Reaction of Diazomethane on a Cobalt Molybdate Catalyst. The Mechanism of Olefin Disproportionation

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Summary Activities of cobalt molybdate catalysts for disproportionation of propene parallel activities for converting diazomethane into nitrogen and ethylene.

THE mechanism involving an adsorbed "cyclobutane" intermediate for the catalytic disproportionation of olefins[1,2] has been criticised by Petit[3] on the grounds that negligible quantities of cyclobutane are obtained; nor does cyclobutane react readily under conditions where labelled ethylene easily disproportionates.

Petit[3] has suggested an alternative mechanism in which the carbon–carbon σ-bonds of the chemisorbed ethylenes are ruptured simultaneously with the π-bonds, so that excited or ground-state cyclobutane is never realized. The suggested transition state for disproportionation therefore approaches a tetracarbene–metal complex. Such a drastic reduction in bond order could arise if there is extensive donation from and back-donation to the bonding and antibonding π-orbitals, respectively, of adsorbed olefins. We report here data from reactions of diazomethane on an olefin disproportionation catalyst in support of Petit's mechanism.

A commercial cobalt molybdate (Laporte "Comox") has optimum activity for propene disproportionation after heating for 2 h at 773 K in oxygen and *in vacuo* for 18 h at

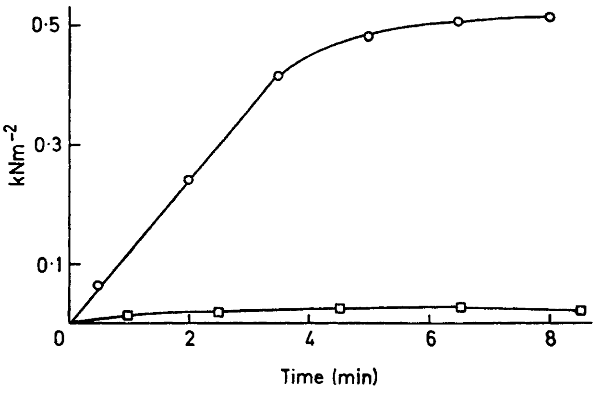

FIGURE. *Conversion of diazomethane into ethylene at* 293 K *on a cobalt molybdate catalyst after evacuation at* 823 K. ○ , 18 h; □, 1 h.

823 K. The half-life of approach to equilibrium between propene and products is about 5 min at 353 K using 0·5 g of catalyst and $5{\cdot}3 \times 10^3\ Nm^{-2}$ of propene in a static reactor ($2{\cdot}0 \times 10^{-4}\ m^3$) coupled by a gas-sampling valve to a g.l.c. unit. Addition of $5{\cdot}3 \times 10^3\ Nm^{-2}$ of ether to the propene had no effect on the reaction rate. When $5{\cdot}3 \times 10^3\ Nm^{-2}$ of a mixture of 20% diazomethane in ether was added to activated catalyst at 293 K completely selective rapid formation of ethylene was observed (Figure). After evacuation the catalyst had the same reactivity for conversion of propene at 353 K. However, a catalyst sample which was heated at 773 K in oxygen for 3 h and *in vacuo* at 823 K for 1 h gave negligible conversion of propene and had very little activity for forming ethylene from diazomethane (Figure).

The results clearly suggest that the sites on molybdate catalysts which disproportionate olefins also selectively convert adsorbed methylenes into ethylene.

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