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Adsorption and Decomposition of Isopropyl Alcohol over Zinc Oxide

Infrared and Kinetic Study

BY OSAMU KOGA, TAKAHARU ONISHI* AND KENZI TAMARU

Department of Chemistry, Faculty of Science,
University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

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The adsorption of isopropyl alcohol and acetone on zinc oxide was studied by an infrared technique which revealed that isopropyl alcohol is dissociatively adsorbed at room temperature to form zinc alcoholate and hydroxyl group on the surface, while the adsorption of acetone takes place in its enolic form. When adsorbed isopropyl alcohol was heated to 363 K, the zinc alcoholate species changed gradually to acetone adsorbed in its enolic form, which further desorbed at higher temperatures as acetone, being replaced by the attacking isopropyl alcohol.

The behaviour of the adsorbed species during decomposition of isopropyl alcohol on zinc oxide was studied in more detail, leading to the overall reaction mechanism described by eqn (V).

The dehydrogenation of isopropyl alcohol over metal oxides is both technically important and is a basic catalytic reaction in view of its selectivity and catalytic activity. Krylov [1] studied a scheme for dehydrogenation of isopropyl alcohol over zinc oxide, a typical dehydrogenating catalyst. He considered the relation between the activity of various catalysts and their properties and suggested an adsorbed alcohol " dissociated at α-hydrogen " and " enol- or keto-type of acetone " as reaction intermediate, and that the dehydrogenation step from dissociated alcohol to adsorbed acetone was rate-determining. Teichner and coworkers [2] measured the pressure increase under various reaction conditions and concluded that the rate determining step is the dehydrogenation of adsorbed alcohol to form acetone, a mechanism similar to that of Krylov. Both, however, obtained no direct information about either the adsorbed species or the reaction sites and assumed some partial equilibrium in their reaction sequences. Desorption of isopropyl alcohol from zinc oxide was studied by Kemball and coworkers [3] who reported that even at temperatures as high as 573 K some species are not removed from the catalyst surface; in particular less acetone was desorbed in comparison with hydrogen.

In this report the adsorption of isopropyl alcohol and acetone on zinc oxide was studied by infrared spectroscopy, and the mechanism of decomposition of isopropyl alcohol to produce acetone is elucidated by measuring not only its rate but also the adsorption and kinetic behaviour of adsorbed species during the reaction.

EXPERIMENTAL

Zinc oxide (Kadox 25 from New Jersey Zinc Co., surface area 10 $m^2 g^{-1}$) was pressed into a self-supporting disc (≈ 0.2 g), which was placed in an infrared cell and connected to a conventional closed circulating system, as reported previously.[4] The catalyst disc was evacuated (10^{-3} N m^{-2}) at 690 K for 2 h and further treated for 2 h at 730 K in 13 kN m^{-2} oxygen being circulated through a trap cooled by liquid nitrogen.

Isopropyl alcohol and acetone were used after purification by repeated distillation. [$^2H_8$]Isopropyl alcohol and [$^2H_6$]acetone were obtained from Merck.

The infrared spectra of the adsorbed species were measured in the region 4000-900 cm^{-1}. If necessary, the 900-600 cm^{-1} range was also measured by putting almost the same amount of catalyst in the reference beam.

The procedure and apparatus employed in measuring the adsorption were similar to those employed previously.[5] Zinc oxide catalyst ($\approx$ 3.0 g) for the kinetic study was used in the form of a disc and treated under the same conditions as for the infrared study. The adsorption and the rate of decomposition of isopropyl alcohol were measured in a circulating system at 363 K.

The amounts of the adsorbed alcohol and acetone were determined by the peak height of the infrared spectra using the reference cell to compensate gas phase absorptions. The calibration curves for adsorbed isopropyl alcohol and acetone shown in fig. 1 were determined by measuring the 1129 and 1500 cm^{-1} bands when known amounts of isopropyl alcohol and acetone were separately adsorbed.

The reactant and product gases were analysed by gas chromatography using a 1 m dioctylsebasate column at room temperature.

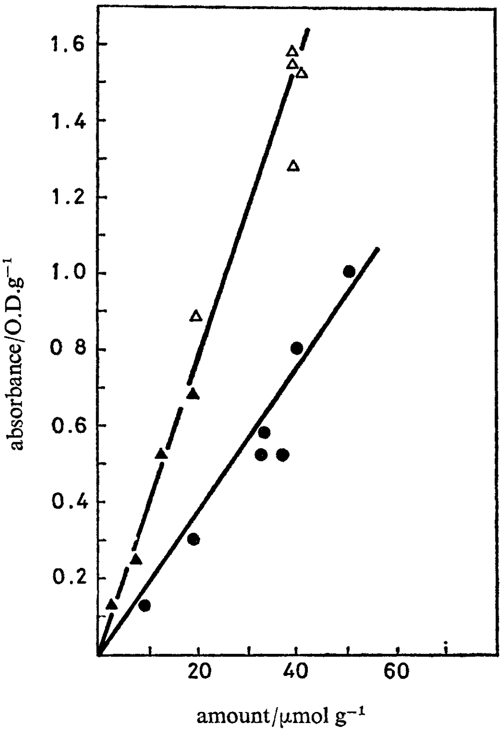


FIG. 1.—Calibration curve of adsorbed species at room temperature (shaded symbols) and 363 K (open symbols). ●, isopropyl alcohol (IPO), 1129 cm^{-1}; ▲, △, acetone (En), 1500 cm^{-1}.

RESULTS AND DISCUSSION

INFRARED STUDY

ADSORPTION OF ISOPROPYL ALCOHOL

The infrared spectra of isopropyl alcohol adsorbed on zinc oxide at room temperature are shown in fig. 2. The amount of saturated adsorption was nearly

60 μmol (g cat)$^{-1}$. The sharp bands at 3616 and 3665 cm^{-1}, due to the hydroxyl group on zinc oxide, decreased on alcohol adsorption and a new broad band around 3300 cm^{-1} increased.

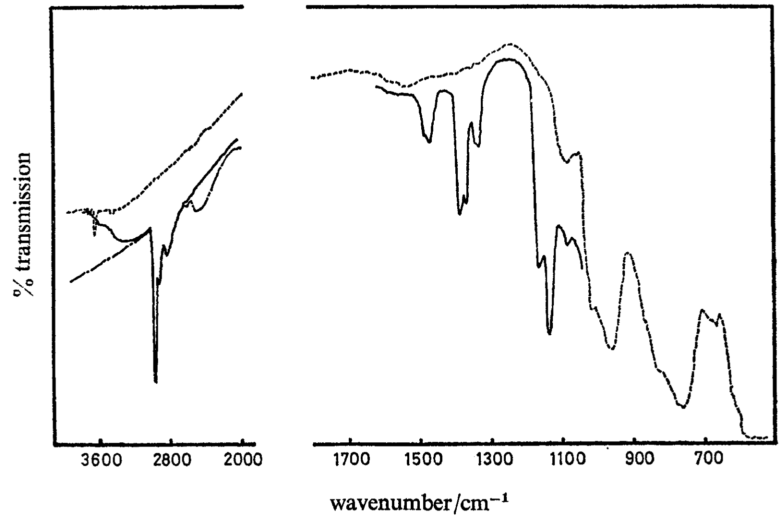


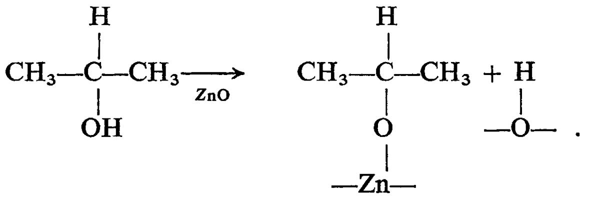
FIG. 2.—Infrared spectra of adsorbed isopropyl alcohol (IPO). - - -, ZnO background; ——, adsorbed alcohol (IPOH); — - —, adsorbed alcohol after exchange with D_2 (IPOD) at room temperature.

TABLE 1.—INFRARED BANDS OF ISOPROPYL ALCOHOL, ITS ZINC ALCOHOLATE AND ITS ADSORBED SPECIES ON ZnO

alcohol[7] (liquid) /cm^{-1}	zinc[6] alcoholate /cm^{-1}	adsorbed species (this work) /cm^{-1}	assignment[7]
1470 vs	1450 vs	1458 vs	$\delta(CH_3)$
1412 m			$\delta(CH)$
1382 vs	1366 vs	1380 vs	$\delta(CH_3)$
1372 vs	1356 vs	1366 vs	$\delta(CH_3)$
1342 s	1330 s	1338 s	$\delta(CH)$
1311 vs			$\delta(OH)$
1162 m	1160 m	1159 m	skeletal
1130 vs	1133 vs	1129 vs	skeletal

The hydrogen exchange reaction between adsorbed alcohol and deuterium gas (13 kN m^{-2}) at room temperature was also studied and revealed that only hydrogen in the hydroxyl group of alcohol was exchanged. The broad band of hydroxyl group around 3300 cm^{-1} was shifted to 2500 cm^{-1} by the exchange reaction, all the other bands staying unchanged (fig. 2).

The spectrum in fig. 2 was compared with those of liquid alcohol and zinc alcoholate in table 1. The table shows that the band positions are reasonably similar to those of alcoholate, which suggests that alcohol is adsorbed dissociatively to form zinc alcoholate and hydroxyl group on the surface, as follows,



$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3 \xrightarrow[ZnO]{} CH_3-\overset{\overset{H}{|}}{\underset{\underset{\underset{-Zn-}{|}}{O}}{\underset{|}{C}}}-CH_3 + \underset{\underset{-O-}{|}}{H} \; . \tag{I}$$

ADSORPTION OF ACETONE ON ZnO

Typical infrared spectra of small amounts of acetone [20 μmol (g cat)$^{-1}$] adsorbed on zinc oxide at room temperature are shown in fig. 3. There was no indication that the adsorbed acetone desorbed during evacuation at 383 K for a few hours.

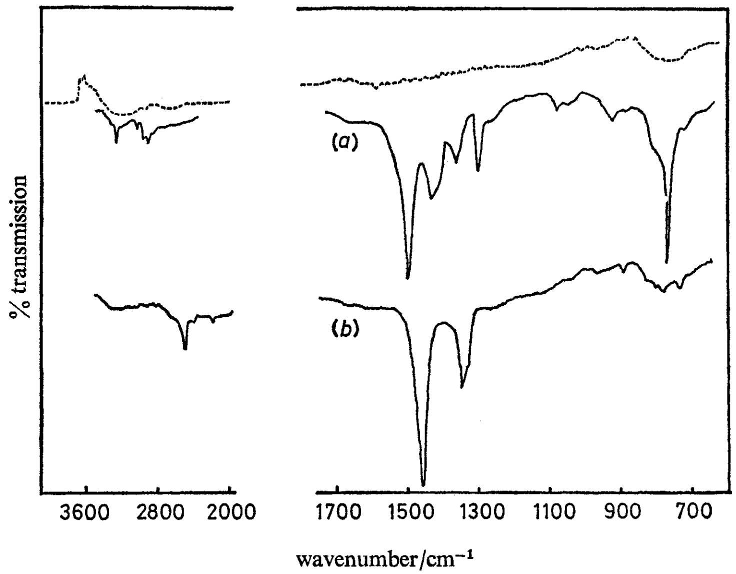


FIG. 3.—Infrared spectra of adsorbed acetone (En). - - -, ZnO background, nearly the same amount of ZnO in the reference beam; (*a*) adsorbed [$^2H_0$]acetone, (*b*) adsorbed [$^2H_6$]acetone.

The spectrum of adsorbed acetone lacks the absorption band characteristic of C═O stretching of acetone vapour at 1745 cm^{-1}. In addition the following new bands appeared in the spectrum of adsorbed acetone; (*a*) a sharp band for OH group at 3360 cm^{-1} with weak absorption of the H—C═ group at 3040 cm^{-1} and (*b*) a strong skeletal vibration band at 1500 cm^{-1}.

To collect more information on the behaviour of hydrogen in the adsorbed state, a hydrogen exchange reaction was carried out at room temperature between deuterium (13 kN m^{-2}) and acetone [20 μmol (g cat)$^{-1}$] adsorbed on zinc oxide. The results of the exchange demonstrated that the hydrogen atoms both in the hydroxyl and in the hydrocarbon group were exchanged, resulting finally in the complete exchange of all the hydrogen atoms in acetone.[8]

As the exchange reaction proceeded, the band around 1500 cm^{-1} shifted gradually to 1465 cm^{-1}. The amounts of hydrogen and/or deuterium in the hydroxyl group of the adsorbed species was estimated from their intensity. In fig. 4 the deuterium content in the hydroxyl group of the adsorbed molecule (OD/OH+OD) is plotted against the peak position of the adsorbed molecule near 1500 cm^{-1}. The skeletal C═C bond shifts linearly with the deuterium content of the hydroxyl group, supporting the idea that the OH group is directly attached to the C═C bond.

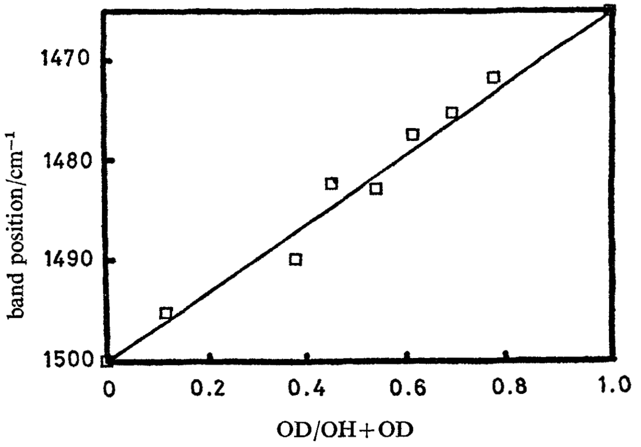
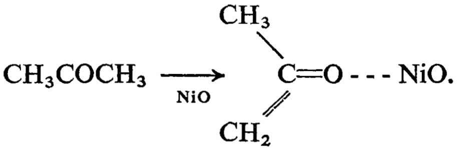


FIG. 4.—Band shift of peak at nearly 1500 cm^{-1} for En under partial deuteration. OH (OD) represents OH (OD) concentration of En from the infrared absorbance at 3360 cm^{-1} (2510 cm^{-1}).

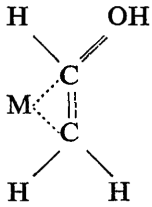
Roginsky and coworkers [9] observed an OH band in the region 3550-3750 cm^{-1} and two strong bands at 1575 and 1515 cm^{-1} in the range characteristic of the C═O stretching vibration in the spectra of acetone adsorbed on NiO. They proposed an enolate type adsorption species as follows:



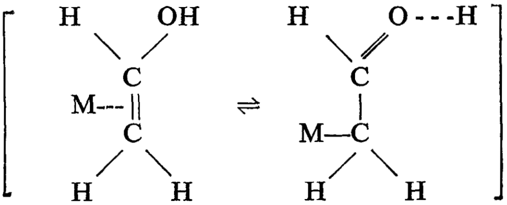
$$CH_3COCH_3 \xrightarrow[\text{NiO}]{} (CH_3)(CH_2)C{=}O\text{---}NiO. \qquad \text{(II)}$$

Kubokawa *et al.*[10] observed a similar adsorbed species on NiO and MgO. However, in the case of ZnO the bands of adsorbed acetone are different from those on NiO and MgO noted above.

Some metal complexes with enol type compounds have been synthesized.[11-14] One of these enol type complexes, Pt-vinyl alcohol complex, was analysed by X-ray diffraction and the geometrical structure (1) is given as follows:



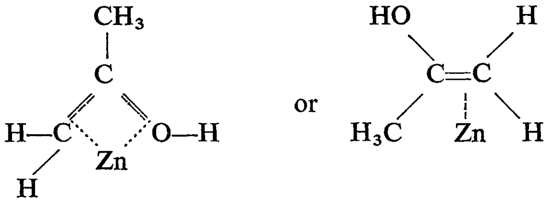
(1)



(2) (3) (III)

which is a hybridized structure of (2) and (3).[13]

In table 2 the characteristic infrared bands of acetone adsorbed on zinc oxide are compared with the enol type molecules. This comparison leads to the conclusion that the adsorbed species on ZnO is an enol type as follows:



(IV)

Nagai and Miyahara [15] studied the infrared spectra of acetone adsorbed on ZnO and found that the adsorbed acetone species is an enolate.

When large amounts of acetone [> 40 μmol (g cat)$^{-1}$] were introduced onto zinc oxide, the spectrum differed from that of fig. 2, as shown in fig. 5. This spectrum, which has a new peak around 1600 cm^{-1}, is similar to that reported by Nagai *et al.* It is known that polymerization of acetone takes place on zinc oxide. Accordingly, the spectrum in fig. 5 can be assigned to a polymerized species of acetone such as acetylacetone.

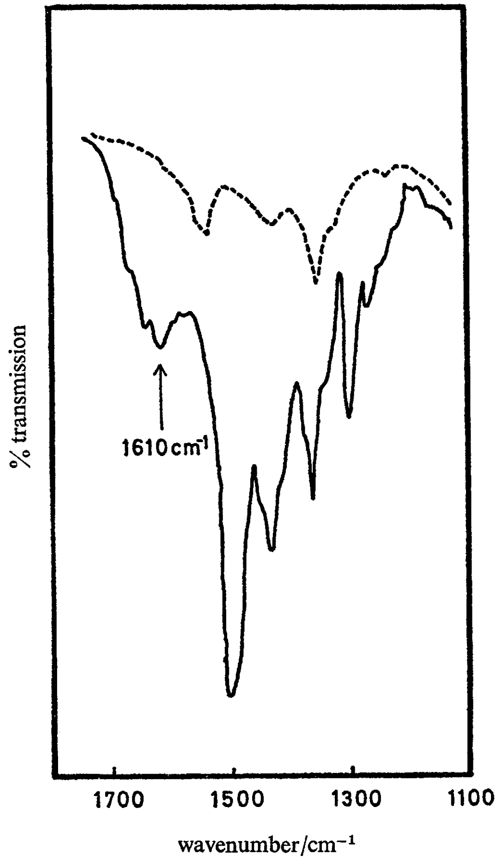
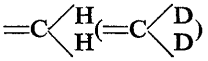


FIG. 5.—Infrared spectra of adsorbed acetone in excess amounts (52 μmol g^{-1}).

TABLE 2.—CHARACTERISTIC BANDS OF ENOL TYPE SPECIES AND ADSORBED ACETONE

		adsorbed species (this work)		
$(RCH_2{=}CMeOH)^+Br^-$ [14]	$C_3H_6Cl_2O—Pt$ [12]	CH_3COCH_3	CD_3COCD_3	assignment
	3300 vs	3360 w	2510 m	—OH(—OD)
	3020 w	3040 w		H—C=
		2960 w	2220 w	$—CH_3(—CD_3)$
		2930 w		$—CH_3$
		2880 w		$—CH_3$
1515 s	1545 s	1500 vs	1465 vs	C=C
		1435 m	1046 w	$—CH_3(—CD_3)$
		1362 m	1350 s	C—O
		1301 s		
		1080 w	940 w	 $=C\begin{smallmatrix}H\\H\end{smallmatrix}(=C\begin{smallmatrix}D\\D\end{smallmatrix})$
		1050 w		
		930 w	900 w	
		765 vs	793 w	
			752 w	

When adsorbed isopropyl alcohol was heated to 363 K, the spectrum of the adsorbed species changed from that in fig. 2 to curve (*a*) in fig. 3; isopropyl alcoholate species on ZnO changed to an enol type acetone species at this temperature, indicating

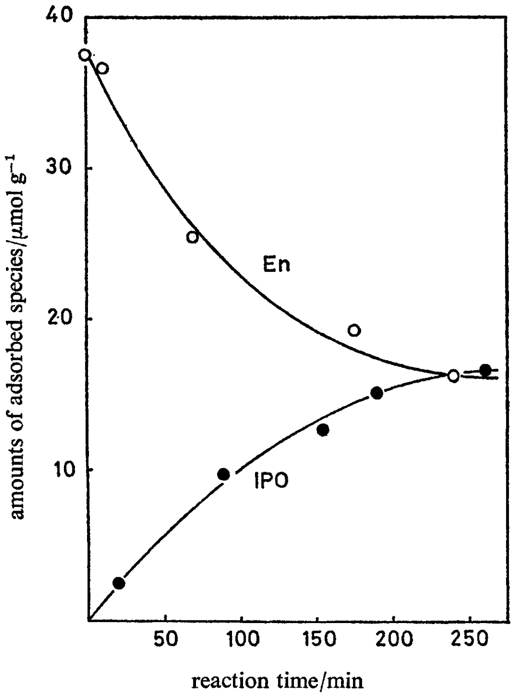


FIG. 6.—Reaction between En(a) and hydrogen (18 kN m^{-2}) to produce IPO(a) on ZnO at 363 K.

that the first step in the decomposition of isopropyl alcohol is the dissociative adsorption to alcoholate and hydroxyl groups on the surface which react further to enol(a) and hydrogen.

When adsorbed acetone, En(a), was heated at 363 K in the presence of 18 kN m^{-2} hydrogen, it was converted into isopropyl alcoholate (IPO) as shown in fig. 6, further supporting the reversible process $H_2 + En(a) \rightleftharpoons IPO(a) + H(a)$.

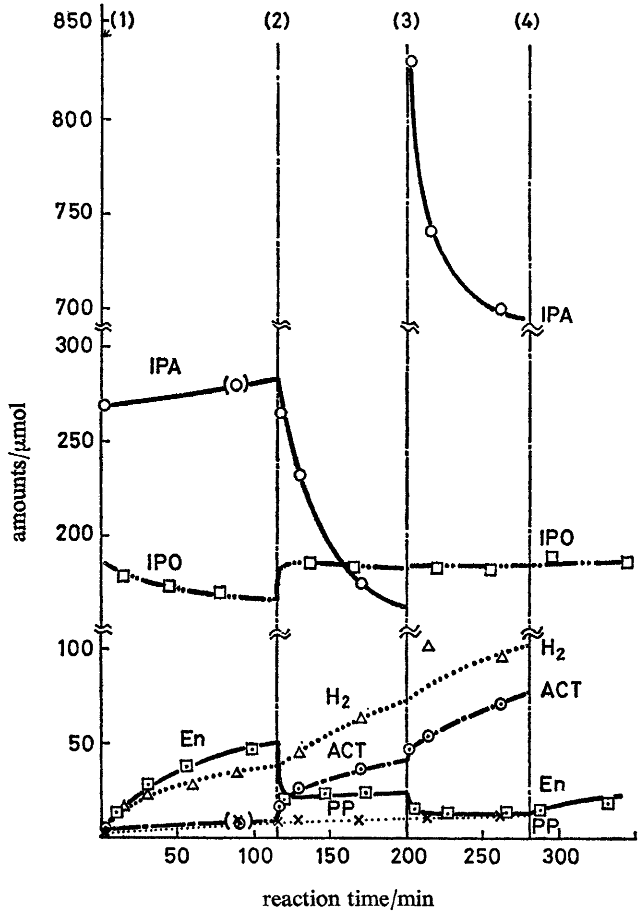


FIG. 7.—Decomposition of isopropyl alcohol on ZnO at 363 K. (1) Gas phase was removed by a liquid nitrogen cold trap just after introducing alcohol to the reaction cell. (2) Release of condensed gases from the trap. (3) Reintroduction of isopropyl alcohol. (4) Evacuation of gas phase. —○—, IPA, isopropyl alcohol in gas phase; —⊙—, ACT, acetone (g); —×—, PP, propylene (g); —△—, H_2 (g); —□—, IPO, adsorbed isopropyl alcohol (alcoholate); —⊡—, En, adsorbed acetone (enol).

KINETIC STUDY OF DECOMPOSITION OF ISOPROPYL ALCOHOL

Isopropyl alcohol decomposes over zinc oxide at 363 K to form mainly acetone and hydrogen ($\approx$ 90 % selectivity) and small amounts of propylene and water (10 %). A typical result of the dynamic study at 363 K is given in fig. 7, where the changes in partial pressure of the reactants and products and the amounts of each adsorbed species are shown. Soon after contact of alcohol with the catalyst, the gas phase components other than hydrogen were removed by circulating the reacting gas and condensing in a liquid nitrogen trap (period 1); after 2 h the condensed gases were released by removing the liquid nitrogen (period 2).

During period 1, the amounts of species adsorbed during reaction were estimated from i.r. intensities, and by measuring the pressure and composition of the ambient gas and the amount of condensate (determined by gas chromatography at suitable time intervals) in the trap. The amount of adsorbed alcohol decreased, while hydrogen in the gas phase and the adsorbed acetone (enol species) increased with time by almost the same amount. The adsorbed acetone desorbed negligibly as Kemball *et al.*[3] observed in the absence of alcohol in the gas phase.

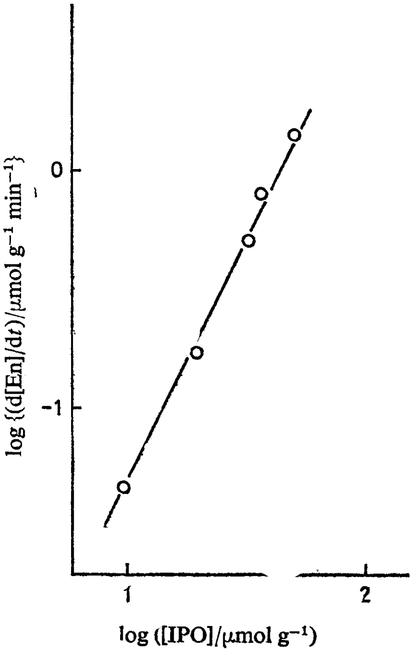


FIG. 8.—Dependence of the initial rate of En formation upon IPO coverages.

At the start of period 2, the adsorbed alcohol increased, whereas the adsorbed acetone decreased desorbing into the gas phase by amounts corresponding to the release of condensed vapours from the trap. The decomposition of alcohol continued subsequently, while adsorbed alcohol and acetone remained almost constant. Thus the following scheme for the overall reaction can be proposed to explain these results:

$$\mathrm{IPOH(g)} \rightleftharpoons \mathrm{IPO(a)} + \mathrm{H(a)} \tag{1}$$

$$\mathrm{IPO(a)} + \mathrm{H(a)} \rightleftharpoons \mathrm{En(a)} + \mathrm{H_2(g)} \tag{2}$$

$$\mathrm{En(a)} + \mathrm{IPOH(g)} \rightleftharpoons \mathrm{IPO(a)} + \mathrm{ACT(g)} \tag{3}$$

where IPOH(g), IPO(a), En(a) and ACT(g) show gaseous isopropyl alcohol, isopropyl alcolate (adsorbed), enol type adsorbate and gaseous acetone, respectively. Step (3) represents the expulsion by alcohol vapour of the enol type acetone adsorbed species which is adsorbed instead on the catalyst surface.

To discover the role of adsorbed alcohol and acetone in dehydrogenation, the rate of reaction (2) was examined at various alcohol and acetone coverages. The results using fresh catalysts are shown in fig. 8.

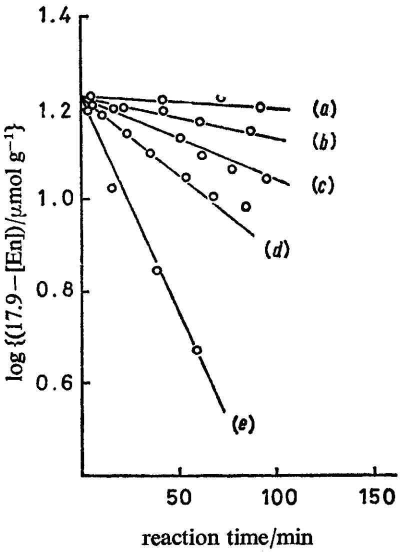
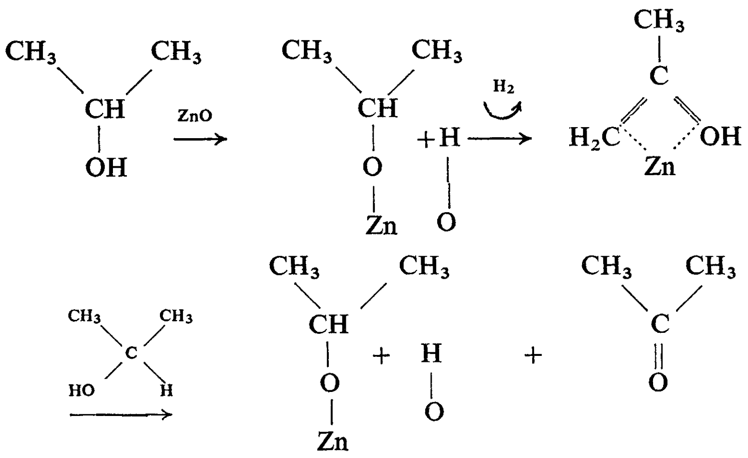


FIG. 9.—Formation of En at various coverages of IPO and En. IPO coverage in μmol (g cat)$^{-1}$. Vacant site (S): 17.9 μmol (g cat)$^{-1}$ (see text). (*a*) IPO = 9.81, (*b*) IPO = 19.7, (*c*) IPO = 32.7, (*d*) IPO = 36.6, (*e*) IPO = 50.8.

The initial rate of formation of enol type adsorbed species was second order with respect to IPO(a) coverage in the initial stage of the reaction, which suggests that initially IPO(a) can react with dissociatively adsorbed hydrogen H(a) to form enol species. The preadsorption of acetone (En) inhibited this reaction, demonstrating that the initial rate of En formation is proportional to the vacant site (S) for En adsorption (fig. 9). Summarizing these data the following equation was obtained

$$d[En(a)]/dt = k[IPO(a)][H(a)][S-En(a)].$$

An overall mechanism for the reaction is thus proposed:



(V)

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