

Infrared Spectroscopic Studies of Adsorption and Catalysis: Acetone and Acetaldehyde on Silica and Silica-Supported Nickel

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Infrared spectral data are presented for the adsorption of acetone and acetaldehyde on silica and silica-supported nickel at various temperatures.

On silica, the hydrogen-bonded interaction between surface hydroxyl groups and the adsorbate carbonyl groups has been confirmed. A new adsorbed species is found on heating acetaldehyde in the presence of silica at 120°C, which can be convincingly identified as crotonaldehyde. It seems likely that this is formed by a surface(acid)-catalyzed aldol condensation reaction between two molecules of acetaldehyde followed by dehydration.

Over silica-supported nickel, slow catalytic reactions have been observed resulting in decomposition to methane and carbon monoxide from acetaldehyde alone at 20° and 120°C, and from acetone and hydrogen at 200°C. The former reactions are very similar to other reported aldehyde decarbonylation reactions studied by nonspectroscopic methods.

INTRODUCTION

Infrared methods have been used by several workers to study the adsorption of these compounds on a variety of surfaces. Acetone has been studied on porous glass (1-4), Aerosil (5), and iron and cobalt suspended in paraffin oil (6). Acetaldehyde has been studied on porous glass (1), 3:1 silica-alumina (7, 8), and iron, cobalt, and nickel in paraffin oil (6). However, none of the earlier work (1-8) has involved parallel measurements of both the C-H stretching and C=O stretching regions of the spectra and this has been an aim of the present work.

Sidorov (2) considered that two types of site were active in adsorption onto silica; surface OH groups which interact with adsorbed molecules by hydrogen bonding (type 1 sites), and surface oxygen or silicon atoms (type 2 sites). He found (1, 2) that both acetone and acetaldehyde are physically adsorbed onto type 1 sites at room temperature, although prolonged evacuation failed to remove them completely.

Folman and Yates (3, 4) measured band intensities of acetone adsorbed onto thin plates of Vycor porous glass and concluded that type 1 sites were operative at 25°C, but at higher temperatures they noticed a hysteresis effect on adsorption-desorption cycles. They accounted for this in terms of a slow migration from type 1 to type 2 sites.

More recently Lorenzelli (5) studied acetone adsorbed on pressed Aerosil and found a similar shift in the $\nu_{\text{O-H}}$ band, but reported a doubling in the $\nu_{\text{C=O}}$ frequency of the adsorbate, which he attributed to a second unspecified type of interaction. He also noticed that after heating adsorbed acetone to 500°C, it could not all be removed by evacuation, whereas the simple hydrogen-bonded interaction is expected to break down at these temperatures. However, since the adsorbate frequencies were unchanged on heating, he concluded that no reaction had taken place, and some acetone remained physically trapped in the pores of the silica.

Fabbri and co-workers (7, 8) found two

adsorbate carbonyl stretching bands for acetaldehyde on silica-alumina and attributed these to interactions with two types of sites, namely Lewis and Bronsted acid centers. The lower frequency band at 1630 cm^{-1} was found to arise from the more strongly held species.

All these previous results indicate that both acetone and acetaldehyde are initially bound to silica surfaces through fairly strong hydrogen bonding, although the situation appears to be more complicated at higher temperatures. From the work described in this paper we conclude that the silica surface is itself catalytically active in promoting condensation reactions of acetaldehyde at higher temperatures, and the products formed are more strongly held than the original compound.

The only results yet reported of infrared studies of acetone or acetaldehyde adsorbed on metals are by Neff (6), using metal films of iron, cobalt, and nickel suspended in paraffin oil. This method has the advantage that no silica support is required, and so effects due to adsorption onto silica are eliminated, as is also the highly absorbing silica background from 1300 to 700 cm^{-1} . However, it has the compensating disadvantage that non-volatile adsorbates or products may be retained dissolved in the paraffin; the presence of the oil medium also prevents observations of the well-characterized $\nu_{\text{C-H}}$ region from 3100 to 2700 cm^{-1} . Neff found that at 25°C acetone was not chemisorbed on nickel, whereas on iron and cobalt the carbonyl bond was opened to form a metal-oxygen bond, giving a surface alkoxide structure. Acetaldehyde when exposed to nickel was almost exclusively decomposed to produce chemisorbed carbon monoxide. Unfortunately, any other products could not be identified. On iron and cobalt no such decomposition was found, the aldehyde also being adsorbed as a surface alkoxide.

EXPERIMENTAL

a. Materials. The Cab-O-Sil powder was pressed for 5 min at 2 tons/sq. inch into

thin discs 1 inch in diameter and weighing about 80–100 mg. The supported-metal discs were prepared in the same way from dried nickel nitrate-silica powder and reduced in a slow stream of dry hydrogen at 300°C for 4 hr; they contained about 10% by weight of nickel metal.

The adsorbates were thoroughly degassed at 10^{-5} torr several times at liquid nitrogen temperature and the gases admitted to the cell at 25°C up to a pressure of 10 torr.

b. Adsorption cell. A double-beam Pyrex glass cell has been developed suitable for use at high and low temperatures, which is detachable from the main vacuum system. By this means spectra can be taken of both the vapor and the adsorbed phase, the former being accurately balanced out at room temperature by use of the two beams of the spectrometer. Vapor pressures between 10^{-1} and 10^{-5} torr were indicated by a Pirani head directly attached to the cell. The optical pathlength of the cell was about 10 cm, and it was sealed with 5 mm thick windows of calcium fluoride affixed by a pigmented alkyd resin.

c. Spectrometer. A Grubb-Parsons double-beam grating instrument type G.S.2 was used throughout, to cover the accessible range from 4000 to 1200 cm^{-1} . The silica support and the calcium fluoride windows used on the cell prevented any investigations at frequencies lower than 1200 cm^{-1} .

d. General procedure. After mounting in the cell, the silica discs were heated at 300°C under vacuum for an hour to remove adsorbed water, and evacuated for a further hour while cooling to 25°C and until a pressure of 10^{-5} torr was maintained. Nickel-on-silica discs were reduced as described above and evacuated for a further hour at 25°C . Spectra of the discs were taken before and after admission of the sample vapor at a pressure of 10 torr. In general the gas phase was left to stand at 25°C for 12 hr over the absorbent; the samples were then evacuated (or heated and then evacuated) and changes in the spectra were recorded. Experiments were

TABLE 1
INFRARED FREQUENCIES OF ACETONE ADSORBED ON CAB-O-SIL

Band	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	Literature values (Ref.)
$\nu_{\text{O-H}}$ (free)	3740	—	3740 (1)
$\nu_{\text{O-H}} \dots \text{O}$	~ 3400	~ 340	3370 (1), ~ 3400 (3,4)
	3003	15	3008 (2), 3020 (4)
ν_{CH_3}	2960	11	2967 (2)
	2920	16	2926 (2), 2935 (4)
$\nu_{\text{C=O}}$	1709	39	1719 (1), 1703, 1690 (5)

also carried out in the presence of hydrogen gas in the cases of adsorption onto nickel samples.

RESULTS

A. Acetone

1. Acetone on Cab-O-Sil

The spectra obtained are in good general agreement with those reported previously on porous glass (1-4) and Aerosil (5) at room temperature. At a pressure of 10 torr and at 25°C the spectra show the bands listed in Table 1.

The bond-stretching modes of free and hydrogen-bonded surface OH groups closely followed the behavior found by Folman and Yates (3, 4), but whereas they reported only two $\nu_{\text{O-H}}$ bands, we have observed three, in agreement with Sidorov (2). We have not found the doubling of the $\nu_{\text{C=O}}$ band noted by Lorenzelli (5).

Figure 1(a) shows the temperature dependence of the optical density for the bond-stretching modes indicated. Values for the $\nu_{\text{O-H}}$ bands have not been presented, since they were of optical density less than 0.1, even at a pressure of 10 torr. On step-wise evacuation from 10 to 10^{-3} torr, the intensity changes closely paralleled the effect of raising the temperature to 200°C.

Although no detailed investigations were made of adsorption-desorption hysteresis phenomena, it was noted that a weak CH band remained after pumping at 10^{-5} torr for an hour at 25°C. By this time the free hydroxyl band at 3740 cm^{-1} had been restored to its original intensity and the

residual ν_{CH} band was the only indication of anything left on the surface.

In Fig. 1(b) is plotted the shift $\Delta\nu$ (cm^{-1}) of the perturbed surface OH group

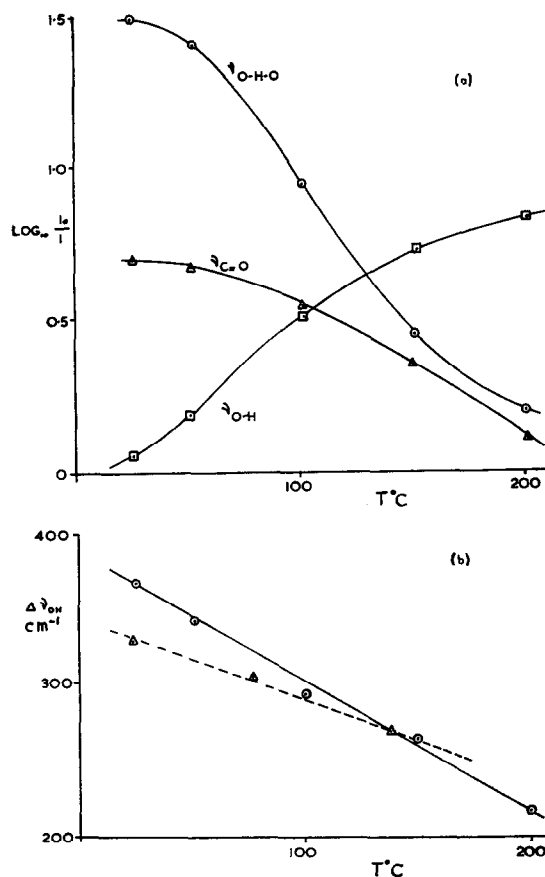


FIG. 1. Adsorption of acetone on Cab-O-Sil at different temperatures: (a) temperature dependence of optical densities; \odot , $\nu_{\text{O-H}} \dots \text{O}$; Δ , $\nu_{\text{C=O}}$; \square , $\nu_{\text{O-H}}$ (free); (b) temperature dependence of $\Delta\nu_{\text{OH}}$; \odot , our results on Cab-O-Sil; Δ , Folman and Yates on porous glass (3).

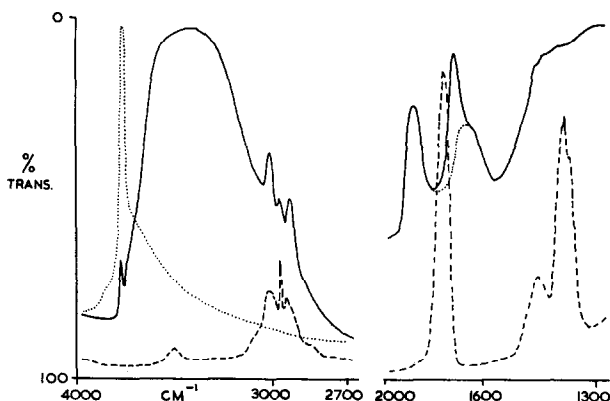


FIG. 2. Infrared spectrum (4000–1300 cm^{-1}) of acetone adsorbed on Cab-O-Sil at 25°C., evacuated surface; ---, acetone vapor (10 torr) in equilibrium with the silica sample; —, adsorbed acetone.

in Cab-O-Sil on adsorption as a function of temperature. The values given by Folman and Yates on porous glass (3) are also shown for comparison.

Figure 2 shows a typical spectrum of adsorbed acetone.

2. Acetone on Silica-Nickel

a. In the absence of hydrogen. No significant differences were observed when acetone was adsorbed onto thoroughly degassed silica-supported nickel, as compared with adsorption onto silica alone. The presence of the metal particles dispersed over the surface considerably reduced the transmission of the samples in the 4000 to 2000 cm^{-1} region, so that the O–H and C–H stretching modes were not observed so clearly. However, weak bands were still seen at 3008, 2960, and 2920 cm^{-1} and the carbonyl band again appeared at about 1710 cm^{-1} . Since evacuation to 10^{-4} torr removed virtually all adsorbed species, as from silica alone, it was concluded that no chemisorption had occurred, in agreement with the results of Neff (6).

b. In the presence of hydrogen gas. At 25°C the addition of hydrogen gas at a pressure of 10 torr either before or after the addition of acetone produced no change in the spectra of either the adsorbed or the vapor phase. However, after heating to 200°C for 1 hr a slow decomposition reaction was observed, producing methane and carbon monoxide. This was established

beyond doubt by the appearance in the spectrum of the gas phase of new absorption bands at 3018 (CH_4) and 2144 cm^{-1} (CO), each with well-defined rotational structure, and also a sharp band at 1306 cm^{-1} (CH_4). These exactly correspond with the vibration frequencies of the pure gases. With the appearance of these new bands, there was a corresponding decrease (by about 50%) in the intensity of the vapor-phase acetone absorption. Moreover, the adsorbed phase also showed a band at 2054 cm^{-1} , characteristic of carbon monoxide adsorbed on nickel, which was not removed by room-temperature evacuation. The cracking reaction did not, however, go to completion even after heating at 250°C for 8 hr.

B. Acetaldehyde

1. Acetaldehyde on Vycor Porous Glass at 25°C

Although the spectra obtained indicate a type of adsorption similar to that found by Sidorov (1), the frequencies of the bands are slightly different. It is difficult to make an accurate comparison of the two results because our sample of glass was more strongly heated before adsorption (12 hr at 800°C and 12 hr at 500°C in air, before evacuation at 300°C), and also because Sidorov did not state the time that the sample had been left in contact with the surface. The glass plate we used was

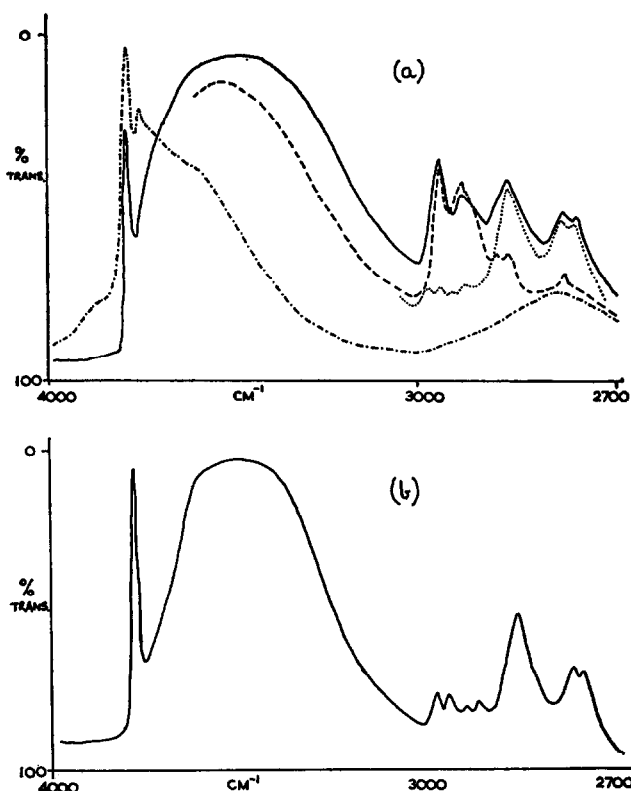


Fig. 3. Infrared spectrum (4000–2700 cm^{-1}) of acetaldehyde adsorbed on silica at 25°C. (a) Porous Vycor glass: — · — · — · — · —, evacuated surface; · · · · ·, immediately after adsorption (10 torr); —, 12 hr after adsorption; - - - - -, on subsequent evacuation to 10^{-5} torr. (b) Cab-O-Sil: —, adsorbate in equilibrium with vapor (10 torr).

0.3 mm thick, and before adsorption the free $\nu_{\text{O-H}}$ band was resolved into two sharp components at 3745 and 3704 cm^{-1} . The same result has been recently reported by Low and Ramasubramanian (9), who have convincingly attributed these two bands to SiOH and BOH groups, respectively.

The spectrum of the 4000–2700 cm^{-1} region immediately after adsorption, which is shown in Fig. 3(a), is very similar to that for adsorption onto Cab-O-Sil at 25°C [see Fig. 3(b)]. After standing for 12 hr there was a slight decrease in the intensity of the aldehydic $\nu_{\text{C-H}}$ bands, whereas the bands at 2981 and 2939 cm^{-1} became much stronger, and could not be removed by room-temperature evacuation. These spectra are also shown in Fig. 3(a), and the changes in optical density are plotted against pressure (in torr) in

Fig. 4(a). The strong background adsorption of porous glass below 2000 cm^{-1} prevented an accurate determination of the intensity of the adsorbate carbonyl band, which was between 1725 and 1730 cm^{-1} . The frequencies of the other bands are listed in Table 2.

There is clearly little difference initially between the room-temperature adsorption of acetaldehyde to Vycor porous glass and to Cab-O-Sil; but after several hours over porous glass the surface spectrum shows absorption bands of alkyl groups, and it is these new groups which cannot be removed rather than the original adsorbate. Since this does not occur over Cab-O-Sil, the porous glass must be chemically active even at 25°C; this may well be caused by the presence of boron in the material.

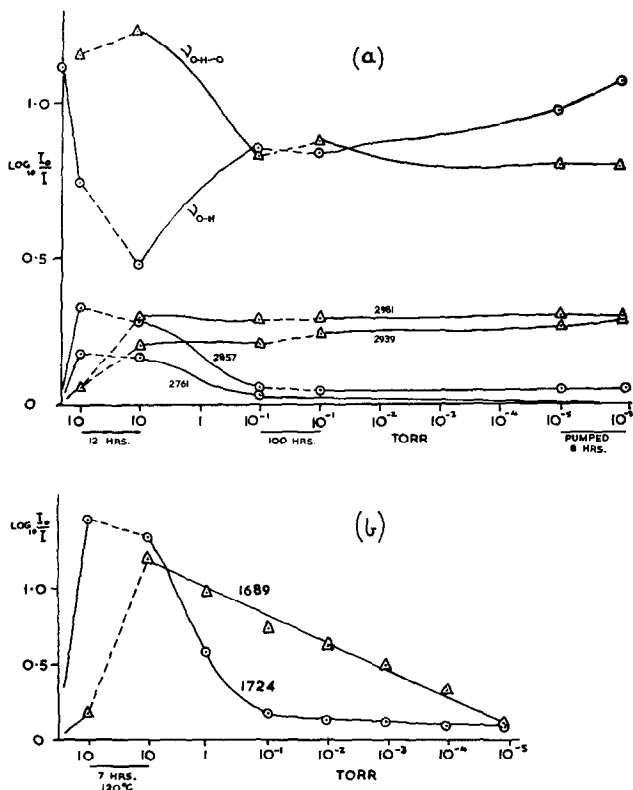


FIG. 4. Infrared intensity changes in the absorption bands of adsorbed acetaldehyde: (a) after standing and evacuation over porous Vycor glass; (b) after heating over Cab-O-Sil; \circ , 1724-cm^{-1} band; Δ , 1689-cm^{-1} band.

TABLE 2
INFRARED FREQUENCIES (cm^{-1}) OF ADSORBED ACETALDEHYDE (10 TORR) AT 25°C

Absorption mode	Gas phase	Porous glass		Cab-O-Sil		
		This work	Sidorov, Ref. (1)	Initially	After 6 hr at 120°C	Crotonaldehyde
$\nu_{\text{C}=\text{CH}}$	—	—	—	—	3045	3042
ν_{CH_2}	{ 3024 (R)	3008 ^a	—	3000	3004	3004
	{ 2996 (P)	2981 ^b	3030	2974	2980	2980
	{ 2967 (Q)	2939 ^b	—	2941	2950	2951
	{ 2926	2878 ^c	—	2920	2924	2924
$\nu_{\text{C}-\text{H}}$	{ 2840 (R)	—	—	—	—	2850
	{ 2822 (Q)	2857	2900	2852	2850	—
	{ 2804 (P)	—	—	—	—	2825
	{ 2736 (R)	2761	—	2762	2760	—
	{ 2704 (P)	2745	2780	2740	2744	2744
$\nu_{\text{C}=\text{O}}$	{ 1763 (R)	—	—	1724	1724	—
	{ 1749 (Q)	—	—	—	1689	1688
	{ 1735 (P)	—	—	—	—	—
$\nu_{\text{C}=\text{C}}$	—	—	—	—	1643	1642
δ_{CH_2}	1352	—	—	1352	1352	—

^a Only visible initially.

^b Both become strong after 12 hr at 25°C .

^c Only visible on evacuation.

2. Acetaldehyde on Cab-O-Sil

The absorption of acetaldehyde has been studied at 25° and 120°C over Cab-O-Sil. It was also found that results with partially deuterated silica (OH:OD about 1:1) were very similar, and that no exchange with acetaldehyde took place either on standing or after heating. The frequencies of the various ν_{CH} bands are listed in Table 2. Figure 3(b) shows a typical spectrum at 25°C between 4000 and 2700 cm^{-1} .

In the region below 2000 cm^{-1} the carbonyl absorption at 25°C showed a single peak at 1724 cm^{-1} , and the C-H angle-deformation bands were also weakly visible between 1300 and 1400 cm^{-1} . Of particular interest are the results obtained at higher temperatures. The most pronounced effect in the spectra was the appearance of a second, strong carbonyl absorption band at 1689 cm^{-1} with a shoulder of variable intensity at 1676 cm^{-1} , found in all cases after heating to 120°C for several hours. Accompanying this new

band, there was also found a third peak at 1643 cm^{-1} which, although considerably weaker than the one at 1689 cm^{-1} , was nevertheless quite sharp, as shown in Fig. 5(b). The changes in the spectra of the 3100–2700 cm^{-1} region are also shown in Fig. 5, together with spectra of crotonaldehyde adsorbed at 25°C under identical conditions. Thus virtually all the new bands in the acetaldehyde spectrum in both regions may be attributed to adsorbed crotonaldehyde formed on the silica surface. For cases (b) and (c), absorption in the ν_{CH} region was significant even after pumping for several hours below 10^{-5} torr at 25°C. The surface residue at this stage, when heated to 300°C without pumping, produced carbon monoxide in the gas phase as the only observable product, leaving the surface clean.

3. Acetaldehyde on Silica-Nickel

The spectra obtained for acetaldehyde on nickel immediately after adsorption showed bands with similar frequencies and intensities to those observed on silica alone. The

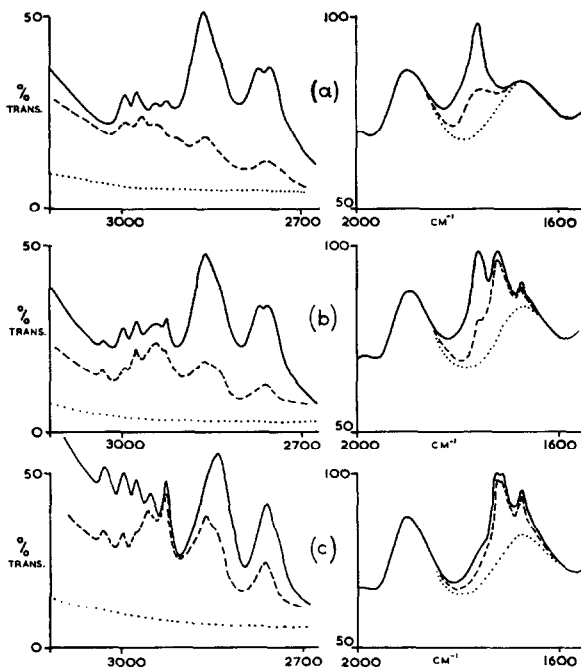


FIG. 5. Infrared spectra (3100–2700 cm^{-1} and 2000–1600 cm^{-1}) at 25°C over Cab-O-Sil: (a) acetaldehyde; (b) acetaldehyde after heating to 120°C for 6 hr; (c) crotonaldehyde;, evacuated surface; ———, adsorbate at 10 torr; - - -, adsorbate at 10^{-1} torr.

resolution and quality of spectra in the 3000-cm⁻¹ region was poorer because of scattering by the nickel particles, resulting in low background transmission. By using a 50% attenuator in the reference beam, spectra of good quality were still obtainable in the 1700-cm⁻¹ region where the carbonyl stretching frequency showed a maximum at about 1710 cm⁻¹, some 14 cm⁻¹ lower than over silica alone.

After standing at 25°C for 12 hr some of the acetaldehyde had decomposed to produce a trace of chemisorbed carbon monoxide and a little methane in the gas phase (the Q branch at 3018 cm⁻¹ and some of the rotational structure were clearly visible). Two weak bands from a new adsorbed species, at about 2970 and 2933 cm⁻¹, were now dominant in the ν_{CH₃} region. The reaction proceeded faster at 100°C, and after an hour carbon monoxide also appeared in the gas phase, with the methane band considerably stronger. However, reaction was not more than 10% complete after 4 hr at 120°C. We therefore concur with the findings of Neff (6), that no stable surface species results from exposure of acetaldehyde to nickel, although even at 25°C and in the absence of hydrogen gas it is decomposed to methane and carbon monoxide. The latter is chemisorbed at 25°C, but is driven off the surface at 120°C.

DISCUSSION

A. Adsorption on Silica

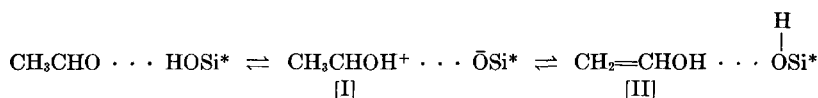
It has been shown that both acetone and acetaldehyde are initially adsorbed to both Cab-O-Sil and Vycor glass by hydrogen bonding through a surface hydroxyl

group and the carbonyl oxygen atom of the adsorbate, in agreement with all previous studies. From our results, this appears to be the main type of interaction between silica and acetone at all temperatures from 20° to 200°C.

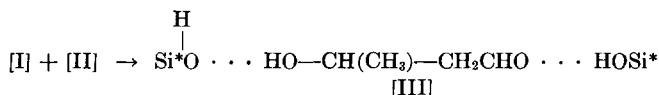
With acetaldehyde the situation is more complicated, because additional surface species are formed on standing over Vycor glass at 25°C, and over Cab-O-Sil at 120°C.

The two low-frequency bands at 1689 and 1643 cm⁻¹ have to be accounted for, as do the changes in intensity and frequency in the ν_{C-H} region and the carbon monoxide produced when the residual surface species was strongly heated. It is difficult at this stage to account satisfactorily for the formation of an alkyl species over Vycor glass at 25°C. However, as mentioned above, we consider that the spectra obtained with Cab-O-Sil at 120°C may be fully interpreted in terms of the formation of crotonaldehyde which remains adsorbed to the surface. This may be accounted for on the hypothesis that the acidity of the surface hydroxyl groups is active in promoting an aldol condensation between two molecules of acetaldehyde. The aldol thus formed may then be dehydrated either immediately or on heating to yield the corresponding unsaturated aldehyde, which in turn may decompose on stronger heating to produce carbon monoxide and a hydrocarbon. In the case of acetaldehyde the products would be acetaldol, crotonaldehyde, and propylene. Following the reaction mechanisms discussed by Noyce and Pryor (10), we propose the following sequence, where Si* indicates a surface silicon atom:

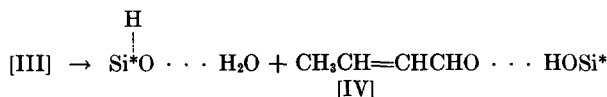
(1) Surface catalyzed keto-enol tautomerism.



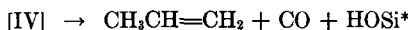
(2) Addition reaction between the enol form and protonated keto molecule to give acetaldol.



(3) Dehydration of acetaldol to crotonaldehyde and water.



(4) Formation of propylene and carbon monoxide from the decomposition of crotonaldehyde at 300°C.



We have confirmed that the spectra obtained at higher temperatures from adsorbed acetaldehyde are consistent with such a scheme by doing preliminary adsorption experiments with crotonaldehyde itself. At 25°C the 5–7 μ region shows three bands at 1688, 1672, and 1642 cm^{-1} with an intensity pattern almost identical with that of the bands found after heating acetaldehyde (see Fig. 5). We have therefore assigned these frequencies to $\nu_{\text{C}=\text{O}}$ (1688 cm^{-1}) and to $\nu_{\text{C}=\text{C}}$ (1642 cm^{-1}) absorption bands of adsorbed crotonaldehyde. The frequencies of the $\nu_{\text{C}-\text{H}}$ bands also correspond well with those of the condensed acetaldehyde residue. Moreover, on heating the adsorbed crotonaldehyde to 300°C, carbon monoxide was found in the gas phase.

Bonino and Fabbri (8) have previously found three bands for crotonaldehyde at 1701, 1667, and 1626 cm^{-1} for adsorption onto 3:1 silica-alumina, which were in that case attributed to interaction with both Lewis and Bronsted-type centers.

It is interesting to compare this proposed sequence of surface reactions with some nonspectroscopic studies. Malinowski and co-workers have made extensive studies of the base-catalyzed aldol condensation reactions of formaldehyde with other aliphatic aldehydes (11), at high temperatures over treated silica. They, too, found crotonaldehyde from the self-condensation of acetaldehyde. Czarny (12) found that crotonaldehyde was produced when acetaldehyde and water vapor were passed together over a treated silica-tantalum oxalate catalyst at 335°C. Others (13) have studied the catalytic action of silica-alumina on acetaldehyde by gas chromatography, and found that at temperatures below 200°C, crotonaldehyde was the

principle product, whereas at higher temperatures cracking predominated and water, carbon monoxide, propylene, and other hydrocarbons were produced. The effect of the tantalum oxalate and the alumina was probably to increase the surface acidity, thus making their combined catalysts more effective than pure silica. Nevertheless, we have shown that the silica itself is active in promoting surface reactions of this type. Such self-condensations should in principle be possible with any aldehyde or ketone provided that it contains at least one α -hydrogen atom. However we failed to observe any analogous effects in the spectra of acetone, even at temperatures as high as 200°C.

B. Adsorption on Supported Nickel

In addition to the reactions observed over silica, our results have shown that slow cracking reactions occur over silica-supported nickel. However, these require milder conditions than the silica-catalyzed condensations and the products are different, so it is likely that the two processes are independent of each other. As stated above, acetaldehyde is decomposed on standing over a bare nickel surface at 25°C, whereas acetone requires the presence of hydrogen gas and a temperature of 200°C.

Such decarbonylation reactions have been noted before but, apart from similar results reported briefly by Neff (6) for acetaldehyde, not supported by any infrared studies of surface phenomena. Böekesen and van Senden (14) in 1913 studied the decomposition of heptanal at 220°C over finely divided nickel supported on pumice and observed carbon monoxide as a gaseous product, together with hexene and hexane. Suen and Fan (15) in 1942

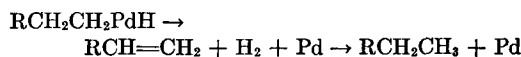
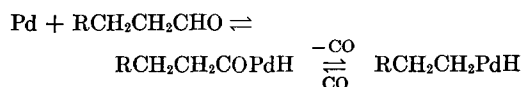
TABLE 3
THERMODYNAMIC FUNCTIONS FOR THE DECARBONYLATION REACTIONS

Reaction	Temp. (°K)	$-\Delta H^\circ$ (kcal/mole)	$-\Delta G^\circ$ (kcal/mole)
$\text{CH}_3\text{CHO} \rightleftharpoons \text{CO} + \text{CH}_4$	298	4.6	13.2
	500	4.6	20.0
$(\text{CH}_3)_2\text{CO} + \text{H}_2 \rightleftharpoons \text{CO} + 2\text{CH}_4$	298	10.5	22.0
	500	10.5	28.3
$(\text{CH}_3)_2\text{CO} \rightleftharpoons \text{CO} + \text{C}_2\text{H}_6$ (not observed)	500	-5.1	11.4

confirmed this and established that over nickel-kieselguhr at 250°C in an atmosphere of hydrogen, *n*-hexane was the main product, any hexene first formed being reduced under these conditions to the paraffin. No heptane was found. According to these authors, Sabatier and co-workers had previously shown that the reduction of benzaldehyde over nickel at 210–235°C to toluene was accomplished by the formation of some benzene and carbon monoxide, which was subsequently reduced to methane. Over copper at 350°C, benzene was the main product.

More recently Tsuji, Ohno, and Kajimoto (16) have confirmed that the decarbonylation of aliphatic aldehydes is a general reaction, which produces a mixture of the corresponding olefin and paraffin, together with carbon monoxide and hydrogen. For example, decanal reacted at 200°C over metallic palladium to give nonene and nonanes. Hemidy and Gault (17) have shown by mass-spectrometric analysis that butanal was cracked to propene and propane over heated palladium. The same reaction required higher temperatures over a platinum catalyst.

Tsuji and others have proposed (16) the following reaction scheme:



The surface intermediates in this series are the acyl and alkyl palladium complexes, but it is stated (16) that there is still no direct evidence of their existence. We have so far been unable to obtain

infrared evidence for these on nickel, but we plan to continue work with aldehydes and ketones on metals in an attempt to obtain direct evidence for or against such species in favorable cases. It does not appear that evidence has previously been obtained for surface-catalyzed decarbonylation reactions of ketones in the gaseous phase.

The decomposition reactions that we have observed are both thermodynamically feasible and exothermic in the gaseous phase, as indicated in Table 3. The values are calculated from standard free energy data taken from Pitzer and Brewer (18). The products are presumably even more stabilized by the surface adsorption of carbon monoxide, which we have shown to occur over nickel. It might have been expected from these values that acetone would be decomposed at 25°C, but it is probably only at higher temperatures that the system acquires the energy of activation necessary for the reaction to proceed.

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