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Base Catalyzed Adsorption of Toluene by Zinc Oxide

In a recent series of publications, the late Professor Kokes and his co-workers reported experimental evidence which indicated that zinc oxide can act as a base in catalytic reactions with unsaturated hydrocarbons. From studies of the interaction of molecular nitrogen (*1*) and molecular hydrogen (*2*) (type III) (*3*) with dissociated hydrogen (type I) (*4*) on zinc oxide, they concluded that the limited number of active zinc and oxide sites are paired. In addition, ethylene (*4*) was observed to chemisorb on zinc oxide rapidly and reversibly, but ir data indicated that the ethylene did not lose its vinyl hydrogen upon adsorption. Therefore, it was concluded that ethylene chemisorption on zinc oxide was nondissociative. In contrast, ir data obtained with deuterium-labeled propylene (*5*) showed that propylene adsorption was dissociative on zinc oxide and involved the rupture of the methyl carbon–hydrogen bond. These studies also provided evidence that the dissociated hydrogen was attached to an oxide ion, whereas the hydrocarbon moiety was probably bound to the zinc ion of the active pair site. Inasmuch as the zinc and oxide ions of the pair are Lewis acids and bases, respectively, it is reasonable to expect that the allyl species will have anionic character and the abstracted hydrogen will have protonic character.

In later reports, Chang and Kokes (*6,7*) showed that the dissociative adsorption of $CH_3—C\equiv CD$ on zinc oxide produced propargyl ions ($^-CH_2—C\equiv CD$) by loss of hydrogen from the methyl group. The cleavage of the methyl carbon–hydrogen bond rather than the acetylenic hydrogen–carbon bond suggested that the methyl hydrogen attained, at least, some allylic nature which they attributed to a change of the alkynic character of methyl acetylene to olefinic character when it chemisorbed. Presumably, the adsorbed species is formed by opening one of the π-bonds. A similar phenomenon was reported by Little *et al.* (*8*) in their adsorption studies of acetylenes on metals.

The chemisorption behavior of butenes was similar to that observed for propylene and acetylenes on zinc oxide: they chemisorbed zinc oxide without dissociation at low temperature (*9*), but rapidly underwent dissociation and then isomerization at room temperature (*10*).

From these results, along with other supplementary information, Kokes suggested that zinc oxide can behave as a base. Moreover, he put forth an acidity series (Table 1) (*11*) based on this concept. This preliminary information suggested that zinc oxide can dissociate acids with a pK less than 36 and cannot dissociate those with pK greater than 36 (*12*). We now report the results for toluene (p$K = 35$) which supports the contention that zinc oxide can be viewed as a basic catalyst.

We have found that toluene readily chemisorbs on zinc oxide. The most characteristic region in the infrared spectrum for the chemisorption of toluene is the region for the vibrations of the aromatic ring at 1605, 1494, and 1460 cm^{-1} (liquid phase) (*13*). In our laboratory, we also observed strong bands at the same frequencies with a liquid sample of 0.02 mm. However, when toluene vapor (25 Torr) was admitted into an empty ir cell of 120 mm, we only observed two strong bands at 1610 and 1500 cm^{-1} with intensities comparable to those obtained from the liquid sample. The band at 1460 cm^{-1} only appeared as a very weak band. Apparently, the intensity

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TABLE 1
Acidities of Carbon Acids

Acid	Anion	p*K*
H_2O	OH^-	16
CH_3CH_2OH	$CH_3CH_2O^-$	18
$RCOCH_2R$	$RCOCHR^-$	19–20
$H{-}C{\equiv}C{-}H$	$H{-}C{\equiv}C^-$	25
NH_3	NH_2^-	34
$CH_3CH{=}CH_2$	$CH_2CH{=}CH_2^-$	35
C_2H_4	$C_2H_3^-$	37

of the 1460 cm^{-1} band is highly sensitive to the state of toluene. With a zinc oxide catalyst disc in the cell, adsorption was confirmed by the persistence of these bands after a brief evacuation of the system when doses of toluene vapor were introduced into the system. Chemisorption was also indicated by the corresponding downward shift of these bands to 1593 and 1487 cm^{-1}, respectively, suggesting the formation of a π-complex. This is similar to the formation of the toluene-copper(II) montmorillonite complex, as observed by Pinnavaia and Mortland (*14*). They also observed bands at 1593 and 1487 cm^{-1}, when toluene was adsorbed on the interlamellar surfaces of copper(II) montmorillonite.

The adsorbed toluene, in time, underwent dissociation as evidenced by the growth of a new O-H band at 3575 cm^{-1}. The formation of this O-H band was accompanied by the growth of two new bands at 1585 and 1482 cm^{-1}. In fact, these two bands result from a further downward shift of the 1595 and 1487 cm^{-1} bands due to stronger chemisorption of the dissociated benzyl species with zinc oxide. This also suggested that the benzyl species was probably adsorbed with its benzene ring parallel to the surface. Initially, dissociation occurred readily as evidenced by the increase in intensity of the three bands at 3575, 1585, and 1482 cm^{-1}. Within 1 hr, about half the surface species was dissociated. A representative example of the chemisorption of toluene on zinc oxide is given in Fig. 1.

Additional adsorption studies with alpha-toluene-$D_3[C_6H_5CD_3]$ indicated that the dissociation of toluene occurred via the rupture of the methyl carbon-hydrogen bond. This was evidenced by the formation of an OD band at 2640 cm^{-1}. This is expected from an isotopic shift of the O-H band at 3575 cm^{-1}. At the same time, no new band was found at or near 3575 cm^{-1} region.

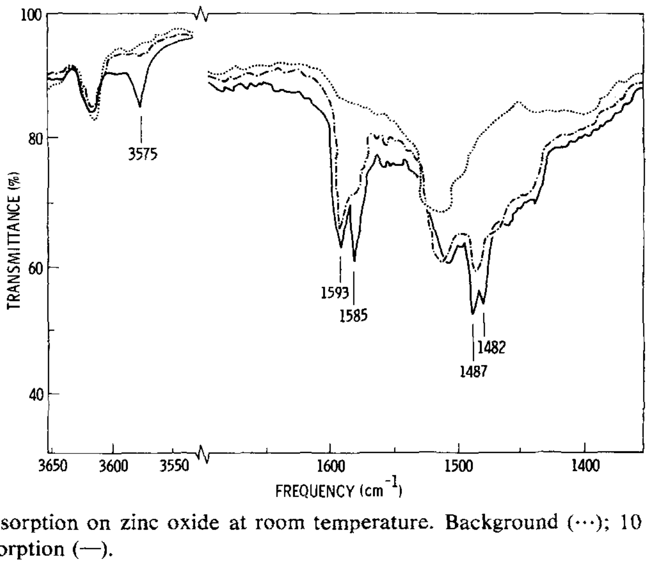

Fig. 1. Toluene adsorption on zinc oxide at room temperature. Background (···); 10 min after adsorption (-·); 60 min after adsorption (—).

Prolonged evacuation at room temperature removed nearly all the π-complex surface species, but little of the dissociated species. This was shown by the disappearance of the infrared bands at 1593 and 1487 cm^{-1}. However, desorption of the dissociated species occurred when the sample was heated to 75°C, as indicated by the simultaneous disappearance of the three bands at 3575, 1585, and 1482 cm^{-1}.

In conclusion, we believe that the preliminary data from *in situ* ir studies strongly supports the view that zinc oxide acts as a base catalyst and its effective "basicity" is comparable to that of the allylic carbanion, but weaker than that of the vinyl carbanion.

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