369. *Reactions of Peroxides in* NN-*Dimethylformamide Solution. Part I. The Induced Decomposition of Benzoyl Peroxide.*

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The thermal decomposition of benzoyl peroxide in *NN*-dimethylformamide solution has been studied between 40° and 70°. A rapid induced decomposition was observed, of first order in benzoyl peroxide. Interaction of benzoyloxy-radicals and the solvent forms $H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}$ radicals which readily attack the peroxide molecules; a chain mechanism in which termination occurs by combination of $H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}$ and benzoyloxy-radicals is thus established. Benzoic acid and *N*-benzoyloxymethyl-*N*-methylformamide are major products; the structure of the latter has been established by synthesis. The significance of these results in polymerization studies in *NN*-dimethylformamide is discussed.

NN-DIMETHYLFORMAMIDE has recently been extensively used as a polymerization solvent and several kinetic studies in this medium, particularly of the polymerization of acrylonitrile, have been reported.[1,2] As we learn more about the mechanism of polymerization we need to know how and how much the amide may participate in the reactions. It may react with polymer radicals or with primary radicals arising directly from the initiator. Chain transfer occurs with several types of polymer radical [3] but the point of radical attack has not hitherto been established. We now report a study of reactions between *NN*-dimethylformamide and primary radicals derived from benzoyl peroxide.

RESULTS AND DISCUSSION

General Features of the Reaction.—Benzoyl peroxide decomposes in *NN*-dimethylformamide solution by a first-order process. Plots of the logarithms of the peroxide concentration against time were linear over at least 90% of the reaction, and had similar slopes over the whole range of initial concentrations studied (4—60 × 10^{-2} mole $l.^{-1}$).

Temp.	40°	60°	69·4°	70°
Half-life (min.)	3000	154	61·5	59
Overall velocity coefficient k (sec.$^{-1}$)	$3{\cdot}86 \times 10^{-6}$	$7{\cdot}50 \times 10^{-5}$	$1{\cdot}88 \times 10^{-4}$	$1{\cdot}96 \times 10^{-4}$

The Table summarizes the rate data obtained at several temperatures. The values of k correspond closely to the Arrhenius relation $k = 3 \times 10^{14} \exp(-28{,}300/\boldsymbol{R}T)$ sec.$^{-1}$. By contrast, the half-life of the decomposition at 69·4° measured in the presence of styrene ($\sim$ 1 mole $l.^{-1}$) is about 30 hr. so, in the absence of a benzoyloxy-radical scavenger such as styrene, a rapid induced decomposition of the peroxide occurs.

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[1] Onyon, *Trans. Faraday Soc.*, 1956, **52**, 80; Barson, Bevington, and Eaves, *Trans. Faraday Soc.*, 1958, **54**, 1678; Thomas, Gleason, and Pellon, *J. Polymer Sci.*, 1955, **17**, 275.

[2] Bamford and Jenkins, *Proc. Roy. Soc.*, 1953, *A*, **216**, 515; Bamford, Jenkins, and Johnston, *ibid.*, 1957, *A*, **239**, 214.

[3] Prévot-Bernas and Sebban-Danon, *J. Chim. phys.*, 1956, **53**, 418; Bamford, Jenkins, Johnston, and White, *Trans. Faraday Soc.*, 1959, **55**, 168; also unpublished work.

The main products of the induced reaction are the ester *N*-benzoyloxymethyl-*N*-methylformamide (I) and benzoic acid. The former was isolated (not quantitatively) in approximately 60 mole % yield, and its constitution has been confirmed by hydrolysis to benzoic acid, methylamine, and formaldehyde, and also by synthesis. The yield of benzoic acid is ~85 mole % throughout the course of the reaction at 60°. Comparatively small amounts of carbon dioxide are formed during the decomposition: at 50° and 60° 10·7 and 11·5 mole % respectively, based on the benzoyl peroxide decomposed.

The primary step in the thermal decomposition of benzoyl peroxide in many solvents is the homolytic fission into benzoyloxy-radicals:

$$(\mathrm{Ph{\cdot}CO{\cdot}O})_2 \longrightarrow 2\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It is well known[4,5] that these radicals may attack further peroxide molecules, causing an induced decomposition of the latter into carbon dioxide, phenyl benzoate, and biphenyl; in *NN*-dimethylformamide no biphenyl or phenyl benzoate could be detected. Since the yield of carbon dioxide is low, most of the benzoyloxy-radicals formed in (1) must attack the solvent, giving rise to reactions (2), (3), and (4):

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + \mathrm{H{\cdot}CO{\cdot}NMe_2} \longrightarrow \mathrm{Ph{\cdot}CO_2H} + \mathrm{H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}} \quad . \quad . \quad . \quad . \quad (2)$$

$$\mathrm{H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}} + (\mathrm{Ph{\cdot}CO{\cdot}O})_2 \longrightarrow \mathrm{H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}O{\cdot}COPh}\ (\mathrm{I}) + \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} \quad . \quad (3)$$

$$\mathrm{H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}} + \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} \longrightarrow \mathrm{H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}O{\cdot}COPh} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Reactions (3) and (4) constitute a chain mechanism responsible for the rapid induced decomposition of the peroxide into the observed products.

Kinetics.—The velocity coefficients of reactions (1)—(4) will be denoted by k_1, k_2, k_3, k_4, and for conciseness P, P•, D, D• will be used to represent benzoyl peroxide, the benzoyloxy-radical, *NN*-dimethylformamide, and the derived radical H•CO•NMe•CH$_2$• respectively. On the basis of the usual stationary-state assumptions we have:

$$\mathrm{d[P{\cdot}]/d}t = 2k_1[\mathrm{P}] - k_2[\mathrm{P{\cdot}}][\mathrm{D}] + k_3[\mathrm{D{\cdot}}][\mathrm{P}] - k_4[\mathrm{P{\cdot}}][\mathrm{D{\cdot}}] = 0 \quad . \quad . \quad (5)$$

$$\mathrm{d[D{\cdot}]/d}t = k_2[\mathrm{P{\cdot}}][\mathrm{D}] - k_3[\mathrm{D{\cdot}}][\mathrm{P}] - k_4[\mathrm{P{\cdot}}][\mathrm{D{\cdot}}] = 0 \quad . \quad . \quad . \quad . \quad (6)$$

These equations may be solved directly for [P•], [D•], and the results used to deduce the following relations:

$$-\frac{\mathrm{d[P]}}{\mathrm{d}t} = \frac{\mathrm{d[A]}}{\mathrm{d}t} = \frac{k_1[\mathrm{P}]}{2}\{1 + (1 + 4y[\mathrm{D}])^{\frac{1}{2}}\} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where [A] represents the concentration of benzoic acid and $y = k_2k_3/k_1k_4$. It is clear from (7) that according to this mechanism the reaction should be of first order in peroxide with an overall velocity constant given by (8):

$$k = \tfrac{1}{2}k_1\{1 + (1 + 4y[\mathrm{D}])^{\frac{1}{2}}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and that the benzoic acid formed should be equivalent to the peroxide decomposed, on a molar basis. These predictions are in satisfactory agreement with observation: spontaneous decarboxylation of a minor proportion of the benzoyloxy-radicals could account for the lower yield of benzoic acid observed and also for the small amount of carbon dioxide formed.

If the reaction is carried out in the presence of a radical scavenger (*e.g.*, styrene) the induced decomposition [reactions (2), (3)] is largely suppressed; very similar behaviour was observed by Nozaki and Bartlett[5] and by Swain, Stockmayer, and Clarke[4] for the decomposition of benzoyl peroxide in a number of other solvents. It thus becomes possible to evaluate k_1 directly; the values obtained at 70° were in the range 6·4—8·0 × 10^{-6} sec.$^{-1}$. Unfortunately, the reaction under these conditions is not quite straightforward since the " first-order constant " varies somewhat with the initial peroxide concentration;

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[4] Swain, Stockmayer, and Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.

[5] Nozaki and Bartlett, *ibid.*, 1946, **68**, 1686.

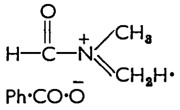
this behaviour, which is not understood, has been observed in other systems containing benzoyl peroxide.[6] For present purposes it will be sufficiently accurate to take $k_1 = 7 \times 10^{-6}$ sec.$^{-1}$. Since k, k_1, and [D] are known, y may be calculated from (8). The value obtained at 70° is 55·1 mole^{-1} l., from which it follows that $k_2k_3/k_4 = 3{\cdot}8 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$. Further evaluation of the individual velocity coefficients is not possible from the present results. The kinetic chain length ν of the induced decomposition, *i.e.*, the number of peroxide molecules decomposed for each P· radical generated in the spontaneous fission (1), is given by

$$\nu = \{(1 + 4y[\mathrm{D}])^{\frac{1}{2}} - 1\}/4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

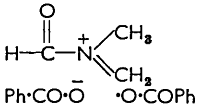
This quantity is therefore independent of the benzoyl peroxide concentration. Its value at 70° in bulk *NN*-dimethylformamide solution is approximately 13.

Chemical Aspects and Significance in Polymerization Studies.—The decomposition of benzoyl peroxide in *NN*-dimethylformamide solution is unusual in that the induced reaction is of first order in peroxide concentration. Generally, the order of an induced decomposition is higher than unity. However, Cass [6,7] observed similar kinetics for the decomposition in diethyl ether, and isolated 1-ethoxyethyl benzoate in good yield, together with benzoic acid. These products clearly arise from a reaction sequence similar to (2), (3), and (4).[4,6,7]

The characteristic kinetic features of the reaction in *NN*-dimethylformamide arise from the dominance of reactions (2), (3), and (4) over other alternatives. The greater strength of the O–H bond than of the C–H bond is consistent with (2) being fast and predominating over decarboxylation of the benzoyloxy-radical. It is noteworthy that, since the O–H bond is also much stronger than the O–C bond, the relative rates of hydrogen abstractions compared to additions to double bonds in polymerization reactions may be much higher for $-\mathrm{O}\cdot$ radicals than for $-\overset{|}{\underset{|}{\mathrm{C}}}\cdot$ radicals. Reactions (2) and (3) may be facilitated by the stabilization of their transition states by polar contributions from structures such as (II) and (III). Further, it is not surprising that (4), involving interaction of electron-donating and -accepting radicals, should predominate over other possible termination reactions.



(II)



(III)

The mechanism may be compared with that of the reactions between amines and benzoyl peroxide which have been studied by Gambarjan [8] and extensively investigated in recent years by Horner and his co-workers.[9] According to Horner, the primary step is the transfer of an electron from the amine to the peroxide. This is a bimolecular process which is not a chain reaction and it is distinct from an induced decomposition of the type found in the present work. (Urry and Juveland [10] have, however, suggested that an induced decomposition may in fact participate in benzoyl peroxide–amine systems in some circumstances.) However, the mechanism of reactions (2) and (3) resembles the primary step in the amine–peroxide reaction postulated by Horner, insofar as these reactions are assisted by the electrophilic characters of the benzoyloxy-radical and the peroxide and the electron-donating properties of *NN*-dimethylformamide and the derived radical $\mathrm{H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}}$. The polar nature of the transition state would, of course, be much more pronounced in the amine–peroxide reaction than in reactions (2) and (3).

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[6] Cass, *J. Amer. Chem. Soc.*, 1946, **68**, 1976.

[7] *Idem, ibid.*, 1947, **69**, 500.

[8] Gambarjan, *Ber.*, 1909, **42**, 4003; 1925, **58**, 1775; Gambarjan and Cialtician, *Ber.*, 1927, **60**, 390.

[9] A concise discussion of Horner's work, with references, is given in Walling, " Free Radicals in Solution," John Wiley and Sons, 1957, p. 590.

[10] Urry and Juveland, *J. Amer. Chem. Soc.*, 1958, **80**, 3322.

The possible occurrence of (2) must be considered when studying vinyl polymerization in *NN*-dimethylformamide; this is particularly necessary when kinetic chain lengths are to be determined by estimation of the number of initiator fragments incorporated into polymer molecules. At low monomer concentrations, reaction (2) may compete significantly with direct initiation by addition of benzoyloxy-radicals to the monomer; initiation may then occur through $H{\cdot}CO{\cdot}NMe{\cdot}CH_2{\cdot}$ radicals, but the polymer will not carry end-groups derived from the initiator. Estimates of the kinetic chain length from end-group determinations will therefore be too high, while initiator efficiencies will appear to be too low. Barson, Bevington, and Eaves,[1] studying the polymerization of acrylonitrile in *NN*-dimethylformamide with labelled benzoyl peroxide as initiator, have, in fact, recorded behaviour of this type. Although the authors account for their results by postulating hydrogen-transfer between benzoyloxy-radicals and the monomer, we consider it much more likely that the radicals react according to (2), since the amide solvent has a higher transfer constant (in the polymerization of acrylonitrile) than the monomer [3,11] and was present in greater concentration.

EXPERIMENTAL

Materials.—Benzoyl peroxide was purified by two precipitations from chloroform solution into methanol and was dried in a vacuum. *NN*-Dimethylformamide was treated with phosphoric oxide several times before vacuum distillation.[2]

Technique.—The decomposition was carried out in the dark under nitrogen, and its progress was followed by titrating samples by the method of Swain, Stockmayer, and Clarke.[4] In some cases the benzoic acid was estimated at intervals during a reaction. For this purpose samples were taken from the reaction mixture, diluted with *NN*-dimethylformamide, and titrated with standard potassium methoxide in benzene–methanol solution to a thymol-blue end-point.

Estimations of the carbon dioxide evolved during the reaction were made by sweeping out the carbon dioxide by a stream of nitrogen, which was then bubbled through standard baryta.

Isolation of N-*Benzoyloxymethyl*-N-*methylformamide* (I).—After decomposition of benzoyl peroxide in *NN*-dimethylformamide most of the solvent was removed by vacuum-distillation, and the residue, in ether solution, was washed with dilute aqueous sodium carbonate to remove benzoic acid. The ethereal extract was then dried ($CaSO_4$), and the ether removed. The liquid residue was distilled in a molecular still and gave a colourless oily product with n_D^{20} 1·5398 (Found: C, 62·5; H, 5·7; N, 7·1. $C_{10}H_{11}O_3N$ requires C, 62·2; H, 5·7; N, 7·3%). An indication of the structure of the *product* was first obtained by hydrolysis. When it was treated with 20% aqueous sulphuric acid, formaldehyde was evolved and identified by its characteristic odour and by formation of its 2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p. 164°). On alkaline hydrolysis (50% aqueous sodium hydroxide) methylamine was formed. It gave a characteristic yellow precipitate with Nessler's reagent and a positive carbylamine test. Benzoic acid was produced in both hydrolyses and was identified by a mixed m. p. determination.

Synthesis of N-*Benzoyloxymethyl*-N-*methylformamide.*—Redistilled *N*-methylformamide (59 g.) was refluxed for 1 hr. in alcohol (100 ml.) with paraformaldehyde (31 g.) and potassium carbonate (1 g.). The alcohol was distilled off, and the liquid residue extracted with ether. The insoluble portion consisted mainly of *N*-hydroxymethyl-*N*-methylformamide together with potassium carbonate, which was filtered off. The unpurified material (yield 72%) was used directly for the preparation of the *benzoate* as follows: 9 g. of it were shaken with redistilled benzoyl chloride (11·5 ml.) and 5% aqueous sodium hydroxide (120 ml.) in the cold. The lower layer was separated, washed with dilute sodium carbonate solution, and dried (yield 52%). The product, when distilled in a molecular still, gave a viscous colourless oil with n_D^{20} 1·5401 (Found: C, 63·0; H, 6·0; N, 7·3. $C_{10}H_{11}O_3N$ requires C, 62·2; H, 5·7; N, 7·3%). On hydrolysis this compound behaved identically with the reaction product described above.

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[11] Bamford, Jenkins, and White, *J. Polymer Sci.*, 1959, **34**, 271.