[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Hydrolysis of Some β-Alkoxypropionitriles[1]

BY ROBERT V. CHRISTIAN, JR.,[2] AND R. M. HIXON

The usual method employed heretofore in the preparation of β-alkoxypropionic acids has involved the hydrolysis[3] of an ester[4] of the desired acid. A variation was introduced by Jones and Powers[5] who obtained sodium β-methoxypropionate from the action of excess sodium methoxide upon β-chloropropionic acid. A single reference to β-alkoxypropionitriles as precursors of acids of this type appears as a patent[6] describing the hydrolysis of di-(2-cyanoethyl)-ether as a step in the preparation of esters of di-(2-carboxyethyl)-ether, although the free acid was not characterized. It should be noted, too, that Kilpi[7] carried out kinetic studies on the hydrochloric acid hydrolysis of β-methoxy- and β-ethoxypropionitrile but did not isolate the products of the reactions.

In the present work, some of the now easily available β-alkoxypropionitriles were examined as intermediates for the preparation of acids of the β-alkoxypropionic type.

Experimental[8]

Materials.—1,4-Pentanediol was prepared by hydrogenation[9] of γ-valerolactone. The other alcohols and glycols were commercially available products which were purified by distillation when necessary. The acrylonitrile (Eastman Kodak Co. Practical Grade) was used without further treatment.

β-Ethoxypropionitrile was prepared by the method of Koelsch.[10] Utermohlen's procedure,[11] employing 40% potassium hydroxide as the catalyst, was followed in the synthesis of the other monofunctional nitriles. Those which have not been described heretofore are listed in Table I with pertinent information. The preparation of 1,4-di-(2-cyanoethoxy)-pentane has been described.[12] The other bifunctional nitriles were obtained in accordance with the procedure of Bruson and Riener.[13]

Alkaline Hydrolysis of β-Alkoxypropionitriles.—1,4-Di-(2-cyanoethoxy)-pentane, when refluxed with 10% sodium hydroxide in the usual manner, gave an undistillable and uncrystallizable oil of neutral equivalent 177 (calculated for the expected dibasic acid, 124). Similar treatment of di-(2-cyanoethyl)-ether with 24% sodium hydroxide gave material from which neither di-(2-carbamylethyl)-ether[13] nor the disodium salt of di-(2-carboxyethyl)-ether[14] could be obtained by suitable procedures.

TABLE I

β-ALKOXYPROPIONITRILES, $ROCH_2CH_2CN$

R	Yield, %	B. p., °C.	Mm.	$n^{20}D$	d^{20}_{20}	Nitrogen, %[a] Calcd.	Found
n-Propyl	84	87–89	24	1.4131	0.9006	12.4	12.2
		84	19				
Isobutyl	81	91	20	1.4143	.8836	11.0	11.1
s-Butyl	79	90	19	1.4156	.8896	11.0	11.3
Isoamyl	82	99	13	1.4218	.8834	9.93	10.1
s-Amyl	70	98	16	1.4205	.8862	9.93	9.85
Allyl	85	95	24	1.4330	.9396	12.6	12.4

[a] By micro Kjeldahl.

β-Ethoxypropionic acid[3b] could not be identified as a product of the hydrolysis of β-ethoxypropionitrile with 22% sodium hydroxide. Upon distillation of the reaction products under reduced pressure, partial decomposition took place and a colorless distillate was collected. This liquid liberated carbon dioxide from dilute sodium bicarbonate and reduced alkaline 2% permanganate. The substance polymerized upon standing to form a transparent, elastic solid which was insoluble in ethanol or chloroform but dissolved slowly in sodium bicarbonate solution, with evolution of carbon dioxide, to yield a clear solution of unusually high viscosity.

Acid Hydrolysis of β-Alkoxypropionitriles.—The procedure consisted in heating a mechanically stirred mixture of the β-alkoxypropionitrile and twice the calculated quantity of concentrated hydrochloric acid. Only representative experiments are described below. Yields of the liquid acids were based upon the neutral equivalents of the once-distilled compounds. Analytical data and physical constants were obtained upon material purified by fractional distillation using a 20-cm. Vigreux column. The information is summarized in Table II. The yields of the solid acids were determined from the neutral equivalents of the crude products whereas recrystallization to constant melting point furnished analytical specimens. These data are presented in Table III.

The monobasic acids were characterized, when possible, by preparation of solid *p*-bromophenacyl esters (Table IV) in accordance with a standard procedure.[15] Thionyl chloride, followed by cold, concentrated ammonium hydroxide, served to convert the dibasic acids to amides (Table V), of which several have been prepared recently by other methods.[13,16]

β-*n*-Propoxypropionic Acid.—A mixture of 79.1 g. (0.7 mole) of β-*n*-propoxypropionitrile and 140 g. (1.4 moles) of concentrated hydrochloric acid was stirred and heated for three hours at 70–80° and then for thirty minutes at 100°. The reaction mixture was evaporated to dryness *in vacuo* with heating on a water-bath. The product was taken up in acetone (or ether) and filtered. The residual ammonium chloride was washed several times with the solvent. Distillation gave 74 g. of colorless liquid boiling at 117–123° (13 mm.) and having the neutral equivalent 130. This represents a yield of 80%.

The corresponding ethoxy-, isopropoxy-, *n*-butoxy-,

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[1] Taken from part of a thesis submitted by Robert V. Christian, Jr., to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] (a) Hamonet, *Compt. rend.*, **132**, 260 (1901); *Bull. soc. chim.*, [3], **33**, 518 (1905); (b) Palomaa, *Ann. Acad. Sci. Fennicae*, [A] **3**, No. 2 (1911); *Chem. Zentr.*, **83**, II, 595 (1912); (c) Fichter and Herndl, *Helv. Chim. Acta*, **14**, 857 (1931); (d) Palomaa and Jaakola, *Ber.*, **67**, 949 (1934); (e) Palomaa and Tukkimäki, *ibid.*, **68**, 887 (1935); (f) Fichter and Schnider, *Helv. Chim. Acta*, **25**, 229 (1942).

[4] Methods for preparing the necessary esters have been reviewed by Rehberg, Dixon and Fisher, THIS JOURNAL, **68**, 544 (1946).

[5] Jones and Powers, *ibid.*, **46**, 2518 (1924).

[6] Bruson, U. S. Patent 2,347,627, April 25, 1944; *C. A.*, **39**, 87 (1945).

[7] Kilpi, *Z. physik. Chem.*, **86**, 672 (1913).

[8] Melting points and boiling points are uncorrected.

[9] Folkers and Adkins, THIS JOURNAL, **54**, 1145 (1932).

[10] Koelsch, *ibid.*, **65**, 437 (1943).

[11] Utermohlen, *ibid.*, **67**, 1505 (1945).

[12] Christian, Brown and Hixon, *ibid.*, **69**, 1961 (1947).

[13] Bruson and Riener, *ibid.*, **65**, 23 (1943).

[14] Wislicenus, *Ber.*, **3**, 809 (1870); *Ann.*, **166**, 10 (1872).

[15] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935, p. 144.

[16] (a) Bruson, U. S. Patent 2,359,708, October 3, 1944; *C. A.*, **39**, 3972 (1945); (b) U. S. Patent 2,372,808, April 3, 1945; *C. A.*, **39**, 4623 (1945).

TABLE II

β-ALKOXYPROPIONIC ACIDS, $ROCH_2CH_2COOH$

R	Yield, %	B. p., °C.	Mm.	$n^{20}D$	d^{20}_4	Analyses, % Calcd. Neut. eq.	Calcd. Carbon	Calcd. Hydrogen	Found Neut. eq.	Found Carbon	Found Hydrogen
Ethyl[a]	86	117–120	17	....	1.0635	118.1	..	...	120.0	..	...
n-Propyl[b]	80	87	1	1.4233	1.0237	132.1	..	...	132.0	..	...
		120	13								
Isopropyl[c]	60	85.5–86	1	1.4202	1.0192	132.1	..	...	131.3	..	...
		118	13								
n-Butyl[d]	69	96–97.5	1	1.4268	0.9929	146.1	57.5	9.67	147.3	57.1	10.0
Isobutyl[d]	67	89–90	1	1.4227	0.9843	146.1	57.5	9.67	146.0	57.0	9.74
s-Butyl	56	90–91.4	1	1.4252	0.9946	146.1	57.5	9.67	146.4	57.3	9.76
Isoamyl[e]	69	100	1	1.4285	0.9697	160.2	..	...	162.7	..	...
		137	12		0.9725(d^{18}_{18})						
s-Amyl	49	100–101	1	1.4289	0.9833	160.2	60.0	10.1	159.4	59.7	10.3
Allyl	33[f]	84	1	1.4423	1.0604	130.1	55.4	7.75	130.8	55.3	8.17
		111–112	6								
2-Methoxyethyl	75	109–110	0.5	1.4356	1.1146	148.2	48.6	8.16	150.8	48.3	8.35

[a] Previously prepared. Palomaa (3b) gives boiling point 119–120° (19 mm.) and d^{20}_4 1.0641. [b] Previously prepared (3e). Nazarov and Romanov (*Bull. acad. sci. U. R. S. S., Classe. sci. chim.*, 1940, 453; *C. A.*, **35**, 3593 [1941]) report boiling point 110–112° (9 mm.) and $n^{19}D$ 1.4230. [c] Previously prepared (3e). Nazarov and Romanov (*loc. cit.*) report boiling point 125–126° (22 mm.) and $n^{20}D$ 1.4202. [d] Previously prepared (3e) but physical constants not reported. [e] Previously prepared. Constants reported are boiling point 135° (12 mm.) (3c, 3f) and d^{18} 0.974 (3a). [f] Reaction temperature was 60–70°.

TABLE III

β-ALKOXYPROPIONIC ACIDS (DIBASIC), $R(CH_2CH_2COOH)_2$

R	Yield, %	M. p., °C.	Analyses, % Calcd. Neut. eq.	Calcd. Carbon	Calcd. Hydrogen	Found Neut. eq.	Found Carbon	Found Hydrogen
—O—	97	60–61[a,b]	81.07	44.5	6.18	81.77	44.8	6.56
$—O(CH_2)_2O—$	94	66[c]	103.1	46.6	6.86	103.5	47.0	7.24
$—O(CH_2)_3O—$	90	86–87[d]	110.1	49.1	7.32	111.1	49.3	7.62
$—O(CH_2)_2O(CH_2)_2O—$	91	Oil[e]	125	..	..	137[f]	..	..

[a] Recrystallized from an ether–petroleum ether (b. p. 60–70°) mixture by cooling to −40°. [b] Boiling point 189–192° (1 mm. or less) with slight decomposition. [c] Recrystallized from benzene containing a little acetone. [d] Recrystallized from benzene containing a little petroleum ether (b. p. 60–70°). [e] Decomposed at about 225° upon attempted distillation at 0.5 mm. or less. [f] Crude product.

TABLE IV

p-BROMOPHENACYL β-ALKOXYPROPIONATES, $ROCH_2CH_2COOCH_2COC_6H_4Br$-*p*

R	Crystalline form[a]	M. p., °C.	Bromine, %[b] Calcd.	Bromine, %[b] Found
Ethyl	Large leaflets	47–48	25.4	25.1
n-Propyl	Shiny leaflets	57–58	24.3	24.2
Isopropyl	Tiny plates	44–44.5	24.3	23.9
n-Butyl	Shiny leaflets	55	23.3	23.0
Isobutyl	Fibrous needles	58–59	23.3	23.2
s-Butyl	Oil	.....	..	..
Isoamyl	Glistening needles	56	22.4	22.2
s-Amyl	Oil	.....	..	..
Allyl	Tiny plates	38–39	24.4	24.3
2-Methoxyethyl	Oil	*ca.* 15	..	..

[a] Recrystallized by dissolution in aqueous ethanol at room temperature followed by cooling to −20°. [b] By micro pearl tube.

TABLE V

β-ALKOXYPROPIONAMIDS (DIBASIC), $R(CH_2CH_2CONH_2)_2$

R	M. p., °C.	Nitrogen, %[f] Calcd.	Nitrogen, %[f] Found
—O—[a]	143.5–144	17.5	17.4
$—O(CH_2)_2O—$[b]	123[d,e]	13.7	13.6
$—O(CH_2)_3O—$	124[d]	12.8	12.5
$—O(CH_2)_2O(CH_2)_2O—$[c]	103–103.5	11.3	11.2

[a] Previously prepared by another method (13). M. p. reported, 146°. [b] Previously prepared by another method (16a). M. p. reported, 123–124°. [c] Previously prepared by another method (16). M. p. reported, 103–104°. [d] Mixed melting point of these two substances was 95–110°. [e] Change in crystal structure at 107°. Melted sharply at 104° without resolidification under rapid heating (10° per minute). [f] By micro Kjeldahl.

isoamyloxy-, *s*-amyloxy-, and 2-methoxyethoxy-compounds were prepared by this method.

β-Isobutoxypropionic Acid.—β-Isobutoxypropionitrile (76.2 g., 0.6 mole) was stirred with 120 g. (1.20 moles) of concentrated hydrochloric acid for four hours at 75–80°. The cooled reaction mixture was diluted with sufficient water to dissolve the precipitate of ammonium chloride. The organic layer was separated and the aqueous solution was extracted with ether. Distillation gave 63 g. of material boiling at 105–110° (5 mm.). The neutral equivalent, 157, indicated a yield of 67%.

The *s*-butoxy- and allyloxy- derivatives were prepared in a similar fashion.

1,3-Di-(2-carboxyethoxy)-propane.—A stirred mixture of 98 g. (0.54 mole) of 1,3-di-(2-cyanoethoxy)-propane and 216 g. (2.16 moles) of concentrated hydrochloric acid was heated at 70–80° for four hours and then at 100° for thirty minutes. The mixture was evaporated to dryness *in vacuo* and extracted with warm acetone. Evaporation of the acetone solution under reduced pressure gave 118.5 g. of sirup which crystallized to a white solid (melting point 65–77°) upon standing overnight. The neutral equivalent was 123, indicating a yield of 90%.

Di-(2-carboxyethyl)-ether, 1,2-di-(2-carboxyethoxy)-ethane, and di-(2-[2-carboxyethoxy]-ethyl) ether were prepared by this method.

Acid Hydrolysis of 1,4-Di-(2-cyanoethoxy)-pentane.—A stirred mixture of 40 g. (0.19 mole) of 1,4-di-(2-cyanoethoxy)-pentane and 76 g. (0.76 mole) of concentrated hydrochloric acid was heated for five hours at 80–90°. Extraction with chloroform gave 40.5 g. of uncrystallizable oil of neutral equivalent 199. This material was esterified by refluxing with absolute ethanol containing a trace of dry hydrogen chloride. Upon distillation the principal fraction consisted of 13 g. of colorless liquid which contained chlorine and was shown by the ferric hydroxamate test[17] to be an ester. The physical constants were boiling point 109–112° (2.5 mm.), d^{25}_4 1.0325, and n^{25}_D 1.4386.

The presence of chlorine in the product suggested that cleavage at an ether linkage might have occurred during the hydrolysis. Under the conditions of the experiment this would likely lead to the formation of an ethyl β-(chloroamyloxy)-propionate. The analytical data lend support to this hypothesis.

Anal. Calcd. for $C_{10}H_{19}O_3Cl$: MR_D, 56.63; C, 53.9; H, 8.60; Cl, 15.9. Found: MR_D, 56.75; C, 53.6; H, 8.82; Cl, 15.2.

1,4-Di-(2-carbethoxyethoxy)-pentane.—Sixty grams (0.16 mole) of coarsely pulverized 1,4-di-(2-cyanoethoxy)-pentane bis-(ethyliminoester hydrochloride)[13] was added in small portions to 200 ml. of distilled water at room temperature. The addition was carried out over a period of twenty minutes and the mixture was stirred continuously. The solid dissolved readily and no change in temperature was observed, but an oil began to separate at once. The mixture was finally heated at 45° for thirty minutes, cooled, and extracted with ether. Distillation of the dried ether extract gave 28 g. (58%) of colorless liquid of boiling point 142–145° (0.5 mm.), d^{25}_4 1.0174, and n^{25}_D 1.4363.

Anal. Calcd. for $C_{15}H_{28}O_6$: sapn. equiv., 152.2; C, 59.2; H, 9.27. Found: sapn. equiv., 151.4, 152.4; C, 59.5; H, 9.54.

Alcoholysis of 1,4-di-(2-cyanoethoxy)-pentane by the methods of Spiegel[18] and Sabetay[19] gave complex mixtures. 1,4-Di-(2-carbethoxyethoxy)-pentane was obtained in 33% yield, however, by a modification of the procedure described by Kimball, Jefferson and Pike[20] for the preparation of ethyl α-phenylacetoacetate.

With a view to characterization of 1,4-di-(2-carbethoxyethoxy)-pentane by conversion to the sodium salt of the corresponding acid, an attempt was made to saponify the ester by gentle warming with the calculated quantity of alcoholic sodium hydroxide. The experiment was abandoned when the reaction mixture began to exhibit a strong odor of ethyl acrylate.

Discussion

The fact that lower yields of β-alkoxypropionitriles were obtained from secondary alcohols is in agreement with the observations of Utermohlen.[11] Furthermore, it was found unnecessary to employ external cooling to hold the reaction temperature below 40° during the addition of *s*-butyl alcohol and *s*-amyl alcohol to acrylonitrile. This suggests a lower reaction rate or a lower heat of reaction for the secondary alcohols.

Failure to obtain the expected products in the three cases in which β-alkoxypropionitriles were treated with aqueous alkali was unexpected, inasmuch as other investigators have successfully employed basic hydrolysis for the conversion of the cyanoethyl derivatives of active methylene compounds,[21] isatin,[22] pyrrole[23] and ammonia[24] to the corresponding acids. It has been established, however, that the base-catalyzed reaction of an alcohol with acrylonitrile produces an equilibrium mixture which contains, in addition to the β-alkoxypropionitrile, appreciable quantities of the reactants.[10] It is suggested that under the conditions of the basic hydrolytic experiments herein described, partial decomposition of the β-alkoxypropionitriles into their generators took place with subsequent formation of complex hydrolysis mixtures. It is deemed significant that one of the products of the basic hydrolysis of β-ethoxypropionitrile exhibited properties suggestive of acrylic acid or one of its derivatives. Hollihan and Moss[25] have reported that acrylonitrile reacts with commercial viscose solutions to form cyanoethyl ethers of cellulose xanthate, and that during the aging process the latter are hydrolyzed by the approximately 3% sodium hydroxide normally present to form carboxyethyl ethers. These hydrolysis conditions are, of course, much less drastic than those employed in the present study.

Although no attempt was made to determine optimum conditions, hydrolysis in acid media appears to be a fairly general method for the conversion of β-alkoxypropionitriles to the corresponding acids. Slightly lower yields were obtained in the preparation of the β-*s*-alkoxypropionic acids and there was a general decrease in yield as the size of the alkyl group increased. No attempt is made to explain the cleavage which apparently took place upon hydrolysis of 1,4-di-(2-cyanoethoxy)-pentane with hydrochloric acid.

The monobasic β-alkoxypropionic acids were colorless liquids having little or no odor. They were all soluble in the common organic solvents. The ethoxy-, isopropoxy-, allyloxy- and 2-methoxyethoxy- derivatives were easily soluble in water whereas β-*n*-propoxypropionic acid was only slightly so. None of the higher homologs were appreciably soluble in water.

The dibasic acids of the β-alkoxypropionic type were very soluble in water, thus displaying, by comparison with acids of similar molecular weight but having a carbon chain uninterrupted by oxygen, the striking effect of the ether linkage upon solubility. These acids were soluble in acetone or ethanol but insoluble in petroleum ether. Di-(2-carboxyethyl)-ether was highly soluble in ether, but insoluble in benzene. 1,2-Di-(2-carboxyethoxy)-ethane was insoluble in ether and slightly soluble in benzene. 1,3-Di-(2-carboxyethoxy)-

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(17) Davidson, *J. Chem. Education*, **17**, 81 (1940).

(18) Spiegel, *Ber.*, **51**, 296 (1918).

(19) Sabetay, *Bull. soc. chim.*, [4] **45**, 534 (1929).

(20) Kimball, Jefferson and Pike, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 284.

(21) Bruson and Riener, THIS JOURNAL, **64**, 2855 (19
18 (1943).

(22) DiCarlo and Lindwall, *ibid.*, **67**, 199 (1945).

(23) Blume and Lindwall, *J. Org. Chem.*, **10**, 255 (

(24) Ford, THIS JOURNAL, **67**, 876 (1945).

(25) Hollihan and Moss, *Ind. Eng. Chem., Ind. Ed.*

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.

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

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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).