

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, TOKYO UNIVERSITY]

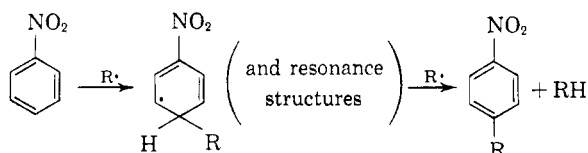
Reactions of Nitro Compounds with 1-Cyano-1-methylethyl Radicals Produced by the Decomposition of α, α' -Azobisisobutyronitrile

NAOKI INAMOTO AND OSAMU SIMAMURA

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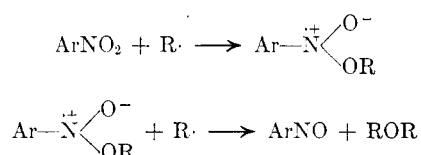
1-Cyano-1-methylethyl radicals attack the nitro group of nitrobenzene, *m*-dinitrobenzene and tetranitromethane yielding hydrogen cyanide, acetone, and, in the case of the first two compounds, *N*-phenyl- and *N*-(*m*-nitrophenyl)-*O,N*-bis(1-cyano-1-methylethyl)hydroxylamines. Nitromethane does not react with this radical. The importance of this reaction in the mechanism of retardation of vinyl polymerization by nitro compounds is pointed out.

Aromatic nitro compounds are effective retarders or inhibitors of the free-radical polymerization of vinyl compounds.¹⁻⁵ Price and Durham have postulated for the retarding action of aromatic nitro compounds a mechanism shown in the following scheme, in which R· denotes a growing polymer radical.



In support of this mechanism, they found that the elements of nitro compounds used as retarders were incorporated in the polymer molecule produced. Further support for the mechanism is that the nuclear methylation of nitro compounds occurs readily in the reaction with various reagents⁶ which are believed to produce methyl radicals on decomposition.

An alternative mechanism involving an attack by a radical on the nitro group has been suggested by Hammond and Bartlett⁴ on the basis of their observations on the benzoyl peroxide-initiated polymerization of allyl acetate:



In connection with the retarder action of nitro compounds their reactions with simple aliphatic radicals seem to be of interest. Hammond and

Ravve⁷ investigated the reaction of triphenylmethyl with nitrobenzene with the result that the former reacted only by abstracting oxygen from the nitro group, whereas Gingras and Waters⁸ reported that 1-cyano-1-methylethyl radicals did not react detectably in boiling toluene solution with 1,3,5-trinitrobenzene and 2,4-dinitrochlorobenzene.

We have now examined reactions of nitrobenzene, *m*-dinitrobenzene, nitromethane, and tetranitromethane with 1-cyano-1-methylethyl radicals, which are generated by thermal decomposition of α, α' -azobisisobutyronitrile and which could be regarded as models of growing polymethacrylonitrile radicals. It has been found that the 1-cyano-1-methylethyl radical can indeed react with the nitro group.

The decomposition of α, α' -azobisisobutyronitrile in nitrobenzene at 100° gave a small amount each of hydrogen cyanide, acetone, and a crystalline compound, C₁₄H₁₇N₃, m.p. 93–94°, besides tetramethylsuccinonitrile and 2,3,5-tricyano-2,3,5-trimethylhexane, the usual products. The crystalline compound was identified as *N*-phenyl-*O,N*-bis(1-cyano-1-methylethyl)hydroxylamine, which was also obtained from nitrosobenzene and α, α' -azobisisobutyronitrile in boiling toluene according to Gingras and Waters.⁸ The amount of the acetone isolated from the reaction mixture as the 2,4-dinitrophenylhydrazone corresponded to 3.4% of 1-cyano-1-methylethyl radicals to be generated from the azonitrile used, and that of the disubstituted phenylhydroxylamine to 2.8%.⁹

Similarly, when α, α' -azobisisobutyronitrile and *m*-dinitrobenzene were boiled in toluene, the evolution of hydrogen cyanide was noticed and acetone was produced together with a yellowish crystalline compound, C₁₄H₁₆N₄O₃, m.p. 159–159.5°. This compound was thought to be *N*-(*m*-nitrophenyl)-*O,N*-bis(1-cyano-1-methylethyl)hydroxylamine on

(1) S. G. Foord, *J. Chem. Soc.*, 48 (1940).(2) C. C. Price and D. A. Durham, *J. Am. Chem. Soc.*, 65, 757 (1943).(3) C. C. Price, *J. Am. Chem. Soc.*, 65, 2380 (1943); C. C. Price and D. H. Read, *J. Polymer Sci.*, 1, 44 (1946); G. V. Schulz, *Chem. Ber.*, 80, 232 (1947).(4) G. S. Hammond and P. D. Bartlett, *J. Polymer Sci.*, 6, 617 (1951); cf. also P. D. Bartlett and H. Kwart, *J. Am. Chem. Soc.*, 72, 1051 (1950).(5) J. W. Breitenbach, *Z. Elektrochem.*, 60, 286 (1956).(6) L. F. Fieser, R. C. Clapp, and W. H. Daudt, *J. Am. Chem. Soc.*, 64, 2052 (1942); R. B. Sandin and W. B. McCormick, *J. Am. Chem. Soc.*, 67, 2051 (1945).(7) G. S. Hammond and A. Ravve, *J. Am. Chem. Soc.*, 73, 1891 (1951).(8) B. A. Gingras and W. A. Waters, *J. Chem. Soc.*, 1920 (1954).

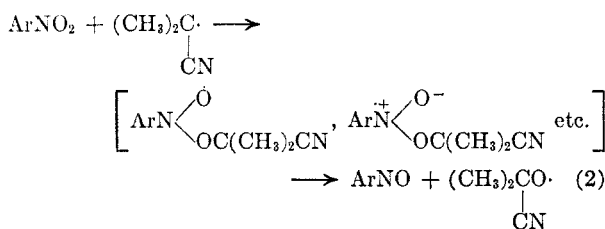
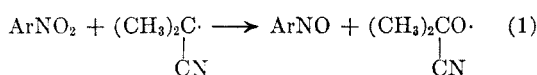
(9) The percentage yields reported in this paper are all based on 1-cyano-1-methylethyl radicals to be generated from the azonitrile used, it being assumed that one molecule of the latter gives two of the former radicals.

the basis of elemental analysis and by analogy with the formation of the corresponding product from the reaction in nitrobenzene. The amounts of the acetone and trisubstituted hydroxylamine isolated were, respectively, 4.6% and 2.2% of 1-cyano-1-methylethyl radicals generated.

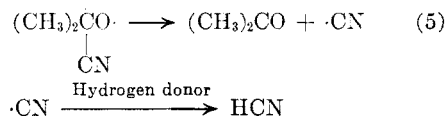
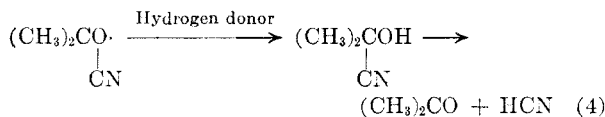
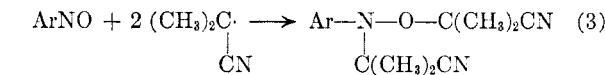
When α,α' -azobisisobutyronitrile was added to boiling nitromethane, neither hydrogen cyanide nor acetone was detected and tetramethylsuccinonitrile and 2,3,5-tricyano-2,3,5-trimethylhexane were obtained in yields of 77.5% and 16%, respectively, on the basis of 1-cyano-1-methylethyl radicals generated. If the latter compound is produced by disproportionation of 1-cyano-1-methylethyl radicals followed by attack of the same radical on the resulting methacrylonitrile,¹⁰ the yield of 16% corresponds to consumption of 21.5% of 1-cyano-1-methylethyl radicals; therefore, 99% of the radical produced is accounted for. Thus, 1-cyano-1-methylethyl radicals do not appear to attack nitromethane.

Unlike nitromethane, tetranitromethane was found to react with 1-cyano-1-methylethyl radicals in toluene at 100° affording 4% of acetone.

It is inferred from the results mentioned above that 1-cyano-1-methylethyl radicals attack an oxygen atom of the nitro group eventually to produce a nitroso compound and a 1-cyano-1-methylethoxy radical. The exact mechanism of the attack by the radical is unknown. The radical may abstract the oxygen atom directly (Equation 1) or alternatively it may add primarily to the oxygen atom as postulated originally by Hammond and Bartlett⁴ to give an intermediate radical as shown below, the latter decomposing subsequently into a nitroso compound and a 1-cyano-1-methylethoxy radical (Equation 2).



The nitroso compound thus formed combines with two 1-cyano-1-methylethyl radicals to yield a trisubstituted hydroxylamine (Equation 3).⁸ The 1-cyano-1-methylethoxy radical gives rise to acetone and hydrogen cyanide probably either through the formation of acetone cyanhydrin (Equation 4) or through decomposition similar to that of *tert*-butoxy radicals (Equation 5).



In the case of tetranitromethane, the formation of 1-cyano-1-methylethoxy radicals can be considered certain, as was evidenced by the isolation of acetone; but the fate of an intermediate from tetranitromethane is as yet unknown. As evolution of some nitrogen dioxide was observed in the course of the reaction, it is possible that the decomposition took place into nitric oxide and nitrogen dioxide. Neither tris(1-cyano-1-methylethyl)hydroxylamine⁸ nor α -nitroisobutyronitrile,¹¹ both of which should have been formed from 1-cyano-1-methylethyl radicals and nitric oxide or nitrogen dioxide, respectively, could be detected, however. It is also unknown why nitromethane does not react with radicals whereas tetranitromethane does.

There is a rough parallelism between the amount of acetone produced in the present reaction and the retarder efficiency of nitro compounds in the polymerization.^{1,5} One nitro group in an aromatic compound gives a strong retardation, and the retarding effect is much stronger with two nitro groups. While tetranitromethane is a strong retarder,⁵ nitromethane is ineffective in retarding both thermal⁵ and benzoyl peroxide-initiated² polymerization of styrene or effective only to a limited extent, if at all, in the peroxide-induced short-chain polymerization of allyl acetate.⁴ It may thus be concluded that the nitro compound takes part in the retardation by reacting with growing polymer radicals as shown in formulas 1, 2, and 3. In the case of aromatic nitro compounds with a replaceable hydrogen atom in the nucleus the mechanism postulated by Price and Durham² cannot be excluded.

EXPERIMENTAL

Reaction of nitrobenzene with α,α' -azobisisobutyronitrile. α,α' -Azobisisobutyronitrile (5.34 g.) was added little by little during 2 hr. to 20 g. of nitrobenzene heated on a boiling water bath and the heating was continued for a further 12 hr. Evolution of nitrogen took place, and hydrogen cyanide was detected by its odor and the Berlin blue reaction. The reaction mixture was distilled with steam, and tetramethylsuccinonitrile was separated from the distillate. On addition of an alcoholic solution of 2,4-dinitrophenylhydrazine to the aqueous distillate 0.53 g. of 2,4-dinitrophenylhydrazone of acetone, m.p. 126°, precipitated. The oily residue of the steam distillation was extracted with ether, the ether re-

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(11) J. F. Tilney-Bassett and W. A. Waters, *Chem. & Ind. (London)*, 957 (1956).

moved from the extract and the residue dissolved in petroleum ether. This solution, after standing in a refrigerator, gave 0.45 g. of *N*-phenyl-*O,N*-bis(1-cyano-1-methylethyl)hydroxylamine, m.p. 93–94° (recrystallized from aqueous alcohol) with no depression on admixture with a sample prepared from nitrosobenzene according to Gingras and Waters.⁸

Anal. Calcd. for C₁₄H₁₇N₃O: N, 17.28. Found: N, 16.94%.

The insoluble part in petroleum ether gave, on filtration, 70 mg. of 2,3,5-tricyano-2,3,5-trimethylhexane, m.p. and mixed m.p. 81–82°.

*Reaction of *m*-dinitrobenzene with α,α' -azobisisobutyronitrile.* To a solution of 6.72 g. of *m*-dinitrobenzene in 20 cc. of toluene heated on a boiling water bath 6.56 g. of α,α' -azobisisobutyronitrile was added in small portions over 2 hr., and the mixture was heated for a further 3 hr. to complete the reaction. Hydrogen cyanide was evolved during the reaction. The reaction mixture was subjected to steam distillation and after recovery of tetramethylsuccinonitrile, acetone was isolated as 2,4-dinitrophenylhydrazone (0.85 g.) from the distillate. The residue from the steam distillation was extracted with ether, the ether removed and the residue was treated with petroleum ether. An insoluble part in this solvent was extracted with benzene and evaporation of the benzene gave 0.5 g. of *N*-(*m*-nitrophenyl)-*O,N*-bis(1-cyano-1-methylethyl)hydroxylamine, m.p. 159–159.5° (from benzene).

Anal. Calcd. for C₁₄H₁₆N₄O₃: C, 58.32; H, 5.59; N, 19.44;

mol. wt., 288. Found: C, 58.62; H, 5.88; N, 19.3%; mol. wt. (Rast), 278.

Reaction of nitromethane with α,α' -azobisisobutyronitrile. α,α' -Azobisisobutyronitrile (8.2 g.) was added gradually during 2 hr. to nitromethane (30 g.) under reflux and the refluxing was continued for a total of 6 hr. No hydrogen cyanide was detected in the nitrogen evolved during this period. The reaction mixture was distilled through a Vigreux column and the recovered nitromethane was shown to contain no acetone. On slow sublimation at 100° of the solid residue from the distillation, 5.27 g. of tetramethylsuccinonitrile was obtained. The residue was extracted with ether and evaporation of the ethereal solution gave 1.09 g. of 2,3,5-tricyano-2,3,5-trimethylhexane, m.p. 81–82°.

Reaction of tetranitromethane with α,α' -azobisisobutyronitrile. To a solution of 4.0 g. of tetranitromethane in 15 cc. of toluene heated on a boiling water bath, 5.0 g. of α,α' -azobisisobutyronitrile was added in small portions during 2 hr. and the mixture was heated for a further 6 hr. Some nitrogen dioxide was evolved. The reaction mixture was distilled with steam and acetone was isolated as 2,4-dinitrophenylhydrazone (0.6 g.) from the distillate after separation of tetramethylsuccinonitrile. No tractable products could be isolated from the viscous residue from the steam distillation.

BUNKYO-KU, TOKYO
JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Oxidation of *n*-Octane with White Fuming Nitric Acid¹

MYRON L. BENDER, JOHN FIGUERAS, JR.,² AND MARTIN KILPATRICK

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The heterogeneous reactions of *n*-octane with white fuming nitric acid at –5°, 4°, and 27° have been investigated, using infrared spectroscopy as the main analytical tool. The effect of added phosphorus pentoxide, nitrogen pentoxide, sulfuric acid, and water was studied. The vigor of the reaction is a function of both the temperature and the concentration of nitrogen pentoxide. It is suggested that the nitrogen pentoxide in the white fuming nitric acid is responsible for its higher reactivity compared with the reactivity of aqueous nitric acid.

The principal products formed from the low temperature reaction include initially an alkyl nitrate (presumably 2-octyl nitrate) and subsequently 2-octanone. At higher temperatures carbon-carbon scission occurs and a mixture of carboxylic acids is obtained.

The reaction of white fuming nitric acid with alkanes is of interest as a model, controllable system for certain hypergolic (spontaneous ignition) reactions. The liquid phase heterogeneous reaction of *n*-octane with white fuming nitric acid has been investigated in order to determine the initial attack involved and the course of the reaction.

Previous work on the liquid phase reactions between alkanes and nitric acid has involved mainly aqueous solutions of nitric acid. The nitration of *n*-octane carried out by Konovalov³ at 130° (sealed tube) with dilute nitric acid (sp. gr. 1.075) produced a fair yield of 2-nitrooctane. Worstall⁴

reported the formation of primary mono- and di-nitrooctanes in the reaction of this hydrocarbon with a mixture of nitric acid (sp. gr. 1.42) and sulfuric acid at the reflux temperature. The use of fuming nitric acid (sp. gr. 1.52) resulted in extensive oxidation of the hydrocarbon.

The literature yields the following generalizations concerning the liquid phase reactions of alkanes and nitric acid. Dilute nitric acid is preferable for nitration,⁵ concentrated nitric acid favors oxidation and polynitroalkane formation,³ while fuming nitric acid leads to both vigorous oxidation and polynitration.^{4,6} Tertiary carbon atoms are nitrated most readily.⁷ In the light of the above data and of Hass' signal successes with

(1) This work was conducted under Office of Naval Research Contract Nonr-630(00).

(2) Present address: Eastman Kodak Co., Rochester, N. Y.

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(4) R. A. Worstall, *Am. Chem. J.*, **20**, 202 (1898).

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(7) W. Markovnikov, *Ber.*, **32**, 1441 (1899).