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The Infrared Spectrum of Glycine Chemisorbed by Supported Nickel

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The infrared absorption spectrum of glycine chemisorbed from the vapor onto silica-supported nickel has been recorded. The NH stretching frequencies appeared at 3350 and 3285 cm^{-1} and the carboxyl stretching frequencies at 1595 and 1405 cm^{-1}. From these bands it is concluded that glycine was present on the surface in the anionic form and that it interacts with the metal through the carboxyl group as well as through the NH_2 group.

INTRODUCTION

Infrared spectroscopy has proved to be a very useful tool in surface chemistry (*1*, *2*). This technique has been particularly valuable in determining the structures of surface adsorption complexes. To our knowledge all studies published to date in this area have considered the adsorption of molecules containing only one functional group. It therefore appears worthwhile to investigate the chemisorption of polyfunctional molecules. It is not known whether bifunctional molecules form chelate-like complexes involving two bonds with one surface atom or whether di-adsorption on two adjacent surface atoms is preferred. If a molecule can form two adsorption bonds, differing in bond strength, the additional question arises whether at high coverage the weaker bond is broken to use these sites for the formation of stronger bonds with additional mono-adsorbed molecules. Finally, the question arises whether the metal atoms of the surface will remain at their original sites or the chemisorption will be of the corrosive type (*3*). Although these problems are of considerable fundamental importance in heterogeneous catalysis, it appears impossible to give an unequivocal answer from the present knowledge of chemisorption.

To initiate this investigation we have chosen an amino acid as the bifunctional adsorbate since amino acids are of considerable importance in biochemistry and biocatalysis. A special application of optically active amino dicarboxylic acids is their use as "modifiers" in asymmetric catalysis (*4*). It is perhaps surprising that the adsorption of amino acids on metal surfaces has not been studied to date. A possible reason for this might be the difficulty for an adsorbens of very low volatility to be chemisorbed on a reactive metal such as nickel. Adsorption from solution is not feasible as the metal surface would be strongly contaminated by the solvent and subsequent reduction at temperatures in excess of 350°C would decompose the surface complex. For the feasibility of the present work it was, therefore, essential to sublime amino acids in vacuum without decomposition. Literature data show that this should be possible (*5*, *6*). From thermodynamic data on the stability of metal amino acid complexes (*7*), amino acids are expected to form strong bonds with transition metals, whereas interactions between amino acids and the silica support are expected to be much weaker. In special experiments preceding the present work we succeeded in finding conditions for subliming glycine (NH_2CH_2COOH) on silica supported nickel and successively desorbing

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the excess glycine (condensed on the metal and on the support) without decomposition of the adsorption complex on the nickel surface.

EXPERIMENTAL

Apparatus

The infrared cell is shown in Fig. 1. It has a body of pyrex glass and contains a stainless steel oven, which can be heated by induction. The temperature is measured by a thermocouple. The Ni/SiO$_2$ disk in its stainless steel holder can be transported from one section to another by means of a winch with gold wires. During the reduction of the sample it is in position b. Sublimation of glycine occurs from the inside of two parallel walls d which can be heated from the outside while the disk is in position d. When a spectrum is recorded the disk is located between the potassium bromide windows e. The windows are attached to the pyrex glass using a mixture of Apiezon wax W40 and Apiezon grease T. The cell is connected to a high vacuum apparatus. A pressure of 1.3×10^{-3} N m^{-2} can be maintained if the apparatus is closed from the pumps.

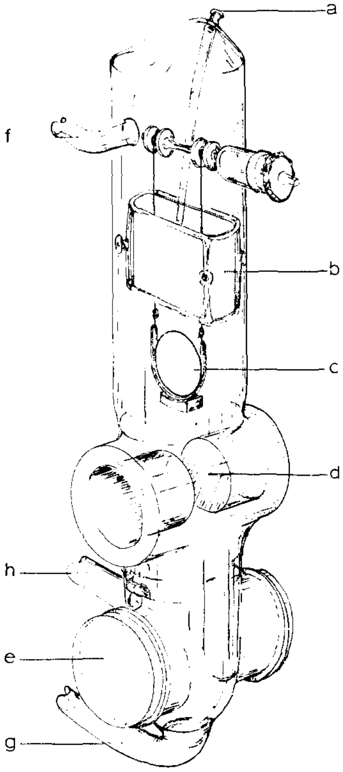


FIG. 1. The infrared cell: (a) thermocouple well; (b) stainless steel oven; (c) disk; (d) subliming walls; (e) KBr windows; (f) hydrogen outlet; (g) hydrogen inlet; (h) connection with the vacuum system.

Sample preparation

The Ni/SiO$_2$ samples were prepared by impregnation. Silica Cabosil and Ni(NO$_3$)$_2$$\cdot$6H$_2$O were mixed with distilled water. The water was then slowly evaporated while the mixture was stirred. The dried impregnated silica was subsequently ground and pressed to give self-supporting disks of 2.8-cm diameter, using a pressure of 8×10^7 N m^{-2}. After reduction the disk had a weight of 50 mg and contained 20% wt % nickel.

Prior to attaching the windows, finely divided glycine was spread on the inside of the walls d of the cell. Reduction at 350°C in the stainless steel oven during 16 hr took place in a flow of hydrogen, purified over a Pt–asbestos catalyst and a trap cooled with liquid nitrogen. After reduction, the temperature of the disk was kept at 350°C while the cell was evacuated to remove chemisorbed hydrogen. Next, the disk was lowered to a position between the two glycine covered walls d. The disk-holder was in contact with the wall heated to 170°C and the disk had approximately the same temperature. Its surface was roughly 1 mm from the wall. In this way glycine was sublimed from the wall to the disk for 20 hr. Subsequently, the disk was brought to the opposite wall and the sublimation procedure was repeated. During sublimation hydrogen appeared in the gas phase. Excess glycine was observed to condense on the neighboring glass parts including the opposite wall d showing that glycine molecules were able to travel through the disk. Subsequently, the disk was lowered to the position between the KBr windows. The infrared spectra were recorded on a Perkin–Elmer infrared spectrophotometer, model 325, using the crossed chopper mode to eliminate radiation from the sample. The reference beam was attenuated to compensate for the low transmittance of the disk (8% at 3000 cm^{-1}).

RESULTS AND DISCUSSIONS

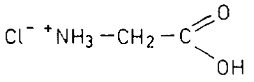
The infrared spectra of the Ni/SiO_2 disk before and after adsorption of glycine are shown in Fig. 2. Due to the strong absorption by the silica support only the frequency region 4000–1350 cm^{-1} could be used. To establish that the spectrum was characteristic of glycine chemisorbed on nickel atoms and not on the silica support, we repeated the adsorption procedure as previously described, but using an unimpregnated disk of pure silica. There was no evidence from the infrared spectra that glycine was adsorbed onto the pure silica surface.

These results prove that glycine can indeed be chemisorbed on a prereduced Ni/SiO_2 sample by subliming from the vapor. The evolution of hydrogen during adsorption of glycine shows that adsorption is dissociative as might be expected from previous results of the adsorption of carboxylic acids such as formic acid (*8*). A question which was uncertain before we started this study and has now been settled was whether the sublimed glycine would be able to migrate over the silica surface until it is trapped by a nickel particle. It seems to us that the techniques used here would be suitable for studying the adsorption of not only amino acids, but also of other compounds of low volatility.

For an interpretation of the infrared spectra of the chemisorption complex a comparison with the infrared spectra of glycine and metal glycine complexes (*9–17*) of known structure appears useful. In the 3500–3000 cm^{-1} region NH_2 and NH_3^+ stretching frequencies occur. Literature data (*16*) show that the charged NH_3^+ group in the zwitterionic form gives rise to absorption bands in the region 3130–3000 cm^{-1}, whereas the uncharged NH_2 group absorbs in the region 3500–3300 cm^{-1}. The NH stretching bands at 3350 and 3285 cm^{-1} in the sorption complex clearly indicate that glycine is not adsorbed on the metal in its zwitterionic form. Further, the data in Table 1 show that coordination of the lone pair of the nitrogen atom of the amino group results in a shift to lower frequencies of the NH bands, related to the free amino group. It would appear, therefore, that in the chemisorption complex the nitrogen atom of the amino acid interacts with the metal.

In the 1700–1350 cm^{-1} region carboxyl stretching frequencies occur. For the carboxyl group two extreme structures are possible:

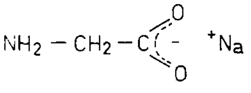
(1) an asymmetric structure as observed for the HCl salt of glycine:



$$Cl^- \; {}^+NH_3-CH_2-C(=O)OH$$

$\nu_{C=O}$ = 1740 cm^{-1}

(2) a symmetric structure as observed for the sodium salt of glycine:



$$NH_2-CH_2-C(\cdots O)_2^- \; {}^+Na$$

ν_{as} = 1600 cm^{-1}

ν_s = 1415 cm^{-1}

As the symmetry of the carboxyl group decreases, the asymmetric mode (ν_{as}) shifts to higher frequencies and the symmetric

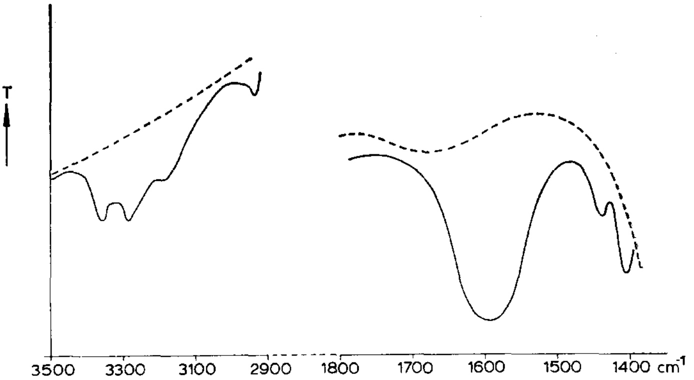


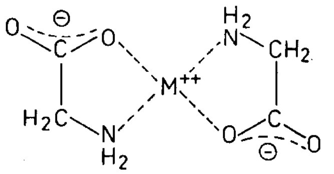
FIG. 2. IR absorption spectra of the Ni/SiO_2 disk: before (- - -), and after (——) adsorption of glycine.

TABLE 1
ASYMMETRIC AND SYMMETRIC STRETCHING FREQUENCIES OF COORDINATED AND FREE NH_2 GROUPS

Compound	ν_{as}(cm^{-1})	ν_s(cm^{-1})	Reference
Na-gly	3400	3360	(*18*)
$Ni(gly)_2$	3355	3302	(*19*)
$Ni(gly)_2 \cdot 2H_2O$	3300	3250	(*20*)
Ni-gly sorption complex	3350	3285	this work
$Pt(gly)_2$ (trans)	3230	3090	(*21*)
methyl ester of glycine (me gly)	3390	3322	(*22*)
$NiCl_2$(me gly)$_2$	3295	3252	(*22*)
$PtCl_2$(me gly)$_2$	3257	3205	(*22*)

mode (ν_s) shifts to lower frequencies; thus the difference $\nu_{as} - \nu_s = \Delta$ increases.

For the sorption complex the carboxyl stretching frequencies are at 1595 and 1405 cm^{-1}, similar to those found for the complex $Ni(gly)_2$ (see Table 2). This is an indication of a symmetric carboxyl group, in which resonance is preserved. However, this does not necessarily mean that the two oxygen atoms are structurally at equivalent positions. In the complexes of several bivalent metal ions with glycine the oxygen atoms have different positions with respect to the metal ions (*23*, *24*).



Nevertheless, the oxygen metal bond is generally believed to be essentially ionic (*18*, *24*), but with some covalent character depending on the metal ion, increasing in the series:

Ni < Zn < Cu < Co < Pd < Pt.

Some data are collected in Table 2.

Furthermore, the infrared spectrum shows bands at 2920 and 1440 cm^{-1}. These are obviously the stretching and bending modes of the CH_2 group, indicating that this group is not dissociatively adsorbed.

A third band in the NH_2 region appears near 3150 cm^{-1}. This band, which is weaker than the bands at 3350 and 3285 cm^{-1}, has also been observed by Rosenberg (*18*) and Sharma *et al.* (*19*) for metal-amino acid complexes, and by Springer and Curran (*22*) for metal-amino acid ester complexes. Springer (*22*) suggests that this band may

TABLE 2
CARBOXYL STRETCHING FREQUENCIES RELATED TO THE SYMMETRY OF THE CARBOXYL GROUP

Compound	ν_{as}(cm^{-1})	ν_s(cm^{-1})	Δ(cm^{-1})	Reference
Glycine	1595	1399	196	(*25*)
	1594	1415	179	(*12*)
$Ni(gly)_2 \cdot 2H_2O$	1599	1410	189	(*26*)
	1609	1408	201	(*25*)
	1589	1411	178	(*21*)
Ni-gly adsorption complex	1595	1405	190	this work
$Cu(gly)_2$	1607	1366	241	(*25*)
$Pd(gly)_2$	1642	1373	269	(*25*)
	1642	1374	268	(*21*)
$Pt(gly)_2$	1643	1374	269	(*21*)

↓ increasing M-O covalency

↑ increasing COO^- symmetry

be due to an overtone of an NH_2 bending vibration, its intensity enhanced and its frequency lowered by Fermi resonance with an NH_2 stretching mode.

CONCLUSIONS

The present data show that the chemisorption of glycine on nickel is dissociative and that the infrared spectrum of the chemisorption complex is very similar to that of the bulk compound Ni $(gly)_2 \cdot 2H_2O$. It therefore appears that the interaction between the glycine and nickel in the chemisorption complex is very similar to that in the compound, the structure of which is known from X-ray diffraction work. Although it is not possible to definitely rule out other possibilities, it appears very likely to us that the deprotonated glycine forms a chelate structure connecting the nitrogen atom and one of the oxygen atoms to the same nickel atom. In view of the high adsorption temperature it is even possible that the chemisorption is corrosive, in which case the nickel atom leaves its lattice position in the nickel crystal surface and forms additional bonds with a second deprotonated glycine molecule. This chemisorption complex then would have the same stoichiometry $Ni^{2+}(gly^{-1})_2$ as the corresponding bulk compound. On the basis of the present data this seems to us a realistic description of the complex resulting from the chemisorption of glycine on reduced nickel at 170°C.

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