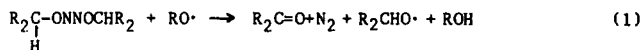


DI-t-BUTYL HYPONITRITE.  
 A CONVENIENT SOURCE OF t-BUTOXY RADICALS (1)

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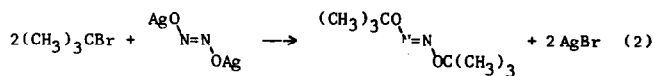
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A few hyponitrites have been described in the literature (2-13) and are used as initiators for polymerizations. However, their usefulness is severely limited by induced decomposition (12) and a tendency to explode (2-10).



Simple tertiary alkyl hyponitrites which contain no hydrogens alpha to oxygen should be much less subject to these drawbacks. The properties of di-t-butyl hyponitrite (DBH) confirm this supposition. Furthermore, the following properties make DBH an excellent initiator. It is easily prepared, safely handled, decomposes cleanly and efficiently, and its convenient decomposition rate ( $t_{1/2} = 29$  minutes at  $65^\circ$ ) may be followed by UV, IR, NMR, and by  $\text{N}_2$  evolution at concentrations of  $10^{-4}$  M (UV) to neat DBH.

DBH is prepared in good yields by adding dry silver hyponitrite to an excess of ice cold t-butyl bromide.



It is a colorless, crystalline compound, which melts at 82° with nitrogen evolution. It is soluble in common organic solvents, insoluble in water, and can be recrystallized from methanol at -65°. Compared to DBPO (di-t-butylperoxyoxalate) (14), it is far less sensitive to shock and seems to be insensitive to scratching (14).

In addition to the usual infrared absorptions of the t-butoxy-group (at 2959, 1368, 1183  $\text{cm}^{-1}$ ), DBH shows a very intense absorption at 995  $\text{cm}^{-1}$  due to an antisymmetric =N-O-stretch (15). Since a study of IR and Raman spectra of both sodium hyponitrite and silver hyponitrite (15) indicate trans configuration, we assume that DBH is also trans as shown in equation 2.

The ultraviolet spectrum of DBH shows a  $\lambda_{\text{max}}$  at 226  $\text{m}\mu$  with an  $\epsilon = 62000$  ( $\log \epsilon = 4.79$ ). The NMR spectrum is a singlet 1.33 ppm. downfield from tetramethylsilane.

The decomposition of DBH at 45° in isooctane yields the same organic products as DBPO under the same conditions, suggesting that the mechanisms of the decompositions are identical (16) (Table 1).

Table 1

Percent yields based on total accounted t-butoxy groups.

	$\bar{M}$	t-Bu <sub>2</sub> O <sub>2</sub>	t-BuOH	Acetone	Isobutyleneoxide
DBH	0.125	10.0	89.0	1	< 0.5
DBPO	0.112	8.1	90.9	1	< 0.5

The product distribution was obtained by g.l.c. analysis. From the formation of di-t-butylperoxide it is evident that 10.0, 8.1% respectively of the starting material has decomposed by a cage reaction.

The rates of decomposition, followed by means of UV- and IR-absorption, are given in table 2.

Table 2

Solvent	T°	k x 10 <sup>4</sup> sec	Deviation	Wavelength	c mol/l
95% Ethanol	65.0	3.93	± 0.02	226 mμ	10 <sup>-4</sup>
Isooctane	65.0	4.00	± 0.02	226 mμ	10 <sup>-4</sup>
	45.0	0.272	± 0.0005	226 mμ	10 <sup>-4</sup>
	55.0	1.07	± 0.006	226 mμ	10 <sup>-4</sup>
	75.0	13.30	± 0.003	226 mμ	10 <sup>-4</sup>
Nujol	65.0	5.17	± 0.06	230 mμ	10 <sup>-4</sup>
t-Butyl Alcohol	65.0	4.68	± 0.008	226 mμ	10 <sup>-4</sup>
n-Butylether	65.0	4.50	± 0.01	226 mμ	10 <sup>-4</sup>
Isooctane	65.0	3.85		10.05 μ	2 x 10 <sup>-1</sup>

Whereas all UV-studies were carried out in concentrations of 10<sup>-4</sup> moles/l, the IR-run was done in 0.2 molar solution. Since a change in concentration from 10<sup>-4</sup> to 2 x 10<sup>-1</sup> moles/l does not affect the rate of decomposition or its kinetic order, the decomposition of DBH does not seem to be induced. All observed rates are accurately first order in [DBH].

The activation parameters calculated from the above rate data are found to be  $\Delta H^\ddagger = 27.9$  kcal and  $\Delta S^\ddagger = 8.2$  cal/deg.

#### Experimental

Preparation: Five ml. of reagent t-butyl bromide was maintained at about 0° and stirred rapidly while 1.0 g. dry silver hyponitrite (17) was added in very small portions. (Addition of t-butyl bromide to silver hyponitrite without solvent results in explosions! The use of ether as solvent drastically reduces the yield.)

After 15 minutes, the AgBr was filtered off, washed with ether and the combined filtrate evaporated at room temperature on a rotary evaporator. The crystalline residue was recrystallized from methanol/water and dried over  $P_2O_5$  for one hour. Yield: 350 mg (75%). To obtain an analytically pure sample, the product was recrystallized three times from methanol under nitrogen at  $-65^\circ$  and pumped at 0.1 mm at  $0^\circ$  for 30 minutes. (At 0.1 mm DBH is volatile at room temperature.) M.p.  $82^\circ$  dec.

Anal. Calcd. for  $C_8H_{18}N_2O_2$ : C, 55.14; H, 10.41; N, 16.07. Found: C, 55.03; H, 10.67; N, 16.30.

Kinetic procedure: For kinetic measurements a Zeiss UV-spectrophotometer, Model PMQ II and a Heathkit EUW-20A recorder were used. In a typical run, two stoppered 1 cm quartz cells containing 2 ml of isooctane each were placed in the thermostatically controlled cell holder for at least 15 minutes. The temperature of the solvent was checked by means of a thermocouple placed in a third cell in the holder and the wavelength set at 226 m $\mu$ . Five-hundredths ml of a concentrated solution of DBH in isooctane were injected with a syringe into the sample cell to give a concentration of approximately  $10^{-4}$  moles/l. The cell was then shaken and the increase in transmittance of the sample, over a range from 20-75% recorded versus time. For determining the rate by IR, 20 ml of a 0.2 molar solution of DBH in isooctane was placed in a constant temperature bath. After the initial warming up period of about 20 minutes, 1 ml samples were taken out at regular

time intervals and cooled immediately in ice. The decrease of DBH was measured at  $995\text{ cm}^{-1}$  by following the increase of transmittance. The first order rate constants were calculated from the slope of the straight line obtained by plotting  $\log A$  versus time.

Products: One ml of a 0.125 molar solution of DBH in isooctane was kept in a sealed ampoule at  $45^\circ$  for 60 hours. The mixture was then analyzed on a F & M gas chromatograph, Model 500, using a 20 foot carbowax 20 M column, at  $75^\circ$ , with a flowrate of 10 ml/min.He. The area ratios of the products were then corrected by a factor  $f$ , obtained from analysis of four different mixtures of known amounts of the same products.

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