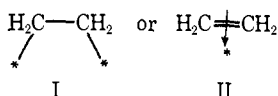Martin A. Schwartz, Robert A. Holton

Department of Chemistry, The Florida State University
Tallahassee, Florida 32306
Received December 17, 1969

Formation of π-Allyl Complexes by Adsorption of Propylene on Zinc Oxide

Sir:

Many of the mechanistic features of heterogeneous hydrogenation catalysts are accommodated by the assumption that adsorbed olefin reacts (reversibly or irreversibly) with an adsorbed hydrogen atom to form a surface alkyl which subsequently reacts with another adsorbed hydrogen atom to form alkane.[1] It is traditionally assumed that the adsorbed olefin is bound to the surface either by two σ bonds (I) or by a single π bond (II), *e.g.*

$$\underset{\underset{*}{/}\ \underset{*}{\backslash}}{H_2C-CH_2} \quad \text{or} \quad \underset{\underset{*}{\Updownarrow}}{H_2C=CH_2}$$

$$\text{I} \qquad\qquad \text{II}$$

where * stands for a surface atom. Isomerization of olefins, which accompanies hydrogenation, is also included in this scheme as follows.
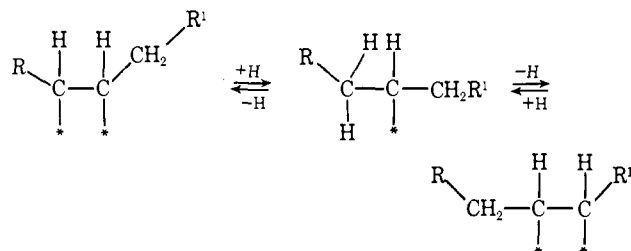
In line with the above, hydrogen is a cocatalyst for the isomerization of olefins over a number of metals.[2,3] Over cobalt,[4] however, isomerization is detectable in the absence of hydrogen (although it proceeds at a much lower rate), and over chromia isomerization of olefins may be faster in the absence of hydrogen than when it is present.[5] Clearly, isomerization in the absence of hydrogen calls for a different mode of olefin adsorption. Burwell, *et al.*,[6] proposed that dissociative adsorption of olefins to form allylic species could explain the results over chromia. Later, Rooney and coworkers[7] suggested that many of the features of exchange, isom-

erization, and racemization reactions related to hydrogenation are better explained if we assume olefins can form a π-allyl complex on the surface. Evidence for such π-allyl species stems largely from mechanistic considerations. In this paper we present infrared evidence that on at least one hydrogenation catalyst, zinc oxide, olefins adsorb to form allyl species in which the π bond appears to contribute to the bonding to the surface. Zinc oxide is particularly well suited for such a study of dissociatively adsorbed olefin because surface hydrogen species (formed from hydrogen adsorption) are known to give rise to strong bands at 3500 and 1710 cm^{-1} which have been assigned to surface OH and ZnH, respectively.[8] Both of these bands are shifted somewhat in the presence of olefins.[9]

At room temperature propylene adsorbs rapidly on zinc oxide to form a species not removable by evacuation at room temperature for 16 hr. This adsorbed species, however, is completely removed by evacuation at 125° for 2 hr, and collection and analysis of the desorbed gas reveal that it is essentially pure propylene. By way of contrast adsorbed ethylene, also recoverable unchanged, can be removed by brief evacuation at room temperature.[9] This dramatic difference in the strength of chemisorption for these two olefins clearly suggests a basically different mode of adsorption.

If the spectrum of the zinc oxide is observed during admission of propylene, one sees the immediate appearance of bands at 3590 and 1545 cm^{-1} as well as bands in the C-H stretching and deformation region. The band at 3590 cm^{-1} can be reasonably assigned to a surface OH, whereas the band at 1545 cm^{-1} occurs in a region characteristic of a weakened C=C bond such as that found in π complexes.[10,11] This assignment can be checked by examination of the spectrum of adsorbed perdeuteriopropylene. A band corresponding to a surface OD appears at 2655 cm^{-1}; the relative isotope shift for this band is essentially the same as that encountered for the OH and OD bands formed by adsorption of H_2 and D_2, respectively.[8,9] As well as the expected shifts for C-D bands, a band appears at 1475 cm^{-1} which corresponds to the 1545-cm^{-1} band for adsorbed C_3H_6. This isotope shift is too small for either a ZnH or CH bond, but it is comparable to the shift in C=C stretch found for gaseous propylene on deuteration, *i.e.*, from 1652 to 1588 cm^{-1}.[12]

Further details on the nature of adsorbed propylene are supplied by the spectra of deuterium-labeled propylenes. Adsorption of 2-deuteriopropylene yields a surface OH band and a spectrum consistent with adsorbed propylene with one C-D stretch; this spectrum does not change over a period of several hours. Absorption of 1,1-dideuteriopropylene yields initially a surface OH band and a spectrum consistent with adsorbed propylene with more than one C-D stretch. In time, however, the spectrum changes; the OH band intensity decreases and an OD band appears. The growth in intensity of the OD band is coordinated with the decrease in in-

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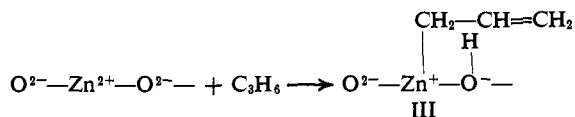
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tensity of the OH band. Slight changes also occur in the C–H and C–D region of the spectra.

The above data clearly show that hydrogen is removed from propylene to form an allyl group. If, following Burwell's picture of adsorption on chromia,[5b] we view hydrogen adsorption on zinc oxide as heterolytic

$$-Zn^{2+}-O^{2-}- + H_2 \longrightarrow \overset{\overset{\displaystyle H}{|}}{-Zn^+}-\overset{\overset{\displaystyle H}{|}}{O^-}-$$
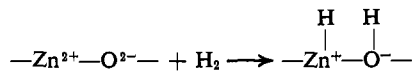
the formation of an allyl species involves a similar heterolytic fission

$$O^{2-}-Zn^{2+}-O^{2-}- + C_3H_6 \longrightarrow O^{2-}-\overset{\overset{\displaystyle CH_2-CH=CH_2}{|}}{\underset{\overset{\displaystyle |}{III}}{Zn^+}}-\overset{\overset{\displaystyle H}{|}}{O^-}-$$

Such a formulation has the advantage that it offers a natural explanation of why no ZnH band is observed: the allyl group blocks the Zn part of the active site. The shift in the C=C bond frequency suggests there is participation of the π bond in the bonding. When manganese carbonyl reacts with allyl chloride to form a σ-allyl complex (III), the double-bond frequency (1620 cm^{-1})[11] is only slightly different from that for gaseous propylene (1652 cm^{-1}).[12] However, when it forms a π-allyl complex (IV), the double-bond frequency shifts dramatically, i.e., to 1505 cm^{-1}.[11] Such behavior is typical of transition metal–allyl complexes. Since the shift in double-bond frequency we observe is pronounced, it seems reasonable to view the surface species as a π-allyl complex bound to zinc. With this interpretation, the changes with time that are found in the spectrum of adsorbed 1,1-dideuteriopropylene can be accommodated by the following.[13]
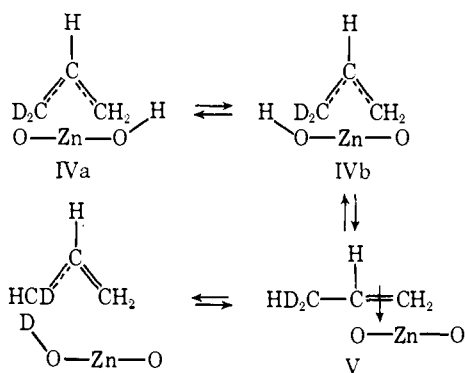
Three further points should be stressed. (1) In the above discussion we include the "dynamic" allyl system (which may be more than one type of species[14]) in the term π-allyl complex; the infrared spectra are not sufficiently diagnostic to differentiate these species.[15]

(2) The bonding to the surface zinc atom involves more π interaction than that found for diallylzinc in

solution; for the latter $\nu_{C=C}$ occurs at 1613 to 1622 cm^{-1}[16] compared to 1545 cm^{-1} for the adsorbed species.

(3) Propylene may form other species on the surface; our results indicate only that the π-allyl complex is the major (and perhaps the only) surface species present.

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A. L. Dent, R. J. Kokes
Chemistry Department, The Johns Hopkins University
Baltimore, Maryland 21218

Self-Reaction of Diethylnitroxide Radicals[1]

Sir:

Although the self-reactions of alkylperoxy radicals have received considerable attention in recent years,[2-6] the self-reactions of the isoelectronic dialkylnitroxide radicals have been almost entirely neglected. We wish to report the results of an esr investigation of the self-reaction of diethylnitroxide carried out over a wide range of temperature. The results show some interesting parallels and differences when compared with the behavior of the alkylperoxy radicals.

The experimental procedure was similar to that employed in our studies of peroxy radicals.[5] The nitroxide was best prepared from 10^{-2} M diethylhydroxylamine in CF_2Cl_2 by direct photolysis at temperatures below $-60°$ and by photolysis in the presence of 10^{-1} M di-t-butyl peroxide above $-60°$. The spectrum was similar to that previously reported for diethylnitroxide formed in the reaction of diethylformamide with hydrogen peroxide.[7] The radicals generally disappeared with reasonably clean second-order kinetics, occasional deviations being observed at the beginning or end of the main decay. These deviations are presumably due to the formation of some radicals having stabilities different from that of the main radical, diethylnitroxide. The same bimolecular rate constant was obtained from decays measured over two orders of magnitude in the initial radical concentration.

The rate constant for the decay of tertiary peroxy radicals decreases rapidly as the temperature is lowered ($E_t = 8–9$ kcal/mol[2-6]). In complete contrast the temperature coefficient for the decay of diethylnitroxide in CF_2Cl_2 is very small or zero.[8] At 30° the bimolecu-

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