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DECOMPOSITION OF 1-PHENOXY-2-PROPANOL OVER ACTIVATED ALUMINA

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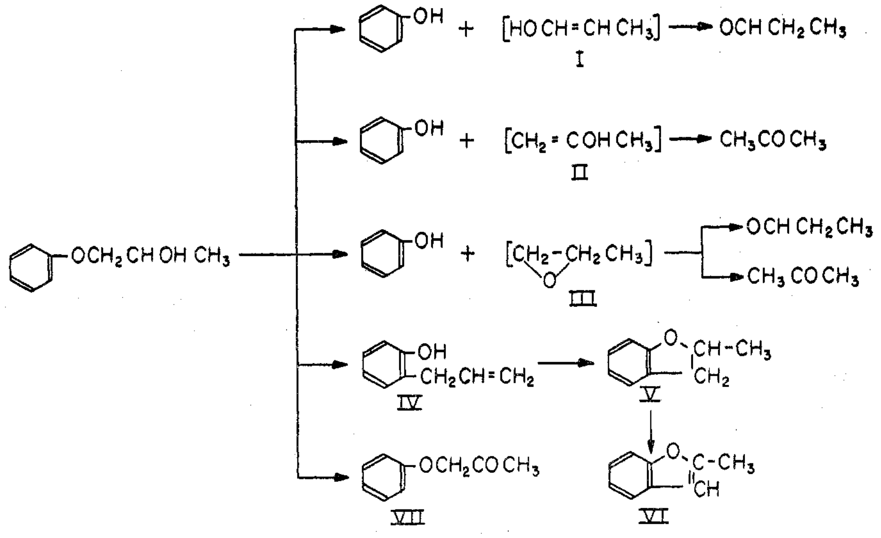
1-Phenoxy-2-propanol (1, 2) decomposed to a variety of products when passed over activated alumina at 400°. The approximate molar amounts of the various decomposition products per mole of 1-phenoxy-2-propanol are listed in Table I.

The decomposition of 1-phenoxy-2-propanol involved mainly the removal of the C_3-side chain and loss of water. The precursors of propionaldehyde and acetone could be enols (I and II) or propylene oxide (III) which has been reported (3, 4, 5) to rearrange to both propionaldehyde and acetone under conditions similar to those of the present study. We have no evidence as to whether dehydration took place before or after hydrolysis (6). There was some β,γ-dehydration-rearrangement to give *o*-allylphenol (IV) and 2-methyldihydrobenzofuran (V), also dehydrogenation of the latter to 2-methylbenzofuran (VI). Some oxidation of the secondary alcohol group occurred to give phenoxyacetone (VII).



EXPERIMENTAL

1-Phenoxy-2-propanol ("Dowanol 2B", product of Dow Chemical Co.) (795 g.) was passed at atmospheric pressure and 400° through a 20-ml. bed of activated alumina ($\frac{1}{8}$ in. × $\frac{1}{8}$-in. pellets) during 16 hours (liquid hourly space velocity 2.4). The catalyst was contained in a vertical 17-mm. o.d. Vycor tube which was heated in a thermostatically-controlled electric furnace. The tube space above the catalyst (*ca.* 75 ml.), packed with Vycor chips, served as vaporizer-preheater. The space below the catalyst was packed with Vycor chips to minimize the residence time of the catalyzate at the elevated temperature. The exit train consisted of a water-cooled receiver followed by two wet-ice traps, a Dry-Ice trap, and a wet-test gas meter. No non-condensable gas was produced, and there was no condensate in the wet-ice traps, but the Dry-Ice trap collected about 1 ml. of liquid. The carbonaceous deposit on the used catalyst contained 1.2 g. of carbon (determined by combustion).

The catalyzate plus the Dry-Ice trap condensate (785 g. total) was distilled at 740 mm. through a 50-plate glass column (packed with glass helices) until the major portion of the phenol had distilled over. The remainder was distilled at 20 mm. through a 27-plate glass column (also packed with glass helices). During the first part of the distillation 2.5 g. of condensable gas (condensed in a Dry-Ice trap) came off; analysis showed it to be a 50-50 mixture of propylene and ethylene. The distillation data are presented in Table II and Figure 1.

TABLE I

DECOMPOSITION PRODUCTS[a] PER MOLE OF 1-PHENOXY-2-PROPANOL

PRODUCTS	MOLE
Propylene and ethylene	0.01
Propionaldehyde	.10
Acetone	.53
n-Propanol	.12
Water	.15
Phenol	.70
2-Methyldihydrobenzofuran	.03
2-Methylbenzofuran	.03
Phenoxyacetone	.04
o-Allylphenol	.05
1-Phenoxy-2-propanol	.06
High-boiling products	.08

[a] Hurd and Perletz (1) reported that the pyrolysis of phenoxyacetone at 650° gave 0.44 mole of phenol, 0.25 mole of methane, 0.06 mole of olefins, 0.46 mole of carbon monoxide, and 0.06 mole of carbon dioxide per mole of phenoxyacetone.

Identification of the components of the distillate was accomplished by chemical and and physical means. All solid derivatives were identified by mixture melting point comparison with authentic specimens; the reported melting points are uncorrected.

Plateau A. Propionaldehyde, b.p. 47.5-49.0° (740 mm.), n_D^{20} 1.3610; identified as the *p-nitrophenylhydrazone*, m.p. 123.5-124.5°.

Plateau B. Acetone, b.p. 55.8-56.2° (740 mm.); identified as the *p-nitrophenylhydrazone,* m.p. 148-149°; essential absence of propionaldehyde shown by methone.

Transition fraction between plateaus A and B. This fraction presumably contained only propionaldehyde and acetone. The presence of prioionaldehyde was shown by methone (m.p. of propionaldehyde derivative, 157-158°). A portion of the transition fraction was oxidized with alkaline permanganate (to convert propionaldehyde to potassium propionate) and then distilled; the distillate contained acetone, identified as the *p-nitrophenylhydrazone.* Fractional crystallization of the mixture of the 2,4-dinitrophenylhydrazones of the transition fraction gave a small yield of acetone 2,4-dinitrophenylhydrazone (m.p. 125-126°), but the majority of the fractions melted rather sharply at 105-107°.

Anal. Calc'd for $C_9H_{10}N_4O_4$: C, 45.37; H, 4.23; N, 23.52; Mol. wt., 238.

Found: C, 45.58; H, 4.44; N, 23.23; Mol. wt., 247.

This 105-107°-melting solid was qualitativelv resolved into the *2,4-dinitrophenylhy-*

TABLE II

Distillation of 1-Phenoxy-2-propanol Catalyzate

FRACTION	B.P., °C. (MM.)	WT.-% OF CHARGE
Gas	Below 45 (740)	0.3
A	45–52 (740)	3.8
B	52–71 (740)	20.0
C	71–92 (740)	4.6
D	92–138 (740)	1.8
E	138–177 (740) 86–106 (20)	47.9
F	106–126 (20)	8.4
G	126–148 (20)	6.3
H	148–170 (20)	2.1
I	Over 170 (20)	4.8

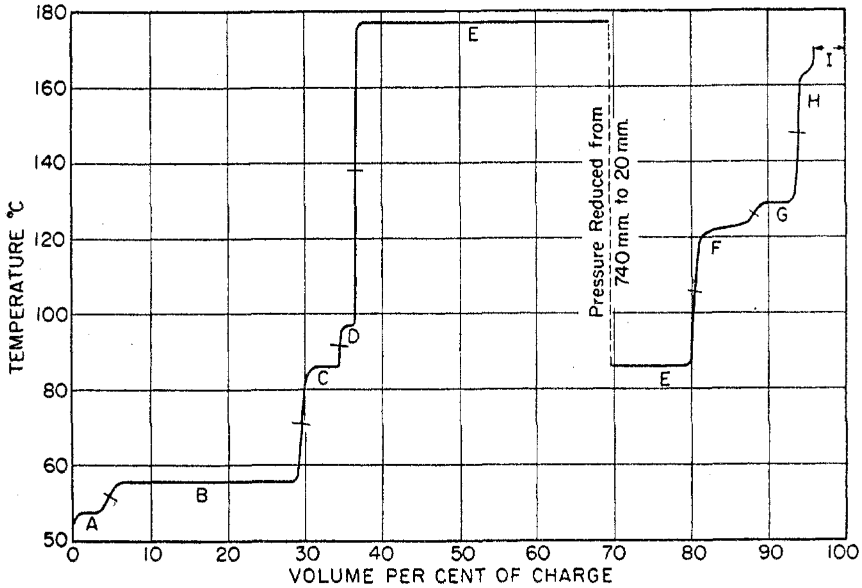


Fig. 1. Distillation of 1-Phenoxy-2-propanol Catalyzate. A = propionaldehyde; B = acetone; C = *n*-propanol-water azeotrope; D = water; E = phenol, 2-methyldihydrobenzofuran, and 2-methylbenzofuran; F = phenoxyacetone and *o*-allylphenol; G = 1-phenoxy-2-propanol; H = unidentified; I = residue.

drazones of propionaldehyde (m.p. 153–154°) and acetone (m.p. 125–126°) by chromatographic adsorption on silica (7).

Plateau C. n-Propanol-water azeotrope, b.p. 85–86.5° (740 mm.); *n*-propanol identified as the *3,5-dinitrobenzoate*, m.p. 73.5–74.5°; also by chromic acid oxidation followed by identification of propionaldehyde.

Plateau D. Water, b.p. 97–99° (740 mm.), d_4^{25} 0.9975, n_D^{25} 1.3328.

Plateau E. Phenol, 2-methydihydrobenzofuran, and 2-methylbenzofuran; b.p. 176–177° (740 mm.) and 85.5–86.5° (20 mm.). This mixture was separated into solid and liquid components by pressure filtration. The solid was shown to be mainly phenol; identified as phenoxyacetic acid, m.p. 99–100.5°. Fractional crystallization of a 10-g. sample of the crude phenoxyacetic acid indicated the essential absence of other phenoxyacetic acids.

The liquid component was washed with aqueous caustic and distilled at 20 mm. to give a heart-cut boiling at 85–89° (d_4^{25} 1.0411, n_D^{25} 1.5426). When subjected to the conditions of the Claisen rearrangement (8), it did not yield *o*-allylphenol, and therefore was not allylphenyl ether. Comparison of the infrared spectrum of the liquid component with the spectra of 2-methyldihydrobenzofuran and 2-methylbenzofuran showed that it consisted of about equal amounts of these compounds.

Plateau F. Phenoxyacetone and *o*-allylphenol, b.p. 106–126° (20 mm.). This mixture was separated into its acidic and neutral components by extraction with aqueous caustic. The alkaline extract was reacted with chloroacetic acid to give a mixture of phenoxyacetic acid (m.p. 99–100.5°) and *o*-allylphenoxyacetic acid which was separated by fractional crystallization from water. *o*-Allylphenoxyacetic acid melts at 148.5–150°.

Anal. Calc'd for $C_{11}H_{12}O_3$: Neut. equiv., 192.2. Found: Neut. equiv., 191.2.

The neutral portion distilled at 123–124° (20 mm.) and the distillate gave the *semicarbazone* of phenoxyacetone, m.p. 173–173.5° (9). Analytical hydrogenation of the distillate showed 1.1 double bonds, and the hydrogenated sample reacted with phenyl isocyanate to give the *phenylurethan* of 1-phenoxy-2-propanol (m.p. 90–91°, crystallized from *n*-heptane).

Anal. Calc'd for $C_{16}H_{17}NO_3$: N, 5.16. Found: N, 5.16.

Plateau G. 1-Phenoxy-2-propanol, b.p. 127–129° (20 mm.); identified as the *phenylurethan*, m.p. 90–91°.

Plateau H. Unidentified, b.p. 162–165° (20 mm.).

SUMMARY

1-Phenoxy-2-propanol decomposes over activated alumina at 400° to give ethylene, propylene, propionaldehyde, acetone, *n*-propanol, water, phenol, 2-methyldihydrobenzofuran, 2-methylbenzofuran, phenoxyacetone, *o*-allylphenol, and a small amount of unidentified, higher-boiling material.

Two new compounds were prepared: *o*-allylphenoxyacetic acid and the phenylurethan of 1-phenoxy-2-propanol.

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