strongly absorbing solution was obtained which possessed peaks at 229 and 282 mμ and a minimum at 245 mμ. This material was hydrolyzed with 2 *N* HCl in the autoclave and again extracted with ether in the above manner. *Ca.* 0.5 mg. of active nicotinic acid was obtained; its specific activity was not determined. The nature of the absorbing substance(s) in the first extract at *p*H 3.0 is unknown.

It was noted that the insolubles from the ethyl nicotinate root cultures, after precipitation with trichloroacetic acid at 100°, were radioactive to the extent of 0.008 mμc./mg. C.[12] This fraction normally contains cellulose, protein and other high molecular weight substances.

Inasmuch as nicotinic acid has recently been shown to originate from nicotine during the fermentation of cigar filler tobacco,[13] it thus appears that whatever relationship the two may have in the living plant is confined to the catabolic side of metabolism and is unconcerned with nicotine biosynthesis.

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[13] W. G. Frankenburg and A. M. Gottscho, *Ind. Eng. Chem.*, **44**, 301 (1952).

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N-Nitrosoacetanilide as Polymerization Initiator

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It has been shown by Blomquist, Johnson and Sykes[3] and by Hey and Misra[4] that substituted N-nitrosoamides will initiate the polymerization of styrene, methyl methacrylate and acrylonitrile. N-Nitrosoacetanilide itself does not appear to have been tested as an initiator. Although the initiator action suggests that free radicals are being produced as shown in the equation

$$\mathrm{ArN(NO)acyl} \longrightarrow \mathrm{ArN{=}NOacyl} \longrightarrow \mathrm{Ar.} + \mathrm{N_2} + \mathrm{acyl}$$

it was found experimentally by both groups of workers that a bromine-containing aryl group gave a bromine-containing polymer but that strangely enough bromine in the acyl group showed much less tendency to become incorporated in the polymer. This result seems to be in marked contrast to the behavior of *p*-bromobenzoyl peroxide[5] with styrene, which leads to incorporation of more bromobenzoate residue than bromophenyl residue.

Since we have been interested in potential sources of free radical intermediates, we have carried out some further polymerization experiments with N-nitrosoacetanilide to see whether this compound might possibly be a cationic initiator (a conceivable explanation of the bromine results) and to get further data about the initiator efficiency. Methyl methacrylate, acrylonitrile and styrene were polymerized, and qualitatively less polymerization occurred in the presence of *sym*-trinitrobenzene. Vinyl acetate and vinylpyridine showed little if any polymerization. Isobutylene was unaffected; there seemed to be no trace even of low molecular weight material such as trimers or tetramers. In six experiments the weight of the residue was zero within the experimental error after subtracting out the weight of the initiator products and of the inhibitor (Table I).

TABLE I

ATTEMPTED POLYMERIZATION OF ISOBUTYLENE

C_4H_8, g.	Nitroso-acetanilide, mmoles	*sym*-Trinitro-benzene, mmoles	Wt. of residue Obsd.	Wt. of residue Expected[a]
7.3	0	0	0	0
6.3	1	0	0.17	0.13
7.4	1	1	.24	.23
6.8	2	0	.33	.26
7.2	2	2	.53	.46
6.9	4	0	.51	.53
6.9	4	4	.93	.93

[a] Allowing for loss of nitrogen from the N-nitrosoacetanilide.

The styrene experiments are reported in Table II. Azo compounds and other products of initiator decomposition made all of the polymers highly colored.

TABLE II

AMOUNT OF POLYSTYRENE FORMED WITH N-NITROSOACETANILIDE AS INITIATOR

87 mmoles (9.2 g., 10 cc.) styrene used in each run

Nitroso-acetanilide, mmoles	*sym*-Trinitro-benzene, mmoles	Wt. polymer + NA residue (+ TNB) I[a]	Wt. polymer + NA residue (+ TNB) II[a]	Net wt. of polymer I[a]	Net wt. of polymer II[a]
0	0	0.00	0.00	0.00	0.00
0.5	0	0.86	0.96	0.79	.89
1	0	1.46	1.14	1.29	.97
2	0	1.55	1.24	1.28	.97
4	0	1.91	1.52	1.38	.99
8	0	2.47	1.93	1.41	.87
0.5	0.25	0.47	0.17	0.34	.04
1	0.5	.64	.34	.40	.10
2	1	.87	.63	.40	.16
4	2	1.42	1.19	.49	.26

[a] I. Tubes allowed to stand at 2–4° in the dark for five days, contents then poured into beakers and allowed to evaporate to constant weight at room temperature and atmospheric pressure. II. Reaction for two days in the dark at room temperature.

The effect of trinitrobenzene and the fact that the acrylates are polymerized readily while styrene is polymerized poorly[6] and isobutylene not at all are consistent with the hypothesis that a free radical rather than a cationic polymerization is taking place.

The low yields of polystyrene may result from such factors as inhibition due to reaction products and to wastage of initiator. But even in the complete absence of these effects only a low yield of polymer is to be expected for such a fast decomposing initiator. For a first order initiation reaction of 100% efficiency and for a bimolecular termination process without inhibition the amount of polymer

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[2] From the M.S. Thesis of Constance S. Savat, 1950.

[3] A. T. Blomquist, J. R. Johnson and H. J. Sykes, THIS JOURNAL, **65**, 2446 (1943).

[4] D. H. Hey and G. S. Misra, *Discussions Faraday Soc.*, **2**, 279 (1947).

[5] P. D. Bartlett and S. G. Cohen, THIS JOURNAL, **65**, 543 (1943).

[6] C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, *ibid.*, **72**, 48 (1950).

expected is given by eq. 1. S_0 and S_∞ are styrene concentrations at zero time and at "infinite" time

$$\log_{10}(S_0/S_\infty) = 2(0.434)k_2(1/k_1k_3)^{1/2}(\mathrm{NA}_0)^{1/2} \qquad (1)$$

NA_0 is the initial nitrosoacetanilide concentration, and k_1, k_2 and k_3 are rate constants for initiation, propagation and termination. Using the reported values of the rate constants ($k_1 = 7.7 \times 10^{-5}$, $k_2 = 44$, $k_3 = 2.4 \times 10^7$)[7,8] the maximum amount of polymer expected is as follows: with nitrosoacetanilide initially at 0.05 M (the 0.5 mmole experiment of Table II) about 37%, at 0.1 M about 48%. The maximum amount of polymer is increased at lower temperatures since k_1 has a higher temperature coefficient than either k_2 or k_3: 22 kcal., as compared with 7 kcal. or less.[7,8]

Experimental Part

N-Nitrosoacetanilide.—This was prepared by the method of DeTar.[9] The monomer samples were distilled before use to remove inhibitor.

Isobutylene Experiments.—A series of tubes of Pyrex glass was prepared, and weighed amounts of N-nitrosoacetanilide and of trinitrobenzene added. Phillips Pure Grade (99 mole % min.) isobutylene was distilled into these tubes which were immersed in a trichloroethylene both at solid carbon dioxide temperature. The tubes were sealed, placed in shields and allowed to remain at room temperature for 24 hours. The tubes were cooled, the capillary tips broken, and the isobutylene allowed to evaporate at room temperature and atmospheric pressure. The top of the tube was cut off, the tube weighed, rinsed thoroughly with methylene chloride, and weighed again in order to determine the weight of residue. The results are given in Table I.

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[7] W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1800 (1934); R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949).

[8] M. S. Matheson, E. E. Aves, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 1704 (1951).

[9] D. F. DeTar, *ibid.*, **73**, 1446 (1951).

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Reactions of N-Nitroso-2-acetamidobenzophenone

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We have been interested in reactions which may produce the *o*-benzoylphenyl radical (and other similar radicals) in our study of the mechanisms of certain free radical reactions.[2] The decomposition of diazotized 2-aminobenzophenone under alkaline conditions is under study at present as a source of these radicals. The thermal decomposition of N-nitroso-2-acetamidobenzophenone is a related reaction which might also be expected to yield the desired radical.[3] A preliminary study of this nitroso compound has given interesting results, but the reactions of this compound are too complex to be useful for our purposes at the present time.

In benzene solution N-nitroso-2-acetamidobenzophenone gives 2-benzoylbiphenyl 15%, fluorenone 7%, and unidentified higher molecular weight products. In methanol acidified with sulfuric acid the products were fluorenone 20%, 2-methoxybenzophenone 40% and 2-aminobenzophenone 40%. In acetic acid the products were fluorenone 23%, 2-acetoxybenzophenone 25% and 45% of 2-aminobenzophenone. The reactions in methanol and in acetic acid thus seem to be ionic reactions.

Experimental Part

N-Nitroso-2-acetamidobenzophenone.—2-Aminobenzophenone was prepared from N-tosylanthranoyl chloride, benzene and aluminum chloride.[4] Acetylation with acetic anhydride gave 2-acetamidobenzophenone, m.p. 87–88.5°; Lothrop and Goodwin[5] report a m.p. of 88°. This was converted to the nitroso compound. To 8 g. of the amide, 12 g. of potassium acetate, 56 ml. of glacial acetic acid, 24 ml. of acetic anhydride was added 4.6 g. of nitrosyl chloride in 13.4 g. of acetic anhydride during ten min. at 5°; after an hour at 0°, the mixture was stirred with 800 ml. of ice-water to precipitate the nitrosoamide. This was recrystallized from 125 ml. of acetic acid plus added water, giving 52% of yellow crystals, m.p. 72° dec. It is not stable at room temperature, but can be preserved for several days at Dry Ice temperature.

Anal. Calcd. for $C_{15}H_{12}O_3N_2$: C, 67.15; H, 4.51; N, 10.44. Found: C, 67.20; H, 4.63; N, 11.07.

Reactions.—The following thermal decomposition reactions of N-nitroso-2-acetamidobenzophenone were studied: 2 g. of the nitrosamide in 20 ml. of benzene for 15 hours at room temp.; 1 g. in 50 ml. of methanolic 0.04 M sulfuric acid for one hour at 50–65° and then for two days at room temp.; 1 g. in 15 ml. of glacial acetic acid for one hour at 100° and then two days at room temperature.

Isolation of and Estimation of Products.—The benzene reaction mixture was subjected to exhaustive steam distillation, yielding fractions of 0.26 g. and 0.23 g. after extraction with methylene chloride. A semi-quantitative analysis was made for fluorenone and for 2-benzoylbiphenyl by measurement of the optical absorbance of ethanol solutions of these fractions at 2300, 2570 and 2650 Å. On evaporation of the ethanol the first residue yielded crystals of 2-benzoylbiphenyl, m.p. 83.3–85.3°, m.p. with authentic material[2] 86–87°, and a small amount of yellow crystalline material, m.p. 83–84°. The yellow crystalline material was subjected to microscopic examination and was identical with fluorenone in the following respects: hexagonal plates, highly birefringent, four angles about 148°, two angles about 64°, parallel extinction. The second fraction yielded only 2-benzoylbiphenyl, m.p. 84.3–85.3°, in crystalline form.

The methanol reaction mixture was neutralized with sodium hydroxide, distilled to remove most of the methanol, water was added, and then the resulting mixture was extracted with methylene chloride. The methylene chloride layer was subjected to exhaustive steam distillation and the distillates, after extraction with methylene chloride and evaporation to dryness, yielded 0.95 g. of residue. The infrared spectra of this residue had peaks characteristic of fluorenone, benzophenone, 2-methoxybenzophenone, 2-aminobenzophenone and one or more unidentified other materials. A semi-quantitative analysis based on absorbance at 2150, 2350 and 2570 Å. was made for fluorenone, 2-aminobenzophenone and 2-methoxybenzophenone.

The acetic acid reaction mixture was distilled to remove most of the acetic acid and the residue was treated with methylene chloride and aqueous sodium hydroxide. The methylene chloride layer was subjected to steam distillation and gave 0.59 g. of neutral residue. Semi-quantitative analysis of an ethanol solution using absorbance at 2350, 2570 and 2650 Å. gave estimates of the amounts of fluorene, 2-aminobenzophenone and 2-acetoxybenzophenone. On evaporation of the ethanol, yellow crystals of fluorenone separated, m.p. 78.5–81.5°, mixed m.p. with authentic fluorenone 79–82°. The infrared spectra of the residue obtained by evaporation of the mother liquor had peaks at 5.87, 6.24, 10.90 and 13.54 characteristic of fluorenone; at 5.70, 6.28, 6.95, 7.78, 7.95, 8.43 and 13.25 characteristic of 2-acetoxybenzophenone, and at 3.07 and 3.50 characteristic of 2-aminobenzophenone. In addition to the listed

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[1] Department of Chemistry, University of South Carolina, Columbia, S. C.

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[3] D. F. DeTar, *ibid.*, **73**, 1446 (1951).

[4] D. F. DeTar and H. Scheifele, *Org. Syntheses*, **32**, 8 (1952).

[5] W. C. Lothrop and P. A. Goodwin, THIS JOURNAL, **65**, 363 (1943).