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Infrared Investigation of Chemisorption of Cyclohexanol and Cyclohexanone on Pt/SiO$_2$

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Adsorption of cyclohexanol on Pt/SiO$_2$ catalyst was investigated by means of ir spectroscopy. At room temperature hydrogen atoms from both OH and tertiary carbons split off easily, resulting in the formation of cyclohexanone held on SiO$_2$ by hydrogen bonds whereas on Pt it is held by a π-bond or through the lone electron pair of oxygen. Dissociation of α-hydrogens in cyclohexanone commences only at circa 353 K. At 393 K bands characteristic of an enolic system were observed, suggesting formation of a π-oxoallylic species during dehydrogenation of cyclohexanone.

1. INTRODUCTION

Infrared investigations are widely used in elucidating the nature of chemisorption. Extensive experimental work has been carried out on aliphatic aldehydes, ketones, and alcohols using silica and silica-supported metal catalysts (*1–5*). The results suggest the formation of an alkoxide (*1–4*), a diadsorbed alkoxide (*1–4*) and a carboxylate structure (*4, 5*) upon interaction of surface alkoxide and CO.

Such measurements supply a valuable contribution to the better understanding of metal-catalyzed transformations of cyclohexanol. This reaction has been studied extensively in our laboratory. Data with respect to nickel (*6*), copper (*7*), and platinum (*8, 9*) have been published so far; a detailed analysis of results obtained with other Group VIIIB metals is to be published soon (*10*).

On Pt, the main reaction route is the formation of phenol and benzene (*8, 9*). Radiotracer measurements (*7, 9*) have demonstrated that the dehydrogenation of cyclohexanol to phenol proceeds via cyclohexanone as well as via a direct pathway. The present paper deals with adsorption and transformation of cyclohexanol on Pt/SiO$_2$ (Cab-O-Sil H5) using the conventional spectroscopic technique. Its aim is to identify the surface species formed in the dehydrogenation of cyclohexanol. Our preliminary ir work (*11*) on Rh and Pt has shown that cyclohexanol chemisorption leads to the formation of chemisorbed CO. The shift of the ν(CO) band (*12, 13*) in the presence of chemisorbed reactant can then be used to determine the electron donor ability of the surface complex formed during dehydrogenation.

2. EXPERIMENTAL

The infrared cell and the apparatus have been described elsewhere (*14*). The Pt/SiO$_2$ samples were prepared by impregnating Cab-O-Sil H5 silica with a solution of H_2PtCl_6. The sample, which contained about 10% Pt by weight, was reduced in the cell at 620 K in a stream of hydrogen for about 5 hr. The pellet was then cooled to the temperature of the measurement and evacuated for about 10 min until residual pressure was about 10^{-7} Pa.

Deuterated cyclohexanone was prepared by exchange with D_2O in the presence of K_2CO_3. Deuterated cyclohexanols were produced via reduction of cyclohexanone with $LiAlD_4$. The substances cyclohexanol-1-d_1, cyclohexanol-0-d-1-d_1, and cyclohexanone-2,2,6,6-d_4 were tested by ir and NMR techniques and showed more than 95% deuterium content in the expected

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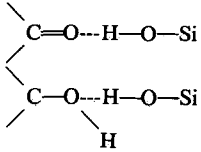
TABLE 1

Infrared Bands of Cyclohexanol and Cyclohexanone (cm^{-1}) Adsorbed on SiO_2 and Pt/SiO_2[a]

A		B	C	D	E	F[b]	G	Assignment
5 min	10 hr							
		3400vs,b						 OH stretching
3300vs,b	3300vs,b							
						3090vw,b 3040w,b		olefinic CH stretching
2940vs	2940vs	2940vs	2940vs	2940s	2940s			$\nu_a(CH_2)$ aliphatic CH
2865s	2965s	2865s	2865s	2865m	2865m			$\nu_s(CH_2)$ stretching
					2175vw[d]			CD stretching
				2060m[c]		1990w,b		adsorbed CO stretching
				1875w,b[c]		1830w,b		
		1703vs	1703sh					>C=O stretching
			1694vs					
		1682sh	1682sh					
	1660sh			1660sh				C=C stretching
	1625w,b			1625w,b				H_2O bending
						1610m		C=C=O "asymmetric" stretching
							1595s 1500m 1475m	monosubstituted aromatic ring vibration

1470wm	1470wm	1470sh	1470w	1470w	1470w		CH$_2$ scissoring
1455vs	1455vs	1455s	1455s	1455s	1455s		
		1434m	1343w				αCH$_2$ scissoring in ketone
		1423m	1423w				
	1415w			1415vm			—HC= in-plane bending
	1400sh			1400w,b			alcohol OH bending
						1400vw	C=C=O "symmetric" stretching
1370s	1370s		1370m	1370m			CH$_2$ wagging in alcohol
1350m	1350m		1350m	1350m			
		1353m	1353m				CH$_2$ wagging in ketone
		1345m	1345sh				
		1311m	1311m				

[a] A, cyclohexanol adsorbed on SiO$_2$ (Cab-O-Sil HS5) at 313 K for 5 min and for 10 hr; B, cyclohexanone on SiO$_2$ at 313 K; C, cyclohexanol on Pt/SiO$_2$ at 313 K; D, hydrogen admitted to C at 313 K; E, cyclohexanol adsorbed at 313 K, then D$_2$ admitted at 313 K; F, cyclohexanone chemisorbed at 393 K; G, cyclohexanol on Pt/SiO$_2$ at 593 K for 2 hr. s, strong; m, medium; b, broad; sh, shoulder; v, very; w, weak.

[b] CD stretchings at 2210 and 2112 cm^{-1} after D$_2$ addition.

[c] Observed on a fresh sample.

[d] The same band was observed after adsorption of cyclohexanol-0-*d*-1-d_1 and cyclohexanol-1-d_1.

positions. H$_2$ and D$_2$ gases were purified by a BASF-11 deoxo contact and by a molecular sieve trap cooled with liquid N$_2$.

Spectra were recorded on a Digilab FTS-14 Fourier transform spectrophotometer. The spectrum of the catalyst after reduction was the first to be taken; it was stored on the disk memory of a Nova-1200 computer and later used as background.

3. RESULTS AND DISCUSSION

3.1. Adsorption on Pure Silica

Spectra of adsorbed cyclohexanol (Fig. 1a and column A in Table 1) on Cab-O-Sil silica were very similar to that of the liquid. However, on a silica pellet standing for about 10 hr in alcohol vapor of relatively high pressure (100 Pa), dehydrogenation is discernible. (Prior to adsorption measurements the silica wafer was evacuated in the cell at 650 K for 3 hr.) A weak shoulder centered at about 1660 cm^{-1} and a weak band at 1415 cm^{-1} can tentatively be assigned as C=C stretching and —HC= in-plane bending of cyclohexene formed in dehydration. The 1625-cm^{-1} band belongs to water deformation. The fact that careful examination of the spectra in the region above 3000 cm^{-1} reveals no signs of C–H stretching bands of an olefinic species is probably because of the low intensity of ν(CH) vibrations.

The shoulder at 1400 cm^{-1} can be assigned to the OH deformation of the hydroxyl group of cyclohexanol physisorbed on SiO$_2$ (*15*). Formation of cyclohexanone was not observed.

The spectrum of the adsorbed cyclohexanone (Fig. 1b and column B in Table 1) was also measured at room temperature and showed no signs of any reaction except H-bonding between the carbonyl group and the hydroxyl groups of the silica surface (Fig. 1c). The ν(CO) band appearing at 1703 cm^{-1} and the shoulder at about 1682 cm^{-1} indicate two different types of H-bonding. If these are compared with the 1716-cm^{-1} ν(CO) frequency of cyclohexanone in CCl$_4$ solution (*16*), it would appear that the H-

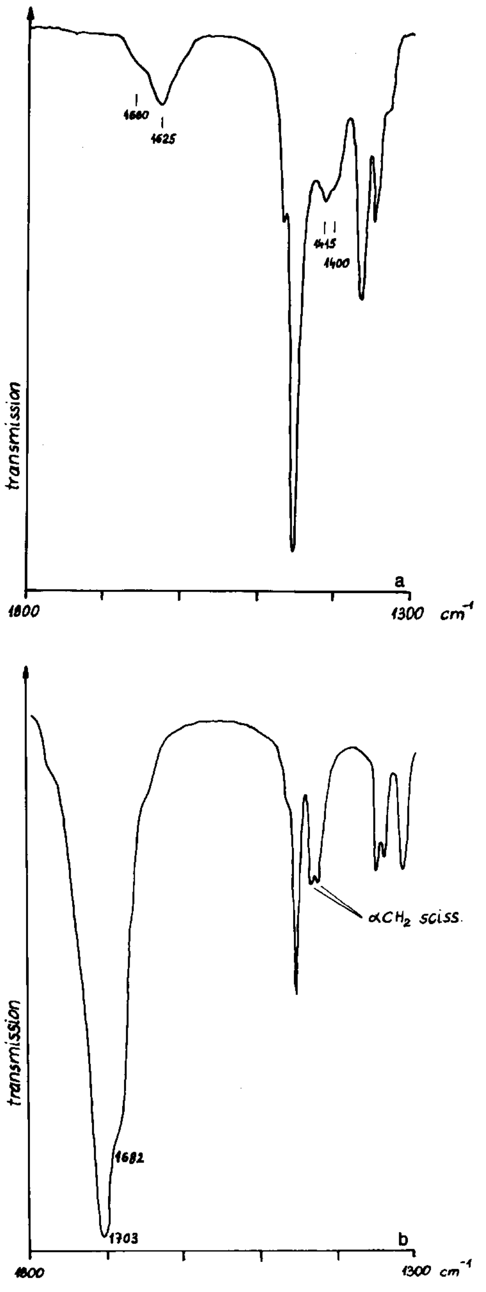


FIG. 1. (a) SiO_2 after exposure to 100 Pa cyclohexanol for 10 hr at 313 K; (b) cyclohexanone (100 Pa) adsorbed on SiO_2 for 5 min at 313 K; (c) same as (b), 2800 to 4000-cm^{-1} spectral region.

bonding caused shifts of 13 and 28 cm^{-1}, respectively. Similar shifts of frequency and doubling of the carbonyl band were

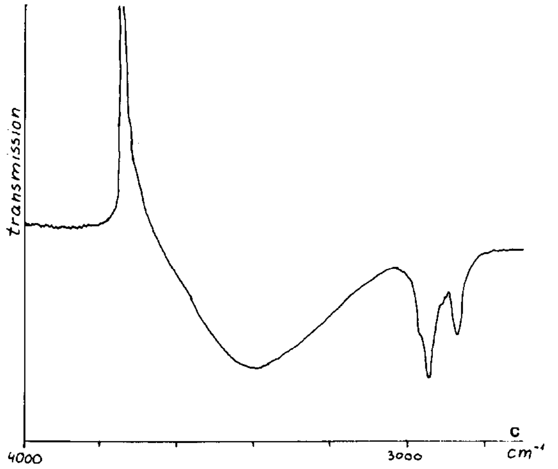


FIG. 1—*Continued*

observed when cyclohexanone was adsorbed on silica from CCl_4 solution (*17*). In agreement with the explanation given by Marshall and Rochester (*13, 17*) our two ν(CO) bands can be assigned to carbonyl groups interacting with isolated surface silanol groups and with pairs of adjacent hydroxyl groups, respectively.

The OH stretching frequencies of the H-bonded silanol groups interacting with the OH groups of the alcohol and with the carbonyl are at about 3300 and 3400 cm^{-1}, respectively. They appear in the expected range reported for similar systems (*18*).

3.2. *Adsorption on Pt/SiO₂ at Room Temperature*

Dehydrogenation of cyclohexanol into cyclohexanone is the main reaction route at room temperature. Some of the recorded spectra are depicted in Figs. 2 and 3. Parallel with cyclohexanone formation, dehydration and cleavage of C–C bonds (CO formation) have been observed on freshly prepared samples. Dehydration is suggested by formation of bands at 1660, 1625, and 1415 cm^{-1} (Fig. 2a). The bands can be assigned, as before, to the C═C stretching, water deformation, and —HC═ in-plane bending, respectively. Spectra showing the presence of CO on the surface are presented in Figs. 4b and c. These spectra,

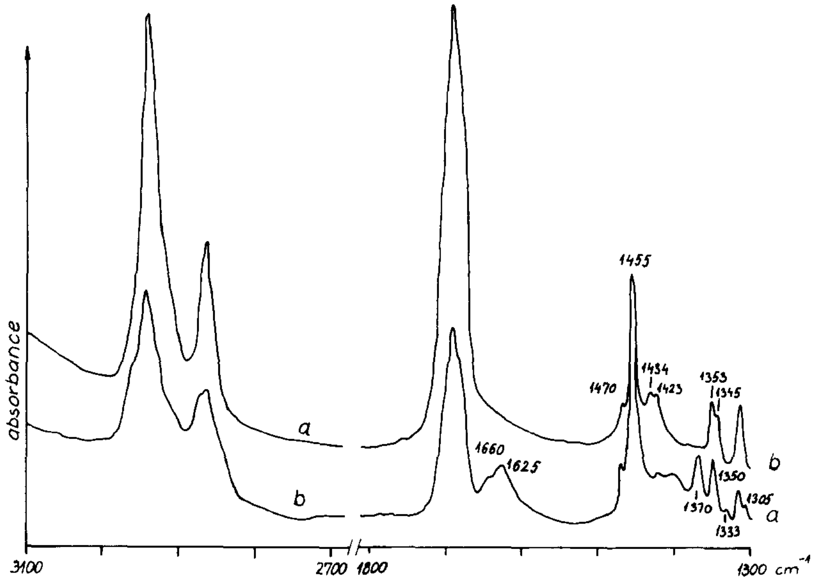


FIG. 2. (a) Cyclohexanol on Pt/SiO$_2$, 53 Pa in the cell for 5 min at 313 K; (b) after 15-min evacuation (10^{-4} Pa).

illustrating the effect of the carbonyl group on the ν(CO) frequency of CO, are discussed at the end of this section. A summary of the observed spectra is given in Table 1 (columns C, D, and E).

If cyclohexanol vapor is introduced into the cell the carbonyl band appears immediately (Figs. 2 and 3), suggesting that part of the adsorbed cyclohexanol has been transformed into cyclohexanone. Bands at 1434, 1423, 1353, 1345, and 1311 cm^{-1} are characteristic of cyclohexanone. The CH$_2$ scissoring modes of the α-methylene groups occur at 1434 and 1423 cm^{-1}; bands at 1353, 1345, and 1311 cm^{-1} belong to different waggings (*12*). The presence of unreacted alcohol or surface alcoholate is indicated by bands at 1370 and 1350 cm^{-1}; they are probably CH$_2$ waggings coupled with C–C stretching vibrations. The bands at 1455 and 1470 cm^{-1}

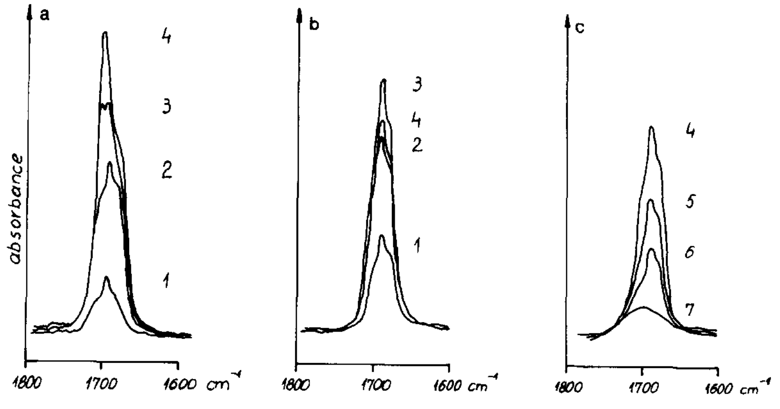


FIG. 3. (a) Cyclohexanol adsorbed for 5 min at 313 K on Pt/SiO$_2$: (1) 20 Pa, (2) 72 Pa, (3) 93 Pa, and (4) 120 Pa cyclohexanol in cell. (b,c) (1) 53 Pa cyclohexanol adsorbed; (2) evacuating the gas phase; (3) after 30-min evacuation; (4) after 60-min evacuation; (5) 30 Pa H$_2$ added; (6) in 46 Pa H$_2$; (7) in 0.33 kPa H$_2$.

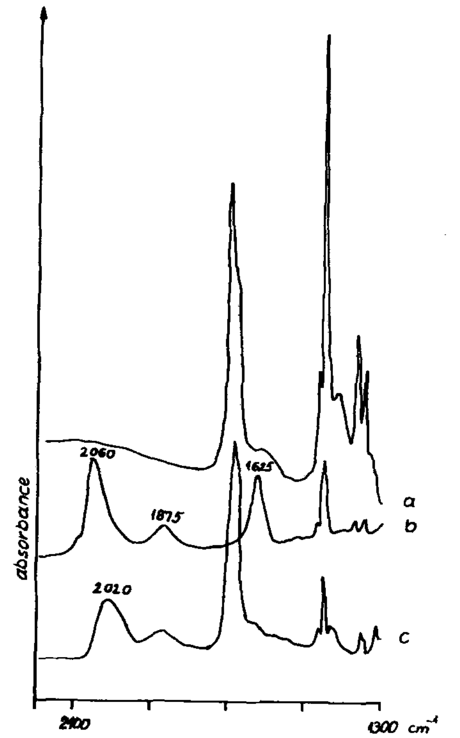
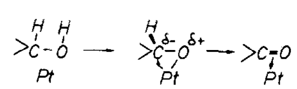


FIG. 4. (a) 106 Pa cyclohexanol in the cell after 6 hr; (b) in H_2 flow after 2 min; (c) after 20-min evacuation.

appear in both the cyclohexanone and the cyclohexanol spectra. These bands can be assigned to the scissoring of CH_2 in the β and γ positions to the carbon atom holding oxygen.

The formation of cyclohexanone takes place via dehydrogenation of the surface alcoholate. Evidence suggesting the presence of alkoxide was obtained by hydrogenation or deuteration of cyclohexanone formed on the catalyst surface. When H_2 was added in small doses the characteristic bands of cyclohexanone around 1700 cm^{-1} and between 1440 and 1300 cm^{-1} disappeared and the 1370-, 1350-cm^{-1} doublet of the adsorbed alcohol was restored. The addition of D_2 instead of H_2 resulted in the appearance of a CD stretching band at 2175 cm^{-1}. After chemisorption of cyclohexanol-1-d_1 and cyclohexanol-0-d-1-d_1 the spectra showed the same CD band. Spectra of cyclohexanol-1-d_1 and cyclohexanol-0-d-1-d_1 in CCl_4 solution, however, revealed CD bands at 2103 and 2122 cm^{-1}, respectively. We suggest therefore that the adsorbed cyclohexanol is bonded to the surface through its oxygen atom. A higher stretching frequency of the CH bond (i.e., it is measured as CD) is found since back-bonding occurs from the metal to the carbon so that the C–H bond order increases. This excess negative charge is then removed when the H atom is abstracted (I). A shift of the CH stretching vibrations in surface alcoholates has been observed on oxide surfaces, too (*19*).



$$>\overset{H}{\underset{}{C}}-\overset{H}{\underset{Pt}{O}} \longrightarrow >\overset{H}{C}{}^{\delta-}-O^{\delta+}{}_{Pt} \longrightarrow >\underset{Pt}{C}=O \qquad \text{(I)}$$

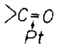
The admission of cyclohexanol in small doses reveals the multiple structure of the ν(CO) band of cyclohexanone (Fig. 3). At low coverage a peak developed at 1694 cm^{-1} having shoulders on both sides at 1703 and 1682 cm^{-1}, respectively. On gradually increasing the pressure the highest-frequency band was quickly intensified until eventually it dominated the 1694-and 1682-cm^{-1} bands (Fig. 3a).

Upon evacuation the intensity of the ν(CH) bands decreased whereas the intensity of the 1694-and 1682-cm^{-1} bands passed through a maximum as a function of time of pumping. The initial enhancement of the ν(CO) band (Figs. 2 and 3b) in the course of the evacuation permits the suggestion that the weakly bonded hydrogen formed by the rupture of the OH bond inhibits dissociation of the CH bond at the tertiary carbon atom. Evacuation removes the weakly held hydrogen from the surface, thereby promoting the dehydrogenation of alcoholate into cyclohexanone. The importance of weakly held hydrogen has already been suggested in the hydrogenation of benzene and olefins (*20–22*). Persistent pumping caused the desorption of all the bands of the whole spectrum, indicating slow desorption of cyclohexanone (Figs. 3b, c).

The admission of H_2 decreased the intensity of the ν(CO) band but a small and very broad band still remained even at high hydrogen pressures (10^4 Pa) around 1700 cm^{-1}. Apparently the intensity of the band component of 1694 cm^{-1} was reduced at the highest rate (Fig. 3c).

The multiple structure of the ν(CO) band suggests that cyclohexanone is attached to the surface by different forces. If the assignment given previously for the carbonyl species adsorbed on silica is kept in mind it is likely that the band at 1694 cm^{-1} arises from cyclohexanone adsorbed on Pt particles, and the other two bands belong to the ketone that formed on Pt and then moved to the support and bonded with the H-bridges.

Since the interaction between the metal and the C=O group is weak (the ν(CO) frequency was shifted by 21 cm^{-1} with respect to that in CCl$_4$ solution), the ketone is probably connected to the Pt surface by a π-bond (**II**) or through one of the lone electron pairs of oxygen (**III**):



$$>\underset{\underset{\text{Pt}}{\downarrow}}{C=O}$$

(II)

$$>C{=}\ddot{O}{:}\!\rightarrow \text{Pt}$$

(III)

A surface complex (**III**) was proposed in the case of adsorption of acetone on supported Ni (*3*). The formation of surface species (**II**) or (**III**) is confirmed by the fact that C–H bonds did not dissociate below 353 K. Since the C–H stretching region of the spectra (Fig. 2b) does not provide convincing evidence for C–H bond rupture, the chemisorption of cyclohexanone-2,2,6,6-d_4 was investigated. No C–D bond rupture was observed at room temperature, in agreement with the observation of Takagi *et al.* (*23, 24*) measured by mass spectroscopy and NMR. When the sample was heated above 350 K the strong OD stretching of silica appeared, indicating that deuterium atoms were abstracted from the ketone and exchanged with the OH groups of the silica surface. This observation suggests that at elevated temperatures chemisorption of cyclohexanone takes place by dissociation of C–H bonds.

The electron donor properties of cyclohexanone are confirmed by the lowering of the ν(CO) stretching frequency of CO formed on fresh Pt/SiO$_2$ pellets. As mentioned previously this "high" activity of Pt could not be recovered after "stabilization" of the pellets, i.e., after repeated oxidation–reduction cycles. It is shown in Fig. 4b that a stream of H$_2$ removed all the physisorbed substances and typical bands of chemisorbed CO appeared at 2060 and 1875 cm^{-1} (*25*). The 1370-, 1350-cm^{-1} bands of adsorbed alcohol are also discernible, i.e., besides decarbonylation a certain amount of alcohol was formed. Stopping the gas flow and evacuating the gas phase resulted in the reappearance of cyclohexanone (Fig. 4c), showing that the reaction is reversible and strongly dependent on the hydrogen coverage of the surface. The carbon monoxide band of higher frequency was shifted to 2020 cm^{-1}, whereas its intensity decreased only slightly. It seems that the frequency shift is caused by the appearance of an electron donor adsorbate (surface species (**II**) or (**III**)) in the neighborhood of the adsorbed CO molecules rather than by the decrease of surface coverage of CO (*12*).

3.3. Reactions at Elevated Temperatures

In order to follow the process of dehydrogenation further, the chemisorption of cyclohexanone at 393 K was investigated (Table 1, columns F, G). The spectra in Figs. 5a and b show the decrease of the frequency of the carbonyl band and formation of very broad bands at about 1610 and 1400 cm^{-1}. These bands are characteristic of an enolic system of a C$\overset{...}{=}$C$\overset{...}{=}$O skeleton containing two "bonds and a half" (*15*). Bands were also observed in the olefinic C–H stretching region at 3090, 3040 cm^{-1} and they diminished when D$_2$ was introduced into the cell. At the same time two CD stretchings grew at 2210 and 2112 cm^{-1}, respectively, and all the bands below 1700 cm^{-1} disappeared (Fig. 5c). These changes can be explained in terms of an extended,

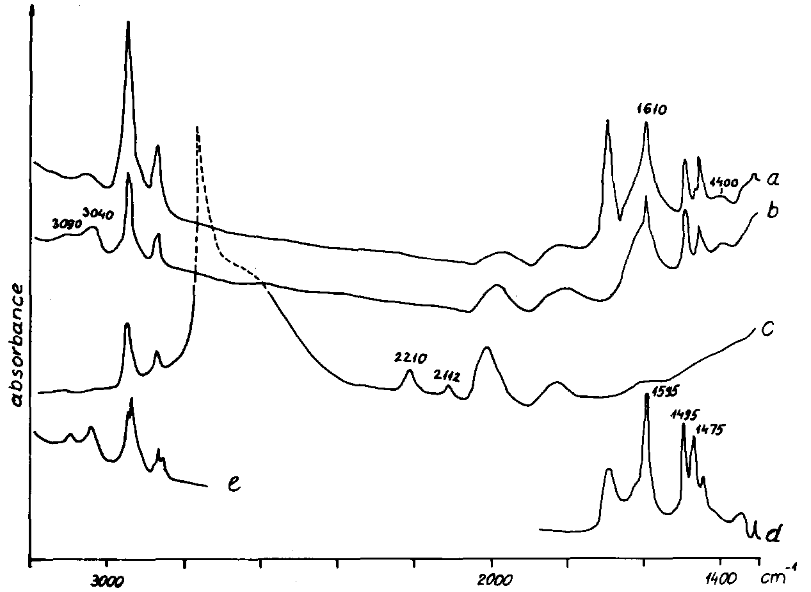
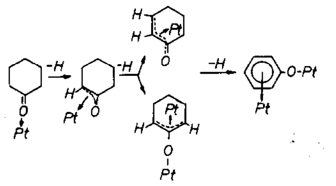


FIG. 5. (a) Pt/SiO_2 exposed to 33 Pa cyclohexanone at 393 K for 5 min; (b) after exposure for 30 min; (c) after introducing 3.33 kPa D_2; (d) Pt/SiO_2 heated in 120 Pa cyclohexanol for 2 hr at 573 K, spectrum recorded after cooling to 323 K; (e) the same as (b) together with the gas phase.

delocalized bond system of the C_6 ring (including the C–O bond as well) that results in the dehydrogenation of the ring. We propose the following scheme, which shows that dehydrogenation of cyclohexanone proceeds through the π-oxoallylic species:



(IV)

The sharp bands at 1600 and 1495 cm^{-1} in Fig. 5b can be compared with bands formed when cyclohexanol vapor is heated with the Pt/SiO_2 sample at 573 K (Fig. 5d). The latter shows well-defined bands at 1595, 1500, and 1475 cm^{-1}. These can be assigned to the characteristic vibrations of a monosubstituted aromatic ring (*15*), i.e., the high-temperature dehydrogenation resulted in the formation of surface phenolate. The presence of a delocalized bond system π-bonded to the Pt surface is strongly suggested by the very low CO stretching frequency of chemisorbed CO showing bands at 1990 and 1830 cm^{-1}. The higher-frequency band shifted to 2020 cm^{-1} when H_2 was added to the system. This very low frequency (1990 cm^{-1}) indicates the presence of strong electron donors (*12*, *13*) on the metal surface, i.e., the π-bonded aromatic ring and those delocalized systems that were depicted before (**IV**).

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