On the Chromophore of Polyacrylonitrile. IV. Thermal Oxidation of Polyacrylonitrile and Other Nitrile-Containing Compounds

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ABSTRACT: Compounds that model certain aspects of the structure of polyacrylonitrile were degraded thermally at 145°. Measurements of the rate of discoloration and of the rate of oxygen uptake have suggested a mechanism for thermal color formation in polyacrylonitrile. The primary attack of the oxygen on the polymeric chain must be at the methylene hydrogens, since the rate of oxygen uptake and of color formation increases with n for the series of compounds $CH_3CH(CN)(CH_2)_nCH(CN)CH_3$ ($n = 0, 1, 2$). The hydroperoxide formed at this point breaks down to yield a β-ketonitrile. Both of these products were quantitatively determined during the course of the thermal treatment. The β-ketonitrile formed will initiate the color-forming polymerization of nitrile groups by a nucleophilic attack on one of the neighboring nitrile groups. The conjugated structure produced will react with atmospheric oxygen and will partially form a polynitrone—the final chromophore.

The thermal degradation of polyacrylonitrile (PAN) has attracted scientific as well as commercial interest. Numerous publications have appeared over the years which dealt mainly with the chemical structure that imparts the yellow-to-brown color to the heat-treated polymer. McCartney,[2a] Burlant and Parsons,[2b] and Grassie and McNeill[3] suggested the polymerization of nitrile groups to produce a partially hydrogenated system of naphthyridine rings. Peebles and Brandrup[4,5] confirmed that the chromophore consists of a system of conjugated $(\text{–C}{=}\text{N–})_x$ and not of $(\text{–C}{=}\text{C–})_x$ bonds. In addition, they showed that this chromophore picks up oxygen to form a nitrone. Since this reaction is not quantitative, they concluded that the chromophore consists of a random copolymer of conjugated imine and nitrone bonds $[(\text{–C}{=}\text{N–})_x\text{-}(\text{–C}{=}\text{N}(\rightarrow\text{O})\text{–})_y]$.

Rather limited and scattered information exists on the mechanism of the formation of this chromophore. Ammonia and amines will initiate the nitrile polymerization in PAN. LaCombe postulated an attack of the amine on a nitrile group forming an amidine.[6] Similarly, Grassie and McNeill showed that all compounds acting as Lewis bases can act as initiators. This was explained as a nucleophilic attack on the nitrile group yielding active species able to initiate the polymerization of nitrile groups.[7] Recently, Conley and Bieron showed that oxygen and heat definitely cause discoloration of PAN.[8] Earlier work had even shown that PAN develops color when heated under nitrogen.[2b,9] The formation of an intermediate azomethine by condensation of a nitrile group with a tertiary hydrogen atom was suggested.[10] Finally, Grassie and Hay suggested that the inability to obtain color-stable PAN might be explained by the action of the tertiary hydrogen atom. This hydrogen might have enough Lewis base character to act as initiator.[11]

Information on this subject is very limited and partly contradictory. Therefore, it was decided to investigate the formation of color in some model compounds of PAN in different environments with special attention to oxygen and the way it enters the molecule.

Results

A. **Model compounds** of two consecutive units in the chain (2,4-dicyanopentane), of a head-to-head link (2,3-dicyanobutane), and of a tail-to-tail link (2,5-dicyanohexane) were prepared and purified. These compounds were heat treated for varying lengths of time in an oil bath at 145° under pure oxygen and under purified nitrogen. After heat treatment, an aliquot was dissolved in Spectrograde ethylene carbonate–propylene carbonate and the ultraviolet absorption was measured. The results obtained are shown in Figure 1 where the absorption at 225 mμ is plotted *vs.* time.[12] Clearly, the discoloration of these model compounds depends on oxygen alone since no coloration of 2,4-dicyanopentane occurred during 1 week at 145° in the absence of oxygen. But the results for different model compounds obtained under oxygen are rather unexpected. Contrary to expectation, 2,3-dicyanobutane is the most stable of the model compounds and 2,5-dicyanohexane is the least stable. Repeated purifications of the model compounds and

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

[2] (a) J. P. McCartney, *Mod. Palst.*, **30**, No. 11, 118 (1953); U. S. National Bureau of Standards Circular 525, U. S. Government Printing Office, Washington, D. C., 1953, p 123; (b) W. J. Burlant and J. L. Parsons, *J. Polymer Sci.*, **22**, 249 (1956).

[3] N. Grassie and I. C. McNeill, *ibid.*, **27**, 207 (1958).

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

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

[6] E. M. LaCombe, *ibid.*, **24**, 152 (1957).

[7] N. Grassie and I. C. McNeill, *ibid.*, **39**, 211 (1959).

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

[9] J. Schurz, A. Ullrich, and H. Zah, *Monatsh. Chem.*, **91**, 741 (1960).

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

[11] N. Grassie and J. N. Hay, *J. Polymer Sci.*, **56**, 189 (1962).

[12] As a referee kindly pointed out, the absorptivity shown in the figures is based on the content of starting material and is therefore not an absolute absorptivity.

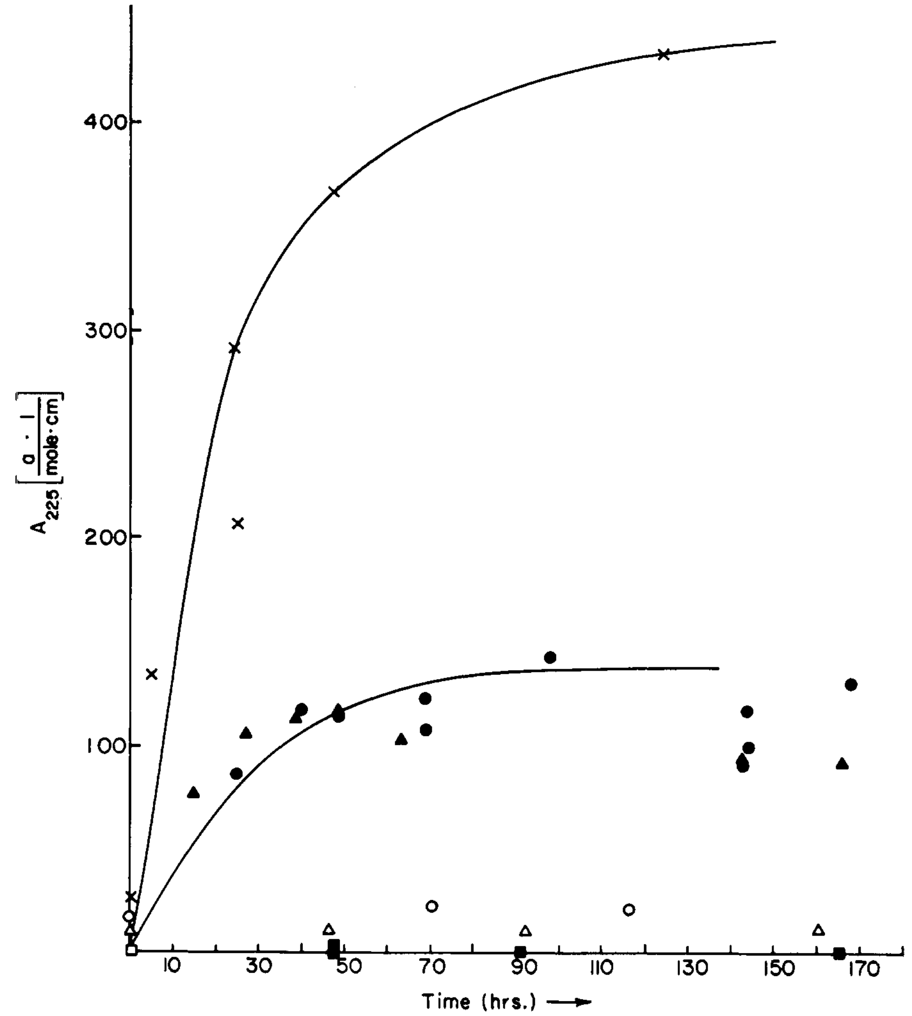
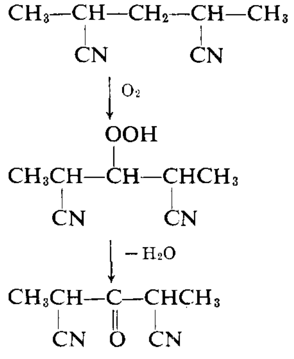


Figure 1. Discoloration of model compounds as measured by the ultraviolet absorption at 225 mμ after different times of degradation at 145°—under oxygen (1000 mm): ×, 2,5-dicyanohexane; ●, *meso*-2,4-dicyanopentane; ▲, racemic 2,4-dicyanopentane; ■, 2,3-dicyanobutane; under nitrogen (1000 mm): ○, *meso*-2,4-dicyanopentane, △, racemic 2,4-dicyanopentane.

varying experimental conditions always yielded identical results.

Thus it was decided to determine the oxygen uptake of these model compounds at 145°, since there existed the possibility that the oxygen would attack the molecule but that the hydroperoxide formed could not break down to colored intermediates. It was, for instance, observed that in the series $CH_3CH(CH_3)(CH_2)_nCH(CH_3)_2$ oxygen was taken up by both tertiary hydrogen atoms independent of *n*, but that the breakdown of these peroxides and the kind of products obtained were dependent on *n*.[13] Therefore, a gas buret was built which allowed the determination of the amount of oxygen taken up by the sample measured as the change in volume at constant pressure and temperature. The results obtained are shown in Figure 2 and it is seen that they essentially duplicate the results obtained by color-formation measurements. 2,3-Dicyanobutane does not take up much oxygen at all within the time given. 2,4-Dicyanopentane takes up more, but 2,5-dicyanohexane takes up the most. Equilibrium values were not obtained within 1 week. The amount of oxygen taken up always constituted a small fraction of that theoretically possible. However, the rates of oxygen uptake are significantly different.

It is apparent from our experiments that the hydrogen in the tertiary position must be rather stable to oxidation, since all compounds tested contain the same amount of tertiary hydrogen atoms but the rates of oxygen uptake and of color formation are drastically different. According to our results, the place of the first oxygen attack must be the hydrogen atoms of the methylene bridge. If this is correct, the hydroperoxide formed initially could break down with elimination of water, yielding a ketone group in β position to the nitrile group.



$$\begin{array}{c} CH_3-\underset{CN}{CH}-CH_2-\underset{CN}{CH}-CH_3 \\ \Big\downarrow O_2 \\ CH_3\underset{CN}{CH}-\overset{OOH}{CH}-\underset{CN}{CH}CH_3 \\ \Big\downarrow -H_2O \\ CH_3\underset{CN}{CH}-\underset{O}{\overset{\|}{C}}-\underset{CN}{CH}CH_3 \end{array}$$

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(13) F. F. Rust, *J. Amer. Chem. Soc.*, 79, 4000 (1957).

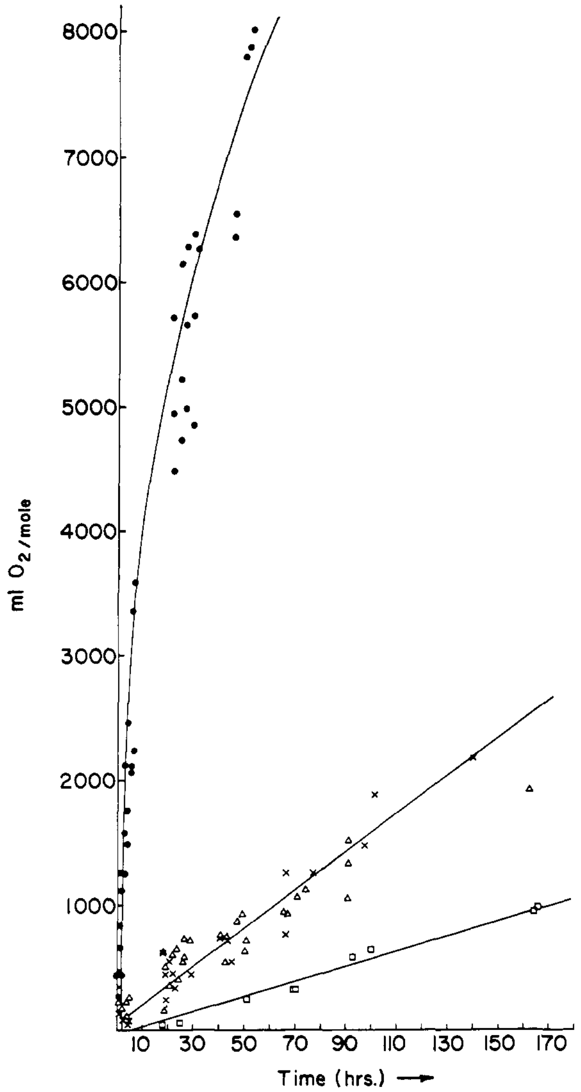

Figure 2. Oxygen uptake of different model compounds at 145° and 610 mm oxygen pressure: ●, 2,5-dicyanohexane; ×, *meso*-2,4-dicyanopentane; △, racemic 2,4-dicyanopentane; □, 2,3-dicyanobutane.

Since we know the spectral behavior of ketonitriles from earlier work (chromophoric weak acid groups of ref 14a, absorption II of ref 14b), this hypothesis could be readily tested: 2,5-dicyanohexane was heated under oxygen at 145° and samples were taken at intervals. The hydroperoxide was titrated iodometrically and the ketonitrile was determined by dissolving the sample in ethylene carbonate–propylene carbonate (EC–PC) and measuring the difference in absorptivity at 265 mμ before and after base addition. The results are shown in Figure 3. Hydroperoxide and ketonitrile are seen to be intermediates during color formation. First the hydroperoxide is produced, then the ketonitrile appears and decreases again, and finally color is developed (measured as the amount of background absorption at 275 mμ). If 2-cyanobutanone, a β-ketonitrile, is added, the induction period for ketonitrile formation is eliminated. This is good evidence for the suggested path of attack of oxygen on the methylene bridge. In addition, the sample became fluorescent during heat treatment. This fluorescence agreed with that observed for polyacrylonitrile.[15] When 2,4-dicyanopentane was subjected to the same experimental conditions, identical results were obtained. As expected, the formation of a β-ketonitrile (absorption II) occurs considerably slower; therefore, the color forms at a much slower rate (Figure 4) in agreement with our earlier observations.

The thermal stability of isobutyronitrile and 2-cyanobutane was compared in a separate experiment. Both compounds were heated in a sealed tube filled with oxygen at 150° for 4 days. The uv spectrum of the resulting brown liquids was measured in EC–PC and the curves in Figure 5 were obtained. While isobutyronitrile shows no titratable uv absorption, 2-cyanobutane shows the presence of a β-ketonitrile impurity. In addition, it degraded much faster than isobutyronitrile as measured by the difference in the intensity of the uv-background absorption. Both compounds showed essentially no uv absorption before heat treatment.

B. Correlation of the Results with the Polymer. Oxygen Uptake of Polyacrylonitrile. Samples of polyacrylonitrile of different origins were investigated for their thermal behavior. A typical oxygen uptake curve of polyacrylonitrile is shown in Figure 6. The initial very rapid apparent oxygen uptake is followed by a slower one which gradually increases in rate. The first steep decrease in volume is due to condensation of water introduced with the sample into the cooler parts of the apparatus. Very carefully dried samples do not contain this steep portion of the curve. This also suggests that the final increase is due to the initiation of evaporation of some reaction products and subsequent condensation in the cooler parts of the apparatus. A large quantity of polymer was heat treated at 145° for 1 week and all volatile materials were condensed in a trap cooled by Dry Ice–acetone. A small quantity of volatile products was indeed observed. The mixture had an almondlike odor and showed several peaks in the gas chromatographic traces. One peak corresponded to water; the others were not determined. The interpretable middle part of the curve is the same for all polymers investigated within the experimental error, as seen in Table I. This is an expected result, since all polymers possess the same structure, neglecting end groups and defects for the moment. The rate of oxygen uptake is *ca.* 6.8 ml/hr per two repeat units (for easier comparison with model compounds used) which is much smaller than that of the comparable model compound, 2,4-dicyanopentane (16 (ml/mol)/hr). We attribute this mainly to the difference in physical state of the materials (heterogeneous polymer *vs.* liquid model compound) and resulting variations in diffusivity.

Discussion

The thermal oxidation of model compounds of type $CH_3CH(CN)(CH_2)_nCH(CN)CH_3$ ($n = 0, 1, 2$) shows that color formation and oxygen uptake both increase

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(14) (a) J. R. Kirby, J. Brandrup, and L. H. Peebles, Jr., *Macromolecules*, 1, 53 (1968), paper II in this series; (b) J. Brandrup, J. R. Kirby, and L. H. Peebles, Jr., *ibid.*, 1, 59 (1968), paper III in this series.

(15) H. N. Friedlander, L. H. Peebles, Jr., J. Brandrup, and J. R. Kirby, *ibid.*, 1, 79 (1968), paper VI in this series.

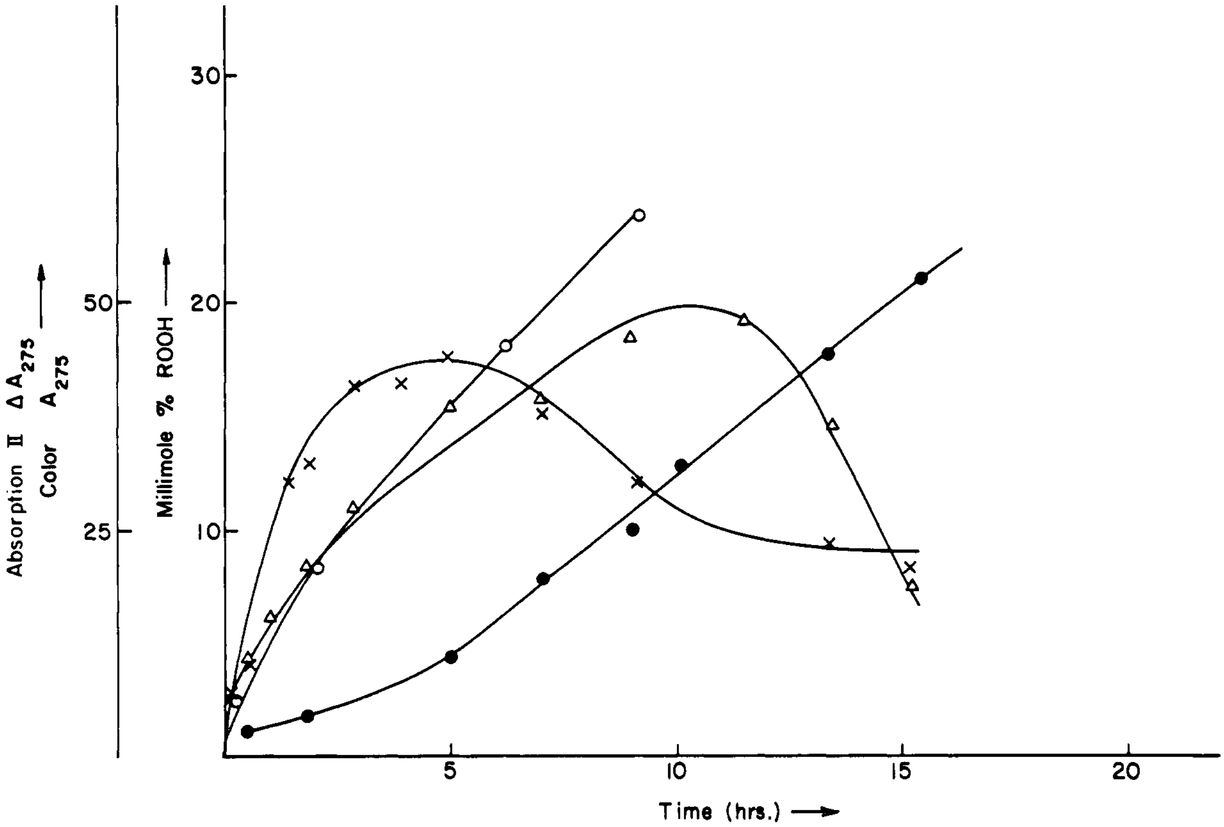

Figure 3. Time dependence of the formation of hydroperoxide (×) and β-ketonitrile (△) intermediates (absorption II) and of the formation of color (●) of 2,5-dicyanohexane. Color formation of 2,5-dicyanohexane is enhanced by addition of 16 wt % 2-cyanobutanone (○).

TABLE I
RATE OF OXYGEN UPTAKE FOR SEVERAL PAN SAMPLES

Remarks	Rate, (ml of O_2/two repeat units[a])/hr	Yellowness index after 8 hr at 145°
Redox-H_2O	5.6	22.6
Bulk polymerization	5.8	35.2
Redox-H_2O	5.1	41.1
Redox-H_2O	8.0	24.1
Peroxide-DMSO	5.4	28.3
Redox-H_2O	8.5	34.2
Redox-H_2O	8.0	20.1
Redox-H_2O	7.8	21.1

[a] Two repeat units facilitate comparison with model compounds used.

with an increase in *n* even though all three compounds have the same number of α-hydrogen atoms. Most theories on polymer degradation in general invoke the tertiary hydrogen atom. This is the place where oxygen attacks hydrocarbon polymers, forming a hydroperoxide which then can break down in numerous ways. The tertiary hydrogen atom was also assumed to play a role in the color formation of PAN by a number of authors. Conley and Bieron state that "the oxidatively most susceptible linkage in the polymer backbone is the tertiary hydrogen activated by the adjacent electron withdrawing nitrile group."[8] Grassie and Hay believe that this tertiary hydrogen atom is acidic enough to act as initiator of the color-forming reaction[11] and Weiss[16] similarly believes that the tertiary hydrogen can easily dissociate and is therefore responsible for the dyeability of PAN.

The results here both on the dinitriles cited above and on the thermal oxidation of 2-cyanobutane and isobutyronitrile indicate that the methylene hydrogens are considerably more susceptible to oxygen attack.

This idea of attack of the oxygen on the secondary hydrogen atoms seems to be contradictory to most other statements in the polymer literature. It is very common today to confuse the ionic lability of a tertiary hydrogen atom with its ability to undergo free-radical reactions (for instance, hydroperoxide formation) and to assume that tertiary hydrogen atoms react more easily than secondary or primary hydrogen atoms under any conditions. This confusion results from work on hydrocarbons and polyolefins (polypropylene) and polystyrene where it was shown that the tertiary hydrogen is more labile to both ionic and free-radical attack.[17] It was assumed to be correct for all other polymers. The extensive work on polyolefins has overshadowed all other results obtained earlier on substitution reactions in low molecular weight chemistry. Therefore, it is useful to recall that earlier work had already established quite different substitution rules when different substituents are already present in the

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(16) W. Weiss, *Mitt. Inst. Textiltechnolog. Chemiefaser Rudolstadt*, **4**, 27 (1960).

(17) W. O. Lundberg, "Autoxidation and Antioxidants," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1961; H. C. Beachell and D. L. Beck, *J. Polymer Sci.*, **A3**, 457 (1965).

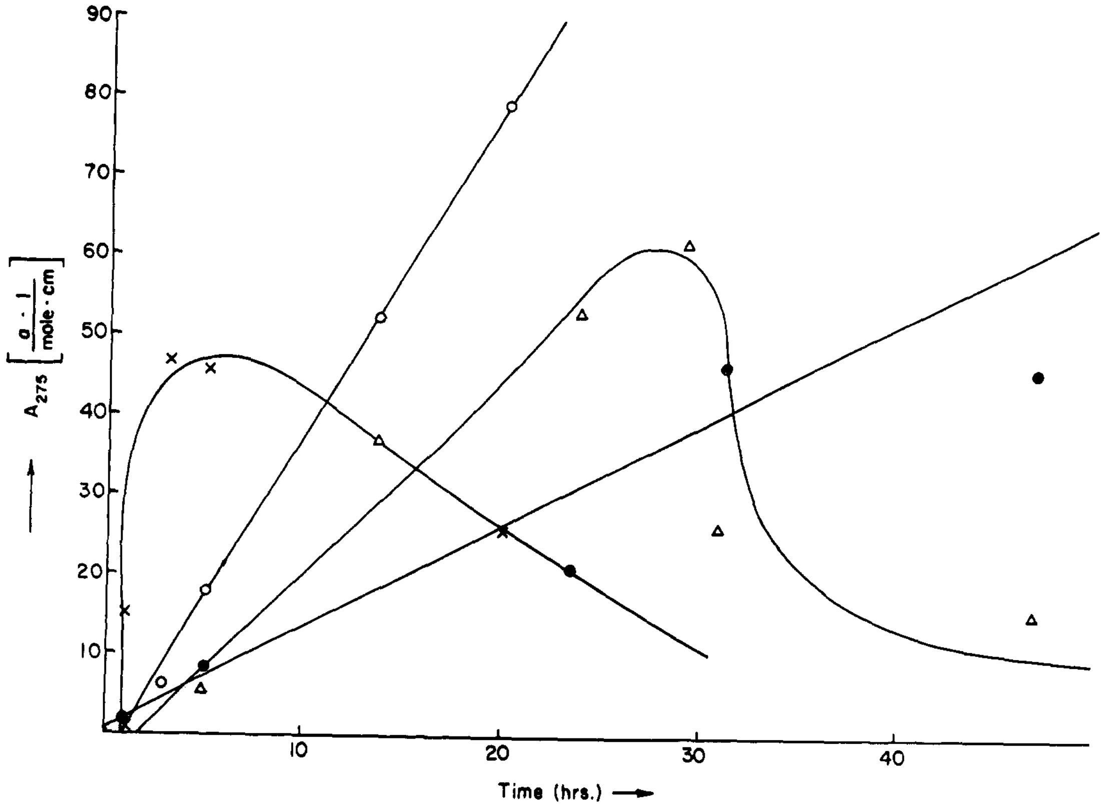

Figure 4. Time dependence of the formation of β-ketonitrile defects (×, △) and of color in 2,5-dicyanohexane (×, ○) and in 2,4-dicyanopentane (△, ●).

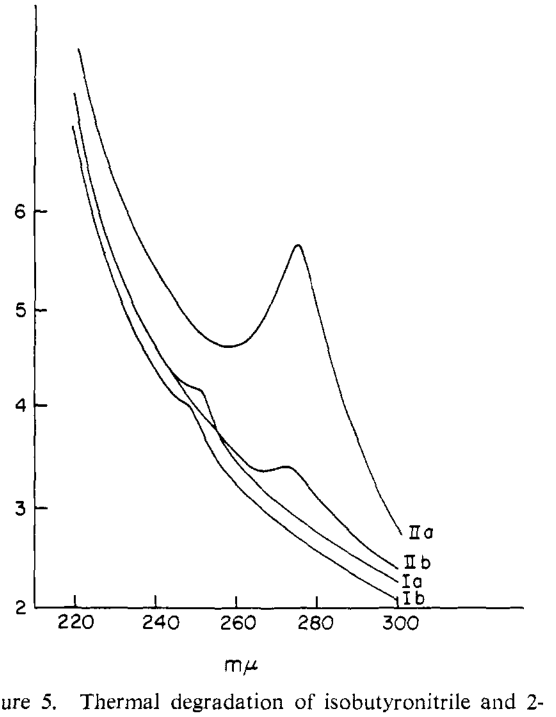

Figure 5. Thermal degradation of isobutyronitrile and 2-cyanobutane as measured by the uv spectra after 4 days at 150°: Ib, isobutyronitrile before addition of base; Ia, isobutyronitrile after addition of base; IIb, 2-cyanobutane before addition of base; IIa, 2-cyanobutane after addition of base.

substrate.[18] Thus tertiary hydrogens are much more stable under certain conditions than primary or secondary hydrogens, as, for instance, work on sulfochlorination by Kharasch, Kane, and Brown demonstrates.[19] Furthermore, substituents in the chain have a directive effect on the placement of the incoming group. Thus, methyl groups will direct the groups close to them, while other substituents may direct them to more remote positions. Rust and Vaughan studied the vapor phase chlorination of lower straight chain monochlorides, such as 1-chlorobutane.[20] They observed that chlorine tends to enter the molecule in positions remote from the seat of the original substituent. Ash and Brown studied the chlorination of a number of substituted hydrocarbons and determined the directive effects of the substituents to the entering chlorine group.[18] Only phenyl and methyl substituents have a larger amount of α substitution. All others (–COOH, -COCl, -Cl, -CN, etc.) try to place the next substituent as distantly as possible. Chlorination of propionitrile yielded predominantly products of β substitution.[21]

Modern theoretical organic chemistry explains these directive forces by the inductive and the resonance effects.[22] These effects tend to decrease or increase the electron density on the atom under consideration which in turn will affect its reactivity toward other compounds. Methyl groups tend to increase the elec-

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(18) A. B. Ash and H. C. Brown, *Rec. Chem. Progr.*, **6**, 15 (1945); **9**, 81 (1948).

(19) M. S. Kharasch, S. S. Kane, and H. C. Brown, *J. Amer. Chem. Soc.*, **64**, 1621 (1942).

(20) W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **5**, 449 (1940); **6**, 479 (1941).

(21) A. Bruylants, M. Tits, C. Dien, and R. Gauthier, *Bull. Soc. Chim. Belges*, **61**, 366 (1952).

(22) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959, p. 200 ff.

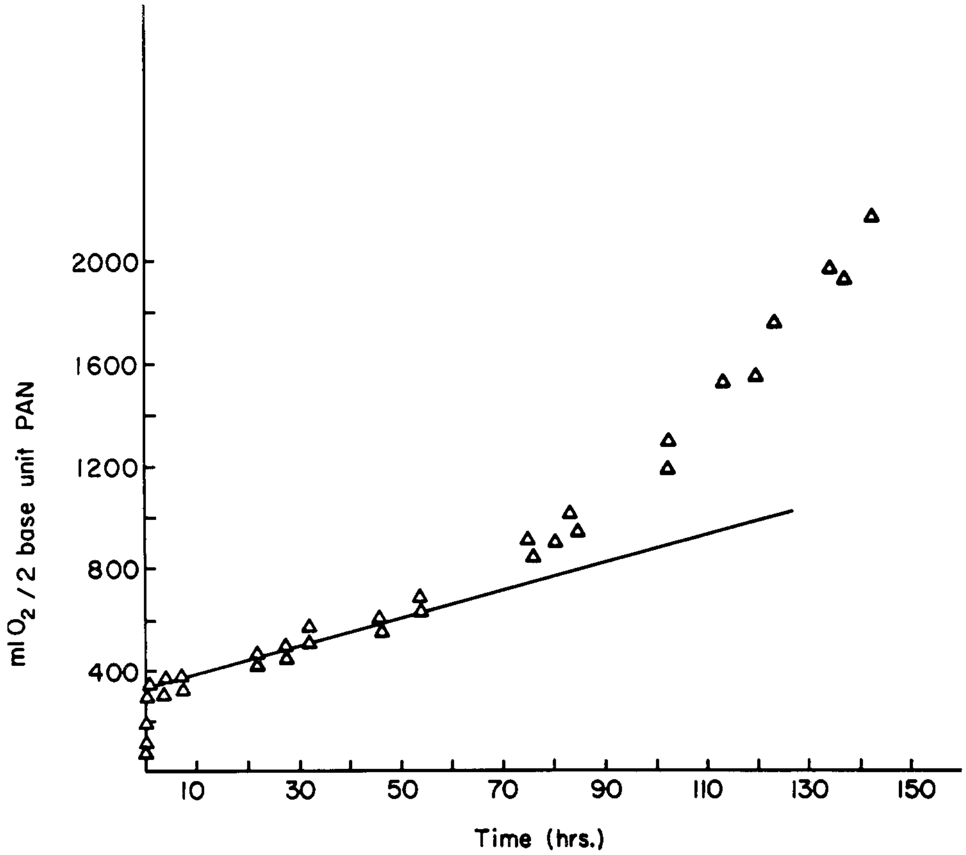

Figure 6. Typical oxygen uptake curve for polyacrylonitrile at 145° and 610 mm oxygen pressure.

tron density on the neighboring hydrogen atom (+R, +I effect), while the cyano groups and most other groups will decrease it (−R, −I effect).[22] Since oxygen is a better electron attractor, *i.e.*, more electronegative, than carbon or hydrogen, it will tend to react with atoms of high electron density. This is the case for the tertiary hydrogen atoms in polyolefins (methyl substituent) and polystyrene (phenyl substituent), but this is not true for tertiary hydrogens close to cyano, chloro, or carboxyl groups. Therefore, our findings here, that the favored places of attack in our compounds are the secondary hydrogen atoms, should also be valid for other substituents or for that matter polymers (polyacrylamide, polyacrylic acid, etc.).

As seen in Figures 1 and 2, 2,3-dicyanobutane takes up oxygen and forms color, but to a much smaller degree than the other models. This cannot be explained with the idea suggested here. Most likely, oxygen attack will occur at the tertiary hydrogen atoms, as shown to be the case for isobutyronitrile.[23] Breakdown of the hydroperoxide will give amides, N-substituted amides, and acids.[23] This idea is confirmed by the much smaller rate and by the smaller amount of color formed per amount of oxygen taken up (Table II). The table gives nearly identical ratios for 2,4-dicyanopentane and 2,5-dicyanohexane (within a factor of 2), demonstrating the similarity of the processes involved, while 2,3-dicyanobutane develops much less color (1:10). This must mean that some of the oxygen was consumed in the formation of colorless products like amides, etc.[23] Therefore, the ratio of color formation or oxygen uptake for 2,3-dicyanobutane and 2,4-dicyanopentane will give the ratio of attack at the tertiary hydrogen to attack at the secondary hydrogen. This ratio is 1:58 according to color measurements (Figure 1) but it is 1:3 according to oxygen uptake measurements (Figure 2). These numbers are not intended to be exact but do demonstrate the predominant attack at the secondary hydrogen atoms.[24]

TABLE II
RATIO OF COLOR TO OXYGEN UPTAKE

	Color (A_{275})/oxygen (ml/mol)
2,3-Dicyanobutane	0.7×10^{-2}
2,4-Dicyanopentane	14×10^{-2}
2,5-Dicyanohexane	7×10^{-2}

If we now turn to the thermal behavior of polymers, we notice that the amount of oxygen taken up by various polymers is nearly identical and that the amount of thermal discoloration is very different for different polymers after identical times of heat treatment, as seen in Table I. This is direct evidence that another active initiator must be present in the polymer. The β-ketonitriles can be formed by two distinctly different reactions: oxidation of the methylene carbon atoms

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(23) J. Brandrup, *Macromoles*, **1**, 72 (1968), paper V in this series.

(24) The ratio determined by color measurements might be even higher since 2,3-dicyanobutane is only very slightly discolored by these conditions whereas degraded 2,4-dicyanopentane is black. The ratio determined by oxygen uptake seems closer to reality since it measures the reactivity of the hydrogen atoms directly and not subsequent reactions.

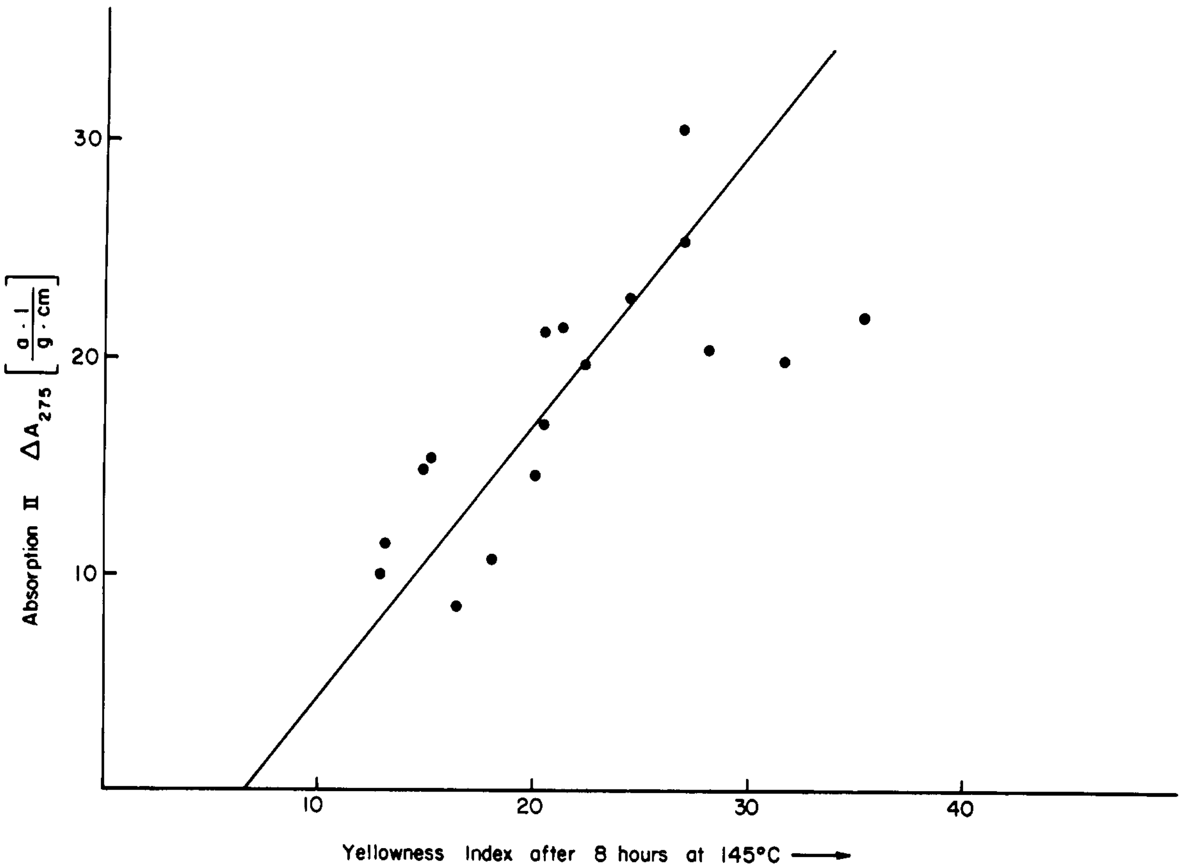

Figure 7. Dependence of the thermal discoloration of PAN on the amount of β-ketonitrile defect present in the polymer (absorption II).

(as shown here) and polymerization through a nitrile group by a growing chain as is shown in paper III of this series.[14b] The β-ketonitrile from either source should then be able to initiate the thermal color formation reaction. To test this hypothesis, polymers containing different amounts of the β-ketonitrile group (absorption II of ref 14b) were heat treated for 8 hr at 145°. The color developed was determined by measuring the yellowness index[25] of the polymer. The amount of β-ketonitrile defect present was determined as chromophoric weak acid group.[14a] Figure 7 shows that the amount of color formed is directly proportional to the amount of the β-ketonitrile defect present in the polymer. But a residual amount of color is also formed when no β-ketonitrile defect is present in the polymer, measured by the intercept on the yellowness axis in Figure 7. This amount of discoloration must be due to the β-ketonitrile formed during thermal oxidation as outlined above. It therefore was not determined before the start of the experiment.

The initiating action of ketonitrile can be explained by its nucleophilic attack on a nitrile group adopting Grassie's and McNeill's results with acids and phenols.[7] This can be visualized as in Scheme I (the nucleophilic center of attack can be either the α-carbon or the enolate oxygen). As indicated earlier, the imine chromophore formed will in part pick up oxygen to form the poly(imine–conitrone) structure—the final chromophore.[4,26]

All the reactions outlined here occur only with a very small fraction of the polymer. But this very small amount of chromophore formed is sufficient to impart a definite color to the polymer. Heat-treated 2,4-dicyanopentane is deep black in color; it was separated into reacted and unreacted species by fractional precipitation by ether–heptane mixtures. The colored part constituted less than 1% of the amount after 1 week at 145°. The recovered 2,4-dicyanopentane had an identical rate of discoloration when retested for its thermal behavior. The fact that the reactions leading to color constitute only a minor part of the whole polymer explains the lack of success of earlier workers, who tried to investigate the color reaction with the polymer itself. This also explains the remaining excellent stability, the lack of a major amount of volatiles, and the stability of the molecular weight.

Experimental Section

A. Description of the Apparatus for Measuring Oxygen Uptake. A gas buret was constructed which measured the

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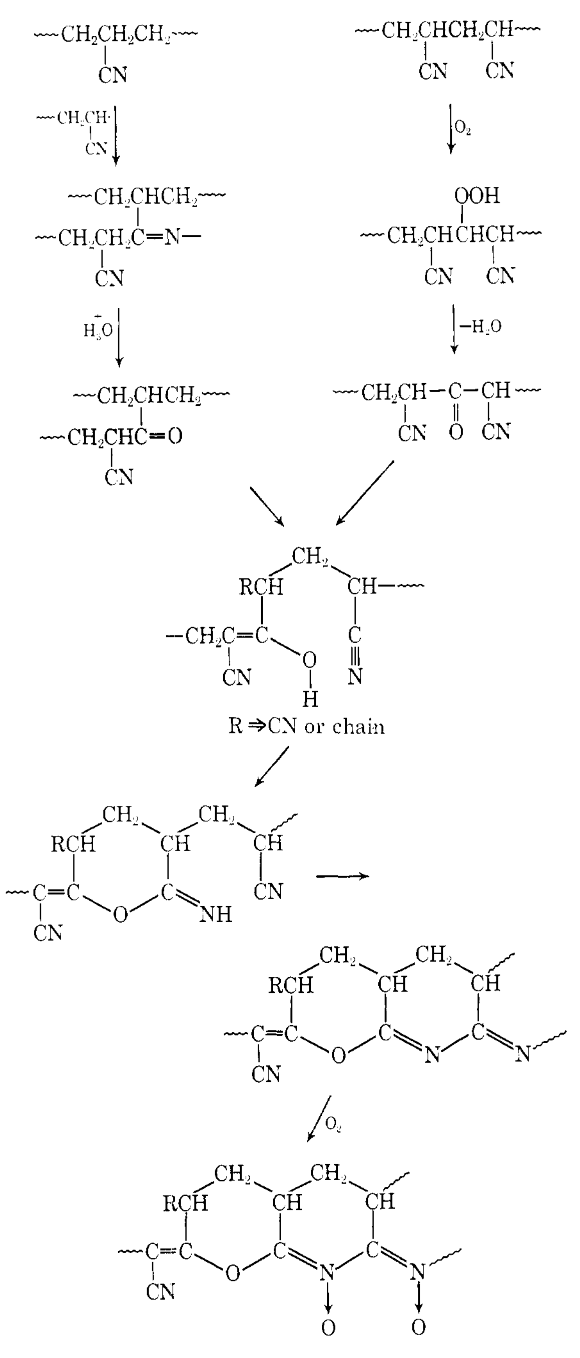
[25] D. B. Judd, "Color in Business, Science and Industry," John Wiley and Sons, Inc., New York, N. Y., 1952, p 165.

[26] We have stated that the ratios of color formation to oxygen uptake for 2,4-dicyanopentane and 2,5-dicyanohexane are nearly identical (within a factor of 2). Thus the structure of the chromophore of the two compounds should be equivalent, a poly(imine–conitrone) of the form $-(C{=}N)_x-(C{=}N(\rightarrow O)-)_y$. While the 2,4-dicyanopentanes can also form a series of six-membered heterocyclic rings, the 2,5-dicyahohexane probably does not form a seven-membered heterocyclic ring. If so, then generally only one nitrile group per molecule participates in the nitrile polymerization reaction. These structural speculations were not pursued further.

SCHEME I



change in volume at constant pressure and temperature. This was achieved by using two manometers filled with mercury as seen in Figure 8. Any decrease in volume caused a rise of the mercury level in legs b and c and a lowering in legs a and d which broke an electrical contact in a. A relay then started a Servo motor which increased the mercury level in d, thereby also raising the level in a. Volume expansion was corrected in a similar way. When the mercury level in a tended to rise, a second contact in a was closed which caused the Servo motor to lower the level in d.

The accuracy of the instrument was determined by the difference in heights of the two contacts in a. Their difference in heights was close to 1 mm, which corresponded to 0.5 ml in volume change. The construction of the instrument allowed the easy determination of leaks in the system, since this caused a continuous lowering of the mercury level. An oxygen uptake, however, corresponded to a continuous increase of the mercury level. Since the gas buret kept the inside pressure constant against the outside pressure, changes in outside pressure were corrected by using an empty gas buret as a control.

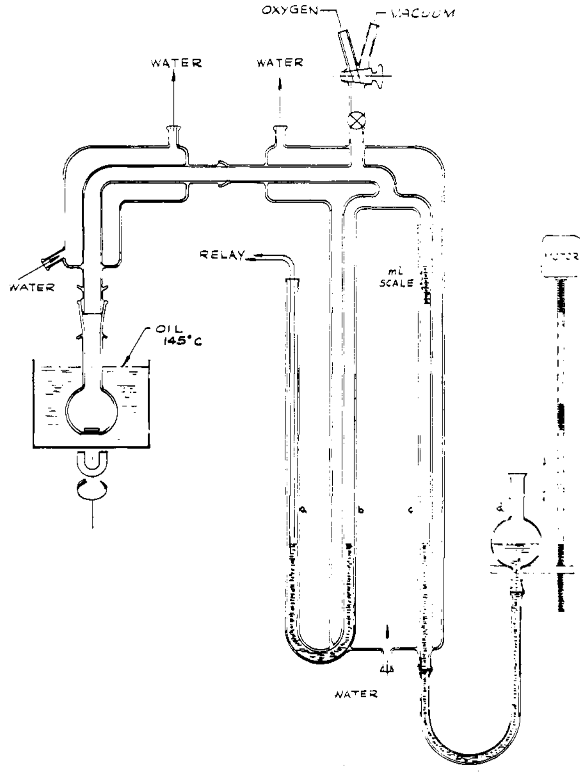


Figure 8. Schematic representation of the oxygen uptake instrument.

The samples were weighed in small tubes, connected with the gas buret, and flushed with vacuum and oxygen several times. After the system was ready, an oil bath (145°) was raised immersing the samples into it. After the immediate volume expansion had ceased, readings of the mercury level were taken every minute, later every hour. These readings were corrected by the change in volume in the standard buret and recalculated into milliliters of oxygen per mole of compound. These dimensions are used in all figures.

B. Preparation of Compounds. 1. 2,5-Dicyanohexane. Smaller amounts of this dinitrile were obtained through the kindness of Dr. M. Baizer, Monsanto, St. Louis, Mo. Larger quantities were prepared by electrodimerization of methacrylonitrile according to Baizer.[27]

2. 2,4-Dicyanopentane was prepared by the methods of Takata[28] and Clark.[29]

3. 2,3-Dicyanobutane was obtained in reasonable yields by a method closely related to Clark's preparation of 2,4-dicyanopentane. Ethyl-α,β-dicyano-α,β-dimethyl propionate was obtained by treating lactonitrile with sodium ethyl cyanoacetate according to Higson and Thorpe.[30] The ester obtained in very good yield was hydrolyzed by cold, ethanolic potassium hydroxide. The free acid was decarboxylated by refluxing it in toluene with copper spirals. This last step was the most difficult one; many side products were obtained. 2,3-Dicyanobutane was obtained in approximately

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(27) M. M. Baizer and J. D. Anderson, *J. Electrochem. Soc.*, **111**, 223 (1964).

(28) J. Takata and M. Taniyama, *Chem. High Polymers* (Tokyo), **16**, 693 (1959).

(29) H. G. Clark, *Makromol. Chem.*, **63**, 69 (1963).

(30) A. Higson and J. F. Thorpe, *J. Chem. Soc.*, **89**, 1455 (1906).

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.

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

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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 $(-\mathrm{C}{=}\mathrm{N}(\rightarrow\mathrm{O})-)_n$. 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-

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

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