propane was insoluble in ether, but easily soluble in warm benzene.

Summary

1. Six hitherto undescribed β-alkoxypropionitriles have been prepared.
2. A reaction mechanism is proposed to account for the fact that alkaline hydrolysis of β-ethoxypropionitrile, di-(2-cyanoethyl)-ether and 1,4-di-(2-cyanoethoxy)-pentane failed to yield the expected β-alkoxypropionic acids.
3. A series of monobasic and dibasic acids of the β-alkoxypropionic type was prepared by acid hydrolysis of the corresponding nitriles. The acids were characterized, when possible, by the preparation of suitable solid derivatives. The dibasic acids and several of the monobasic acids are described for the first time.
4. Hydrolysis of 1,4-di-(2-cyanoethoxy)-pentane with hydrochloric acid yielded a chlorine-containing acid which was isolated as the ethyl ester. The analysis of this ester was in close agreement with that calculated for an ethyl β-(chloroamyloxy)-propionate.
5. Hydrolysis of 1,4-di-(2-cyanoethoxy)-pentane-bis-(ethyliminoester hydrochloride) or ethanolysis of 1,4-di-(2-cyanoethoxy)-pentane at low temperatures gave 1,4-di-(2-carbethoxyethoxy)-pentane.

WICHITA, KANSAS RECEIVED NOVEMBER 21, 1947

[CONTRIBUTION FROM THE EMERYVILLE LABORATORIES OF SHELL DEVELOPMENT COMPANY]

Decompositions of Di-*t*-alkyl Peroxides. III. Kinetics in Liquid Phase

BY JOHN H. RALEY, FREDERICK F. RUST AND WILLIAM E. VAUGHAN

In the first papers of this set,[1,2] the decomposition of di-*t*-butyl peroxide in the vapor phase was shown to be a clean-cut, first order process, the rate determining step of which was the scission of the peroxy-oxygen linkage. The resultant radicals, *t*-butoxy and the methyl derived therefrom, can react with copresent molecules by steps which follow the generally accepted patterns of chain initiation, propagation and termination. This work has now been extended to a study of decompositions in condensed phases.

It is well established[3a,b,4,5] that the rate of decomposition of benzoyl peroxide varies profoundly with the solvent; further, the first order rate is complicated by higher order processes which become increasingly important at higher concentrations. In contrast, the present work reveals that even in such diverse solvents as cumene, *t*-butylbenzene and tri-*n*-butylamine, the rates of decomposition of di-*t*-butyl peroxide are closely the same and, importantly, nearly equal to that in the vapor phase. Likewise the energies of activation in solution and vapor are approximately equivalent. This implies, obviously, that the same simple dissociation step is rate determining in all cases.

Although these condensed environments do not alter the rate, their differing abilities to donate hydrogen atoms give rise to varying amounts of *t*-butyl alcohol in relation to acetone in the competing steps 2 and 3a

$$(CH_3)_3CO{-}OC(CH_3)_3 \longrightarrow 2(CH_3)_3CO{-} \quad (1)$$

$$(CH_3)_3CO{-} + R'H \longrightarrow (CH_3)_3COH + R' \quad (2)$$

$$(CH_3)_3CO{-} \longrightarrow (CH_3)_2CO + CH_3 \quad (3a)$$

$$CH_3 + R'H \longrightarrow CH_4 + R' \quad (b)$$

Further, in all of the solvents, with increasing temperature the *t*-butoxy radical increasingly dissociates to acetone and methyl (3a). The data permit a rough estimate of the difference in the activation energies of the steps 2 and 3a for the hydrocarbon solvents.

Experimental

Materials

Di-*t*-butyl peroxide, prepared by the method of Vaughan and Rust[6] and vacuum distilled ($n^{20}D$ 1.3890), was used for both the decomposition experiments and calibration of the infrared spectrograph. By titration it analyzed 98% pure. The several solvents were chosen for convenience of boiling points (avoidance of undue pressure build-up in the bombs), obtainability, ease of purification and, importantly, differing abilities as hydrogen donors to free radicals. Commercial **cumene** was carefully distilled and a fraction of b. p. 152° and $n^{20}D$ 1.4912 was collected and stored under nitrogen. ***t*-Butylbenzene** (Eastman Kodak Co.) was similarly treated (b. p. 169°, $n^{20}D$ 1.4922). **Tri-*n*-butylamine** (Eastman) was treated with 3 *N* hydrochloric acid and the water-insoluble impurities removed; the amine was regenerated with aqueous sodium hydroxide, washed, dried, and distilled (b. p. 214°; $n^{20}D$ 1.4291).

Method

The decompositions were carried out in heavy-walled glass bomb tubes (capacity 40 cc.) in an oil-bath regulated to ±0.1°. The seven or more bombs for a given experiment were filled from a stock solution of the peroxide in the particular solvent, chilled, evacuated, sealed, and immersed. After a short equilibration period, they were withdrawn at specified intervals, quenched, and prepared for analysis. They were then opened in an inert atmosphere, the density of the solution determined by pycnometer, and analysis performed by infrared spectrometry. Time "zero" is defined as the time of withdrawal of the first sample. Duplicate experiments were performed in nearly all cases.

Evidence that the decomposition is independent of the

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[1] Raley, Rust and Vaughan, THIS JOURNAL, **70**, 88 (1948).

[2] Rust, Seubold and Vaughan, *ibid.*, **70**, 95 (1948).

[3] (a) Nozaki and Bartlett, *ibid.*, **68**, 1686 (1946); (b) Bartlett and Nozaki, *ibid.*, **69**, 2299 (1947)).

[4] Cass, *ibid.*, **68**, 1976 (1946).

[5] Barnett and Vaughan, *J. Phys. Coll. Chem.*, **51**, 926, 942 (1947).

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

vapor volume in the tubes was obtained from the following pair of experiments. Two sets of bombs were charged with a stock solution of the peroxide in cumene, one set having a vapor volume of 35% and the other 66%. The decompositions were then carried out at 135 ± 0.1° to at least 50% completion. The first order constants were 5.1 and 5.2 × 10^{-5} sec.$^{-1}$, respectively, and the *t*-butyl alcohol–acetone ratios, 1.51/0.49 = 3.1 and 1.41/0.59 = 2.4.

Analysis

Analyses were performed by an infrared spectrometric procedure developed for di-*t*-butyl peroxide and its decomposition products, acetone and *t*-butyl alcohol. The bands utilized in the method are found at the (uncorrected) wave lengths of 11.46 μ, 5.88 μ and 2.925 μ, respectively. Tests showed the method to be applicable in the three solvents studied. Since the spectral procedure yields concentrations in terms of unit volume, the density of the sample was needed for conversion to terms of unit weight. This basis is used for expressing concentrations since the weight rather than the volume or total number of moles remains constant throughout the decomposition. The weight of methane which could escape when the bombs were opened was negligible.

Results

Figure 1 gives an example of the precision of measurement in several runs and Fig. 2 that of the correlation of a set of experiments. The reaction is first order to conversions as high as 85% (Fig. 3). In Table I are summarized all of the data and included therein are corresponding values for the vapor phase for the sake of ready comparison. The small variation of the rates in the four media at a given temperature is striking and argues

TABLE I

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE IN VARIOUS ENVIRONMENTS

	Cumene 0.799 mole DTBP/kg. soln. $k = 0.63(10^{16})e^{-37,500/RT}$			*t*-Butylbenzene 0.775 mole DTBP/kg. soln. $k = 1.1(10^{16})e^{-38,000/RT}$		
		Stoichiometry[d]			Stoichiometry	
Temp., ±0.1° C.	$k \times 10^5$[b] sec.$^{-1}$	*t*-Butyl alcohol	Acetone	$k \times 10^5$[b] sec.$^{-1}$	*t*-Butyl alcohol	Acetone
125	1.6 ± 0.1	1.61	0.39	1.5 ± 0.2	0.75	1.25
135	5.2 ± 0.3	1.51	0.49	5.0 ± 0.3	0.56	1.44
145	15.6 ± 1.3	1.23	0.77	15.1 ± 2.2	0.46	1.54

	Tri-*n*-butylamine 0.867 mole DTBP/kg. soln. $k = 0.35(10^{16})e^{-37,000/RT}$			Vapor phase[a] 52–386 mm. $k = 3.2(10^{16})e^{-39,100/RT}$		
		Stoichiometry[f]			Stoichiometry	
Temp., ±0.1° C.	$k \times 10^5$[b] sec.$^{-1}$	*t*-Butyl alcohol	Acetone	$k \times 10^5$[c] sec.$^{-1}$	*t*-Butyl alcohol	Ketones[e]
125	1.7 ± 0.3	*ca.* 1.9	*ca.* 0.1	1.1	0	2.0
135	4.2 ± 0.4	*ca.* 1.9	*ca.* 0.1	3.6	0	2.0
145	16.0 ± 2.1	*ca.* 1.9	*ca.* 0.1	11.5	0	2.0

[a] Interpolated and extrapolated from Ref. (1): temp. range 139.8–159.8° (±0.04°). [b] Calculated from data for the first 50% decomposition. [c] Calculated from data for the first 33% decomposition. [d] Products from one molecule of ROOR (R = *t*-butyl); see equations (2) and (3a) + (3b). [e] Principally acetone with *ca.* 5% methyl ethyl and higher ketones. [f] Acetone formation with this solvent is too small to allow precise determination of the stoichiometry.

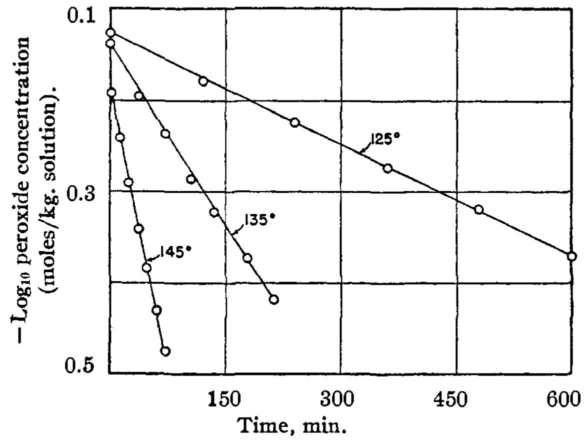

Fig. 1.—Decomposition of di-*t*-butyl peroxide in *t*-butylbenzene: initial concentration, 0.775 mole/kg. solution.

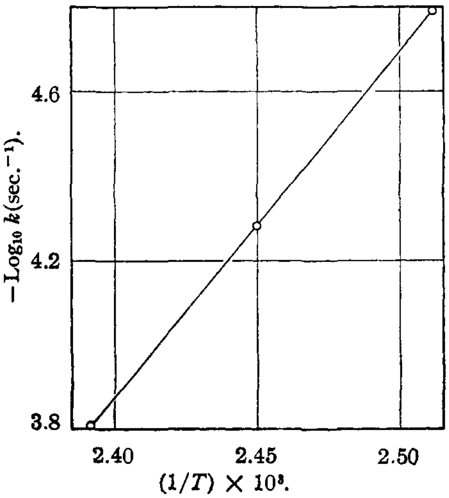

Fig. 2.—Effect of temperature on di-*t*-butyl peroxide decomposition in cumene; initial concentration, 0.799 mole/kg. solution.

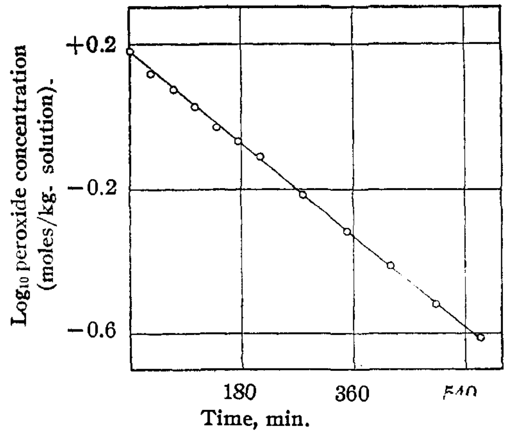

Fig. 3.—Decomposition of di-*t*-butyl peroxide 85% decomposition: temperature, 135°; init tration, 1.618 moles/kg. solution.

strongly for the unimolecularity of the decomposition,[7] especially in light of the large differences in the fate of the *t*-butoxy radicals. There is a slight trend of *k* with concentration (Table II), but this variation is no greater than that exhibited by the decomposition of nitrogen pentoxide in carbon tetrachloride.[8]

TABLE II

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE IN CUMENE

Temp. 135.0 ± 0.1°

Initial concentration (moles/kg. soln.)	$k \times 10^{5a}$ (sec.$^{-1}$)
0.455	4.9 ± 0.4
0.799	5.2 ± .1
1.62	5.0 ± .2
2.35	5.7 ± .4

[a] Calculated from data for the first 50% decomposition.

The regular behavior in tri-*n*-butylamine is especially interesting in view of Nozaki and Bartlett's[3,9] finding of explosive reactions of benzoyl peroxide in nitrogen-containing solvents. Di-*t*-butyl peroxide does not behave as an oxidizing agent in the usual sense of the expression.

The trends in the stoichiometries enable one to calculate roughly the differences in the activation energies of the steps 2 and 3a. The values of ($E_{3a} - E_2$) are *ca.* 16 kcal. for cumene and 11 for *t*-butylbenzene. It should be mentioned that calculation shows that step 3a is endothermic to the extent of *ca.* 5 kcal.

Acknowledgment.—The authors wish to thank Mr. William R. Harp and Dr. Robert S. Rasmussen of the Spectroscopic Department of this Company for their extensive coöperation, without which the analytical procedures would have been far more complicated and less accurate. Thanks are also due Mr. Charles E. Fuller and Miss Betty J. Benell for their assistance.

Summary

The small variation in the first order rates of decomposition of di-*t*-butyl peroxide in cumene, *t*-butylbenzene and tri-*n*-butylamine solution and in the vapor state is strong evidence that the same process is rate-determining in all cases. This is thought to be unimolecular scission of the peroxy-oxygen linkage. With increasing temperature the *t*-butoxy radicals become more subject to loss of methyl rather than abstraction of hydrogen from solvent molecules.

EMERYVILLE 8, CALIFORNIA RECEIVED OCTOBER 6, 1947

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[7] For comparison with the thermal decomposition of N_2O_5 in various solvents, see F. Daniels, "Chemical Kinetics," Cornell University Press, Ithaca, N. Y., 1938, pp. 100–107.

[8] Eyring and Daniels, THIS JOURNAL, 52, 1472 (1930).

[9] Also private communication from Dr. Nozaki.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Effect of Salts on the Solubilization of Insoluble Organic Liquids by Cetylpyridinium Chloride

BY PAUL H. RICHARDS AND JAMES W. MCBAIN

Solutions of colloidal electrolytes and of similar non-electrolytic detergents have the power of dissolving otherwise insoluble substances by putting them into or upon the colloidal micelles of the detergent. Salts promote the formation of colloidal micelles of the detergent. Salts promote the formation of colloidal micelles and probably change even their sizes and relative proportions. Therefore they also affect solubilization. Heretofore[1–6] salts have always been reported to enhance solubilization, as well as produce it in solutions of detergents otherwise too dilute to contain colloidal particles.

Materials.—The detergents used in these experiments were cetylpyridinium chloride, obtained in very pure form through the courtesy of Wm. S. Merrell Company, Emulsol 607L (Emulsol Corporation), and Triton X-100 (Röhm and Haas); compare previous publications using these detergents.[3,5,7] The relative effects of a number of detergents with a series of insoluble organic liquids has already been reported.[7]

The organic compounds used were benzene (Kahlbaum "K," thiophene free), *n*-octane (Eastman Kodak Co.) and *n*-octyl alcohol (Eastman Kodak), as well as others previously referred to.[7] The salts employed in the investigation were Kahlbaum sodium and potassium chloride "zür Analyse."

Method.—The method of determining the solubilization of the organic compound by the detergent has been fully described.[7] The turbidimeter was used to detect the saturation or inflection point where solubilization in the clear solution was complete, and any excess of organic liquid began to appear as emulsified droplets. The solutions were shaken in a thermostat maintained at 25° for from ten to twenty hours before readings were taken. The solutions of the detergent and of the salts were prepared at double the desired concentration and 5 cc. of each solution was pipetted

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[1] Hartley, *J. Chem. Soc.*, 1968 (1938).

[2] McBain, Merrell and Vinograd, THIS JOURNAL, 63, 675 (1941).

[3] McBain and Merrill, *Ind. Eng. Chem.*, 34, 915 (1942).

[4] McBain, in "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942, pp. 129, 131.

[5] McBain and Green, THIS JOURNAL, 68, 1731 (1946).

[6] McBain, Wilder and Merrill, *J. Phys. Chem.* 52, 12 (1948).

[7] McBain and Richards, *Ind. Eng. Chem.*, 38, 642 (1946).