

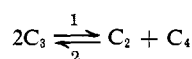
Direct Transformation of Ethylene to Propylene on an Olefin Metathesis Catalyst

Sir:

Olefin metathesis is now a well-established reaction for a variety of homogeneous and heterogeneous catalysts, consisting of complexes of molybdenum, or of some of its neighbors, in the transition series of metals.^{1,2}

We report here evidence for the novel direct transformation of ethylene to propylene on an olefin metathesis catalyst prepared from Mo(CO)₆ and Al₂O₃.

Reactions were carried out at 80° using propylene (40 mm) in a static reactor (200 ml) coupled by a gas sampling valve to a glc unit. A fresh sample of catalyst was used in each experiment unless otherwise indicated. A cobalt molybdate catalyst (Laporte Comox) activated at 500° for 2 hr and *in vacuo* at 550° for 18 hr caused rapid disproportionation to equal amounts of ethylene and butenes, as expected from the following reversible reactions. However, very different distri-



butions were obtained using a catalyst prepared from molybdenum hexacarbonyl and Laporte type A alumina. A typical sample consisted of 0.5 g of alumina pretreated in air at 500°, cooled in a desiccator, intimately dry mixed with 0.0668 g of molybdenum hexacarbonyl, and activated by evacuation at 90° for 2 hr. The samples were bright yellow but activation at higher temperatures caused a change to sandy brown. Product distributions for two successive runs on the same sample, with evacuation between runs for 15 min at 90°, are shown in Figure 1.

The striking feature is that the C₄ yields greatly exceed those of C₂. In the second run the difference was much smaller and in subsequent runs the catalyst changed more to sandy brown, with the C₄/C₂ ratios slowly approaching unity. The C₄/C₂ ratios in initial runs also declined in like fashion with increasing activation temperature above 90°. The large ratios cannot be explained by reactions 1 and 2 alone. Ethylene produced by reaction 1 must be reacting further by either reaction 3 or 4.



Ethylene cannot give new products by reaction 1, but when used as reactant was very slowly converted to propylene at 80°. The temperature was then raised to 210° over a period of 2 hr and the product distributions observed are shown in Table I.

Table I

Temp, °C	C ₂ , %	C ₃ , %	C ₄ , %	C ₅ , %
130	95.6	4.4		
150	91.0	9.0		
165	77.3	18.7	4.0	
210 ^a	39.5	8.7	3.5	48.3

^a Per cent C₂-C₅ normalized to 100%.

(1) R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**, 170 (1964).

(2) E. A. Zuech, *Chem. Commun.*, 1182 (1968).

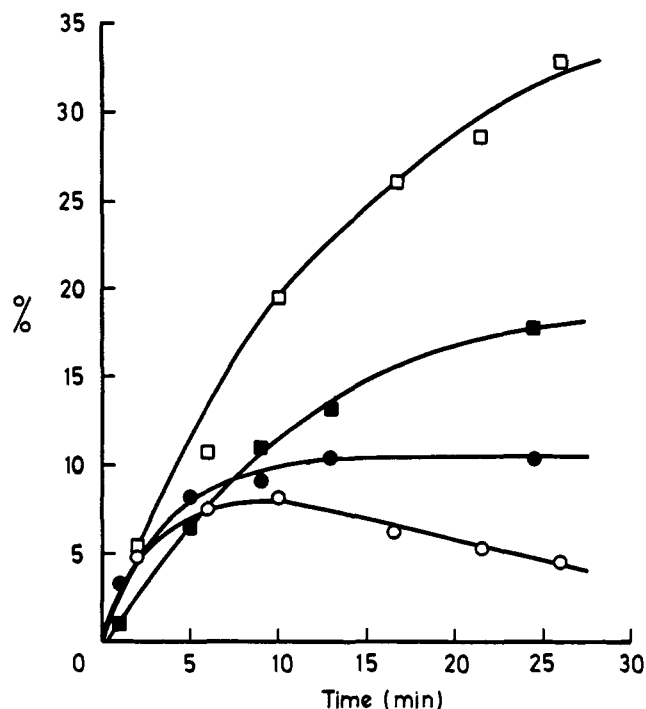


Figure 1. Reaction of propylene on Mo(CO)₆-Al₂O₃: first run, C₂H₄(○), C₄H₈(□); second run, C₂H₄(●), C₄H₈(■).

The most striking feature is the large yield of pentenes at 210° (also small amounts of hexenes and heptenes) in contrast to the low yield of butenes. If metathesis is responsible the pentenes should be formed from but-1-ene and propylene, so the results indicate that the pentenes arise from addition of C₂ to C₃.

When an equimolar mixture of C₂ and C₃ was used at 80°, reactions of both were also very slow, as with ethylene itself. Propylene was then reacted until there were 5.5, 82, and 12.5% of C₂, C₃, and C₄, respectively, and a dose of ethylene added. Ethylene now reacted readily and the percentage yields of butenes and especially propylene rose as shown in Figure 2.

These results are more in accord with reaction 3 than 4. Reaction 3 was conclusively proved by the following experiment. Perdeuteriopropylene was allowed to react at 80° in a static vessel, coupled by a leak to a mass spectrometer, until substantial amounts of butenes were observed. A large dose of ethylene-*d*₀ was then added. It decreased rapidly with a corresponding large increase in propylene-*d*₀ but not in butene-*d*₀.

When ethylene was added to activated Comox at 80° very slow formation of propylene was also observed and the yield increased with temperature (21% C₃ at 300°), but the only other products were negligible amounts of butenes.

Catalysts prepared from molybdenum hexacarbonyl and alumina are variable in activity and the sites labile compared to Comox. Thus, Kemball and coworkers³ reported wide variations in rates of a standard reaction of propylene at 25° on the same type of catalyst. Several features are noteworthy in the present work. (i) Ethylene is converted very slowly to propylene and also poisons disproportionation of propylene if added prior to or simultaneously with propylene to the catalyst. Ethylene is therefore more strongly bonded to

(3) E. S. Davie, D. A. Whan, and C. Kemball, *ibid.*, 1202 (1971).

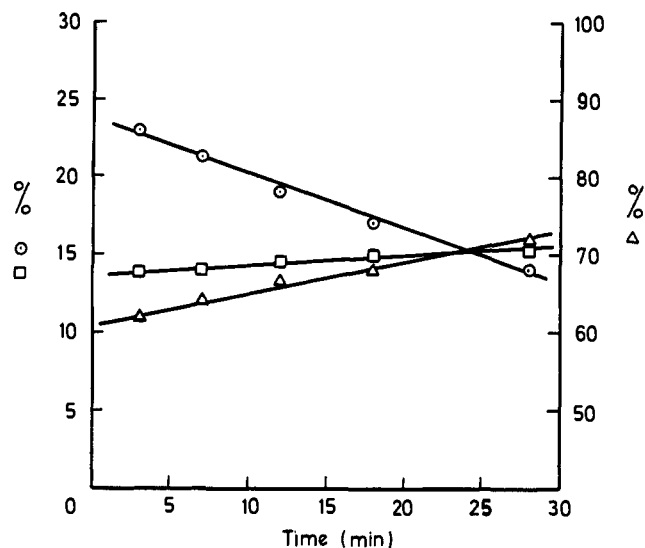
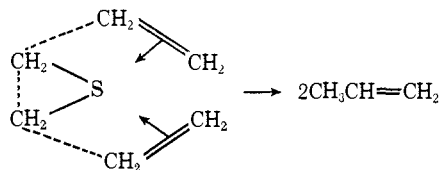


Figure 2. Product distribution on admission of ethylene to a propylene reaction: \circ , C₂H₄; Δ , C₃H₆; \square , C₄H₈.

the sites than higher alkenes. (ii) Reaction 3 is quite rapid when ethylene is added to a system where propylene has already been reacting for some time. (iii) The sites which cause reaction 3 are more labile than those which can only give reactions 1 and 2. (iv) The catalyst is also distinguished from Comox by formation of high yields of pentenes from ethylene at higher temperatures.

The following is an attempt to outline mechanisms involving methylene complexes for reaction 3. The splitting of one ethylene into methylenes, and addition of each of the latter to another ethylene, followed by rearrangement of the resulting trimethylene, seems to be the most straightforward pathway for directly converting ethylene to propylene. However, the possibility that a very different type of mechanism is responsible cannot be discounted. If only two ethylenes are allowed per site then adsorbed methylene is an intermediate. A concerted reaction of three ethylenes per site is also possible. The following diagram attempts to illustrate this without specifying complete details of coordination and bonding.



The influence of prior addition of propylene is intriguing. Formation of π -allyl complexes is indicated. This would enrich electron density on the metal, thereby enhancing back-donation of charge to π^* orbitals of adsorbed olefin, with consequent easier rupture of ethylene to methylene. In view of the novel arene molybdenum π -allyl derivatives recently described by Green and coworkers,⁴ it is possible that allyl and three ethylenes are ligands of one molybdenum which is attached to the support by coordination to one or two oxide or hydroxide ions. π -Allyl could also be the key intermediate in the addition of ethylene to propylene, giving pentenes.

(4) M. L. H. Green, J. Knight, L. C. Mitchard, G. C. Roberts, and W. E. Silverthorn, *Chem. Commun.*, 1619 (1971).

Pettit⁵ has argued that the transition state in olefin metathesis is a tetracarbene-metal complex rather than an adsorbed "cyclobutane." Thus, reaction 3 may also have significance in attempting to prove whether carbene complexes can form from olefins on such catalysts, even though the site responsible for different reactions may not be identical.

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(5) G. S. Lewandos and R. Pettit, *Tetrahedron Lett.*, 789 (1971).

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Sodium Magnetic Resonance in Lyotropic Nematic Phases and the Implications for Observation in Living Systems

Sir:

Flautt and Lawson¹ have described the first lyotropic nematic phase which could be used as a solvent for oriented molecule nmr spectra.^{2,3} The recommended phase corresponds to the middle soap structures^{4,5} in a ternary phase to which sodium sulfate was added for ease of preparation. The ordering of the nematic structure of the phase in a magnetic field has a long relaxation time of several hours and the optic axis is perpendicular to the magnetic field direction.¹ We have investigated the ²³Na nmr signals at 8.0 MHz in this phase with and without the addition of sodium sulfate. Typical results are presented in Figure 1. In a ternary phase without addition of sodium sulfate, the signal is a triplet of intensity ratios 3:4:3 arising from an incompletely averaged quadrupole interaction tensor,⁶ first order with respect to a nuclear Zeeman splitting. The separation of the outer components of the triplet is given by⁶

$$\Delta\nu = \nu_Q \langle 3 \cos^2 \theta - 1 \rangle = 2\nu_Q S_{zz} \quad (1)$$

ν_Q is half the quadrupole coupling constant (e^2qQ/h) and θ is the angle between the magnetic field and the principal axis of the electric field gradient (EFG) tensor (axial symmetry). S_{zz} represents the degree of orientation of the EFG axis. The central peak of this triplet is 40% the intensity of the signal from the same concentration sodium ion in water, which has no quadrupole splitting. The intensity of the outer transitions is thus properly accounted for with a ratio 3:4:3. On first observation when inserted into the magnet there is some evidence of the "powder type" spectrum in which the two outer components are broadened and the derivative curve tails toward the central peak. The central peak is always sharp, since it is unaffected by any randomization of the direction of partially averaged

(1) K. D. Lawson and T. J. Flautt, *J. Amer. Chem. Soc.*, 89, 5489 (1967).

(2) K. D. Lawson, P. J. Black, and T. J. Flautt, *Mol. Cryst. Liquid Cryst.*, 7, 201 (1969).

(3) K. D. Lawson and T. J. Flautt, *J. Phys. Chem.*, 72, 2066 (1968).

(4) V. Luzzati, H. Mustacchi, and A. Skoulios, *Discuss. Faraday Soc.*, 25, 43 (1958).

(5) L. Mandell, Krister Fontell, and P. Ekwall, *Advan. Chem. Ser.*, No. 63, 89 (1967).

(6) M. H. Cohen and F. Reif, *Solid State Phys., Suppl.*, 5, 321 (1962).