3. Insoluble material is attributable, principally, either to incomplete disorganization of the associated material in the granule or to retrogradation. Both conspire to give the erroneous impression that potato starch contains a non-dispersible fraction comparable to the alpha-amyloses of the cereal starches.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Alpha Substituted Ethyl n-Butyl Ethers[1]

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In this Laboratory the alpha chloroalkyl ethers have been studied for the past several years with two major purposes in mind: (1) to extend the series[2] through the synthesis of additional members, as far as seemed practically desirable, securing rather complete physical data relative to the properties of all new compounds; and (2) to investigate the utilization of these alkoxy derivatives in the preparation of new examples of compounds of bifunctional type. In this investigation the preparation, from alpha chloroethyl n-butyl ether[2] or alpha cyanoethyl n-butyl ether, of representative examples of the more important alkoxy types was effected. The use of the chloro ether in further syntheses was limited because of its rapid hydrolysis and extreme tendency toward complete decomposition upon brief contact with mildly alkaline reagents. However, the cyano derivative is a stable substance which served well as an intermediate for the preparation of other and more important compounds. From the data of the vapor pressures of these new compounds the latent heats of vaporization were calculated. Thermodynamical data have not previously been reported in the literature for compounds of the types of alkoxy ketones, alkoxy esters, etc.

Experimental

Di-n-butyl Acetal.—The method of Descudé[3] was adopted, with slight modification, for the synthesis of di-n-butyl acetal. Forty-seven grams of alpha chloroethyl n-butyl ether was added slowly with shaking and cooling to a solution of twelve grams of sodium in 200 cc. of n-butyl alcohol. The mixture was heated on the water-bath at 100° for about fifteen minutes, filtered, washed with distilled water, dried over anhydrous sodium sulfate, and fractionated; b. p. 51° (12 mm.) (corr.); d_4^{20} 0.8296; n_D^{20} 1.4079; M_R calcd., 51.36; M_R found, 51.78.

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 68.89; H, 12.73. Found: C, 69.35; H, 12.71.

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[1] An abstract of the dissertation submitted by John T. Murchison to the Faculty of the University of Texas, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1933.

[2] Henze and Murchison, THIS JOURNAL, **53**, 4077 (1931).

[3] Descudé, *Bull. soc. chim.*, [3] **27**, 1216 (1902).

α-*n*-Butoxyethyl Acetate.—The method of Friedel[4] was employed in this synthesis. A mixture of 49 g. of fused sodium acetate and 48 g. of alpha chloroethyl *n*-butyl ether in 50 cc. of dry benzene was warmed at 60° for fifteen minutes with vigorous shaking. After twelve hours the material was filtered, dried over calcium chloride and distilled under reduced pressure; b. p. 54–54.5° (19 mm.) (corr.); d_4^{20} 0.9122; n_D^{20} 1.4062; M_R calcd., 42.32; M_R found, 43.14.

Anal. Calcd. for $C_8H_{16}O_3$: C, 59.96; H, 10.07. Found: C, 60.02; H, 9.96.

α-Cyanoethyl *n*-Butyl Ether.—The method used by Gauthier[5] was found satisfactory for this preparation. One hundred and twenty-three grams of cuprous cyanide was suspended in 150 cc. of dry benzene and 150 g. of alpha chloroethyl *n*-butyl ether was added slowly with stirring. The material was warmed at 74–76° for one and one-half hours, cooled, filtered and distilled; b. p. 170–172° (750 mm.) (corr.); d_4^{20} 0.8616; n_D^{20} 1.4040; M_R calcd., 35.81; M_R found, 36.08.

Anal. Calcd. for $C_7H_{13}ON$: C, 66.08; H, 10.31; N, 11.01; Found: C, 66.02; H, 10.40; N, 11.25.

Preparation of Esters of α-*n*-Butoxypropionic Acid.—A mixture of alpha cyanoethyl *n*-butyl ether, a few drops of water and an excess of the appropriate alcohol was saturated with dry hydrogen chloride, boiled under reflux for ten to fifteen minutes, cooled, filtered, washed with water, and dried over anhydrous potassium carbonate. The dried carbon tetrachloride extract of the wash water was then added and the whole distilled at reduced pressure. The esters were colorless liquids of pleasant odor. The five esters synthesized, together with data concerning them, are listed in Table I.

TABLE I

ESTERS OF α-*n*-BUTOXYPROPIONIC ACID, $CH_3CH(OC_4H_9)COOR$

R	B. p., °C. (corr.)	Mm.	d_4^{20}	n_D^{20}
Methyl	168–169	750	0.9346	1.4090
Ethyl	117–118	52	.9145	1.4100
n-Propyl	204–205	750	.9112	1.4174
n-Butyl	219–221	750	.9058	1.4208
n-Amyl	132–134	38	.9073	1.4268

R	Molecular refractivity Calcd.	Molecular refractivity Obs.	Analyses, % Carbon Calcd.	Analyses, % Carbon Found	Analyses, % Hydrogen Calcd.	Analyses, % Hydrogen Found
Methyl	42.33	42.35	59.97	60.22	10.07	10.00
Ethyl	46.94	47.17	62.02	62.28	10.42	10.46
n-Propyl	51.56	51.97	63.73	63.95	10.70	10.57
n-Butyl	57.18	56.57	65.28	65.18	10.96	10.79
n-Amyl	60.79	61.15	66.60	65.97	11.19	10.95

α-*n*-Butoxypropionamide.—A mixture of 34.5 g. of alpha cyanoethyl *n*-butyl ether, 20 cc. of *n*-propyl alcohol and 40 cc. of dry ether was saturated with dry hydrogen chloride, then warmed on the water-bath, washed with water and dried with anhydrous sodium sulfate. The dried ether extract of the wash water was added and the mixture distilled, b. p. 140–141° (35 mm.); m. p. 24–26°; d_4^{20} 0.9706; n_D^{20} 1.4465; M_R calcd., 42.24; M_R found, 41.27.

Anal. Calcd. for $C_7H_{15}O_2N$: C, 57.94; H, 10.34; N, 9.65. Found: C, 57.47; H, 10.37; N, 9.80.

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(4) Friedel, *Ber.*, **10**, 492 (1877).

(5) Gauthier, *Compt. rend.*, **138**, 89 (1904).

α-*n*-Butoxypropionic Acid.—A mixture of 34.5 g. of α-*n*-butoxypropionitrile and 100 g. of barium hydroxide in 800 cc. of water was boiled under reflux. After four hours it had become homogeneous; after twenty-three hours it was cooled, acidified with sulfuric acid and filtered. The butoxypropionic acid, which did not separate, was extracted by shaking with two 20 cc. quantities of carbon tetrachloride, dried with calcium chloride and distilled under reduced pressure; b. p. 129–130° (38 mm.); d_4^{20} 0.9842; n_D^{20} 1.4258; M_R calcd., 37.71; M_R found, 38.03.

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.50; H, 9.65. Found: C, 57.30; H, 9.47.

The preparation of the butoxypropionic acid from the nitrile by acid hydrolysis was effected but proved less satisfactory than the method recorded above. This acid was also obtained from the α-*n*-butoxypropionamide by saponification with barium hydroxide and subsequent acidification.

Preparation of α-*n*-Butoxy Ketones.—The ketones were obtained from the alpha *n*-butoxypropionitrile by means of the Grignard reaction. The Grignard reagent was prepared in the usual manner, the cyano ether was added gradually with cooling and the mixture was permitted to stand for about sixteen hours. After this material was hydrolyzed by acid the ether layer was separated, washed with sodium bicarbonate solution and dried with anhydrous sodium sulfate. It was possible to distil the methyl, ethyl and *n*-propyl ketones at atmospheric pressure without excessive decomposition but those of higher molecular weight could only be obtained by distillation at reduced pressures.

The ketones synthesized were all liquids of light yellow color, characteristic odor and were miscible with the usual organic solvents. The carbonyl group does not appear to be very reactive for, although the compounds slowly produced a magenta color with Schiff's reagent, not even the methyl ketone could be made to yield a solid bisulfite addition product. All members of this series apparently reacted with phenylhydrazine, *p*-nitrophenylhydrazine and semicarbazide, producing oils which showed no tendency to crystallize. Hence, no further attempt was made to characterize them by preparing other derivatives. The names of the ketones synthesized and the data concerning them are listed in Table II.

TABLE II

n-BUTOXY KETONES, $CH_3CH(OC_4H_9)COR$

R	B. p. °C. (corr.)	Mm.	d_4^{20}	n_D^{20}
Methyl	164–166	750	0.8758	1.4125
Ethyl	80–82	35	.8693	1.4143
n-Propyl	195–197	750	.8685	1.4200
n-Butyl	114–116	35	.8669	1.4247
n-Amyl	129–130	35	.8657	1.4287

R	Molecular refractivity		Analyses, %			
			Carbon		Hydrogen	
	Calcd.	Obs.	Calcd.	Found	Calcd.	Found
Methyl	40.68	40.99	66.51	66.38	11.20	10.96
Ethyl	45.30	45.48	68.29	68.28	11.47	11.51
n-Propyl	49.92	50.16	69.70	69.03	11.71	11.68
n-Butyl	54.54	54.88	70.90	70.76	11.91	11.80
n-Amyl	59.15	59.57	71.93	71.97	12.08	11.91

Vapor Pressures of Alkoxy Compounds.—Although a considerable number of investigators have synthesized examples of various types of alkoxy derivatives, the data concerning the physical properties of these compounds are extremely inadequate, being chiefly limited to a record of boiling point temperatures and, in a few instances, densities and refractive indexes. Since the vapor pressure and latent heat of vaporization are among the more important properties of liquids, these data were secured, as far as was practical, for these derivatives of ethyl *n*-butyl ether.

The vapor pressures, at selected temperatures, of several liquids prepared in the course of this investigation were determined by means of the isoteniscope method suggested by Smith and Menzies.[6] The data so obtained were plotted upon a large scale (curve not shown) using the conventional log $p_{\text{mm.}}$ *vs.* $1/T$ graph, and, selecting the

TABLE III

VAPOR PRESSURE DATA

t, °C.	1/*T*	V. P., mm.	Log V. P.
α-Cyanoethyl *n*-Butyl Ether			
A, 46700; *B*, 8.418			
50	0.003095	7	0.8451
75	.002873	27	1.4314
100	.002680	76	1.8808
125	.002512	197	2.2945
150	.002364	443	2.6464
α-*n*-Butoxypropionic Acid			
A, 52830; *B*, 8.508			
100	0.002680	13	1.1139
125	.002512	38	1.5798
150	.002364	82	1.9138
165	.002282	128	2.1072
200	.002114	474	2.6758
Methyl α-*n*-Butoxypropionate			
A, 51930; *B*, 9.337			
75	0.002873	35	1.5441
100	.002680	95	1.9777
125	.002512	310	2.4914
144	.002398	749	2.8745
Ethyl α-*n*-Butoxypropionate			
A, 53140; *B*, 9.171			
75	0.002873	8	0.9031
100	.002680	54	1.7324
125	.002512	190	2.2788
150	.002364	417	2.6201
165	.002282	682	2.8338
n-Propyl α-*n*-Butoxypropionate			
A, 44190; *B*, 7.647			
100	0.002680	35	1.5441
125	.002512	71	1.8513
150	.002364	154	2.1875
175	.002232	313	2.4955
200	.002114	635	2.8028
n-Butyl α-*n*-Butoxypropionate			
A, 40810; *B*, 6.813			
100	0.002680	12.5	1.0969
125	.002512	28.5	1.4548
n-Amyl α-*n*-Butoxypropionate			
A, 47320; *B*, 7.621			
100	0.002680	10	1.0000
125	.002512	26	1.4150
2-Butoxybutanone-3			
A, 37860; *B*, 7.819			
50	0.003095	50	1.6990
75	.002873	136	2.1385
100	.002680	315	2.4983
125	.002512	711	2.8519
2-Butoxypentanone-3			
A, 38760; *B*, 7.833			
60	0.003002	57	1.7559
75	.002873	115	2.0607
100	.002680	263	2.4200
125	.002512	542	2.7340
135	.002450	747	2.8733
2-Butoxyhexanone-3			
A, 39490; *B*, 7.783			
60	0.003002	39	1.5911
75	.002873	85	1.9294
100	.002680	171	2.2330
125	.002512	378	2.5775
144	.002395	697	2.8432
2-Butoxyheptanone-3			
A, 10330; *B*, 3.546			
100	0.002680	125	2.0969
125	.002512	154	2.1875
2-Butoxyoctanone-3			
A, 10330; *B*, 3.130			
100	0.002680	48	1.6812
125	.002512	68	1.8325

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[6] Smith and Menzies, THIS JOURNAL, **32**, 1420 (1910).

best straight line through the points so obtained, the constants A and B in Young's equation, $\log p_{\text{mm.}} = -0.05223\,A/T + B$, were determined by substituting the values of $\log p_{\text{mm.}}$ and $1/T$ selected from the curves. The data from which the latter were plotted and the values obtained for A and B are collected in Table III.

Latent Heats of Vaporization.—The value of the constant A obtained from Young's equation was used in making the calculation, independent of variation in temperature, of the latent heat of vaporization by means of the appropriate form of the Clausius equation $\Delta H = (2.303 \times 1.987 \times 0.05223)A$. The values so obtained are recorded in Table IV.

TABLE IV

LATENT HEATS OF VAPORIZATION

Name	A	ΔH
Alpha cyanoethyl *n*-butyl ether	46700	11160
Alpha *n*-butoxypropionic acid	52830	12630
Methyl alpha *n*-butoxypropionate	51930	12412
Ethyl alpha *n*-butoxypropionate	53140	12700
n-Propyl alpha *n*-butoxypropionate	44190	10562
n-Butyl alpha *n*-butoxypropionate	40810	9754
n-Amyl alpha *n*-butoxypropionate	47320	11310
2-Butoxybutanone-3	37860	9049
2-Butoxypentanone-3	38760	9264
2-Butoxyhexanone-3	39490	9438
2-Butoxyheptanone-3	10330	2469
2-Butoxyoctanone-3	10330	2469

Summary

1. The preparation and properties of the following new compounds are reported: α-cyanoethyl *n*-butyl ether, α-*n*-butoxypropionamide, α-*n*-butoxypropionic acid, the methyl through *n*-amyl esters of this acid, the methyl through *n*-amyl α-*n*-butoxyethyl ketone series, α-*n*-butoxyethyl acetate and the di-*n*-butyl acetal.

2. Vapor pressures were determined at selected temperatures for certain of these compounds and, from these data, the corresponding latent heats of vaporization have been calculated.

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