically to oxidize the ferrous iron added slowly. After completion of the slow addition, the persulfate remaining was determined by adding rapidly an excess of ferrous iron and then back-titrating with ceric sulfate after complete reaction had taken place. The reproducibility of the experiments is poor; therefore, no exact calculations can be made of the extent of the induced decomposition. The results show, however, that in acid, neutral and pyrophosphate medium an induced decomposition of persulfate occurs upon slow addition of ferrous iron.

Rapid Mixing in the Absence of Oxygen in the Presence of Organic Substances.—Rapid mixing of nitrogen-saturated solutions has been carried out by the method described previously.[2] As mentioned above, with several concentrations of ferrous iron and persulfate, in the absence of organic compound, stoichiometric results have been obtained upon rapid mixing (reaction ratios of 1.98 to 2.00). Results obtained in the presence of ethanol are given in Table II. It is evident that in the presence of ethanol, persulfate is consumed by some reaction other than with ferrous iron. Aldehyde determinations carried out in several reaction mixtures have shown that the principal reaction is the oxidation of ethanol to acetaldehyde (reaction (II)). Similar results had been found previously with hydrogen peroxide[2]; however, the extent of the induced oxidation of ethanol is several fold smaller with persulfate than with hydrogen peroxide, under comparable conditions.

TABLE II

RAPID MIXING OF PERSULFATE, FERROUS IRON, AND ETHANOL, IN THE ABSENCE OF OXYGEN. INITIAL MOLAR CONCENTRATION OF PERSULFATE EXACTLY ONE-FOURTH THAT OF FERROUS IRON (EXCEPT AS NOTED); SULFURIC ACID 0.5 M THROUGHOUT

Initial concentrations (M) Fe^{++}	Ethanol	Molar reaction ratio, R: $\Delta Fe^{++}/\Delta S_2O_8^=$		k_3/k_2	Aldehyde formed ($M \times 10^3$) Calculated		Found	
5.5×10^{-4}[a]	0.10	0.49	0.49	0.015	....		....	
1.0×10^{-3}	.010	1.64	1.66	.017	....		....	
1.0×10^{-3}	.10	0.68	0.70	.015	....		....	
1.0×10^{-2}	.10	1.54	1.56	.023	....		....	
2.0×10^{-2}	.10	1.67	1.69	.030	0.82	0.78	0.75	0.64
1.0×10^{-1}	.10	1.90	1.92	.036	1.2	1.0	1.2	1.0

[a] Initial concentration of persulfate, 2.5×10^{-4} M.

Merz and Waters[5] have pointed out that, if the simple reaction scheme given by equations (1), (2), (3) and (4) is followed, the consumption ratio of persulfate to *promoter* should be nearly constant during the reaction, so that the over-all consumption ratio is

$$\frac{\Delta[S_2O_8^=]}{\Delta[EtOH]} = 1 + \frac{k_2[Fe^{++}]}{k_3[EtOH]} \qquad (6)$$

Calculating the consumption of ethanol on the basis of the reaction ratio R given in Table II, and with the assumption that reactions (I) and (II) are the only over-all reactions occurring, we obtain

$$\frac{k_3}{k_2} = \frac{(2 - R)[Fe^{++}]}{R[EtOH]} \qquad (7)$$

In the calculations of k_3/k_2, Fe^{++} has been taken as the arithmetical average of the initial and final concentrations of ferrous iron.

The limiting value found for k_3/k_2 is 0.015. A somewhat lower value (0.0062) was found by Merz and Waters,[4] very likely due to the presence of oxygen in their experiments (as discussed above), which would result in too high a value for R, or too low a value for k_3/k_2.

Results obtained in the combined presence of ethanol and several compounds which were tried as "suppressors" are shown in Table III. Blank experiments with each of these compounds (including bromide) in the same concentrations as used in Table III, but in the absence of ethanol, gave stoichiometric reaction ratios (1.96–2.00). It is seen that acetic acid and acetone, which are suppressors in the hydrogen peroxide–ferrous iron reaction (2) exert no suppressing effect in the persulfate–ferrous iron induced oxidation of ethanol. This means that the ratio of rate constants corresponding to k_3/k_2 for these compounds is much lower than for ethanol; that the ratios are not quite zero, however, is shown by the experiments in the presence of oxygen (Table VII). Chloride and bromide ions, on the other hand, show characteristic suppressing action.

Table III

Effect of Various Compounds Tried as Suppressors, under Conditions of Rapid Mixing as in Table II. Initial Concentrations of Ferrous Iron and Persulfate: 1.0×10^{-3} M and 2.5×10^{-4} M, Respectively, Throughout

Initial concentrations (M) Ethanol	Added compound	Molar reaction ratio, R: $\Delta Fe^{++}/\Delta S_2O_8^{-}$	k_8/k_2
0.010	......	1.65	....
.10	......	0.69	....
.010	Acetic acid (0.10)	1.59	....
.010	Acetic acid (1.0)	1.60	....
.10	Acetic acid (1.0)	0.69	....
.010	Acetone (0.10)	1.56	....
.10	Acetone (.10)	0.58	....
.10	NaCl (.10)	1.04, 0.87	0.0048
.010	KBr (.010)	1.93	.33[a]
.10	KBr (.010)	1.62, 1.64	.58
.10	KBr (.10)	1.93, 1.93	.40[a]

[a] These values are of low accuracy, since R is close to 2.00.

The simplest interpretation of the suppressing action of the halides is that the halide ion competes with both ethanol and ferrous iron for reaction with SO_4^{-}, according to the steps

$$SO_4^{-} + X^- = SO_4^{=} + X\cdot \qquad (8)$$

$$X\cdot + Fe^{++} = X^- + Fe^{+3} \qquad (9)$$

Consideration of these steps, together with those given previously, leads to the expression

$$\frac{k_8}{k_2} = \left[\frac{(k_3/k_2)R}{2 - R} - \frac{[Fe^{++}]}{[EtOH]}\right]\frac{[EtOH]}{[X]} \qquad (10)$$

on the basis of which the values of k_8/k_2 given in Table III have been derived (taking $k_3/k_2 = 0.015$). The bromide ion is the only compound which we have found to exhibit a reactivity with the sulfate radical-ion comparable to that of ferrous iron.

As has been pointed out elsewhere,[8] a fundamental difference exists between the behavior of ethanol and of vinyl monomers such as acrylonitrile, since reaction of a sulfate radical-ion with the former leads to a chain reaction in which radicals are continually re-formed, while radicals reacting with monomers are effectively removed from the system by incorporation in a growing polymer chain which is terminated in a separate phase by reaction with another radical or growing chain. Thus, if the reaction between persulfate and ferrous iron is carried out in the presence of increasing amounts of ethanol, the lower limit of the reaction ratio $\Delta Fe^{++}/\Delta S_2O_8^{=}$, should be zero; while if acrylonitrile is used in place of ethanol, the lower limit should be unity (corresponding to step (1) followed by removal of the sulfate radical-ion). Experimental results obtained in the presence of acrylonitrile are given in Table IV. Acrylonitrile was used both alone and together with the promoters, ethanol and glucose, the results in the presence of glucose being of particular importance in connection with various polymerization recipes of current interest in which the initiating system is composed of an iron salt, a sugar and a peroxide.[3]

Table IV

Rapid Mixing of Persulfate and Ferrous Iron with Acrylonitrile and Ethanol or Glucose, in the Absence of Oxygen. Initial Concentrations of Reagents: $FeSO_4$, 5.5×10^{-3} M; $K_2S_2O_8$, 2.5×10^{-3} M; H_2SO_4, 0.5 M

Initial concentrations (M) Acrylonitrile	Ethanol	Glucose	Molar reaction ratio, R: $\Delta Fe^{++}/\Delta S_2O_8$			Approx. wt. of polymer formed (g.)		
1.26[a]	...	...	1.15	1.18	1.21	3.0	3.1	2.7
..	1.0	...	0.38	0.38		...	...	
1.26[a]	1.0	...	1.03	1.02	...	1.9	1.8	
..	...	1.0	0.98	0.70	0.70	...	...	
1.26[a]	...	1.0	1.10	1.07	...		...	

[a] Corresponds to 10 g. of acrylonitrile in the reaction vessel.

It is seen that the reaction ratio with 1.26 M acrylonitrile is close to the predicted limiting ratio of 1.0 (Table IV). Acrylonitrile exerts a kind of "suppressing" action on the reaction with glucose and ethanol; that is, the reaction between SO_4^{-} and acrylonitrile replaces the reaction between SO_4^{-} and glucose or ethanol, this action being particularly evident in the experiments with ethanol. The effect of ethanol in lowering the yield of polymer is not readily interpreted.

Experiments carried out in alkaline pyrophosphate solution are summarized in Table V. The effectiveness of removal of oxygen is shown by the stoichiometric reaction ratios in the absence of organic compounds. The extent of the induced oxidation of ethanol is of the same order of magnitude in alkaline pyrophosphate as in sulfuric acid

Table V

Rapid Mixing of Persulfate and Ferrous Iron in Alkaline Pyrophosphate Medium, in the Absence of Oxygen. Initial Concentrations of Reagents: $FeSO_4$, 5.5×10^{-3} M; $K_2S_2O_8$, 2.5×10^{-3} M; $Na_4P_2O_7$, 0.10 M

Initial concentrations (M) Ethanol	Acrylonitrile	Molar reaction ratio, R: $\Delta Fe^{++}/\Delta S_2O_8^{=}$	
..	..	2.00	2.06
0.10	..	1.25	1.02
..	1.26[a]	1.95	

[a] Less than 1 g. of polymer formed.

medium (*cf.* Table II). On the other hand, acrylonitrile gives little induced reaction in pyrophosphate medium, and less polymer was found than in acid; this agrees with the observations of Bacon.[13]

Slow Addition in the Presence of Promoters.—Slow addition of ferrous iron to persulfate solutions in the absence of promoters has been described above (Table I). Slow addition experiments in the presence of ethanol and of acrylonitrile are described in Table VI. While the technique was similar to that used in the experiments of Table I, in that a portion of the ferrous iron was added slowly, and the remainder rapidly, no exact calculations can be made for the reaction during the slow addition, since the reaction during the rapid addition is not stoichiometric in the presence of ethanol or acrylonitrile; therefore, the reaction ratios given in Table VI are over-all ratios of the ferrous iron and persulfate consumed during the entire addition of ferrous iron (both slow and rapid). The consumption ratios with ethanol under these conditions, are lower than those obtained with slow addition in the absence of promoters, or than those obtained with rapid addition in the presence of ethanol. As in Table IV, acrylonitrile competes successfully with ethanol for reaction with sulfate radical-ion, so that reaction ratios in the presence of both ethanol and acrylonitrile are in the neighborhood of 1.0 (or higher). There is no correlation between the experimental conditions and the extent of polymerization of the acrylonitrile; and, indeed, the amounts of polymer formed in these slow addition experiments are comparable to those formed under conditions of rapid mixing (Table IV). Acetic acid has virtually no effect in either the presence or absence of ethanol.

TABLE VI

SLOW ADDITION OF FERROUS IRON TO PERSULFATE IN THE PRESENCE OF ORGANIC COMPOUNDS EXPERIMENTS CARRIED OUT WITH "PADDLE" STIRRING, IN A NITROGEN ATMOSPHERE INITIAL CONCENTRATIONS THROUGHOUT: H_2SO_4, 0.5 *M*; $K_2S_2O_8$, 2.5×10^{-3} *M*. TIME OF ADDITION OF FERROUS IRON BETWEEN 2.5 AND 3.5 HOURS THROUGHOUT

Initial concn. (*M*) EtOH	AcOH	CH_2=CHCN	Total Fe^{++} added (*M*)	Fraction of Fe^{++} added slowly	Over-all reaction ratio, *R*		Polymer formed (g.)
..	...	..	5.5×10^{-3}	0.09	1.85		...
0.10	...	..	5.5×10^{-3}	.09	0.15	0.16	...
..	...	1.26	5.5×10^{-3}	.09	1.79		2.4
.10	...	1.26	5.5×10^{-3}	.09	1.48		1.9
.10	...	..	5.5×10^{-3}	.4	0.19		...
..	...	1.26	5.5×10^{-3}	.4	1.53		2.5
.10	...	1.26	5.5×10^{-3}	.4	1.13		2.2
.10	...	..	5.5×10^{-3}	1.0	0.31		...
..	...	1.26	5.5×10^{-3}	1.0	1.37		1.4
.10	...	1.26	5.5×10^{-3}	1.0	1.35		4.2
..	...	..	1.0×10^{-2}	0.09	1.94		...
.10	...	..	1.0×10^{-2}	.09	0.15		...
..	1.0	..	1.0×10^{-2}	.09	1.85		...
.10	1.0	..	1.0×10^{-2}	.09	0.14		...

Rapid Mixing of Persulfate and Ferrous Iron in the Presence of Oxygen.—The reaction between ferrous iron and hydrogen peroxide has been shown to induce oxidation of the ferrous iron by molecular oxygen, if present in the system.[2] Analogous results with persulfate are given in Table VII. As with hydrogen peroxide, various organic compounds (including to a minor extent those which are without effect in the absence of oxygen) lead to induced oxygen oxidation of the ferrous iron; while chloride suppresses this oxidation. Bromide exerts a particularly powerful suppressing action. This effect is of particular importance in the determination of persulfate in the presence of organic compounds. It has been reported[14] that the determination of persulfate in the filtrate of coagulated GR-S latex by reaction with ferrous iron gave poor results in the presence of air; this was attributed to the presence in the latex filtrate of "some substance which induces the air oxidation of ferrous iron during its reaction with persulfate." In the latex study it was found[14] that stoichiometric results could be obtained by the exclusion of oxygen; the behavior of the interfering organic matter in the latex is thus indicated to be similar to that of acetic acid and acetone, which do not affect the stoichiometry of the reaction between ferrous iron and persulfate in the absence of oxygen, but which cause a high reaction ratio in the presence of oxygen (Table VII).

TABLE VII

RAPID MIXING OF PERSULFATE AND FERROUS IRON IN OXYGEN-SATURATED SOLUTIONS (0.5 *M* IN SULFURIC ACID). INITIAL CONCENTRATIONS OF REAGENTS: $FeSO_4$, 1.0×10^{-3} *M*; $K_2S_2O_8$, 2.5×10^{-4} *M*

Initial concentrations (*M*) Ethanol	Acetic acid	Acetone	NaCl	NaBr	Mole reaction ratio, *R*: $\Delta Fe^{++}/\Delta S_2O_8^{=}$	
..	..	..	...	..	2.02	
0.01	..	..	...	..	3.12	
.02	..	..	...	..	3.30	
.05	..	..	...	..	3.29	
.10	..	..	...	..	3.64	3.64
..	0.10	..	...	..	2.13	
..	1.0	..	...	..	2.36	2.10
..	5.0	..	...	..	2.58	
..	..	0.10	...	..	2.26	2.28
..	..	..	1.0	..	2.00	2.00
..	..	..	...	0.10	1.98	1.98
.10	1.0	..	...	..	3.66	3.68
.10	..	1.0	...	..	3.67	3.68
.10	..	..	1.0	..	2.22	2.22
.10	..	..	...	0.010	2.40	2.40
.10	..	..	...	.10	2.00	2.00

Experimental Details

In general, and unless otherwise specified below, the apparatus, reagents and techniques were as described in the papers on hydrogen peroxide.[3]

Reagents.—Potassium persulfate: Merck and Co., Inc., C.P., twice recrystallized from purified water, then dried *in vacuo* at 50°. Acrylonitrile: Eastman Kodak Co. technical grade was fractionally distilled.

Analytical Methods.—The persulfate solutions were standardized by reaction with excess ferrous solution in the presence of air, followed by back titration of the excess ferrous solution with standard ceric sulfate, to the ferrous phenanthroline end-point.

Aldehyde determinations were carried out by measurement of the color formed with Schiff reagent, using a Leitz-

---

(13) R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946).

Rouy Photrometer. A semi-quantitative procedure for the determination of aldehyde in the presence of iron salts has been described previously[2]; based on this, the following quantitative procedure was developed and found satisfactory for determinations under the conditions of Table II. In this procedure, the *p*H is critical, since the extent of precipitation of ferric iron (as phosphate), the intensity of the rose color of the unreacted fuchsin, and the development of the purple color of the fuchsin–aldehyde compound are all quite sensitive to *p*H. In the present work, therefore, the acid and buffer concentrations were closely controlled, and by use of the glass electrode it was established that the *p*H values of the colored mixtures were in each case within 0.05 *p*H unit of the nominal value (2.00). The Schiff reagent was prepared as previously[2]; the phosphate buffer was prepared by dissolving 234.6 g. of $Na_2HPO_4 \cdot 7H_2O$ and 17.27 g. of $NaH_2PO_4 \cdot H_2O$ in water and making up to one liter at 50°; aliquots were always removed at 50°. Procedure: a 5.0-ml. aliquot of reaction mixture, 0.5 *M* in sulfuric acid, was added to 4.0 ml. of buffer (at 50°); 2.0 ml. of Schiff reagent was added, and the transmittancy of the mixture was measured at one-minute intervals, using a filter with maximum transmission at 550 mμ. From the minimum transmittancy, usually obtained after 3–5 minutes, the aldehyde concentration was estimated by means of an empirical calibration curve. If a precipitate of ferric phosphate formed, it was removed by centrifuging before addition of the Schiff reagent; with reaction mixtures as high as 0.05 *M* in ferric iron, results accurate within 5% were obtained by this procedure.

Slow Addition Technique.—The apparatus of Fig. 1 (with paddle stirrer) was designed to permit introduction of a very slow stream of oxygen-free ferrous solution into a vigorously stirred persulfate solution, also oxygen-free. The rate of addition of ferrous solution was controlled by the mercury drive system. Experiments were carried out as follows.

A solution of ferrous sulfate was nitrogen-saturated separately in a vessel containing inlet and outlet tubes. The tube and capillaries shown at the extreme left in Fig. 1 were filled with mercury to the desired height. The air in the graduated column and delivery tube of the apparatus was displaced by mercury by raising the lower leveling bulb. The drawn-out tip of the delivery tube was then immersed in the nitrogen-saturated ferrous iron solution and the graduated column and delivery tube filled with ferrous solution to the bottom calibration mark by lowering the lower leveling bulb. The delivery tip was then placed under water and a fraction of a milliliter of water added to prevent interdiffusion of the solutions of iron and persulfate. The ferrous solution was held in the apparatus by closing clamps N and N′ and stopcock D. A reaction vessel was fixed in position as shown in Fig. 1 and slow addition of ferrous iron solution

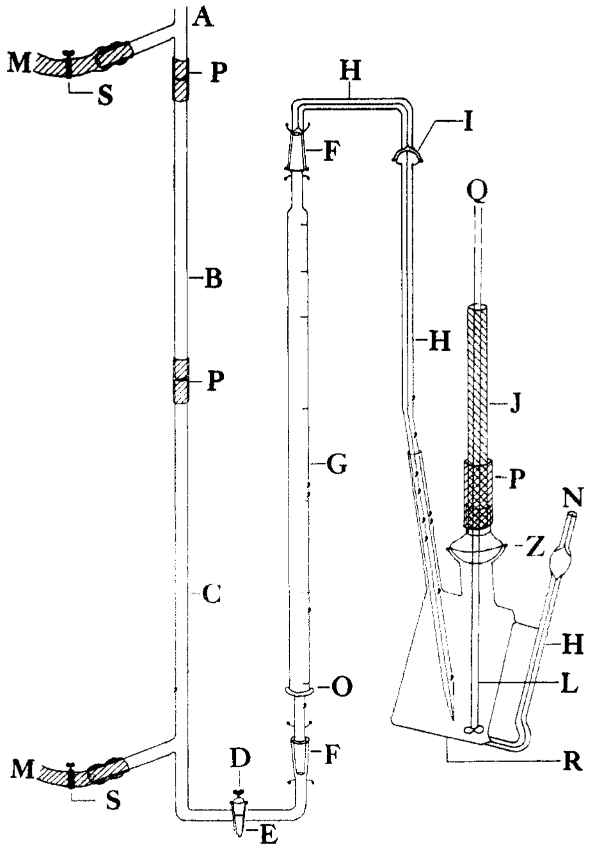

Fig. 1.—Slow addition apparatus with paddle stirrer: A, tubing, Pyrex, 8 mm. i.d.; B, tubing, Pyrex, capillary, < mm. i.d.; C, tubing, Pyrex, 8 mm. i.d.; D, stopcock, No. 2; E, stopcock adapter, Cat. No. 38800 A, Arthur S. La Pine and Co.; F, joint, 10/30; G, tube, Mohr, graduated, calibrated; H, tubing, Pyrex, capillary, 1 mm. i.d.; I, joint, ball and socket, No. 12/1, hand lapped; J, bronze bearing; K, joint, No. 35/20; L, stirrer, glass; M, to mercury leveling bulb; N, to nitrogen; O, ring support; P, rubber sleeve; Q, to stirring motor; R, reaction vessel; S, screw clamp.

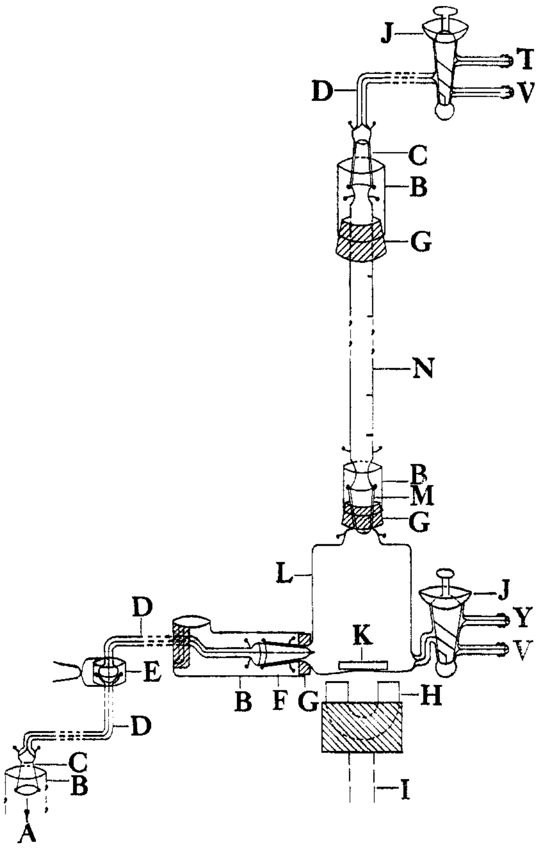

Fig. 2.—Slow addition apparatus with magnetic stirrer: A, apparatus, mercury drive, for delivering ferrous iron solution and mercury; B, tubing, Pyrex, approximately 1 in. o.d.; C, joint, No. 10/30, provided with springs and mercury seal; D, tubing, capillary, Pyrex, 1 mm. i.d.; E, joint, No. 12/1, hand lapped, provided with clamp and mercury seal; F, joint, hand lapped provided with springs and mercury seal; G, rubber tubing, heavy wall, or rubber stopper; H, magnet, Cenco "Little Giant," Cat. No. 78326-C.; I, motor shaft; J, stopcock, vacuum type, 3 way; K, stirring rod, magnetized, platinum covered, length 1.25 in.; diameter 0.25 in.; L, reaction vessel, volume approximately 200 ml.; M, joint, No. 14/35, provided with springs and mercury seal; N, tube, 25-ml., graduated and calibrated; T, to evacuated bulb; U, to vacuum; Y to mercury.

to the reaction mixture effected by opening stopcock D and clamp N. The rate of delivery was reasonably constant, since a high head of mercury (30″) was used; and stirring was quite vigorous, at approximately 1800 r.p.m. Nitrogen was passed through during the entire addition. The volume of solution delivered between the calibration marks was measured in blank runs at the same delivery speed. After addition of the approximately 25-ml. portion of ferrous solution from the delivery tube, the latter was removed from the reaction vessel, and a second portion of ferrous solution (normally ten times as concentrated as the first), was added rapidly from an ordinary volumetric pipet in order to consume the persulfate and leave an excess of ferrous solution which could be titrated.

The apparatus shown in Fig. 2 was designed to permit the collection of any oxygen which might be evolved in the slow addition experiments. The solutions were freed from oxygen before the start of the experiment by evacuation for 20 minutes. The technique employed for the slow addition was similar to that used with the apparatus of Fig. 1. After completion of the reaction, the contents of the reaction vessel were forced up into the evacuated buret N and any gas which had formed was there measured.

Calculations.—The calculations for the rapid mixing experiments (Tables II–V) are straightforward. For the slow addition experiments of Table I the calculations were performed as follows: Let A = ml. Ce^{+4} equivalent to total volume of Fe^{+2} added rapidly. Let B = ml. Ce^{+4} equivalent to Fe^{+2} remaining in reaction mixture at end of rapid reaction. Then $A - B = C$ = ml. Ce^{+4} equivalent to portion of rapidly added Fe^{+2} which reacted = ml. Ce^{+4} equivalent to $S_2O_8^=$ left unreacted after slow addition.

Let D = ml. Ce^{+4} equivalent to total $S_2O_8^=$ taken. Then $D - C = E$ = ml. Ce^{+4} equivalent to total $S_2O_8^=$ reacted.

Let F = Ce^{+4} equivalent to total vol. of Fe^{+2} added slowly. Then $F/E \times 2 = Fe^{+2}$ reacted/$S_2O_8^{-2}$ reacted = molar reaction ratio during slow addition. For the slow addition experiments of Table VI, the over-all reaction ratio was calculated simply as $((A + F) - B)^2/D$.

MINNEAPOLIS, MINN. RECEIVED NOVEMBER 8, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF PENNSYLVANIA]

Conductivity Studies in Methanol[1,2]

BY E. CHARLES EVERS AND ANDREW G. KNOX

The conductance of dilute solutions of a number of quaternary ammonium and other 1–1 salts was investigated in methanol. Limiting equivalent conductances and ion–ion pair equilibrium constants have been evaluated using the methods of Kraus and Fuoss and of Shedlovsky; the merits of the two methods are considered and the results are discussed in the light of what is known regarding these ions in other solvents. Limiting ionic conductances have been evaluated by the method of Kraus and Fowler and compared with values obtained by Hartley from transport data. Methanol has been purified to the point where its specific conductance has ranged between 2 and 7 × 10^{-9} mho.

Introduction

The following investigation was undertaken to secure accurate data on the conductivity of dilute solutions of 1–1 salts in methanol, particularly those of the quaternary ammonium type which have been given thorough investigation in water and in various non-aqueous solvents largely by Kraus and his co-workers.[3]

The most reliable data in methanol previously reported appear to have been obtained by Hartley and his co-workers.[4] These investigators examined a large number of salts of the alkali and alkaline earth metals as well as several salts of the tetramethylammonium and tetraethylammonium types. We have checked the conductivity of several of these salts and have obtained particularly good agreement with their data for potassium chloride.

The conductance data were analyzed using the extrapolation methods of Fuoss and Kraus[5] and of Shedlovsky.[6] Both methods lead substantially to the same values for the limiting equivalent conductance, Λ_0; but in methanol the value of the dissociation constant for the ion-ion pair equilibrium K, computed by the method of Fuoss, is generally twice that obtained by the Shedlovsky method. As these authors have pointed out recently[7] such a difference is to be expected in a solvent of fairly high dielectric constant.

Limiting equivalent ionic conductances have been computed by the method first suggested by Fowler and Kraus[8] which consists of halving the conductance of a salt whose anion and cation conductances are assumed equal; *n*-octadecyltrimethylammonium *n*-octadecylsulfate was employed as the standard electrolyte in this study.

Finally, we have been able to purify methanol to a point where its specific conductance has ranged between 2 and 7 × 10^{-9} mho; consequently, the conductance of the solvent usually was negligible and this has largely eliminated uncertainties associated with the application of a correction for solvent conductance.

Experimental

1. **Salts.**—Spectroscopically pure potassium chloride was kindly supplied us by Dr. K. Krieger of this Laboratory.

Sodium chloride was Mallinckrodt Analytical Reagent Grade salt which was further purified by precipitation from solution with hydrogen chloride, only the middle third portion being retained. The product was recrystallized from conductivity water.

Potassium picrate was prepared by mixing stoichiometric amounts of picric acid with alcoholic potassium hydroxide. The salt was recrystallized from water and from 50% ethanol.

Potassium *n*-octadecylsulfate prepared by Dr. W. E. Thompson was obtained from Dr. C. A. Kraus. It was re-

---

(1) Taken from the Thesis of Andrew G. Knox submitted in partial fulfillment of the requirements for the Ph.D. degree, June, 1950.

(2) Presented before the Meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, in Detroit, Michigan, April, 1950.

(3) C. A. Kraus, *Ann. N. Y. Acad. Sci.*, **51**, 789 (1949).

(4) (a) J. E. Frazer and H. Hartley, *Proc. Roy. Soc.* (*London*), **A109**, 351 (1925); (b) H. Hartley, A. Unmack and D. M. Murray-Rust, *ibid.*, **A127**, 228 (1930); (c) A. Unmack, E. Bullock, D. M. Murray-Rust and H. Hartley, *ibid.*, **A132**, 427 (1932); (d) E. D. Copley and H. Hartley, *J. Chem. Soc.*, 2488 (1930); (e) T. H. Mead, O. L. Hughes and H. Hartley, *ibid.*, 1207 (1933).

(5) R. M. Fuoss, THIS JOURNAL, **57**, 488 (1935); R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 476 (1933).

(6) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(7) R. M. Fuoss and T. Shedlovsky, THIS JOURNAL, **71**, 1496 (1949).

(8) D. L. Fowler and C. A. Kraus, *ibid.*, **62**, 2237 (1940).