(b) (**As the Hydrochloride**).—The refluxing of a mixture of 4.4 g. of the aminoketone hydrochloride and 18 ml. of 85% hydrazine hydrate yielded 52% of the theoretical nitrogen after two hours, and 85% after six hours. Gas evolution had virtually ceased by the end of this time. On working up as in the previous case there was obtained 2.7 g. (88%) of crude product, m.p. 80.5–83°. One recrystallization from ethanol gave, as before, needles of the hydrazone, m.p. 83–84°, interspersed with a few yellow needles of the azine, m.p. 197–198°. In this experiment the exit gases had been passed through 100 ml. of 1.16 *N* sulfuric acid. Titration showed that 2.6 moles of amine had been adsorbed per mole of nitrogen collected.

Cleavage of *p*-Hydroxydimethylaminoacetophenone.—A mixture of 1.1 g. of the aminoketone hydrochloride and 5 ml. of 85% hydrazine hydrate was refluxed in an oil-bath maintained at 130–140°. After two hours 53% of the theoretical nitrogen had been collected, and after six hours, the evolution had practically ceased (83%). The reaction mixture solidified on cooling. It was broken up, filtered, and washed with cold water. There remained 0.5 g. (66%) of crude *p*-hydroxyacetophenone hydrazone, m.p. 145–152°. The filtrate and wash water were extracted with ether and yielded an additional 0.11 g. (14%) of the crystalline hydrazone, m.p. 145–150°. Recrystallization from ethanol afforded colorless, stout prisms of the pure hydrazone, m.p. 154–155°. A mixed melting point with *p*-hydroxyacetophenone hydrazone (m.p. 154–155°), prepared directly from *p*-hydroxyacetophenone, showed no depression.

***o*-Hydroxy-N,N-dimethylphenethylamine.**—To a mixture of 7.6 g. of the aminoketone hydrochloride and 7 ml. of 85% hydrazine hydrate which had refluxed for one hour was added 36 g. of powdered potassium hydroxide. After 90 minutes of continued heating, 104% of the theoretical nitrogen (on basis of the hydrazone decomposition without deamination) had been evolved. The reaction mixture was cooled, although nitrogen was still being evolved, and poured into water. The solution was acidified, washed with ether, made basic with sodium bicarbonate and extracted with four portions of ether. On drying and evaporation of the ether there was obtained 1.2 g. of oily residue, which yielded 0.7 g. (12%) of product; b.p. 82–85° (0.5 mm.).

Anal. Calcd. for $C_{10}H_{15}ON$: N, 8.48. Found: N, 8.46.

The product was not very soluble in water, but dissolved in 10% sodium hydroxide and in dilute hydrochloric acid. It formed a chloroplatinate, m.p. 159–161°, and a picrate, m.p. 148–149°.[16]

Anal. of picrate. Calcd. for $C_{16}H_{18}O_7N_4$: N, 14.21. Found: N, 14.32.

Identity of I and VI.—*α*-Dimethylaminoacetophenone, hydrazine, acetic acid and water were permitted to react under the conditions specified by Jacob and Madinaveitia.[3] There was isolated a solid compound which melted after two recrystallizations from alcohol at 209–210°. Stolle's directions[7] for the preparation of VI were followed, and yielded a compound melting at 209–210°. The melting point of a mixture of these two compounds was also 209–210°.

Base Decomposition of VI.—Compound VI (1.76 g.) was added to a solution of approximately 1 g. of potassium hydroxide in 15 cc. of absolute ethanol. The major portion of VI remained undissolved. When the mixture was refluxed on a steam-bath, nitrogen was evolved at a constant rate (1.14 cc. per min.) until 93% of the theoretical amount (base on two moles of nitrogen per mole of compound) had been liberated. At this point gas evolution abruptly ceased and no more gas was evolved even though the refluxing was continued. During this heating period compound VI dissolved and formed a red-brown solution in the alcohol. Extraction and distillation (0.3 mm.) of the brownish-yellow oil which formed when the solution was added to water gave a light yellow distillate that crystallized to a large extent on standing. Recrystallization of the solid portion from alcohol yielded a yellow solid, m.p. 122–122.5°. The melting point of acetophenone azine prepared independently[4] and also a mixed melting point for these two substances was the same.

Stolle describes a similar reaction in which he isolated material which melted at 121°, but he failed to characterize it as the azine, apparently as a result of a faulty combustion analysis.

Acknowledgment.—This work was supported by the Research Corporation. Analyses were made by C. Brauer and J. Sorensen.

[16] J. v. Braun and O. Bayer, *Ber.*, **57**, 913 (1924), reported melting points of 144° and 142° for the chloroplatinate and picrate, respectively. Analyses were reported for neither.

EVANSTON, ILLINOIS RECEIVED JULY 20, 1951

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

The Effect of Oxygen on the Polymerization of Acrylonitrile[1]

BY KENNETH C. SMELTZ AND ELIZABETH DYER

Studies were made of the effect of oxygen on acrylonitrile in aqueous solutions using potassium persulfate, in non-aqueous solutions with benzoyl peroxide, in bulk systems with benzoyl peroxide and in photosensitized systems with diacetyl as initiator. In all cases normal polymerization was inhibited if the mixture was agitated in the presence of 100% oxygen. The rate of absorption of the oxygen varied with the initial concentrations of the initiator and of the acrylonitrile, and with the solvent. In aqueous systems the absorption of oxygen was initially first order with respect to the persulfate concentration and three-halves order with respect to the acrylonitrile. Over long periods of time the order with respect to persulfate changed from first order for the lowest concentration to three-halves order for the highest. A highly unstable peroxide, of molecular weight approaching that of a trimer, was isolated from non-aqueous experiments. This was shown to give the same decomposition products as were obtained from the aqueous experiments, namely, hydrogen cyanide, carbon dioxide, formaldehyde, the cyanohydrin of glycolic aldehyde and glycolic acid. Evidence was also obtained for the presence of carbon monoxide and a solid substance with terminal unsaturation. Quantitative data from experiments in aqueous solution showed that for every three moles of oxygen absorbed, three moles of hydrogen cyanide, one mole of formaldehyde and one mole of carbon dioxide were produced.

Because of the increasing interest in the effect of oxygen on vinyl polymerizations,[2] an investigation was made of this effect with acrylonitrile. Bacon[3] showed that oxygen inhibited the aqueous solution polymerization of acrylonitrile by causing an induction period which varied with the oxygen content of the system, the temperature and the concentration of initiator. Morgan[4] found that the induction period was inversely proportional to the initial persulfate concentration. Baxendale, Evans and Park,[5] who studied the polymerization of acrylonitrile with hydrogen peroxide–ferrous salt

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[1] From the Ph.D. dissertation of Kenneth C. Smeltz, University of Delaware, June, 1951. This research was supported in part by the Office of Naval Research under contract N7-onr-492.

[2] (a) F. A. Bovey and I. M. Kolthoff, THIS JOURNAL, **69**, 2143 (1947); (b) C. E. Barnes, R. M. Elofson and G. D. Jones, *ibid.*, **72**, 210 (1950); (c) V. Gutmann, *J. Polymer Sci.*, **3**, 336 (1948); (d) H. E. Worrell, M. S. Thesis, University of Delaware, June, 1950.

[3] R. G. R. Bacon, *Trans. Faraday Soc.*, **42**, 141 (1946).

[4] L. B. Morgan, *ibid.*, **42**, 169 (1946).

[5] J. H. Baxendale, M. G. Evans and G. S. Park, *ibid.*, **42**, 155 (1946).

systems, stated that oxygen was absorbed only when all three substances, monomer, peroxide and ferrous ion, were present. The sole report as to the nature of the products resulting from the attack of oxygen on acrylonitrile was that of Kern and Fernow,[6] who obtained hydrogen cyanide from the benzoyl peroxide initiated polymerization, presumably done in air. The object of the present investigation was to secure data on the kinetics of the oxygen absorption and the nature of the oxidation products, using various types of polymerization systems.

Kinetics of Oxygen Absorption

Atmospheres containing 100% oxygen were used in all cases, which caused the inhibition of normal polymerization and the absorption of oxygen by the acrylonitrile in aqueous and non-aqueous solutions containing initiators, and in bulk systems with and without initiators. In aqueous systems, oxygen was absorbed as long as the solution was agitated when acrylonitrile, potassium persulfate and water were all present; no oxygen was absorbed when any two of the above compounds were used alone.

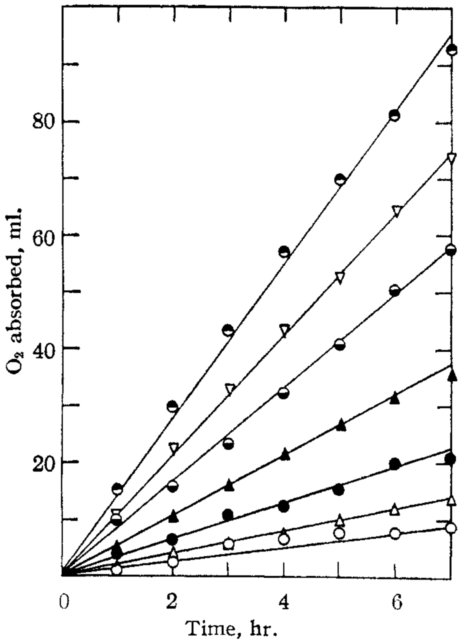

Fig. 1.—Rate of oxygen absorption by aqueous acrylonitrile at 50° with varying amounts of $K_2S_2O_8$. Concn. of $K_2S_2O_8$ (moles × 10^3/100 ml.): ○, 0.185; △, 0.370; ●, 0.925; ▲, 1.85; ⊖, 3.70; ▽, 5.55; ◓, 7.40.

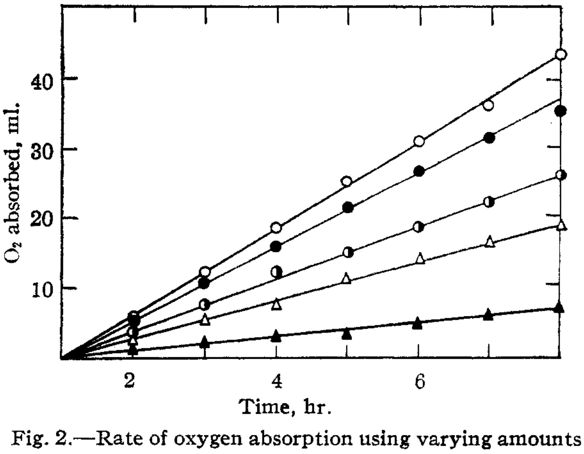

Fig. 2.—Rate of oxygen absorption using varying amounts of acrylonitrile in aqueous solutions with potassium persulfate at 50°. Concn. of acrylonitrile (moles × 10^2/100 ml.): ▲, 1.88; △, 4.71; ◑, 6.60; ●, 9.43; ○, 11.31.

If the stirring was stopped, normal polymerization took place after a definite induction period, which was found to be inversely proportional to the initial concentration of persulfate and due solely to oxygen.[7] This is in agreement with the findings of Kolthoff and Dale[8] on styrene and Morgan[4] on acrylonitrile.

Measurements of oxygen absorption were made during the period of stirring, called the inhibition period; the initial persulfate concentration was varied while the initial acrylonitrile concentration was kept constant, and *vice versa*. The plots of the absorption data, shown in Figs. 1 and 2, gave straight lines for all experiments, which indicates apparent zero order reactions for these seven-hour periods. Similar results were obtained by Kolthoff and co-workers[2a,8] for the absorption of oxygen by styrene.

The relative importance of the concentrations of initiator and of monomer in controlling the absorption of oxygen was determined by plotting the log of the oxygen absorbed in seven hours against the log of the initial persulfate concentration and against the log of the initial acrylonitrile concention, respectively, as in Fig. 3. (Other types of plots gave curves.) The ratio of the slopes of the lines based on monomer and initiator concentrations is 1.48. Hence the acrylonitrile concentration is about 1.5 times as important as the persulfate concentration in the absorption of oxygen.

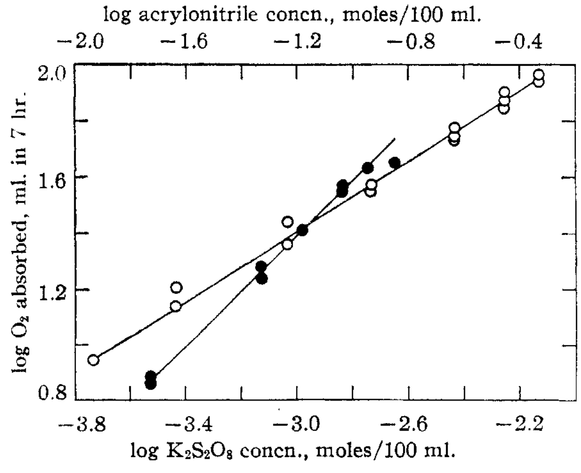

Fig. 3.—The effect of initial acrylonitrile and persulfate concentrations on the absorption of oxygen by acrylonitrile at 50°, ○, $K_2S_2O_8$; ●, acrylonitrile.

Unfortunately it was not possible to follow the rate of disappearance of acrylonitrile in these re-

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(6) W. Kern and H. Fernow, *J. prakt. Chem.*, **160**, 281 (1942).

(7) Induction periods for polymerization of acrylonitrile under nitrogen but with non-deaerated water could be predicted from oxygen absorption data. K. C. Smeltz, M.S. Thesis, University of Delaware, June, 1949.

(8) I. M. Kolthoff and W. J. Dale, THIS JOURNAL, **69**, 441 (1947).

actions. However, the rate of disappearance of the persulfate in the presence of acrylonitrile and oxygen was found by Heinaman[9] to be first order through 70% decomposition for 0.0185 *M* potassium persulfate in unbuffered aqueous solution in the presence of 0.94 *M* acrylonitrile and oxygen at 50°. The velocity constant was 2.06×10^{-4} liter mole^{-1} min.^{-1}; in the absence of acrylonitrile it was 1.07×10^{-4}. The effect of acrylonitrile is not so great as that of methanol, studied by Bartlett and Cotman.[10]

A comparison of the data on oxygen absorption and on persulfate decomposition showed that, for each initial concentration of persulfate, the amount of oxygen absorbed was proportional to the amount of persulfate decomposed. Three experiments were done by taking measurements of oxygen absorption over long periods, using varied initial persulfate concentrations and constant initial acrylonitrile concentrations. Data from these long runs, given in Fig. 4, indicate that the oxygen absorption was not zero order over long periods. As shown in Table I, the oxygen absorption was first order for the lowest concentration of initiator, and somewhat higher, approaching three-halves order, for higher concentrations of initiator. This is probably due to the occurrence of more complex reactions, caused by induced decomposition of the persulfate at the higher concentrations.

TABLE I

OVER-ALL ORDER OF OXYGEN ABSORPTION USING VARIED INITIAL PERSULFATE CONCENTRATIONS AND A CONSTANT ACRYLONITRILE CONCENTRATION[a]

Initial $K_2S_2O_8$, mole/100 ml.	Factors used[b]	*n* calcd.[c]	*n* graph.[d]
0.00185	12	1.01[e]	1
.00370	6	1.21	Neither 1 nor 1.5
.00740	3	1.46	1.5

[a] Acrylonitrile concentration of 0.0943 mole per 100 ml. [b] Factors are the ratio of moles of oxygen absorbed to moles of persulfate decomposed, and give a value of 22.2×10^{-2} mole of oxygen that would be absorbed at infinity in each case. This value was used to calculate the "concentration" of oxygen, *i.e.* the fraction absorbed in a given period. [c] Order of reaction determined by the differential[11] method. [d] Order of reaction determined graphically. [e] The *k* value is 1.30×10^{-4} liter mole^{-1} min.^{-1}.

In all of these long oxygen experiments the rate of oxygen absorption was first order initially with respect to oxygen and first order through the period investigated (67% completion) for the lowest concentration of persulfate. Because of the interdependence of oxygen absorption and persulfate decomposition, it can be assumed that the rate of oxygen absorption is initially first order with respect to persulfate. The oxygen absorption is also dependent on acrylonitrile concentration, which was shown to be 1.5 times as important as the persulfate concentration. Hence for the initial stages the following kinetic expression can be suggested

$$dO_2 \text{ absorbed}/dt = k'(K_2S_2O_8)(CH_2{=}CHCN)^{1.5}$$

Since the pressure of oxygen on the system was kept constant, its concentration is included in the *k'*.

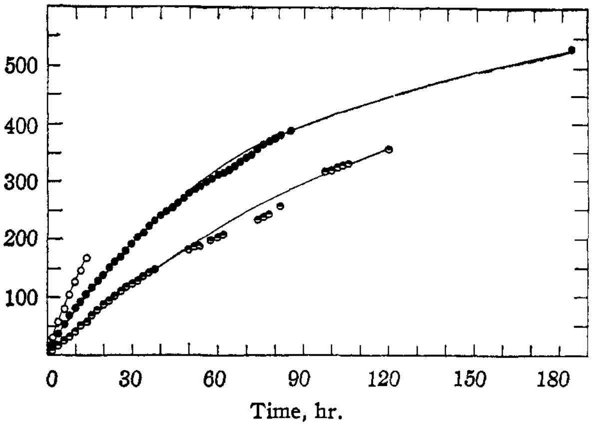

Fig. 4.—Rate of oxygen absorption by aqueous acrylonitrile with varying amounts of $K_2S_2O_8$ at 50° over long periods of time. Concn. of $K_2S_2O_8$ (moles × 10^3/100 ml.): ◐, 1.85; ●, 3.70; ○, 7.40.

A few measurements of oxygen absorption by acrylonitrile in non-aqueous solutions were made, using benzoyl peroxide as initiator. Table II shows that the rates of oxygen absorption varied greatly with the solvent.

TABLE II

EFFECT OF SOLVENT ON OXYGEN ABSORPTION BY ACRYLONITRILE IN THE PRESENCE OF BENZOYL PEROXIDE AND ON THE DECOMPOSITION OF BENZOYL PEROXIDE

Solvent	O_2 absorbed,[a] ml. in 7 hr. at 50°	Decomp. of Bz_2O_2,[b] % in 1 hr. at 80°
Toluene	7.9	17.4
Acetone	9.3	28.5
Ethyl acetate	14.5	53.5
Dioxane	39.4	82.4

[a] A solution containing 0.943 mole of acrylonitrile and 0.00185 mole of benzoyl peroxide in 100 ml. was shaken in the rapid shaker.[2a] [b] Data of Nozaki and Bartlett.[12]

For comparison the rates of decomposition of benzyl peroxide are given, as determined by Nozaki and Bartlett[12] for the same solvents. Even though the temperatures are not the same, it is significant that the two sets of values increase in the same order, which indicates that the rate of oxygen absorption is dependent on the rate of free radical production by decomposition of the peroxide.

Oxidation and Degradation Products

It is well known that molecular oxygen reacts with vinyl monomers, forming polymeric peroxides.[2] The stability and ease of formation of these peroxy polymers varies with the monomer used and appears to increase with the increasing ease of oxygen absorption by the monomer. Data on the rate of oxygen absorption by three different monomers are given in Table III.

A comparison of the apparent stability of the peroxy polymers formed from the monomers used in Table III may be seen by the fact that no peroxy polymer but only decomposition products were found by Heinaman using methyl acrylate,[9]

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[9] W. S. Heinaman, M.S. Thesis, University of Delaware, June 1950.

[10] P. D. Bartlett and J. D. Cotman, THIS JOURNAL, **71**, 1419 (1949).

[11] S. Glasstone, "Textbook of Physical Chemistry," Second Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1066.

[12] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

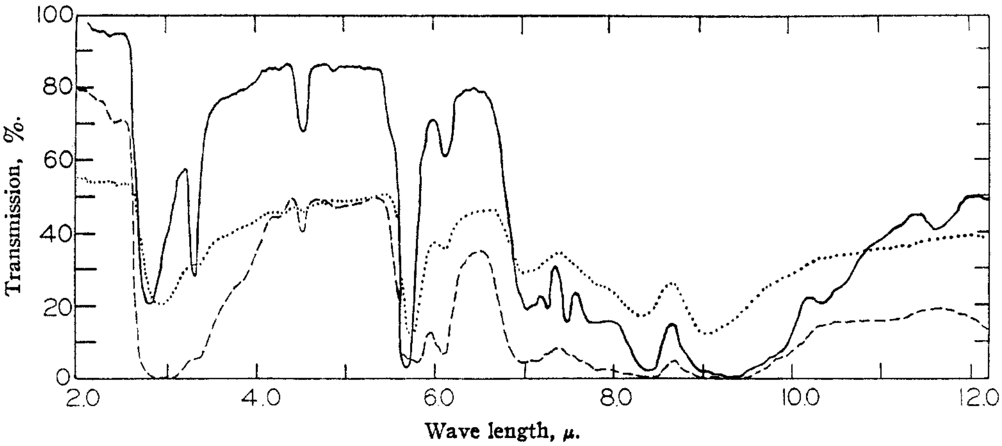

Fig. 5.—Infrared absorption of acrylonitrile polymeric peroxide: —, sample done immediately after isolation; — — —, same sample 2 hr. later; ...., same sample 2.5 hr. after isolation.

very little peroxy polymer and mostly decomposition products were found in this investigation using acrylonitrile and that more peroxy polymer and lesser amounts of decomposition products were obtained by Worrell from α-methacrylonitrile.[2b] Likewise, in an emulsion system using styrene under oxygen at 50°, the data of Bovey and Kolthoff[2a] show that more polymeric peroxide was formed than decomposition products.

TABLE III

OXYGEN ABSORPTION BY VARIOUS VINYL MONOMERS USING POTASSIUM PERSULFATE AS INITIATOR IN AQUEOUS SYSTEMS AT 50°

Monomer	Monomer mole/100 ml.	$K_2S_2O_8$, mole/100 ml.	O_2 absorbed,[a] ml. in 7 hr.
α-Methacrylonitrile[2d]	0.033	0.0074	121.5
Acrylonitrile	.094	.0074	91.7
Methyl acrylate[9]	.133	.0074	51.3

[a] Atmosphere of 100% oxygen.

It is interesting to note that when these monomers as well as those used by Barnes, *et al.*,[2d] are arranged in order of increasing stability of the polymeric peroxide, the order is the reverse of that showing the relative ease of normal polymerization of these monomers, as given by Mayo, Lewis and Walling.[13] For example, methyl acrylate polymerizes the most rapidly but absorbs oxygen the most slowly and has the least stable polymeric peroxide; whereas, methacrylonitrile, which is further down the list, polymerizes more slowly but absorbs oxygen much faster and forms a more stable polymeric peroxide.

Since acrylonitrile is next to methyl acrylate at the top of Mayo's list, it is not surprising that its polymeric peroxide is extremely unstable. Only very small amounts of a yellow-orange tacky peroxidic polymer were isolated from aqueous experiments. However, it was possible to isolate larger quantities of the substance from bulk runs using as initiators benzoyl peroxide or ultraviolet light with diacetyl.

The substance puffed over an open flame and in one case exploded at room temperature, liberated iodine from an acidified solution of potassium iodide, reacted with ferrous salts, and initiated polymerization. It had an apparent cryoscopic molecular weight in dioxane of about 177. This figure is undoubtedly low due to the rapid decomposition of the peroxide after isolation. The peroxidic substance had either a carboxylic acid or hydroperoxidic end group since the substance gave acid tests and was very soluble in alkali as well as acetone; it was also partly soluble in water.

This peroxide decomposed thermally into hydrogen cyanide, carbon dioxide, formaldehyde and an unidentified reddish-black acidic, non-crystalline substance; traces of carbon monoxide and water were also formed. These decomposition products, as well as glycolic acid and the cyanohydrin of glycol aldehyde and/or the dicyanohydrin of glyoxal were present in the reaction mixtures of both aqueous and non-aqueous experiments. In some cases a volatile peroxide was also obtained.

The extreme instability of the peroxide material is shown by the infrared absorption curves given in Fig. 5. The solid line was obtained immediately after the peroxide was isolated, the broken line two hours later on the same sample after standing in air, and the dotted line one-half hour after the broken line. It is seen that the cyanide band at 4.5 μ and the peroxide band at 11.6 μ disappeared completely in this time. Also, the hydroxyl band at 2.8 μ became widened with hydrogen bonding taking place. Bands at 5.7 and 6.1 μ indicate the presence of carbonyl and of double bonds.

Some quantitative data were obtained for the gaseous decomposition products when the experiments were carried out in aqueous solution. The results of these determinations are shown in Table IV.

Because of such a complex mixture of products, it was not possible to get quantitative data on all the various substances present. However, the data does show that for every mole of oxygen absorbed, a mole of hydrogen cyanide, a third of a mole of carbon dioxide and a third of a mole of formaldehyde were found. The missing oxygen can be at least partially accounted for by the glycolic acid and cyanohydrins present. An

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(13) F. R. Mayo, F. M. Lewis and C. Walling, THIS JOURNAL, 70, 1532 (1948).

TABLE IV

COMPARATIVE QUANTITATIVE DATA ON SOME OXIDATION PRODUCTS OF ACRYLONITRILE FROM AQUEOUS EXPERIMENTS USING VARYING INITIAL AMOUNTS OF POTASSIUM PERSULFATE AT 50°

$K_2S_2O_8$ initially,[a] moles × 10^3	Moles O_2 absorbed[b]	Moles HCN formed	Moles HCHO formed	Moles CO_2[c] formed
1.85	3.00	2.99		1.16
1.85	3.00	3.01		
1.85	3.00	3.28		1.23
3.70	3.00			1.63
5.55	3.00		1.04	1.05
7.40	3.00	2.98	0.99	1.18
Average	3.00	3.04	1.01	1.25

[a] With 9.43×10^{-2} mole of acrylonitrile in 100 ml. of solution. [b] From the actual experimental data, all values in this table were calculated to the basis of three moles of oxygen absorbed. [c] The values in this column are slightly high since the gravimetric determination was done in air.

estimate of the amount of acrylonitrile used in oxidation showed that approximately two moles of acrylonitrile were used for every mole of hydrogen cyanide formed. This bit of evidence was gotten through the amount of polymer formed when the oxidation reactions were stopped by stopping the stirring.

It is evident that no complete mechanism can be given to account for such a complex mixture of products and the many reactions that undoubtedly take place. However, certain postulations can be made, which are in accord with the kinetic data and the products found. It is probable that the process in aqueous solution is initiated by both sulfate ion free radicals (formed from the persulfate) and hydroxyl free radicals. The latter, which appeared in such products as glycolic acid, might have been formed by hydrolysis of the sulfate groups. Since evidence for a terminal methylene group was also obtained, a third type of initiating free radical may have been present, formed by the reaction of acrylonitrile with the persulfate as follows

$$S_2O_8^{--} + CH_2{=}CHCN \longrightarrow CH_2{=}\dot{C}(CN) + SO_4\dot{-} + HSO_4^-$$

The increased rate of decomposition of the persulfate in the presence of acrylonitrile suggests such an interaction, which is similar to the interpretation given by Bartlett and Cotman for the effect of methanol on persulfate.[10]

The following tentative mechanism gives rate equations which are in agreement with the kinetic data. P represents persulfate ion, M is acrylonitrile, R· is a radical which can combine with either monomer or oxygen, Z· is a radical which can combine only with monomer (*e.g.*, $SO_4\dot{-}$ or $HOCH_2CH(CN)OO.$), and X, Y and ZH are termination products. The assumption that a peroxy radical cannot combine with oxygen, and that there may hence be an alternation of acrylonitrile and peroxide units in the peroxy polymer is supported by the findings of Bovey and Kolthoff on styrene.[2a] Reaction (3) occurs to a negligible extent, since no normal polymer was formed and the peroxy polymer was of low molecular weight.

$$P \longrightarrow 2Z^{\cdot} \quad (1)$$
$$P + M \longrightarrow Z^{\cdot} + R^{\cdot} \quad (2)$$
$$R^{\cdot} + M \longrightarrow R^{\cdot} \quad (3)$$
$$R^{\cdot} + O_2 \longrightarrow Z^{\cdot} \quad (4)$$
$$Z^{\cdot} + M \longrightarrow R^{\cdot} \quad (5)$$
$$R^{\cdot} + R^{\cdot} \longrightarrow X \quad (6)$$
$$Z^{\cdot} + R^{\cdot} \longrightarrow Y \quad (7)$$
$$Z^{\cdot} + RH \longrightarrow ZH + R^{\cdot} \quad (8)$$
$$Y \longrightarrow 2R^{\cdot} \quad (9)$$

Solution of these equations for dR/dt, dZ/dt and $-dO_2/dt$, assuming stationary states, and making certain approximations, gives expressions in which the oxygen absorption is proportional to the first power of the persulfate concentration, and to a power of the monomer concentration which lies between first and second. The observed three-halves dependence on acrylonitrile concentration is within these limits. It is recognized, however, that this is undoubtedly an average figure resulting from a number of consecutive reactions.

Termination may occur by abstraction of a hydrogen atom from monomer or solvent, as in (8), or by combination of radicals as in (6) or (7). More probably, an intramolecular decomposition may occur, as shown below. This possible scheme, which accounts for the more important products, would not change the kinetics from that of eq. 7.

$$HOCH_2CH(CN)OOCH_2CH(CN)OO\cdot \longrightarrow HOCH_2CH(CN)O\cdot + HCN + CO_2 + HCHO$$
$$HOCH_2CH(CN)O\cdot \longrightarrow HOCH_2CO\cdot + HCN$$
$$HOCH_2CH(CN)O\cdot + H_2O \longrightarrow HOCH_2CH(CN)OH + HO\cdot$$
$$HOCH_2CO\cdot + \cdot OH \longrightarrow HOCH_2COOH$$

Experimental

Materials. Acrylonitrile.—Eastman Kodak Co. acrylonitrile was dried over calcium chloride and distilled through a 35-cm. Vigreux column immediately before use. The fraction used boiled at 77.2 to 77.4° at 760 mm.; $n^{25}D$ 1.3886. Previous authors[14,15] reported $n^{25}D$ 1.3884 and 1.3888.

Potassium Persulfate.—Baker and Adamson Reagent Grade was recrystallized from water at 50°; iodimetric analysis indicated a purity of 99.6%.

Benzoyl Peroxide.—Eastman benzoyl peroxide, after recrystallization from chloroform–methanol, was 99.5% pure.

Diacetyl and Organic Solvents.—These were reagent grade materials that were dried and distilled before use.

Procedures. A. Experiments in Aqueous Solutions.—The recipe used contained 100 ml. of solution, with varying amounts of acrylonitrile and persulfate (as indicated in the graphs and tables). The reaction flask was fitted with a mercury-sealed stirrer running at about 500 r.p.m. and a dropping funnel, and was connected with a water-jacketed, mercury-filled gas buret and a manometer containing dibutyl phthalate. The reaction flask and gas buret were kept at a temperature of 50 ± 0.2°. At the start of an experiment the persulfate and part of the water were introduced, the stirrer started, the system flushed out with oxygen preheated at 50°, and then the acrylonitrile and the rest of the water introduced through the dropping funnel. After about 45 minutes, when the system was reaching temperature and pressure equilibrium, the buret showed a constant reading for 5 minutes when the pressure was equalized with

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[14] H. S. Davis and O. F. Wiedeman, *Ind. Eng. Chem.*, **37**, 482 (1945).

[15] American Cyanamid Company, "The Chemistry of Acrylonitrile," Beacon Press, Inc., New York, N. Y., 1951, p. 12.

the atmosphere. This was taken as the zero reading. Measurements of oxygen absorption were made at hourly intervals, with the pressure kept at atmospheric by regular manual adjustment of the mercury levels.

B. Experiments in Non-Aqueous Systems.—For the oxygen absorption measurements a closed system was used in which a vessel of 160-ml. capacity was shaken at about 300 strokes per minute in an apparatus similar to that described by Bovey and Kolthoff.[2a] After the reaction mixture was placed in the container, the system was alternately evacuated and flushed with oxygen at least five times before immersion in the bath at 50°. Measurements of oxygen absorption were made as before.

For many of the studies of oxidation products open systems were used in which oxygen was bubbled through the acrylonitrile in a flask fitted with a 600-mm. spiral, water-jacketed condenser and thermometer well. Various chemical and cold traps were connected to the system through the top of the condenser. Either heat or ultraviolet light (from a General Electric R. S. reflector sunlamp) was applied to the system. When heat was used, the temperatures were in a range of 50 to 77° and 0.025% benzoyl peroxide was used as initiator. Previous experiments showed that in the absence of an initiator, 100 ml. of acrylonitrile absorbed only 22 ml. of oxygen after shaking 31 hours at 50°. When ultraviolet light was used, the temperature was held between 40 and 65° and 0.1% of diacetyl was used as initiator, since very little reaction took place in two days in its absence.

Oxidation Products. Polymeric Peroxide.—This was isolated from benzoyl peroxide-initiated or diacetyl initiated-photosensitized experiments by evaporation of the reaction mixture (250 ml. treated with oxygen for three or four days) under reduced pressure in a bath at 30–35°. The residue, consisting of from 1 to 5 g. of a tacky, yellow-orange substance was dissolved in acetone, filtered and reprecipitated with petroleum ether. This peroxidic material was highly unstable, beginning to decompose (in one case explosively) as soon as it was isolated. It was soluble in acrylonitrile, acetone, dioxane, dimethylformamide[16] and aqueous alkalies; it was partially soluble in water, ethyl ether and nitrobenzene, and insoluble in petroleum ether and cyclohexane. A molecular weight determination by the freezing point lowering of dioxane gave a figure of 177 (calcd. for $(C_3H_3NO)_3$, 187). Determination of available oxygen by iodimetry gave values of 0.9 and 1.3%, which could be very low because of both the instability of the peroxide and the known inadequacy of the method for polymeric peroxides.[2b]

Carbon Dioxide, Hydrogen Cyanide and Formaldehyde.—Carbon dioxide was identified by passing the gases of a reaction mixture through barium hydroxide solution. Hydrogen cyanide, the odor of which was apparent in all reaction mixtures, was confirmed by the formation of prussian blue. Formaldehyde was identified by the chromotropic acid test,[17] and the formation of its 2,4-dinitrophenylhydrazone and dimedon derivatives.

Glycolic Acid.—Evidence for this from all runs was obtained in sirups which gave positive tests for hydroxyl and carboxyl groups and a positive chromotropic acid test on heating (specific for glycolic acid[18]). The substance was isolated by vacuum distillation as the white crystalline hydrate and converted to the anhydride, m.p. 129–131°, which did not lower the melting point of a known sample of glycolic acid anhydride.

Cyanohydrin of Glycol Aldehyde and/or the Dicyanohydrin of Glyoxal.—The sirupy residues from the aqueous experiments gave no aldehyde tests when in an acid condition, but released hydrogen cyanide and gave aldehyde tests when made just basic. (If made strongly basic and heated, ammonia was evolved.) A 2,4-dinitrophenylhydrazone was obtained which, after recrystallization from nitrobenzene and ethanol did not lower the melting point of the known bis-2,4-dinitrophenyl osazone of glycol aldehyde, m.p. 301–302.5°. Glyoxal would give the same substance. Evidence for the glycol aldehyde cyanohydrin is that in some cases the reaction with the 2,4-dinitrophenylhydrazine went in two stages, with the formation first of a yellow precipitate which changed to the orange-red osazone; the yellow could be the monodinitrophenylhydrazone of glycol aldehyde.[19]

Evidence for Terminal Unsaturation.—This is based on the fact that basic and acidic potassium permanganate solutions were reduced at once and bromine in carbon tetrachloride was decolorized by the residual sirups. When the reduced permanganate solution was filtered, the filtrate made acid and distilled, the distillate contained formaldehyde.

Similar evidence was obtained for the presence of terminal double bonds on the polymer chains of normal polyacrylonitrile made in the presence of potassium persulfate and a nitrogen atmosphere. This polymer had been washed with water and methanol and dried to constant weight *in vacuo* to remove all traces of acrylonitrile. When the polymer was subjected to alkaline hydrolysis, both the aqueous solution of the resulting polyacrylic acid and the solution of its sodium salt reduced a weak solution of potassium permanganate. When the reduced solutions were filtered and the filtrate distilled, the distillate again showed the presence of a small amount of formaldehyde.

Evidence for Carbon Monoxide.—Carbon monoxide may have been present in small amounts as shown by the change of color in an indicating tube containing a silico-molybdate complex and a palladium catalyst put out for this purpose by the Mine Safety Appliances Company.[20] Further evidence was found in the liberation of free iodine from heated iodine pentoxide. In both of these reactions it was necessary to scrub the gases with silver nitrate and cold traps since hydrogen cyanide and acrylonitrile react with both indicators.

Quantitative Determination of Gaseous Products.—Carbon dioxide, hydrogen cyanide and formaldehyde were determined in the aqueous reaction mixtures. The stirrer was stopped to permit polymerization of unoxidized monomer. Without opening the apparatus, now cooled to room temperature, nitrogen was passed through the system and into two traps containing barium hydroxide. Barium carbonate was filtered and the cyanide precipitated with nitric acid and silver nitrate. No formaldehyde was found in these traps. The reaction mixture was then filtered from polymer and treated successively with barium hydroxide, acid and silver ions. The filtrate from the silver cyanide was distilled and the formaldehyde determined spectrophotometrically.[17] Since the barium-containing precipitate was contaminated with barium sulfate, it was treated with hydrochloric acid to determine barium carbonate by difference.

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