Vapor Phase Oxidation of Alkyl Benzenes[1]

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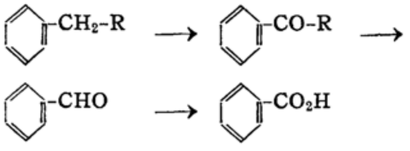
Phthalic anhydride is produced commercially by vapor phase oxidation of naphthalene. By the same process, maleic anhydride is obtained from benzene, anthraquinone from anthracene. Production of benzoic acid from toluene and of phthalic anhydride from *o*-xylene by the oxidation has been studied, but the oxidation of benzene which contains an alkyl group with a longer chain than the methyl group has not been examined.

It has been published that, based on liquid phase oxidation of ethyl benzene, the mechanism of vapor phase oxidation of alkyl benzenes is assumed to be as follows[2]:



R: alkyl group

The author studied the mechanism of vapor phase oxidation of alkyl benzenes and others.

Experimental

Apparatus.—As shown in Fig. 1, a reactor was a steel U tube 18 mm. in diameter, immersed in a molten nitrate bath.

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[1] This is a summary of the report published in *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1746 (1957); **79**, 1081, 1230, 1406 (1958).

[2] L. F. Marek and D. A. Hahn, "The Catalytic Oxidation of Organic Compound in the Vapor Phase", Am. Chem. Soc. Monograph No. 61, Chemical Catalog Co., New York (1932), p. 356.

TABLE I. PHYSICAL CONSTANTS OF SUBSTANCES

		°C	d_4^{20}
Toluene	b.p.	110.5	0.864
Ethyl benzene	b.p.	136.2	0.867
Styrene	b.p.$_{40}$	44.5～45.5	0.908
n-Propyl benzene	b.p.	159.6	0.862
iso-Propyl benzene	b.p.	152.5	0.862
n-Butyl benzene	b.p.	183.2	0.860
sec-Butyl benzene	b.p.	173.5～173.8	0.862
tert-Butyl benzene	b.p.	170.0～170.5	0.866
sec-Amyl benzene	b.p.	192.0～192.8	0.862
3-Phenyl pentane	b.p.	191.0	0.864
tert-Amyl benzene	b.p.	189.0～189.5	0.873
n-Hexyl benzene	b.p.	225.4	0.857
2-Phenyl-*n*-hexane	b.p.	214	0.861
Dodecyl benzene	b.p.$_{20}$	165～185	0.862
Phenyl cyclohexane	b.p.	235～236	0.943
Diphenyl	m.p.	70.3	—
Propiophenone	b.p.	218	1.005
Phenyl acetone	b.p.	216	1.004
Hydrocinnamic acid	m.p.	48	—
Cinnamic acid	m.p.	133	—
α-Hydrindone	m.p.	41	—
Butyrophenone	b.p.	220～221	0.988
Benzyl ethyl ketone	b.p.$_{16}$	109～111	1.001
Benzyl acetone	b.p.$_{13}$	115	0.985
γ-Phenyl butyric acid	m.p.	51	—
Tetralone	b.p.$_{13}$	127	1.092

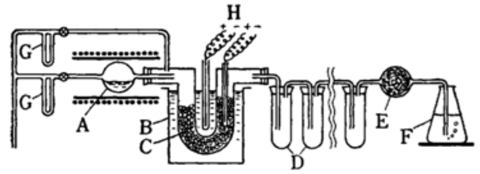

Fig. 1. Apparatus used for vapor phase oxidation.

- A. Evaporator
- B. Salt bath
- C. Reactor
- D. Air condensers and ice-cooled condensers
- E. Glass wool
- F. Water bubbler
- G. Flowmeters
- H. Thermocouples

Catalyst.—The Catalyst was, throughout the present experiments, a mixture of vanadium pentoxide and molybdenum trioxide on pumice stone, which was prepared from ammonium metavanadate (5 g.), ammonium molybdate (5 g.) and puric stone (100 ml.) by the method described before³⁾.

Experimental Conditions.—The air rate was 150 l./hr. and the feed rate of reactants 1.5 g./hr.; the range of reactor temperatures was 300～500°C and the volume of catalyst was 50 ml. Duration of an experimental run was 3 hr. Substances oxidized are listed in Table I.

Analysis of Reaction Products.—Oxidation products, mainly a mixture of phthalic and maleic anhydrides and benzoic acid, after having been dissolved in hot water (and filtered, if necessary,) were dried in vacuo and weighed. Then, using a portion of the dried product, the neutralization equivalent of the whole mixture was ascertained. Another portion of the product was taken, benzoic acid was removed completely by microsublimation apparatus at 65～70°C, and the neutralization equivalent of the remaining product was ascertained. From these values the amounts of phthalic, benzoic, and maleic acids were figured out.

The same procedure was repeated using a known mixture of three acids and the experimental values were found to be within 15% of the theoretical values.

Results and Discussion

Vapor Phase Oxidation of Monoalkyl Benzenes.—Toluene, ethyl benzene, propyl benzenes butyl benzenes, amyl benzenes, hexyl benzenes, and dodecyl benzenes were oxidized under the same conditions. The mole percentage yields of products are listed in Table II.

Table II shows that

1) Ethyl benzene is more easily oxidized

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3) H. Sasayama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **56**, 281 (1953).

TABLE II. EXPERIMENTAL RESULTS OF VAPOR PHASE OXIDATION OF ALKYL BENZENES

	Reaction temp. °C	Products		
		Phthalic anhydride mol. %	Benzoic acid mol. %	Maleic anhydride mol. %
Toluene	300	0	7	8
Toluene	350	trace	12	45
Ethyl benzene	300	0	35	12
Ethyl benzene	400	0	9	41
Styrene	300	0	35	5
Styrene	400	0	trace	49
n-Propyl benzene	350	18	6	34
n-Propyl benzene	400	24	2	35
iso-Propyl benzene	400	0	21	38
n-Butyl benzene	350	27	7	25
n-Butyl benzene	400	26	2	30
sec-Butyl benzene	350	35	9	23
sec-Butyl benzene	400	36	3	26
tert-Butyl benzene	400	trace	0	24
sec-Amyl benzene	350	23	5	22
sec-Amyl benzene	400	24	1	29
3-Phenyl pentane	400	20	2	30
tert-Amyl benzene	350	3	0	38
tert-Amyl benzene	400	4	trace	44
n-Hexyl benzene	350	14	1	50
n-Hexyl benzene	400	19	trace	65
2-Phenyl-*n*-hexane	350	7	3	25
2-Phenyl-*n*-hexane	400	35	1	26
Dodecyl benzene	400	17	1	45
Phenyl cyclohexane	400	8	2	20*
Phenyl cyclohexane	500	10	0	16
Diphenyl	400	14	2	35

* and 18 mol. % of diphenyl is produced.

than toluene. And benzoic acid and maleic anhydride are obtained from ethyl benzene in the same yields as that from styrene.

2) When the number of carbons in the longest chain of the alkyl group is three or more, for instance, *n*-propyl, *n*-butyl, *sec*-butyl, amyl, hexyl, etc., phthalic anhydride (25∼36%), benzoic acid and maleic anhydride are obtained by vapor phase oxidation. When it is two or less, for instance, methyl, ethyl, *i*-propyl, no phthalic anhydride is obtained.

3) The yield of phthalic anhydride obtained from *n*-alkyl benzenes is lower than that from *sec*-alkyl benzenes, and that from *tert*-alkyl benzenes is very small.

4) No benzoic acid is obtained from *tert*-alkyl benzenes by vapor phase oxidation.

The Reaction Mechanism of Vapor Phase Oxidation of *n*-Propyl Benzene and *n*-Butyl Benzene. — *n*-Propyl benzene or *n*-butyl benzene has only one alkyl group. Oxidation of either of these two compounds produces phthalic anhydride in which the benzene ring has two side chains containing carbon atoms. This strange phenomenon, however, can not be explained by the mechanism that has been advocated by Marek, Hahn[2] and others so far.

The range of temperatures of vapor phase oxidation is 350∼500°C and a reactant is passed with air through the vanadium pentoxide catalyst zone in vapor phase. Therefore, it is supposed that oxidation, pyrolysis and condensation would occur at the same time.

Concerning the above-mentioned strange reaction the author examined accordingly the following three mechanisms *a*, *b* and *c*.

Mechanism a. — *n*-Propyl benzene or *n*-butyl benzene would be oxidized to benzaldehyde. The two molecules of the aldehyde may be condensed to form anthraquinone as Parks[4] observed, and then this would be oxidized to from phthalic anhydride.

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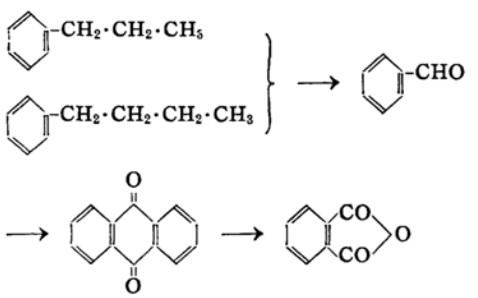
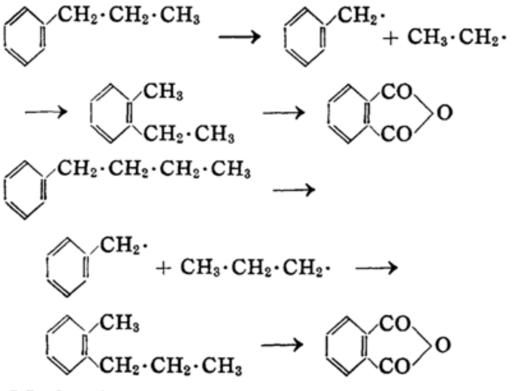
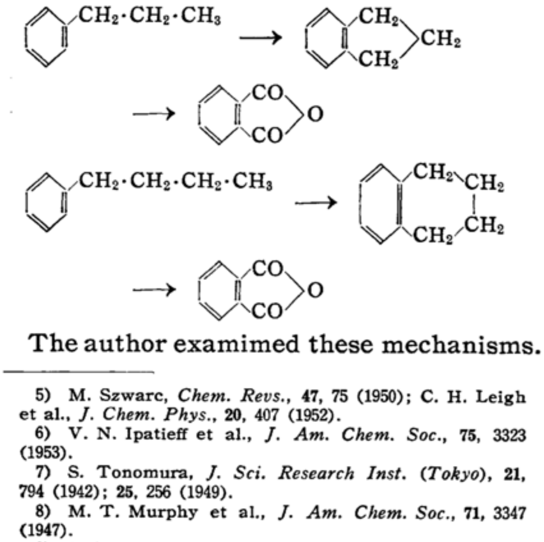
[4] W. G. Parks et al., *Ind. Eng. Chem.*, **33**, 891 (1941); C. R. Downs, *J. Soc. Chem. Ind.*, **46**, 388, T (1927).



Mechanism b. — *n*-Propyl benzene or *n*-butyl benzene would be dissociated to form benzyl and ethyl or propyl radicals, as given in the papers by Szwarc5), then the alkyl radical would be attached to the ortho position of benzyl radical to form dialkyl benzene6). This would be oxidized to phthalic anhydride.



Mechanism c.—As already reported by Tonomura7), Murphy8) and Nametkin9), *n*-propyl benzene or *n*-butyl benzene would produce hydrindene or tetralin by cyclization and then this would be oxidized to phthalic anhydride.



The author examimed these mechanisms.

On mechanism a.—Oxidation products of *n*-propyl benzene or *n*-butyl benzene contained no anthraquinone, and when the mechanism is true, ethyl benzene would have to produce phthalic anhydride through the same mechanisms. But the experimental results showed that no phthalic anhydride was produced from ethyl benzene. From these facts, it is supposed that this mechanism is not true.

On mechanism b.—If this mechanism is correct, ethyl benzene must produce phthalic anhydride by the oxidation. The experiments showed that ethyl benzene did not produce it, and therefore this mechanism is not correct. To ascertain this conclusion, ethyl benzene was oxidized in the vapor phase with air containing vapor of methanol or ethanol, etc., both of which are liable to form a free radical10), but no phthalic anhydride was obtained.

On mechanism c.—*n*-Propyl benzene was passed through the pumice (carrier) bed which contained no vanadium pentoxide under the same conditions as those of the oxidation (temperature, air rate and feed rate). The ultraviolet spectrum of the product showed that it contained styrene but no hydrindene. Moreover, when this product was oxidized in the liquid phase with aqueous solution of potassium permanganate11), only benzoic acid was found but no phthalic acid. As to *n*-butyl benzene, the spectrum showed the presence of alkenyl benzene (presumably propenyl benzene). Thus the mechanism *c* is incorrect.

With these three mechanisms, the formation of phthalic anhydride from *n*-propyl benzene or *n*-butyl benzene by the oxidation can not be explained.

The author studied the following reactions.

Mechanism d·1.—The first carbon atom attacked by oxygen in the alkyl group of *n*-propyl benzene, and *n*-butyl benzene.

Propiophenone $C_6H_5\cdot CO\cdot CH_2\cdot CH_3$, phenyl acetone $C_6H_5\cdot CH_2\cdot CO\cdot CH_3$, hydrocinnamic acid $C_6H_5\cdot CH_2\cdot CH_2\cdot CO_2H$, butyrophenone $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_3$, benzyl ethyl ketone $C_6H_5\cdot CH_2\cdot CO\cdot CH_2CH_3$, benzyl acetone $C_6H_5\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$ and γ-phenyl butyric acid $C_6H_5\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$ were oxidized in vapor phase under the same conditions. The experimental results are given in Table III.

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5) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950); C. H. Leigh et al., *J. Chem. Phys.*, **20**, 407 (1952).

6) V. N. Ipatieff et al., *J. Am. Chem. Soc.*, **75**, 3323 (1953).

7) S. Tonomura, *J. Sci. Research Inst.* (*Tokyo*), **21**, 794 (1942); **25**, 256 (1949).

8) M. T. Murphy et al., *J. Am. Chem. Soc.*, **71**, 3347 (1947).

9) S. S. Nametkin, *Chem. Abstr.*, **42**, 3339 (1948).

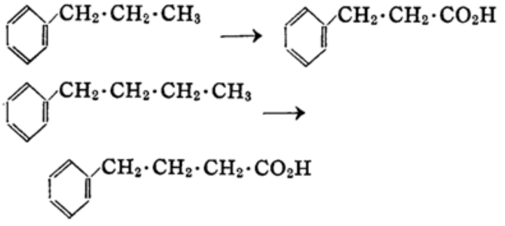
10) W. A. Waters, "The Chemistry of Free Radicals.", Clarendon Press, Oxford (1948), p. 127.

11) S. P. Mulliken, "Identification of Pure Organic Compounds", Vol. I, John Wiley & Sons, Inc., New York, p. 197.

TABLE III. EXPERIMENTAL RESULTS OF VAPOR PHASE OXIDATION OF COMPOUNDS RELATED TO ALKYL BENZENE

Material	Reaction temp. °C	Products: Phthalic anhydride mol. %	Products: Benzoic acid mol. %	Products: Maleic anhydride mol. %
Propiophenone	300	0	45	39
Propiophenone	400	trace	2	49
Phenyl acetone	400	trace	20	42
Hydrocinnamic acid	400	20	2	44
Cinnamic acid	400	15	2	55
α-Hydrindone	400	77	0	11
Butyrophenone	300	trace	62	29
Butyrophenone	400	trace	6	42
Benzyl ethyl ketone	300	0	18	23
Benzyl ethyl ketone	400	0	6	43
Benzyl acetone	400	18	3	46
γ-Phenyl butyric acid	400	30	trace	22
Tetralone	400	62	trace	12

As shown in Table III, propiophenone, butyrophenone, phenyl acetone and benzyl ethyl ketone, of which C_1 or C_2 contains oxygen atom, produced no phthalic anhydride. While hydrocinnamic acid, benzyl acetone and γ-phenyl butyric acid whose C_3 or C_4 has an oxygen atom, produced phthalic anhydride in a yield of 20∼30%. From these results, it is concluded that only when the oxidation was initiated at C_3 of *n*- propyl benzene or at C_3 or C_4 of *n*-buthyl benzene, phthalic anhydride was obtained. The waste gas of oxidation of *n*-propyl benzene had a strong odor of hydrocinnamic acid. *n*-Butyl benzene was passed with air through the catalyst bed which contained a very small quantity of vanadium pentoxide, and the presence of γ-phenyl butyric acid was confirmed by the ultraviolet spectrum of the product.



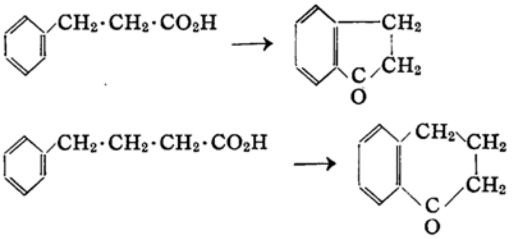
The mechanism given in *d·1* is different from the already published mechanism where only C_1 is oxidized in liquid phase or vapor phase oxidation.

Mechanism d·2.—On cyclization of hydrocinnamic acid and γ-phenyl butyric acid.

Hydrocinnamic acid produces hydrindone by cyclization in the presence of hydrogen fluoride[12], poly-phosphoric acid[13] or 80% phosphoric acid[14] catalyst, and tetralone is obtained from γ-phenyl butyric acid by the action of concentrated sulfuric acid[15]. However, it has not been reported that the cyclization takes place under conditions of vapor phase oxidation.

The author performed the experiment that a mixture of hydrocinnamic acid or γ-phenyl butyric acid vapor and air was passed through the bed of catalyst at 400°C which contained a very small quantity of vanadium pentoxide. Among the reaction products hydrindone and tetralone were identified as phenyl hydrazone and 2, 4-dinitrophenylhydrazone, respectively.

This indicates that cyclization took place. To ascertain this results, the reaction product was oxidized by aqueous solution of potassium permanganate, and phthalic acid was obtained.



Mechanism d·3.—On vapor phase oxidation of hydrindone and tetralone.

By catalytic air oxidation hydrindone and tetralone gave phthalic anhydride in yields of 77, 62% and maleic anhydride 11, 12%, respectively. From these results (*d·1*, *d·2* and *d·3*), the mechanism through

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[12] F. Fieser et al., *J. Am. Chem. Soc.*, **61**, 2172 (1937).

[13] M. R. Snyder et al., ibid., **72**, 2965 (1950); E. C. Horning, ibid., **73**, 5879 (1951).

[14] J. C. Hillyer, *J. Org. Chem.*, **17**, 600 (1952).

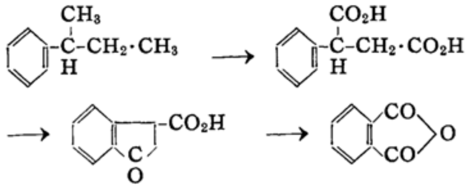
[15] K. Krollpfeiffer et al., *Ber.*, **56**, 620 (1922).

which phthalic anhydride is obtained by the oxidation of *n*-propyl benzene and *n*-butyl benzenes, is as follows:

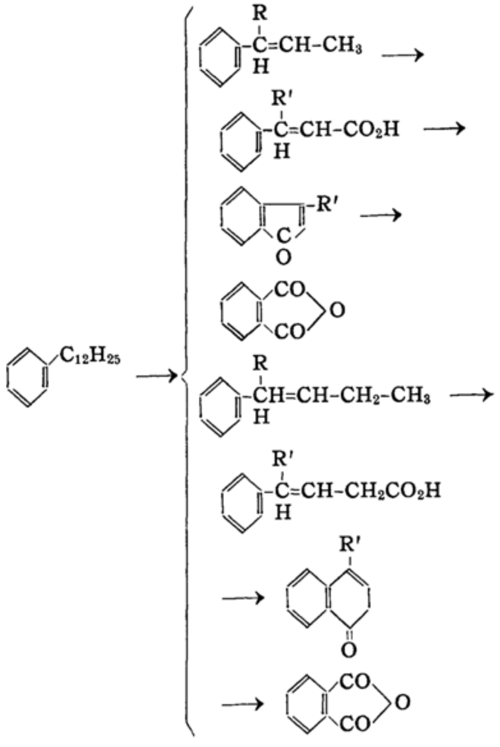
n-propyl benzene → hydrocinnamic acid
→ α-hydrindone → phthalic anhydride
n-butyl benzene → γ-phenyl butyric acid
→ tetralone → phthalic anhydride

iso-Propyl benzene and *tert*-butyl benzene gave no phthalic anhydride by the oxidation. They have only two carbon atoms in the longest chain of the alkyl group, and therefore cyclization will be impossible to occur.

The yield of phthalic anhydride from *sec*-butyl benzene was higher than that from *n*-propyl benzene. This will probably be due to the fact that cyclization of hydrocinnamic acid takes place more easily when it has a substituent group than when it has none[16].



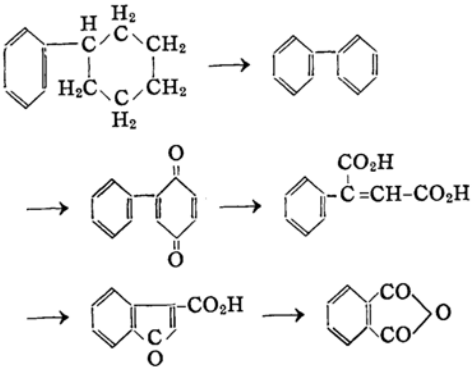
Vapor Phase Oxidation of Amyl Benzenes, Hexyl Benzenes and Dodecyl Benzenes and Others.—The number of carbons in the longest chain of these alkyl groups is at least 3 or more. For the same reason, phthalic anhydride is obtained by the oxidation of these alkyl benzenes (Table II). The product that was obtained by passing dodecyl benzene through the pumice stone (carrier) zone at 400°C, was separated by distillation into three fractions, boiling at about 162, 182 and 230°C, respectively. These produced benzoic acid by oxidation with aqueous solution of potassium permanganate and were absorbed by 90% sulfuric acid and their ultraviolet spectra were characteristic. These were possibly alkenyl benzene (the number of carbons of the alkenyl group was 4—6). As the result it is apparent that such long-chain alkyl benzene as dodecyl benzene is decomposed by heat into short-chain alkenyl benzenes and then phthalic anhydride is produced by oxidation through the above mentioned mechanism.



R: H, CH_3. R′: H, CO_2H.

Benzoic acid was not produced from *tert*-alkyl benzenes. This is possibly due to dissociation[17] into benzene nucleus and the alkyl group.

It is supposed that phenyl cyclohexane produced phthalic anhydride by oxidation through the following mechanism.



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[16] Richter-Anschütz, "Organishe Chemie", Band II. Friedrich Cohen Bonn (1913), p. 615.

[17] N. Tanaka et al., *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **55**, 443 (1952).