[Contribution from the Frick Chemical Laboratory, Princeton University and Gordon Hall, Queen's University, Kingston, Ontario]

The Preparation of Phthalyl Peroxide and its Decomposition in Solution

By K. E. Russell

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The preparation of monomeric phthalyl peroxide is described. The thermal decomposition of the peroxide has been studied in the solvents toluene and xylene and in the monomers methyl methacrylate and styrene. In methyl methacrylate solution, the efficiency of phthalyl peroxide in producing long chain polymer is shown to be very low and this is ascribed partly to the induced decomposition of the peroxide and partly to its decomposition into diradicals which undergo self-termination after adding only a few monomer units.

Cyclic peroxides such as phthalyl peroxide are of interest as sources of diradicals. In principle they can be prepared by the reaction of the appropriate acid chloride with sodium peroxide. However, when pure *sym-o*-phthalyl chloride is shaken with an aqueous solution of sodium peroxide, the product is a polymeric peroxide insoluble in solvents such as benzene and chloroform.[1,2] This polymeric peroxide has been used as a radical source by Shah, Leonard and Tobolsky,[2] but because of the insolubility of the peroxide in monomeric styrene, it was not possible to obtain a homogeneous initiation of long chain polymer. In addition, the polymeric peroxide is essentially a source of monoradicals and does not allow the process of self-termination of diradicals to compete with the propagation reaction.[3]

It is clear that the uncertainties in previous work can be avoided by the use of monomeric phthalyl peroxide as this would be soluble in the reaction medium and the expected products of decomposition are diradicals which should be sufficiently reactive to initiate polymerization. The monomeric peroxide is prepared readily by modifying the procedure of Pechmann and Vanino. A dilute solution of phthalyl chloride in chloroform is added to a dilute aqueous solution of sodium peroxide. The system is buffered to prevent undue decomposition of the peroxide.[4] The monomeric peroxide is produced in about 55% yield and remains dissolved in the chloroform layer.

Decomposition studies have been made on the peroxide in toluene, xylene, styrene and methyl methacrylate. The disappearance of peroxide was followed by iodometric analysis. The initiation of polymerization by the peroxide in the two monomers also was studied.

Experimental

Materials.—Phthalyl chloride (Matheson Co.) was distilled at a pressure of 18 mm. (b.p. 143°) in a concentric tube column. It was frozen by cooling to 0° and, on melting, the clear phthalyl chloride was decanted from the small quantity of white solid which had appeared at the bottom of the container.

Benzene for molecular weight studies was thiophene-free and was purified by fractional freezing and fractional melting. Its melting point was 5.50°.

Styrene (Dow N-99) was distilled at 20 mm. pressure and transferred to a vacuum apparatus. It was degassed three times and twice distilled *in vacuo*. It was stored at −80°.

Methyl methacrylate (Rohm and Haas Co.) was freed from inhibitor by washing with sodium hydroxide solution, washed with water and dried over potassium carbonate. It was distilled at 100 mm. pressure, transferred to the vacuum apparatus, degassed three times and distilled three times *in vacuo*. It was stored at −80°.

Toluene (sulfur-free, Eastman Kodak Co.) and xylene (J. T. Baker Analyzed Reagent) were used without further purification.

Preparation of Phthalyl Peroxide.—A solution of approximately 15 g. each of sodium dihydrogen phosphate and disodium hydrogen phosphate in 400 ml. of water was cooled to 5° in an ice-water-bath. Eight grams of sodium peroxide was added to the stirred solution, followed by a solution of 14 ml. of phthalyl chloride in 300 ml. of chloroform, also cooled to 5°. Stirring was continued for 15 minutes. The chloroform layer was separated off, washed twice with water, and evaporated down to about 30 ml. with a stream of air at room temperature. On cooling to about −50°, the peroxide crystallized out. It was filtered off, washed with petroleum ether and dried in a vacuum desiccator. The yield of crude material was 8.9 g. (55%).

The peroxide was purified by recrystallizing twice from a benzene-petroleum ether mixture. The crystals were colorless needles and melted at 126°, occasionally explosively; this compares with 134–135° for the decomposition point of the polymeric peroxide.[2] It was very soluble in chloroform and in aromatic solvents such as benzene and toluene, and also dissolved readily in the monomers styrene and methyl methacrylate.

Anal.[5] Calcd. for $C_8H_4O_4$: C, 58.57; H, 2.46. Found: C, 58.35; H, 2.64.

On heating, the peroxide left no residue and it gave a negative test for chlorine. The molecular weight was determined by measurement of the freezing point depression of benzene; values of 161 and 163 were obtained (calcd. for $C_8H_4O_4$, 164). The peroxide content was determined by the iodometric method of Wagner, Smith and Peters.[6] Twice-recrystallized material gave a peroxide content corresponding to 98.7% phthalyl peroxide being present, and further recrystallization did not significantly change this figure.

Thermal Decomposition.—The decomposition was studied in toluene, xylene, styrene and methyl methacrylate at temperatures ranging from 60 to 75°. Solutions of peroxide were made up in the concentration range 0.04 to 0.1 mole/liter, and were degassed; the reaction tubes were sealed off *in vacuo*. They were transferred to a thermostat and after appropriate time intervals were analyzed for peroxide content.

No difficulty arose from iodine analysis in the presence of unsaturated compounds,[6] but the formation of polymer in the methyl methacrylate system made it impossible to carry analysis of the decomposition beyond 30%.

The peroxide was used as an initiator for the polymerization of methyl methacrylate and styrene. Solutions of the peroxide in the monomer were made up *in vacuo* and after heating for a known time, they were cooled and the long chain polymer precipitated in methanol. It was dried *in vacuo* at 60°.

Results and Discussion

The reaction of *sym-o*-phthalyl chloride with sodium peroxide under the conditions described leads

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(1) H. V. Pechmann and L. Vanino, *Ber.*, **27**, 1511 (1894).

(2) H. A. Shah, F. Leonard and A. V. Tobolsky, *J. Polymer Sci.*, **7** 537 (1951).

(3) B. H. Zimm and J. K. Bragg, *ibid.*, **9**, 476 (1952).

(4) R. H. McKee, U. S. Patent 1,614,037 (Jan. 11, 1927).

(5) Analysis by Joseph F. Alicino, Metuchen, N. J.

(6) C. D. Wagner, R. H. Smith and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

to a 55% yield of phthalyl peroxide. It is probable that the phthalyl chloride contains traces of its unsymmetrical isomer, but it is unlikely that the product contains any of the monomeric peroxide derived from this isomer, because of the difficulty of forming a three-membered peroxide ring.

The peroxide group forms part of a six-membered ring, and, from a model, a small amount of strain is expected in the ring. By analogy with benzoyl peroxide whose decomposition has been investigated in detail,[7-9] the thermal decomposition of phthalyl peroxide is expected to go through an initial stage in which the O–O linkage is broken to give a diradical, possibly followed by the splitting off of carbon dioxide.

Thermal Decomposition.—The decomposition of phthalyl peroxide in the solvents toluene and xylene does not follow a simple law. In any single reaction the initial order of reaction is less than one (approximately zero in toluene) and it becomes approximately one after 50% reaction. Rates of the reaction therefore have been expressed as the extent of decomposition during the first hour of reaction and some typical values are given in Table I.

TABLE I

DECOMPOSITION OF PHTHALYL PEROXIDE IN SOLUTION

Solvent	Temp., °C.	Decompn. rate (%/hr.)
Toluene	60	9
Toluene	70	26
Xylene	60	25
Methyl methacrylate	75	5
Styrene	75	90%/5 min.

The rate of decomposition of 9%/hr. for phthalyl peroxide in toluene corresponds to an estimated value of about 1%/hr. for benzoyl peroxide in toluene at 60°. The activation energy for the breakdown of phthalyl peroxide in toluene is lower than for benzoyl peroxide, an approximate value of 24 kcal./mole being derived from the above figures.

The rate of decomposition of peroxide varies considerably with the solvent. A similar effect has been observed with benzoyl peroxide, and has been ascribed[8] to the attack on the peroxide of radicals other than those formed in the primary cleavage of the O–O bond. The induced decomposition of benzoyl peroxide is retarded by molecular oxygen, and it is observed that oxygen also cuts down the rate of breakdown of phthalyl peroxide. It thus seems probable that phthalyl peroxide undergoes both a unimolecular and an induced decomposition in solution. The observed kinetics are difficult to explain; it is possible that the reaction products take part in the induced decomposition.

Initiation of Polymerization.—The rate of polymerization of methyl methacrylate in the presence of 0.053 mole/liter phthalyl peroxide was 5.4×10^{-5} mole/liter/sec. at 75°. The rate of polymerization of the pure monomer was negligible. The efficiency of initiation of long-chain polymer assuming that each peroxide molecule gives two radicals is between 0.1 and 0.2%. This low efficiency can be ascribed to two factors. The first is the induced decomposition of the peroxide in which much of the peroxide may well be converted to inert products rather than to radicals which can induce polymerization. The second is the failure of most of the diradicals produced in the unimolecular decomposition to grow appreciably, because of undergoing self-termination to form low polymer after the addition of one or two monomer units.[3,10]

The phthalyl peroxide was recrystallized further to determine whether the long chain polymer arose from the peroxide or from some impurity. Extra recrystallizations did not significantly reduce the rate of polymerization suggesting that the radicals which grow do in fact come directly or indirectly from the peroxide decomposition.

The rate of decomposition of phthalyl peroxide in styrene was very high and the reaction may proceed almost entirely by way of an induced decomposition. The rate of polymerization for styrene containing phthalyl peroxide was only slightly greater than for the pure monomer and the efficiency of initiation was therefore very low.

KINGSTON, ONTARIO, CANADA

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[7] J. H. McClure, R. E. Robertson and A. C. Cuthbertson, *Can. J. Research*, **20B**, 103 (1942).

[8] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

[9] W. E. Cass, *ibid.*, **68**, 1976 (1946).

[10] K. E. Russell and A. V. Tobolsky, *ibid.*, **76**, 395 (1954).