the rate of decomposition of benzoyl peroxide varies widely with solvent and concentration.

These compounds are highly efficient photosensitizers as well as thermal initiators for free radical reactions. An absorption band has its peak at 3500 Å. (measurements on 2-azo-bis-isobutyronitrile) so that the compounds are especially suited for work using the 3660 Å. line of the mercury arc. Table III illustrates some results obtained in irradiations with Type A Hanovia mercury arc light filtered through Pyrex. Because of the characteristics of the absorption, the absorbed light is > 80% 3660 Å. Slightly smaller values than those given in the Table have been found for 2-azo-bis-isobutyronitrile using monochromatic 3660 Å. radiation. The quantum yields show the aliphatic azo nitriles to be superior in efficiency to such a photosensitizer as biacetyl.[4] The first six compounds in the table vary little in efficiency in styrene, and the variations in vinyl acetate are probably less than shown, as it is believed the reactions with vinyl acetate overheated several degrees. These polymerizations were carried out *in vacuo* to eliminate the effects of oxygen. Light intensities were measured with the uranyl oxalate actinometer.

TABLE III

PHOTOPOLYMERIZATION WITH AZO SENSITIZERS AT 3660 Å.[a] AND 30°

Sensitizer (~0.038 m./l.)	Quantum yield polymerization[b] Vinyl acetate	Styrene
2-Azo-bis-isobutyronitrile	360	55
2-Azo-bis-propionitrile (unstable)	. . .	50
Dimethyl-2-azo-bis-isobutyrate	>600	50
1-Azo-bis-1-cyclohexanecarbonitrile	600	50
2-Azo-bis-2-methylheptonitrile	230	55
2-Azo-bis-2-methylbutyronitrile	255	60
4-Azo-bis-4-cyanopentanoic acid	284	. . .
2-Azo-bis-propane[c]	80	2.80
Biacetyl	10.3	1.4[d]

[a] λ>3000 Å. but largely 3660 Å. absorbed so quantum yield calculated on basis of 3660 radiation absorbed. [b] Molecules monomer polymerized per quantum of 3660 Å. radiation absorbed by sensitizer. Quantum yield cor. to 3.94×10^{-5} einstein/hr./cc. ~50% of 3660 Å. light absorbed in 1 cm. with sensitizer concentrations used. [c] This azo compound does not initiate polymerizations at room temperature in the absence of light. [d] With monochromatic 3660 Å.

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(4) C. L. Agre (U. S. Patent 2,367,660, Jan. 23, 1945, to du Pont.)

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Reaction of Hydrogen Bromide with Di-*t*-butyl Peroxide

BY NICHOLAS A. MILAS AND CHARLES N. WINNICK[1]

Vaughan and Rust[2] claimed the preparation of di-*t*-butyl peroxide by the vapor oxidation of isobutane in the presence of hydrogen bromide. More recently Raley, Rust and Vaughan[3] reported that hydrogen chloride sensitizes the vapor phase decomposition of di-*t*-butyl peroxide, but that under comparable conditions hydrogen bromide has little effect on this decomposition. However, the behavior of hydrogen bromide with liquid di-*t*-butyl peroxide is different. We have found recently that at 0° it reacts rapidly and exothermically with di-*t*-butyl peroxide in accordance with the equations

$$(CH_3)_3COOC(CH_3)_3 + 4HBr \longrightarrow 2(CH_3)_3CBr + Br_2 + 2H_2O \quad (1)$$

$$(CH_3)_3CBr + Br_2 \text{ (peroxide)} \longrightarrow (CH_3)_2CBrCH_2Br + HBr \quad (2)$$

The validity of the second reaction was determined experimentally by allowing *t*-butyl bromide to react with bromine in the presence of di-*t*-butyl peroxide as a catalyst. A yield of 64% of isobutylene dibromide was obtained.

Experimental

Reaction of Di-*t*-butyl Peroxide with Hydrogen Bromide.—A sample (16.4 g., 0.181 mole) of di-*t*-butyl peroxide prepared and purified according to directions given elsewhere[4] was cooled to 0° and a slow stream of hydrogen bromide (Dow Chemical Co.) from a tank was allowed to come in contact with the peroxide. The reaction, which was immediate and exothermic, was continued for three hours, the temperature being kept as close to 0° as possible. At the end of this period the mixture separated into two distinct layers which were separated and weighed. The bromine was estimated in each layer iodimetrically and the hydrogen bromide plus bromine by titration against standard alkali. The water in the aqueous layer was estimated by difference. The remainder of the non-aqueous layer was washed with concentrated sodium bisulfite solution, dried over anhydrous magnesium sulfate, then fractionated. A fraction (24 g.) boiling at 72–73° was collected; $n^{25}D$ 1.426. This was identified as *t*-butyl bromide. Another fraction (21.4 g.) was collected at 143–145° which was refractionated through a six-plate Podbielniak column; b. p. 145–148°; $n^{25}D$ 1.5050; $d^{25}{}_{25}$ 1.7426. From the analysis and physical constants, this fraction was identified as isobutylene dibromide. *Anal.* Calcd. for $C_4H_8Br_2$: C, 22.22; H, 3.70; Br, 74.07. Found: C, 22.44; H, 3.87; Br, 74.62. In addition to the two bromides, a black residue remained in the distillation flask.

From 26.4 g. (0.181 mole) of di-*t*-butyl peroxide and excess hydrogen bromide, we obtained 0.1685 mole (92.2%) of bromine (free 0.0695 mole; reacted, 0.099 mole), 0.35 mole of water (96.6%), and 0.274 mole of *t*-butyl bromide (0.175 mole) plus isobutylene dibromide (0.099 mole).

Catalyzed Bromination of *t*-Butyl Bromide.—A mixture of 50 g. of *t*-butyl bromide and 5 g. of di-*t*-butyl peroxide was cooled to 0° and to it was added slowly with frequent shaking 58 g. of liquid bromine. No apparent reaction was noticed during the first few minutes of bromine addition, then a vigorous reaction set in with copious evolution of hydrogen bromide. The reaction mixture was allowed to stand overnight at 0°, then shaken with anhydrous potassium carbonate and distilled. Only 7 g. distilled below 90°, 76 g. between 90–160° and a small tarry residue remained in the distilling flask. The main product was fractionated and the fraction (51 g., 64%) boiling at 148–151° collected and identified as isobutylene dibromide; $n^{26}D$ 1.5075.

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(1) Research Assistant under a special grant from the Union Bay State Chemical Company; present address, Department of Chemistry, University of Illinois.

(2) Vaughan and Rust, U. S. Patent 2,403,771, July 9 (1946).

(3) Raley, Rust and Vaughan, THIS JOURNAL, **70**, 2767 (1948).

(4) Milas and Surgenor, *ibid.*, **68**, 205 (1946).