

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CONTRIBUTION NO. 1239]

Kinetics of the Oxidation of Hypophosphorous Acid by Iodate Ion

BY PHILIP HAYWARD AND DON M. YOST

Introduction.—The rates of oxidation of hypophosphorous acid, H_3PO_2 , to phosphorous acid, H_3PO_3 , with various oxidizing agents have been the subject of a number of investigations.^{1,2} An interesting feature was found to be common to all these reactions, namely, that the rate of reaction became independent of the concentration of oxidizing agent when this was made sufficiently large. To explain this phenomenon, the hypothesis has been made that hypophosphorous acid in aqueous solution exists in both a "normal" and an "active" form, the latter being much more reactive, and that the conversion of the normal to the active form occurs at a measurable rate. These suppositions lead to a rate law which agrees well with experiment; however, the nature of the postulated active form is unknown, although the present consensus is that it contains a univalent phosphorus atom. It seemed of interest, however, to extend the range of investigations on hypophosphorous acid in the hope of gaining a better understanding of its reactions.

Experimental

The choice of iodate as the oxidizing agent leads to a rather complicated system, from the kinetics point of view. After the initial iodate-hypophosphorous acid reaction (1) has begun, there may also take place; (2) the iodate-iodide reaction; (3) the iodate-phosphorous acid reaction; (4) the iodine-hypophosphorous acid reaction; (5) the iodine-phosphorous acid reaction. Reaction (2), being very rapid in acid solution, is the chief trouble-maker, and any scheme for suppressing it would of course also dispose of (4) and (5). Reaction (3) seems to be unavoidable, but fortunately was found to be of minor importance. Our attention was therefore devoted mainly to minimizing the contribution of the iodate-iodide reaction. Successive approaches to this problem consisted of (1) measuring initial rates, abandoning a run as soon as a definite iodine color had appeared; (2) stirring the reaction mixture with finely divided silver chloride (several grams in 200-300 ml. of solution), a procedure which served to keep down the iodide ion concentration; (3) carrying out the reaction in the presence of small amounts of *n*-propanol, a substance which apparently inhibits the iodate-iodide reaction.³

C. p. chemicals were used throughout, and solutions were made up using ordinary distilled water. For about half of the experiments, stock solutions of hypophosphorous acid were prepared, either by treating phosphorus with barium hydroxide and obtaining the acid from barium hypophosphite, or as was suggested by Professor L. C. Pauling, by converting sodium hypophosphite to the acid by means of an Amberlite ion-exchange column. These solutions contained various amounts of phosphorous acid, the mole percentage being in no case higher than 4. For the rest of the experiments, stock solutions of sodium hy-

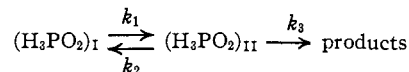
phosphite were used; these always contained negligible amounts of phosphite. Sulfuric acid was used when additional acid was needed. On occasion, the ionic strengths of the reaction mixtures were varied by adding potassium nitrate.

The reactions were usually carried out in glass-stoppered flasks placed in a water-bath, the temperature of which was kept constant within 0.02°. Samples of the reaction mixture were analyzed for iodate by running them into acidified potassium iodide solution and immediately titrating the iodine liberated with thiosulfate. Experiment showed that the error caused by the iodine-hypophosphorous acid reaction in this procedure is negligible.

Calculations.—The rate law upon which calculations were based is of the form given by Mitchell¹

$$-d(\text{IO}_3^-)/dt = \frac{k_1(\text{H}^+)(\text{H}_3\text{PO}_2)}{1 + k_2(\text{H}^+)/k_3(\text{IO}_3^-)}$$

where the constants k_1 , k_2 , k_3 refer to the reactions



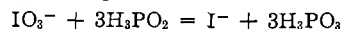
Here $(\text{H}_3\text{PO}_2)_I$ denotes the normal form of hypophosphorous acid, $(\text{H}_3\text{PO}_2)_{II}$ the active form. It should be observed that since the k_1 and k_2 reactions have been shown to be subject to general acid catalysis,² the above rate law is really a special case of a more inclusive expression, which may be written

$$-d(\text{IO}_3^-)/dt = \frac{(\Sigma k[\text{HA}])(\text{H}_3\text{PO}_2)}{1 + \Sigma k_2^a[\text{HA}]/k_3(\text{IO}_3^-)}$$

Here HA is any substance capable of furnishing a proton, such as water, bisulfate ion, undissociated hypophosphorous acid, etc., and k^a is the corresponding catalytic coefficient. The simpler form of the rate law, however, was found to express the results sufficiently well for our purpose.

The reaction rates in this discussion are all given with respect to iodate ion, the units being moles per liter and hours. For purposes of calculation, the iodate concentrations were plotted against time on a large scale, and a smooth curve was drawn through the points. From these graphically smoothed data the rates of reaction at various times were found by numerical differentiation. These rates were also smoothed graphically, and the smoothed values used in the calculation of rate constants.

The stoichiometry of the iodate-hypophosphorous acid reaction was found experimentally to be expressed by the equation



The concentration of hypophosphorous acid at any time could therefore be obtained from the corresponding iodate concentration, provided the hydrogen ion concentration and the dissocia-

(1) Mitchell, *J. Chem. Soc.*, **117**, 1322 (1920), and succeeding papers, 1921-1924.

(2) Griffith and McKeown, *Trans. Far. Soc.*, **530** (1934); Griffith, McKeown and Taylor, *ibid.*, **36**, 752 (1940).

(3) Neogi and Sen, *J. Ind. Chem. Soc.*, **8**, 725 (1931); *C. A.*, **26**, 1178 (1932).

tion constant of hypophosphorous acid were known. It is here that the calculations are subject to considerable error. Dissociation constants of the acid at various ionic strengths were taken from the paper of Griffith, McKeown and Taylor.² Where sulfuric acid of sulfate-bisulfate buffer solutions were used, the data of Harned and Hamer⁴ were used to calculate dissociation constants of bisulfate ion. The acidity at any time was assumed to be due solely to the hypophosphorous and sulfuric acids present, no correction being made either for the production of phosphorous acid during a run or for possible incomplete dissociation of iodic acid. Neglect of the first factor is justified both because hypophosphorous and phosphorous acids are of approximately equal strengths and because actual pH measurements during the course of the reaction showed (with an exception to be mentioned later) no significant change in acidity.

Results and Discussion. 1. Determination of Initial Rates.—In these experiments the attempt was made to determine the order of the reaction with respect to the various reactants. Figure 1 gives the results of a set of experiments designed to test simultaneously the dependence of the order on the hydrogen ion concentration and the concentration of (undissociated) hypophosphorous acid. In these experiments, the iodate concentration and the total concentration of hypophosphorous acid (undissociated acid plus hy-

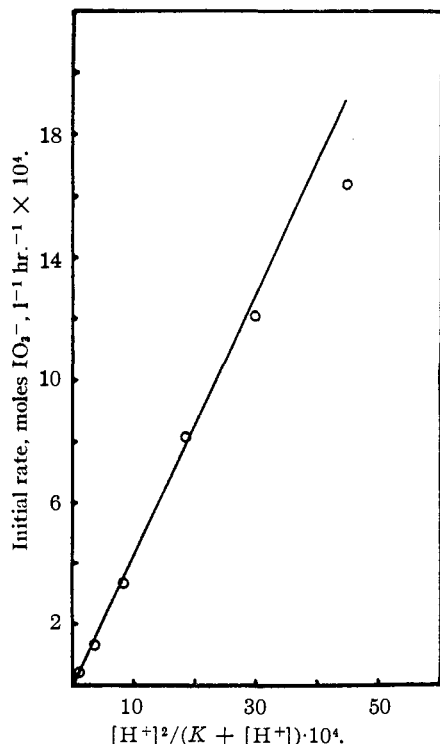


Fig. 1.—Dependence of initial rate on $[H^+][H_2PO_2]$ in the oxidation of hypophosphorous acid by iodate ion.

(4) Harned and Hamer, *THIS JOURNAL*, **57**, 27 (1935).

pophosphite ion) were kept constant, and the acidity varied by adding sulfuric acid. If the rate were proportional to the first power of both hydrogen ion and hypophosphorous acid concentrations, a straight line should result from plotting initial rate against $(H^+)^2 / (K + (H^+))$, where K is the ionization constant of hypophosphorous acid. It is seen that there is a linear relationship at lower acidities, but evidence of a falling off from this linear increase in rate at higher acidities. This, of course, is to be expected if the rate law derived by Mitchell is adhered to in this case, for when the ratio $(H^+) / (IO_3^-)$ becomes sufficiently large, the rate becomes independent of (H^+) .

Another set of experiments, in which the iodate concentration was made small compared to the hypophosphorous acid concentration, was designed to test the dependence of rate on iodate concentration. Under such conditions, the assumed rate law can be written

$$\frac{1}{\text{initial rate}} = \frac{1}{k_1(H^+)(H_2PO_2)} + \frac{k_2}{k_3k_1(H_2PO_2)} \times \frac{1}{(IO_3^-)} = C + \frac{D}{(IO_3^-)}$$

where C and D are constants. Figure 2 shows the data plotted in conformity with this relation; the expected linearity is fairly apparent. However, it must be remarked that the subsequent evaluation of k_1 leads to a value of about 2.3×10^3 for the intercept C , instead of to a value of approximately zero, as shown in Fig. 2. In other words, the initial rates are higher than the rate law would predict. The major part of this discrepancy can probably be explained by the fact that the reaction mixtures were heavily buffered with phosphate, the catalytic effect of which in this case is considerably greater than that of hydrogen ion alone. Using the catalytic coefficients given by

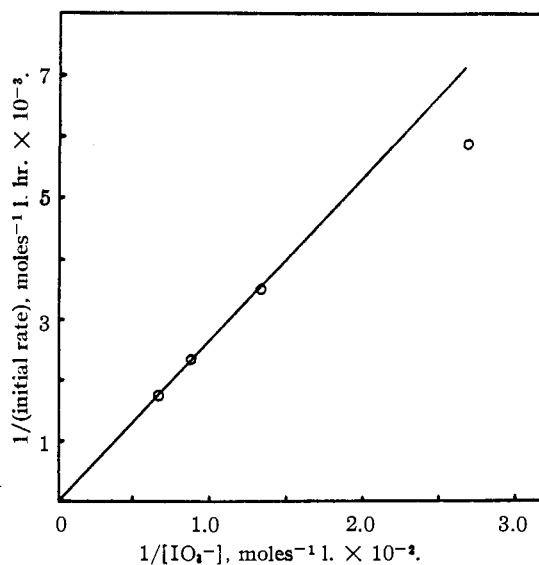


Fig. 2.—Dependence of initial rate on $[IO_3^-]$ in the rate of reduction of iodate ion by hypophosphorous acid.

Griffith, McKeown and Taylor,² we find the value of C to be reduced to about 0.2×10^3 , which, in view of the uncertainties in the initial rates, is now in reasonable agreement with the value found graphically. These phosphate buffers were not used in other experiments, which are therefore not subject to such a major correction.

The rate law can be written in the form

$$k_1 = \frac{\text{rate}}{(\text{H}^+)(\text{H}_2\text{PO}_2)} + \frac{\text{rate}}{(\text{IO}_3^-)(\text{H}_2\text{PO}_2)} \frac{k_2}{k_3} = A + B \frac{k_2}{k_3}$$

The experimentally determined quantities A and B determine the intercept and slope of a straight line, any point of which gives a pair of values of k_1 and k_2/k_3 . Altering the experimental conditions should, by altering A and B , give a family of straight lines which intersect in a point, the coördinates of which are the required values of k_1 and k_2/k_3 . The results given by this procedure are presented in Table I.

TABLE I
"INTERSECTION" VALUES OF k_1 AND k_2/k_3 AT 30°

k_1 , moles ⁻¹ l. hr. ⁻¹	k_2/k_3
8.1	0.50
8.5	.54
8.7	.57
10.4	.82
9.0	.84
10.0	.42
9.4	.40
9.4	.37
9.3	.35
8.7	.31
7.9	.20

Average 9.0 ± 0.7 0.48 ± 0.19

2. The Reaction in the Presence of Silver Chloride.—By stirring the reaction mixtures with silver chloride, it was found possible, if the acidity and iodate concentration were not too high, to prevent entirely the appearance of iodine. Blank experiments showed that oxidation of hypophosphorous acid by silver ion under these conditions was not appreciable, nor was there any evidence for precipitation of silver iodate. This procedure widened considerably the range of practicable initial conditions; also, since the reaction could now be followed through a greater portion of its course, k_1 and k_2/k_3 could be estimated from each experiment. From the rate law written in the form

$$(\text{H}_2\text{PO}_2)/\text{rate} = \frac{1}{k_1(\text{H}^+)} + \frac{k_2}{k_3 k_1} \times \frac{1}{(\text{IO}_3^-)}$$

it can be seen that plotting the left-hand side against $1/(\text{IO}_3^-)$ should give a straight line from whose intercept and slope the values of k_1 and k_2/k_3 could be obtained.

This linearity was always found, at least during the first part of a run. Later on, the slopes of the curves often decreased markedly, an effect which is probably to be attributed to the iodate-phosphorous acid reaction, since the reaction mixtures

usually began to give positive tests for phosphate at about the point where the curves began to drop off. It is possible that the phosphorous acid produced is responsible also because its catalytic effect is about twice that of hypophosphorous acid.² Table II and Fig. 3 give the results obtained from one of the best runs of this kind.

TABLE II
THE IODATE-HYPOPHOSPHITE REACTION AT 30.06° IN THE PRESENCE OF SILVER CHLORIDE
[$\Sigma \text{H}_2\text{PO}_2$]₀ = 0.0525, $K_{\text{H}_2\text{PO}_2}$ = 0.076, $[\text{H}^+] = 0.037$, $\mu = 0.13$, temp., 30.06°

Time, hours	$[\text{IO}_3^-], \times 10^2$	$[\text{H}_2\text{PO}_2], \times 10^2$	Rate, moles l ⁻¹ hr. ⁻¹ , $\times 10^4$
0	11.59	1.73	3.38
0.25	10.72	1.64	3.12
0.50	9.95	1.56	2.85
0.75	9.23	1.49	2.60
1.0	8.51	1.42	2.37
1.25	7.90	1.36	2.15
1.50	7.35	1.31	1.96
1.75	6.83	1.26	1.79
2.0	6.35	1.21	1.65
2.25	5.93	1.17	1.53
2.50	5.55	1.13	1.43
2.75	5.17	1.09	1.32
3.0	4.86	1.06	1.23

The averages of thirty-nine determinations of k_1 and k_2/k_3 , both by the method just indicated and by the "intersection" method previously described, are 12.2 ± 3.0 moles⁻¹ l. hr.⁻¹ and 0.48 ± 0.25 , respectively.

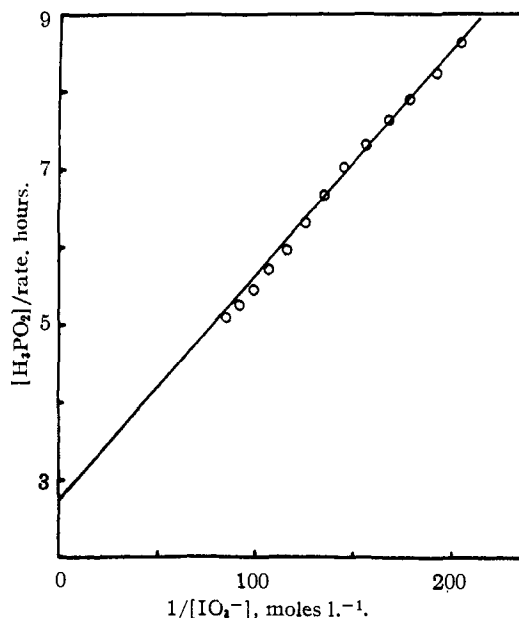


Fig. 3.—The rate of oxidation of hypophosphorous acid by iodate ion in the presence of solid AgCl.

3. The Reaction in the Presence of *n*-Propanol.—In these experiments small concentrations (never more than 7 volume per cent.) of

n-propanol were added to the reaction mixture. Tests showed that varying the concentration of alcohol in this range did not appear to have a significant influence on the rate, that there was no reaction between iodate and *n*-propanol, and that its presence did not interfere with the thiosulfate titrations. The dielectric constants of the solutions were lowered by as much as four per cent. by the addition of the alcohol,⁵ but the error thus introduced into the calculations of hydrogen ion and hypophosphorous acid concentrations is hard to estimate quantitatively. At any rate, it was considered to be negligible, in view of the already considerable uncertainty in these quantities.

It was found that, while there was no apparent retardation of the reaction rate between iodate and hypophosphorous acid, the time of appearance of iodine was indeed delayed to an extent which, other things being equal, was quite accurately proportional to the amount of *n*-propanol added. It was noticed also that, while in previous experiments the acidity remained sensibly constant, in these experiments it dropped continuously, as shown by a *pH* meter. On this account, sodium sulfate-sodium bisulfate buffer solutions were used in some of the experiments designed to evaluate k_2/k_3 ; in other cases, when the acidity was not sufficiently well controlled, the calculated hydrogen ion concentrations were made proportional to their measured values.

It was now possible to work with such high iodate concentrations that a good first approximation to k_1 could be determined directly from the limiting form of the rate equation

$$k_1 = \text{rate}/(\text{H}^+)(\text{H}_2\text{PO}_2)$$

Using an average value of k_1 determined thus, values of k_2/k_3 could be found from experiments at lower iodate concentrations. These were used to correct the values of k_1 , which in turn gave a final small correction in k_2/k_3 . The values of the rate constants obtained using this technique agreed more closely among themselves than did those

TABLE III

THE IODATE-HYPOPHOSPHITE REACTION AT 30.06° IN THE PRESENCE OF *n* PROPANOL

$[\Sigma\text{H}_3\text{PO}_2]_0 = 0.0960$, $K_{\text{H}_2\text{PO}_2} = 0.078$, $[\Sigma\text{H}_2\text{SO}_4]_0 = 0.0172$, $\mu = 0.46$, concn. *n*-propanol = 7 vol. per cent.

Time, hours	$[\text{IO}_3^-]$	Rate, moles $\times 10^3$, $\text{l.}^{-1} \text{hr.}^{-1}$	$[\text{H}^+] \times 10^2$	$[\text{H}_2\text{PO}_2] \times 10^2$	k_1 (uncor.)
0.0	0.1433	2.70	1.60	1.63	10.35
0.25	.1426	2.58	1.58	1.58	10.33
0.50	.1420	2.45	1.55	1.53	10.32
0.75	.1413	2.32	1.52	1.46	10.52
1.0	.1407	2.19	1.49	1.41	10.42
1.25	.1402	2.06	1.47	1.37	10.22
1.50	.1396	1.93	1.45	1.33	10.00
1.75	.1391	1.80	1.42	1.28	9.92
2.00	.1387	1.67	1.40	1.25	9.55
2.25	.1382	1.54	1.37	1.20	9.38

(5) Åkerlöf, THIS JOURNAL, 54, 4125 (1932).

from the other experiments, and we therefore believe them to be the most reliable. Table III presents data from a representative experiment.

For k_1 , the average value at 30.06° was found to be 9.7 ± 0.8 moles⁻¹ l. hr.⁻¹, and for k_2/k_3 , 0.44 ± 0.03 . These are to be compared with the values determined by Mitchell for the iodine reaction, which when adjusted to 30° and converted to these units amount to 9.0 and 0.012, respectively. The two values for k_1 are the same, within the limits of error, but k_2/k_3 is very different in the two cases. Recalling the interpretation of this constant, and assuming that k_2 has the same value in both reactions, we should conclude from this that the reaction of the active form of hypophosphorous acid with the halogens and mercuric ion is about thirty-five times faster than with iodate. It is interesting to point out in this connection that the iodate ion is unlike the other oxidizing agents studied in that it is not a simple neutral molecule or cation.

Increasing the ionic strength from 0.27 to 0.65 had no significant effect on the magnitude of k_1 , and an increase from 0.66 to 1.29 cause k_2/k_3 to decrease from 0.47 to 0.42—a change which is also probably not significant, in view of the uncertain effects of changing ionic strength on the hydrogen ion and hypophosphorous acid concentrations. It is to be noted that the indifference of k_2/k_3 to changes in ionic strength is in accord with the postulated reaction-mechanism, in which both the k_2 and k_3 reactions involve a neutral molecule—*i. e.*, the active form of hypophosphorous acid.

The rate constants were also determined by means of similar experiments at 20.27°, the values being 3.66 for k_1 and 0.35 for k_2/k_3 ; these represent temperature coefficients of 2.7 and 1.3 per 10.4°, respectively. The corresponding activation energies are 17 and 4.5 kcal. The value for the temperature coefficient of the k_1 reaction is considerably below that of 3.14 per 10° found by Mitchell for the iodine reaction. Also, he states that the temperature coefficient of k_2/k_3 is "approximately unity"; lacking the data on which he based this statement, it may be that his value is compatible with the one found here.

Acknowledgments.—We wish to thank Professor E. H. Swift for help with analytical problems, Dr. Norman Davidson for general criticism, and Mr. Fred Ordway for the construction of a nomograph which materially shortened the labor of calculation. We also acknowledge the courtesy of the International Resin Corporation in supplying a sample of Amberlite IR-100 ion exchange resin for the preparation of hypophosphorous acid. The work was supported by a grant from The Research Corporation, and we are greatly indebted to them for this aid.

Summary

The hypothesis that a normal and an active form of hypophosphorous acid coexist in aqueous

solution, and that the conversion of the normal to the active form can be a rate-determining step in its reactions with oxidizing agents, is supported by a study of the kinetics of its oxidation by iodate ion. The rate law

$$-d(\text{IO}_3^-)/dt = \frac{k_1(\text{H}^+)(\text{H}_2\text{PO}_2)}{(1 + k_2(\text{H}^+)/k_3(\text{IO}_3^-))}$$

is found to be in agreement with observation, the

best values of the constants at 30° being 9.7 moles⁻¹ l. hr.⁻¹ for k_1 and 0.44 for k_2/k_3 . The respective activation energies are 17 and 4.5 kcal.

It is probable that iodate ion reacts with the active form of hypophosphorus acid at a much slower rate than do other substances conforming to this rate law.

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An Oxidation-Reduction Cycle in Emulsion Polymerization Systems¹

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Introduction

The physical and chemical properties of synthetic polymers depend markedly upon the conditions under which they are made, particularly upon the temperature of polymerization.³ In certain instances a superior product is obtained when the polymerization is carried out at low temperatures, but the rate of reaction may be so slow that the process is impractical. For this reason considerable effort has been directed toward activating polymerization catalyst systems to obtain substantial rates of polymerization at reduced temperatures.

For a polymerization taking place through a free radical mechanism, the over-all rate of reaction depends, among other things, upon the concentration of free radicals present. It would appear, therefore, that a high rate of polymerization might be attained at low temperatures if a sufficiently high concentration of free radicals could be realized. Unfortunately, the thermal decompositions of certain free radical producing compounds such as benzoyl peroxide are so slow⁴ at reduced temperatures that they exhibit little or no catalytic effect under those conditions.⁵ However, it is found that the formation of free radicals from benzoyl peroxide can be considerably hastened by the presence of ferrous iron. Since ferrous iron is a reducing agent and the peroxide an oxidizing agent, the combination is said to constitute a "Redox" system, and the increased catalytic effect of the peroxide is said to be the result of reduction activation.

(1) This investigation was carried out in part under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program, and was first reported on October 30, 1947. ADDED IN PROOF: Since the preparation of this manuscript, the authors have learned of some work by Werner Kern, "Die makromolekulare Chemie," B1, 199-268 (1948), dealing with topics closely related to those discussed in the present paper. Kern's findings are entirely compatible with those here indicated, although the cyclical aspect of the behavior was not emphasized.

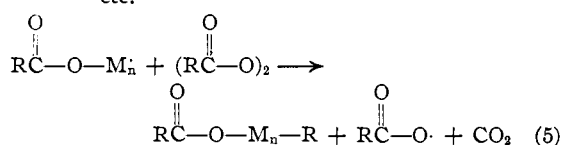
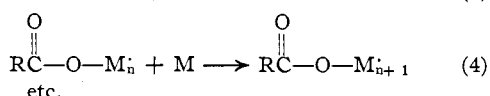
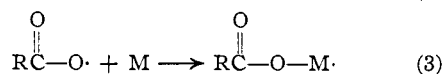
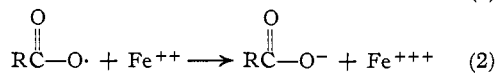
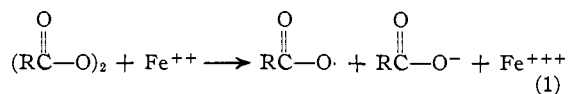
(2) Firestone Tire and Rubber Company research fellow.

(3) Private communication from the Office of Rubber Reserve.

(4) McClure, Robertson and Cuthbertson, *Canadian J. Research*, 20B, 103 (1942); Cass, *This Journal*, 68, 1976 (1946).

(5) Nozaki and Bartlett, *ibid.*, 68, 1686 (1946).

The fundamental work of Haber and Weiss⁶ on the reactions of iron with hydrogen peroxide forms the basis for the chemical aspects of reduction activation. Baxendale, Evans and Parks⁷ made use of an iron-hydrogen peroxide system for the polymerization of acrylonitrile. If one employs an organic peroxide in place of hydrogen peroxide, the following reactions can be expected to occur in a polymerization system activated with ferrous iron



Reaction (1) involves the formation of one free radical and one acid ion, the latter being combined in some form of salt. (The use of the ionic nomenclature in this connection is for the purpose of designating the states of oxidation instead of the actual states of matter which are not necessarily in ionized form.) Reaction (2) represents the destruction of the initially formed free radicals by ferrous ions. It is clear that unless some other reaction intervenes to prevent (2) from occurring, the final result will simply be the complete reduction of the peroxide by the iron. If some polymerizable monomer is present, then reactions (3) and (4), which are precisely the polymer chain growth reactions, can occur. More-

(6) Haber and Weiss, *Proc. Roy. Soc. (London)*, 147A, 332 (1934).

(7) Baxendale, Evans and Parks, *Trans. Far. Soc.*, 42, 155 (1946).