[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

N-Nitrosoacylarylamines as Catalysts in Addition Polymerization[1]

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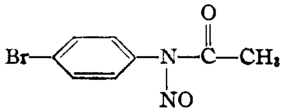
The most widely accepted mechanism for addition polymerization of vinyl derivatives under the influence of peroxide catalysts is the free radical chain reaction originally proposed by Staudinger[2] and substantiated by a number of other investigators.[3] A variety of compounds have been studied as sources of free radicals for the initiation of the addition polymerization. Thus it has been shown that the polymerization of styrene[4,5,6,7] and methyl methacrylate[4] is catalyzed by free radicals formed in the dissociation of tetraphenylsuccinonitrile,[8] benzene azotriphenylmethane,[9] *p*-bromobenzoyl-, anisoyl- and chloroacetyl peroxide,[4] *p*-bromobenzenediazonium hydroxide,[5] 3,4,5-tribromobenzoyl peroxide,[6] and chlorobenzoyl peroxide.[7]

The suggestion of Waters and Hey[10] that N-nitrosoacylarylamines dissociate thermally to give active free radicals has been supported by a certain amount of conclusive evidence.[10,11,12] The present study was undertaken to obtain additional experimental data for this free radical mechanism in the decomposition of N-nitrosoacylarylamines. If the free radicals are formed, then addition polymerization should be catalyzed by the N-nitroso derivatives of the acylarylamines. A number of these compounds were prepared and studied as catalysts in the polymerization of styrene, methyl methacrylate, and acrylonitrile. All of the N-nitrosoacylarylamines were found to act as catalysts for the polymerization.

It was of interest in view of the observations of Price[4,6] and of Bartlett and Cohen[7] on the *p*-bromobenzoyl peroxide catalyzed polymerization of styrene to determine the number of free radicals which were incorporated in the polymer molecule and further to establish whether the aryl or the acid radicals were so involved. Accordingly, the N-nitrosoacylarylamines used in this study contained bromine in two different parts of the molecule. One series of compounds contained a bromine atom attached to the aryl portion of the molecule [N-nitroso-*p*-bromoacetanilide (I) and N,N′-dinitroso-4,4′-dibromosuccindianilide (II)]. The second series contained bromine in the acyl portion of the molecule [N-nitroso-α-bromoisovaleranilide (III) and N-nitroso-N-phenyl-*m*-bromobenzamide (IV)].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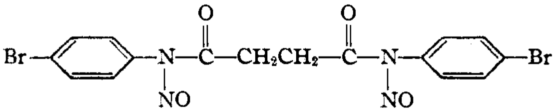
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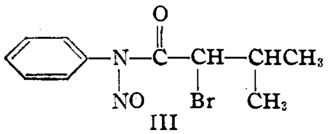
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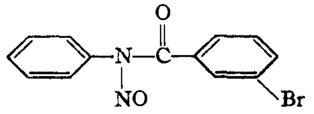
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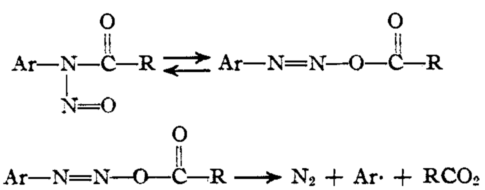
When catalysts containing bromine in the aryl portion of the molecule were used, bromine was always found in the polymers. This was true in the polymerization of styrene, methyl methacrylate, and acrylonitrile using N-nitroso-*p*-bromoacetanilide as the catalyst, and in the polymerization of styrene using N,N′-dinitroso-4,4′-dibromosuccindianilide as a catalyst. However, when the catalysts N-nitroso-N-phenyl-*m*-bromobenzamide and N-nitroso-α-bromoisovaleranilide were used in the polymerization of methyl methacrylate and acrylonitrile, no bromine was found in the resulting polymers. These latter catalysts contained bromine in the acyl portion of the molecule. It appears therefore that in the free radical decomposition of N-nitrosoacylarylamines according to the scheme



$$\mathrm{Ar{-}\underset{\displaystyle N{=}O}{\underset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R \rightleftarrows Ar{-}N{=}N{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R}$$

$$\mathrm{Ar{-}N{=}N{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R \longrightarrow N_2 + Ar\cdot + RCO_2}$$

only the active free aryl radicals are incorporated in the polymer molecules. In each experiment in which N-nitroso-N-phenyl-*m*-bromobenzamide was used as the catalyst *m*-bromobenzoic acid was isolated from the reaction mixture. No attempt was made to isolate α-bromoisovaleric acid from

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(1) This paper is an abstract of a portion of the doctoral dissertation of Harry J. Sykes submitted to the Graduate Faculty of Cornell University in October, 1943.

(2) Staudinger, *Trans. Faraday Soc.*, **32**, 97 (1936).

(3) Marvel and Horning, "Organic Chemistry," by Gilman, second edition, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 771–777.

(4) Price, Kell and Krebs, THIS JOURNAL, **64**, 1103 (1942).

(5) Price and Durham, *ibid.*, **64**, 2508 (1942).

(6) Price and Tate, *ibid.*, **65**, 517 (1943).

(7) Bartlett and Cohen, *ibid.*, **65**, 543 (1943).

(8) Schulz and Wittig, *Naturwissenschaften*, **27**, 387, 456 (1939).

(9) Schulz, *ibid.*, **27**, 659 (1939).

(10) Waters and Hey, *Chem. Rev.*, **21**, 179 (1937).

(11) Grieve and Hey, *J. Chem. Soc.*, 1797 (1934).

(12) Waters, *ibid.*, 113 (1937).

the reaction mixtures in which it should have been formed.

From the calculations based on the bromine content and molecular weights of the polymers (viscosity method) it was found that the fragments of the catalyst contained in the polymers varied over a wide range. Although several of the polymers contained one fragment per polymer molecule, others were obtained which appeared to contain two or more such fragments. In view of the recent studies of Flory[13] on the molecular weights of polyisobutylenes the calculated molecular weights for the higher polymers are probably too low. This would explain a figure of 3.5 obtained for the number of catalyst fragments per polymer molecule observed for one of the polystyrenes (Table II). Nevertheless, it is possible that more than one path might be followed in stabilization of a free radical polymer chain. There may be, for example, disproportionation of hydrogen with some other polymer radical in the solution or combination with a second free radical from the catalyst, and so on.

The N-nitrosoacylarylamines used in this investigation were all prepared by the recent method of France, Heilbron and Hey[14] using nitrosyl chloride in the presence of fused potassium acetate.

$$\mathrm{ArNHCOR + NOCl + CH_3CO_2K \longrightarrow ArN(NO)COR + KCl + CH_3CO_2H}$$

This method is of more general applicability than the nitrous-fume method and gives the desired products in higher purity and improved yield. A number of new N-nitrosoacylarylamines were prepared by this method and are described in the experimental part.

Experimental

Preparation of N-Nitrosoacylarylamines.—The general method of France, Heilbron and Hey[14] was used to prepare all the nitroso compounds. The detailed procedure is given for the nitrosation of fumardianilide. Table I lists the new nitroso compounds prepared by this method.

Nitrosation of Fumardianilide.—A finely divided suspension of fumardianilide (2.6 g., 0.01 mole) in 90 cc. of glacial acetic acid and 30 cc. of acetic anhydride, containing about 8 g. of fused potassium acetate and about 2 g. of phosphorus pentoxide, was stirred and cooled to +7°. To the slurry there was added slowly 25 cc. of a 20% solution of nitrosyl chloride (5 g.. 0.08 mole) in acetic anhydride.[15] Stirring was continued for two hours. the temperature being maintained at 7–12°. Much of the suspended material dissolved.

The reaction mixture was poured into 500 cc. of ice water while stirring vigorously. The nitroso compound which separated as a fine yellow precipitate was filtered, washed thoroughly with cold water (using about 1 liter of water), air-dried on the filter for three hours, and finally dried in a vacuum desiccator over calcium chloride. There was obtained 2.4 g. (88% yield) of product melting at 121° (uncor.) with explosive decomposition.

Anal. Calcd. for $C_{16}H_{12}O_4N_4$: N, 17.3. Found: N, 17.6.

TABLE I

N-NITROSOACYLARYLAMINES PREPARED BY THE NITROSYL CHLORIDE METHOD[a]

Acylarylamine	Product	M. p., °C. (uncor.)[b]	Nitrogen, % Calcd.	Nitrogen, % Found
Fumardianilide	Dinitroso	121	17.3	17.6
Succindianilide[c]	Dinitroso	111	..	..
4,4′-Dibromosuccindianilide	Dinitroso	116	11.6	11.7
4,4′-Dichlorosuccindianilide	Dinitroso	95	14.2	13.8
α,α′-Dibromosuccindianilide	Dinitroso	110	11.6	11.3
N,N′-Diphenylsuccindiamide	Dinitroso	127	11.7	12.0
N,N′-β-Naphthylsuccindiamide	Dinitroso	118	13.2	12.9
N-Phenyl-*m*-bromobenzamide	Nitroso	61	9.6	9.3
α-Bromoisovaleranilide[d]	Nitroso	59	..	..

[a] Attempts to prepare the nitroso derivatives of α-trichloroacetanilide and 2-acetamido-6-chlorobenzothiazole were unsuccessful. [b] Melting points were taken by inserting the sample at a temperature about 5° below the decomposition point and raising the temperature four to five degrees per minute. [c] Prepared by Haworth and Hey[14] by the use of nitrous fumes. [d] This derivative could not be obtained in sufficient purity to give consistent analytical data.

Polymerization Studies.—It was necessary to use freshly prepared catalysts in the polymerization experiments in order to obtain consistent results. N-Nitroso compounds which had been stored in a refrigerator at −10° for several days were unsatisfactory catalysts as they decomposed slowly with the liberation of oxides of nitrogen.

The molecular weights of the polymers were obtained by viscosity measurements of benzene solutions of the polymers. With the styrene polymers calculations were made using the revised equation[16]

$$M = \frac{\log n_r \times K_{em}}{C}$$

$$K_{em} = 0.45 \times 10^4 \text{ for polystyrene in benzene}$$

The original Staudinger equation was used in calculating the molecular weights of the methyl methacrylate polymers. $M = n_{sp}/C \times K_m$; $K_m = 1.7 \times 10^{-4}$ for polymethyl methacrylate in benzene. Molecular weight measurements were not made on the acrylonitrile polymers due to the great insolubility of these products.

Polymerization of Styrene.—A. With N-nitroso-*p*-bromoacetanilide as a catalyst: a few test experiments with the nitroso compound as a catalyst showed that styrene could be polymerized under conditions which did not lead to polymers in the absence of the catalyst. Thus a 10-g. sample of freshly distilled styrene containing 0.2 g. of N-nitroso-*p*-bromoacetanilide gave 3 g. of polystyrene when allowed to stand at room temperature in a sealed tube in the dark for ten days. A sample of uncatalyzed styrene gave no polymer under these conditions. Other polymerization experiments with styrene are given in Table II which summarizes the experimental data from a variety of experiments.

B. With N,N′-dinitroso-4,4′-dibromosuccindianilide as a catalyst: a mixture of 5 g. of styrene and 0.5 g. of the catalyst was kept in a sealed tube under nitrogen at room temperature (27°) for two days. The experiment was carried out in the absence of light. The polystyrene was precipitated and purified by the usual precipitation procedure. The polystyrene (2.5 g.) was light cream colored.

Anal. Calcd. for $BrC_6H_4(C_8H_8)_{16}$: C, 88.32; H, 7.30; Br, 4.38; mol. wt., 1,820. Found: C, 87.89; H, 7.26; Br, 4.33; mol. wt., 1,970 (visc.).

Polymerization of Methyl Methacrylate.—A. With N-nitroso-*p*-bromoacetanilide as a catalyst: a 20-g. sample of freshly distilled methyl methacrylate was treated at room temperature (26°) with 5 g. of freshly prepared

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[13] Flory, THIS JOURNAL, **65**, 372 (1943).

[14] France, Heilbron and Hey, *J. Chem. Soc.*, 369 (1940).

[15] The nitrosyl chloride was furnished through the courtesy of Dr. E. D. Crittenden of the Solvay Process Co., Hopewell, Va.

[16] Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

TABLE II

SUMMARY OF SIGNIFICANT DATA ON FORMATION OF THE POLYMERS

N-Nitroso catalyst	Concn., moles/liter	Monomer	Concn., moles/liter	Temp., °C.	Time, hrs.	Yield, %	Analyses, % Br[e]	Mol. wt. (visc.)	Approx. fragments/polymer molecule
p-Br-acetanilide	0.18	Styrene	8.72	90	12	53	1.85[a]	15,400	3.56
	0.23	Styrene	8.72	75	24	35	6.45	1,665	1.34
4,4′-Dibromosuccindianilide	0.18	Styrene	8.72	27	48	50	4.33[b]	1,970	1.07
p-Br-acetanilide	1.10	Methyl methacrylate	10.00	26	16	A. 35 B. 45	A. 0.80[c] not anal.	12,100	1.21
	3.10	Methyl methacrylate	2.70	65	7.5	A. 18.5 B. 18.4	A. 3.00 not anal.	5,660	2.12
Same	0.25	Acrylonitrile	15.00	40–60	2	60	5.24	....	..
Same	0.15		1.50	50	2	45	7.50[d]	....	..

[a] *Anal.*[f] C, 90.63; H, 7.68; Br, 1.85. [b] *Anal.* C, 87.89; H, 7.26; Br, 4.33. Calcd. for $BrC_6H_4(C_8H_8)_{16}$: C, 88.32; H, 7.30; Br, 4.38; mol. wt., 1820. [c] *Anal.* C, 59.53; H, 8.00; Br, 0.80; O, 31.67 (diff.). Calcd. for $BrC_6H_4(C_5H_8O_2)_{116}$: C, 59.44; H, 8.04; O, 31.83; Br, 0.69; mol. wt., 11,660. [d] *Anal.* C, 68.03; H, 7.18; Br, 7.50. [e] Bromine analyses by Parr bomb combustion and Volhard titration. [f] Carbon and hydrogen analyses by Robert Holley.

catalyst. Within a few minutes the mixture warmed spontaneously. After thirty minutes the reaction had become so vigorous that strong external cooling was required to prevent loss of material from the reaction flask. After holding the reaction mixture at 26° for sixteen hours it set to a solid mass. The crude polymer (9 g.) obtained on adding methyl alcohol to a dioxane solution of the reaction mixture was purified in the usual way by three precipitation treatments. The purified polymer (3 g.) was white.

Anal. Calcd. for $BrC_6H_4(C_5H_8O_2)_{116}$: C, 59.44; H, 8.04; O, 31.83; Br, 0.69; mol. wt., 11,660. Found: C, 59.53; H, 8.00; Br, 0.80; O, 31.67; mol. wt., 12,100 (visc.).

See Table II for other pertinent experimental data on polymethyl methacrylate prepared using N-nitroso-*p*-bromoacetanilide as a catalyst.

B. With N-nitroso-α-bromoisovaleranilide as a catalyst: with this catalyst methyl methacrylate was polymerized by standing at room temperature (26°) for six hours. Examination of the polymer, isolated and purified in the usual way, showed that no halogen was present (negative Beilstein test and negative test in the qualitative analysis for bromine by sodium fusion).

C. With N-nitroso-N-phenyl-*m*-bromobenzamide as a catalyst: The addition of 1.4 g. of catalyst to 10 g. of methyl methacrylate at 26° resulted in the formation of a very viscous liquid within twenty minutes. After allowing the mixture to stand for twelve hours the polymer was isolated and purified in the usual way. The polymer gave a negative Beilstein test and qualitative analysis after fusion with sodium showed no bromine in the polymer.

From the dioxane filtrates a small amount of *m*-bromobenzoic acid (m. p. 153°) was isolated by extraction with cold dilute alkali followed by acidification.

Polymerization of Acrylonitrile. A. With N-nitroso-*p*-bromoacetanilide as a catalyst: the addition of 1.5 g. of catalyst to 20 g. of acrylonitrile at room temperature initiated polymerization with an accompanying rise in temperature. The mixture was held at 60–65° by external cooling. A dark yellow solid mass was formed which was insoluble in boiling dioxane and in acetone. After long extraction with methyl alcohol and ether in a Soxhlet extractor the polymer remaining contained 5.24% Br.

A sample of acrylonitrile containing no catalyst gave no polymer when heated at 65° under control conditions.

A second polymerization was carried out on a solution of 22 g. of acrylonitrile in 100 cc. of benzene at 50°. After two hours the mixture was cooled to room temperature and 10 g. of dry polymer was obtained. Five grams of the crude polymer was extracted with ether until the solvent came through colorless (three hours). Less than 0.5 g. of polymer was removed by this extraction. The composition of the remaining polymer was determined.

Anal. Found: C, 68.03; H, 7.18; Br, 7.50; N, 27.29.

B. With N-nitroso-α-bromoisovaleranilide as a catalyst: Polymerization of 8 g. of acrylonitrile in 50 cc. of petroleum ether (b. p. 60–70°) was effected at room temperature for eight hours using 1 g. of catalyst. The resulting polymer was washed well with petroleum ether, ethyl ether, and dried at 80° for one hour. This polymer gave a negative Beilstein test for halogen. Qualitative analysis for bromine by sodium fusion was also negative.

C. With N-nitroso-N-phenyl-*m*-bromobenzamide as a catalyst: Ten grams of acrylonitrile in 50 cc. of benzene was polymerized by adding 0.6 g. of the catalyst and allowing the solution to stand at room temperature under nitrogen. The solution was kept at 27–30° by external cooling. The resulting polymer gave negative tests for bromine by the usual methods.

Evaporation of the filtrates from the polymerization reaction was carried out at room temperature. From the resulting residue *m*-bromobenzoic acid was isolated by extraction with dilute alkali.

Summary

1. It has been shown that the N-nitrosoacylarylamines will effect the polymerization of styrene, methyl methacrylate, and acrylonitrile.

2. The number of catalyst fragments contained in the polymers varied. Although some polymers showed only one catalyst fragment attached per polymer molecule, others were formed which contained two or more such fragments.

3. Only the active free aryl radicals produced in the decomposition of the N-nitrosoacylarylamines are incorporated in the polymer molecules. The free acid radicals do not appear to be involved in the polymer formation.

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