[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reaction of Chloranil with the Decomposition Products from Azonitriles

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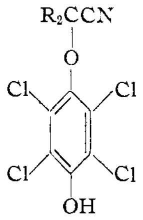
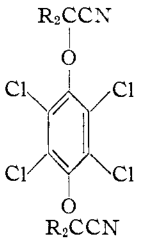
The decomposition of azo-bis-isobutyronitrile or azo-bis-diethylacetonitrile in toluene containing chloranil leads to the production of the monobenzyl ether of tetrachlorohydroquinone in addition to the mono- and dicyanoalkyl ethers derived from the azonitrile. No dibenzyl ether or unsymmetrical diether is formed. It is suggested that the precursor of the benzyl ether is not a semiquinone ether but rather a molecular complex of chloranil and the benzyl radical.

The radicals produced in the decomposition of azo-bis-isobutyronitrile (AIBN) and azo-bis-diethylacetonitrile (AIDN) are structurally closely related to the growing chain radicals involved in the polymerization of methacrylonitrile and are somewhat related to growing methacrylate radicals. Because of this relationship the reactions of decomposing azonitriles with polymerization inhibitors and regulators are of considerable interest. In the course of a study of the reactions of these radicals with chloranil, a typical polymerization inhibitor, we have encountered an apparent anomaly which was not described by other workers[1] who have reported results which duplicate many of our own observations. Because it is possible that our results fit the pattern of behavior[2] which seems to be developing for the interactions of radicals with aromatic substrates, we wish to report our findings at this time.

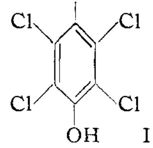
Results and Discussion

As was observed by Bickel and Waters,[1] the decomposition of AIBN in chlorobenzene containing chloroanil leads to the formation of the tetrachlorohydroquinone ethers, Ia and IIa, and the corresponding compounds (Ib and IIb) are produced from AIDN. When toluene is used as the decomposition solvent, the principal phenolic constituent produced by the decomposition of *either* azonitrile is the monobenzyl ether of tetrachlorohydroquinone, III. Despite a careful examination of all neutral products of the reaction by infrared methods we could find no evidence for the presence of the symmetrical diether or the unsymmetrical diether. The relevant yield data are summarized in Table I.

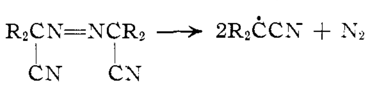

I


II

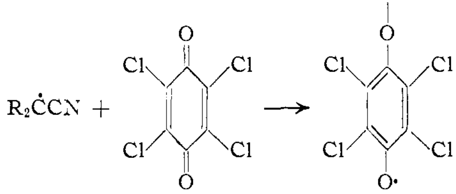
a, R = CH_3
b, R = C_2H_5


III

These observations do not permit any simple interpretation. The products containing the initiator fragments could arise as indicated by equations 1–5. Benzyl radicals must be produced in some reaction such as 5 since there is adequate evidence from this and other work[1,3] to show that the radicals from the initiator do not attack toluene. If benzyl radicals are captured by chloroanil with the production of the semiquinone ether V, it would certainly be expected that this radical should show chemical properties very similar to those of IV. To assert that the observed differences in results are due to the variation in properties between the two ether radicals would require a remarkable faith in long range steric or electronic effects.

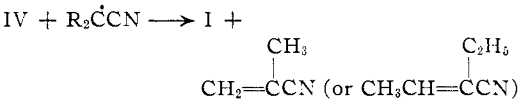


$$\underset{CN}{R_2C}N{=}N\underset{CN}{CR_2} \longrightarrow 2R_2\dot{C}CN + N_2 \quad (1)$$


(2)

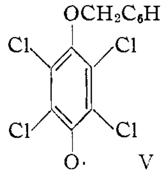
IV

$$IV + R_2\dot{C}CN \longrightarrow II \quad (3)$$



$$IV + R_2\dot{C}CN \longrightarrow I + CH_2{=}\overset{CH_3}{C}CN\ (\text{or } CH_3CH{=}\overset{C_2H_5}{C}CN) \quad (4)$$

$$IV + C_6H_5CH_3 \longrightarrow I + C_6H_5CH_2\cdot \quad (5)$$


V

Two types of explanation have occurred to us. The first derives from the observation that the only diether produced is that involving two initiator fragments. It has been found that the primary products from the decomposition of AIBN destroy each other at a rate which is fast enough to be competitive with the rate at which they diffuse apart.[3] It is conceivable that a pair of radicals produced in

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[1] A. W. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 312 (1950).

[2] G. S. Hammond, C. E. Boozer, C. E. Hamilton and C. L. Peterson, THIS JOURNAL, **77**, in press (1955).

[3] G. S. Hammond, J. N. Sen and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

the primary decomposition step might react with bifunctional scavengers at a very rapid rate. If chloranil functions in this way, it could account for the formation of the diether. However, there has been no evidence for bifunctional scavenging of radical pairs by very reactive substances such as iodine[3] and oxygen.[4]

Another interesting possibility is that V is never formed but that chloranil and the benzyl radicals form molecular complexes which react with cyanoalkyl radicals by disproportionation to produce the monobenzyl ether. The complexes would be similar to the complexes believed to be formed from alkyl peroxy radicals and phenols or aromatic amines[2] except that the donor–acceptor roles of the radical and substrate would be reversed. It may be that cyanoalkyl radicals do not form complexes with chloroanil or, if they do so, it would not be surprising to find that the radical complexes have chemical properties which are quite sensitive to the nature of the complexing radicals. Similarly, the failure to produce a benzyl ether by the decomposition of AIBN in toluene containing trichlorobenzoquinone[5] might be attributed to the inferior complexing ability of the latter quinone.

Experimental

Toluene (Baker and Adamson, Reagent Grade) was distilled through a six-foot column packed with glass helices. The fraction boiling at 109–110° (uncor.) was used in subsequent work.

Chlorobenzene (Paragon Division, Matheson Chemical Co.) was used without further purification.

Chloranil (Eastman Kodak Yellow Label) was recrystallized from glacial acetic acid and dried over sodium hydroxide in a vacuum desiccator.

Azo-bis-diethylacetonitrile was prepared by the method of Dox[6] in 60% yield, m.p. after two recrystallizations from ethanol 74–75°.

Azo-bis-isobutyronitrile was prepared by the method of Dox[6] in 70% yield. After two recrystallizations the product melted at 101–102°.

Decomposition of AIDN in Toluene.—Three and three-tenths grams (0.015 mole) of AIDN was dissolved in 50 ml. of toluene and the solution was refluxed for 15 hours. The toluene was then stripped under reduced pressure at head temperatures below 50°. After standing 3–4 hours at room temperature the residue deposited crystals of tetraethylsuccinonitrile. The distillation of toluene then was resumed and after the removal of a small amount a second crop of dinitrile was obtained. The total yield was 2.09 g. (73%) which melted at 47–48° after recrystallization from ethanol–water. Neither the distillate nor recrystallization residues appeared to contain *sym*-diphenylethane.

Decomposition of AIDN in Toluene Containing Chloranil.—Two and two-tenths grams (0.010 mole) of AIDN and 2.48 g. (0.010 mole) of chloranil were dissolved in 100 ml. of toluene and heated at reflux for 15 hours. The solution was then cooled and extracted with 5% aqueous sodium hydroxide until the extract was colorless. The extract was deep red in color due to the formation of chloranilic acid. Upon acidification with 5% hydrochloric acid a dirty brown solid was precipitated. After repeated recrystallization from glacial acetic acid, this product gave white crystals of tetrachlorohydroquinone monobenzyl ether. The yield was 0.53 g. (16%). *Anal.* Calcd. for $C_{13}H_3O_2Cl_4$: C, 46.3; H, 2.47; Cl, 42.1. Found: C, 46.6; H, 2.48; Cl, 41.6.[7]

The organic layer from the extraction was steam distilled and the distillate which contained all of the toluene was extracted with ether and the extract was dried over anhydrous sodium sulfate. After drying, the toluene–ether solution was distilled under reduced pressure as in the previous experiment. The residue, worked up as in the control, gave 0.6 g. (31%) of tetraethylsuccinonitrile.

The residue from the steam distillation was recrystallized from a large volume of ethanol and gave 1.55 g. (45% based on AIDN) of tetrachlorohydroquinone di-(3-cyano-3-pentyl) ether, m.p. 166–167°. *Anal.* Calcd. for $C_{18}H_{20}O_2N_2Cl_4$: C, 49.3; H, 4.56; Cl, 32.4; N, 6.39. Found: C, 50.1; H, 4.42; Cl, 31.7; N, 6.32.

TABLE I

DECOMPOSITION OF AZONITRILES IN THE PRESENCE OF CHLORANIL

Moles azonitrile × 10^2	Moles chloranil × 10^2	Solvent (50 ml.)	Yields (moles × 10^2) ether Monocyanoalkyl	Dicyanoalkyl	Monobenzyl	Dinitrile
		Azo-bis-diethylacetonitrile				
1.5	None	Toluene	...	...	...	1.09
1.0	1.3	Toluene	0.45	...	0.16	0.31
1.3	1.3	Chlorobenzene	0.67	0.06	...	.47
		Azo-bis-isobutyronitrile				
1.0	None	Toluene	...	...	...	.86
0.94	1.0	Toluene	0.27	0.036	0.032	.36
1.1	0.53	Chlorobenzene	0.29	0.037	...	.46

Decomposition of AIDN in Chlorobenzene Containing Chloranil.—The reaction was carried out and products were isolated by a procedure essentially identical with that described above for the experiment in toluene. The phenolic product obtained was not identical with that obtained in toluene solution, and on the basis of elementary analysis, was assigned the structure tetrachlorohydroquinone mono-(3-cyano-3-pentyl) ether, m.p. 165°; yields and material balance are included in Table I. *Anal.* Calcd. for $C_{12}H_{11}O_2NCl_4$: N, 4.08; Cl, 41.4. Found: N, 4.17; Cl, 40.7

Decomposition of AIBN in Toluene Containing Chloranil.—The decomposition was carried out as above. The solution after heating was extracted with 10% aqueous sodium hydroxide. On acidification the extract gave an amorphous precipitate. The solid was separated into two constituents by fractional crystallization from glacial acetic acid. The less soluble constituent was the monobenzyl ether of tetrachlorohydroquinone identical with the material produced in the similar experiment with AIDN. Samples from the two runs gave no mixed melting point depression and had identical infrared spectra. The mother liquors from the separation of the benzyl ether gave a material which was amorphous but had an infrared spectrum identical with that of an authentic sample of the 2-cyano-2-propyl ether of tetrachlorohydroquinone. The spectrum showed no significant absorption at 13.25μ indicating the absence of the monobenzyl ether.

The steam distillate from the reaction mixture was examined for bibenzyl in the following manner. The last fraction from the recrystallization of tetramethylsuccinonitrile was dried and the infrared spectrum was determined in a Nujol mull. The spectrum was identical to that of pure dinitrile and showed no absorption at 13.25 μ (characteristic of all benzyl compounds studied including bibenzyl). The steam distillation residue gave tetrachlorohydroquinone di-[2-cyano-2-propyl] ether, m.p. 166–167°. The crude residue gave a spectrum which had no absorption at 13.25μ.

Decomposition of AIBN in chlorobenzene containing chloroanil was carried out and the products were worked up as described for other experiments. Yields are summarized in Table I.

Attempted Syntheses of Tetrachlorohydroquinone Monobenzyl Ether.—Several attempts were made to prepare this compound by the alkylation of the hydroquinone with benzyl chloride. With aqueous or alcoholic sodium hydroxide or with potassium carbonate and dry acetone, only unreacted hydroquinone and the diether could be isolated. With sodium hydride in dry ether the starting materials were recovered unchanged.

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(4) C. E. Boozer and G. S. Hammond, unpublished observations.

(5) F. J. L. Aparicio and W. A. Waters, *J. Chem. Soc.*, 4666 (1952).

(6) A. W. Dox, THIS JOURNAL, **47**, 1473 (1925).

(7) All analyses by Drs. Weiler and Straus, Microanalytical Laboratory, Oxford, England.

Preparation of Tetrachlorohydroquinone Dibenzyl Ether.—Eight g. (0.03 mole) of tetrachlorohydroquinone was added to 2.6 g. (0.065 mole) of sodium hydroxide in 100 ml. of water. The solution was heated to reflux and 9.0 g. (0.07 mole) of benzyl chloride was added dropwise. After the addition was complete the solution was refluxed for two more hours. On cooling a precipitate formed which was recrystallized from 95% ethanol, m.p. 173.5–173.8°. *Anal.* Calcd. for $C_{20}H_{14}OCl_4$: C, 56.0; H, 3.28; Cl, 33.2. Found: C, 57.8; H, 3.47; Cl, 31.8.

Structure of Tetrachlorohydroquinone Monobenzyl Ether.—The potentiometric titration of the substance in water solution indicated an equivalence point at *p*H 8.4. The neutral equivalent found was 332 as compared with the calculated value of 337. Since the compound could not be made easily by alkylation, the monoether was converted to the diether. A 0.5-g. sample of the product from the decomposition of AIDN in toluene containing chloranil was dissolved in the minimum volume of 5% aqueous sodium hydroxide and heated to reflux. Then 0.2 ml. of benzyl chloride was added dropwise and the solution was refluxed for four hours. A solid separated during the heating period, and after cooling it was extracted with ether. The ether was evaporated and the solid residue was recrystallized from 95% ethanol, m.p. 173–175°, no depression on admixture with authentic material. The infrared spectrum was also identical with that of the authentic material.

Alkylation of Tetrachlorohydroquinone Mono-[3-cyano-3-pentyl] Ether.—The proof of structure of the monobenzyl ether by conversion to the dibenzyl ether involves the assumption that some other ether would not be cleaved and then dibenzylated under the reaction conditions. Since it is especially important to demonstrate that the substance was not the cyanoalkyl ether a small sample of the latter compound, from the reaction of AIDN with chloranil, was benzylated under identical conditions. The white product was recrystallized from methanol and melted at 230–250° but depressed the melting point of authentic dibenzyl ether.

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[CONTRIBUTION FROM THE ROHM & HAAS CO.]

Reactive Nitrile Groups. II. The Reaction of Cyanoesters with Aqueous Amines[1]

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Methyl cyanoacetate and methyl β-cyanopropionate were found to differ from the corresponding dinitriles, malononitrile and succinonitrile, in their reactions with aqueous amines, in that hindered primary amines, such as 1,1,3,3-tetramethylbutylamine and cyclohexylamine, did not react with the nitrile group but yielded the corresponding salts of the cyanoalkanoic acids. The product from aqueous piperidine and methyl β-cyanopropionate at reflux was piperidinium succinamate. Unhindered primary amines and morpholine gave N,N′-substituted diamides as expected. A comparison of the reaction of a variety of amines in water with, respectively, succinic anhydride, succinimide, methyl β-cyanopropionate and succinonitrile allows the postulation of a consistent cyclic scheme of aminolysis and hydrolysis for succinic acid derivatives. The aminolysis of malonic acid derivatives is thought to result from a chain effect.

In a previous article[2] it was shown that the uncatalyzed attack of an amine on a nitrile group, normally unsuccessful, will take place in the case of structures $NC(CH_2)_xCN$ where x is 1, 2 or 3. The present work was based on the expectation that if one of the –CN groups were replaced with the –COOR group, the nitrile group would react again regardless of whether the driving force were furnished by an inductive effect transmitted through the chain, or by a reaction path involving a cyclic imide intermediate. The study of methyl cyanoacetate and of methyl β-cyanopropionate in reactions of the same type as previously described has led to a further elucidation of the routes by which all of these reactions proceed.

The reaction of methyl cyanoacetate with aqueous benzylamine at reflux gave a 92% yield of N,N′-dibenzylmalonamide. Cyanoacetamide gave a 95% yield of the same compound.[3] These aminolytic reactions should involve a polarizing effect transmitted through the chain[4]; a reaction path involving a four-membered ring is not favored. Neither benzonitrile[2] nor phenylacetonitrile reacted under the same conditions with benzylamine, indicating that the activation would have to be of a major sort. Methyl cyanoacetate reacted with 1,1,3,3-tetramethylbutylamine in the presence of water to give a 50% yield of 1,1,3,3-tetramethylbutylammonium cyanoacetate by simple hydrolysis of the ester group. Cyanoacetamide also gave the same product. No further base attack on the negatively charged cyanoacetate ion is seen to take place. As in the case of succinonitrile[2] with this hindered primary amine, no products of amine attack were obtained.

Reactions of methyl β-cyanopropionate with aqueous amines were not entirely analogous to reactions of succinonitrile with the same amines. The usual aliphatic amines did give the diamides, in better yields and more rapidly than with succinonitrile (Table I). Again morpholine gave the dimorpholide in 23% yield, and piperidine gave piperidinium succinamate in 40% yield. However, 1,1,3,3-tetramethylbutylamine gave 1,1,3,3-tetramethylbutylammonium β-cyanopropionate, and cyclohexylamine gave only a small yield (3%) of the diamide, and as the major product cyclohexylammonium β-cyanopropionate (80%). Benzylamine yielded the diamide as the major product (Table I) but also a small amount of some intractable benzylammonium salt, probably also that of β-cyanopropionic acid.

In the two groups of reactions, with methyl β-cyanopropionate and with succinonitrile, respectively, there are thus some rather surprising differences with small changes in base strength, along with other differences which are obviously the result of the steric nature of the amine. If the reac-

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[1] Given in part at the 126th Meeting of the American Chemical Society, New York, N. Y., September 14, 1954.

[2] L. J. Exner, M. J. Hurwitz and P. L. de Benneville, THIS JOURNAL, **77**, 1103 (1955).

[3] The high yields clearly indicate that the lower yields with malononitrile[2] were due to base-catalyzed self-condensation reactions.

[4] The reaction of ammonia with cyanogen is known to proceed at quite low temperatures; H. M. Woodburn, B. A. Morehead and C. M. Chih, *J. Org. Chem*. **15**, 535 (1950).