

Infrared Spectra of Some Amino Acids Adsorbed on Silica and on Silica-Supported Nickel

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The ir spectra have been recorded of (L) α -alanine, (DL) 2-amino butyric acid, (DL) 3-amino butyric acid, and 4-amino butyric acid on silica-supported nickel. A striking dependence of the resulting adsorption complexes on the position of the NH_2 group in the amino acid molecule has been found. 2-Amino acids are adsorbed more strongly on nickel than on silica; their ir spectra resemble very closely those of the corresponding nickel salts. Quite differently 3-amino butyric acid and 4-amino butyric acid are adsorbed more strongly on silica than on nickel. The adsorbate on Ni/SiO₂ differs, however, from that on SiO₂ in the exchangeability of the H atoms against gaseous D₂. The spectra of the amino acids adsorbed on silica show striking differences: the 2-amino acids form a hydrogen-bridged complex and a surface ester containing an NH_2 group, 3-amino butyric acid forms a similar ester, but with an NH_3^+ group linked in an intramolecular 6-membered ring, and 4-amino butyric acid forms exclusively a hydrogen-bridged complex.

INTRODUCTION

In a previous article (1) we described the adsorption of glycine on silica-supported nickel. It was found that the infrared spectrum resembles closely that of the solid salt $\text{Ni}(\text{gly})_2 \cdot 2\text{H}_2\text{O}$. We concluded that the chemisorption was probably of the corrosive type. In view of the low volatility of glycine (2) we had developed a special sublimation technique to prepare the adsorption complex under well defined conditions in the infrared cell. In the present paper we report results obtained with higher amino acids on Ni/SiO₂, using the same technique. The acids investigated include α -alanine, 2-amino butyric acid, 3-amino butyric acid, and 4-amino butyric acid. Especially 3-amino butyric acid and 4-amino butyric acid are of interest. The nickel (II) complex of the former is less stable than that of its isomer 2-amino butyric acid (3), whereas the latter does not form a nickel (II) chelate to our knowledge. From the thermodynamic data of metal-amino acid complexes (4) it is clear

that the 5-membered ring formed by 2-amino acids is more stable than the 6- or 7-membered ring which would result from chelating metal ions with 3-amino acids and 4-amino acids, respectively. The difference in free energy is mainly due to the different entropies of 5-membered and larger rings, respectively. The reaction of a mono amino acid molecule with two dissolved nickel ions is accompanied by a decrease in degrees of freedom of the nickel ions. This is not true, however, for the reaction of an amino acid molecule with two nickel atoms fixed in a metal surface resulting in a six- or seven-membered ring. Such a bridged structure, therefore, can not be excluded for the entropy reasons which might make it unfavourable in the case of dissolved ions.

In this case one can visualize a complex where a molecule is linked by its two functional groups to different metal atoms. For large amino acid molecules one may further expect that with larger distance between the amino group and the carboxyl group, the adsorption of each group on the

surface will become more independent of the other.

Carboxylic acids and their derivatives are known to form strong bonds with a silica surface, forming surface esters or hydrogen bonds with OH-groups (5). In the case of glycine (1) no adsorption on the silica support could be detected. Nevertheless, it seems reasonable to assume that amino acids, being derivatives from carboxylic acids, are able to interact with surface silanol groups. Particularly if chelating with the nickel metal is not favourable, adsorption on silica would be the main reaction to occur.

EXPERIMENTAL

The infrared cell has been described elsewhere (1). Two modifications were introduced, namely, a different window attachment using brass window holders sealed to the Pyrex glass with vacseal (Varian) and a simple Pyrex device shielding the windows from evaporating amino acid (see Fig. 1). This device also ensured that the catalyst disk was placed in the infrared beam in a reproducible manner. Catalyst preparation was carried out according to Erkelens and Liefkens (6). Decomposition of the nickel nitrate to nickel oxide, prior to introduction of the pressed disk into the cell, results in disks with better transmission properties, while inner parts of the cell (windows!) are not contaminated by NO₂. It was further observed by Van Hardeveld and Hartog (7) that silica impregnated with Ni(NO₃)₂·6H₂O should not be stored

for prolonged periods because recrystallization is then likely to occur, leading to a decreasing number of small particles. This will not happen with NiO on silica. The disk was heated in a flow of purified hydrogen at 350°C and subsequently evacuated at 330°C to about 10⁻² N m⁻² for 2 hr to remove adsorbed hydrogen. The Ni/SiO₂ disk had a weight of 35 mg and contained about 20% by weight Ni. Transmittance at 3000 cm⁻¹ was 10–15%. Infrared spectra were run from 3800 to 1300 cm⁻¹ on a Perkin Elmer spectrophotometer model 325.

In the case of glycine (1) the material had been sublimed from a glass wall kept at 170°C during 20 hr. During this time glycine evaporated onto the disk, migrated through its pores and finally all glycine not adsorbed on Ni disappeared from the heated zone. For the higher amino acids mentioned in the Introduction this procedure failed. If the temperature was raised too rapidly no amino acid was retained on the disk. In order to observe good spectra a large excess of amino acid (about 15 mg each side) had to be sublimed onto the disk at the lowest possible temperature. Subsequently the temperature was slowly raised in steps of 10°C while the cell was connected to the pump. After each heating period a spectrum was recorded so that successive stages of desorbing excess amino acid could be followed until only firmly adsorbed amino acid remained in the sample. The spectra drawn in Fig. 2 did not show any change in peak position upon

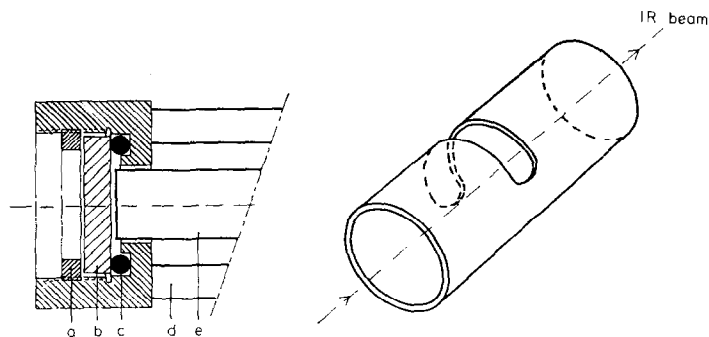


FIG. 1. Window-attachment (left) and window-protector (right). a: Screw ring; b: KBr window; c: viton O-ring; d: pyrex infrared cell; e: window-protector.

further heating, only the intensity decreased owing to decomposition or desorption of the adsorbed molecules. Chemisorption is obviously an activated process, which has no chance to occur if the temperature is raised too rapidly because the amino acid then evaporates before the surface reaction occurs.

RESULTS

Figure 2 shows the infrared spectra of (L) α -alanine, (DL) 2-amino butyric acid, (DL) 3-amino butyric acid, and 4-amino butyric acid on Ni/SiO₂ and on SiO₂. The temperatures indicated are the highest at which the disk was treated, although most spectra could be observed already at lower temperature. Before a spectrum was recorded the disk was cooled to room tem-

perature. The spectra have been corrected for background absorption and scattering. Since different reference beam attenuation has been used, no exact values are given for the transmittance. Though relative intensities may slightly change, different reference beam attenuation does not influence peak positions. Roughly estimated we would say that minimum transmittance for the amino bands is 90% and for carboxyl bands 50%, which means that about 1.5 mg amino acid is adsorbed on the disk. We recorded the spectra from 3800 to 1300 cm⁻¹ but Fig. 2 only shows the 3500–2800 cm⁻¹ (NH, CH stretch) and the 1800–1350 cm⁻¹ (CO stretch, NH and CH deformations) regions, since other regions appeared to be less interesting. Table 1 summarizes the results with the four amino acids studied.

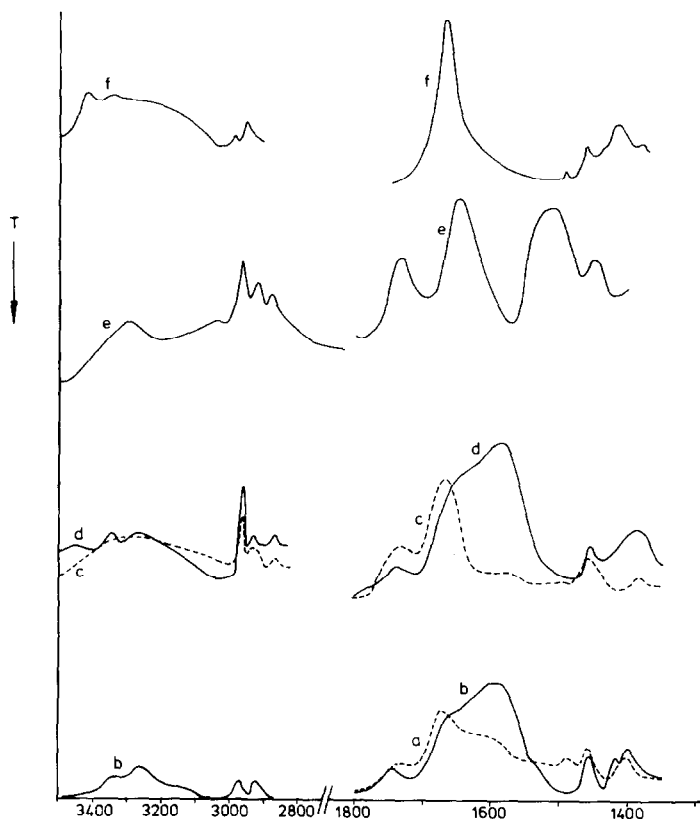


FIG. 2. Infrared spectra (ν in cm⁻¹) of adsorbed amino acids. *a*: α -Alanine on SiO₂ (150°C); *b*: α -alanine on Ni (215°C); *c*: 2-amino butyric acid on SiO₂ (160°C); *d*: 2-amino butyric acid on Ni (220°C); *e*: 3-amino butyric acid on SiO₂ (150°C); *f*: 4-amino butyric acid on SiO₂ (180°C).

TABLE 1
AMINO AND CARBOXYL STRETCHING FREQUENCIES (cm⁻¹) OBSERVED
IN THE ADSORPTION COMPLEXES^a

Compound	Amino group	Carboxyl group	$\nu_{C=O}$
α -Alanine			
On Ni/SiO ₂	3340, 3265	1590, 1400	
On SiO ₂			1740, 1675
2-Amino butyric acid			
On Ni/SiO ₂	3350, 3270	1590, 1390	
On SiO ₂	3300		1735, 1660
3-Amino butyric acid			
On SiO ₂	3300, 3050		1740, 1650
4-Amino butyric acid			
On SiO ₂	3450, 3350		1675

^a See Fig. 1.

1. Alanine (Spectrum a, b)

Sublimation starts at about 130°C.

From the NH bands at 3340 and 3265 cm⁻¹ and the COO bands at 1600 and 1400 cm⁻¹ we conclude that the chemisorption complex of (L) α -alanine on Ni is very similar to the bulk complex Ni(ala)₂ as could be expected from the result of glycine (1). A small peak at 1740 cm⁻¹ and a shoulder at 1660 cm⁻¹ can be attributed to alanine adsorption on the silica support as follows from spectrum a. In the amino region of α -alanine on silica a very broad band appeared with low intensity which is not shown in spectrum a.

2. 2-Amino Butyric Acid (Spectrum c, d)

Sublimation starts at about 120°C.

This compound shows qualitatively the same behaviour as the other two α -amino acids, glycine, and α -alanine. On the Ni/SiO₂ disk at lower temperature we could easily distinguish between adsorption on the metal and adsorption on the silica. Upon heating, bands due to adsorption on silica disappeared more readily than metal-amino acid bands.

3. 3-Amino Butyric Acid (Spectrum e)




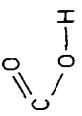

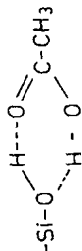
Sublimation starts at about 110°C.

In Fig. 2 only one spectrum is shown, the spectra after adsorption on Ni/SiO₂ and on SiO₂ being identical. Evidently adsorption is stronger on silica than on nickel. A weak band at about 3050 and a strong

band at 1515 cm⁻¹ point to a structure with an NH₃⁺ group. To establish the origin of the band at 1515 cm⁻¹ we carried out a H/D exchange experiment, using a pressure of 1×10^3 N m⁻² D₂ gas and a temperature of 160°C for 1 hr. This experiment revealed a striking difference between the SiO₂ disk and the Ni/SiO₂ disk. Whereas with the SiO₂ disk no change in the infrared spectrum of adsorbed 3-amino butyric acid was observed, marked changes were found with the Ni/SiO₂ disk. Here the bands at 1515, 3300, 3050, and 3745 cm⁻¹ disappeared, while simultaneously new bands appeared at 2500, 2425, and 2755 cm⁻¹. It is conceivable that the amino acid molecules adsorbed on the support exchange some of their hydrogen atoms with those of the surface OH groups. As this hydrogen is able to exchange with hydrogen adsorbed on the nickel particles as a consequence of the so-called spillover effect (16), a reaction pattern is present allowing isotopic exchange between the amino acid molecules and gaseous hydrogen. At any rate the experimental fact that upon isotopic exchange of hydrogen these bands disappear and are replaced by other bands, provides unambiguous evidence for the assignment of these bands, in particular it proves that the 1515 cm⁻¹ band involves a hydrogen atom.

As this experiment showed further that bands in the CH stretching region (3000–2850 cm⁻¹) remained unchanged it seems

TABLE 2
 SOME GENERALLY ACCEPTED N-H AND C-O STRETCHING FREQUENCIES (cm^{-1})

Structure	Molecule	NH ₂				COO	Remarks	Ref.
		ν_{as}	ν_{s}	ν_{as}	ν_{s}			
	CH ₃ NH ₂ (gas)	3470	3360			Free NH ₂ group	8	
	Pt(gly) ₂ (solid)	3236	3145			Strongly coordinated NH ₂	9	
	Ni(ala) ₂	3361	3284	1590	1414		10, 11	
	Ni(2-NH ₂ butyric acid)	3390, 3345	3276	1581	1401		10, 11	
	Amino acid zwitter ions	3130-3030					8	
	Sodium salt glycine			1600	1415	Symmetric structure	12	
	Glycine-HCl				1740	Asymmetric structure	12	
	Surface ester Acetic acid on silica				1760		5	
	Acetic acid physically ad- sorbed on silica				1724		5	

safe to conclude that the 1515 cm⁻¹ band has to be assigned to an NH₃⁺ vibration.

4. 4-Amino Butyric Acid (Spectrum f)

Sublimation starts at 90°C.

As for 3-amino butyric acid the spectra with a Ni/SiO₂ and a SiO₂ disk were identical but some remarkable differences appeared, compared with adsorption of other amino acids on silica: (a) The amino absorption bands appear at higher frequency (3450 and 3350 cm⁻¹). (b) The C=O stretching band at 1675 cm⁻¹ is sharper than in the case of other amino acids and no band at 1740 cm⁻¹ appears. (c) The adsorption complex did not decompose completely upon heating to 350°C for 16 hr, while usually heating for 20 min at 350°C was sufficient to decompose all adsorbed amino acids.

DISCUSSION

The observed bands have been assigned by making use of the relevant infrared results in the literature. Some data are compiled in Table 2. Upon comparing these literature data with our experimental results (Table 1, Fig. 2) we are able to propose structures for the adsorbed amino acids. Absorption bands due to CH vibrations are not included in Table 2 since they appear in the usual region for aliphatic saturated compounds and do not change upon adsorption and exposure to deuterium. We therefore conclude that CH groups do not interact chemically with the surface.

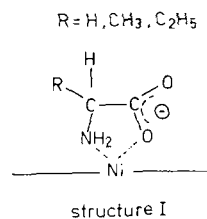
We shall discuss the following adsorption complexes:

1. Amino acid adsorption on nickel
2. Amino acid adsorption on silica
 - (a) 2-Amino acids
 - (b) 3-Amino butyric acid
 - (c) 4-Amino butyric acid

1. Amino Acid Adsorption on Nickel

From the infrared spectra of α -alanine (Fig. 2a) and 2-amino butyric acid (Fig. 2c) on nickel it is clear that qualitatively the absorption bands are the same as in the corresponding nickel chelates. As in the

case of glycine (1) our conclusion is therefore that these amino acids are adsorbed in their anionic form, having the same structure as the salts:



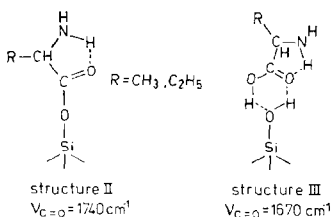
The spectra do not allow us to decide whether the nickel atom is still part of the metal lattice. In view of the high adsorption temperature (up to 200°C) it cannot be excluded that the chemisorption is corrosive which means that the nickel atom is pulled out of its lattice position to form the two-dimensional salt. However, it is not likely that the complex completely loses contact with the metal because the NH₂ group still undergoes H/D exchange with D₂ gas. Another reason for rejecting the model of a salt phase without chemical interaction with the nickel can be based on a result reported by Izumi (13), who found that upon washing the modified catalyst several times the amino acid was not removed from the surface.

2. Amino Acid Adsorption on Silica

Although this study was motivated by the problem of the chemisorption complex with nickel the data obtained also provide interesting and unexpected information with respect to the chemisorption of amino acids on silica. With 2-amino acids some bands in the spectra on Ni/SiO₂ are due to adsorption on SiO₂. From the weakness of these bands, however, it is concluded that interaction is stronger with nickel than with silica. In particular, if one takes into account that the silica surface of a Ni/SiO₂ disk exceeds that of the metal by two orders of magnitude, it is significant that the bands characteristic for adsorption on the metal have by far the greatest intensity in the spectrum. However, a completely different result is obtained for 3-amino butyric acid and 4-amino butyric

acid which are much more strongly adsorbed on silica than on nickel. For these acids the spectra obtained with a SiO_2 disk are identical with those on a Ni/SiO_2 disk. This shows not only that the 6- or 7-membered rings which these molecules might form with one nickel atom in analogy to structure I are unfavourable but also that diadsorbed complexes with two different Ni atoms are less stable for these molecules than the adsorption complexes with silica. Further, some remarkable differences appear to exist in the spectra of the three isomers of amino *n*-butyric acid. In discussing these the strong bands in the 1750–1350 cm^{-1} region are particularly relevant while the NH_2 stretching bands which appear in all spectra have a low intensity, especially in the case of amino acids on silica. They are, moreover, broadened by an interaction of NH_2 with carbonyl oxygen atoms or surface OH groups. Another reason why NH_2 stretching bands are less suited as a base for a structural proposal is that they overlap with the broad band at 3300 cm^{-1} due to disturbed OH groups.

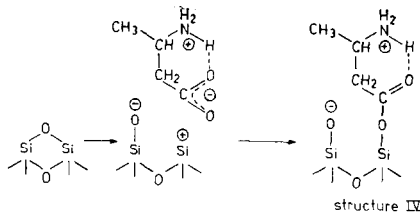
a. 2-Amino acids on silica. The infrared spectra of α -alanine and 2-amino butyric acid on silica show $\text{C}=\text{O}$ stretching frequencies at 1740 and 1670 cm^{-1} . This shows that two types of adsorption complexes exist on the silica surface. According to Young (5) the highest frequency is attributed to a surface ester and the lowest frequency to a hydrogen bonded complex:



b. 3-Amino butyric acid. The spectrum of 3-amino butyric acid on silica shows an intense band at 1515 cm^{-1} . In this region usually the NH_3^+ groups absorb. Upon exchange with deuterium on a Ni/SiO_2 disk the band at 1515 cm^{-1} disappears, in agreement with the assignment to an NH_3^+ group. The resulting formation of the ND_3^+

group cannot be observed because the spectral region at about 1170 cm^{-1} where it is expected is opaque due to absorption by the silica support. Since the $\text{C}=\text{O}$ stretching frequencies appear, as for other amino acids, at 1740 and 1650 cm^{-1} we must conclude that in this adsorption complex the amino group is protonated but the carboxyl group has not been transformed into a carboxylate ion with two equivalent oxygen atoms as in the usual zwitterionic structure. This complex thus contains an NH_3^+ group in combination with either a COOH group or an ester group, like structure II. The former possibility, however, is difficult to reconcile with the known weak acidity of surface OH groups which makes the transition of a proton from SiOH to the zwitterionic COO^- group, resulting in a COOH group, highly unlikely. We therefore suggest that the complex containing the NH_3^+ group is linked to the surface by

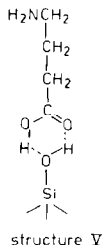
an $\text{C}=\text{O}-\text{Si}$ bond. This could easily result from the adsorption of a gaseous zwitterion on a highly dehydrated silica surface, containing strained $\text{Si}-\text{O}-\text{Si}$ bridges, which may cleave to form SiO^- and Si^+ sites (see refs. 14 and 15).



If a proton is subsequently transferred from the NH_3^+ group in IV to the surface, a complex similar to II would result. Our results do not exclude that such a complex is present on the surface in addition to IV; they also appear to show that some molecules are adsorbed in a structure analogous to III as is evidenced by the 1650 cm^{-1} band.

c. 4-Amino butyric acid on silica. Since one $\text{C}=\text{O}$ stretching band appears (at 1675 cm^{-1}), 4-amino butyric acid only forms one type of adsorption complex on silica. The NH_2 stretching bands at 3450

and 3350 cm⁻¹ point to a free amino group. Also the sharpness of the C=O stretching band indicates little interaction with other groups. The high thermal stability as compared to other amino acids adsorbed on silica indicates that interaction of the NH₂ group and C=O weakens the adsorption of structure III. Accordingly the structure proposed for the adsorption complex of 4-amino butyric acid is



In conclusion it can be stated that the present results have revealed a remarkable dependence of the adsorption complex structure on the position of the amino group in amino acids. They have also shown that the sublimation technique permits the investigation of adsorption complexes of materials with low volatility.

ACKNOWLEDGMENTS

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