Vapor Phase Oxidation of Methyl Naphthalenes[1]

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In 1916, Wohl[2] and Gibbs & Conover[3] discovered that, in the presence of vanadium pentoxide, naphthalene is oxidized to phthalic anhydride at 350 to 550°C. The ever-increasing demand for phthalic anhydride has in recent years stimulated the search for alternative raw materials. A patent claim was made that phthalic anhydride appears in the products of the catalytic air oxidation of methyl naphthalenes and phenanthrene. Methyl naphthalene oil[4] (a mixture of methyl naphthalene isomers, naphthalene and others) gave phthalic anhydride in the yield of 50~60%, but both pure 1- and 2-methyl naphthalenes[5] produced it in 30~40%. This yield is very low, in comparison with that from naphthalene (60~80%)[6]. The cause has not been studied. Reaction heat from methyl naphthalenes to phthalic anhydride is 605 kcal./mol. and is larger than that from naphthalene (450 kcal./mol.). Some investigators[7] accordingly proposed that the catalyst zone was superheated and phthalic anhydride once produced was decomposed, and the yield was lowered as a consequence.

The author studied the reaction mechanism of the vapor phase oxidation of methyl naphthalenes and related compounds and clarified the cause of the low yield.

Experimental

Apparatus.—It is the same as that reported before[8].

Experimental Conditions.—The air rate was 150 l. per hour, the feed rate 1.5 g. per hour; the range of reaction temperatures was 350~500°C, and the catalyst volume was 50 ml.

The method of preparing the catalyst[9] was also reported before (V_2O_5-MoO_3-pumice stone).

The physical constants of reactants are listed in Table I.

Results and Discussion

Vapor Phase Oxidation of Methyl Benzenes.—Methyl naphthalenes have two benzene rings condensed, whereas phthalic anhydride has one. Therefore, in order for methyl naphthalenes to produce phthalic anhydride by vapor phase oxidation, one of the two benzene rings of methyl

TABLE I. PHYSICAL CONSTANTS OF MATERIAL USED FOR VAPOR PHASE OXIDATION

Materials	°C	°C
Naphthalene	m.p. 80.3	
1-Methyl naphthalene	f.p. −32.0	b.p. 245.0
2-Methyl naphthalene	m.p. 32.0	b.p. 241.6
o-Xylene	f.p. −26	b.p. 143~144
1, 2, 3-Trimethyl benzene	f.p. −19.8	b.p. 173.4~174.5
1, 2, 4-Trimethyl benzene	b.p. 168.0~168.5	d_4^{20} 0.8755
1, 2, 4-Benzene-tricarboxylic acid	b.p. 216~217	
Naphthalene-1-carboxylic acid	m.p. 160.5	
Naphthalene-2-carboxylic acid	m.p. 183.5~184.0	
Tetralone	b.p.$_{13}$ 127	d_4^{20} 1.092
2-Methyl-1, 4-naphthoquinone	m.p. 34.2	
2, 6-Dimethyl naphthalene	m.p. 109.5~110.0	
2, 7-Dimethyl naphthalene	m.p. 95.5~96.5	
Dimethyl naphthalene oil	b.p. 260~268	
Acenaphthene	m.p. 94.5	

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[1] This is a summary of reports published in *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 509, 514 (1959).

[2] A. Wohl, Ger. Pat., 379,882 (Sep. 4, 1916).

[3] H. D. Gibbs and C. Conover, Brit. Pat., 119,518 (Oct. 1, 1918).

[4] J. Shelmerdine et al., *J. Appl. Chem.*, **3**, 513 (1953); T. Yatagai, *J. Japan, Tar Ind. Assoc.* (*Coal Tar*), **9**, 648, (1957).

[5] R. Norris et al., *Ind. Eng. Chem.*, **35**, 279 (1943); C. R. Kinney et al., ibid., **43**, 3880 (1951).

[6] L. F. Marek and D. A. Hahn, "The Catalytic Oxidation of Organic Compound in the Vapor Phase", American Chemical Society Monograph No. 61., Chemical Catalog Co., New York (1932), p. 404.

[7] H. Sasayama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **46**, 1225 (1943).

[8] S. Morita, This Bulletin, **33**, 309 (1960); O. Hibino and S. Morita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1766 (1957).

TABLE II. VAPOR PHASE OXIDATION OF METHYL BENZENES AND THE RELATED COMPOUNDS

Materials	Reaction temp. °C	Products: Phthalic anhydride mol. %	Products: Maleic anhydride mol. %	Products: Benzene tricarboxylic acid	Material unreacted
o-Xylene	400	66	7	0	0
1, 2, 3-Trimethyl benzene	400	0	3	trace	0
1, 2, 4-Trimethyl benzene	400	0	3	trace	0
1, 2, 4-Benzene-tricarboxylic acid	400	0	5	0	0

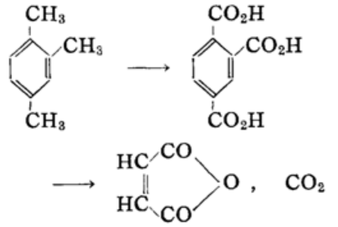
naphthalenes has to be cleaved to form benzene containing two side chains, followed by oxidation to the acid. The author studied the behavior of the side chains of the benzene ring during the vapor phase oxidation.

Toluene, *o*-xylene, 1, 2, 3- and 1, 2, 4-trimethyl benzenes were oxidized in vapor phase under the same conditions mentioned earlier. The results are listed in Table II.

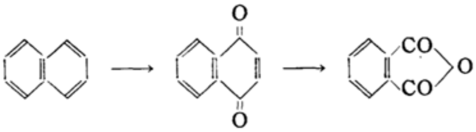
As shown in Table II, phthalic anhydride was produced from *o*-xylene, and benzoic acid from toluene. Therefore, it is apparent that the methyl group is oxidized to carboxylic acid before the benzene ring is cleaved. Sasayama[9] reported that oxidation of trimethyl benzene proceeded stepwise as follows:

trimethyl benzene → benzene-tricarboxylic acid
→ phthalic anhydride → benzoic acid
→ benzene → maleic anhydride.

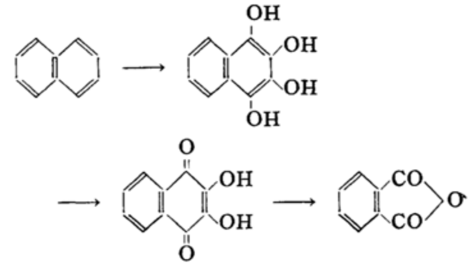
The results obtained by the author showed that both 1, 2, 3- and 1, 2, 4-trimethyl benzenes, on vapor phase oxidation, gave maleic anhydride (in 3% yield) and carbon dioxide, accompanied by very small amounts of 1, 2, 3- and 1, 2, 4-benzene-tricarboxylic acids, respectively, but gave neither phthalic anhydride nor benzoic acid. Furthermore, 1, 2, 4-benzene-tricarboxylic acid gave no phthalic anhydride, but only maleic, anhydride (in 5% yield) and carbon dioxide and no unreacted material was found. The yield of maleic anhydride in this case was comparable with that from 1, 2, 4-trimethyl benzene; therefore, benzene-tricarboxylic acid was presumably formed as an intermediate in the oxidative degradation of trimethyl benzene. However, decarboxylation of the extra carbonyl group did not ensue and the benzene ring was cleaved by the oxidation to form maleic anhydride and carbon dioxide.



Vapor Phase Oxidation of Methyl Naphthalenes and their Related Compounds.—The mechanism[10] of the vapor phase oxidation of naphthalene is described as follows:



Meanwhile, Pongratz[11] proposed the following route:



In either case, a carbon-hydrogen bond in one of two benzene rings is broken and a new carbon-oxygen bond is formed in its place, and then the benzene ring containing oxygen is cleaved.

Two benzene rings of naphthalene are equivalent reaction-wise but those of methyl naphthalenes are not, due to the presence of the methyl group in one ring.

Pongratz[11] studied the vapor phase oxidation of chloro-, nitro-, and hydroxy-naphthalenes and found that both 1- and 2-chloronaphthalenes produced phthalic anhydride and monochlorophthalic anhydride. These results show that chlorinated as well as unsubstituted benzene rings were cleaved, but he also obtained phthalic anhydride from 1, 5-dichloronaphthalene and concluded that dechlorination took place during the oxidation.

So far, no report has been made on the mechanism of vapor phase oxidation of methyl naphthalenes. The author examined four conceivable mechanisms (**a**, **b**, **c** and **d**) of vapor phase oxidation of methyl naphthalenes.

Mechanism ***a***.—Kato[12] and coworkers obtained naphthalene-carboxylic acids in 86% yield

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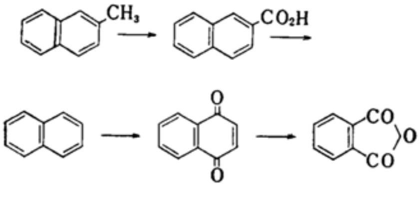
[9] H. Sasayama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **56**, 281 (1953).

[10] C. R. Downs, *J. Soc. Chem. Ind.*, **46**, 383 T(1927).

[11] A. Pongratz, *Angew. Chem.*, **54**, 22 (1941).

[12] S. Kato et al., " Abstracts of the 11th Annual Meeting of Chem. Soc. Japan ", Tokyo (1958), p. 18.

by heating methyl naphthalenes to 250°C with an aqueous solution of sodium dichromate in an autoclave. Pickering[13] et al. obtained the acid by oxidation of alkyl naphthalene with barium permanganate. In the same manner, in the vapor phase methyl naphthalene would first be oxidized to naphthalene-carboxylic acid, and then phthalic anhydride is produced as follows:



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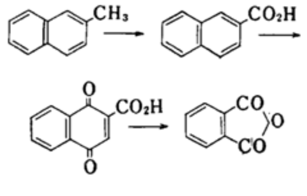
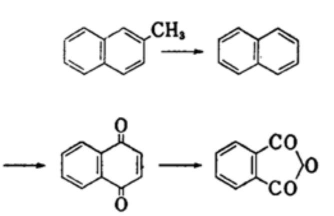
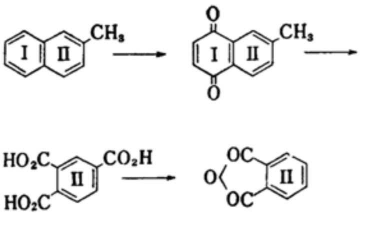


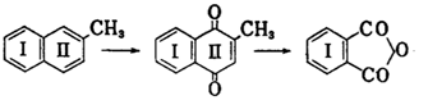
Mechanism b.—Madison[14] obtained naphthalene by one-hour pyrolysis of 1- or 2-methyl naphthalene at 475°C, whereas Kynaston[15] obtained the same compound by passing acenaphthene with steam over a catalyst such as zinc oxide, chromium oxide or alumina. In the same way, methyl naphthalene would produce naphthalene by demethylation as an initial step and naphthalene would then be oxidized to phthalic anhydride:



Mechanism c.—Unsubstituted benzene ring (I) of methyl naphthalene would be oxidized and produce phthalic anhydride with the concomitant decarboxylation of one of the three carboxyl groups.



Mechanism d.—Benzene ring bearing the methyl group would be cleaved by oxidation and produce phthalic anhydride:



The author will discuss these four mechanisms.

On mechanism a.—2-Methyl naphthalene was catalytically oxidized in the vapor phase under the same conditions at 350°C and the product contained 2-methyl-1, 4-naphthoquinone (identified as 2, 4-dinitrophenyl-hydrazone; m.p. 274°C uncor., no depression in mixed m.p.) but no naphthalene carboxylic acid. This result agrees with that obtained by Fieser[16].

Since decarboxylation is assumed in this mechanism, the possible occurrence of decarboxylation was examined. Naphthalene-1- or 2-carboxylic acid was passed through a reaction tube filled with pumice stone containing no vanadium pentoxide under the same conditions as in vapor phase oxidation (temperature, feed rate and air rate). The product did not contain naphthalene at all. In the same way, the acids were passed through the oxidation catalyst zone with a stream of carbon dioxide instead of air under the same conditions, but naphthalene was not obtained. Therefore, decarboxylation does not occur in the oxidation of naphthalene-carboxylic acid. This result is similar to the one obtained in the case of benzene-tricarboxylic acid.

From these results, it is supposed that mechanism **a** is incorrect.

On mechanism b.—In order to check the assumption of demethylation, the following reaction was performed: methyl naphthalene was passed through a pumice stone zone with air or through an oxidation catalyst zone with carbon dioxide instead of air under the same conditions as in the vapor phase oxidation (temperature, feed rate and gas rate).

The products were carefully distilled, but naphthalene was not found. The density and refractive index of the product were identical with those of the starting material.

Madison's experiment[14] showed the formation of naphthalene from methyl naphthalenes but the heating period in his case was more than one hour. In vapor phase oxidation, the contact time was less than one second, and it is assumed that naphthalene was not formed in such a short time.

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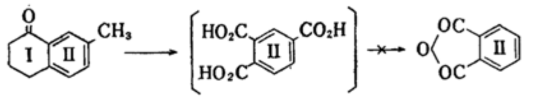
[13] G. B. Pickering et al., *Rec. trav. chim.* **69**, 535 (1950); *Chem. Abstr.*, **44**, 838 (1950).
[14] J. J. Madison et al., *Ind. Eng. Chem.*, **50**, 237 (1958).
[15] W. Kynaston, *J. Soc. Chem. Ind.*, **68**, 225 (1949).
[16] L. F. Fieser, *J. Am. Chem. Soc.*, **75**, 4377 (1953).

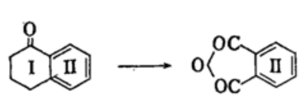
TABLE III. VAPOR PHASE OXIDATION OF METHYL NAPHTHALENES AND THEIR RELATED COMPOUNDS

Materials	Reaction temp. °C	Products: Phthalic anhydride mol. %	Maleic anhydride mol. %	Benzene tricarboxylic acid	Others	Material unreacted
Naphthalene	450	68	7	0	—	0
1-Methyl naphthalene	400	26	4	trace	a)	0
2-Methyl naphthalene	450	42	6	trace	b)	0
Naphthalene-1-carboxylic acid	400	27	21	—	—	4
Naphthalene-2-carboxylic acid	400	36	16	—	—	2
Tetralone	400	62	8	0	—	0
2-Methyl-1, 4-naphthoquinone	400	65	8	0	—	0
7-Methyl tetralone	400	0	3	trace	—	0

a) Trace of quinones
b) Trace of 2-methyl-1, 4-naphthoquinone

On mechanism **c**.—If the oxidation proceeds according to mechanism **c**, 1, 2, 4-benzene-tricarboxylic acid must produce phthalic anhydride. Consequently mechanism **c** is unlikely. To ascertain this conclusion, 7-methyl tetralone and tetralone were catalytically oxidized in the vapor phase under the same conditions. Tetralone produced phthalic anhydride in the same yield as that from naphthalene, but 7-methyl tetralone did not (Table III). The hydrogenated benzene ring of tetralone has an oxygen atom, and, on oxidation, this ring must have been cleaved in order to form phathalic anhydride. If the reaction proceeds similarly in the case of 7-methyl tetralone, the hydrogenated ring containing oxygen would be cleaved. This is the same course which 2-methyl naphthalene follows when it is oxidized through mechanism **c**.





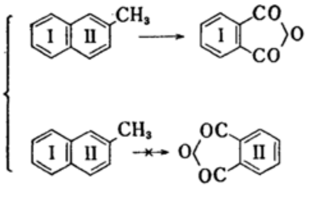
The oxidation products of 2-methyl naphthalene and 7-methyl tetralone caught in the hot part of an air condenser (collector of product) contained a trace of 1, 2, 4-benzene-tricarboxylic acid, which was identified by its melting point and neutralization equivalent. Thus, it is obvious that the benzene ring of methyl naphthalenes having no methyl group was cleaved, but no phthalic anhydride was produced.

On mechanism **d**.—If the benzene ring (II) of methyl naphthalenes having the methyl group is cleaved first and the resulting benzene ring (I) containing two side chains is oxidized, phthalic anhydride would be produced in the same way as from *o*-xylene. The benzene ring (II) of 2-methyl-1, 4-naphthoquinone which has a methyl group, contains two oxygen atoms. Therefore, by catalytic vapor phase oxidation, the benzene ring (II) is cleaved and the reaction follows only mechanism **d**.

The experiment showed that 2-methyl-1, 4-naphthoquinone produced phthalic anhydride in the yield of 65% which is the same as that obtained in the case of naphthalene and *o*-xylene. Accordingly, it is obvious that methyl naphthalenes produce phthalic anhydride only when it is oxidized through mechanism **d**.

From these experimental results it is seen that methyl naphthalenes do not produce phthalic anhydride by mechanism **c** but produce it in 60∼70% yield by mechanism **d**.

The yield of phthalic anhydride obtained from methyl naphthalenes is about 30∼40% by the catalyst used in these experiments (V_2O_5-MoO_3-pumice), German catalyst (V_2O_5-K_2SO_4-silica gel) or American catalyst (V_2O_5-alumina) and is about one half of that from naphthalene. It is conceivable that both reactions through mechanism **c** and **d** occur simultaneously to the same extent, as the presence of a trace of benzene-tricarboxylic acid was confirmed in the products.



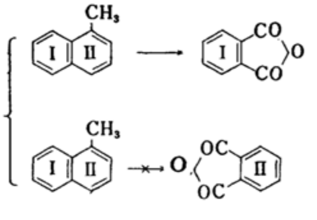
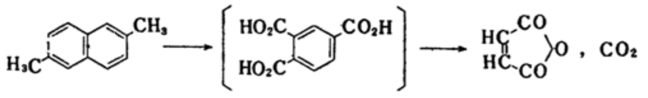
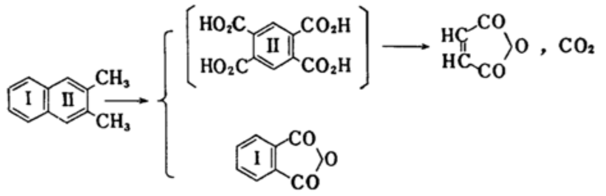


TABLE IV. VAPOR PHASE OXIDATION OF DIMETHYL NAPHTHALENES AND OTHERS

Materials	Reaction temp. °C	Products			
		Phthalic anhydride mol. %	Maleic anhydride mol. %	Naphthalic anhydride mol. %	Benzene tricarboxylic acid
2, 6-Dimethyl naphthalene	450	0	18	0	trace
2, 7-Dimethyl naphthalene	450	0	20	0	trace
Acenaphthene	450	0	14	39	0
Dimethyl naphthalene oil	400	15	8	0	trace
2, 3-Dimethyl naphthalene[a]	375	43	7	0	—

a) This result was obtained by Kinney et al. (V_2O_5-K_2SO_4-silica gel).





If it is desired to produce phthalic anhydride in high yield from methyl naphthalenes, it is necessary to find the catalyst that is capable of cleaving only the benzene ring of methyl naphthalenes which have a methyl group.

Vapor Phase Oxidation of Dimethyl Naphthalenes and Others.—Kinney[5] and coworkers obtained phthalic anhydride from 2, 3-dimethyl naphthalene in yields of 43% and 28% by the American and the German catalysts, respectively. Furthermore they obtained the anhydride in a 30% yield from a fraction (boiling in the 235∼270°C range) of coal tar.

The author oxidized 2, 6- and 2, 7-dimethyl naphthalenes and obtained no phthalic anhydride but maleic anhydride in yields of 18 and 20%, respectively, and very small amounts of benzenetricarboxylic acid. He also obtained phthalic anhydride in a 15% yield by vapor phase oxidation of dimethyl naphthalene oil (boiling range, 260∼268°C) of coal tar (Table IV).

Each of the two benzene rings of 2, 6-dimethyl naphthalene has one methyl group. Therefore, when either of them is cleaved by the oxidation, the resulting benzene ring has three side chains, and no phthalic anhydride would result according to the above-mentioned mechanism **c**. This conclusion agrees with the experimental results.

In the case of 2, 3-dimethyl naphthalene, one (II) of the two benzene rings has two methyl groups, and the other (I) has none. Therefore, when the benzene ring (II) which has two methyl groups is cleaved by vapor phase oxidation, phthalic anhydride would be produced by mechanism **d**, but when a benzene ring having no methyl group is cleaved, no phthalic anhydride would be produced by mechanism **c**. This conclusion agrees with the experimental results obtained by Kinney et al.

Acenaphthene is the compound that has an ethylidene group connecting positions 1 and 8 of naphthalene. Therefore, it is not conceivable that phthalic anhydride is formed. The author obtained naphthalic and maleic anhydrides but no phthalic anhydride.

From all the experiments mentioned above, it is concluded that the stability of rings and substituents against vapor phase oxidation in the decreasing order is as follows:

benzene ring > methyl group
> naphthalene ring > ethylidene group

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