15–20% yield in a rather impure form, bp 61° (1 mm). Peaks at 1715 and 1730 cm^{-1} indicated ketonic impurities. These could be removed partially by shaking an ethereal solution with dilute base. The remaining peak at 1730 cm^{-1} could not be removed by several distillations or reactions with Girard's reagent. Finally, a gas chromatographically pure product was obtained by chromatographing it on a silica gel column from a mixture of hexane and ether. The gas chromatograph showed only two equally strong peaks indicating the two isomers. The nmr spectrum agreed with the chemical structure.

Anal. Calcd for $C_6H_8N_2$: C, 66.35; H, 7.41; N, 25.82. Found: C, 66.66; H, 7.44; N, 26.07.

Acknowledgment. We wish to thank Mr. D. C. Westall for experimental assistance.

On the Chromophore of Polyacrylonitrile. V. The Oxidation of Isobutyronitrile

J. Brandrup[1]

Contribution No. 311 from the Chemstrand Research Center, Inc., Durham, North Carolina. *Received October 27, 1967*

ABSTRACT: The thermal degradation of polyacrylonitrile was studied with the aid of model compounds. Isobutyronitrile was used as model for a single pendant nitrile group in polyacrylonitrile and was thermally degraded under oxygen at 150°. The brown, viscous reaction product showed the presence of 30 different compounds according to gas chromatography, 16 of which have been characterized. These 16 constitute all of the major and several minor compounds. The main products were acetamide, isobutyramide, N-methylpropionamide, and the corresponding acids. In addition, a fiber-forming water-soluble polymer was recovered whose behavior and spectral characteristics agree with the structure of a polynitrone $(-C{=}N(\rightarrow O)-)_n$. A possible mechanism for the formation of these products is outlined. All these reactions occur very slowly (less than 5% conversion in 3 days) and confirm again that the predominant place of oxygen attack in polyacrylonitrile cannot be the tertiary hydrogen atom in the repeat unit.

Paper IV in this series has shown that the predominant oxygen attack on polyacrylonitrile (PAN) occurs at the methylene bridge forming a hydroperoxide at this position with subsequent breakdown to a β-ketonitrile.[2] But 2,3-dicyanobutane which does not have the methylene link also slowly absorbs oxygen but discolors only slightly. Apparently, the tertiary hydrogen also reacts slowly with oxygen, but yields different products. Thus, it was of interest to investigate the resulting products. Since isobutyronitrile is the closest model for a single pendant nitrile group in the chain, it was justified to assume similar reactions to occur in PAN and isobutyronitrile during oxidative heat treatment at 150°. This paper describes the products obtained from thermal oxidation of isobutyronitrile and gives a possible mechanism for their formation.

Results

The thermal oxidation of isobutyronitrile had to be carried out under high pressure because of the low boiling point of isobutyronitrile (107°). Isobutyronitrile was heated to about 150° under an oxygen pressure of 600–1000 psi for varying times. After this oxidation, isobutyronitrile had turned yellow, or black, depending on the extent of degradation. A complex, viscous mixture was obtained. A sample, which was heat treated for 3 days, for instance, showed about 30 different reaction products in the gas chromatographic spectrum (Figure 1) but the sum of all these products represented only *ca.* 5% conversion. These 5% products were sufficient to turn the starting material deep black and viscous. Besides the products shown in the gas chromatographic spectrum, a crystalline inorganic solid was recovered from the bomb.

The mixture obtained was separated into several fractions by repeated vacuum distillations. Comparison of the ir, nmr, and gc spectra of these fractions with pure standards permitted us to assign a structure to all major products and some of the by-products. Major products were recovered, purified, and identified. Smaller peaks were identified by their retention time in the gas chromatograph only. The following products were identified: (a) gases—CO, CO_2; (b) inorganic compounds—water (major), ammonium carbamate (the crystalline, inorganic solid); (c) organic compounds—acetone (not a direct product, but produced on standing), methacrylonitrile (very little), acetic, propionic, and isobutyric acids (minor), acetamide and isobutyramide (both major), N-methylacetamide (minor), and N-methylpropionamide (major). In addition the following compounds were isolated: a hydroperoxide (I), a high-boiling compound $C_8H_{15}N_3O_3$ (II) (major), and a fiber-forming polymer $(C_4H_7NO)_x$ (III) (major).

Intermediate Hydroperoxide (I). The presence and content of a hydroperoxide intermediate were established by iodometric titration. The analysis of the structure was not pursued.

Compound $C_8H_{15}N_3O_3$ (II). A water- and acetone-

---

[1] Farbwerke Hoechst, Kunststoff-Forschung, Frankfurt am Main, Germany.

[2] J. Brandrup and L. H. Peebles, Jr., *Macromolecules*, 1, 64 (1968), paper IV in this series.

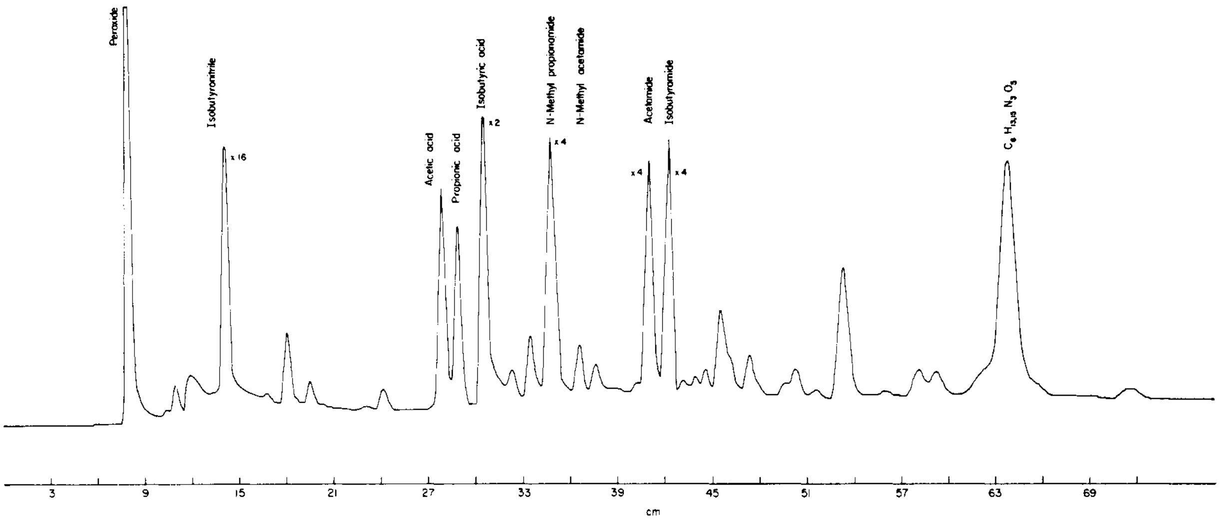


Figure 1. Gas chromatographic spectrum of isobutyronitrile heat treated at 150° for 3 days under oxygen.

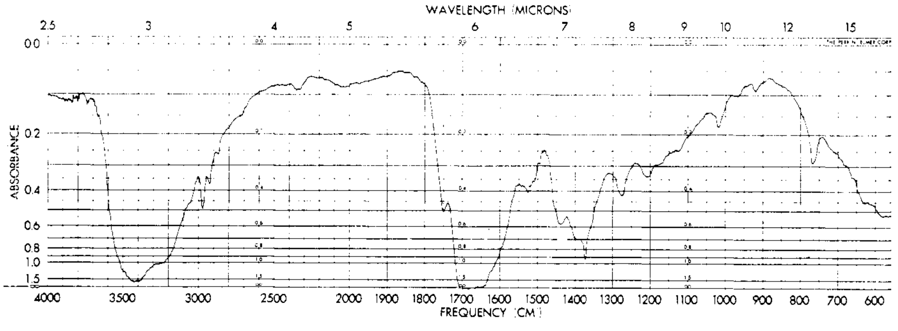


Figure 2. Infrared spectrum of polyisobutyronitrile $(C_4H_7NO)_x$.

soluble, stable compound was recovered in major amounts, bp 170° (1 mm), and was purified by recrystallization from benzene, mp 172°. The 60-Mc nmr spectrum in deuterated dimethyl sulfoxide (DMSO) showed one single, sharp peak at 95 cps (1.6 ppm) and a broad small peak at 490 cps (8.2 ppm). The infrared spectrum showed sharp peaks at 1695, 1725, and 1755 cm^{-1} and broad peaks at 3200 and 3450 cm^{-1}. One weak acid group per molecule could be determined potentiometrically. The compound resisted hydrolysis by concentrated hydrochloric acid but liberated gases (N_2 or N_2O) from an aqueous solution of sodium nitrite. The elemental analysis indicated a high oxygen content, which yielded the formula $C_8H_{15}N_3O_3$. The analysis of its structure was not pursued.

Polymer $(C_4H_7NO)_x$ (III). A brown polymer was obtained as the residue of the vacuum distillation. It had a rather high molecular weight since it was fiber forming. It was water soluble and partially soluble in DMSO but insoluble in DMF and other organic solvents. The infrared spectrum was similar to that of heat-treated PAN with broad absorption bands between 1650 and 1750 cm^{-1} (Figure 2). The nmr spectrum showed an unsymmetrical doublet at 81 cps[3] (Figure 3). This indicated that the isopropyl groups are intact in the polymer. Therefore, the isopropyl group has not participated in polymer formation and must remain as a pendant side group. Since the polymer is deep brown, it contained conjugated sequences. Furthermore, the polymer was bleached by basic hydrogen peroxide, a reaction shown to occur with conjugated $(-C{=}N-)_x$ sequences but not with conjugated $(-C{=}C-)_x$ sequences.[4] Based on all these

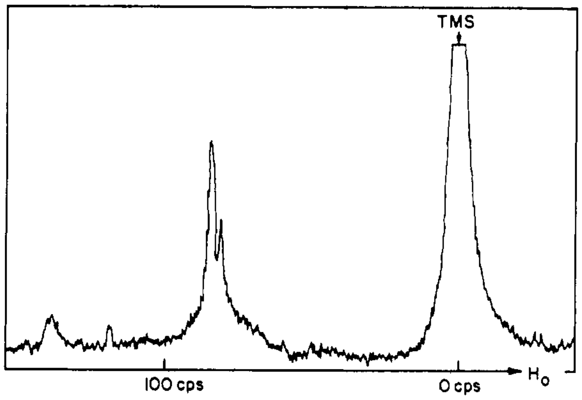


Figure 3. Nmr spectrum of polyisobutyronitrile dissolved in DMSO-d_6 at 105° to make a 11.7 wt % solution. The signals from 100 cycles downfield are due to nondeuterated DMSO.

---

[3] The broad absorption band at 140 cps is due to small traces of undeuterated DMSO in the solvent.

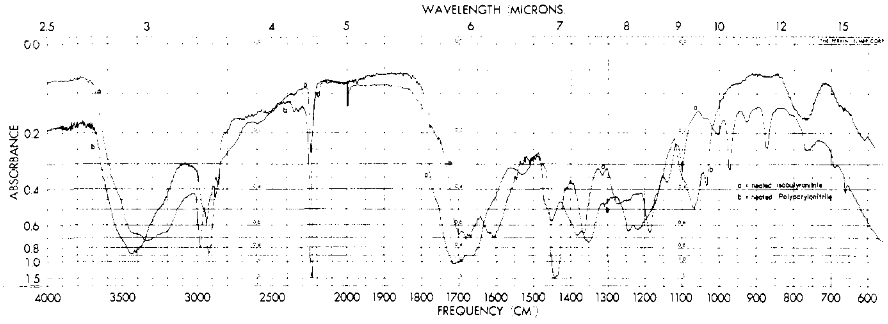


Figure 4. Infrared spectra of heat-treated isobutyronitrile and of heat-treated polyacrylonitrile.

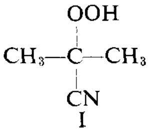
facts the structure of a polynitrone $(\text{-C}{=}\text{N}(\rightarrow\text{O})\text{-})_x$ was suggested as already described in detail.[4]

Discussion

Thermal Degradation of the Model Compound Isobutyronitrile. The oxidation and thermal behavior of low molecular weight nitriles has attracted comparatively little interest. Rabinovitch and Winkler[5a] pyrolyzed acetonitrile and propionitrile at 675 and 865°. Hydrogen, methane, hydrogen cyanide (half the theoretical amount), and several cyano-containing molecules were obtained. Kharasch and Sosnovsky[5b] investigated the oxidative behavior of aromatic nitriles and found ketones and dimers as reaction products. Simple aliphatic nitriles did not react under their experimental conditions. The reaction of nitriles with hydrogen peroxide[5c] is a preparative method for the formation of amides. Hydroperoxides react with nitriles to give amides.[6]

We were interested in the oxidation of isobutyronitrile because of its close similarity to a single pendant nitrile group in polyacrylonitrile. The thermal degradation of isobutyronitrile also produced amides, as described for other nitrile-containing compounds,[6] but, in this case, several amide-containing compounds were obtained, indicating the complexity of the reactions occurring. In addition a whole variety of intermediates and other stable end products was formed as shown in Figure 1. Since they were only present in minor amounts they were not all investigated. The infrared spectrum of the over-all mixture was similar to that of heat-treated PAN (Figure 4) which permitted the conclusion that similar reactions are occurring in the polymer and the model compounds. Therefore, an analysis of the mechanism of oxidation seemed justified.

The thermal breakdown of isobutyronitrile must occur *via* the hydroperoxide intermediate observed. Simple hydrolysis of the nitrile cannot occur, at least during the early stages of the reaction, because the starting material is dry and heat treatment of the same material under nitrogen does not produce any degradation products. The place of oxygen attack must be the tertiary hydrogen atom, since pivalonitrile, which has a methyl group at this position, does not form any color or other degradation products under comparable experimental conditions. The structure of the intermediate hydroperoxide therefore must be

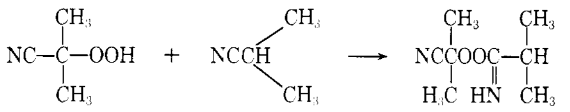

$$\text{CH}_3\text{—}\overset{\text{OOH}}{\underset{\text{CN}}{\text{C}}}\text{—CH}_3$$

I

The breakdown of this hydroperoxide to different intermediates and their subsequent reaction will give the products observed.

The time of appearance of the major intermediates and end products is shown in Figure 5. It is clearly seen that the hydroperoxide is formed nearly instantly. The highest amount (0.39%) is observed after 1 hr at 150°. As this hydroperoxide slowly disappears, two unknown intermediates are formed. Finally, the concentration of these intermediates decreases and the end products acetamide, isobutyramide, and N-methylpropionamide appear. Acetic acid and isobutyric acid increase slowly in concentration, always remaining minor products. Therefore, they cannot be essential for the mechanism, but are formed by slow hydrolysis of the starting material or the amides formed. A mechanism which accounts for all these facts is outlined in Scheme I. Details relating to the major products follow.

Isobutyramide is found in small amounts after 1 hr. It cannot originate from simple hydrolysis of the nitrile since the starting material was dried with P_2O_5 and the same material does not yield amides if heated under nitrogen. Its formation could be visualized by an attack of the original hydroperoxide on the nitrile group of another molecule (Scheme I, path B) similar to the mechanism given by Wiberg for the reaction of nitriles with hydrogen peroxide.[5c]


$$\text{NC—}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{—OOH} + \text{NCCH}(\text{CH}_3)_2 \longrightarrow \text{NC}\overset{\text{CH}_3}{\underset{\text{H}_3\text{C}}{\text{C}}}\text{OO}\underset{\text{HN}}{\overset{\|}{\text{C}}}\text{—}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}}}$$

IV

This intermediate can break down to radicals, which rearrange and pick up hydrogen, most likely from unreacted isobutyronitrile.

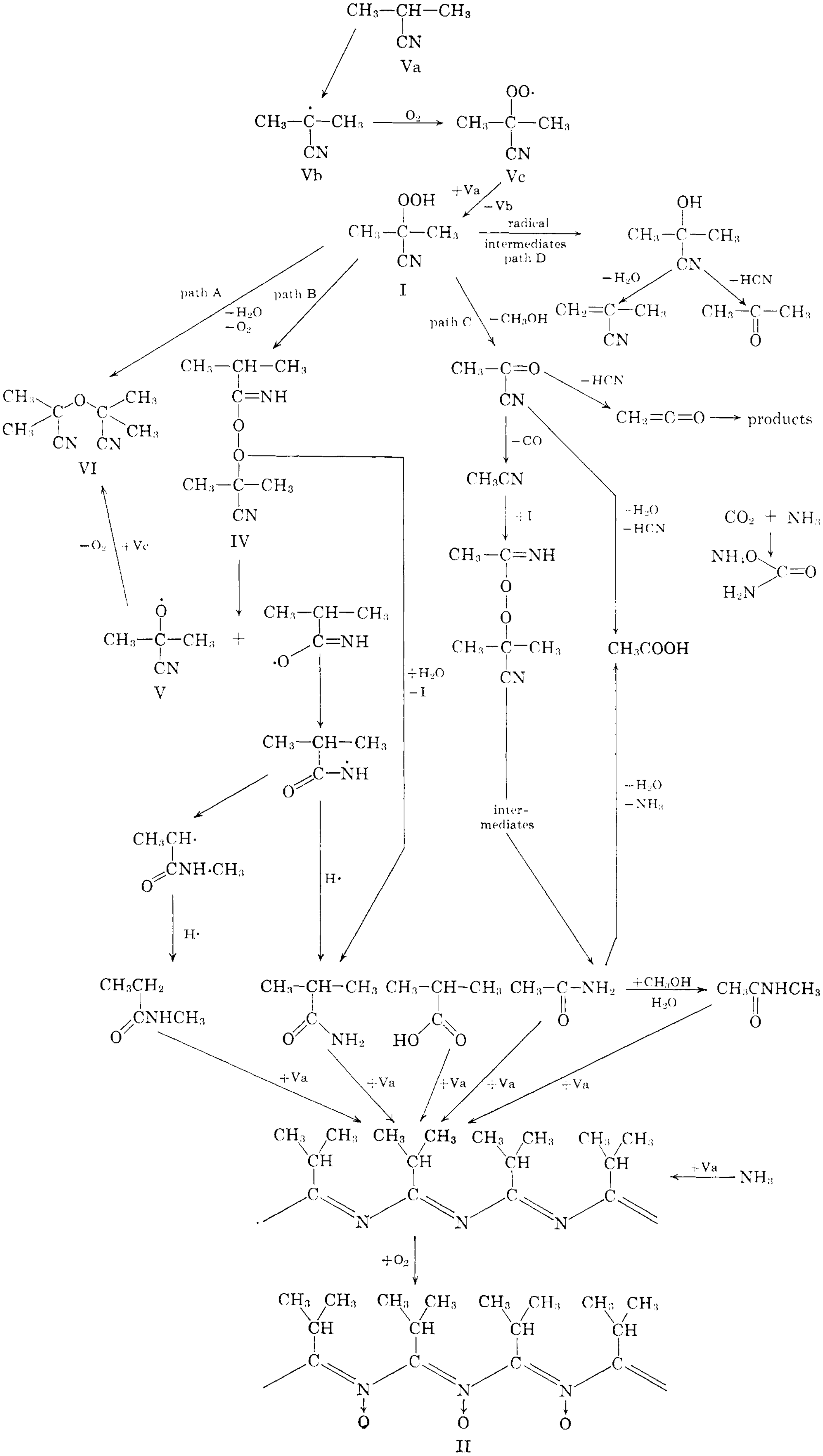
---

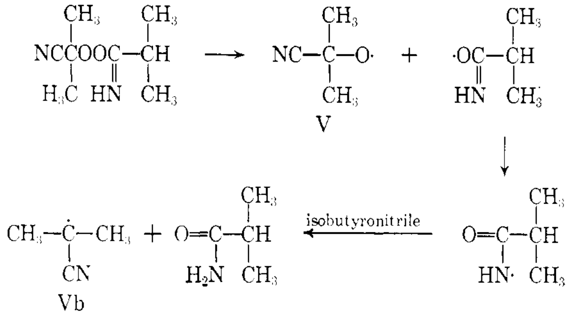
(4) L. H. Peebles and J. Brandrup, *Makromol. Chem.*, **98**, 189 (1966).

(5) (a) B. S. Rabinovitch and C. A. Winkler, *Can. J. Res.*, **20B**, 69 (1942); (b) M. S. Kharasch and G. Sosnovsky, *Tetrahedron*, 3, 97, 105 (1958); (c) K. B. Wiberg, *J. Amer. Chem. Soc.*, 77, 2519 (1955); H. Henecka and P. Kurtz in Houben-Weyl's "Methoden der organischen Chemie," Vol. 8, 4th ed, George Thieme, Stuttgart, 1952, p 663; H. Rupe and K. V. Majewski, *Chem. Ber.*, **33**, 3403 (1900); "Organic Syntheses," Coll. Vol II, John Wiley and Sons, Inc., New York, N. Y., p 586.

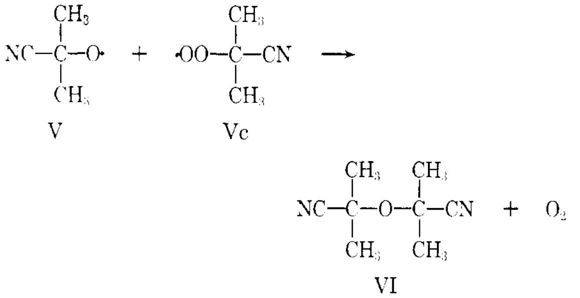
(6) H. Berger, *Trans. Faraday Soc.*, **58**, 1137 (1962).

SCHEME I: MECHANISM OF THERMAL OXIDATION OF ISOBUTYRONITRILE



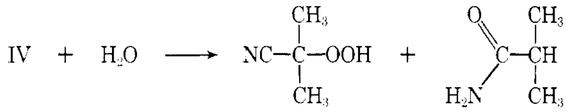


The isobutyronitrile radical Vb can continue the original hydroperoxide-forming chain reaction. The acetone cyanohydrin radical V may react with the hydroperoxide radical.



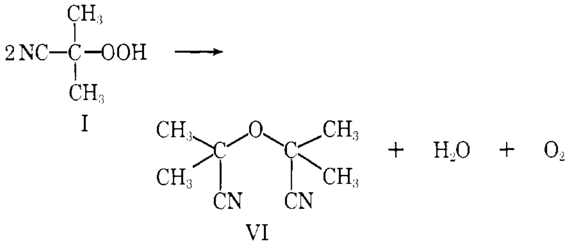
$NC{-}C(CH_3)_2{-}O\cdot + \cdot OO{-}C(CH_3)_2{-}CN \longrightarrow NC{-}C(CH_3)_2{-}O{-}C(CH_3)_2{-}CN + O_2$

The intermediate IV may also be hydrolyzed by water yielding isobutyramide.

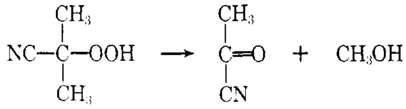


$IV + H_2O \longrightarrow NC{-}C(CH_3)_2{-}OOH + (CH_3)_2CH{-}C(=O)NH_2$

The water necessary for this reaction could originate from the dimerization of two hydroperoxide molecules (Scheme I, path A).



Acetamide. Hydroperoxides are known to break down to ketones by the reaction[7]

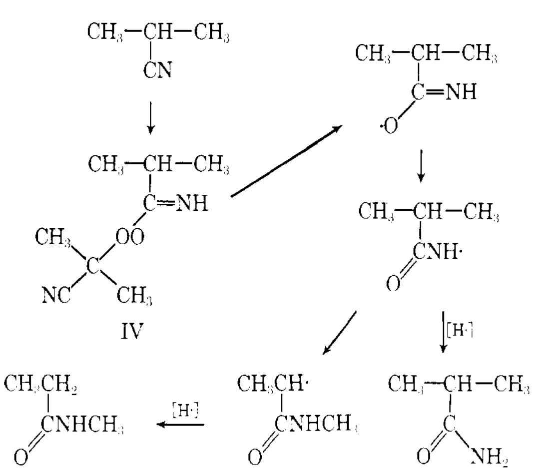


$NC{-}C(CH_3)_2{-}OOH \longrightarrow CH_3{-}C(=O){-}CN + CH_3OH$

to form pyruvonitrile (Scheme I, path C). Methanol was not found in the mixture but this is not thought to be important because of the many side reactions it can undergo (oxidation to formaldehyde, methylation of amides, etc.). Pyruvonitrile is known to eliminate CO (found) and to form acetonitrile.[8] It may also break down to a ketone and hydrogen cyanide to a minor extent. The acetonitrile formed will undergo a similar reaction with the hydroperoxide as isobutyronitrile does, acetamide being formed.

N-Methylpropionamide most likely is the product of rearrangement of an intermediate radical. Radicals are known to undergo numerous rearrangements under proper conditions.[9] The formation could be visualized as given in Scheme II.

SCHEME II



Ammonium carbamate appears after prolonged heating of isobutyronitrile (3–4 days). Complete oxidation of isobutyronitrile has yielded CO_2, H_2O, and NH_3. High temperature and pressure are the conditions of the commercial synthesis of urea from these starting materials, ammonium carbamate being an intermediate.

Acetic, propionic, and isobutyric acids form after extended reaction times. Water exists in larger amounts according to gas chromatography. Simple hydrolysis of nitriles and amides seems to be the reaction path.

Water. Major amounts of water most likely are formed by path A and path D in Scheme I.

Poly(isobutyronitrile) $(C_4H_7NO)_x$. The formation of this polymer must occur by nucleophilic attack of acids, amides, and NH_3 formed during oxidation on unreacted isobutyronitrile. The addition of nucleophiles to polyacrylonitrile starts a similar condensation reaction of the pendant nitrile groups.[10] A conjugated $(-C{=}N-)_x$-containing polymer is expected to form which is oxidized further to a polynitrone $(-C{=}N(\rightarrow O)-)_x$. Experimental evidence for this last reaction was presented already.[4]

Correlation of the Results Obtained for the Model Compound with the Thermal Degradation of Polyacrylonitrile. The close similarity between isobutyronitrile and one pendant nitrile group in PAN suggests that similar reactions must occur in the polymer. However, simultaneous but faster attack of oxygen at the methylene bridge screens the reactions occurring at the tertiary hydrogen atoms in the polymer.[2] Oxygen attack at the tertiary hydrogen atom will produce amides as outlined for the model compound (Scheme III). Further hydrolysis will also yield acids. All

---

(7) M. S. Kharasch, E. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 753 (1950).

(8) R. N. Bennett, E. Jones, and P. D. Ritchie, *J. Chem. Soc.*, 2628 (1956).

(9) A. Fish, *Quart. Rev.* (London), **18**, 243 (1964).

(10) N. Grassie and J. N. Hay, *J. Polymer Sci.*, **56**, 189 (1962).

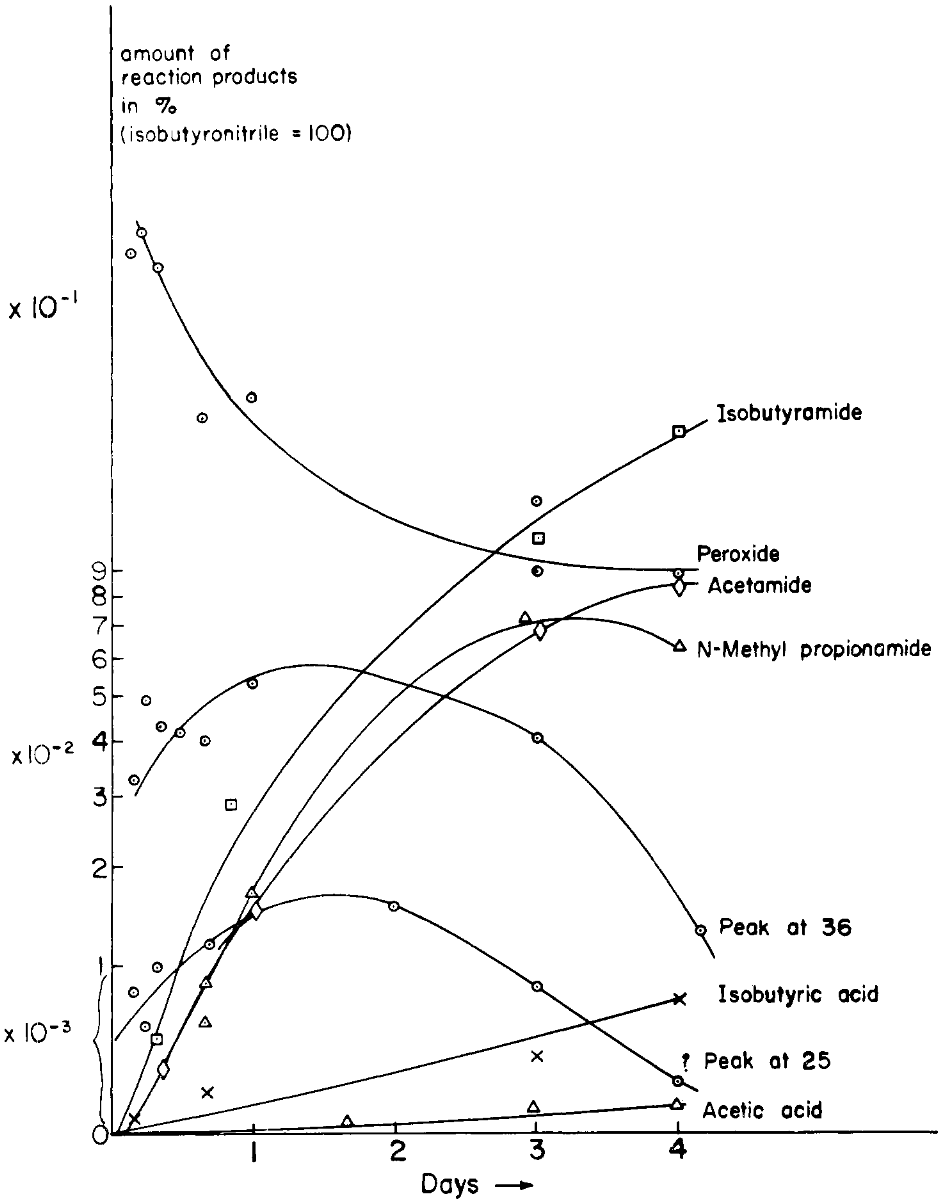
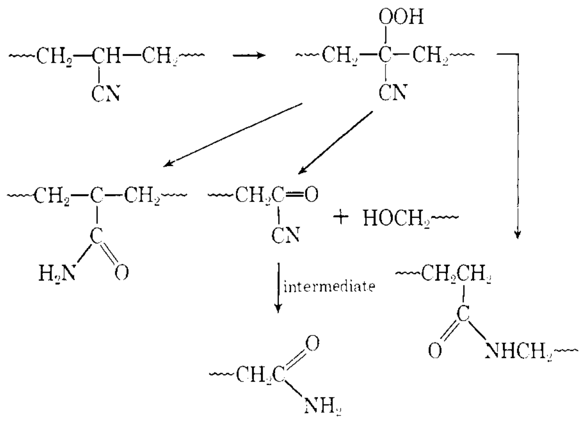


Figure 5. Time dependence of major gas chromatographic peaks of isobutyronitrile heat treated at 150°.

these products form part of the chain and therefore cannot be separately identified. Only volatile compounds observed like NH_3, HCN, and water were already detected by earlier work.[11–13]

SCHEME III



All the oxidation products mentioned have the ability to act as nucleophilic initiators of the color-forming polymerization of nitrile groups[10] (Scheme IV). The conjugated nitrile chain will then pick up oxygen at most of the conjugated nitrile links and form the very stable polynitrone, the final chromophore.[4] Since a polynitrone will be insoluble in organic solvents but soluble in water, an explanation is offered for the increasing insolubility of PAN during heat treatment.[14]

---

(11) W. J. Burlant and J. L. Parsons, *J. Polymer Sci.*, **22**, 249 (1956).

(12) S. L. Madorsky, "Thermal Degradation of Organic Polymers," Interscience Publishers Inc., New York, N. Y., 1964, p 194.

(13) H. Zahn and P. Schäfer, *Makromol. Chem.*, **30**, 225 (1959).

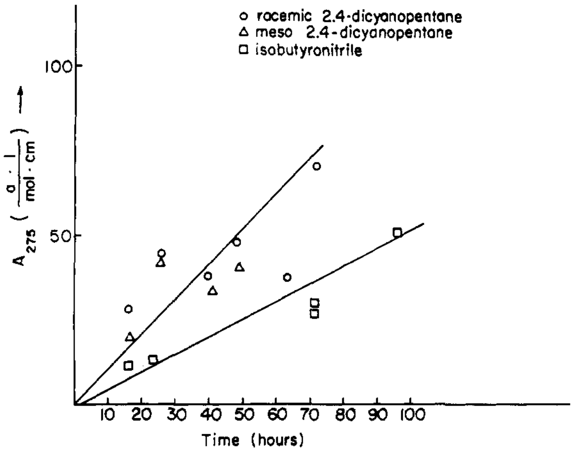
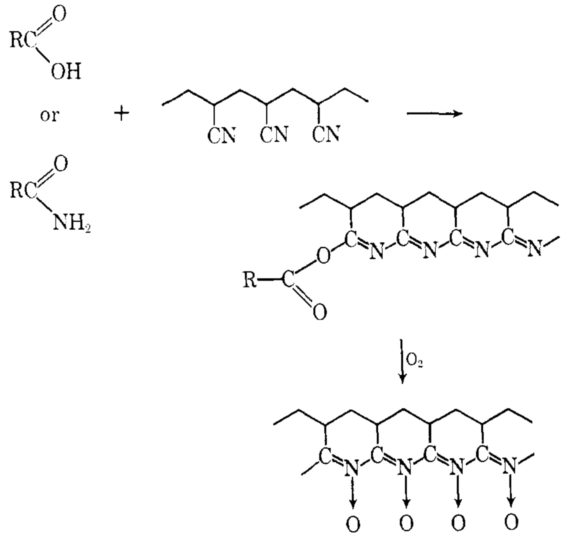


Figure 6. Change in the ultraviolet spectrum of model compounds with extent of degradation at *ca.* 145°.

Scheme IV



The ratio of oxygen attack at the tertiary *vs.* the secondary hydrogen atoms would be of interest. The previous paper had given a ratio of 1:3 based on the oxygen uptake of 2,3-dicyanobutane *vs.* 2,4-dicyanopentane. The discoloration of isobutyronitrile cannot be directly compared with the discoloration of the other model compounds investigated because of rather different experimental conditions. Isobutyronitrile was oxidized at 600–1000 psi O_2 and 150°; the other models were oxidized at 7.9 psi (1.5 atm) O_2 and 150°. Nevertheless, Figure 6 shows that in spite of the more severe experimental conditions isobutyronitrile discolors slower than 2,4-dicyanopentane as judged by the time dependence of the transmission in the ultraviolet region. The difference in degradation rate between isobutyronitrile and 2-cyanobutane already was described.[2]

All these experiments clearly show the subordinate role of the tertiary hydrogen atom contrary to expectation and show that the predominant place of oxygen attack in PAN is the methylene bridge.

Experimental Section

Isobutyronitrile was heated to about 150° under an oxygen pressure of 600–1000 psi for varying times in a 300-ml rocking steel autoclave. The bomb was opened after cooling and gases were collected in an infrared cell and investigated. Depending on the extent of oxidation, the complex, viscous mixture was yellow, brown, or black. In addition, a crystalline, inorganic solid was recovered from the bomb. This solid was separated from the liquid, washed with acetone and ether, and dried. The compound was unstable and released NH_3 with time; addition of acid yielded CO_2—the typical behavior of ammonium carbamate. The melting point in a sealed tube (151°) was in agreement with literature reports.

The liquid mixture obtained was separated into several fractions by repeated vacuum distillations under nitrogen and the fractions were investigated further by gas chromatography. An F & M gas chromatograph, Model 500, and a 14-ft long column filled with 20% Carbowax 20M on Gaschrom P and an 18-ft long column filled with 5% Carbowax 20M terephthalate on Chromosorb G 45–60 mesh AW-DMCS treated were used.

1. Fraction, Bp 26–28° (88 mm). This fraction contained five components according to gas chromatography. They were identified as water, methacrylonitrile, isobutyronitrile, and a hydroperoxide intermediate. The presence of the latter was established by iodometric titrations. The analysis of its structure was not pursued.

2. Fraction, Bp 95° (3 mm). This fraction contained three major peaks and solidified upon cooling. Recrystallization from hexane yielded white fluffy crystals of mp 128° which agreed with the melting point of isobutyramide (129°).

Anal. Calcd for C_4H_9NO: C, 55.17; H, 10.34; N, 16.09. Found: C, 55.0; H, 9.95; N, 16.01.

Ir and nmr spectra were in agreement; hydrolysis with HCl yielded isobutyric acid. The liquid of the isobutyramide recrystallization from hexane separated a colorless liquid upon concentrating which solidified. Its melting point (81°) and ir, nmr, and gc spectra agreed with acetamide.

Anal. Calcd for C_2H_5NO: C, 40.67; H, 8.47; N, 27.12. Found: C, 40.80; H, 8.40; N, 27.30.

The third peak could never be isolated completely because of very similar behavior. Repeated vacuum distillation gave a fraction enriched with this component. The nmr spectrum showed the presence of the $-NHCH_3$ group (doublet at 265 cps) and the ir spectrum showed the typical pattern of a secondary amide (peaks at 3100, 3300, 1660, and 1550 cm^{-1} in the solid state, which change in dilute chloroform solution to 3460, 3350 (broad), 1680, and 1520 cm^{-1}).[15] A synthetic mixture of isobutyramide and N-methylpropionamide gave identical ir, nmr, and gc spectra with this fraction, but a mixture with N-methylformamide, N-methylacetamide, N-methylbutyramide, and N-methylisobutyramide did not. This was taken as sufficient evidence for N-methylpropionamide.

3. Fraction, Bp 160° (1 mm). A water- and acetone-soluble, stable compound was recovered in major amounts, bp 170° (1 mm), and was purified by recrystallization from benzene (mp 172°). The 60-Mc nmr spectrum in deuterated DMSO showed one single, sharp peak at 95 cps (1.6 ppm) and a broad peak at 490 cps (8.2 ppm) due to one single hydrogen. The infrared spectrum showed sharp peaks at 1695, 1725, and 1755 cm^{-1} and broad peaks at 3200 and 3450 cm^{-1}. One weak acid group per molecule could be determined potentiometrically. The compound resisted hy-

---

(14) As a referee pointed out, increasing insolubility of heat-treated polyacrylonitrile could also be explained by even a slight amount of cross-linking by the proceeding condensation of nitrile groups. This is certainly correct.

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 208, 211, and 219.

drolysis by concentrated hydrochloric acid but liberated gases from an aqueous solution of sodium nitrite. The elemental analysis indicated a high oxygen content, which yielded the formula $C_8H_{15}N_3O_3$.

Anal. Calcd for $C_8H_{15}N_3O_3$: C, 47.76; H, 7.46; N, 20.90; O, 23.88. Found: C, 47.26; H, 7.50; N, 21.06; O, 24.48.

The oxygen was actually determined. The molecular weight in a vapor phase osmometer was determined as 201 in acetone.

4. Fraction, Residue of Distillation. After removal of all components by high-vacuum distillation, major amounts of a brown-black residue remained which apparently was polymeric, since fibers could be pulled from the melt. The polymer was purified by precipitation in acetone and high-vacuum treatment in a molecular still to remove all low-boiling components.

The polymer was soluble in water and partially soluble in DMSO. The nmr spectrum showed one doublet at 81 cps and the ir band showed broad absorption bands in the C=N region around 1600 cm^{-1}.

The elemental analysis of the polymer indicated a high nitrogen and oxygen content.

Anal. Calcd for $(C_4H_7NO)_x$: C, 56.47; H, 8.2; N, 16.47; O, 18.82. Found: C, 55.95; H, 7.9; N, 17.05; O, 19.7.

Hydrolysis with concentrated hydrochloric acid yielded isobutyric acid; treatment with basic hydrogen peroxide destroyed the brown color. The product obtained was highly hygroscopic but could not be identified. Based on these facts, the polymer was identified as a polynitrone.

Acknowledgment. We wish to thank Professor W. H. Urry for many helpful discussions.

On the Chromophore of Polyacrylonitrile. VI. Mechanism of Color Formation in Polyacrylonitrile

H. N. Friedlander, L. H. Peebles, Jr.,[1a] J. Brandrup,[1b] and J. R. Kirby

Contribution No. 482 from the Chemstrand Research Center, Inc., Durham, North Carolina. *Received October 27, 1967*

ABSTRACT: The formation of color in polyacrylonitrile is shown to be due to the formation of partially hydrogenated naphthyridine-type rings produced by linking up of adjacent nitrile units. This structure absorbs oxygen rapidly but not completely to form polynitrone $(\text{-C}{=}\text{N}(\rightarrow\text{O})\text{-})_n$ units. The polymerization of the nitrile units is initiated by products resulting from oxygen attack, by defects in the polymer chain, and by nucleophilic agents. Oxygen forms a hydroperoxide at the methylene carbon which forms a ketonitrile by elimination of water. A similar β-ketonitrile is produced by polymerization of the growing chain radical through a pendant nitrile group on the formed polymer. The cyanoenamine produced first is hydrolyzed to a β-ketonitrile when polymerization is conducted in an acidic aqueous medium. These defects may initiate the polymerization of adjacent nitrile groups. The amount of color formed is directly proportional to the number of these defects in the absence of other initiators. The fluorescence of polyacrylonitrile, described by many observers, is shown to be due to the presence of these ketonitrile groups in the polymer chain.

The thermal discoloration of polyacrylonitrile has received considerable attention during recent years. The main interest of previous publications was to establish the nature of the chromophore causing the color of the heat-treated polymer.[2-11] Since this work relied mostly on spectral evidence, no final conclusion could be drawn. Furthermore, relatively little work had been done on the mechanism of initiating the chromophore formation. The action of amines,[12] bases,[13,14] and the tertiary hydrogen atoms of the polymer itself[15] was considered. The initiating action of the latter was inferred by Grassie and Hay because all polyacrylonitriles developed color despite extensive purification of the monomer while polymethacrylonitrile did not discolor at high temperatures when it was prepared from purified monomers and extraneous material was excluded.[15,16]

In contradiction to this, we would like to show that the monomeric unit of polyacrylonitrile itself will not initiate the color formation reaction, but that it is converted into species which will initiate the color formation.

This paper summarizes the work carried out in this laboratory on the formation of color in polyacrylonitrile

---

(1) (a) To whom all correspondence should be addressed; (b) Farbwerke Hoechst, Kunststoff-Forschung, Frankfurt am Main, Germany.

(2) (a) R. C. Houtz, *Textile Res. J.*, **20**, 786 (1950); (b) J. R. McCartney, *Mod. Plast.*, **30**, No. 11, 118 (1953).

(3) W. J. Burlant and J. L. Parsons, *J. Polymer Sci.*, **22**, 249 (1956).

(4) N. Grassie and I. C. McNeill, *ibid.*, **27**, 207 (1958).

(5) J. Schurz, *ibid.*, **28**, 438 (1948).

(6) W. Skoda, J. Schurz, and H. Bayzer, *Z. Phys. Chem.* (Leipzig), **210**, 35 (1959).

(7) R. T. Conley and J. F. Bieron, *J. Appl. Polymer Sci.*, **7**, 1757 (1963).

(8) A. A. Berlin, A. M. Dubinskaya, and Y. S. Moshkovskii, *Vysokomolekul. Soedin.*, 1938 (1964).

(9) W. Fester, *Textil Rundschau*, **20**, 1 (1965).

(10) L. H. Peebles, Jr., and J. Brandrup, *Makromol. Chem.*, **98**, 189 (1966).

(11) L. H. Peebles, Jr., *J. Polymer Sci.*, *A-1*, **5**, 2637 (1967).

(12) E. M. LaCombe, *ibid.*, **24**, 152 (1957).

(13) H. Stübchen and J. Schurz, *Monatsh. Chem.*, **89**, 234 (1958).

(14) T. Takata, I. Hiroi, and M. Taniyama, *J. Polymer Sci.*, A2, 1567 (1964).

(15) N. Grassie and J. N. Hay, *ibid.*, **56**, 189 (1962).

(16) N. Grassie and I. C. McNeill, *ibid.*, **39**, 211 (1959).