Naphthalene as an Isolatable Reaction Intermediate in the Catalytic Vapor-phase Oxidation of Methylnaphthalenes to Phthalic Anhydride

By Charles J. NORTON

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Naphthalene has not been reported previously as a reaction intermediate in the heterogeneous vapor-phase oxidation of either monomethylnaphthalenes or dimethylnaphthalenes with air over vanadia catalyst at reactions which yield phthalic anhydride[1-3]. Recently, Morita tried unsuccessfully to detect naphthalene as an intermediate in the oxidation of 2-methylnaphthalene and naphthalene-1- and 2-carboxylic acid. For this reason, he concluded that naphthalene is not a reaction intermediate in the oxidation of methylnaphthalenes to phthalic anhydride[4].

The purpose of this communication is to report the discovery and isolation of naphthalene as an isolatable reaction intermediate under reaction conditions which are well known to effect its further oxidation to phthalic anhydride[1-6].

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TABLE I. FLUID-BED OXIDATIONS IN AIR OVER VANADIA CATALYST[1]

Free	Reaction condition			Mol. % coversion to various product					
	Temp. °C	Contact time sec.	Air-to-feed ratio l.(air)/g.(feed)	PA[2]	MA[3]	NQ[4]	HC[5]	N[6]	CO_2[7]
A. Oxidations at conditions for good phthalic anhydride pronduction									
Naphthalene	375	0.69	29	50.5	2.2	1.4	25.8[8]	—	20.1
22% 1-Methylnaphthalene 78% 2-Methylnaphthalene	375	0.66	91	30.9	2.6	3.1	3.8	(0.5)[10]	59.6
22% 1-Methylnaphthalene 78% 2-Methylnaphthalene	375	0.45	82	37.4	2.3	1.8	19.5	(2.3)[10]	39.1
2-Methylnaphthalene	375	0.49	99	37.8	5.9	3.6	13.4	(1.7)[10]	39.3
1,2-Dimethylnaphthalene	375	0.48	148	19.7	22.7	4.2	13.2	(1.0)[10]	40.2
1,7-Dimethylnaphthalene	375	0.48	165	15.5	3.0	1.1	4.9	(0.0)[10]	75.5
2,3-Dimethylnaphthalene	375	0.41	133	49.0	2.5	2.9		8.8[11]	36.8
B. Oxidations at milder conditions than required for good phthalic anhydride production									
1-Methylnaphthalene	324	0.26	7.34	low[9]	—	—	—	4.02[12]	—
1-Methylnaphthalene	324	0.15	6.78	low[9]	—	—	—	4.34[12]	—
1-Methylnaphthalene	347	0.10	4.71	low[9]	—	—	—	.2.18[12]	—

1) Davison powdered vanadia oxidation catalyst, 100~200 mesh, activated in air at 430°C for 2 hr.
2) PA=Phthalic anhydride
3) MA=Maleic anhydride
4) NQ=Naphthoquinone
5) HC=Total recovered hydrocarbons
6) N=Naphthalene
7) CO_2 determined by difference
8) Largely naphthalene
9) Phthalic anhydride produced in low yield, but not determined.
10) Determined by elution chromatography; too little to confirm by auxiliary analyses.
11) Determined by elution chromatography and confirmed by melting point and infrared and ultraviolet spectrometry.
12) Determined by gas-liquid chromatographic analyses.

The experiments related below were carried out in a laboratory fluid-bed catalytic flow reactor equipped with air and liquid feed devices, and a temperature controller. The condensable reaction products were caught in a series of traps and analyzed by a combination of gravimetric, spectrometric, and chromatographic procedures. Experimental conditions a reults are summarized in Table I.

Naphthalene was first isolated in an 8.8 mol. per cent conversion in the reaction product mixture obtained from 2, 3-dimethylnaphthalene under conditions which gave a 49.0 weight per cent conversion to phthalic anhydride. This naphthalene was separated from the product mixture by means of elution chromatography with petroleum ether over alumina. The identity and purity of the reaction product were established by m. p., 80.1~80.7°C, and gas-liquid chromatographic, infrared and ultraviolet spectrometric comparisons with an authentic sample of naphthalene.

Only small amounts of naphthalene were detected by elution chromatograms in the product mixtures obtained from the oxidation of 1-methylnaphthalene under the reaction conditions for good phthalic anhydride yields. However, improved conversions of 2.18 to 4.34 mol. per cent naphthalene were obtained under milder reaction conditions, which gave low yields of phthalic anhydride (see Part B, Table I). These reaction product mixtures were distilled to obtain a 15.2 g. naphthalene cut, b. p. 214~223°C/629 mmHg, which on recrystallization from ethanol gave an infrared spectrum entirely superimposable with one of an authentic naphthalene sample.

These experimental results conclusively demonstrate that naphthalene is an isolatable reaction intermediate in the heterogeneous vapor-phase oxidation of 2, 3-dimethylnaphthalene to phthalic anhydride. Although the naphthalene conversions were too small to be confirmed under conditions favoring good phthalic anhydride production from either 1- or 2-dimethylnaphthalene, larger naphthalene conversions were demonstrated and confirmed in the oxidation of 1-methylnaphthalene at milder reaction conditions, which are less favorable for good phthalic anhydride production. Consequently, any reaction mechanism or kinetic analysis for the heterogeneous vapor-phase oxidation of methylnaphthalenes over vanadia must consider naphthalene as an isolatable reaction intermediate which is produced in sufficient quantities to be desorbed from the catalyst and detected.

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The Denver Research Center
The Ohio Oil Company
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