

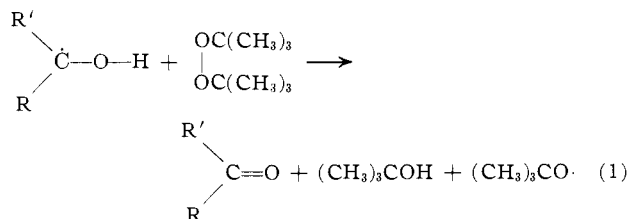
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KAN.]

Induced Decompositions of Di-*t*-butyl Peroxide in Primary and Secondary Amines¹BY EARL S. HUYSER, CORWIN J. BREDEWEG,² AND RICHARD M. VANSCOY

RECEIVED MARCH 2, 1964

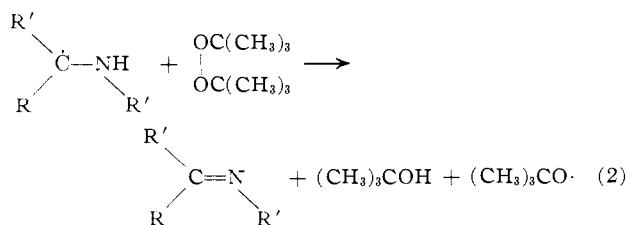
Although tertiary amines have no appreciable effect on the rate of thermal decomposition of di-*t*-butyl peroxide, an induced decomposition of this peroxide is found in primary and secondary amines. The primary and secondary amines are oxidized to imines in these reactions. A mechanism involving transfer of a nitrogen-bonded hydrogen atom from an α -aminoalkyl radical to the peroxide linkage is proposed to account for the induced decomposition of the peroxide. Tertiary amines, having no nitrogen-bonded hydrogen, cannot participate in such a reaction. Similarly, γ -collidine does not cause any induced decomposition of di-*t*-butyl peroxide whereas a very marked induced decomposition of the peroxide is observed in the oxidation of dihydro-3,5-dicarboethoxy-2,6-lutidine to the corresponding pyridine derivative with di-*t*-butyl peroxide.

Earlier kinetic studies concerning the rates of decomposition of di-*t*-butyl peroxide in solution indicated that for the most part the rate of this reaction was independent of the solvent.³ Among the solvents cited as having no effect on the rate of decomposition of di-*t*-butyl peroxide was tri-*n*-butylamine. More recent studies have shown that primary and secondary alcohols cause an induced decomposition of this dialkyl peroxide.⁴ In this study it was proposed that the aldehyde or ketone produced resulted from the interaction of an α -hydroxyalkyl radical obtained from the alcohol with the oxygen-oxygen linkage of the peroxide. The absence of any participation of α -alkoxyalkyl radicals with the peroxide as evidenced by the lack of any observable induced decomposition of di-*t*-butyl peroxide in ethers led to the conclusion that the reaction of the α -hydroxyalkyl radical with the peroxide linkage involved the oxygen-bonded hydrogen atom of the free radical. Abstraction of an α -hydrogen from a primary



R = alkyl and R' = alkyl or hydrogen

or secondary amine⁵ would yield an α -aminoalkyl radical with a hydrogen bonded to nitrogen. Such a radical might be expected to interact with the di-*t*-butyl peroxide in a manner similar to that postulated for the α -hydroxyalkyl radicals producing an imine as a reaction product of the amine.



(1) This work was supported in part by a grant (No. 5620) from the National Institutes of Health.

(2) National Science Foundation Cooperative Fellow, 1961-1963. This paper is taken in part from the thesis submitted by C. J. B. in partial fulfillment of the requirements for the Ph.D. degree from the University of Kansas, 1963.

(3) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 88 (1948).

(4) E. S. Huyser and C. J. Bredeweg, *ibid.*, **86**, 2401 (1964).

(5) W. H. Urry, O. O. Juveland, and F. W. Stacey, *ibid.*, **74**, 6155 (1952); W. H. Urry and O. O. Juveland, *ibid.*, **80**, 3323 (1958).

Although tertiary amines,⁶ as well as ethers,⁷ increased the decomposition rates of diacyl peroxides (although very likely by different mechanisms), tri-*n*-butylamine was an unfortunate choice for the dialkyl peroxide studies. The radicals produced by hydrogen abstraction from a tertiary amine are not capable of such a reaction and are analogous to the α -alkoxyalkyl radicals obtained from ethers. For this reason, we have investigated the decomposition rates of various primary, secondary, and tertiary amines and examined the products in one case to see if imines were indeed formed in these reactions.

The rates of decomposition of di-*t*-butyl peroxide at 125° in the amines in Table I were followed by the gas chromatographic method described previously.⁴ This method is quite reliable well past the first half-life of the peroxide in most cases. First-order plots of the data obtained for these amines as well as for toluene, a solvent in which no induced decomposition of di-*t*-butyl peroxide occurs, are shown in Fig. 1. Calculation of the first-order rate constants and the half-lives of the peroxide in these solvents were made from the slopes of the "best-fit" straight lines drawn through the experimental points.

TABLE I
RATE DATA FOR THE DECOMPOSITION OF DI-*t*-BUTYL
PEROXIDE IN AMINES AT 125°

Solvent	Initial molar ratio of solvent:peroxide	$k' \times 10^5$, sec. ⁻¹ ^a	$t_{1/2} \times 10^5$, sec.
Toluene	9.07	1.62	4.27
N-Methylpiperidine	9.00	1.54	4.49
γ -Collidine	10.8	1.67	4.14
Piperidine	10.2	3.49	1.98
N-Ethylcyclohexylamine	8.92	4.01	1.73
Cyclohexylamine	9.01	5.50	1.32

^a The term k' refers to the quantities found in the brackets of eq. 9 for the last three items. For the other items, $k' = k_s$, the reaction rate constant for the unimolecular decomposition.

Examination of the experimental plots in Fig. 1 shows that the rate of decomposition of di-*t*-butyl peroxide is increased only in cyclohexylamine, piperidine, and N-ethylcyclohexylamine, namely, those amines which can give an α -aminoalkyl radical having at least one nitrogen-bonded hydrogen atom. In N-methylpiperidine and γ -collidine, the rate of decomposition of the peroxide is apparently not influenced to any significant extent by the solvent. Treatment of the reaction mixture obtained by decomposing di-*t*-butyl peroxide in

(6) C. Walling and N. Indictor, *ibid.*, **80**, 5814 (1958); references to other work can be found in this article.

(7) W. E. Cass, *ibid.*, **69**, 500 (1947).

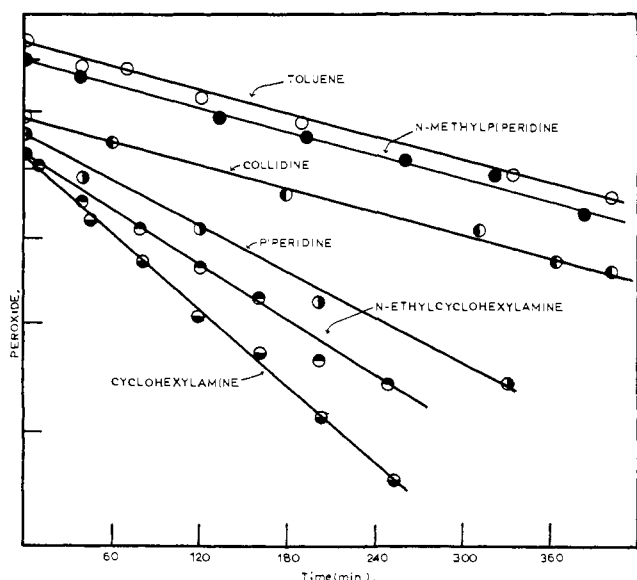
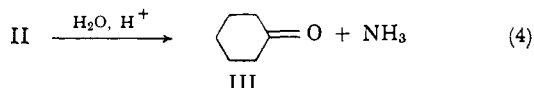
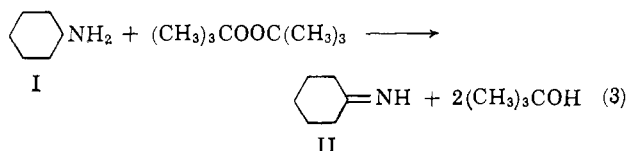
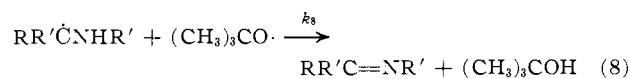
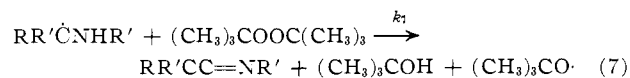
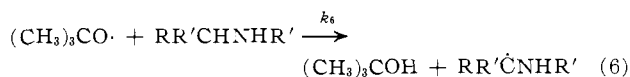
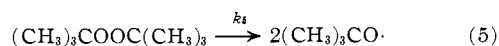


Fig. 1.—First-order plots for decomposition of di-*t*-butyl peroxide at 125°

cyclohexylamine (I) with water and a catalytic amount of acid resulted in the formation of ammonia and cyclohexanone (III). The ketone was recovered by gas chromatographic separation of the resulting mixture and identified by its infrared spectrum and by conversion to its semicarbazone. These products are consistent with the postulated formation of cyclohexylimine (II) in the reaction of cyclohexylamine with di-*t*-butyl peroxide.



The following mechanism, which accounts for both induced decomposition and the formation of an imine, is proposed for the reaction of di-*t*-butyl peroxide with primary and secondary amines



R = alkyl and R' = alkyl or hydrogen

Reactions 6 and 7 comprise a free-radical chain sequence involving both the amine and the di-*t*-butyl peroxide. The participation of the peroxide in this chain reaction could well account for the fact that it is consumed in these reactions at a rate considerably greater than the simple unimolecular decomposition rate observed in inert solvents. Support for the proposed interaction

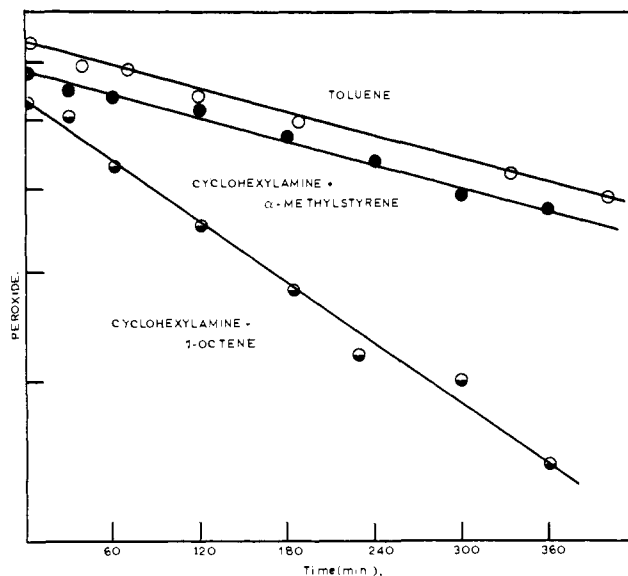


Fig. 2.—First-order plots for decomposition of di-*t*-butyl peroxide in cyclohexylamine plus 1-octene and α -methylstyrene at 125°.

of the α -aminoalkyl radical with the peroxide as shown in reaction 7 comes from the observation that the peroxide apparently does not undergo any appreciable amount of induced decomposition in cyclohexylamine if α -methylstyrene is present. Examination of the first-order plots for the decomposition of di-*t*-butyl peroxide in cyclohexylamine and α -methylstyrene (initial molar ratio of amine:peroxide:olefin = 4:1:1) in Fig. 2 shows that the peroxide decomposes at essentially the same rate as observed in toluene. Urry and his co-workers have shown that α -aminoalkyl radicals add to olefinic linkages (reaction 9).⁵ A logical ex-

$$\text{RR}'\dot{\text{C}}\text{NHR}' + \text{CH}_2=\text{CHR} \longrightarrow \text{RR}'\text{C}(\text{NHR}')\text{CH}_2\dot{\text{C}}\text{HR} \quad (9)$$

planation for this lack of induced decomposition of the peroxide is that the α -aminoalkyl radicals prefer to add to the double bond of α -methylstyrene rather than react with the peroxide and consequently the peroxide is consumed only in the unimolecular decomposition (reaction 5). Figure 2 shows that the peroxide decomposes at an enhanced rate, however, in the presence of 1-octene (initial molar ratio of amine:peroxide:olefin = 4:1:1). Examination of the gas chromatograms obtained in the analyses showed that the 1-octene, an olefin much less reactive toward addition by free radicals than α -methylstyrene,⁵ reacted at a rate approximately one-fourth that of the peroxide. It must be concluded that if the peroxide is more reactive than the 1-octene toward reaction with α -aminoalkyl radicals, the chain sequence 6 and 7 leading to the formation of the imine is very likely operative. It is interesting to note that Urry and Juveland reported the formation of imines in the di-*t*-butyl peroxide induced reactions of amines to olefins.⁵ They concluded that these imines were formed in a disproportionation reaction of two α -aminoalkyl radicals in a chain-termination reaction. Although some of these imine-type products found in the reactions of amines with alkenes could have been formed in a termination process (see next paragraph), the kinetic data suggest that they

(8) M. S. Kharasch and M. Saga, *J. Org. Chem.*, **14**, 537 (1949); M. S. Kharasch, E. Simon, and W. Nudenberg, *ibid.*, **18**, 328 (1953).

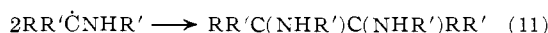
were formed to a large extent in the chain reaction of the amine and peroxide.

The observed first-order kinetics with respect to the peroxide in each case where induced decomposition occurs is consistent with the cross-termination process shown in reaction 8. The derived rate expression for the rate of decomposition of the peroxide in such a chain reaction in which cross termination operates is

$$\frac{-d[\text{Per}]}{dt} = \left[k_7 + \left(\frac{k_7}{k_5} \pm \frac{k_5}{2k_7} \sqrt{1/4 + \frac{2k_7k_8[\text{RR}'\text{CHNHR}']}{2k_5k_8}} \right) \right] [\text{Per}] \quad (10)$$

The quantities in the brackets of this equation constitute a constant, provided, of course, there is no change in the concentration of the amine. In our studies, about a tenfold excess of amine was used and the change in its concentration during the course of one half-life of the peroxide could not have amounted to more than 5% of its initial concentration.

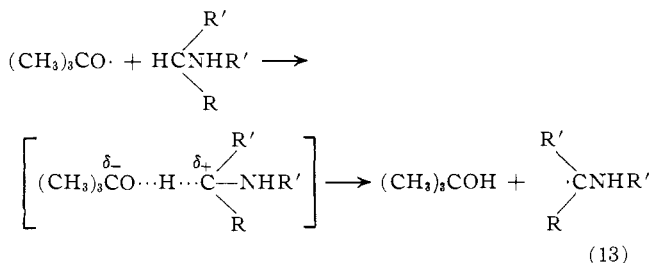
If termination of the chain sequence resulted from the coupling of two α -aminoalkyl radicals, as shown in 11, the rate would not be first-order in peroxide.



The derived rate expression in such a case would be

$$\frac{-d[\text{Per}]}{dt} = k_5[\text{Per}] + k_7 \left(\frac{k_5}{2k_{10}} \right)^{1/2} [\text{Per}]^{1/2} \quad (12)$$

Cross termination is not unexpected in reactions which involve radicals that can display opposite polar effects in their chain-propagating reactions.⁹ In the abstraction of an α -hydrogen from the amine by a *t*-butoxyl radical (reaction 6 of the chain sequence), the transition state very likely involves a polar contribution in which the alkoxy radical acts as an electron acceptor

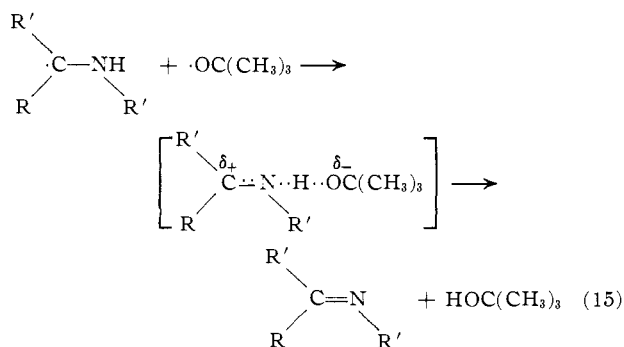
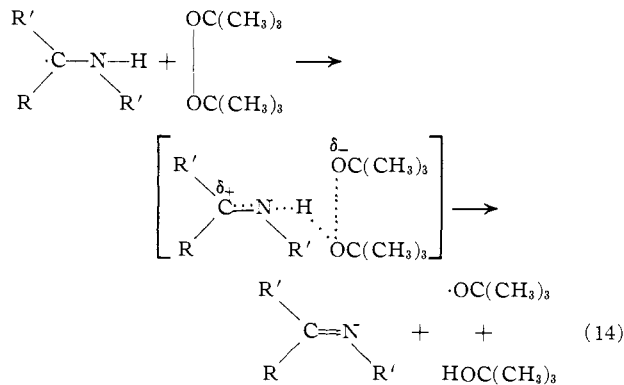


and the amine as a donor substrate.¹⁰ The α -aminoalkyl radical can act as a donor radical in its reaction with di-*t*-butyl peroxide which would have acceptor properties in the transition state of this reaction eq. 14). In the transition state of the termination reaction, the activation energy requirement would be lowered by polar contributions from a donor and acceptor radical.

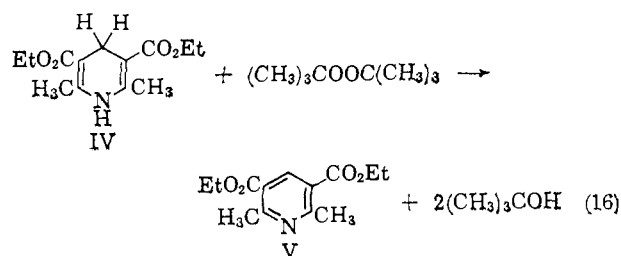
Pyridines, having no nitrogen-bonded hydrogen atoms, behave in a manner similar to other tertiary amines in these reactions as shown by the fact that there is no induced decomposition of di-*t*-butyl peroxide in γ -collidine. On the other hand, dihydropyridine

(9) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 146.

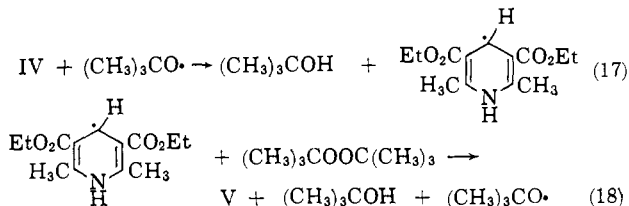
(10) Hydrogen abstraction from amines by the *t*-butoxyl radical is so facile that very little acetone is produced by the reaction $(\text{CH}_3)_3\text{CO}\cdot \longrightarrow \cdot\text{CH}_3 + \text{CH}_3\text{COCH}_3$. See also J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948).



derivatives might be expected to induce the decomposition of di-*t*-butyl peroxide since a radical with a nitrogen-bonded hydrogen can be formed. We found that the oxidation of dihydro-3,5-dicarboethoxy-2,6-lutidine (IV) to 3,5-dicarboethoxy-2,6-lutidine (V) can be performed in high yields using di-*t*-butyl peroxide as the oxidizing agent. Evidence that the oxidation of the



dihydropyridine proceeds by the following chain sequence comes from the very marked effect the presence of even a relatively small amount of this compound has on the rate of decomposition of di-*t*-



butyl peroxide. Figure 3 shows the rates of decomposition of di-*t*-butyl peroxide in γ -collidine and in the same solvent with about one-half of a mole of IV per mole of peroxide present. That such a low concentration of the dihydropyridine can so dramatically affect the rate of decomposition of the peroxide suggests that the kinetic chain length of the sequence 17 and 18 may be very long. Both steps of this sequence are reactions that might be expected to proceed quite readily. The

abstraction of an allylic hydrogen from IV by the *t*-butoxyl radical would be quite favorable both from the standpoint of the bond-dissociation energies involved and the polar factor. The transfer of a hydrogen atom from the monohydropyridyl radical to the peroxide would involve not only the energy and polar factors making the hydrogen atom transfer favorable with other amines but also the energy resulting from the formation of the aromatic ring.

Experimental¹¹

Materials.—The following commercial materials were used in this work: toluene, piperidine, cyclohexylamine, *N*-methylpiperidine, *N*-ethylcyclohexylamine, γ -collidine, and di-*t*-butyl peroxide. In each case, the material was redistilled under vacuum until it gave a single gas chromatographic peak. Dihydro-3,5-dicarboethoxy-2,6-lutidine was prepared by the reaction of ethyl acetoacetate, formaldehyde, and ammonia in the manner described¹² previously with the exception that concentrated ammonium hydroxide was used in place of ammonia gas. After two recrystallizations from ethanol, the material melted at 182–184°, reported¹³ 183–185°.

Apparatus.—The gas chromatographic analyses for the kinetic studies were performed with an Aerograph A-90-P using a 15 ft. by 0.25 in. column packed with 15% of the polyethylene glycol, E-600 (Dow Chemical Co.), on 30–60 mesh Chromosorb P. The chromatograms were traced on a Sargent Recorder (Model SR) fitted with a disk integrator.

Kinetic Measurements.—The rates of decomposition of di-*t*-butyl peroxide at 125° in toluene, piperidine, *N*-methylpiperidine, cyclohexylamine, and *N*-ethylcyclohexylamine were performed using the gas-chromatographic technique described previously.⁴ The rates of decomposition of di-*t*-butyl peroxide in γ -collidine both in the presence and the absence of dihydro-3,5-dicarboethoxy-2,6-lutidine were determined in the following manner: The solution, consisting in each case of the amounts of reagents shown in Table I, was about equally distributed into several Pyrex tubes. The tubes were sealed and placed in a constant temperature oil bath maintained at 125 ± 0.2°. At the times indicated in the figure, a tube was withdrawn from the bath and cooled immediately to 0°. A portion of the resulting reaction mixture was accurately weighed out along with a known amount of ethyl acetate. The resulting mixture was subjected to gas chromatographic analysis. The amount of di-*t*-butyl peroxide remaining in the reaction mixture at the time the tube was withdrawn from the oil bath was determined from a comparison of the gas chromatographic areas of the peroxide and ethyl acetate. The correction factor necessary to adjust the peak area ratios to mole ratios was determined from the gas chromatographic peak areas of mixtures of ethyl acetate and di-*t*-butyl peroxide of known composition.

Decomposition of Di-*t*-butyl Peroxide in Cyclohexylamine.—A mixture consisting of cyclohexylamine (17.0 g., 0.172 mole) and di-*t*-butyl peroxide (6.2 g., 0.04 mole) was heated in several sealed Pyrex tubes for 26 hr. at 125°. On opening the tubes after cooling, the strong odor of ammonia was noted. The contents of the tubes were hydrolyzed with a dilute hydrochloric acid solution. The organic materials remaining after hydrolysis were extracted from the acid-soluble materials with ether. The ether layer was washed once with dilute hydrochloric acid, twice with a sodium bicarbonate solution, and twice with water. After drying the ether solution over anhydrous magnesium sulfate, the ether was removed by distillation. The remaining liquid showed a gas chromatographic peak with a retention time the same as that of cyclohexanone. The cyclohexanone was separated in a pure state by chromatographing the mixture on an Aerograph A-700 Autoprep using a 20 ft. by 3/8 in. column packed

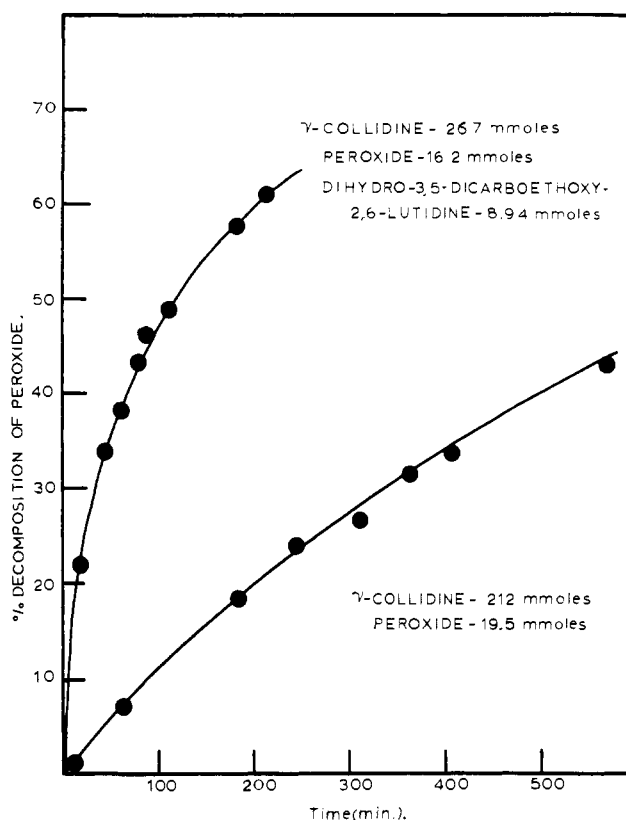


Fig. 3.—Rates of decomposition of di-*t*-butyl peroxide in γ -collidine and in γ -collidine with dihydro-3,5-dicarboethoxy-2,6-lutidine present.

with 30% E-600 on Chromosorb P at a column temperature of 130°. The resulting liquid had an infrared spectrum identical with that of an authentic sample cyclohexanone and gave the semicarbazone of cyclohexanone, m.p. 166–167°, reported¹⁴ m.p. 166°.

Reaction of Dihydro-3,5-dicarboethoxy-2,6-lutidine with Di-*t*-butyl Peroxide (in Chlorobenzene).—A mixture consisting of dihydro-3,5-dicarboethoxy-2,6-lutidine (5.0 g., 0.02 mole) and di-*t*-butyl peroxide (4.4 g., 0.03 mole) in 30 ml. of chlorobenzene was heated at reflux temperature (130°) for 12 hr. At the end of this period, gas chromatographic analysis showed a large *t*-butyl alcohol peak but only a trace of acetone could be detected. The chlorobenzene solution was extracted three times with 10 ml. each of a 10% hydrochloric acid solution. The resulting aqueous extractions were extracted once with ether. The solution was made alkaline with dilute sodium hydroxide solution and the 3,5-dicarboethoxy-2,6-lutidine, which precipitated, was filtered out, washed with water, and dried, amounted to 4.0 g. (80% of theory), m.p. (from ethanol) 72°, reported¹⁴ 72°; m.p. of the picrate 118°, reported¹⁵ 118–119°.

(In Dimethylformamide).—A mixture consisting of dihydro-3,5-dicarboethoxy-2,6-lutidine (2.5 g., 0.01 mole) and di-*t*-butyl peroxide (2.2 g., 0.015 mole) in 18 ml. of dimethylformamide was heated for 12 hr. at 125° in an oil bath. Gas chromatographic analysis of the reaction mixture indicated the presence of only trace quantities of acetone and a large amount of *t*-butyl alcohol. A small amount of unreacted di-*t*-butyl peroxide, which was present in an amount in excess of the required for the oxidation, was also detected. The reaction mixture was diluted with water which caused the 3,5-dicarboethoxy-2,6-lutidine to precipitate out of solution. The yield was 2.3 g. (92% of theory), m.p. (from ethanol) 72°.¹⁴

(11) All melting points are uncorrected.

(12) A. Singer and S. M. McElvain, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 214.

(13) E. Knoevenagel and J. Fuchs, *Ber.*, **35**, 1791 (1902).

(14) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 136.

(15) R. Schiff and P. Proiso, *Gazz. chim. ital.*, **25** [II], 65 (1895).