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Letter to the Editors

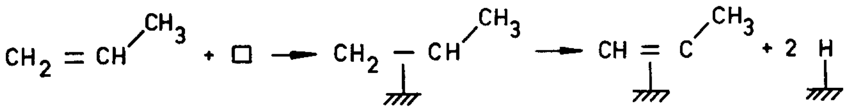
On the Mechanism of the Disproportionation of Olefins

In studies on the disproportionation (or dismutation) of olefins, a new catalytic process developed by Banks and Bailey (*1*), Bradshaw *et al.* (*2*) suggest that the reaction proceeds via a "quasi-cyclobutane" intermediate. We have studied the mechanism of this process and particularly the disproportionation of propylene.

$$2C_3H_6 \rightleftarrows C_2H_4 + C_4H_8$$

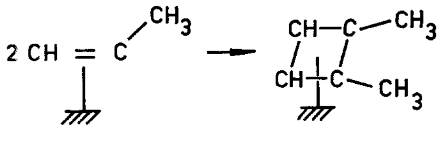
Active catalysts for the disproportionation are MoO_3, WO_3, $Mo(CO)_6$, $W(CO)_6$, and Re_2O_7 on alumina or silica (*1*, *3*)

We propose the following mechanism. First propylene is adsorbed on the surface of the catalyst with a π-bond and hydrogen abstraction takes place.



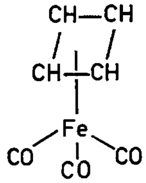
Here, □ is a vacancy at the surface. The π-bond is formed by overlap of the π-bonding and π-antibonding orbitals of the propylene molecule with, respectively, the e_g and t_{2g} orbitals of the metal.

Hereafter a 1,2-dimethylcyclobutadiene intermediate is formed.



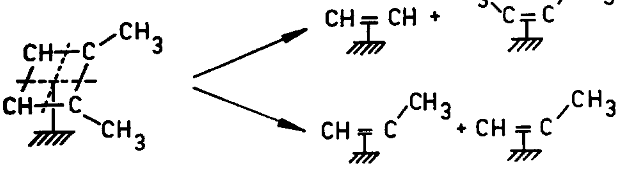
The 1,2-dimethylcyclobutadiene is aligned to the catalyst surface by overlap of the individual p_z orbitals of the carbon atoms of the ring with the d orbitals of the metal, or by overlap of a linear combination of the p_z orbitals with the metal d orbitals.

The structure of the intermediate may be analogous to that of cyclobutadieneiron tricarbonyl, described by Pettit *et al.* (*4*, *5*).



Pettit *et al.* report data which indicate that this complex has an aromatic character.

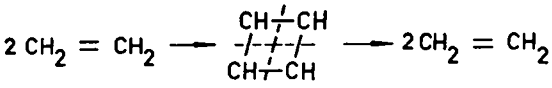
At last, if all steps are reversible, the intermediate will be broken along one of the dotted lines.



After recombination with hydrogen, propylene, ethylene, and 2-butene will appear in the gas phase.

The distribution of the disproportionation products of propylene matches in detail this mechanism. Nearly equimolar amounts of ethylene and butene are formed, while there is evidence that of the butenes primarily only 2-butene is formed. The percentage of 1-butene in the reaction mixture draws near to zero at short contact times, while the percentage of 2-butene increases. The formation of *cis*-2-butene is favored and particularly at short contact times the cis/trans ratio is larger than thermodynamics predicts.

The proposed mechanism explains also that ethylene is virtually inert towards disproportionation catalysts.



In our opinion the cyclobutadiene intermediate, proposed in the above, is the "quasi-cyclobutane" intermediate, suggested by Bradshaw *et al.*

It should be noted that our considerations, as well as those of Bradshaw, are based on the supposition of the formation of a four-membered carbon ring intermediate. We successfully proved this supposition for the disproportionation of propylene in submitting a ^{14}C-tagged propylene, viz. propylene-2-^{14}C, to this reaction; the butene formed was radioactive in contrast with the ethylene formed, which showed no radioactivity at all.

REFERENCES

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