[CONTRIBUTION FROM THE ORGANIC BASIC RESEARCH DEPARTMENT, THE DOW CHEMICAL CO.]

The Addition of Chlorine to Acrylonitrile

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The type of products obtained when chlorine is added to acrylonitrile is dependent upon the presence or absence of hydrogen chloride during the reaction. The radiation of a tungsten lamp between 3000 and 4000 Å is the most effective radiation range for catalyzing the addition of chlorine to acrylonitrile.

The literature describing the conditions and products for the addition of chlorine to the double bond of acrylonitrile presents conflicting data. Sumner[1] has stated in a patent that chlorine reacts with acrylonitrile in the presence of visible light and in the absence of oxygen and water to give a 65 to 79% yield of 2,3-dichloropropionitrile. He reports that if solvents were used the desired molar amount of chlorine was about one third the amount of acrylonitrile present as the use of a higher ratio of chlorine favored the formation of by-products. Emphasis was placed on the need for anhydrous conditions. Yet the effect of a small amount of water did not appear to be a sufficient reason for the absence of 2,3-dichloropropionitrile in the products when the work of D'Ianni[2] is considered. In his study of the action of chlorine water on acrylonitrile, D'Ianni obtained a 26% yield of 2,3-dichloropropionitrile as a by-product when he added chlorine to a solution of one mole of acrylonitrile dissolved in twenty-two moles of water. Krzikalla and Flickinger[3] have stated that "chlorination of acrylonitrile with two atoms of chlorine does not yield 2,3-dichloropropionitrile as expected, but a mixture of about one half mole of 3-chloropropionitrile and one half mole of 2,2,3-trichloropropionitrile." A similar statement was made in a patent by Clifford and D'Ianni.[4]

Brintzinger, Pfannstiel, and Koddebusch[5] reported a 95% yield of 2,3-dichloropropionitrile and 100% acrylonitrile conversion when chlorine was added in the dark to acrylonitrile (1.04 moles) in the presence of pyridine (0.18 mole). This work has been repeated in this laboratory but their very high yield was not achieved. It is important in this procedure that all of the pyridine be removed by the water wash as only trace amounts of pyridine hydrochloride causes continuous dehydrohalogenation of 2,3-dichloropropionitrile to 2-chloroacrylonitrile during distillation.

Since published reports are conflicting, a detailed study of the chlorination of acrylonitrile was undertaken. It is now evident that the conditions of chlorination may be altered to obtain two kinds of products: (1) A mixture of 3-chloropropionitrile and 2,2,3-trichloropropionitrile, and (2) 2,3-dichloropropionitrile.

The concentration of hydrogen chloride in the chlorination mixture was an important factor in determining the nature of the product formed. When acrylonitrile was treated with chlorine and chlorination was continued after the mixture became saturated with hydrogen chloride, the product was a mixture of 3-chloropropionitrile and 2,2,3-trichloropropionitrile which on prolonged chlorination led to high yields of 2,2,3-trichloropropionitrile. When the reaction was stopped before the solution became saturated with hydrogen chloride, the major product was always 2,3-dichloropropionitrile.

EXPERIMENTAL

Influence of hydrogen chloride on the reaction. Since the reaction proceeds very slowly in the dark, visible light (150-watt Sylvania bulb with built-in reflector) was employed as specified by Sumner.[1]

Commercial acrylonitrile that contained 0.5 to 0.7% water was used in all experiments.

The experiments were carried out in a cylindrical Pyrex reactor that was placed in and against the side of a larger Pyrex beaker which contained ice water. A magnetic stirrer was used in the reactor. The light source was placed 6 inches away from the section where the beaker and reactor touched. Chlorine was added to a 200-ml. (3.3 moles) charge of acrylonitrile at a rate of 16–18 g./hr. and 8-ml. samples were withdrawn at half-hour intervals. These were analyzed by infrared spectroscopy by measuring the intensity of the band at 11.0 μ for 3-chloropropionitrile, 13.3 μ for 2,2,3-trichloropropionitrile, and 13.6 μ for 2,3-dichloropropionitrile. Several runs were made, and the results of a typical run are given in Fig. 1. In each run hydrogen chloride was evolved when, or just after, the maximum concentration of 2,3-dichloropropionitrile was reached. The 3-chloropropionitrile appeared at approximately the same time.

If the accumulation of hydrogen chloride is a major factor in determining the course of the reaction, the addition of a base to neutralize the acid as it forms should make possible a higher conversion of acrylonitrile to 2,3-dichloropropionitrile. An experiment was run exactly as before but with 20 ml. (0.25 mole) of pyridine added to the initial acrylonitrile charge. The point of attainment of saturation with hydrogen chloride and corresponding appearance of 3-chloropropionitrile and 2,2,3-trichloropropionitrile was delayed by more than 2 hr., as shown in Fig. 2.

To determine the effect of hydrogen chloride in a direct manner, 11 g. of the gas was added (with cooling) to 200 ml. of acrylonitrile in 2 min. This was immediately followed

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[1] J. K. Sumner, U. S. Patent 2,390,470 (1945).

[2] J. D'Ianni, U. S. Patent 2,231,360 (1941).

[3] H. Krzikalla and E. Flickinger, Office of the Publication Board, PB Report 638.

[4] A. M. Clifford and J. D. D'Ianni, U. S. Patent 2,384,889 (1945).

[5] H. Brintzinger, K. Pfannstiel, and H. Koddebusch, *Angew. Chem.*, A60, 311 (1948).

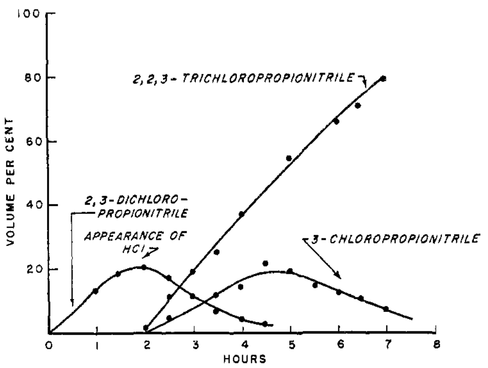

Fig. 1. Effect of time on distribution of products of the reaction of acrylonitrile and chlorine

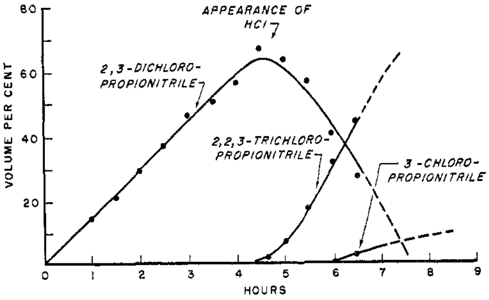

Fig. 2. Effect of time on distribution of products of the reaction of chlorine and acrylonitrile containing pyridine

by the addition of chlorine at a rate of 16–18 g./hr. in the presence of light from the 150-watt lamp. At the end of 30 min. the major product was 2,2,3-trichloropropionitrile, the minor product was 3-chloropropionitrile, and there was neither chlorine nor 2,3-dichloropropionitrile present.

In order to establish the effect of hydrogen chloride on further chlorination of 2,3-dichloropropionitrile, 6 g. of chlorine was dissolved in 200 g. of the compound. This solution was left at room temperature, in the dark, for 4 hr. and no reaction was noted. A like sample of 2,3-dichloropropionitrile was first saturated with hydrogen chloride and then chlorine was added (cooling was required immediately). In 4 hr. all of the 2,3-dichloropropionitrile was converted to 2,2,3-trichloropropionitrile. These two experiments were repeated starting with 3-chloropropionitrile and the results were the same.

Fig. 1 indicates that the relative rate of chlorination of 2,3-dichloropropionitrile is much higher than that of 3-chloropropionitrile. The 3-chloropropionitrile is chlorinated to 2,2,3-trichloropropionitrile but the concentration of the intermediate 2,3-dichloropropionitrile is not great enough to be detected by infrared spectrometry. Results of chlorinating a mixture of equal volumes of 2,3-dichloropropionitrile and 3-chloropropionitrile (mole ratio: 6.7 to 5.4, respectively) are plotted in Fig. 3. The reaction mixture was first saturated with hydrogen chloride and then chlorine was added at a constant rate in the absence of light. During the time (1 hr.) it took to chlorinate 30% by volume of 2,3-dichloropropionitrile only 2% of the 3-chloropropionitrile was chlorinated.

Identification of the photochemically effective radiation. Since the tungsten lamp that was used emitted radiation over a broad portion of the spectrum, standard glass radiation filters were used to locate the most effective portion of the spectrum. A piece of aluminum foil shaped like a funnel was used as a means of channeling the light through the filter. The 150-watt bulb was placed in the large end of the funnel and 6 inches away from the small end where one of the standard 2″ × 2″ glass filters was placed. Thus the light passed through the filter, Pyrex beaker, and reactor. In each run 200 ml. of acrylonitrile was used and chlorine was added at a rate of 12–14 g./hr. for 35 min. In all runs there was an excess of chlorine. The composition of the sample was immediately determined by infrared measurements. The results are in Table I. (A small amount[6] of radiation is emitted by the tungsten lamp between 2800 and 3100 Å and no measure of its effectiveness was made.)

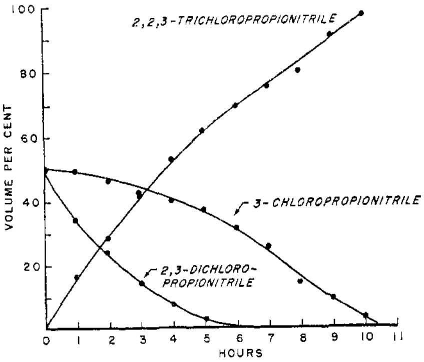

Fig. 3. Effect of time on distribution of the products of the reaction between chlorine and 2,3-dichloropropionitrile and 3-chloropropionitrile in the presence of hydrogen chloride and the absence of light

TABLE I

EFFECT OF LIGHT ON PRODUCT DISTRIBUTION

Filter No.	Wave Length[a]	Relative Concentration: 2,3-Dichloropropionitrile	Relative Concentration: 2,2,3-Trichloropropionitrile
Complete darkness	—	5	0
2540[b]	7500	5	5
3389[b]	4000	50	5
7380[b]	3400	65	0
Optical Pyrex	3100	100[c]	0

[a] The number indicates the lower limit in angstroms of 90% of the radiation. [b] Corning Glass Co. [c] The conditions of this experiment gave the highest concentration (actual 4% vol.) of 2,3-dichloropropionitrile and this was assigned an arbitrary value of 100.

Preparation of 2,3-dichloropropionitrile in a solvent. Three moles of chlorine was added in 1 hr. to 3 moles of acrylonitrile and 1 g. of hydroquinone dissolved in 500 ml. of carbon tetrachloride. An ice water bath was used to maintain a reaction temperature of 10–25°. The solution was illuminated with the lamp placed 4 inches from the reactor. The mixture was stirred an additional 0.5 hr. after the addition of chlorine was stopped. The carbon tetrachloride was removed by distillation at 200 mm. and then the distillation was continued at 7–10 mm. to obtain the product. The yield of 2,3-dichloropropionitrile was 75%.

Preparation of 2,3-dichloropropionitrile without a solvent. To a solution of 2 g. of hydroquinone in 11.9 moles of acrylonitrile was added 150 g. (2.1 moles) of chlorine in 70 min. The reaction mixture was cooled with an ice water bath and illuminated with a 150-watt bulb. The light was left on for 20 min. after the addition of chlorine was stopped.

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(6) L. R. Koller, *Ultraviolet Radiation*, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 101.

TABLE II

PHYSICAL PROPERTIES OF THE CHLOROPROPIONITRILES

	3-Chloropropionitrile	2,3-Dichloropropionitrile	2,2,3-Trichloropropionitrile
B.p. (10 mm.)	59°	58°	47°
B.p. (50 mm.)	93	91	79
B.p. (100 mm.)	110	108	96
d_{25}	1.137	1.327	1.426
n_D^{25}	1.4360	1.4633	1.4655
		(Literature)	
B.p.	75–76°/20 mm.[9]	61°/13 mm.[5] 80°/25 mm.[2] 86–87°/36 mm.[1]	53°/14 mm.[5] 80–81°/63 mm.[8] 156–157°/atm.[7]
Density	1.1272/20°[9]	1.303/25°[2]	
Refractive index	n_D^{20} 1.4370[9]	n_D^{26} 1.4638[2]	n_D^{20} 1.4677[7]

The reaction mixture was first distilled at 150 mm. and 8.5 moles of unchanged acrylonitrile was recovered. Then 1.5 moles of 2,3-dichloropropionitrile was obtained at 8 mm. pressure. The distillation residue appeared to be polymerized acrylonitrile. The 44% yield of 2,3-dichloropropionitrile based on unrecovered acrylonitrile undoubtedly could be improved.

Pyridine-catalyzed preparation of 2,3-dichloropropionitrile. Ten moles of chlorine was added at a rate of 1.5–2.0 moles/hr. to a stirred mixture of 10 moles of acrylonitrile and 100 ml. (1.24 moles) of pyridine. External cooling was used and the reaction was run in the dark. During the first hour a very viscous lower layer formed which was difficult to stir. This layer gradually disappeared. After all of the chlorine had been added, the crude reaction product was washed four times with 800-ml. portions of water, dried over calcium chloride and distilled at 8–10 mm.; yield of 2,3-dichloropropionitrile was 69%.

Preparation of 2-chloroacrylonitrile. The pyridine-catalyzed preparation was repeated but the reaction material was not water-washed. It was heated under reflux at 50 mm., the flask temperature was not allowed to exceed 90°. The 2-chloroacrylonitrile (b.p. 20°, 50 mm.) which was continuously formed was allowed to escape through the condenser and was collected in a large Dry Ice trap. The hydrogen chloride passed out of the system through a water aspirator as it was formed. The material caught in the Dry Ice trap was redistilled at 150 mm. to give a 60% yield of 2-chloroacrylonitrile, b.p. 44° (150 mm.), b.p. 88°, (760 mm.), d_{25} 1.088, n_D^{25} 1.4284 (lit.[7] b.p. 88°, n_D^{20} 1.4294).

Physical properties of the chloropropionitriles. The physical properties of the three chloropropionitriles prepared in this investigation are in Table II. The properties were determined on samples that were 99% pure as shown by vapor chromatography. The three chloropropionitriles did not form azeotropes with each other. Mixtures of 3-chloropropionitrile and 2,3-dichloropropionitrile could not be separated by distillation owing to the nearness of their boiling points. It is interesting to note that as the number of chlorine atoms in the molecule increased, the boiling point decreased.

DISCUSSION

The cursory use of light filters indicates that the most effective wave length for promoting the addition reaction between chlorine and acrylonitrile is between approximately 3000 to 4000 Å instead of the visible region as previously reported.[1] This presents a combination of opposed factors that must be considered when chlorine is added to the double bond of acrylonitrile. Without the radiation the addition is extremely slow. Radiation at about 3100 Å accelerates the addition, but it also promotes the undesired substitution of hydrogen by chlorine. Ultraviolet light is known also to cause acrylonitrile polymerization, which in this case is detrimental.

The use of pyridine[5] as a catalyst is unique because it both catalyzes the addition reaction and eliminates the hydrogen chloride. That pyridine hydrochloride will effect continuous dehydrohalogenation of 2,3-dichloropropionitrile to give 2-chloroacrylonitrile seems unusual; however, Spence[7] points out that a catalytic amount of an aliphatic amine hydrohalide will do the same.

When light was used for the reaction catalyst, the following scheme is proposed as the reaction path:

$$\mathrm{Cl_2} \xrightarrow{\mathrm{uv}} \mathrm{2Cl\cdot} \qquad (1)$$

$$\mathrm{CH_2{=}CHCN + Cl\cdot \longrightarrow CH_2Cl\dot{C}HCN} \qquad (2)$$

$$\mathrm{CH_2Cl\dot{C}HCN + Cl_2 \longrightarrow CH_2ClCHClCN + Cl\cdot} \qquad (3)$$

$$\mathrm{CH_2ClCHClCN + Cl\cdot \longrightarrow CH_2Cl\dot{C}ClCN + HCl} \qquad (4)$$

$$\mathrm{CH_2Cl\dot{C}ClCN + Cl_2 \longrightarrow CH_2ClCCl_2CN + Cl\cdot} \qquad (5)$$

$$\mathrm{CH_2Cl\dot{C}HCN + HCl \longrightarrow CH_2ClCH_2CN + Cl\cdot} \qquad (6)$$

Step (1) can occur in the presence of ultraviolet radiation or blue visible light and is the initiation step. The chlorine radical then adds as in steps (2) and (3) to give 2,3-dichloropropionitrile. Step (4) leads to the formation of hydrogen chloride and loss of 2,3-dichloropropionitrile. Step (6) shows how as the concentration of hydrogen chloride builds up the formation of 3-chloropropionitrile becomes appreciable as does 2,2,3-trichloropropionitrile.

The presence of hydrogen chloride was shown to catalyze the chlorination of 3-chloropropionitrile and 2,3-dichloropropionitrile in the dark. (Kabisch[10] disclosed that acetonitrile saturated with hydrogen chloride was chlorinated readily in the dark to

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(7) L. U. Spence, U. S. Patent **2,385,550** (1945).

(8) J. G. Lichty, U. S. Patent **2,231,838** (1941).

(9) A. Brylants, M. Tits, C. Dieu, and R. Gauthier, *Bull. soc. chim. Belg.*, **61**, 366–392 (1952).

(10) G. Kabisch, U. S. Patent **2,745,868** (1956).

trichloroacetonitrile.) These chlorinations may be interpreted on an ionic basis as follows:

$$HCl + CH_2{=}CHCN \longrightarrow CH_2ClCH_2CN \tag{7}$$

$$CH_2ClCH_2CN + H^+ \longrightarrow CH_2ClCH_2\overset{+}{C}{=}NH \overset{-H^+}{\rightleftharpoons} CH_2ClCH{=}C{=}NH \xrightarrow{Cl_2} CH_2ClCHClCN + HCl \tag{8}$$

$$CH_2ClCHClCN + H^+ \longrightarrow CH_2ClCHCl\overset{+}{C}{=}NH \overset{-H^+}{\rightleftharpoons} CH_2ClCCl{=}C{=}NH \xrightarrow{Cl_2} CH_2ClCCl_2CN + HCl \tag{9}$$

Step (7) is known to take place in the absence of light.[11] The rate of step (9) should be greater than step (8) because the carbonium ion of step (9) should eject a proton more readily than the corresponding carbonium ion of step (8). This is in agreement with the observation that the 2,3-dichloropropionitrile is chlorinated at a higher rate than 3-chloropropionitrile.

Acknowledgment. The author wishes to thank J. H. Brown, Jr., Professor Lewis Hatch, and Professor Harry Walborsky for their advice and help.

FREEPORT, TEX.

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[11] R. Stewart and R. H. Clark, *J. Am. Chem. Soc.*, **69**, 713 (1947).

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., RESEARCH AND ENGINEERING DIVISION]

Ozonation of Azo and Azomethine Double Bonds

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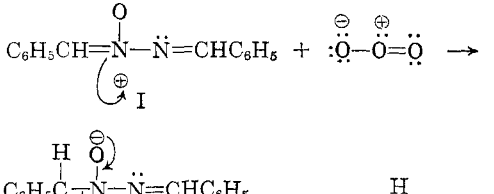
The ozonolysis of the azomethine double bond with ozone-oxygen mixtures has been investigated. Cleavage was the principal reaction with azines and Schiff bases. Carbonyl compounds were isolated in reasonably good conversions. These reactions were also accompanied by a variety of other products, which are best accounted for by an ozone-initiated autoxidation as a secondary reaction. Oxanilide, formanilide, and s-diphenylurea were isolated from the ozonolysis of *N*-cinnamylideneaniline. Azobenzene was unexpectedly resistant to ozonolysis.

The literature[1] indicates significant differences in the ease of ozonolysis of azo and azomethine linkages. An unsuccessful attempt in these laboratories to ozonize azobenzene prompted a further investigation of the reaction of azo and azomethine compounds with ozone-oxygen mixtures. Azobenzene was recovered nearly quantitatively on treatment with one, four and eight molar equivalents of ozone in oxygen mixtures at −40 to 34°. Trace amounts of glyoxal and a compound (isolated as the 2,4-dinitrophenylhydrazone, m.p. 252–255° dec.), possibly salicylaldehyde, were the only products isolated from the water-soluble oils obtained from these reactions (see table). Azoxybenzene formation was not detected. The ozonation reaction is in contrast to the peracetic acid oxidation of azobenzenes which yields azoxybenzenes.[2] However, it has been stated[3] that the ozonation of hydrazobenzene yielded azobenzene without "noteworthy" formation of other products.

The ozonation of benzalazine, on the other hand, resulted in a facile cleavage of the carbon-nitrogen double bond. An excellent conversion of benzaldehyde was obtained (see table). This reaction was characterized by the rapid development of a blue color, attributed to the formation of dinitrogen trioxide, which persisted throughout the oxonation. It has recently been observed that a blue to green color also resulted during the ozonation of nitrones, which was shown to be due to the formation of nitroso compounds.[1b]

Since this coloration does not result during ozonation of Schiff bases, the initial reaction of ozone with benzalazine must involve an electrophilic attack on the nitrogen atom of the carbon-nitrogen double bond followed by the loss of oxygen



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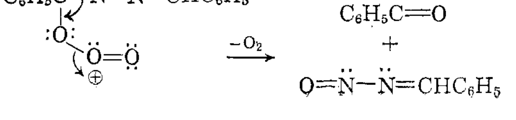

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[1] The literature is reviewed by (a) P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958); (b) A. H. Riebel, R. E. Erickson, C. J. Ashire, and P. S. Bailey, *J. Am. Chem. Soc.*, **82**, 1801 (1960).

[2] (a) A. Angeli, *Atti. accad. Lincei*, **19**, 794 (1910); (b) P. Gagnon and B. T. Newbold, *Can. J. Chem.*, **37**, 366 (1958).

[3] W. Strecker and M. Baltes, *Ber.*, **54B**, 2693 (1921).