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

$$-d(IO_3^-)/dt = \frac{k_1(H^+)(H_3PO_2)}{(1 + k_2(H^+)/k_3(IO_3^-))}$$

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.

PASADENA, CALIFORNIA RECEIVED AUGUST 30, 1948

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

An Oxidation-Reduction Cycle in Emulsion Polymerization Systems[1]

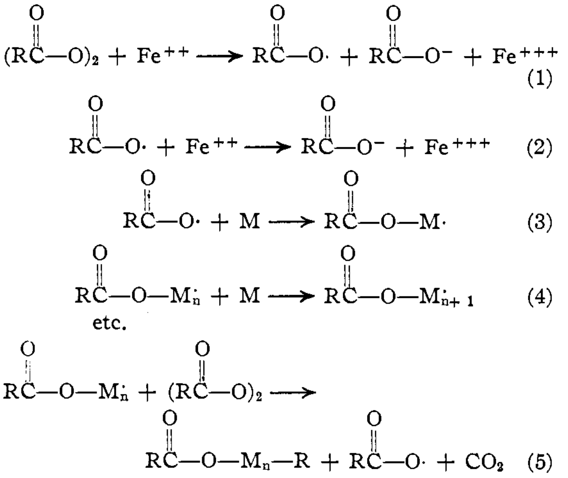
BY F. T. WALL AND T. J. SWOBODA[2]

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 slow[4] 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.

The fundamental work of Haber and Weiss[6] on the reactions of iron with hydrogen peroxide forms the basis for the chemical aspects of reduction activation. Baxendale, Evans and Parks[7] 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



$$(R\overset{O}{\overset{\|}{C}}-O)_2 + Fe^{++} \longrightarrow R\overset{O}{\overset{\|}{C}}-O\cdot + R\overset{O}{\overset{\|}{C}}-O^- + Fe^{+++} \tag{1}$$

$$R\overset{O}{\overset{\|}{C}}-O\cdot + Fe^{++} \longrightarrow R\overset{O}{\overset{\|}{C}}-O^- + Fe^{+++} \tag{2}$$

$$R\overset{O}{\overset{\|}{C}}-O\cdot + M \longrightarrow R\overset{O}{\overset{\|}{C}}-O-M\cdot \tag{3}$$

$$R\overset{O}{\overset{\|}{C}}-O-M_n^{\cdot} + M \longrightarrow R\overset{O}{\overset{\|}{C}}-O-M_{n+1}^{\cdot} \tag{4}$$

etc.

$$R\overset{O}{\overset{\|}{C}}-O-M_n^{\cdot} + (R\overset{O}{\overset{\|}{C}}-O)_2 \longrightarrow R\overset{O}{\overset{\|}{C}}-O-M_n-R + R\overset{O}{\overset{\|}{C}}-O\cdot + CO_2 \tag{5}$$

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-

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(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).

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

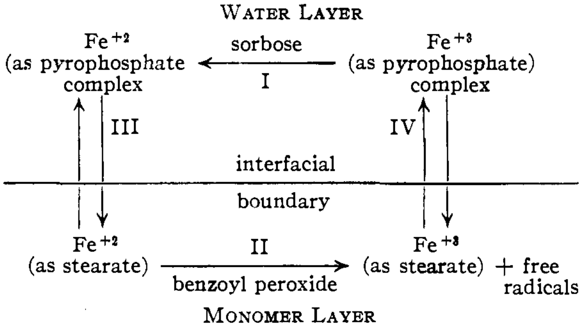
(7) Baxendale, Evans and Parks, *Trans. Far. Soc.*, **42**, 155 (1946).

over, once a monomer of the vinyl type has added to the initial free radical, the resulting free radical is no longer subject to the reaction represented by equation (2), since a stable salt can no longer be formed. However, a polymeric free radical can undergo reaction (5) which is equivalent to the induced free radical decomposition discussed by Nozaki and Bartlett.[5] Reaction (5) is also equivalent to chain transfer or modification so it is apparent that a peroxide can serve both as a catalyst and as a modifier[8] in a polymerization system.

If an appreciable amount of ferrous iron is brought into contact with an organic peroxide, reactions (1) and (2) take place so rapidly that the catalyst is soon spent. Accordingly, if reduction activation is to be of any use for promoting polymerization, some means must be found for controlling reaction (1) and for minimizing reaction (2) which does no good in a polymerization system. A solution to this problem can be found by keeping the iron concentration very low relative to the concentrations of the peroxide and of the monomer, since under these circumstances the rate of reaction (1) would be reduced to a reasonable value and reaction (3) would predominate over reaction (2). This pattern suggests that continuous addition of small amounts of ferrous iron to the polymerization recipe might give rise to the desired state of affairs. Although such addition by mechanical means is highly impractical, the same result can fortunately be accomplished in an emulsion system when appropriate auxiliary reagents are present. Thus certain highly effective "Redox recipes" for the preparation of a variety of polymers, such as the copolymer of butadiene and styrene, have actually been devised by polymerization technologists.[3] These recipes are complex reaction systems which involve a variety of substances in addition to the monomer, peroxide, and iron. The work reported here was undertaken to establish the role of each of the reagents in these recipes. It is our conclusion that a certain reaction cycle, to be called the "Redox Cycle," takes place, and that each of the reagents present in the simplest effective recipe serves a definite purpose in this cycle.

The Emulsion "Redox" System

A typical recipe[9] for a "Redox" polymerization consisting only of those reagents which are necessary and sufficient is: 20 g. monomer, 40 g. water, 0.1 g. benzoyl peroxide, 0.1 g. ferric ammonium sulfate, 0.1 g. sorbose, 0.1 g. sodium pyrophosphate, 1.0 g. sodium stearate. In place of ferric ammonium sulfate, it is permissible to substitute ferrous ammonium sulfate for reasons which will be made clear presently. As we have already seen, if ferrous iron is present, such iron can react with benzoyl peroxide to form free radicals. Those free radicals then combine with monomer ultimately building up polymer molecules. It remains to be seen how the above recipe controls the decomposition of benzoyl peroxide to sustain a smooth and rapid polymerization at reduced temperature. As a result of this investigation, it appears that the following cycle properly describes the behavior of the system



The iron in the emulsion is originally present as ferric iron which is tied up for the most part as the pyrophosphate complex in the aqueous phase. But the ferric iron can be reduced by sorbose or some other reducing sugar to form ferrous iron, a large portion of which also remains as a pyrophosphate complex in the water layer. However, limited amounts of both ferrous and ferric iron will tend to pass into the oil phase, presumably as the stearate salts, since ferrous and ferric stearates are oil soluble compounds. The distribution between the phases will occur in accordance with the usual laws governing distribution of solutes between immiscible solvents. In the oil phase the ferrous iron can react with benzoyl peroxide to form free radicals and ferric iron. The free radicals start the polymerization going and the ferric iron ultimately passes back into the water layer to maintain distribution equilibrium. Since the iron finally returns to its original form, the net result of the whole process is the reduction and decomposition of benzoyl peroxide by sorbose.

Several factors contribute to the effectiveness of the cycle described above. First of all, the amount of iron present in a form capable of reacting with the peroxide is quite small. This means that reaction (1) will proceed at a moderate rate and will be followed almost exclusively by reaction (3), because of the large excess of monomer. Nevertheless, the total amount of iron in the system is appreciable, and hence can be readily controlled for reproducible results. The pyrophosphate serves to tie up most of the iron in complex form, thus providing a reservoir of iron to be drawn from as needed. If the pyrophosphate were not present, too much of the ferrous iron would be solubilized in the organic phase with the result that the peroxide would be decomposed too rapidly for sustained polymerization. Moreover, in the absence of pyrophosphate there would be little tendency for the ferric iron to be drawn into the water layer

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[8] Snyder, Stewart, Allen and Dearborn, THIS JOURNAL, **68**, 1422 (1946); Wall, Banes and Sands, *ibid.*, **68**, 1429 (1946).

[9] Marvel, Deanin, Overberger and Kuhn, *J. Polymer Sci.*, **3**, 128 (1948).

TABLE I

DESCRIPTION OF EXPERIMENTS

Experiment	I	II	III	IV	V[b]	VI	VII	VIII	IX
	Approximate concentrations of ingredients, moles per liter								
Chloroform phase[a]									
Benzoyl peroxide	0.05	0.05	0.01	0.05			0.01	0.01	0.01
Ferric stearate						0.01			
Water phase[a]									
Ferrous ammonium sulfate	.05	.05	.01	.05					
Ferric ammonium sulfate					0.01		.01	.01	.01
Sorbose					.01	.01	.01	.01	.01
Sodium pyrophosphate				.10	.02	.02	.02		.02
Sodium stearate	.10	.05	[c]	.05	.04	.04	.04	.04	[c]
Benzyltrimethylammonium hydroxide			.04						.04

[a] Equal volumes of two phases used. [b] No chloroform phase included in this experiment. [c] Sodium stearate added later during course of experiment.

where it can be reduced by the sorbose which is present for that purpose. If no sorbose is added, the system can still be made to function providing the original recipe contains a large amount of ferrous iron with sufficient pyrophosphate to handle it. The over-all operation under these conditions would lose its cyclical aspect, and the effective concentration of reducing iron would not be maintained at nearly as uniform a level.

The sodium stearate has a dual role in the "Redox" system, and it is largely because of this coincidence that the "Redox" system actually operates. Ordinarily sodium stearate would be added for emulsification purposes, and it does serve that function with the "Redox" recipe as well. Equally important, however, is the solubilization of the ferrous iron in the oil phase which is brought about by the formation of oil soluble ferrous stearate in the presence of soap. If the iron were not solubilized in the oil phase to a sufficient extent, then the entire cycle would break down. In fact, if certain cationic emulsifying agents such as the quaternary ammonium salts are substituted for sodium stearate without other changes in the recipe, the "Redox" system fails for the obvious reason that the iron is not brought into contact with the peroxide.

Experimental

The validity of the cycle described above was established by a series of separate experiments which were designed to test every aspect of the cycle. To avoid the complications of actual polymerization, which would overshadow the reactions in the "Redox" cycle, chloroform was used in place of monomer. Thus there was obtained an emulsion system which simulated the polymerization system in all respects except that reaction (2) would take place instead of reactions (3), (4), and (5). Under these experimental circumstances, the stoichiometry of the cycle could be well established. Among the experiments carried out were the reaction of ferrous stearate with benzoyl peroxide, the reduction of ferric iron with sorbose, and the transfer of iron from one phase to the other. Other experiments involved the omission of one or more critical reagents. A description of the experiments which were performed is presented in Table I. Each experiment was carried out at room temperature in the absence of oxygen with vigorous agitation of the emulsion. The data for these experiments are given in Table II. The results of all the experiments were compatible with the cycle proposed, so the conclusions given above are considered correct.

Since the solubilization of ferrous iron in the oil phase of a reaction emulsion appears to be an important factor in the operation of the "Redox" system, several experiments were carried out to investigate this aspect of the system. The first experiments were of a qualitative nature designed to prepare ferrous stearate in chloroform or benzene solution and to observe its reaction with peroxide in such single phase oil systems. Solutions of ferrous stearate (0.01–0.02 molar) were simply prepared by adding, in the absence of oxygen, an aqueous solution of ferrous ammonium sulfate in slight excess to an agitated emulsion consisting of chloroform or benzene with water and sodium stearate. The phases were permitted to separate; then the water layer was discarded and the organic layer filtered. The experiments were continued by introducing benzoyl peroxide into these solutions of ferrous stearate. A very rapid decomposition of the peroxide with accompanying oxidation of the iron was observed.

After establishing the qualitative results described above, further quantitative experiments were carried out which involved the reaction of benzoyl peroxide with ferrous iron in an emulsion medium. For Experiment I an emulsion

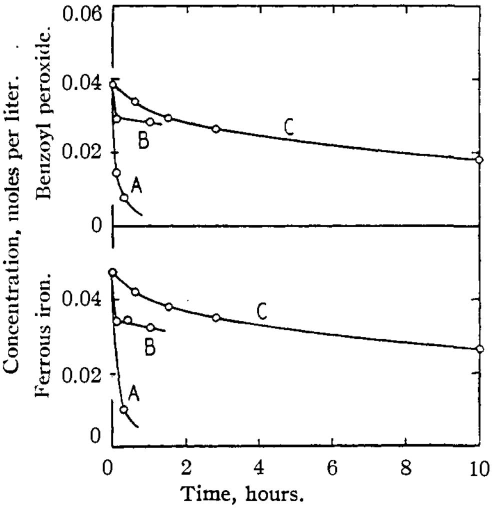

Fig. 1.—Peroxide–ferrous iron systems: curves A, equivalent amount of soap; curves B, half equivalent amount of soap; curves C, half equivalent amount of soap plus pyrophosphate.

TABLE II

SUMMARY OF RESULTS

Expt.	Time, hr.	Concentrations	
		Benzoyl peroxide[a]	Ferrous iron[b]
I	0	0.0389	0.0475
	0.1	.0146	.....
	0.3	.0078	.0100
II	0	.0389	.0475
	0.1	.0293	.0343
	0.4	.....	.0345
	1.0	.0285	.0323
III	0	.01003	
	1.3	.00990	
	4.6	.00970	
	5.2	added sodium stearate (40% equivalent of ferrous iron)	
	5.3	.00859	
	5.9	.00720	
	6.8	.00613	
	10.6	.00460	
	11.4	added sodium stearate (large excess)	
	11.8	.00355	
IV	0	.0389	0.0475
	0.6	.0340	.0420
	1.5	.0295	.0380
	2.8	.0264	.0350
	10.0	.0181	.0265
V	0		0
	2.3		0.00124
	5.7		.00236
	9.8		.00320
VI	0		0
	4.3		0.00048
	6.7		.00088
	10.6		.00168
	22.4		.00360
VII	0	.00925	
	6.0	.00780	
	17.8	.00573	
	27.2	.00280	
VIII	0	.01112	
	4.9	.01063	
	9.0	.01051	
	16.1	.01020	
IX	0	.01025	0[c]
	1.3	.01034	.....
	1.6	.....	0.0012
	2.7	.01038	.....
	3.0	.....	.0017
	3.1	added sodium stearate (10% equivalent of ferric iron)	
	3.2	.00990	.....
	3.3	.....	.0014
	4.2	.00975	.....
	4.3	.....	.0010
	5.6	.00960	.....
	5.7	.....	.0009
	8.1	.00945	.....
	8.2	.....	.0009

[a] Total moles calculated per liter of chloroform; obtained by iodometric titration. [b] Total moles calculated per liter of water; obtained by dichromate titration. [c] Initial ferric iron concentration, 0.01069; subsequent concentrations, as plotted in Fig. 5, obtained by difference.

was prepared consisting of chloroform, water, benzoyl peroxide, ferrous ammonium sulfate, and sodium stearate with the latter three substances present in stoichiometrically equivalent amounts. In this experiment, the results of which are illustrated in Fig. 1, a rapid decomposition of peroxide occurred, accompanied by a rapid oxidation of ferrous iron to the ferric state.

Experiment II was identical to Experiment I except that only one half the equivalent amount of sodium stearate was included. The results of this experiment, also illustrated in Fig. 1, show the same rapid initial reaction observed for Experiment I. But when one half the reactants were consumed, the rate of reaction abruptly decreased to a very small value. These experiments demonstrate conclusively that the iron must actually get into the organic phase to be truly effective as a reduction activator and that the sodium stearate serves as the solubilizing agent.

Further evidence supporting the conclusion drawn above was obtained in Experiment III which involved a similar emulsion, except that no sodium stearate was initially included. In its place there was substituted an equivalent amount of benzyltrimethylammonium hydroxide, which is a cationic emulsifying agent incapable of solubilizing iron. The data as shown in Fig. 2 show that no significant amount of reaction occurred with this system. However, after 5.2 hours a 40% equivalent of sodium stearate was added, whereupon the rate of reaction immediately became very rapid but then slowly diminished due to the insufficiency of sodium stearate. A further addition of a large excess of sodium stearate at 11.4 hours caused another surge of reaction. Thus the dual role of sodium stearate as emulsifier and solubilizer is established.

The undesirably rapid reaction which ensues between benzoyl peroxide and ferrous iron, as in Experiment I, is effectively controlled by holding a large part of the ferrous iron in the water phase in the form of the stable water soluble pyrophosphate complex,[10] $Fe_2(P_2O_7)_3^{-8}$. The effect of the addition of sodium pyrophosphate on the reaction is to be seen by comparing the results of Experiment II with those of Experiment IV given in Fig. 1. The experiments were identical except that in Experiment IV there was added an amount of sodium pyrophosphate 50% in excess of that required to hold all the ferrous iron in the pyrophosphate complex. The data show that, although the total amounts of reaction in the experiments are comparable, for Experiment IV the reaction between the benzoyl peroxide and ferrous iron proceeded at a more moderate rate and continued over a longer period of time.

The behavior exhibited by the reaction mixture of Experiment IV suggests that it would be capable of satisfactory polymerization initiation, a fact which is borne out by experience. However, the characteristics of the reaction between benzoyl peroxide and ferrous iron can be further improved by including in the system a means for generating ferrous iron as it is needed during the course of the reaction, and thus eliminating the need for a large water phase reservoir of ferrous iron. The water phase reduction of ferric iron by sorbose accomplishes this task and makes up the remainder of the "Redox" cycle, which will now be considered. First it should be noted that the behavior of ferric iron is quite similar to that of ferrous iron with respect to its solubilization in the organic phase of the emulsion as ferric stearate and its ability to form the stable water soluble pyrophosphate complex,[10] $Fe_2(P_2O_7)_3^{-6}$. Two experiments were performed which indicate the characteristics of the reaction between sorbose and ferric iron. In Experiment V, equivalent amounts of ferric iron and sorbose were permitted to react in a single phase water system containing sodium stearate and so-

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[10] Freed and Kasper, THIS JOURNAL, **52**, 2632 (1930); Pascal. *Ann. chim. phys.*, [8] **16**, 359 (1909).

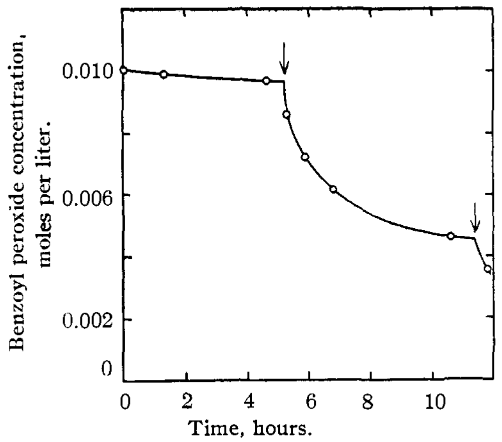

Fig. 2.—Peroxide-ferrous iron system with cationic emulsifier; soap added at times indicated by arrows.

dium pyrophosphate. (The composition of this reaction mixture is close to that of the water phase of a polymerization emulsion.) Experiment VI differed from Experiment V by the inclusion of a chloroform layer and the introduction of ferric iron as ferric stearate dissolved in the chloroform. The data for these experiments appear in Fig. 3. Both of these experiments show that the reaction between sorbose and ferric iron proceeds at a rate which is commensurate with the rate observed for the reaction between benzoyl peroxide and ferrous iron in the presence of pyrophosphate. The second of these two experiments demonstrates in particular the ability of the ferric iron to transfer from the organic to the water phase and to engage in the reaction with sorbose in an emulsion medium.

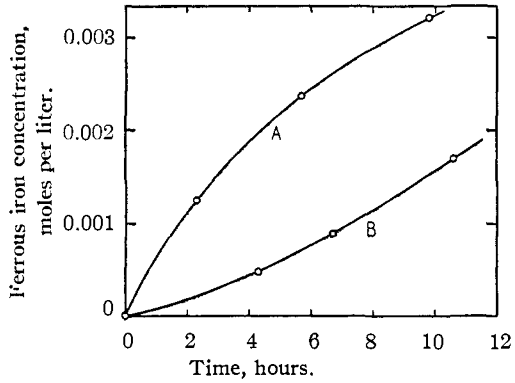

Fig. 3.—Sorbose–ferric iron systems: curve A, aqueous system; curve B, emulsion system.

With experimental verification of each step in the proposed "Redox" cycle completed, Experiment VII, involving the entire monomer free "Redox" system, was next considered. The reaction mixture of this experiment consisted of equal volumes of a chloroform phase, containing benzoyl peroxide and ferric stearate, and a water phase, containing sorbose, sodium stearate, and sodium pyrophosphate. The decomposition of benzoyl peroxide obtained in this experiment was moderate and uniform over an extended period, as shown by the data of Fig. 4. The desirability of this system is confirmed by its highly successful performance as a polymerization initiator.[9]

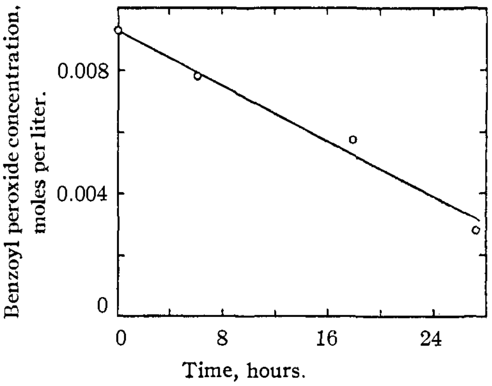

Fig. 4.—Peroxide decomposition for complete "Redox" system.

Two additional experiments involved interrupting certain steps in the "Redox" cycle to show that such interruptions result in almost complete breakdown of the mechanism leading to the decomposition of the benzoyl peroxide. Experiment VIII was equivalent to Experiment VII except that the pyrophosphate was eliminated. While this omission does not prevent the benzoyl peroxide-ferrous iron reaction from occurring, it renders difficult the transference of ferric iron from the organic to the water layer. The results of this experiment showed that, although some benzoyl peroxide did decompose, the rate of the decomposition was considerably reduced as compared with Experiment VII. Notwithstanding the small amount of benzoyl peroxide decomposition which occurred, the results are significant for the omission of the pyrophosphate does not positively assure the absence of small amounts of ferric iron in the water phase.

Experiment IX was also similar to Experiment VII, except that the reaction mixture initially contained a cationic emulsifying agent, benzyltrimethylammonium hydroxide, in place of sodium stearate. Here the only restriction placed on the system was to prevent the transfer of the ferrous iron from the water phase into the organic phase. The data for this experiment, appearing in Fig. 5, show that in the initial period no benzoyl peroxide decomposition occurred, even though the unrestricted sorbose-ferric iron reaction built up an appreciable ferrous iron concentration in the aqueous phase. At the end of 3.1 hours an amount of sodium stearate equivalent to 10% of the ferric iron originally present was added. Reaction immediately took place, giving rise to an abrupt drop in the benzoyl peroxide

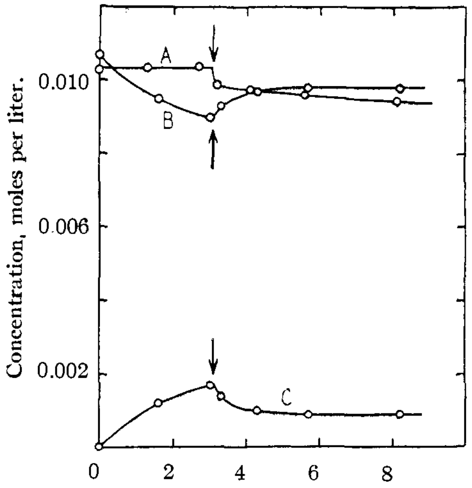

Fig. 5.—Peroxide-ferric iron–sorbose–pyrophosphate system with cationic emulsifier; soap added at time indicated by arrows: curve A, peroxide concn.; curve B, ferric iron concn.; curve C, ferrous iron concn.

concentration and an accompanying decrease in the ferrous iron concentration and increase in the ferric iron concentration. Following these adjustments the system approached a steady state in which the benzoyl peroxide concentration continued to decline at a slow rate while the ferrous and ferric iron concentrations became constant. This behavior can be readily interpreted in terms of the proposed "Redox" cycle. For given concentrations of benzoyl peroxide and sorbose, the rates of the various reactions will depend primarily upon the concentrations of the ferrous and ferric iron. But since the reaction which produces ferrous iron consumes ferric iron, and vice versa, it is obvious that the reaction system will approach a steady state in which the rates of the benzoyl peroxide–ferrous iron and the sorbose–ferric iron reactions become equal and the concentrations of the ferrous and ferric iron become constant.

Summary

A mechanism is proposed for the reduction activation of polymerizations in emulsion systems. It is found that ferrous iron, solubilized in the oil phase as the stearate, promotes the decomposition of benzoyl peroxide into free radicals which are capable of initiating polymerization. In this process the ferrous iron is oxidized to the ferric form which is subsequently transferred to the aqueous phase where it exists as a pyrophosphate complex. The ferric iron is then reduced by an appropriate water soluble reducing agent such as sorbose. The reduced ferrous iron is ultimately transferred back to the oil phase to resume the cycle.

Sodium stearate is used as an emulsifying agent, but it does more than promote emulsification since it also renders the iron salts oil soluble. Omitting any of the reagents mentioned above or replacing the soap by a cationic emulsifying agent which is incapable of solubilizing the iron in oil, disrupts the smooth operation of the cycle. The net result of the entire cycle is the reduction of organic peroxides into free radicals and acid ions by a reducing sugar with iron serving as the effective intermediary.

URBANA, ILLINOIS RECEIVED AUGUST 12, 1948

[CONTRIBUTION FROM GELATIN PRODUCTS DIV., R. P. SCHERER CORP.]

Absorption Spectra of Steroid–Antimony Trichloride Reaction Products[1]

BY ALEXANDER MUELLER

It has been reported by numerous workers that sterols give color reactions with various reagents.[2] The employment of antimony trichloride has been shown to give a greater specificity for quantitative determinations.[3] Examinations in this laboratory[4,5] have revealed that the spectra of the colors developed with the widely used antimony trichloride reagent are highly characteristic and have reasonably high extinction coefficients with magnitudes at specific wave length maxima directly related to the structure of the steroid molecule. Measurements on thirty-four steroids, mostly cholesterol derivatives, to confine the study to a homologous series, are reported in this communication. The interrelationships between molecular groupings and resulting spectra are summarized and the applicability of the measurements in characterization of molecular structure is indicated.

Experimental

A 1-ml. aliquot of the steroid[6] solution in purified chloroform was pipetted into a 25-ml., glass-stoppered cylinder, 10 ml. of antimony trichloride reagent[7] added, and the reaction mixture thoroughly shaken. The solution is poured into one pair of matched 10-mm. corex cells while the second or reference cell is filled with 1 ml. of chloroform and 10 ml. of antimony trichloride reagent. The absorption spectra were determined with a Beckman spectrophotometer, Model DU, using an incandescent lamp as the source of illumination and varying the slit width to accord with the region of the spectrum examined.

Throughout the measurements, reaction periods were determined with a stopwatch and optimum concentrations of steroid solutions were ascertained as the result of adjustments in preliminary trials. For additional manipulative details see reference.[5] From the optical densities determined for the solutions at the respective time intervals and wave length maxima, corresponding extinction coefficients, $E(1\%, 1\text{ cm.})$, were calculated. The values are summarized in the accompanying table and graphs.

Discussion

The compounds in Table I are arranged according to the following order: (1) saturated hydrocarbons with one or more substituents (excepting hydrogen) on Rings I and II; (2) one double bond with no substituents on Rings I and II; (3) one double bond with one substituent (such as hydroxy, keto, ester or halogen) on Rings I and II; (4) one double bond with two substituents on Ring I or II; (5) two double bonds with no substituents on Ring I or II; (6) two double bonds with one substituent on Ring I or II; (7) unclassified (calciferol and sex hormones).

Comparing the magnitude of absorption intensities of the various antimony trichloride reaction products, calciferol (Fig. 8), with an exo-

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(1) Presented in part before the Division of Organic Chemistry, American Chemical Society, Chicago, Illinois, September 9 to 13, 1946.

(2) Sobotka "The Chemistry of the Steroids," The Williams and Wilkins Co., Baltimore, 1938) has reviewed applications of the qualitative aspects.

(3) G. Pincus, *Endocrinology*, **32**, 176 (1943).

(4) A. Mueller, *Ind. Eng. Chem. Anal Ed.*, **18**, 214 (1946).

(5) F. W. Lamb, A. Mueller and G. W. Beach, *ibid.*, **18**, 187 (1946).

(6) The compounds examined were prepared in the Fine Chemicals Division of the R. P. Scherer Corp., and the purity verified by elemental analysis, melting point, optical rotation and ultraviolet absorption spectra.

(7) The solvent and reagent were prepared according to D. T. Ewing, G. V. Kingsley, R. A. Brown and A. D. Emmett, *Ind. Eng. Chem. Anal. Ed.*, **15**, 301 (1943).