gaseous products and the reaction appeared to be unsuited as a synthetic method. To complete the series, methylene chloride also was tried but did not react at the boiling point of ether. These results indicate a marked difference in the reactivity of vicinal chlorides at the trichloro level. This is of interest in connection with the behavior of chloral for which only reduction at the carbonyl group with aliphatic Grignard reagents containing β-hydrogen atoms has been reported[2] and the behavior of monochloroacetone which was found to react with isoamylmagnesium bromide at the chlorine atom as well as adding on the reagent at the carbonyl group.[3]

Considering the violence of the reaction of carbon tetrachloride, even at −78°, carbon tetrafluoride was also treated with *n*-butylmagnesium chloride at the boiling point of ether. However, no reaction was observed.

Experimental

1,1,1-Trichloropentane.—*n*-Butylmagnesium chloride was prepared from one mole of *n*-butyl chloride, one gram atom of magnesium and 300 ml. of dry ether. The solution was forced by means of dry nitrogen under pressure, into a stirred mixture of 2 moles of carbon tetrachloride and 300 ml. of dry ether cooled in a bath of Dry Ice and acetone. A vigorous reaction occurred with the formation of a white precipitate and a gas which decolorized bromine in carbon tetrachloride. White fumes were also formed which settled on the walls of the flask as a white solid. Since this was very soluble in water it was concluded that it was magnesium chloride. After the reagent had been added the cooling bath was removed and the mixture allowed to come to room temperature and stand for two hours. It was then refluxed gently for forty-five minutes and after cooling was decomposed with ice-water. Some basic magnesium precipitate was filtered out with suction and the organic layer separated, dried with calcium chloride and distilled to 100° to remove ether and excess carbon tetrachloride. The residue weighed about 30 g. and constituted a crude yield of 16.5%. On continuing the distillation, hydrogen chloride was evolved copiously at about 140°; consequently, the residue was vacuum distilled. Refractionation at 20 mm. through a 10-plate column packed with glass helices gave a heart-cut boiling at 56–57°. The index of refraction was n^{20}_D 1.4540.

Anal. Calcd. for $C_5H_9Cl_3$: Cl, 60.5. Found: Cl, 60.2, 60.1.

Acknowledgments—The authors are indebted to Mr. H. L. Lovell for the analysis reported above and to the Fluorine Laboratories of The Pennsylvania State College for the sample of carbon tetrafluoride used.

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(2) Gilman and Abbott, *J. Org. Chem.*, **8**, 224 (1945); Floutz, This Journal, **67**, 1615 (1945).

(3) Kinney and Spliethoff, to be published in the *Journal of Organic Chemistry*.

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Received October 4, 1948

Decomposition of Aliphatic Azo Compounds

By Frederick M. Lewis and Max S. Matheson

Certain aliphatic azo compounds have several properties which make them especially suitable as sources of free radicals for kinetic investigations. These properties include stability, clean first order decompositions nearly independent of reaction media, and the ability to act as efficient photosensitizers in the near ultraviolet.

The decomposition rates (Table I) as measured by nitrogen evolution, were in all cases first order after a short induction period, probably due to a thermal adjustment after sample addition and to the disappearance of oxygen traces introduced with the sample. Thiele and Heuser[1] and Dox[2] have described the method of preparation of these compounds. Further, it has been shown that 2-azo-bis-isobutyronitrile heated at 110° in high boiling petroleum ether quantitatively splits out nitrogen, tetramethyl succinonitrile being formed in 50% yield.[1] Of course such fragments of the azo compound as initiate polymerization in the presence of monomer will not appear as tetramethyl succinonitrile.

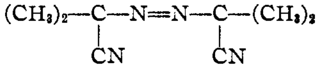
Table I

Decomposition of Azo Compounds in Xylene at 80°

Material, 0.1–0.3 mole/l.	*k*, min.⁻¹	*Ea*, kcal.
2-Azo-bis-isobutyronitrile	0.0092	31.3
2-Azo-bis-2-methylbutyronitrile	.00598	29.4
2-Azo-bis-2-methylheptonitrile	.0107	30.2
1-Azo-bis-1-cyclohexanecarbonitrile	.000282	39.9
Dimethyl-2-azo-bis-isobutyrate	.00653	35.8
4-Azo-bis-4-cyanopentanoic acid	.00538[a]	34.0

[a] In water, insoluble in xylene.

Table II shows that there is little change in rate for 2-azo-bis-isobutyronitrile (sold as Porofor N by Naugatuck Chemical Division of U. S. Rubber Co.) with widely different reaction solvents, and



$$(CH_3)_2\underset{CN}{C}-N{=}N-\underset{CN}{C}-(CH_3)_2$$

even a powerful inhibitor (tetrachloroquinone) has little effect. Accordingly these materials offer several advantages over peroxides as free radical sources when a constant rate of production of radicals is desired. (As an example of free radical activity 0.096 g./l. of Porofor N in purified vinyl acetate induces 4.7% polymerization per hour at 50°.) Several authors[3] have shown that

Table II

Solvent Effect in the Decomposition of 2-Azo-bis-isobutyronitrile

(∼0.3 mole/l.) at 80°

Solvent	*k*, min.⁻¹
Xylene	0.0092
Xylene contg. 0.012 mole/l. tetrachloroquinone	.00898
Glacial acetic acid	.00914
N-Dimethylaniline	.011
Dodecyl mercaptan	.00875
Carbon tetrachloride	.00725 (77°)

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(1) Thiele and Heuser, *Ann.*, **290**, 1 (1896).

(2) Dox, This Journal, **47**, 1473 (1925).

(3) Nozaki and Bartlett, *ibid.*, **68**, 1686 (1946); Cass, *ibid.*, **68**, 1976 (1946).

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	Quantum yield polymerization[b] 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.)

CONTRIBUTION 80 FROM THE
UNITED STATES RUBBER CO.
PASSAIC, NEW JERSEY RECEIVED OCTOBER 11, 1948

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; $n^{25}\text{D}$ 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°; $n^{25}\text{D}$ 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; $n^{26}\text{D}$ 1.5075.

CAMBRIDGE, MASSACHUSETTS
RECEIVED SEPTEMBER 14, 1948

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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).