THE INITIATION OF POLYMERISATION PROCESSES BY REDOX CATALYSTS

By R. G. R. BACON, A.R.C.S., PH.D.
(SENIOR LECTURER IN ORGANIC CHEMISTRY,
THE QUEEN'S UNIVERSITY OF BELFAST)

General Features

Historical.—In a monograph which appeared in 1937 [1] it was possible to tabulate some hundreds of published processes for polymerising olefinic compounds, but at that date, as the authors pointed out, the investigation of mechanisms of polymerisation had not reached a stage where an acceptable co-ordinating theory could be recognised. Subsequently the principles of polymerisation initiation by free-radical mechanisms [2, 3, 4, 5, 6] or by ionic mechanisms [6, 7, 8] became generally accepted. Redox-initiated polymerisations belong to the first category. Their study has contributed to the recognition in recent years that short-lived free radicals may be intermediates in many kinds of aqueous-phase reactions.

During the period 1920—1940 the use of catalytic amounts of peroxidic substances was found to be the most generally useful method for converting vinyl compounds and dienes, with reasonable rapidity, into polymers of high molecular weight. About 1940, workers in at least three industrial laboratories independently demonstrated that the polymerisation speeds which were customary with peroxides could be vastly increased by the use of mixtures of oxidising agents and reducing agents as initiators. In one laboratory this new technique was described as " reduction activation ",[9] but the terms " redox catalysis " and " redox polymerisation " are now in common use and they will be employed throughout this Review.

Descriptions of redox methods were not published until after the war. In 1946 the Reviewer described the effects of using mixtures of persulphate* with numerous reducing agents for the polymerisation of vinyl compounds in aqueous media,[9, 10] whilst Morgan described the effects of three-component

---

[1] Burk, Thompson, Weith, and Williams, " Polymerisation ", Reinhold, New York, 1937.

[2] For a general account of the polymerisation of olefinic compounds see, *e.g.*, Bawn, " The Chemistry of High Polymers ", Butterworths, London, 1948.

[3] Waters, " The Chemistry of Free Radicals ", Oxford Univ. Press, Oxford, 1946.

[4] " The Labile Molecule ", *Discuss. Faraday Soc.*, 1947, **2.**

[5] " The Reactivity of Free Radicals ", *ibid.*, 1953, **14.**

[6] Discussion on Macromolecules, *J.*, 1947, 252—306.

[7] Plesch, " Cationic Polymerisation ", Heffer, Cambridge, 1953.

[8] Pepper, *Quart. Rev.*, 1954, **8,** 88.

[9] Bacon, *Trans. Faraday Soc.*, 1946, **42,** 140.

[10] Imperial Chemical Industries Limited, with Bacon, Morgan, *et al.*, B.P. 573,270, 573,317, 573,366, 573,369, 574,449, 574,482, 575,616, 576,160, 583,166, 586,988, 599,472. *Note.* Apart from these and some other early examples (ref. 18), no attempt has been made, in this Review, to deal with the extensive patent literature which now exists.

* Throughout this Review the term " persulphate " will be used for the ion $S_2O_8{}^{2-}$ (peroxodisulphate).

initiators comprising persulphate, reducing agent, and heavy-metal salt.[11] At the same time, Baxendale, M. G. Evans, and their collaborators described their important associated investigations of vinyl polymerisations, which involved the hydrogen peroxide–ferrous salt system (Fenton's reagent).[12] In Germany, following an observation that fast polymerisations of 2-chlorobuta-1 : 3-diene (chloroprene) could be initiated by mixtures of oxygen and a reducing agent, a group of chemists studied several types of redox polymerisation processes between about 1940 and 1944. Some of their results were mentioned in F.I.A.T. reports [13] and the work was later fully reviewed by Kern.[14, 15, 16] In the U.S.A. the earliest investigations of redox polymerisations originated in an attempt to obtain synthetic rubbers by using catalysts which simulated the oxidation–reduction systems of enzymes in plant cells.[17, 18]

Most of the post-war investigations of redox polymerisations have been carried out in the U.S.A. and Canada. The types of redox systems principally studied there have been those which have found application in the North American synthetic rubber industry. Since this industry is based largely on a particular pair of monomers, butadiene and styrene, which are copolymerised in aqueous emulsion, some of the more important chemical features of this copolymerisation are summarised on p. 293.

The essence of redox polymerisation is that initiation occurs simultaneously with, and in consequence of, oxidation–reduction reactions between a system of catalyst components. The practical result is that polymerisations may occur so rapidly that it becomes feasible to conduct them at low temperatures, or with very small concentrations of initiators, or in equipment designed to function continuously. There may be consequential changes in the molecular weights and in the properties of the polymers produced. Redox techniques appear to be most effective in aqueous media, but they can be employed in organic solvents or in bulk monomers.

Redox systems which have been successfully used to initiate polymerisations are very numerous, and their number is probably capable of almost indefinite extension. The great variety of systems so far explored is one of the chief impressions to be gained from a study of the literature. The Reviewer has tried to demonstrate this variety in the present survey, which

---

[11] Morgan, *Trans. Faraday Soc.*, 1946, **42**, 169.

[12] Baxendale, Evans, and Park, *ibid.*, p. 155 ; see also refs. 27, 29, 50, and 51.

[13] F.I.A.T. Reports, 618, 717, 898, 916 (1945—1946) ; see also ref. 61.

[14] Kern, pp. 175—213, in F.I.A.T. Review of German Science, 1939—1946, " Preparative Organic Chemistry ", Part 3, edited by Ziegler, Dieterich, Wiesbaden, 1948 ; see also Konrad and Becker, *idem.*, pp. 229—238.

[15] Kern, reviews of German experimental work : (*a*) *Makromol. Chem.*, 1948, **1**, 209 ; (*b*) *ibid.*, p. 249 ; (*c*) *ibid.*, 1948, **2**, 48.

[16] Kern, discussions of polymerisation theory : (*a*) *ibid.*, 1948, **1**, 199 ; (*b*) *ibid.*, p. 229.

[17] Semon, XIth International Congress of Pure and Applied Chemistry, London, 1947.

[18] W. D. Stewart and B. F. Goodrich Co., U.S.P. 2,380,473—4—5—6—7, 2,380,617—8, 2,380,710, 2,383,425, 2,388,372—3.

deals with publications up to the early part of 1954. By that date there appeared to be a diminution in output, except in the patent literature. Many publications have concerned practical polymerisation "recipes", which have been arrived at semi-empirically. Their chemical complexity is such that their study does not readily lead to advances in fundamental redox-initiation theory. Contributions to the theory must be sought rather in that smaller proportion of the literature dealing with the simpler reaction systems.

There is no commonly accepted method of classifying redox initiators. On p. 294 *et seq.* they have been subdivided in accordance with the nature of their main oxidising component.

General Features of Redox Mechanisms.—(a) *Free-radical reaction theory.* The best-investigated type of redox initiator is a two-component system, comprised of a peroxidic oxidising agent and a reducing agent. With hydrogen peroxide, persulphate, or an organic peroxide as the oxidant, the primary step is usually formulated as a single-electron transfer, with cleavage of the –O–O– bond, to form a free radical. Thus, if the reducing agent is a metal ion, such as M^{2+} :

$$M^{2+} + RO{\cdot}OR \longrightarrow M^{3+} + RO\cdot + :OR^- \quad . \quad . \quad (1)$$

In the presence of a suitable monomer, $CH_2{:}CHX$, this process is followed by the usual stages of initiation, chain-propagation, and chain-termination : [19]

$$CH_2{:}CHX + RO\cdot \longrightarrow RO{\cdot}CH_2{\cdot}CHX\cdot \quad . \quad . \quad (2)$$

$$\begin{aligned} CH_2{:}CHX + RO{\cdot}CH_2{\cdot}CHX\cdot &\longrightarrow RO{\cdot}CH_2{\cdot}CHX{\cdot}CH_2{\cdot}CHX\cdot \\ &\longrightarrow RO{\cdot}[CH_2{\cdot}CHX]_n\cdot \quad . \quad . \quad (3) \end{aligned}$$

$$\begin{aligned} RO{\cdot}[CH_2{\cdot}CHX]_n\cdot + RO{\cdot}[CH_2{\cdot}CHX]_m\cdot &\longrightarrow \\ RO{\cdot}[CH_2{\cdot}CHX]_n{\cdot}[CHX{\cdot}CH_2]_m{\cdot}OR& \quad . \quad . \quad (4) \end{aligned}$$

Alternatively to (4), the growth of the polymer chain may be terminated by several other processes,[19] including radical-transfer with a sufficiently reactive molecule which may be present in the system, *e.g.* :

$$RO{\cdot}[CH_2{\cdot}CHX]_n\cdot + HA \longrightarrow RO{\cdot}[CH_2{\cdot}CHX]_n{\cdot}H + A\cdot \quad . \quad (5)$$

In such cases, HA could be a reducing component of a redox catalyst.

In competition with the initiation process (2) the radical ·OR may be consumed by reaction with M^{2+}, *i.e.*, the oxidation may go to completion as it would in the absence of monomer :

$$M^{2+} + \cdot OR \longrightarrow M^{3+} + :OR^- \quad . \quad . \quad . \quad (6)$$

The initiation may also be in competition with a reaction between ·OR and HB (representing any readily oxidisable substance which may be present) :

$$HB + \cdot OR \longrightarrow HOR + B\cdot \quad . \quad . \quad . \quad (7)$$

Steps (1) and (7) are commonly postulated when a redox mixture is employed as an oxidant instead of as a polymerisation catalyst.

The close relation (through the common intermediary ·OR) of polymerisation effects (2—4) with oxidation effects (7) has certain consequences.

---

[19] For a general account of these processes see Burnett, *Quart. Rev.*, 1950, **4**, 292.

Thus, evidence for reaction mechanisms, obtained from polymerisation processes, may be relevant to related oxidation processes, or *vice versa* ; a good example is provided by the hydrogen peroxide–ferrous ion system (p. 294). Another consequence, which does not appear to have been much developed as yet, is that systems which have been found effective as redox catalysts may find novel applications in preparative chemistry ; for example, unusual reactions have lately been effected by using mixtures of peroxidic oxidising agents and sodium hydrogen sulphite.[20] A related practical application, which has been appreciated since the discovery of redox catalysis, is that the ready response to polymerisation of a water-soluble monomer, like acrylonitrile, provides a sensitive means of detecting free radicals, whether formed as transient entities in oxidation processes or in other ways ; some aspects of the method have been discussed by Dainton.[21] An aqueous solution of acrylonitrile is convenient for this purpose since polymerisation is sharply marked by precipitation of polymer particles, which are readily isolable at any stage of the reaction.

(b) *Systems of three or more components.* The intervention of traces of impurities, and particularly of heavy-metal ions, is a familiar feature of oxidation–reduction processes. For example, adventitious traces of cupric ion very strongly accelerate the persulphate–thiosulphate reaction [22] and the persulphate-argentous ion–oxalate reaction.[23] The controlled addition of such supplementary catalysts to redox initiators was studied at an early stage in the investigations made in several laboratories and resulted, as expected, in a further increase in polymerisation rate.

Three-component systems commonly contain metal ions which may react with both the oxidising and reducing components of the system. The catalytic action of small amounts of the ion is thus apparently explained by the easy interconversion of its two forms :

$$\text{Peroxidic compound (P)} + \mathrm{M}^{2+} \longrightarrow \text{Reduced P} + \mathrm{M}^{3+} \quad . \qquad (8)$$

$$\text{Reducing agent (R)} + \mathrm{M}^{3+} \longrightarrow \text{Oxidised R} + \mathrm{M}^{2+} \quad . \qquad (9)$$

Examples of such systems are persulphate–cupric–thiosulphate [11, 22] and " cumene hydroperoxide "*–ferrous–reducing sugar.[24] Free radicals could be formed in processes (8) or (9) ; further sources of radicals are the direct reaction of peroxide and reducing agent, and the reaction of the latter with radicals formed in process (8). The elucidation of detailed mechanisms may clearly be very difficult. The difficulty is greater in the even more complex mixtures which, as pointed out in the last section, are often used

---

[20] Soloway and Friess, *J. Amer. Chem. Soc.*, 1951, **73,** 5000 ; Bamann and Schriever, *Chem. Ber.*, 1953, **86,** 996.

[21] Dainton, Tilden Lecture, *J.*, 1952, 1533.

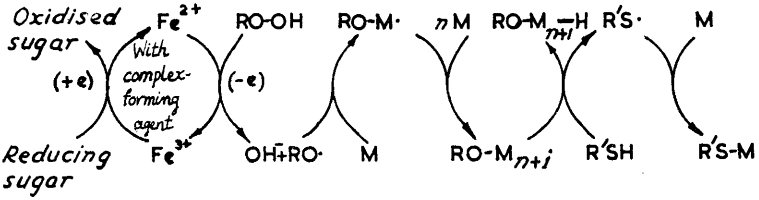
[22] King and Steinbach, *J. Amer. Chem. Soc.*, 1930, **52,** 4779 ; Sorum and Edwards, *ibid.*, 1952, **74,** 1204 ; cf. also ref. 11.

[23] King, *J. Amer. Chem. Soc.*, 1928, **50,** 2089 ; T. L. Allen, *ibid.*, 1951, **73,** 3589.

[24] Orr and Williams, *Canad. J. Chem.*, 1951, **29,** 949 ; this includes a review of the extensive earlier literature.

* Throughout this Review the compound αα-dimethylbenzyl hydroperoxide will be called " cumene hydroperoxide ", as in the original literature.

in manufacturing processes. A proposal has been made [25] to represent the interlinked processes of multicomponent systems with the curved-arrow symbolism which is used by biochemists to depict enzyme reactions ; a typical complicated type of redox-initiation then appears as :



(M represents monomer, R'SH a thiol)

An important aspect of the use of metals is that they frequently exist in solution as complex ions. Complexed forms have often been postulated as intermediates in redox reactions, as, for example, in the systems examined by King and Steinbach [22] and by Allen.[23] In other cases the reactivity of the metal may be deliberately modified by introducing it into the redox system in the form of a complex ion ; examples are the use of ferricyanide and of iron complexes with pyrophosphate (p. 303). Less conventional modes of metal-complexing are stressed in some recent developments in inorganic chemistry.[26] It is recognised that entities such as ferrous ion are inaccurately represented as bare ions and should properly be considered, when mechanisms are formulated, as solvated ions or members of ion-pairs. Furthermore, it appears that transfers of atoms or groups from complexes are plausible alternatives to electron transfer in some oxidation–reduction reactions which have been studied.

Some General Factors influencing Aqueous-phase Polymerisations.—Whatever the initiator used, the course of aqueous-phase polymerisations is influenced by a variety of factors which require brief comment before the effects specific to redox initiation are discussed.

Fundamental to all types of polymerisation is the effect of monomer structure on polymerisability, and the well-known differences which are observed in this respect with conventional peroxide initiators [2] appear to apply similarly to redox initiation. Thus, monomers of types $CH_2{:}CHX$ or $CH_2{:}CXY$ (X or Y being polar groups), such as acrylic and methacrylic compounds, or vinyl and vinylidene halides, or vinyl esters, undergo the fastest polymerisations, whilst styrene and diene hydrocarbons polymerise with moderate ease, and ethylene with difficulty.

Most common monomers have low water-solubility. For example, Evans and his co-workers studied the kinetics of polymerisation of methyl methacrylate (with Fenton's reagent as catalyst) in homogeneous aqueous solution at a concentration limited to about 0·1M.[27] This polymerisation

---

[25] Patrick, *J. Polymer Sci.*, 1952, **9**, 467.

[26] " Kinetics and Mechanism of Inorganic Reactions in Solution ", Chemical Society Special Publication, No. 1, 1954.

[27] Baxendale, Evans, and Kilham, *Trans. Faraday Soc.*, 1946, **42**, 668.

cannot be carried out with a much higher proportion of methacrylate unless the monomer is emulsified. By conducting the process with agitation, and in the presence of a suitable emulsifying agent, the monomer : water ratio being in practice perhaps 1 : 2, the initial emulsion of monomer droplets may be converted into a stable dispersion of polymer particles, often called a latex. The function of soaps and similar emulsifying agents in emulsion polymerisation has been extensively studied, especially for styrene and diene hydrocarbons. In modern theory, due particularly to Harkins,[28] two modes of action are distinguished. The dispersion systems are considered to be stabilised through the soap's forming adsorbed monolayers on the original monomer droplets, and on the final polymer particles, and on the monomer–polymer particles which exist at intermediate reaction stages. Secondly, soap micelles in the aqueous phase solubilise monomer molecules and provide centres where the initiation and propagation of polymerisation occur.

These considerations are relevant for a review of redox processes from two points of view. It frequently happens that the oxidant (for example, an organic peroxide) is soluble in the monomer phase but is practically insoluble in water, whilst the reducing agent is soluble in water but not in the monomer. The components of the redox system are thus separated, and their interaction is partly regulated by distribution and diffusion factors. Secondly, it seems possible that, in addition to functioning physically, emulsifying agents may sometimes show chemical reactivity towards an oxidant used as catalyst. Even when the system is initially a homogeneous solution, the presence of an emulsifying agent may profoundly affect the rate of polymerisation. Thus, in the case of the methyl methacrylate solutions to which reference has just been made, Evans observed [27] that small amounts of cetyltrimethylammonium bromide greatly increased the speed of the reaction. The kinetics, however, were unaffected and in this instance it was concluded [29] that the effect was physical, being due to the maintenance of the growing polymer chains in colloidal solution ; coagulation was prevented. In another case, Kolthoff and Miller showed [30] that when persulphate was present in aqueous soap solutions decarboxylation of the fatty acid occurred (cf. p. 302). It seems possible that free radicals thus formed from the soap may have an effect on the polymerisation of butadiene conducted in this system.[31] There are abundant data in technological literature to show that the success of emulsion polymerisations may vary greatly when the emulsifying agent (anionic, cationic, or non-ionic) is varied.[32] The cause of a particular effect can occasionally be traced (*e.g.*, to the chemical reactivity of certain unsaturated acids in the emulsify-

---

[28] Harkins, *J. Chem. Phys.*, 1945, **13,** 381 ; *J. Polymer Sci.*, 1950, **5,** 217.

[29] Baxendale, Evans, and Kilham, *ibid.*, 1946, **1,** 466.

[30] Kolthoff and Miller, *J. Amer. Chem. Soc.*, 1951, **73,** 5118.

[31] Kolthoff, Meehan, and Carr, *J. Polymer Sci.*, 1951, **7,** 577 ; cf. *idem, ibid.*, 1951, **6,** 73 ; cf. also ref. 87*a*.

[32] *E.g.*, Wilson and Pfau, *Ind. Eng. Chem.*, 1948, **40,** 530 ; Mast and Fisher, *ibid.*, 1949, **41,** 790 ; Azorlosa, *ibid.*, p. 1626 ; Helin, Gyenge, Beadell, Boyd, Mayhew, and Hyatt, *ibid.*, 1953, **45,** 1330.

ing agent), but commonly it is uncertain whether the effect is due to physical or to chemical causes, or to both.

In both redox and non-redox systems the dependence of polymerisation rates on pH is well known and has great practical importance. For example, with a typical redox catalyst (persulphate–sulphite) acrylonitrile required acid conditions, whilst the rate of vinyl chloride polymerisation showed a peak at pH 8, and styrene reacted at a fairly uniform rate except at high pH.[9] Explanations have been advanced in relatively simple cases. For example, it was suggested [33] that differences in the propagation rate for ionised and undissociated methacrylic acid account for the pH-dependence observed in the polymerisation of this monomer with persulphate as catalyst. In general however the significance of pH effects in relation to polymerisation mechanisms has not been explained. In an emulsion system, the pH range required for physical stability of the dispersion is a major factor influencing the choice of working conditions.

Finally, reference may be made to the numerous chemicals which influence polymerisation as " inhibitors " and " retarders " [34] and as " modifying agents ".[35] All appear to function by reacting with free radicals at some stage in a polymerisation process. Among inhibitors are substances, such as quinol or oxygen, which, under appropriate conditions, can act as components of redox initiators, and thereby promote polymerisation instead of retarding it. Among modifying agents are substances, particularly thiols, which may have a dual function in a polymerisation (see p. 301), acting both as chain-terminating agents and as redox components.

Butadiene–Styrene Copolymerisation.—General accounts of the application of redox catalysis to this industrially important reaction are included in two symposia.[36] Features of main chemical interest may be summarised as follows. It has long been known [37] that emulsion copolymerisation [38] of butadiene with styrene, in a weight ratio of about 3 : 1, yields polymers of high molecular weight with rubber-like properties. Intensive research has been carried out with numerous other monomers,[35] but butadiene–styrene copolymers still provide by far the most important synthetic substitutes for natural rubber. However, whereas the latter is a linear polyisoprene with regular 1 : 4-links, —CH_2·CMe:CH·CH_2—, and with exclusively *cis*-olefinic bonds, the copolymers are more net-like than linear and contain some 1 : 2-linked diene units, —CH_2·CH(CH:CH_2)— (typically about 20%), mixed with the 1 : 4-linked units, —CH_2·CH:CH·CH_2—, which may have *cis*- or *trans*-forms. These structural differences are

---

[33] Pinner, *J. Polymer Sci.*, 1952, **9**, 282 ; cf. Katchalsky and Blauer, *Trans. Faraday Soc.*, 1951, **47**, 1360.

[34] Bovey and Kolthoff, *Chem. Rev.*, 1948, **42**, 491 ; *J. Amer. Chem. Soc.*, 1948, **70**, 791 ; *J. Polymer Sci.*, 1950, **5**, 569.

[35] Starkweather, Bare, Carter, Hill, Hurka, Mighton, Sanders, Walker, and Youker, *Ind. Eng. Chem.*, 1947, **39**, 210.

[36] *Ibid.*, 1949, **41**, 1553—1632 ; 1952, **44**, 724—756.

[37] The essential features appear in B.P. 339,255 (1929) (I.G. Farbenind. A.G.).

[38] For general theory of copolymerisation see Alfrey, Bohrer, and Mark, " Copolymerization ", Interscience, New York, 1952.

reflected in the differing physical properties of the natural and synthetic materials.

When a simple catalyst, such as persulphate, is used, the copolymerisation is a fairly slow process, 12—24 hours being typical times required at 40—50°. The application of various redox methods enables moderately fast reactions to be effected at quite low temperatures. Redox methods and lower temperatures apparently do not appreciably lessen the proportion of 1 : 2-linkages,[39, 40] but *X*-ray data show the molecules to be more linear,[40, 41] and, on the whole, the physical properties approach more closely to those of natural rubber.[36] By using aqueous emulsions in which methanol, ethylene glycol, glycerol, etc., are present to prevent freezing, the redox-catalysed copolymerisations have been carried out at temperatures as low as − 40°. At 5°, which is a common operating temperature, hydroperoxide–ferrous ion–reducing agent systems enable reaction periods of 3—5 hours to be attained,[42, 43] and, with high concentrations of initiators,[43] or with initiators of high activity,[43a] polymerisations can be completed in less than half an hour. Further references will be made in the subsequent sections to butadiene–styrene copolymerisations.

Redox Catalysts containing Particular Oxidants

Hydrogen Peroxide.—In most investigations of redox systems containing hydrogen peroxide, this oxidant has been used in conjunction with iron salts, with which it reacts rapidly. It is believed that hydroxyl radicals are intermediates in these reactions, as well as in some other types of hydrogen peroxide decomposition. It may be noted that in certain circumstances the decomposition may be ionic in character; for example, a study of the kinetics of oxidation of unsaturated ketones by hydrogen peroxide, under alkaline conditions, indicated that the ion HO_2^- [cf. step (12)] is an intermediate.[44]

Numerous studies of the decomposition of hydrogen peroxide by iron salts or other compounds have shown the reaction steps to be complicated. The subject has been very fully reviewed by Baxendale[45] and, in some of its aspects, by Medalia and Kolthoff.[46] The step which is of chief concern here is the electron-transfer proposed by Haber and Weiss[47] for the initiation of decomposition by ferrous ions:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO\cdot + OH^- \qquad . \quad . \quad (10)$$

Their suggestions represented a development of Haber and Willstätter's

---

[39] Kolthoff, Lee, and Mairs, *J. Polymer Sci.*, 1947, **2**, 220.

[40] Johnson, Brown, and Bebb, *Ind. Eng. Chem.*, 1949, **41**, 1617.

[41] Johnson and Bebb, *ibid.*, p. 1577.

[42] Howland, Neklutin, Provost, and Mauger, *ibid.*, 1953, **45**, 1304.

[43] Pryor, Harrington, and Druesedow, *ibid.*, p. 1311.

[43a] Miller and Diem, *ibid.*, 1954, **46**, 1065.

[44] Bunton and Minkoff, *J.*, 1949, 665; cf. ref. 4, p. 207, and Waters, in Gilman's "Organic Chemistry", Vol. 4, Wiley, New York, 1953, p. 1171.

[45] Baxendale, *Adv. Catalysis*, 1952, **4**, 31.

[46] Medalia and Kolthoff, *J. Polymer Sci.*, 1949, **4**, 377.

[47] Haber and Weiss, *Naturwiss.*, 1932, **20**, 948; *Proc. Roy. Soc.*, 1934, *A*, **147**, 332.

theory[48] of free-radical mechanisms for reactions promoted by metal-containing enzymes. With excess of ferrous ion, the oxidation shown in step (10) is completed by :

$$Fe^{2+} + HO\cdot \longrightarrow Fe^{3+} + OH^- \quad . \quad . \quad . \quad (11)$$

Alternatively, with small amounts of iron, hydrogen peroxide is decomposed to oxygen. For this oxygen-producing reaction a sequence of steps, initiated by HO· (from 10) was postulated by Haber and Weiss[47] and, in a revised form, by Baxendale and his co-workers.[49] The same groups of workers[47, 49] investigated the decomposition of hydrogen peroxide to oxygen which occurs under the influence of ferric salts. The postulated first step is (12), involving production of the radical $HO_2\cdot$ from the ion HO_2^-, which is formed by dissociation of the peroxide :

$$H_2O_2 \rightleftharpoons HO_2^- + H^+$$
$$Fe^{3+} + HO_2^- \longrightarrow Fe^{2+} + HO_2\cdot \quad . \quad . \quad . \quad (12)$$

There is little information concerning the possible significance of ferric-catalysed decomposition of hydrogen peroxide for polymerisation processes.

Baxendale and Evans examined redox-catalysed polymerisations of vinyl compounds[12] in the light of the Haber–Weiss mechanism. They concluded that in catalysis by ferrous ion–hydrogen peroxide the monomer competes with ferrous ion for the hydroxyl radical produced in step (10) and that, when monomer is present in sufficient excess, step (11) is completely suppressed. The number of ferrous ions oxidised per molecule of peroxide fell from a maximum of two to a minimum of one when monomer concentration was increased from zero. Methyl acrylate proved somewhat less efficient than acrylonitrile in this competition for hydroxyl radicals. It was also demonstrated that oxidation of glycollic acid by the ferrous ion–hydrogen peroxide system was greatly reduced when acrylonitrile was polymerised in the same medium, this indicating that hydroxyl radicals are responsible for both polymerisation and oxidation. The proposed polymerisation mechanism for vinyl compounds (steps 1—4, $R = H$) was supported by the observed kinetics of methyl methacrylate polymerisation[27] and also by the agreement between measured molecular weights of the polymer and the values calculated, assuming mutual chain termination (step 4), from the amount of hydrogen peroxide decomposed.[50] Molecular weights of polystyrene, likewise prepared by initiation with this system, showed fairly similar values, when determined by osmotic-pressure measurements, as when calculated, again assuming mutual chain termination, from the content of hydroxyl end-groups.[51] End-group determination was carried out by reaction with methylmagnesium iodide but it was pointed out that this method has limited reliability because of inherent experimental difficulties.

Much evidence of other kinds may be quoted in support of the postulated

---

[48] Haber and Willstätter, *Ber.*, 1931, **64**, 2844.

[49] Barb, Baxendale, George, and Hargrave, *Trans. Faraday Soc.*, 1951, **47**, 462, 591.

[50] Baxendale, Bywater, and Evans, *ibid.*, 1946, **42**, 675.

[51] Evans, *J.*, 1947, 266.

initiation of polymerisation by hydroxyl radicals. The photolysis of hydrogen peroxide, for which the process : $H_2O_2 \xrightarrow{h\nu} 2\ {\cdot}OH$ was suggested in 1929,[52] can be used for the hydroxylation of olefinic bonds,[53] as in the reaction :

$$CH_2{:}CH{\cdot}CH_2{\cdot}OH + 2\ {\cdot}OH \rightarrow HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$$

When photolysis is carried out in presence of acrylonitrile, polymerisation occurs, as Dainton [54] and others have demonstrated. Dainton has also effected polymerisation by irradiating aqueous acrylonitrile solution with γ- or X-rays.[55] In this case his kinetic results suggested that reaction with a free radical was responsible for chain-termination, as well as for initiation. The presence of OH (or OD) end-groups was demonstrated by infrared absorption spectra.[21] The formation of hydrogen atoms and hydroxyl radicals from water by high-energy irradiation had previously been suggested by Weiss [56] who studied the behaviour of the resulting radicals in numerous chemical reactions.[57] Closely related to these various radiation experiments is the generation of radicals, including ·OH, by the photochemical excitation of ion-pairs (p. 307).

Finally, there is the evidence to be obtained by using the redox system, Fe^{2+}–H_2O_2 (Fenton's reagent) as an oxidant for organic molecules such as aromatic compounds and aliphatic hydroxy-acids (cf. the use of glycollic acid in Evans's experiments). The reagent has been used in preparative organic chemistry since 1894, and mechanisms of the resulting oxidations, which include oxidative coupling ($RH + {\cdot}OH \rightarrow R{\cdot} + H_2O$; $2R{\cdot} \rightarrow R{\cdot}R$), hydroxylation, and other processes have been well explored by Waters and others in recent years.[58] The data are consistent with the view that hydroxyl radicals are intermediates. Both the polymerisation and the oxidation reactions are subject to interference by atmospheric oxygen (cf. p. 306). Thus, Evans found [12] that oxygen was absorbed during the initiation of polymerisation of vinyl compounds by ferrous ion–hydrogen peroxide, and Kolthoff and Medalia found [59] that oxygen was absorbed during the oxidation of organic substrates such as alcohols.

Apart from the work of Evans's school, studies of hydrogen peroxide redox-catalyst systems are relatively few, partly because these catalysts are not the most efficient which can be used for polymerisations. Some experiments by Marvel [60] involving butadiene–styrene copolymerisation in emulsion at 50° showed big differences from the results obtained by Evans

---

[52] Urey, Dawsey, and Rice, *J. Amer. Chem. Soc.*, 1929, **51**, 1371.

[53] Milas, Kurz, and Anslow, *ibid.*, 1937, **59**, 543.

[54] Dainton, *J. Phys. Colloid Chem.*, 1948, **52**, 490.

[55] *Idem, Nature*, 1947, **160**, 268 ; Collinson and Dainton, " Radiation Chemistry ", *Discuss. Faraday Soc.*, 1952, **12**, 212.

[56] Weiss, *Nature*, 1944, **153**, 748.

[57] Weiss *et al.*, *J.*, 1949, 3241 and later papers.

[58] Waters, ref. 3 ; Waters *et al.*, ref. 4, p. 179 ; *J.*, 1949, 2427 and later papers; Weiss *et al.*, *ibid.*, p. 2074 and later papers ; Baxendale and Magee, ref. 5, p. 160.

[59] Kolthoff and Medalia, *J. Amer. Chem. Soc.*, 1949, **71**, 3777, 3784.

[60] Marvel, Deanin, Claus, Wyld, and Seitz, *J. Polymer, Sci.*, 1948, **3**, 350.

with vinyl compounds. Ferrous or ferric salts were equivalent in their activating effect on hydrogen peroxide; the activity of both kinds of salts was increased by complex-formation with pyrophosphate; and polymerisation did not begin for an hour, during which time the hydrogen peroxide completely disappeared and some organic peroxide was formed. Some examples of the initiation of butadiene–styrene copolymerisation by the three-component system hydrogen peroxide–ferrous ion–sorbose were briefly recorded by Kern.[15b] Other German workers reported that ammonia or aliphatic amines activated the polymerisation of *N*-vinylpyrrolidone initiated by hydrogen peroxide in aqueous solution.[61]

Polymerisation of methyl acrylate in acidic aqueous solution has recently been effected with mixtures of hydrogen peroxide and sodium nitrite.[62] Reaction appears to involve the intermediate formation of pernitrous acid, which decomposes to give hydroxyl radicals and nitrogen dioxide:

$$\mathrm{HO{\cdot}OH + HO{\cdot}NO \longrightarrow HO{\cdot}O{\cdot}NO + H_2O}$$
$$\mathrm{HO{\cdot}O{\cdot}NO \longrightarrow HO{\cdot} + NO_2}$$

This system acts both as a hydroxylating agent and a nitrating agent for aromatic nuclei.

Persulphates.—Persulphates, such as the potassium salt, $K_2S_2O_8$, are excellent polymerisation initiators in aqueous solution. By analogy with hydrogen peroxide, their activity could be attributed to sulphate radical-ions, $\cdot SO_4^-$, formed by homolytic fission:

$$\mathrm{^-O{\cdot}SO_2{\cdot}O{\cdot}O{\cdot}SO_2{\cdot}O^- \longrightarrow 2\ {}^-O{\cdot}SO_2{\cdot}O{\cdot}} \quad . \quad . \quad . \quad (13)$$

Some data relating to this process will be summarised before redox systems containing persulphate are considered.

The kinetics of persulphate decomposition in aqueous solution, which, in the absence of oxidisable or polymerisable substances, leads to oxygen evolution, have been studied by several workers. One of the most recent investigations, by Kolthoff and Miller,[63] included the use of a tracer technique, with $H_2{}^{18}O$, to discover the source of the evolved oxygen. A first-order, acid-catalysed reaction was found. It was suggested that oxygen-formation involved two paths: (*a*) through sulphate radical-ions and hydroxyl radicals; (*b*) in the case of acid-catalysed decomposition, through sulphur tetroxide (a known, but unstable compound), which was considered to give rise to oxygen, or, at high acid concentrations, to Caro's acid:

$$\begin{array}{lrcll}
(a) & \mathrm{S_2O_8{}^{2-}} & \longrightarrow & \mathrm{2\ {\cdot}SO_4{}^-} \quad . \quad . \quad . \quad . & (13) \\
 & \mathrm{{\cdot}SO_4{}^- + H_2O} & \longrightarrow & \mathrm{HSO_4{}^- + HO{\cdot}} \quad . \quad . \quad . & (14) \\
 & \mathrm{2HO{\cdot}} & \longrightarrow & \mathrm{H_2O + \tfrac{1}{2}O_2} & \\
(b) & \mathrm{S_2O_8{}^{2-} + H^+} & \longrightarrow & \mathrm{HS_2O_8{}^-} & \\
 & \mathrm{HS_2O_8{}^-} & \longrightarrow & \mathrm{HSO_4{}^- + SO_4} & \\
 & \mathrm{SO_4} & \longrightarrow & \mathrm{SO_3 + \tfrac{1}{2}O_2} &
\end{array}$$

Route (*a*) had previously been suggested by Bartlett and Cotman.[64]

---

[61] Fikentscher and Herrle, B.I.O.S. Report 354, Item 22.

[62] Halfpenny and Robinson, *J.*, 1952, 928, 939.

[63] Kolthoff and Miller, *J. Amer. Chem. Soc.*, 1951, **73**, 3055.

[64] Bartlett and Cotman, *ibid.*, 1949, **71**, 1419.

Several other workers have suggested $\cdot SO_4^-$ as an intermediate when discussing mechanisms of polymerisation or oxidation promoted by aqueous persulphate. On the other hand Levitt, studying the oxidation of thiols,[65] has suggested sulphur tetroxide as the intermediate for oxygen-formation, oxidation, and polymerisation, and has further proposed its generation by the process :

$$S_2O_8^{2-} \longrightarrow SO_4^{2-} + SO_4$$

His views have been contested by Eager and McCallum.[65a]

Steps (2—4) ($OR = SO_4^-$) would result in the incorporation of sulphate end-groups in polymers of high molecular weight. This has been detected by using isotopically labelled persulphate, $K_2{}^{35}S_2O_8$, as catalyst [66] in chloroprene polymerisation, but only to the extent of one group per 8—17 polymer molecules. Two sulphate groups per molecule were indicated by results from polystyrene.[67] Failure of a similar demonstration when tetrafluoroethylene was the monomer was attributed to ready hydrolysis of sulphate from $\cdot CF_2 \cdot SO_4H$ groups.[68] There is some uncertainty about these experiments, especially in their quantitative aspects, because of the low sulphur contents of the polymers and because of the difficulty of removing adsorbed impurities from them. Good evidence for sulphate end-groups resulted from a study of persulphate-initiated emulsion polymerisation of allyl acetate, which gave chains containing only fourteen monomer units ; 75% of the value calculated for one sulphate group per molecule was recorded.[69] If ethylene is subjected to the action of aqueous persulphate it forms even shorter polymers, with two or more monomer units, and these molecules have been found to contain sulphate, sulphonate, or hydroxyl groups.[70] When persulphate is used to oxidise organic molecules it occasionally forms isolable organic sulphates, as in the Elbs persulphate reaction,[71] but more generally it leads to oxidatively coupled products, or to products which are hydroxylated or otherwise oxygenated. In the latter reactions, as also in cases where the presence of hydroxyl may be claimed in polymers prepared with persulphate, there is uncertainty as to the steps by which the hydroxyl is introduced. It could arise, for example, by hydrolysis of an initially formed sulphate, or step (14) might occur, the hydroxyl radical then becoming the entity responsible for oxidation or polymerisation.

From the time when the mechanism of redox catalysis first came under discussion the formation of the sulphate radical-ion by electron-transfer between persulphate and reducing agent has been considered.[72] If, analogously to the reaction between persulphate and reducing agent, electron-

---

[65] Levitt, *Canad. J. Chem.*, 1953, **31,** 915.

[65a] Eager and McCallum, *ibid.*, 1954, **32,** 692.

[66] Mochel and Peterson, *J. Amer. Chem. Soc.*, 1949, **71,** 1426.

[67] W. V. Smith and Campbell, *J. Chem. Phys.*, 1947, **15,** 338 ; W. V. Smith, *J. Amer. Chem. Soc.*, 1949, **71,** 4077.

[68] Berry and Peterson, *ibid.*, 1951, **73,** 5195.

[69] Bartlett and Nozaki, *J. Polymer Sci.*, 1948, **3,** 216.

[70] Hopff, Goebel, and Kern, *Makromol. Chem.*, 1950, **4,** 240 ; cf. ref. 90.

[71] Sethna, *Chem. Rev.*, 1951, **49,** 91.

[72] *E.g.*, Discussion on Oxidation, *Trans. Faraday Soc.*, 1946, **42,** 190—197.

transfer were to occur between persulphate and monomer, then, instead of (13) as the primary step in ordinary persulphate initiation, the following process could be postulated :

$$S_2O_8^{2-} + M \longrightarrow (^{-}SO_4\text{-}M\cdot) + \cdot SO_4^{-} \quad . \quad . \quad . \quad (15)$$

To test this, Kolthoff [73] studied the persulphate-catalysed polymerisation of allyl acetate in presence and absence of simple alcohols. From his results, taken in conjunction with Bartlett's,[64] an argument was developed to show that step (15) does not occur.

The Reviewer reported [9] that the persulphate-initiated polymerisation of vinyl compounds is very greatly accelerated by compounds which react with persulphate, including metals, oxidisable metal salts, hydrazine and hydroxylamine, hydrogen sulphide and thiols, salts of various oxy-acids of sulphur, such as sulphite, dithionite, and thiosulphate, and polyhydric phenols. Similar observations were made in Germany.[14, 15] One of the best-investigated of such redox systems is ferrous ion–persulphate. Both Kolthoff [74] and Williams [75] have investigated the kinetics and have postulated the primary process :

$$Fe^{2+} + S_2O_8^{2-} \longrightarrow Fe^{3+} + SO_4^{2-} + \cdot SO_4^{-} \quad . \quad . \quad (16)$$

In the absence of other reactive substances, the oxidation is completed by the step :

$$Fe^{2+} + \cdot SO_4^{-} \longrightarrow Fe^{3+} + SO_4^{2-}$$

In the presence of a monomer (Williams used acrylonitrile) the sulphate radical-ion is diverted to polymerisation initiation (steps 2—4 ; $OR = SO_4^{-}$), or, in the presence of an oxidisable substrate (Kolthoff used ethanol or glucose), it is diverted to the hydrogen-abstraction step with which oxidation is believed to begin :

$$RH + \cdot SO_4^{-} \longrightarrow R\cdot + SO_4H^{-} \quad . \quad . \quad . \quad (17)$$

As with the ferrous ion–hydrogen peroxide system, the ferrous ion–persulphate reaction induces consumption of atmospheric oxygen. Bromide or chloride ions suppress oxidation of a substrate,[74] presumably by competing for the radical-ions :

$$\begin{aligned} \cdot SO_4^{-} + Br^{-} &\longrightarrow SO_4^{2-} + Br\cdot \\ Fe^{2+} + Br\cdot &\longrightarrow Fe^{3+} + Br^{-} \end{aligned}$$

Merz and Waters [76] had previously studied the action of both the ferrous ion–hydrogen peroxide and the ferrous ion–persulphate system in the oxidation of alcohols, and had pointed out the similarity of the primary processes (10) and (16). Kolthoff differed from their conclusions with respect to the steps succeeding (17), which result in the conversion of the radical from the alcohol (R = *e.g.* $CH_3\cdot\dot{C}H\cdot OH$) into aldehyde.

The system argentous ion–persulphate provides another useful redox catalyst for vinyl polymerisations.[9, 11] Small accelerating effects have

---

[73] Kolthoff, Meehan, and Carr, *J. Amer. Chem. Soc.*, 1953, **75**, 1439.

[74] Kolthoff, Medalia, and Raaen, *ibid.*, 1951, **73**, 1733.

[75] Fordham and Williams, *ibid.*, p. 4855.

[76] Merz and Waters, ref. 4, p. 179.

been reported for it in the emulsion polymerisation [77] of butadiene. In the light of data available at the time, Morgan suggested [11] that the reactive entity in this system might be the hydroxyl radical, but from subsequent developments it appears simpler to formulate the primary steps as giving the sulphate radical-ion, analogously to the iron reaction :

$$\begin{aligned} Ag^+ + S_2O_8{}^{2-} &\longrightarrow Ag^{2+} + SO_4{}^{2-} + \cdot SO_4{}^- \\ Ag^{2+} + S_2O_8{}^{2-} &\longrightarrow Ag^{3+} + SO_4{}^{2-} + \cdot SO_4{}^- \end{aligned}$$

There is evidence from many sources for the existence of bi- and ter-valent silver salts [78] and Yost suggested some time ago [79] that these higher-valency ions are intermediates in silver-catalysed oxidation by persulphate of manganous, chromic, and vanadous ion, ammonia, and hydrazine. It has been known for some time that silver salts possess a strong catalytic action in the persulphate oxidation of organic compounds. The use of this reaction has recently been extended [80] in various directions. As with Fenton's reagent, and with uncatalysed persulphate oxidations, the products may be the result of oxidative coupling, or may show hydroxylation and other forms of oxygenation. There is evidence that, in some cases at least, sulphates may be the intermediates which lead to oxygen-containing end-products ; for example, in the following reaction [81] the *iso*propyl hydrogen sulphate is stable enough to be obtained in about 70% yield :

$$\begin{aligned} CHMe_2{\cdot}CO_2H &\xrightarrow{S_2O_8{}^{2-}/Ag^+} CHMe_2{\cdot}SO_4H + CO_2 \\ CHMe_2{\cdot}SO_4H + H_2O &\longrightarrow CHMe_2{\cdot}OH + H_2SO_4 \end{aligned}$$

An uncertain feature of these silver-catalysed oxidations is the reactivity of the higher-valency silver ions. There are reasons for suspecting that they are able to act directly as oxidants, Ag^+ thereby being regenerated. Similarly Ag^{2+} or Ag^{3+} may be able to initiate polymerisations (cf. p. 310) ; here too the mechanisms are uncertain.

There is also a good deal of work, not of a highly quantitative character, concerning the use of complex salts of heavy metals as activating agents for persulphate-initiated polymerisations ; examples are ferricyanide [35] and various cobalt complexes.[82] Little is known about the chemistry of these processes, which are complicated by the fact that some multivalent metal ions appear to be able to initiate polymerisation without the aid of peroxidic compounds (cf. p. 310).

Thiols are the best-investigated of non-metal activating agents for

---

[77] Rainard, *J. Polymer Sci.*, 1947, **2**, 16.

[78] Kleinberg, " Unfamiliar Oxidation States ", University of Kansas Press, Lawrence, U.S.A., 1950.

[79] Yost, *J. Amer. Chem. Soc.*, 1926, **48**, 152 ; Dekker, Lévy, and Yost, *ibid.*, 1937, **59**, 2129.

[80] Bacon, Bott, Doggart, Grime, and Munro, *Chem. and Ind.*, 1953, 897 ; Bacon, Grime, and Munro, *J.*, 1954, 2275.

[81] Bacon and Bott, *Chem. and Ind.*, 1953, 1285.

[82] Marvel, Inskeep, Dearborn, Saunders, Johnston, Shepherd, Deutschman, Damman, and Oppegard, *J. Polymer Sci.*, 1948, **3**, 181.

persulphate, but principally in relation to butadiene–styrene copolymerisation. Thiols were introduced as " modifiers " for this reaction before the advent of redox catalysts and their function was explained [83] as restriction of polymer growth through radical transfer (step 5) :

$$X{\cdot}[CH_2{\cdot}CHX]_n{\cdot} + RSH \longrightarrow X{\cdot}[CH_2{\cdot}CHX]_n{\cdot}H + RS{\cdot}$$

This releases a thiol radical, which is believed capable of initiating further polymerisation :

$$CH_2{:}CHX + RS{\cdot} \longrightarrow RS{\cdot}CH_2{\cdot}CHX{\cdot}$$

There is a considerable literature [3] concerning the reactivity of thiol radicals, *e.g.*, towards olefinic bonds. It is noteworthy that they cause polymerisation [84] when generated, in presence of acrylonitrile, by photolysis of disulphides ($RS{\cdot}SR \longrightarrow 2\ RS{\cdot}$), a reaction which recalls the behaviour of hydrogen peroxide. Kolthoff has shown [85] that thiols not only modify the properties of the polymer but also increase polymerisation speed. The effect varies with the structure of the thiol and was found to be greatest for dodecanethiol. It appears uncertain to what extent this " promoter " action is due to direct reaction between thiol and persulphate. This process has been suggested for the initiation of chloroprene polymerisation.[66] Eager and Winkler [86] studied the kinetics of the thiol–persulphate reaction in homogeneous aqueous solution and formulated it as :

$$S_2O_8{}^{2-} \underset{}{\overset{\text{(Slow)}}{\rightleftharpoons}} 2\ {\cdot}SO_4{}^-$$

$$RSH + {\cdot}SO_4{}^- \xrightarrow{\text{(Fast)}} RS{\cdot} + SO_4H^-$$

Levitt [65] regarded sulphur tetroxide as the reactive intermediate in this reaction. However, the reactions which may occur in the typical system : monomer–soap–persulphate–thiol are complicated and include, as shown by Kolthoff,[87] addition of the thiol to the olefinic bond of the monomer and the formation of disulphides, $(RS)_2$. Various related sulphur compounds, such as thiol-esters, $RS{\cdot}COR'$,[88] and diaroyl disulphides, $(S{\cdot}COR)_2$,[89] may successfully replace simple thiols in the copolymerisation of butadiene and styrene.

While this Review was being prepared for the press, Kolthoff reported a long and difficult investigation which has led to some revision of his previously published views.[87a] Like some earlier workers, he used persulphate containing radioactive sulphur as a tracer and applied it to the emulsion polymerisation of styrene in the presence of dodecane-1-thiol. The results indicate that the free radicals responsible for the initiation

---

[83] Snyder, J. M. Stewart, R. E. Allen, and Dearborn, *J. Amer. Chem. Soc.*, 1946, **68,** 1422 ; Wall, Banes, and Sands, *ibid.*, p. 1429.

[84] Birch, Cullum, and Dean, *J. Inst. Petroleum,* 1953, **39,** 206.

[85] Kolthoff and Harris, *J. Polymer Sci.*, 1947, **2,** 41, 49, 72, 82.

[86] Eager and Winkler, *Canad. J. Res.*, 1948, **26,** *B*, 527.

[87] Kolthoff and Miller, *J. Amer. Chem. Soc.*, 1952, **74,** 4419.

[87a] Kolthoff, O'Connor, and Hansen, *J. Polymer Sci.*, 1955, **15,** 459.

[88] Frank, Drake, P. V. Smith, and Stevens, *ibid.*, 1948, **3,** 50.

[89] Frank, Blegen, and Deutschman, *ibid.*, p. 58.

reaction are provided solely by the dissociation of persulphate ions; there appears to be no contribution, at the initiation stage, due to free radicals from reaction of persulphate with thiol, or with fatty acid, or with monomer (as in the hypothetical step 15).

The system persulphate–sulphite (or –hydrogen sulphite) is a convenient and potent redox catalyst for vinyl compounds [9] and has been successfully used for butadiene copolymerisations; [90] little is known about the mechanisms involved. The activating effect is enhanced by small amounts of heavy-metal ions, such as iron (used, *e.g.*, for tetrafluoroethylene [68]) and silver (used, *e.g.*, for chlorotrifluoroethylene [91]). In the case of tetrafluoroethylene [68] the labelled reagents, $K_2{}^{35}S_2O_8$ and $NaH^{35}SO_3$, were used and the resulting polymer end-groups examined. It was concluded that, in decreasing order of effectiveness, radical-producing reactions were:

$$Fe^{2+} + S_2O_8{}^{2-} \longrightarrow Fe^{3+} + SO_4{}^{2-} + \cdot SO_4{}^- \quad . \quad (16;\ \text{cf. } 8)$$

$$Fe^{3+} + HSO_3{}^- \longrightarrow Fe^{2+} + HSO_3\cdot \quad (\text{cf. } 9)$$

$$S_2O_8{}^{2-} + HSO_3{}^- \longrightarrow SO_4{}^{2-} + \cdot SO_4{}^- + HSO_3\cdot$$

The related system, persulphate–thiosulphate, studied by Morgan,[11] is an effective polymerisation catalyst and is greatly enhanced in activity by a suitable third component, such as small amounts of the ions cupric, ferrous, or iodide. Morgan was unable to formulate a precise mechanism, whilst Bunn [92] advanced a tentative scheme with the primary step:

$$S_2O_8{}^{2-} + S_2O_3{}^{2-} \longrightarrow SO_4{}^{2-} + \cdot SO_4{}^- + \cdot S_2O_3{}^-$$

but he encountered difficulties in interpreting the kinetic data.

Diacyl Peroxides.—There is much well-known evidence [3] for the formation of free radicals, $R\cdot CO_2\cdot$ or $R\cdot$, by the thermal dissociation of diacyl peroxides, $(R\cdot CO\cdot O)_2$. Benzoyl peroxide, $(Ph\cdot CO\cdot O)_2$, and allied compounds have long been used [1] as polymerisation catalysts, sometimes in aqueous emulsions, but more particularly for undiluted monomer or for solutions of monomer in organic solvents. Used alone, their activity in aqueous media is generally much less than that of persulphates, but, as reported by Kern,[14, 15a, 15b] German investigators found them to be very effective when used in redox systems, in both aqueous and non-aqueous media, and with or without a heavy-metal salt as a third catalytic component. Like Evans, Kern based his theory of the reaction on Haber's earlier suggestions [48] and formulated the production of radicals as an electron-transfer process; *e.g.*, for a three-component catalyst (YH_2 = reducing agent):

$$Fe^{2+} + (R\cdot CO\cdot O)_2 \longrightarrow Fe^{3+} + R\cdot CO\cdot O^- + R\cdot CO\cdot O\cdot$$

$$Fe^{3+} + YH_2 \longrightarrow Fe^{2+} + YH\cdot + H^+$$

$$Fe^{3+} + YH\cdot \longrightarrow Fe^{2+} + Y + H^+$$

$$R\cdot CO\cdot O\cdot + YH_2 \longrightarrow R\cdot CO\cdot OH + YH\cdot,\ \text{etc.}$$

For cases where the reducing agent (*e.g.*, a tertiary amine) was incapable of converting ferric into ferrous ion, the metal was presumed to function by complex-formation (involving either Fe^{2+} or Fe^{3+}) with the reducing

---

[90] *E.g.*, Willis, *Ind. Eng. Chem.*, 1949, **41**, 2272.

[91] Hamilton, *ibid.*, 1953, **45**, 1347.

[92] Bunn, ref. 72, p. 190.

agent, whereby the reactivity of the latter towards the oxidant was increased :[93]

$$\begin{aligned} Fe^{2+} + XH &\rightleftharpoons Fe^{2+}(XH) \\ Fe^{2+}(XH) + (R{\cdot}CO{\cdot}O)_2 &\rightarrow Fe^{2+}(X) + R{\cdot}CO{\cdot}O{\cdot} + R{\cdot}CO{\cdot}OH \\ Fe^{2+}(X) &\rightleftharpoons Fe^{2+} + X \end{aligned}$$

Polymer-chain initiation appears to be due to the radicals $R{\cdot}CO{\cdot}O{\cdot}$, since Kern showed,[94] for the polymerisation of styrene or 2 : 3-dimethylbuta-1 : 3-diene, using *p*-bromobenzoyl peroxide to provide a labelling atom, that the number of *p*-bromobenzoate end-groups was the same for the redox system peroxide–ferric ion–benzoin as it was when the peroxide was the sole initiator.

The German investigations of emulsion copolymerisation of butadiene and styrene with diacyl peroxide systems were repeated and extended by Marvel[95] and by Johnson and Bebb.[96] These reactions are very sensitive to small changes in components and procedure ; optimum conditions are determined empirically and vary from one monomer to another. As an example of reaction rates attainable, 80% polymerisation may be effected in 3 hours at 30°. Many different diacyl peroxides are effective, including some, such as acetyl peroxide, which are water-soluble. Thus, separation of peroxide and reducing agent in different phases is not essential. α-Ketols, containing the system $\cdot CO{\cdot}CH(OH)\cdot \rightleftharpoons \cdot C(OH){:}C(OH)\cdot$, are especially effective as the reducing-agent components ; examples are benzoin, dihydroxyacetone, or, preferably, ketoses, such as sorbose and fructose. It has been suggested that the sugars may undergo alkali-induced fission, to give simpler reducing agents, but, in any case, the oxidative degradation of sugars by mixtures of peroxides and iron salts is a known reaction. Metal-ion catalysis of the peroxide–sugar reaction appears to be restricted to iron and cobalt salts. Ferrous salts can also be used effectively in the absence of sugars ; *i.e.*, the catalyst system may be acyl peroxide–ferrous ion. The emulsion-polymerisation is conducted in an alkaline medium, but is markedly sensitive to pH ; an optimum rate has been reported at pH 8·5. Under alkaline conditions iron would be precipitated, but it is maintained as a soluble complex by adding pyrophosphate, or other complexing agent, the use of which is essential in order for effective catalysis to occur. Part of the iron is believed to be present as a ferrous soap, which is produced by reaction with the emulsifying agent, and which is soluble in the monomer. The chemistry of emulsion-polymerisations containing the redox system benzoyl peroxide–iron pyrophosphate–sorbose was examined by Wall and Swoboda,[97] who suggested that the essential reaction occurs between peroxide and ferrous soap in the monomer droplets, but Kolthoff,[98] in a later

---

[93] Details of the change XH → X are not given ; for a more specific treatment of a similar type of reaction see ref. 117.

[94] Kern, Schulz, and Stallmann, *Makromol. Chem.*, 1951, **6**, 216.

[95] Marvel, Deanin, Overberger, and Kuhn, *J. Polymer Sci.*, 1948, **3**, 128 ; Marvel, Deanin, Kuhn, and Landes, *ibid.*, p. 433.

[96] Johnson and Bebb, *ibid.*, p. 389.

[97] Wall and Swoboda, *J. Amer. Chem. Soc.*, 1949, **71**, 919.

[98] Kolthoff and Youse, *ibid.*, 1950, **72**, 3431.

examination of the system, suggested that the locus of this reaction is the monomer present in the soap micelles.

Benzoyl peroxide provides the best-known illustration of an initiator responding to redox-activation in non-aqueous polymerisation media. The reported examples, which come mainly from the German investigators [14, 15a, 15b] represent relatively simple reaction systems, which could profitably be further investigated. The bulk-polymerisation of several vinyl compounds and dienes, initiated by benzoyl peroxide, was found to be strongly accelerated by various reducing agents, such as sulphinic acids, α-ketols, formic acid, thiols, hydrazines, and tertiary amines.[99] The activity of such systems could be enhanced by incorporating some soluble metal compounds as third components. The relative efficiency of the metals was somewhat dependent on the type of metal derivative used. In the case of metal naphthenates, the reported order of activity was as follows, with lead, surprisingly, showing the biggest effect:

$$Pb > Fe > Co > Ni > Mn > Cu > Zn > Ce$$

Hydroperoxides.—The preparation and reactions of organic hydroperoxides, RO•OH, have been reviewed by Hawkins.[100] They have been much studied as polymerisation catalysts since 1948, when "cumene hydroperoxide", $Ph{\cdot}CMe_2{\cdot}O{\cdot}OH$, was reported [101] to be a very active catalyst in redox systems for butadiene–styrene copolymerisation. This compound has continued to be the main subject of later work, though still greater catalytic activity has been found in some related hydroperoxides, such as compounds of the type p-$X{\cdot}C_6H_4{\cdot}CMe_2{\cdot}O{\cdot}OH$, where X is chlorine, *iso*propyl, *tert.*-butyl, etc.[102] Cumene hydroperoxide is water-soluble to the extent of 0·0914M at 25°,[103] and it is therefore distributed between both fluid phases in emulsion polymerisation.

Kharasch, who has carried out extensive studies of hydroperoxides,[104] has shown that the cumene derivative can be decomposed in several ways, involving either free-radical or ionic mechanisms, and giving a variety of end-products. Its thermal decomposition in solution is autocatalytic and occurs, depending on the solvent, in the range 70—130°, to give either free radicals or ions.[105] Williams found that in styrene solution the decomposition temperature can be lowered to 30° by adding salts or complexes of various heavy metals, but it seems that the metal does not necessarily undergo a valency change. Williams suggested that this decomposition is ionic, for practically no polystyrene was formed.[106] Several investigators

---

[99] For further data on the use of amines see Horner and Schwenk, *Kunststoffe*, 1949, **39**, 292; *Angew. Chem.*, 1949, **61**, 411; *Annalen*, 1950, **566**, 69; see also ref. 117.

[100] Hawkins, *Quart. Rev.*, 1950, **4**, 251.

[101] Vandenberg and Hulse, *Ind. Eng. Chem.*, 1948, **40**, 932.

[102] Wicklatz, Kennedy, and W. B. Reynolds, *J. Polymer Sci.*, 1951, **6**, 45; Fryling and Follett, *ibid.*, p. 59.

[103] Kolthoff and Medalia, *J. Amer. Chem. Soc.*, 1949, **71**, 3789.

[104] Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, 1950, **15**, 748, and later papers by Kharasch *et al.*

[105] *Idem, ibid.*, 1951, **16**, 113; Fordham and Williams, *Canad. J. Res.*, 1949, **27**, *B*, 943.

[106] *Idem, ibid.*, 1950, **28**, *B*, 551.

have examined the reaction which readily occurs between the peroxide and ferrous salts at ordinary temperatures and have formulated the primary step, in the usual manner, as a one-electron transfer :[107]

$$Fe^{2+} + PhCMe_2{\cdot}O{\cdot}OH \longrightarrow Fe^{3+} + PhCMe_2{\cdot}O{\cdot} + OH^-$$

On the other hand, Williams has suggested,[108] on the basis of kinetic data obtained with the hydroperoxide from *iso*propyl- or *tert.*-butyl-cumene, that this decomposition occurs with intermediate complex-formation :

$$Fe^{2+} + RO{\cdot}OH \longrightarrow \underset{\overset{\cdot\cdot}{Fe^{2+}}}{RO{\cdot}OH} \longrightarrow RO{\cdot} + \underset{\overset{\cdot\cdot}{Fe^{2+}}}{{\cdot}OH}$$

Formation of RO· radicals in the reaction between *tert.*-butyl hydroperoxide (or other hydroperoxides) and ferrous salt is indicated by the fact that, with butadiene present, compounds such as $Bu^tO{\cdot}[CH_2{\cdot}CH{:}CH{\cdot}CH_2]_2{\cdot}OBu^t$ are obtained.[109]

The radicals formed from cumene hydroperoxide can initiate polymerisation, can induce decomposition of further peroxide, can oxidise an organic substrate, or can induce oxidation by atmospheric oxygen.[107] These features are similar to those of ferrous ion–hydrogen peroxide or –persulphate systems in aqueous media, but, under appropriate conditions, some differences from these systems may appear. For example, in alkaline media the decomposition may have an ionic character.[110] Also, with cobalt as catalyst, there is evidence[111] for generation of the radical $PhCMe_2{\cdot}O{\cdot}O{\cdot}$, attributed to the process :

$$Co^{2+} + PhCMe_2{\cdot}O{\cdot}OH \longrightarrow Co^{3+} + PhCMe_2{\cdot}O{\cdot} + OH^-$$
$$Co^{3+} + PhCMe_2{\cdot}O{\cdot}OH \longrightarrow Co^{2+} + PhCMe_2{\cdot}O{\cdot}O{\cdot} + H^+$$

The general features of the three-component system, cumene hydroperoxide–ferrous ion–sugar,[24, 112] which has been much used in butadiene–styrene copolymerisation, are similar to those which have been discussed for corresponding systems containing benzoyl peroxide. Besides pyrophosphate, other agents, such as ethylenediaminetetra-acetic acid, have been employed to form complexes with the iron.[113] Diverse reducing agents, such as dihydroxyacetone, sodium sulphide, hydrazine, and sodium formaldehyde sulphoxylate, have been used, in conjunction with iron salts, as alternatives to sugars.[114] Another variation is provided by some catalysts

---

[107] Kolthoff and Medalia, ref. 103 ; Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, 1950, **15,** 763 ; Fordham and Williams, *J. Amer. Chem. Soc.*, 1950, **72,** 4465 ; 1951, **73,** 1634.

[108] Orr and Williams, *Canad. J. Chem.*, 1952, **30,** 985.

[109] Kharasch, Arimoto, and Nudenberg, *J. Org. Chem.*, 1951, **16,** 1556.

[110] Fordham and Williams, ref. 107 ; Frank, *Chem. Rev.*, 1950, **46,** 155.

[111] Kharasch, Fono, Nudenberg, and Bischof, *J. Org. Chem.*, 1952, **17,** 207 ; Kharasch, Pauson, and Nudenberg, *ibid.*, 1953, **18,** 322.

[112] Kolthoff and Medalia, *J. Polymer Sci.*, 1950, **5,** 391 ; Kolthoff, Medalia, and Youse, *ibid.*, 1951, **6,** 93.

[113] Mitchell, Spolsky, and Williams, *Ind. Eng. Chem.*, 1949, **41,** 1592.

[114] Kolthoff and Medalia, *J. Polymer Sci.*, 1951, **6,** 189, 209 ; Kolthoff and Meehan, *ibid.*, 1952, **9,** 343, 433 ; Brown, Bawn, Hansen, and Howland, *Ind. Eng. Chem.*, 1954, **46,** 1073.

containing nitroprusside,[115] *e.g.*, the system *iso*propyl-αα-dimethylbenzyl hydroperoxide–nitroprusside–hydroxylamine–thiol in which a complicated series of reactions occurs. Certain amines, particularly polyamines, of the general formula $NH_2 \cdot [CH_2 \cdot CH_2 \cdot NH]_n \cdot H$, have great practical importance as reducing agents in conjunction with cumene hydroperoxide and ferrous salts.[116] Some data are available concerning the course of reaction between peroxidic compounds and various kinds of amines.[99] From a study of the kinetics of the interaction of cumene hydroperoxide with diethylenediamine, triethylenetetramine, or tetraethylenepentamine, in the presence or absence of methyl methacrylate, Orr and Williams concluded [117] that the function of the ferrous ion is purely catalytic in the classical sense. It forms complexes with the amine and thereby, it was supposed, renders the N–H bond more reactive. Formation of free radicals was then postulated :

$$RO \cdot OH + R' \cdot NH_2 : A \longrightarrow RO \cdot + R' \cdot NH \cdot + H_2O + A$$
$$[A = Fe^{2+},\ Fe(OH)^+,\ \text{or}\ Fe(OH)_2]$$

Oxygen.—Reference has been made in preceding sections to the generally adverse effect of oxygen on the rates of polymerisation processes. Early in the study of redox initiators the Reviewer investigated [9] whether the extremely fast polymerisations which were being observed with acrylonitrile were due merely to removal of oxygen by the reducing agent. It was concluded that this was not the case since (*a*) with persulphate as sole initiator, prior de-aëration of the system led to elimination of the induction period without increase in polymerisation rate, whilst (*b*) some reducing agents, such as thiosulphate, which were unlikely to be efficient removers of oxygen, proved strong accelerators of polymerisation. Logemann and other German workers came to similar conclusions.[14, 15a] If the reducing agent can react with oxygen, destruction of inhibitor will certainly contribute to elimination of the induction period, and, in some of these cases, another contributing factor may be free-radical formation between oxygen and reducing agent. For example, there may be a subsidiary production of radicals from sulphite and atmospheric oxygen as an accompaniment to a main production between sulphite and persulphate.

Redox catalysts in which oxygen provided the sole oxidant were developed, especially for butadiene–styrene copolymerisation, by the German investigators,[14, 15c] who called this technique " autox catalysis ". Suitable reducing agents were dithionite, sulphinic acids, thiols, and α-ketols, and their effect was enhanced by iron salts, usually as complexes with pyrophosphate. As might be expected, polymerisation rates passed through maxima at empirically determined concentrations of oxygen, falling to low values, or to zero, at higher and lower concentrations. Chloroprene is an example of a monomer which very easily forms a peroxide with oxygen,

---

[115] Kolthoff and Meehan, *J. Polymer Sci.*, 1953, **11**, 71.

[116] Whitby, Wellman, Floutz, and Stephens, *Ind. Eng. Chem.*, 1950, **42**, 445, 452 ; Spolsky and Williams, *ibid.*, p. 1847 ; Embree, Spolsky, and Williams, *ibid.*, 1951, **43**, 2553.

[117] Orr and Williams, ref. 5, pp. 170, 237 ; cf. ref. 99.

and in such a case it is uncertain as to what extent this peroxide is the real source of free radicals in reaction with the reducing agent. In other cases, the source of radicals must lie in an autoxidation process, involving oxygen and reducing agent ; this kind of reaction has been widely studied in other connections and has been interpreted in terms of free-radical intermediates.[3]

Some modifications to the German " autox " systems made by Marvel [118] included the use of a cobalt salt as an additional catalyst component and also the use, as reducing agents, of long-chain alkane-1-sulphinic acids, which had been found to be reactive impurities in some alkanesulphonic acids employed as emulsifying agents. An independent investigation by Sully [119] demonstrated that the emulsion-polymerisation of styrene was promoted by sulphite in presence of traces of air and copper salts ; a mechanism based upon the classical work of Bäckström was suggested :

$$Cu^{2+} + SO_3{}^{2-} \longrightarrow Cu^{+} + {\cdot}SO_3{}^{-}$$

The sulphite radical ion was considered to initiate polymerisation and the cuprous ion to become reoxidised by oxygen. Thus, in this case, it was the interaction of reducing agent and metal ion which was the presumed source of free radicals.

The broader issues of catalysis and inhibition by oxygen are outside the scope of this Review and have been discussed elsewhere.[16, 34] Some instances of interference by oxygen in redox processes have been noted in preceding sections ; this seems to occur especially readily when ferrous salts are employed.[12, 120] Several investigators [12, 16, 34] have discussed chain-termination by oxygen as involving the formation of products such as $R{\cdot}[CH_2{\cdot}CHX]_n{\cdot}O{\cdot}O{\cdot}$, whilst others [121] have demonstrated the production of fairly stable polyperoxides, such as $\cdot[CH_2{\cdot}CHPh{\cdot}O{\cdot}O]_n$— from styrene and oxygen.

Non-peroxidic Oxidising Agents.—(a) *Multivalent metals.* Certain metals, in their complexed higher-valency states, can replace peroxidic compounds in redox catalysts. Examples are potassium ferricyanide [122] and carbonatotetramminecobaltic nitrate,[123] both being used in conjunction with thiols ; reaction mechanisms have not been proposed. A much simpler type of initiation, and one which is important from the viewpoint of chemical theory, is that which occurs on photo-excitation of aqueous solutions of vinyl monomers containing ion-pairs, such as $Fe^{3+}\ OH^{-}$, an active species in aqueous ferric perchlorate.[124] The free hydroxyl radical, which is

---

[118] Marvel and Keplinger, *J. Polymer Sci.*, 1951, **6**, 83 ; Marvel and Meinhardt, *ibid.*, p. 733.

[119] Sully, *J.*, 1950, 1498.

[120] Hobson and D'Ianni, *Ind. Eng. Chem.*, 1950, **42**, 1572.

[121] Bovey and Kolthoff, *J. Amer. Chem. Soc.*, 1947, **69**, 2143 ; Barnes, Elofson, and Jones, *ibid.*, 1950, **72**, 210 ; Kern and Stallmann, *Makromol. Chem.*, 1951, **7**, 199.

[122] Kolthoff and Dale, *J. Polymer Sci.*, 1948, **3**, 400 ; 1950, **5**, 301.

[123] Deanin, Lindsay, and Leventer, *ibid.*, 1948, **3**, 421.

[124] Evans and Uri, *Nature*, 1949, **164**, 404 ; *J. Soc. Dyers and Colourists*, 1949, **65**, 709 ; Evans, Santappa, and Uri, *J. Polymer Sci.*, 1951, **7**, 243 ; Orgel, *Quart. Rev.*, 1954, **8**, 422.

produced by transfer of an electron from the anion to the cation :

$$\mathrm{Fe^{3+}OH^-} \overset{h\nu}{\rightleftharpoons} \mathrm{Fe^{2+}OH} \longrightarrow \mathrm{Fe^{2+}} + \cdot\mathrm{OH}$$

is responsible for initiating the polymerisation, or, alternatively,[125] it may be used to hydroxylate an organic substrate, such as benzoic acid. Other heavy-metal ions, such as Ce^{4+}, Pb^{2+}, or $UO_2{}^{2+}$ may replace Fe^{3+}, whilst the reducing anion may alternatively be Cl^- or $N_3{}^-$.

(b) *Chromate.* Lang and Zwerina showed some years ago [126] that the oxidation of manganese(II) was induced in acid solution by interaction of chromate and arsenite. Kolthoff and Meehan have recently used the same chromate–arsenite system [127] to induce copolymerisation of butadiene and styrene. They suggested that initiation was due to the unstable intermediate ions, chromium(IV) or chromium(V), *e.g.* (M = monomer) :

$$\begin{aligned} \mathrm{Cr^{VI} + As^{III}} &\longrightarrow \mathrm{Cr^{IV} + As^{V}} \\ \mathrm{Cr^{IV} + M} &\longrightarrow \mathrm{Cr^{III} + M\cdot} \end{aligned}$$

(c) *Hydroxylamine.* Hydroxylamine promotes polymerisation when acting as a reducing agent in conjunction with peroxidic compounds.[9, 14] In aqueous acidic solutions of strong reducing agents, such as titanous or chromous ion, hydroxylamine acts as an oxidant. Davis, Evans, and Higginson showed [128] that such redox systems will likewise induce vinyl polymerisations and they produced evidence to suggest that initiation was due to $\cdot NH_2$ radicals, which, until then, had apparently not been reported as reaction intermediates in aqueous solution :

$$\mathrm{Ti^{3+} + HO\cdot NH_3{}^+ \longrightarrow Ti^{4+} + \cdot NH_2 + (HO^- + H^+)}$$

Uri has stated [129] that vinyl polymerisations may be initiated by $\cdot NH_2$ radicals formed by the photodissociation of hydrazine.

(d) *Halogen compounds.* Two examples will be cited. Polymerisation was initiated by reaction between ferrous salts and hypobromous acid.[130] The kinetics suggested that this was due, not to hydroxyl radicals, but to bromine atoms :

$$\begin{aligned} \mathrm{Fe^{2+} + HO\cdot Br} &\longrightarrow \mathrm{Fe^{3+} + OH^- + Br\cdot} \\ \mathrm{CH_2{:}CHX + Br\cdot} &\longrightarrow \mathrm{CH_2Br\cdot CHX\cdot} \end{aligned}$$

In the second case, polymerisation of acrylonitrile was initiated in aqueous solution by the crystalline addition product of trimethylamine and chlorine.[131] This reaction was formulated as involving initiation by chlorine atoms :

$$\begin{aligned} \mathrm{Cl\cdot NMe_3{}^+ + Cl^-} &\rightleftharpoons \mathrm{{:}NMe_3 + Cl{:}Cl} \\ \mathrm{{:}NMe_3 + Cl{:}Cl} &\longrightarrow \mathrm{\cdot NMe_3{}^+ + Cl^- + Cl\cdot} \end{aligned}$$

(e) *Miscellaneous inorganic oxidants.* Kern briefly reported [14, 15a] that

[125] Bates, Evans, and Uri, *Nature*, 1950, **166**, 869.

[126] Lang and Zwerina, *Z. anorg. Chem.*, 1928, **170**, 389.

[127] Kolthoff and Meehan, *J. Polymer Sci.*, 1952, **9**, 327.

[128] Davis, Evans, and Higginson, *J.*, 1951, 2563.

[129] Uri, *Chem. Rev.*, 1952, **50**, 375.

[130] Evans, Baxendale, and Cowling, ref. 4, p. 206.

[131] Horner and Podschus, *Angew. Chem.*, 1951, **63**, 531 ; cf. Böhme and Krause, *ibid.*, p. 531.

chlorate, hypochlorite, permanganate, or manganese dioxide had been found by Monheim to act as the oxidant components of redox initiators.

(f) *Enzymic systems.* The readiness with which polymerisations occur when promoted by redox systems led Kern [132] to revive, in a new form which stressed the catalytic action of enzymic redox systems, the old hypothesis that rubber is formed in plant cells from isoprene. Results recently reported concerning the catalytic activity of enzyme systems on polymerisations *in vitro* are therefore of interest. Polymerisation of methyl methacrylate was initiated by xanthine oxidase (XO) in presence of formaldehyde, a reaction which was formulated [133] as involving catalysed transfer of hydrogen atoms from formaldehyde to monomer:

$$\begin{aligned} \mathrm{XO} + \mathrm{CH_2(OH)_2} &\rightleftharpoons \mathrm{XOH} + \mathrm{CH_2(OH)\text{—}O\cdot} \\ \mathrm{XOH} + \mathrm{M} &\rightarrow \mathrm{H\text{—}M\cdot} + \mathrm{XO} \\ \mathrm{CH_2(OH)\text{—}O\cdot} + \mathrm{M} &\rightarrow \mathrm{H\text{—}M\cdot} + \mathrm{HCO_2H} \end{aligned}$$

Peroxidase used in conjunction with hydrogen peroxide has been reported [134] to catalyse initiation of isoprene polymerisation, though, according to Dainton,[21] neither peroxidase nor catalase functions as a polymerisation catalyst.

Variations in Mode of Reaction

Redox processes described in preceding sections have been represented in what is probably a simplified form ; they have generally been shown as one-electron transfers between catalyst components, succeeded by reaction between the resulting free radicals and monomer molecules. A less simple view of the reactions would take account of (*a*) participation of complexed forms of molecules, ions, or free radicals, (*b*) the influence of concurrent side-reactions, and (*c*) possible initiation by entities other than the free radicals which have been discussed. Mention has already been made, in various sections, of the first of these factors ; brief examples will now be given concerning the other two.

Concurrent side-reactions may be important because they lead to removal of one of the catalyst components, or because they provide an additional source of radicals, or because their products act as catalysts or inhibitors. For example, some reducing agents, if used in systems containing very reactive monomers, may be partly consumed in forming addition products at the double bond ; sodium hydrogen sulphite or thiosulphate acts in this way towards acrylonitrile.[9, 11, 135, 135a] Redox polymerisations of vinyl

[132] Kern, *Makromol. Chem.*, 1948, **2**, 63.

[133] Parravano, *J. Amer. Chem. Soc.*, 1951, **73**, 183.

[134] Clark, MacLean, Henderson, Barton, Johnson, Grunlund, and W. L. Reynolds, *Canad. J. Res.*, 1950, **28**, *F*, 351.

[135] Morton and Landfield, *J. Amer. Chem. Soc.*, 1952, **74**, 3523.

[135a] J. H. M. Hill and the Reviewer have recently proved (unpublished work) that the Bunte salt, $S_2O_3Na\cdot CH_2\cdot CH_2\cdot CN$, results from the addition of thiosulphate to acrylonitrile ; some other vinyl compounds react similarly. The Bunte salt, however, may itself influence polymerisation in conjunction with persulphate ; *i.e.*, the kinetics may be even more complicated than has been supposed.

compounds conducted on textile fibres [136] provide another kind of illustration; it appears that some kinds of fibre molecules, such as reduced wool,[137] may participate in the redox processes instead of acting as inert carriers. Oxidative degradation, such as may occur, for example, between acrylonitrile and oxygen,[138] is another type of side-reaction, leading commonly to aldehydes and acids. The possible significance of the oxidation, by persulphate, of the fatty acids provided by soaps has already been mentioned.[30, 31, 87a]

The possible initiation of polymerisation by the direct action of heavy-metal ions is an example of factor (*c*). There is some evidence that such reactions occur, but their detailed course has not yet been formulated. The suggested mechanism for catalysis by chromate (p. 308) involves initiation directly by transient types of chromium ions. Higher-valency silver ions may function analogously in the argentous ion–persulphate system (p. 299), whilst the ferrous ion–hydrogen peroxide system (p. 294) can be supposed to react through an intermediate ferryl ion, FeO^{2+}, if Bray and Gorin's [139] view be accepted. Some fragmentary supporting evidence for initiation processes of this kind is supplied by observations with stable types of multivalent ions. The catalytic effect of ceric salts on the polymerisation of acrylonitrile in aqueous solution,[9] and of ferric soaps on the polymerisation of styrene or methyl methacrylate in benzene,[140] have been reported. The observed catalysis of vinyl polymerisation by silver perchlorate [141] is suspected to be an example of ionic catalysis, whilst the polymerisation of acrylonitrile by large amounts of silver nitrate appears to be a special case, and has been interpreted by an electron transfer occurring within an argentous ion–nitrile complex.[142]

To summarise: Redox initiation refers to processes of polymerisation induced by numerous different chemical reactions; in general, these processes may be co-ordinated by the theory that intermediate reaction steps between catalyst components involve single-electron transfers; future modifications of the theory may lie in the more precise characterisation of the reactive entities and perhaps in the recognition of a variety of reaction paths.

---

[136] Lipson and Speakman, *Nature*, 1946, **157**, 590, 736; Landells and Whewell, *J. Soc. Dyers and Colourists*, 1951, **67**, 338.

[137] Lipson and Hope, *Austral. J. Res.*, 1950, *A*, **3**, 324.

[138] Smeltz and Dyer, *J. Amer. Chem. Soc.*, 1952, **74**, 623.

[139] Bray and Gorin, *ibid.*, 1932, **54**, 2124.

[140] Sen and Palit, *Nature*, 1950, **166**, 603; *J. Indian Chem. Soc.*, 1953, **30**, 150.

[141] Richards and Eley, ref. 4, p. 378.

[142] Salomon, *Rec. Trav. chim.*, 1949, **68**, 903.