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ACETOPHENONE IN THE GAS PHASE OXIDATION OF ETHYLBENZENE WITH PALLADIUM CATALYST

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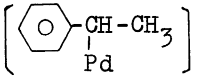
Acetophenone was obtained selectively accompanied by small amounts of styrene and carbon dioxide in the gas phase oxidation of ethylbenzene with palladium catalyst below 140°C. Acetophenone was postulated to form from the direct oxidation of ethylbenzene since styrene was not oxidized under similar conditions even at higher temperature.

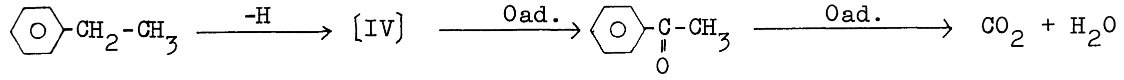
In a recent year, numerous novel reactions catalyzed by palladium metal have been widely investigated.[1)] A typical example is the production of vinyl acetate from ethylene[1-a)] and this process has been commercialized since 1968. We also studied this reaction extensively and proposed the reaction mechanism.[2)]

It is also well known that unsaturated hydrocarbons are generally oxidized to carbon dioxide and water with oxygen by palladium metal catalyst.[3)] In fact, we also found that aromatic hydrocarbons such as benzene, toluene, xylenes, isopropylbenzene, and n-butylbenzene, were oxidized quantitatively to carbon dioxide and water under these conditions. Partial oxidation products such as carbonyl compounds and/or carboxylic acids were scarcely formed in these oxidations.

Surprisingly, ethylbenzene was exceptional, and afforded partial oxidation products. Thus, acetophenone (I) was formed selectively accompanied by small amounts of styrene (II) and carbon dioxide (III) below 140°C, as shown in Table 1. Table 1 indicates clearly that acetophenone is produced selectively under the following conditions ; 1) at lower temperature 2) greater molar ratio of ethylbenzene to oxygen 3) lower concentration of catalyst 4) in the absence of water.

Preliminary experiments showed independently that acetophenone was easily oxidized to carbon dioxide with the same catalyst over 140°C, and no oxidation product was formed from styrene even at 180°C and in the presence of water.

These results suggest that acetophenone is not formed via styrene in the present reaction. Acetophenone may be formed by the direct oxidation of ethylbenzene via an intermediacy,  (IV), which is derived from abstraction of α-hydrogen of ethylbenzene by palladium.[4)]



(Oad. ; adsorbed oxygen)

Table 1 . Gas Phase Oxidation of Ethylbenzene with Palladium Catalyst

Exp.	Pd	Gas Composition(%)				Temp.	Rate of Product Formation[b)]			Selectivity(%)[c)]		
No.	conc.[a)]	PhEt	O_2	N_2	H_2O	(°C)	(I)	(II)	(III)	(I)	(II)	(III)
1	2	10	19	71	0	130	1.35	0.20	2.00	74.9	11.1	14.0
2	2	10	19	71	0	150	0.94	0.95	37.0	14.5	14.6	70.9
3	2	61	8	31	0	130	1.08	0.01	1.12	87.5	0.8	11.7
4	2	61	8	31	0	200	0.48	0.33	13.65	19.1	13.1	67.8
5	0.1	10	19	71	0	130	0.75	0.10	0.48	82.4	11.0	6.6
6	0.1	10	19	71	0	200	0.68	0.92	3.27	33.9	45.8	20.3
7	0.1	8	14	57	21	130	0.03	0.14	0.32	14.3	66.4	19.3
8	0.1	8	14	57	21	200	0.09	0.80	4.31	7.4	56.6	36.0

a) wt% (for carrier (Al_2O_3)), b) (mmol/cat. g .hr) x 10^{-1}

W/F ; 2.53 x 10^{-2} (cat.g.hr/mmol), c) $\frac{(I)\ (\text{or } II,\ III)}{(I)+(II)+1/8(III)} \times 100$

In this communication, catalyst was prepared as previously reported1) and all reactions were performed using a usual flow system.

REFERENCES

1) a) Bayer, Belg. 627888 ; National Distillers, U. S. 3190912.

b) S. Nakamura and T. Yasui, Synthetic Commun., 1, 137 (1971).

c) T. Kunugi, T. Matuura, and T. Kono, Kogyo Kagaku Zasshi, 71, 1517 (1968).

d) H. J. Arpe and L. Härnig, Erdöl und Kohle, 23, 79 (1970).

2) S. Nakamura and T. Yasui, J. Catal., 17, 366 (1970) ; ibid., 23, 315 (1971).

3) For example ; H. H. Voge and C. R. Adams, "Advances in Catalysis", 17, 208 (1967).

4) For example ; G. C. Bond and P. B. Wells, "Advances in Catalysis", 15, 91 (1964).

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