The Catalytic Synthesis of Olefins from Aldehydes and Ketones over Manganese Dioxide

By D. H. PIEHL

(Research Department, R. J. Reynolds Tobacco Co., Winston-Salem, North Carolina 27102)

A NOVEL vapour-phase conversion of aliphatic aldehydes and ketones into olefins over a supported manganese dioxide catalyst has been observed. In previous reports of similar reactions, either the conversions have been performed in a hydrogen atmosphere or longer-chain olefins were formed through condensation.[1] This is the first report of the direct catalytic conversion of aldehydes and ketones into the corresponding olefins in a non-reducing atmosphere.

The reactions were carried out with a pulsed micro-catalytic reactor similar to the one described by Pines.[2] The reaction temperature was 550° at a pressure of 50—75 lb./in.[2] of nitrogen with contact times less than 1 sec. 1 μl. Samples of low-molecular-weight aliphatic aldehydes and ketones were pulsed over Harshaw (Mn-0201T) manganese dioxide (1 g.) supported on 1/8 in. alumina pellets. The effluent was analysed directly by g.l.c. and retention times and i.r. analysis of samples obtained from multiple injections were used to identify the products.

The following conversions were obtained without optimizing the conditions:

Isobutyraldehyde	→ Isobutene	40%
n-Butyraldehyde	→ But-1-ene	25%
Acetone	→ Propene	45%
Crotonaldehyde	→ Butadiene	25%
n-Heptaldehyde	→ Hept-2-ene	~5%
Pentan-2-one	→ Pent-1-ene	62%
Cyclohexanone	→ Cyclohexene	22%

The method appears to be of general application based on a limited number of reactions, but reactions on the macro-scale have not been examined as yet.

$$RCH_2 \cdot CO \cdot R \rightarrow RCH : CHR$$
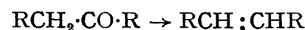
A kinetic study of the formation of isobutene from isobutyraldehyde was carried out by varying the reactant concentration in tetrahydrofuran from 30 to 70% by volume. It appeared that the reaction is one-half order in aldehyde. At a concentration of 10% there was an almost quantitative conversion and yield.

An Arrhenius plot of isobutene formation gave an approximate activation energy of 13 kcal.mole[-1].

[1] R. H Griffith, J. Chem. Soc., 1945, 715; V. I. Komarewsky and T. H. Kritchevsky, J. Amer. Chem. Soc., 1943, 65, 547; C. Capitani and E. Mugnaini, Ital. P. 526142. (May 14th, 1955).
[2] P. Steingaszner and H. Pines, J. Catalysis, 1966, 5, 356.