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Dehydration of Formic Acid on Titanium Dioxide. Application of NMR to the Study of Formic Acid Adsorbed on Electron-Donor Centers

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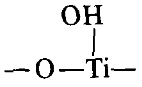
Using the example of formic acid adsorbed on TiO_2, we point out the interest of NMR for studying chemisorption on electron-donor sites. From the chemical shifts $\delta(^1H)$ and $\delta(^{13}C)$ of the total adsorbate (physical and chemical adsorption) one can determine the shifts characteristic of the chemisorbed phase alone, then the corresponding electron–nucleus coupling constants a_H and $a_{^{13}C}$, and consequently the electron spin density transferred from the electron-donor site and the deformation of the adsorbed molecule.

INTRODUCTION

Titanium dioxide is essentially a dehydration catalyst for formic acid (*1*). The active centers in this reaction are the electron-donor sites (abbreviated to EDS) the nature of which depends on the temperature T_t of thermal pretreatment of the oxide. At relatively low temperatures these sites are the oxygen atoms or the hydroxyls of



$$\overset{\mathrm{OH}}{\overset{|}{-\mathrm{O}-\mathrm{Ti}-}}$$

groups arising from partial dehydration of the surface (*1, 2*). They are diamagnetic and consequently cannot be detected directly by ESR. For high T_t values these EDS are Ti^{3+} ions formed by reduction of the surface in the reaction

$$2\,Ti^{4+} + O^{2-} \rightarrow V_a + \tfrac{1}{2}\,O_2 + 2\,Ti^{3+}, \quad (1)$$

where V_a is an anionic vacancy.

In agreement with results of other authors (*3*), the ESR signal detected ($g_\perp$ = 1.967, $g_\parallel$ = 1.948) is characteristic of Ti^{3+} ions subjected to an axially symmetrical crystal field with tetragonal distortion. The variation of this ESR signal with adsorption of formic acid ($g_\perp$ = 1.973, $g_\parallel$ = 1.948) clearly demonstrates that there is a bond between these Ti^{3+} ions and one or two HCO_2H molecules. However, because of the low natural abundance of the ^{17}O and ^{13}C isotopes it is not possible to detect hyperfine coupling by ESR and to obtain thereby further information about the form of the chemisorbed complex. The final NMR result will reveal, moreover, that even with sufficiently high nuclear concentrations the ESR components due to the electron–nucleus coupling could not be resolved, the ESR signal of Ti^{3+} in the Ti^{3+}–HCO_2H complex being too broad.

In contrast, with modern NMR spectrometers it is possible to detect signals of nuclear spins even at very low concentration. Moreover, in paramagnetic systems the NMR chemical shifts give not only the value of the coupling constant but also its sign, impossible to obtain with ESR. We shall show in the study of HCO_2H adsorbed on TiO_2 that the electron spin density at each nucleus of the adsorbate can be determined and, consequently, the mechanism of adsorbent–adsorbate bond formation. We should point out, however, that the interpretation of the spectra is much more

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complex in the case of NMR than in that of ESR.

EXPERIMENTAL

Materials and Procedures

The titanium dioxide used is the amorphous microporous solid AM (*1*) prepared by the hydrolysis of $TiCl_4$ by NaOH following the method of Kennedy *et al.* (*4*).

The NMR experiments were carried out mainly on samples designated AM-250 and AM-400, these being AM pretreated at 250 and 400°C, respectively, under vacuum. At these temperatures this catalyst has a maximum in its catalytic activity and in the number of EDS (*1*). The NMR spectra of formic acid adsorbed on the oxide were recorded on a Brucker CXP FT spectrometer at 90 MHz. Chemical shifts were measured by the substitution method (*5*). The reference for the proton shifts of the adsorbed phase is the molecule in the gas phase; that of ^{13}C is the position of the liquid acid. Proton shift corrections for the bulk magnetic susceptibility of the samples were made following the method proposed by Bonardet *et al.* (*6, 7*). Those for ^{13}C shift are negligible.

RESULTS

Protons

At high surface coverage the spectra consist of two lines: one is rather narrow, characteristic of ^1H–C, the other much broader, due to acid O–^1H. When the coverage decreases, the latter rapidly becomes so broad that it can no longer be detected. For this reason we have only studied the proton resonance of H–C. The number n of molecules adsorbed per square meter of surface is always much greater than the number n_s of EDS estimated by ESR (*1*).

For sample AM-400, n is between 3 and 11×10^{18} molecules/m², whereas n_s is 10.75×10^{16}/m². Under these conditions, for each experimental temperature T_e between 25 and 90°C, the spectrum has only one line characteristic of ^1H–C, the magnitude of whose *upfield* chemical shift $\delta(^1H)$ decreases monotonically when n increases. Figures 1 and 2 show that $\delta(^1H)$ is linearly dependent on $1/n$ and $1/T_e$. Analogous

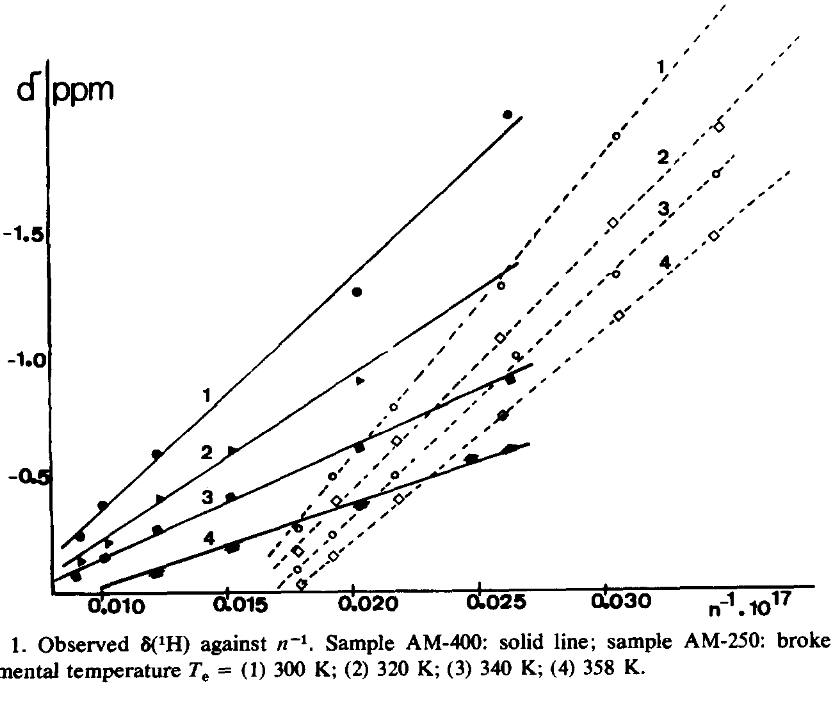


FIG. 1. Observed $\delta(^1H)$ against n^{-1}. Sample AM-400: solid line; sample AM-250: broken line; experimental temperature T_e = (1) 300 K; (2) 320 K; (3) 340 K; (4) 358 K.

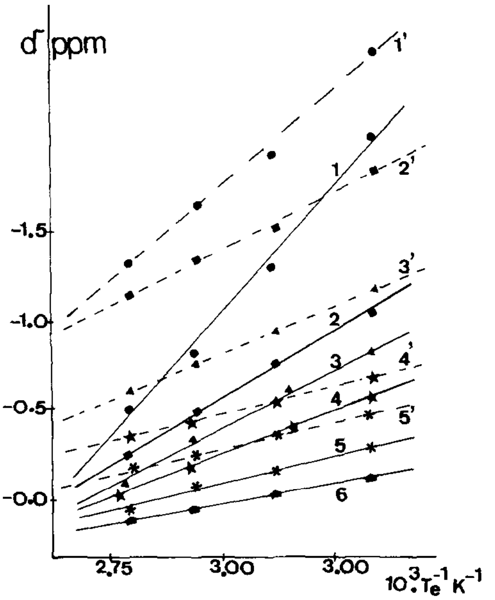


FIG. 2. Observed $\delta(^1H)$ vs T_e^{-1}. Sample AM-400 (solid line), $n \times 10^{-16}$ = (1) 380; (2) 490; (3) 662; (4) 817; (5) 980; (6) 1100. Sample AM-250 (broken line); $n \times 10^{-16}$ = (1') 290; (2') 327; (3') 385; (4') 460; (5') 522.

results are obtained for sample AM-250 (Figs. 1 and 2).

Carbon

The most interesting data provided by NMR come from the comparison of the chemical shifts observed for the different nuclei. This is why we have studied ^{13}C resonance. However, owing to the low abundance of this isotope and to the relatively small amount of acid in the sample, it was sometimes necessary to accumulate several hundred thousand times for one spectrum. We have, therefore, only considered the case of AM-400 at $T_e = 25°C$. As in the case of protons, only one line is observed, and its *downfield* chemical shift δ (^{13}C) decreases also with increase in n and depends linearly on $1/n$ (Fig. 3).

DISCUSSION

Sample AM-400

We shall firstly discuss sample AM-400 because it was studied the most. The number of adsorbed molecules n is much greater than the number of EDS, n_s. On the surface, there are therefore molecules chemisorbed on these centers and others adsorbed elsewhere, physically for example. Now, for each experimental temperature T_e there is only one line in the ^1H and ^{13}C spectra. This proves that the physically and chemically adsorbed molecules exchange rapidly (on the NMR time scale). In fact we chose a high surface coverage in order to narrow the spectral components by such a rapid exchange between the different adsorbed molecules. The chemical shift δ of the total adsorbed phase depends on the theoretical shifts, δ_p and δ_{ch} and the numbers, n_p and n_{ch}, of physically and chemically adsorbed molecules, respectively:

$$\delta = \frac{n_p\ \delta_p + n_{ch}\ \delta_{ch}}{n_p + n_{ch}} \tag{2}$$

where $n = n_p + n_{ch}$.

For light atoms, the chemical shift due to physical adsorption is negligible; therefore, $\delta_p = \delta_{\text{reference}} = 0$ and

$$\delta = \frac{n_{ch}}{n}\ \delta_{ch}. \tag{3}$$

When the surface coverage is very high, all the chemisorption sites (assuming they are sufficiently strong) are occupied; consequently, n_{ch} is independent of n, and δ is a linear function of $1/n$. These rapid ex-

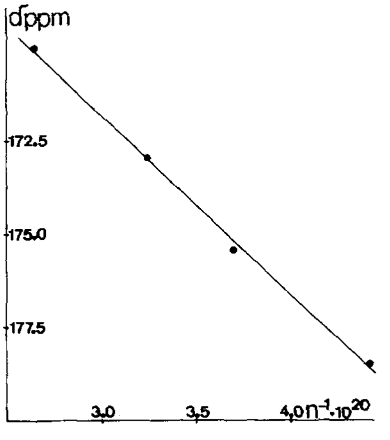


FIG. 3. Observed $\delta(^{13}C)$ against n^{-1}. Sample temperature T_e = 300 K.

change properties have already been used in the study of diamagnetic (*8, 9, 22*) and paramagnetic (*10, 11*) adsorbents.

The linear dependence of $\delta(^1H)$ on $1/T_e$ proves that the chemisorbed molecules interact with the paramagnetic centers which cannot be other than Ti^{3+}. Assuming then that the only chemisorption centers are precisely these Ti^{3+} ions analysed by ESR (*1*), using Eq. (3) where $n_{ch} = n_s$, for each T_e we can calculate the shift $\delta_{ch}(^1H)$ of the chemisorbed phase alone. For example, at 25°C

$$\delta_{ch}(^1H) = -75 \pm 3 \text{ ppm} \quad \text{(upfield).}$$

In the same way we find

$$\delta_{ch}(^{13}C) = +3934 \pm 25 \text{ ppm} \quad \text{(downfield).}$$

We have verified that $\delta_{ch}(^1H)$ is also linear with $1/T_e$ (Fig. 4).

The chemical shifts can be due to the anisotropic interaction δ_{ani} ("pseudo-contact" (*12*)) or (and) isotropic Fermi contact interaction δ_I (*13, 14*) between the spin S of the unpaired electron of Ti^{3+} and the nuclear spins I of ^1H and ^{13}C of the HCO_2H molecule adsorbed on this site. In the example considered it is impossible to determine the share of these two interactions. We have therefore calculated the effect δ_{ani} on different plausible models of the structure of the chemisorbed HCO_2H-Ti^{3+} complex. For each of them, the structure factor $(3 \cos^2\theta - 1)/r^3$ (where θ is the angle between the axis of the complex and the vector r which joins the electronic and nuclear spins) which occurs in δ_{ani} is small. Moreover, the values of $g_\perp$ and $g_\parallel$ are not very different; we have therefore assumed that the pseudo-contact interaction is small if not completely negligible, and we have attributed the δ_{ch} values to the Fermi contact interaction. The corresponding hyperfine coupling constants, deduced from the above δ_{ch} values are

$$a_H = -2.85 \text{ MHz} \quad \text{or} \quad -1.019 \text{ G},$$

$$a_{^{13}C} = +37.30 \text{ MHz} \quad \text{or} \quad +13.330 \text{ G}.$$

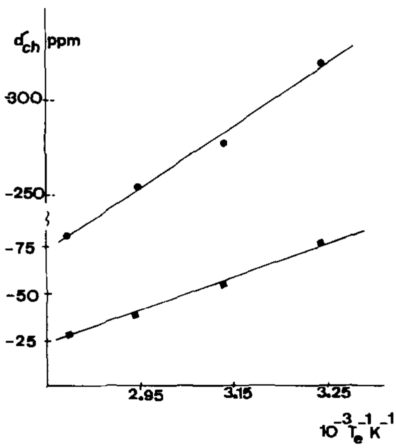


FIG. 4. Calculated δ_{ch} of chemisorbed molecules vs T_e^{-1}. ■, AM-400; ●, AM-250.

We shall now show how the electronic state and the structure of the chemisorbed complex can be determined on the basis of these coupling constants.

Assume firstly that the HCO_2H molecules remain planar after adsorption. The above results can only be explained as follows. Formation of a $(Ti^{3+}-HCO_2H)$ π-complex transfers positive electron spin density ρ_π directly into the $\pi^* -$ MOs of the molecule. By polarisation of the spins along the σ(C–H) bond, this density $\rho_\pi{}^C$, near the carbon, induces a spin density which is positive on ^{13}C and consequently negative on ^1H (Fig. 5). From the value of the coupling constant a_H it is possible to calculate $\rho_\pi{}^C$ in the $\pi^* -$ MO at the carbon atom by using McConnell and Chesnut's relationship (*15*)

$$a_H \text{ (gauss)} = -25\rho_\pi{}^C,$$

whence

$$\rho_\pi{}^C = 4 \times 10^{-2}. \qquad (4)$$

We have shown by quantum mechanical study of $(HCO_2H)^-$ that the spin density $\rho_\pi^{O(2)}$ differs only a little from $\rho_\pi{}^C$, whereas $\rho_\pi^{O(4)}$ is very small (*16*). Consequently, a spin density of about 0.1 is transferred into the $\pi^* -$ MO of HCO_2H. Since Ti^{3+} is a d^1 ion this spin density is equal to the electronic charge density 0.1*e*.

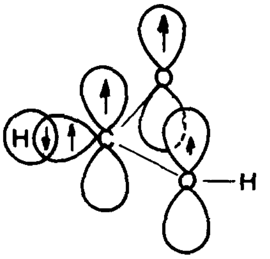


FIG. 5. Spin polarization in the (C–H) bond induced by the transferred spin density in the HCO_2H π^* – MO.

However, when the carbon atom is sp^2 hybridised (planar configuration) and the positive and negative spin densities on C and H, respectively, are due uniquely to spin polarisation along the σ(C–H) bond induced by the electron density $\rho_\pi{}^C$, the absolute values of the coupling constants $|a_H|$ and $|a_{^{13}C}|$ are of the same order of magnitude (*12, 16*). To explain why $|a_{^{13}C}|$ is much greater than $|a_H|$ we have to assume that a part of the electron spin density on the π^* – MO is directly transferred into the $2s$(C) orbital, and therefore, that the adsorbed species $(HCO_2H)^{\epsilon-}$ is no longer planar. The deviation from planarity, α, can be calculated from the following equation (*17*):

$$a_C(\alpha)\ \text{(gauss)} = [a_C(0) + 1190 \cdot 2\tan^2\alpha]\rho_\pi{}^C, \quad (5)$$

where

$a_C(\alpha)$ is the true coupling constant,
$a_C(0)$ is the coupling constant corresponding to the theoretical planar structure,
α is the angle between the bonds and the plane normal to the C_3 symmetry axis, treating $(HCO_2H)^{\epsilon-}$ as a CH_3 group.

One could take for $|a_C(0)|$ the value found for $|a_H|$, but in this case one would be neglecting the polarisation S^C of the spins of the $1s^{(C)}$ electrons and the spin density in the π^* – MO at the oxygen atoms. The value of $a_C(0)$ for the planar structure must therefore be calculated from Karplus and Fraenkel's relationship (*17*):

$$a_C(0) = (S^C + 2Q_{CO}{}^C + Q_{CH}{}^C)\,\rho_\pi{}^C + Q_{OC}{}^C \cdot \rho_\pi^{O(2)} + Q_{OC}{}^C \cdot \rho_\pi^{O(4)}, \quad (6)$$

where $Q_{ij}{}^i$ are the σ-π spin polarisation constants.

We have confirmed that $\rho_\pi^{O(2)} \sim \rho_\pi{}^C \gg \rho_\pi^{O(4)}$ (*15*). From literature values (*17, 18*),

$$S^C = -12.5\ \text{G}, \qquad Q_{CH}{}^C = 19.5\ \text{G},$$
$$Q_{CO}{}^C = 17.2\ \text{G}, \qquad Q_{OC}{}^C = -27.1\ \text{G},$$

one finds

$$a_C(0) = 0.57\ \text{G}.$$

and, consequently, from Eq. (5),

$$\alpha = 6.5°.$$

This distortion is of the same order of magnitude as those determined by ESR for the formation of carboxyl radical ions $(R\ CO_2H)^-$ by irradiation of acids below 150 K [(*19*), L-alanine: 8°; succinic acid: 10°] (*20*). Assuming that $(HCO_2H)^{\epsilon-}$ adopts C_3 symmetry the bond angles of this ion are then 119°. This value is very close to that obtained by ab initio SCF study of $(HCO_2H)^-$ (*16*).

Admittedly these calculations can only be approximate. In fact, while the spin polarisation of the $1s$(C) electrons is fairly insensitive to variations in the structure of the complex because of the localisation of this orbital, that of the $2s$(C) electrons (coefficients $Q_{ij}{}^i$ in Eq. (6)) must be affected by the hybridisation type and by the bond lengths. However, these calculations give with sufficient precision the order of magnitude of the distortion of $(HCO_2H)^{\epsilon-}$ relative to the theoretical plane.

We have mentioned that the ^{1}H-NMR signal of the acidic OH cannot be detected when the surface coverage is not very high, because the characteristic signal is considerably broadened. This broadening could be due to the interaction between the acid and the surface which decreases the mobility of the adsorbed species and therefore increases the dipolar interactions. However, we do not have much faith in this hypothesis which should also lead to considerable broadening of the other NMR components.

This broadening could be due also to the fact that in such a nonplanar structure of $(HCO_2H)^{\epsilon-}$, $\rho_\pi{}^C$ and $\rho_\pi^{O(2)}$ must directly induce a spin density on the OH proton by hyperconjugation (*12*). (The spin density on the OH oxygen is negligible (*16*).) The interactions between $H^{(5)}$ and these spin densities on C and O(2) depend on the angle between the –COO plane and the C . . . $H^{(5)}$ and O(2) . . . $H^{(5)}$ directions. The deformation of $(HCO_2H)^{\epsilon-}$ will not be uniform for all the chemisorption sites; there should be a distribution of $H^{(5)}$ chemical shifts, and consequently, broadening of the corresponding NMR signal.

However, in our opinion the rather marked broadening of the $H^{(5)}$ signal must be primarily the consequence of a greater paramagnetic effect on the relaxation of $H^{(5)}$. Although it is partially transferred to HCO_2H, the odd electron is preferentially localised on Ti^{3+} ($\epsilon \sim 0.1e$). One can therefore write for the chemisorbed phase alone

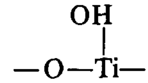
$$\frac{\Delta H_{\mathrm{ch}}(\mathrm{H}^{(3)})}{\Delta H_{\mathrm{ch}}(\mathrm{H}^{(5)})} = \frac{T_{2,\mathrm{ch}}(\mathrm{H}^{(5)})}{T_{2,\mathrm{ch}}(\mathrm{H}^{(3)})} \sim \left[\frac{r(\mathrm{Ti}^{3+}\text{–}\mathrm{H}^{(5)})}{r(\mathrm{Ti}^{3+}\text{–}\mathrm{H}^{(3)})}\right]^6,$$

where r denotes the distance between $H^{(5)}$ or $H^{(3)}$ and Ti^{3+}, ΔH_{ch} and $T_{2,\mathrm{ch}}$ the linewidths and the transverse relaxation times of each proton.

Unfortunately, it is difficult, impossible even, to measure the widths of the two signals ($H^{(5)}$ and $H^{(3)}$) together, except at very high surface coverage. By studying the adsorption of DCO_2H and HCO_2D and the relaxation, it should be possible to elucidate this point. One can only say that at very low coverage, $\Delta H(H^{(5)})/\Delta H(H^{(3)})$ is at least about 10. If this is the case (which remains to be confirmed) one could then affirm that $(Ti^{3+}\text{–}H^{(5)}) < (Ti^{3+}\text{–}H^{(3)})$, more precisely $(Ti^{3+}\text{–}H^{(3)}) \geq 1.5\ (Ti^{3+}\text{–}H^{(5)})$. Taking into account firstly the NMR results (spin density on C and $H^{(3)}$, deformation of the adsorbed molecule, $Ti^{3+}\text{–}H^{(3)} > Ti^{3+}\text{–}H^{(5)}$) and, secondly those of quantum mechanics (deformation of HCO_2H^-, spin density distribution, and particularly $\rho_\pi^{O(2)} \gg \rho_\pi^{O(4)}$) one could suggest the form for the adsorbed complex shown in Fig. 6.

Sample AM-250

We have not studied the ^{13}C-NMR of this sample. We cannot therefore determine the exact geometry of the adsorbed complex. However, apart from this, the ^{1}H-NMR results are absolutely identical with those for AM-400. They prove that in this case also a charge transfer complex is formed when HCO_2H is adsorbed on the oxygen or the OH's of the

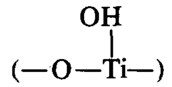


$$\overset{\text{OH}}{\underset{}{-\text{O}-\overset{|}{\text{Ti}}-}}$$

EDS (diamagnetic), and that this results in a dissymmetric distribution of the spin densities as is the case when electron acceptors such as TCNE or TNB are adsorbed on these EDS (*1*).

The spin density transferred from these EDS into the π^* – MO of HCO_2H is much greater than that transferred from Ti^{3+}. For example, at $T_e = 25°C$, $\delta_{\mathrm{ch}}(^1H) = 320$ ppm against 75 ppm for AM-400. The electron density transferred is at least equal to the spin density. It is therefore greater than or equal to $0.4e$. The difference between these two samples probably explains why the dehydrating activity by EDS is much greater for AM-250.

Kinetics studies of the dehydration of HCO_2H on AM-250 indicate that the EDS



$$(-\text{O}-\overset{\text{OH}}{\overset{|}{\text{Ti}}}-)$$

are the active centers in this reaction (*1*). However, Munuera (*21*) has noticed that

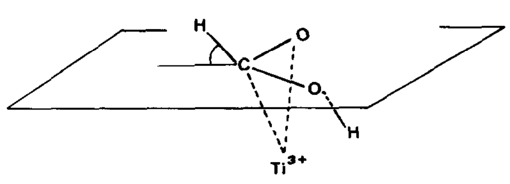
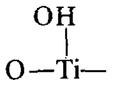


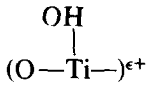
FIG. 6. $HCO_2H\text{–}Ti^{3+}$ chemisorbed complex.

the intensities of the ir bands characteristic of certain surface OH groups decrease markedly upon adsorption of HCO_2H on TiO_2 (rutile). He deduced that the active centers in this reaction could be the Brønsted acid sites. Now, we have shown that the OH groups on Ti are negative and must therefore be weakly acidic (*2*). But this acidity could very well be increased after electron transfer from



$$\mathrm{O{-}\overset{\overset{OH}{|}}{Ti}{-}}$$

to HCO_2H, and proton capture by the adsorbate would then be assisted both by the now positive character of



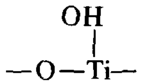
$$\mathrm{(O{-}\overset{\overset{OH}{|}}{Ti}{-})^{\epsilon+}}$$

and the negative character of $(HCO_2H)^{\epsilon-}$. These two types of result are therefore not necessarily incompatible.

CONCLUSION

Application of NMR to the study of the adsorption of formic acid on TiO_2 treated at 400°C confirms the existence of the strong interaction between the surface Ti^{3+} centers and HCO_2H, already demonstrated by ESR. However, we have been able to define the form of the chemisorbed complex better. In fact, from the chemical shifts $\delta(^1H)$ and $\delta(^{13}C)$ of the total adsorbate (physical and chemical adsorption) we have determined the shifts characteristic of the chemisorbed phase alone (HCO_2H–Ti^{3+}). Therefore we can calculate the corresponding electron–nucleus coupling constants a_H and $a_{^{13}C}$, and consequently, deduce from them the spin density ρ_π (and in this particular case the electronic charge ϵ) transferred from Ti^{3+} into the $\pi^* -$ MO of HCO_2H. Comparison of these two coupling constants has, moreover, shown that $(HCO_2H)^{\epsilon-}$ no longer has a planar structure; the mean value of the bond angles is about 118°.

The diamagnetic electron-donor centers (O and OH) of the



$$\mathrm{{-}O{-}\overset{\overset{OH}{|}}{Ti}{-}}$$

groups give similar results and indicate that in this case also there is electron transfer from the surface into the $\pi^* -$ MO of HCO_2H. The electron transferred is actually higher than in the case of Ti^{3+}. This difference may explain why the dehydrating activity of these centers is greater than that of Ti^{3+}.

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