New Catalytic Synthesis of Ketones by the Oxidation of Olefins

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(Received September 4, 1968)

It is well known that α-olefins are oxidized to ketones by a palladium chloride catalyst with copper chloride in the presence of hydrogen chloride and water.1) However, in the heterogeneous oxidation of olefins, allylic oxidation has been mainly reported to occur and no catalyst effective in forming ketones has yet been found. In this communication we wish to report a new catalytic synthesis of ketones by the gas-phase oxidation of olefins in the presence of steam.

The catalyst used in the present synthesis is composed of tin- or cobalt oxide combined with molybdenum trioxide. The atomic ratio of the tin or the cobalt to the molybdenum in the catalyst is usually larger than unity. Sn-90/Mo-10 and Co-90/Mo-10 catalysts were used in this experiment. The catalyst was prepared by the thermal decomposition of a mixture of tin- or cobalt hydroxide and an aqueous solution of ammonium molybdate. It was molded into cylindrical tablets and was fired in air at 550°C for 5 hr before the run. The reactions were carried out in a flow system at an atmospheric pressure. The reaction products were separated by gas chromatography and were identified by mass spectrometry. Typical experimental results are tabulated in Table 1.

Propylene, *n*-butenes, and 1-pentene were converted to acetone, methyl ethyl ketone, and methyl propyl ketone (including diethyl ketone), respectively. When the reactions were carried out at higher temperatures, the per-pass conversion of olefins increased, whereas the selectivity to ketones was decreased by the side reactions forming acetaldehyde, acetic acid, and carbon dioxide.

Ethylene did not react under the same conditions and gave only carbon dioxide at higher temperatures. Isobutene, which has no corresponding ketone, was converted mainly to tertiary butanol and diisobutene under the same conditions, and to α-methylacrolein and carbon dioxide at higher temperatures. On both the tin and cobalt catalysts, primary and secondary alcohols were easily oxidized to the corresponding aldehydes and ketones respectively. These results suggest that ketones, were formed *via* the hydration of olefins to form alcoholic intermediates followed by oxydehydrogenation. Since it has been established that acid catalysts are effective for the hydration of olefins, and since tin-molybdenum and cobalt-molybdenum heteropolyacids are known, it seems that the heteropolyacid is responsible for the first step of the reaction.

Some binary oxides, such as Cr_2O_3-MoO_3, Fe_2O_3-MoO_3, and CuO-MoO_3, were also effective in forming acetone from propylene, however, the selectivities to acetone were far lower than in the cases of SnO_2-MoO_3 and Co_3O_4-MoO_3.

TABLE 1. REACTIONS OF OLEFINS OVER SnO_2-MoO_3 AND Co_3O_4-MoO_3 CATALYSTS

Olefin	Ketone	Catalyst	Reaction temp. (°C)	Conversion of olefin (%)	Selectivity to ketone* (%)
$CH_2=CHCH_3$	CH_3COCH_3	Sn-Mo	135	9.0	85.3
		Co-Mo	210	4.0	75.3
$CH_2=CHC_2H_5$	$CH_3COC_2H_5$	Sn-Mo	135	4.8	85.3
		Co-Mo	240	2.2	60.8
$CH_3CH=CHCH_3$	$CH_3COC_2H_5$	Sn-Mo	155	9.2	58.8
(trans)		Co-Mo	233	2.5	26.7
$CH_2=CHC_3H_7$	$CH_3COC_3H_7$**	Sn-Mo	158	8.0	65.4

Experimental condition.
Catalyst, 16—20 g. GHSV, 400—450.
Reactant gas composition, Olefin 20 vol%, O_2 30%, H_2O 30%, N_2 20%.
* Values exclusive of isomerization.
** Including diethyl ketone.

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1) J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Ruttinger and H. Kojer, *Angew. Chem.*, **71**, 176 (1959); **74**, 93 (1962).