Benzaldehyde by Autoxidation of Dibenzyl Ether

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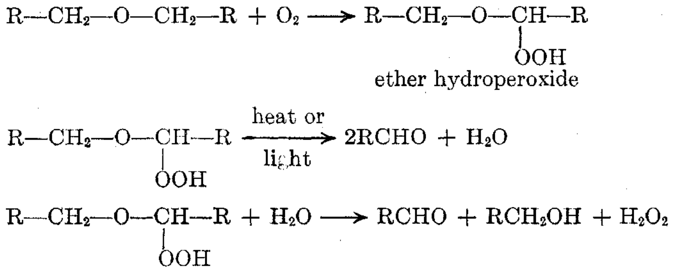
The noncatalytic oxidation of dibenzyl ether by air has been studied over a temperature range of 40° to 250° C., and a process has been developed for the conversion of this ether to benzaldehyde, benzoic acid, and benzyl benzoate in 80 to 85% yield.

IN THE manufacture of benzyl alcohol by saponification of benzyl chloride, a considerable amount of dibenzyl ether is formed as a by-product. Dibenzyl ether has relatively little industrial importance, and its formation may represent an economic loss. This ether, when exposed to the air for an extended period of time, develops an odor of benzaldehyde. This phenomenon was first observed by Cannizzaro (*1*) and later studied by Clover (*2*), Milas (*3*), and Rieche and Meister (*5*).

Milas studied the absorption of oxygen by various ethers at 40° C. and found that dibenzyl ether, with the exception of *tert*-butyl benzyl ether, had the highest rate of oxygen absorption. Iodine, benzoquinone, and picric acid were found to be inhibitors, whereas iron, gold, water, silver, copper, and mercury, in increasing order, catalyzed the autoxidation. Monohydroxybenzyl peroxide, benzaldehyde, and benzoic acid were found in the autoxidized ether.

The formation of the products obtained by the autoxidation of ethers may be formulated as follows:



$$R{-}CH_2{-}O{-}CH_2{-}R + O_2 \longrightarrow R{-}CH_2{-}O{-}\underset{OOH}{\underset{|}{CH}}{-}R$$

ether hydroperoxide

$$R{-}CH_2{-}O{-}\underset{OOH}{\underset{|}{CH}}{-}R \xrightarrow[\text{light}]{\text{heat or}} 2RCHO + H_2O$$

$$R{-}CH_2{-}O{-}\underset{OOH}{\underset{|}{CH}}{-}R + H_2O \longrightarrow RCHO + RCH_2OH + H_2O_2$$

The object of this investigation was to study the noncatalytic oxidation of dibenzyl ether by air over a broad range of temperatures and to develop, if possible, a process for converting this ether to such desirable products as benzaldehyde and benzoic acid.

MATERIALS

Dibenzyl ether was obtained by the distillation in vacuo of residues obtained from the manufacture of benzyl alcohol. Material boiling at 135–137° C., under a vacuum of 5 mm. of mercury, was washed with potassium iodide and sodium thiosulfate solutions to remove all peroxides. The peroxide-free material was then washed with 10% sodium bisulfite solution to remove aldehydes, with 10% sodium carbonate solution to remove acidic material, and then with water until neutral. The ether was distilled under vacuum through a 12-inch Vigreux column. Material boiling at 135° C. (5 mm. of mercury) was then put into brown bottles, and nitrogen bubbled through the liquid for one minute. The bottles were tightly stoppered and stored in a dark closet.

The constants of the material were: specific gravity, 25°/25° C., 1.0418–1.0419; refractive index at 20° C., 1.5610–1.5615; chlorine, free (Beilstein flame test).

APPARATUS AND PROCEDURE

The apparatus (Figure 1) consisted of a 500-ml. three-necked flask, *A*, equipped with a coarse fritted-glass gas dispersion tube, a thermometer for measuring the temperature of the contents of the flask, and a propellor agitator with a shaft speed of 1000 r.p.m. Clean, dry air at constant rates was bubbled through weighed amounts of dibenzyl ether contained in the electrically heated oxidation flask, *A*.

The volatile products of oxidation, unreacted ether, and excess air were passed through a column, *G*, which was 1 inch in diameter and packed to a depth of 9 inches with $^3/_{32}$-inch glass helices. The purpose of this column was to fractionate out the unreacted ether and return it to oxidation flask, *A*.

The vapors were condensed by a 4-inch Friedrich type condenser, *H*, the condensate being collected in a 250-ml. flask, *J*. The noncondensables, consisting of excess air saturated with oxidation products, were led to the bottom of a glass absorber, *K*. This abosrber was 1 inch in diameter and was packed to a depth of 15 inches with $^1/_4$-inch glass Raschig rings. For the duration of oxidation, mineral oil was trickled down the column and was collected in a 250-ml. Erlenmeyer flask.

The residue remaining in flask *A* at the termination of the oxidation was weighed and then analyzed for acid and saponification values. The distillate in flask *J* was separated from the small amount of water, weighed, and analyzed for percentage benzaldehyde, acid value, and saponification value. The composition of the distillate was determined by fractionation of a sample (usually 50 ml.), previously dried over anhydrous sodium sulfate, in a 12-inch insulated Vigreux column at atmospheric pressure.

Products were recovered by combining the distillates from a series of oxidations, washing them free of acid with 10% sodium carbonate solution and water, drying them over anhydrous sodium sulfate, and then fractionating them in an 18-inch column. This column was 1 inch in diameter and packed with $^3/_{32}$-inch glass helices. The column was insulated by magnesia pipe covering. The low boilers were removed atmospherically, and the high boilers were then distilled under vacuum.

Similarly, the residues from a series of oxidations were combined, washed free of acid, dried, and distilled under vacuum. Benzoic acid, recovered from the alkaline washes by acidification, was washed and dried.

METHODS OF ANALYSIS. Benzaldehyde was determined by a method described in the National Formulary (*4*). Benzyl benzoate and benzoic acid were determined by methods described in the U. S. Pharmacopoeia (*6*).

YIELDS

The effect of mechanical agitation was determined by running duplicate experiments with and without the agitator. Agitation was employed in experiments 1, 4, 5, 7, and 9 but not for the duplicate experiments 2, 3, 6, 8, and 10.

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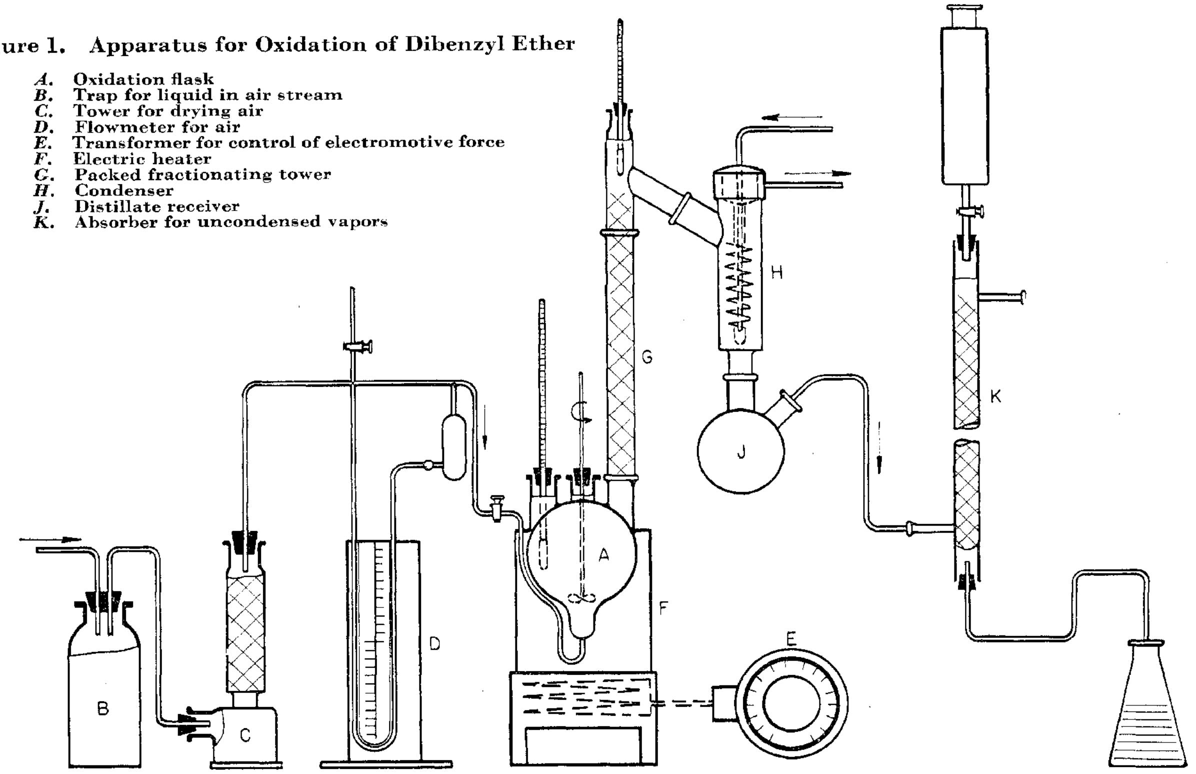


Figure 1. Apparatus for Oxidation of Dibenzyl Ether

A. Oxidation flask
B. Trap for liquid in air stream
C. Tower for drying air
D. Flowmeter for air
E. Transformer for control of electromotive force
F. Electric heater
G. Packed fractionating tower
H. Condenser
J. Distillate receiver
K. Absorber for uncondensed vapors

Similarly, the effect of insulation of the column of the oxidizer was determined by employing an uninsulated column for experiments 1 to 7 and an insulated column for the others. Insulation was provided by wrapping the column with a single layer of $^3/_8$-inch asbestos rope.

A constant flow of air was maintained until distillation had ceased, except in experiments 21 to 24. It became apparent during the course of these low-temperature runs that it would be impossible to determine when distillation had stopped, since the rate of distillation was extremely low. It was therefore decided to run these experiments for 400 to 450 minutes, approximately the same time employed for the runs at higher temperatures.

The results appear in Table I. The compositions of the distillates obtained from experiments 1 to 20 were determined by the method previously described. Since the amounts of distillates obtained in experiments 21 to 26 were small, fractionation was not attempted; the compositions were determined solely by analysis.

The amount of benzoic acid and benzyl benzoate in each residue (experiments 1 to 20) was calculated from the acid and saponification values. The residues from experiments 21 to 26 were fractionated, after removal of the benzoic acid with dilute alkali.

As a check on the validity of the analyses, the distillates having a high percentage of high boilers (experiments 14, 15, 17, and 18) were combined and reanalyzed: d_{25}^{25}, 1.0215; benzaldehyde, 66.0%; benzoic acid, 5.25%.

This material was then washed and fractionated as previously described. From 470 grams of combined distillates the following were obtained:

Material	Weight, Grams	Analysis	Exptl.	Literature	% Recovered from Distillates
Toluene	68.8	B.P., ° C.	110-111	110.80	14.6
		n_D^{20}	1.4967	1.49685	
Benzaldehyde	299.7	d_{25}^{25}	1.0461	1.0460	63.8
		n_D^{20}	1.5451	1.5460	
Benzoic acid	23.0	Purity, %	100	121.4	4.9
		M.P., ° C.	122	...	
Benzyl alcohol	26.6	n_D^{20}	1.5400	1.53955	5.7
Residue	16.7	...	...	...	3.6
					92.6

Since the recovery of benzaldehyde was 96.7% of the analyzed amount and the benzoic acid recovery was 93.5%, it may be assumed that the methods of analysis are reliable. Additional quantities of products could undoubtedly have been recovered from the wash water and thereby improved agreement between the analyzed and isolated quantities. The amount of toluene recovered corresponds approximately to the average of the amounts in the individual distillates as determined by the boiling ranges—i.e., 14.6% compared to a 13% average.

The residues from experiments 12 to 19 were combined and reanalyzed. The acid value was 95.2 and the saponification value 251, corresponding to 20.7% benzoic acid and 59% benzyl benzoate. The acid was removed with dilute alkali and recovered. The neutral material was then fractionated. Two redistillations were necessary for the recovery of a benzyl benzoate of high purity.

The 250-gram residues yielded: 46.6 grams of benzoic acid (98.6% purity, 120–121.5° C. melting point), corresponding to a

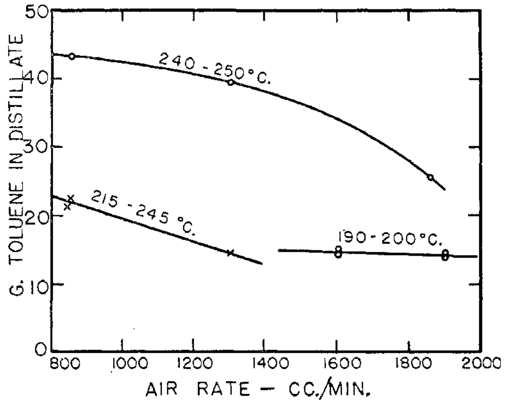


Figure 2. Amount of Toluene in Distillate as a Function of Air Rate at Different Temperatures

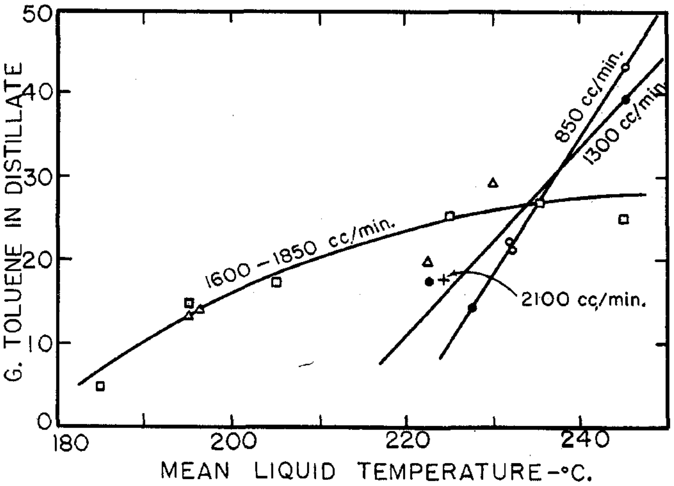


Figure 3. Amount of Toluene in Distillate as a Function of Temperature at Different Air Rates

90% recovery of the analyzed amount; 121.9 grams of benzyl benzoate (98.0% purity, $n_D^{20} = 1.5685$), corresponding to an 81% recovery; 23.7 grams of dibenzyl ether ($n_D^{20} = 1.565$); 22.5 grams of high boilers (unidentified semisolid); 30.2 grams of residue (unidentified dark brown solid and tars).

DISCUSSION OF RESULTS

The data of Table I show that there is no advantage in providing agitation other than that afforded by the air. No benefit was derived by operating the column without insulation, the efficiency being sufficient to reduce the high boilers to less than 5% in most cases.

In Figure 2 a comparison of the 240° to 250° C. with the 190° to 200° C. data indicates that the effect of air rate is more pronounced at higher temperatures; this is undoubtedly due to the relatively greater increase in the rate of the fission reaction compared to the rate of oxidation at elevated temperatures. Figure 3 indicates that elevated temperatures increase the rate of fission of the ether, the effect being more pronounced at low air rates. The fission may be formulated as:

$$(C_6H_5CH_2)_2O \xrightarrow{\text{heat}} C_6H_5CHO + C_6H_5CH_3$$

The yields shown in Table II do not include material recovered or recoverable from the absorber. Here again the increase in toluene formation at higher temperatures is evident. The value at 240° to 250° C. is lower than at 230° to 240°, but this is believed to be due to experimental error and abnormally high losses in the effluent gases. Figure 4 indicates the time of oxidation for the data in Table II.

The data of Table II were plotted, and smoothed values of the yields of products obtained for various temperatures. Since 1 mole of dibenzyl ether is equivalent to 1 mole of benzyl benzoate, or 2 moles of toluene, benzaldehyde, benzyl alcohol, or benzoic acid, the number of moles of the latter were divided by 2 in calculating the moles of ether required for their formation. In Figure 5 the cumulative moles of ether equivalent to the products are plotted against temperature; thus, for any temperature, the relative amounts of the various products are given by the vertical distances between the curves. Figure 5 shows that, although maximum formation of benzaldehyde occurs at approximately 220° C., the maximum yield of total oxidation products occurs at 190° to 200°.

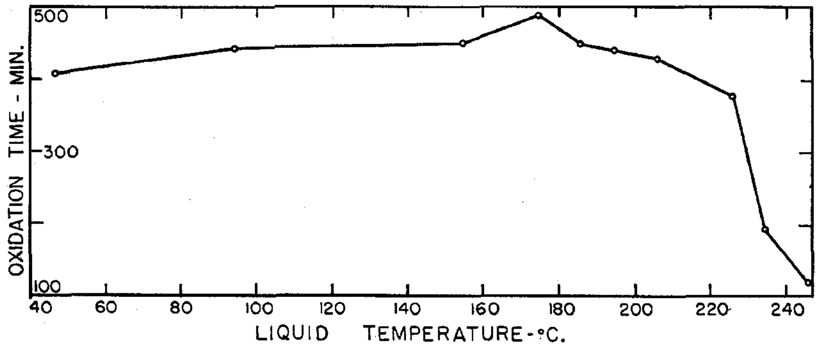


Figure 4. Oxidation Time for Various Temperatures at Air Rate of 1850 Cc. per Minute

TABLE I. OXIDATION OF DIBENZYL ETHER

[Charged 200 grams of dibenzyl ether (1.01 moles); scrubber liquid, 200 ml. of mineral oil]

Expt. No.[a]	Liquid Temp., ° C.	Vapor Temp., ° C.	Air Rate, Cc./Min.	Oxidation Time, Min.	Distillate, Grams			Residue, Grams					Benzaldehyde in Mineral Oil, Grams
					Toluene	Benzaldehyde	Heavies	Benzaldehyde	Benzyl alcohol	Benzoic acid	Benzyl benzoate	Dibenzyl ether	
1A	215–240	55–100	1300	355	14.5	97.5	8.4	...	...	7.7	14.5	...	5.6
2	210–235	50–100	1300	475	17.3	104.0	2.2	...	...	15.9	48.6	...	5.6
3	220–245	60–100	850	475	23.1	104.5	0.9	...	...	19.0	37.5	...	6.1
4A	220–240	75–105	850	435	21.1	108.3	2.6	...	...	16.6	11.0	...	5.1
5A	215–230	55–105	1600	420	20.0	117.2	5.5	...	...	10.7	34.9	...	5.4
6	225–235	75–105	1600	355	29.3	110.3	7.0	...	...	15.2	35.5	...	4.6
7A	190–200	60–70	1600	380	13.5	75.5	1.3	...	...	20.4	40.7	...	6.1
8	195–200	50–85	1600	430	15.0	91.0	1.6	...	...	18.8	44.8	...	7.1
9A	190–200	70–85	1850	430	14.6	93.3	4.5	...	...	14.9	58.5	...	5.8
10	190–200	50–80	1850	450	14.8	104.6	3.8	...	...	18.7	43.1	...	6.1
11	200–210	70–90	1850	430	17.4	112.7	4.0	...	...	16.8	40.8	...	5.6
12	240–250	50–135	850	240	43.5	100.6	0.8	...	...	6.9	24.3	...	...
13	240–250	60–130	1300	195	39.5	105.9	12.3	...	...	6.5	19.7	...	...
14	240–250	120–160	1850	120	25.5	104.8	39.9	...	...	1.6	16.4	...	...
15	230–240	60–120	1850	195	27.2	102.1	21.8	...	...	6.1	26.3	...	...
16	220–230	90–100	1850	325	25.4	110.4	5.5	...	...	10.5	31.3	...	...
17L	220–230	100–115	2100	300	17.2	103.5	22.9	...	...	2.9	21.9	...	...
18	220–230	100–115	2100	260	18.2	109.0	24.1	...	...	7.8	20.7	...	...
19	180–190	65–100	1850	450	5.1	92.3	5.4	...	...	25.0	55.0	...	...
20	180–190	60–100	1850	450	3.7	92.4	9.5	...	...	21.1	48.9	...	...
21	90–100	...	1850	445		6.6 g. semisolid		9.4	7.4	8.3	...	159.1	...
22	90–100	...	1850	450		4.4 g. semisolid		12.0	5.7	7.9	...	160.5	...
23	40–50	...	1850	405	0	0	0	3.5	2.3	0.1	...	188.0	...
24	40–50	...	1850	410	0	0	0	3.4	2.2	0.7	...	184.5	...
25	150–160	38–41	1850	450	...	14.1	3.1[b]	4.8	1.8	14.2	35.0	106.5	...
26	170–180	45–60	1850	490	...	45.6	4.6[b]	8.1	...	35.6	57.0	32.8	...

[a] A = agitation employed in these experiments, not in others; L = leak in joint of apparatus, some volatile material lost. Experiments 1–7 employed uninsulated column; column was insulated for other runs.

[b] Acid.

Table II. Yields of Products from 200 Grams of Ether (1.01 Moles) at Various Temperatures for Air Rate of 1850 Cc. per Minute

Liquid Temp., ° C.	Toluene		Benzaldehyde		Benzoic Acid		Benzyl Alcohol		Benzyl Benzoate		Unoxidized Ether		Oxidation Time, Min.
	Grams	Mole	Grams	Moles	Grams	Mole	Grams	Mole	Grams	Mole	Grams	Mole	
40–50	0.0	0.0	3.5	0.033	0.1	0.0008	2.3	0.021	0.0	0.0	188.0	0.950	405
90–100	0.0	0.0	9.4	0.088	8.3	0.068	7.4	0.068	0.0	0.0	159.1	0.803	445
150–160	0.0	0.0	18.9	0.178	17.3	0.142	1.8	0.017	35.0	0.165	106.5	0.538	450
170–180	...	...	53.7	0.506	40.2	0.329	...	...	57.0	0.269	32.8	0.166	490
180–190	5.1	0.055	92.3	0.872	28.0	0.229	2.4	0.022	55.0	0.259	...	...	450
190–200	14.7	0.160	99.0	0.933	21.7	0.178	0.8	0.007	50.8	0.240	...	...	440
200–210	17.4	0.189	112.7	1.063	20.6	0.169	0.2	0.002	40.8	0.192	...	...	430
220–230	25.4	0.276	110.4	1.041	12.2	0.100	3.8	0.035	31.3	0.147	...	...	325
230–240	27.2	0.296	102.1	0.962	11.2	0.092	8.6	0.079	26.3	0.124	8.1[a]	0.041	195
240–250	25.5	0.277	104.8	0.988	12.4	0.102	9.7	0.090	16.4	0.077	19.4[a]	0.098	120

[a] Determined by fractionation of the heavy fraction obtained from the distillates.

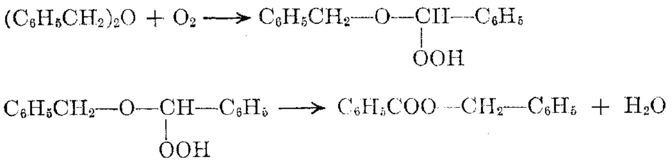
OVER-ALL YIELD

At 200° C. with an air rate of 1850 cc. per minute, the time of oxidation was about 435 minutes. Dibenzyl ether consumed was 1.01 − 0.06 or 0.95 mole; production was:

	Moles	Yield, % of Theory
Benzaldehyde	1.02	53.7
Benzoic acid	0.16	8.4
Benzyl benzoate	0.23	24.2
Benzyl alcohol	0.01	0.5
Toluene	0.17	9.0
		95.8

Assuming a 90% recovery of products for commercial practice, the over-all yield would be about 86% of theory. By employing suitable absorbers, this yield may be increased, as shown.

High temperatures (above 220° C.) reduced the time required for oxidation, but this advantage was offset by the increased formation of toluene, which has relatively little value. The formation of benzyl benzoate may be explained by the following reactions:



$$(C_6H_5CH_2)_2O + O_2 \longrightarrow C_6H_5CH_2{-}O{-}\underset{\displaystyle OOH}{\underset{|}{CH}}{-}C_6H_5$$

$$C_6H_5CH_2{-}O{-}\underset{\displaystyle OOH}{\underset{|}{CH}}{-}C_6H_5 \longrightarrow C_6H_5COO{-}CH_2{-}C_6H_5 + H_2O$$

or

$$2C_6H_5CHO + O_2 \longrightarrow 2C_6H_5COOH$$

$$C_6H_5COOH + C_6H_5CH_2OH \longrightarrow C_6H_5COOCH_2C_6H_5 + H_2O$$

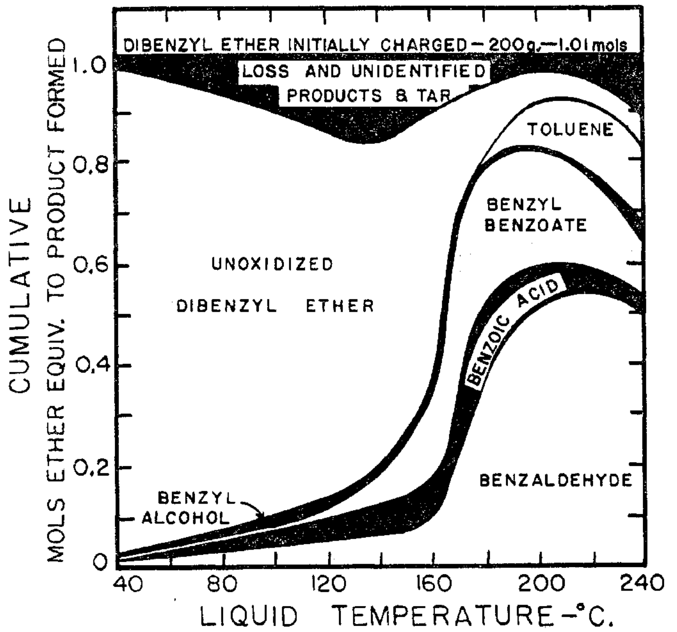


Figure 5. Cumulative Moles of Ether, Equivalent to Each Product, Which Are Formed at Different Temperatures

SUMMARY

The oxidation of dibenzyl ether by atmospheric oxygen was investigated over a temperature range of 40° to 250° C. The study was made in glass equipment, air being blown through the ether at rates of 850 to 2100 cc. per minute.

The products of oxidation were benzaldehyde, benzyl alcohol, benzoic acid, and benzyl benzoate. At high temperatures the disproportionation of the ether was significant:

$$(C_6H_5CH_2)_2O \longrightarrow C_6H_5CHO + C_6H_5CH_3$$

The effects of temperature and air rate on the time required for oxidation and on the yields of the various products were determined. The optimum air rate was found to be in the range 1600 to 1850 cc. per minute for a charge of 1.01 moles dibenzyl ether. The maximum yield of benzaldehyde was obtained at 220° C. At this temperature, however, approximately 13% of the ether was thermally decomposed. The maximum yield of total products of oxidation was obtained at 190° to 200° C., only 4 to 8% of the ether having been disproportionated at this temperature range. Yields were approximately: 53% benzaldehyde, 8% benzoic acid, 24% benzyl benzoate, 1% benzyl alcohol, and 9% toluene, or a total of 95% on the dibenzyl ether consumed.

Since the formation of toluene is accompanied by the formation of benzaldehyde, there was no great reduction in the yield of benzaldehyde at higher temperatures. The yields of benzoic acid and benzyl benzoate were, however, adversely affected. High temperatures reduced the time required for oxidation, but this advantage was offset by the increased formation of toluene.

It was also found that an efficient column for returning unoxidized ether to the oxidizer was necessary. This was especially true for high temperatures and air rates.

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