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## N. M. R. CHEMICAL SHIFTS AND REACTIVITY OF SOLID SURFACES

By

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### Abstract

By means of a few examples, we show the interest of NMR in the study of the interactions between gas and solids (dia- and paramagnetic). Thus, it is possible to characterise Brönsted acidity of oxides, just as in homogeneous phases, by calculating the dissociation coefficient of the OH bonds in the presence of other molecules and by determining the chemical shift of the acidic hydrogen. On the other hand the NMR study of  $Ti^{3+}$ -HCOOH interaction has shown that in certain cases NMR gives much more informations than ESR on chemisorbed paramagnetic complexes: electron nuclear coupling, electron spin densities, *etc.*, and leads to an understanding of the mechanism of heterogeneous catalytic reactions.

### I. Introduction

High-resolution NMR studies carried out some twenty years ago<sup>1)</sup> on molecules adsorbed on diamagnetic solid surfaces indicated that proton resonance frequencies differ from free molecule values. This shift, due to a disturbance of the electron distribution, varies with the nature of the functional group, especially when there is a preferred orientation of the chemisorbed molecule with respect to the surface.

On the other hand, since adsorption decreases molecular motion, apart from changes in  $\delta$ , we should observe a broadening of the spectral components which will be greater or smaller depending on the component and whether it is associated with a group fixed on the surface or sufficiently remote for it to preserve a certain number of degrees of freedom.

However studies of this sort were for a long time not very numerous for several reasons.

#### I.1 *Experimental difficulties*

The experimental difficulties and in particular the lack of spectrometer sensitivity with continuous irradiation. The appearance of the new pulsed

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Fourier transform spectrometers has almost completely eliminated this problem and makes it possible to study several nuclei such as  $^{13}\text{C}$  or  $^{15}\text{N}$  for example, often at low natural abundance.

### I.2 *Difficulty of calculating the real chemical shift*

It was possible to follow the variation of the spectrum of an adsorbed phase in terms of different parameters but the intrinsic positions of the lines with respect to the standard references were unknown. Indeed, for a variety of reasons (wide lines, competitive adsorption, *etc.*) only the method of substitution can be used for measuring NMR chemical shifts of adsorbed phases.<sup>2)</sup> It is necessary, therefore, to correct the observed chemical shift for the bulk magnetic susceptibility of both the solid and the adsorbed gas. Unfortunately, because of the small quantity of powder used and inadequate knowledge of the apparent density of a powder, it was difficult to estimate the small volume susceptibility of powders accurately by conventional techniques.

Now, the bulk susceptibility of the adsorbent can be measured directly by NMR: one determines the variation of the observed chemical shift of a physisorbed gas in terms of the surface coverage, this shift being measured with respect to the gas phase. The value of this shift extrapolated to zero coverage gives the susceptibility correction of the solid.<sup>3,4)</sup> In the case of nuclei other than the proton, and for certain adsorbents such as zeolites, Michel and Pfeifer<sup>5)</sup> have shown that this term contains in part the non-negligible effect of Van der Waals type interactions. Our current work on the adsorption of inert gases confirms these results.<sup>6)</sup> In any case, whatever the component of this correction factor, its measurement is absolutely essential to the determination of the chemical shifts, especially when these are of the order of a few ppm.

### I.3 *Line broadening at low surface coverage*

Originally, chemists wished to work with very low surface coverages, in order to determine specifically the interaction between the surface and the molecules of the first adsorbed layer. As the strongly chemisorbed molecules are not very mobile, the spectra obtained were very broad and very difficult to use when the adsorbed molecules were other than very simple ones. Fig. 1 shows a spectrum obtained in

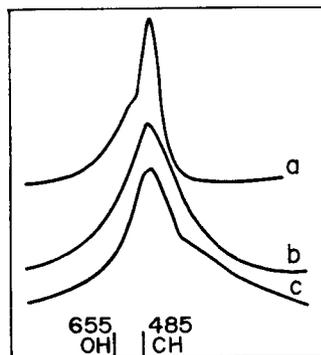


Fig. 1. NMR signals of formic acid adsorbed on silica-alumina.

- a:  $p/p_0 > 0.2$ , room temperature;
- b:  $p/p_0 < 0.1$ , room temperature;
- c:  $p/p_0 < 0.1$ , 75°C.

this way<sup>6a)</sup>; it corresponds to the chemisorption of formic acid on silica-alumina containing acidic OH groups at the surface. The signal detected at room temperature corresponds to the CH group proton. In the old HR-NMR spectrometers, the band width of the scanning field was very small (1000 Hz). Because they are too broad relative to this scanning field the OH group signals of the solid or the chemisorbed acid could not be detected at room temperature. This is a clear indication that chemisorption is operating by interaction of the carboxylic OH group with the surface.

At 75°C, the CH signal becomes narrower and a second signal appears upfield (Fig. 1 c). This is characteristic of a rapid exchange between the protons of the OH groups of chemisorbed formic acid (broad signal at 11 ppm) and those of the solid OH (very broad signal at about 4 ppm) through the  $\text{HC(OH)}_2^+$  species which is intermediate in the dehydration of the acid on such catalysts.

This example points out the interest of setting the species in motion; in this way one can detect a signal characteristic of the site exchange of two protons which cannot be detected separately.

## II. Equilibrium Between Chemically and Physically Adsorbed Molecules. Chemisorption Equilibrium Constant and Chemical Shift

The spectral components could be narrowed either by the use of new techniques or with rapid exchange, at high surface coverage, between the different adsorbed species. This second method seems particularly interesting when we want to investigate the kinetics of heterogeneous catalytic reactions and therefore to study the system at a temperature close to that of the reaction. We report a few examples of chemisorption studies by this second method.

It is well known that in homogeneous media the form and the width of HR-NMR spectra are very sensitive to time-dependent processes. In the case of rapid site exchange of two spins A and B associated with chemical shifts  $\delta_A$  and  $\delta_B$ , the NMR spectrum consists of a single more or less narrow line whose position  $\delta$  depends on  $\delta_A$  and  $\delta_B$  and the number of spins  $n_A$  and  $n_B$  (2)

$$\delta = \frac{n_A \delta_A + n_B \delta_B}{n_A + n_B} \quad (1)$$

Conversely this result can be used to determine the theoretical position of a signal (for example  $\delta_B$ ) when the other quantities are known.

J. FRAISSARD

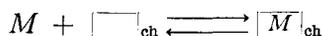
The case of chemically ( $n_{\text{ch}}, \delta_{\text{ch}}$ ) and physically ( $n_{\text{p}}, \delta_{\text{p}}$ ) adsorbed molecules is formally very similar to the preceding case.

$$\delta = \frac{n_{\text{p}} \delta_{\text{p}} + n_{\text{ch}} \delta_{\text{ch}}}{n_{\text{p}} + n_{\text{ch}}} \quad (2)$$

But the 'ch' component is often very broad. The chemical shifts are generally measured relative to the gas ( $\delta_{\text{gas}}=0$ ). Moreover, since physical adsorption does not perturb the system very much:  $\delta_{\text{p}} \sim \delta_{\text{gas}}$ . Consequently

$$\delta = \frac{n_{\text{ch}}}{n_{\text{ch}} + n_{\text{p}}} \delta_{\text{ch}} \quad (3)$$

Let us consider the adsorption equilibrium



number of species at equilibrium:  $n_{\text{p}} \quad S - n_{\text{ch}} \quad n_{\text{ch}}$

where  $\square_{\text{ch}}$  denotes the chemisorption sites and  $S$  denotes the total number of  $\square_{\text{ch}}$ . The equilibrium constant is

$$K = \frac{n_{\text{ch}}}{n_{\text{p}}(S - n_{\text{ch}})} \quad (4)$$

$$n_{\text{ch}} = \frac{K n_{\text{p}} S}{1 + K n_{\text{p}}}$$

Consequently

$$\delta = \frac{K(n_{\text{p}}/n) S}{1 + K n_{\text{p}}} \quad \text{with} \quad n = n_{\text{ch}} + n_{\text{p}} \quad (5)$$

At high surface coverage

$$n_{\text{p}} \gg n_{\text{ch}} \quad \text{then} \quad n_{\text{ch}} + n_{\text{p}} = n \sim n_{\text{p}} \quad \text{and} \quad \delta = \frac{K S}{1 + K n} \delta_{\text{ch}} \quad (6)$$

Kazansky *et al.*<sup>7)</sup> have confirmed for paramagnetic systems that

$$\delta \sim S/n \delta_{\text{ch}} \quad \text{for strong chemisorption} \quad (7)$$

$$\delta \sim K S \delta_{\text{ch}} \quad \text{for weak chemisorption} \quad (8)$$

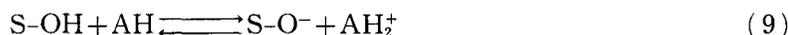
### III. Example on a Diamagnetic Solid

#### III.1 Acid-Base reactions at a solid surface

Let us consider a surface  $S$  consisting of a certain number of acidic OH groups denoted  $S\text{-OH}$ . Because of the strong dipolar interactions of

spins, the NMR lines of these OH groups are very wide (of the order of one gauss).

On this surface let us adsorb a molecule AH (base) which can capture a surface proton by equilibrium



If rapid exchange occurs between the surface proton S-OH and those of the adsorbed molecule AH, the acid proton must affect the chemical shift of the adsorbed phase. The  $^1\text{H}$  spectrum should contain only one line at  $\delta_{\text{obs}}$  due to the coalescence of the lines at  $\delta_{\text{AH}}$ ,  $\delta_{\text{AH}_2^+}$  and  $\delta_{\text{OH}}$ . Thus

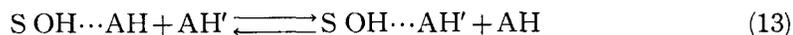
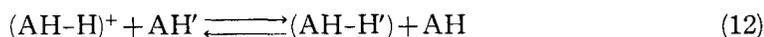
$$\delta_{\text{obs}}(^1\text{H}) = P_{\text{OH}}\delta_{\text{OH}}^{\text{H}} + P_{\text{AH}}\delta_{\text{AH}}^{\text{H}} + P_{\text{AH}_2^+}\delta_{\text{AH}_2^+}^{\text{H}} \quad (10)$$

For the same reason

$$\delta_{\text{obs}}(\text{A}) = P'_{\text{AH}}\delta_{\text{AH}}^{\text{A}} + P'_{\text{AH}_2^+}\delta_{\text{AH}_2^+}^{\text{A}} \quad (11)$$

where  $P_i$  and  $P'_i$  are the concentrations of H and A nuclei in the group  $i$ . Knowing  $\delta_{\text{AH}}^{\text{A}}$  and  $\delta_{\text{AH}_2^+}^{\text{A}}$ , the relative concentrations,  $P'_{\text{AH}}$  and  $P'_{\text{AH}_2^+}$ , and the dissociation coefficient of S-OH in the presence of AH can be calculated from eq. 11. By eq. (10) it is possible to calculate  $\delta_{(\text{S-OH})}^{\text{H}}$  which could not be measured directly.

In fact the study is more complex than is indicated by the above analysis which assumes that all the AH molecules are adsorbed on the S-OH. At high coverage, physical adsorption is important and gives rise to many equilibria such as:



Furthermore, several types of sites for chemisorbing AH can coexist on the surface (for example Brönsted and Lewis acid sites). The problem then becomes above all a chemical one since, amongst this more or less complex set of equilibria, the characteristics of reaction<sup>9)</sup> alone have to be determined.

### III. 2 Examples

#### III. 2. 1 $\text{NH}_4\text{Y}$ zeolite

The line width of  $^1\text{H}$  due to  $\text{NH}_4^+$  is 32 kHz at  $-196^\circ\text{C}$  (rigid lattice) and 8 kHz at room temperature. Bonardet *et al.*<sup>9)</sup> have shown that after ammonia adsorption there is only one signal whose position and width de-

J. FRAISSARD

pend on the relative concentrations of the  $\text{NH}_4^+$  and  $\text{NH}_3$  species. This signal is characteristic of the exchange :



Extrapolating to zero concentration of adsorbed ammonia, the real chemical shift of the ammonium zeolite proton is  $7.0 \pm 0.1$  ppm relative to  $\text{NH}_3$  gas. In solution  $\delta_{\text{H}}(\text{NH}_4^+) = 6.9$  ppm and  $\delta_{^{15}\text{N}}(^{15}\text{NH}_4) = 43.5$  ppm. This shows - firstly that the effect of chemical exchange on the shift  $\delta$  is independent of the signal widths (before exchange) and on their overlap - secondly, that the ammonium ion is associated with the same chemical shift whether it is in solution or in zeolite cages.

### III. 2. 2 *HY zeolite (9)*

After adsorption of ammonia, the chemical shift observed must depend on the shift  $\delta_i$  and on the concentration of each of the species present ( $\text{NH}_3$ ,  $\text{NH}_4$ ,  $\text{OH}$ ), and on the dissociation coefficient of  $\text{OH}$  in the presence of  $\text{NH}_3$  (eq. 9). Conversely, the value of  $\delta$  increases with the desorption of ammonia. But at the limit of vacuum desorption the number of  $\text{NH}_3$  remaining chemisorbed is close to that of the initial number of  $\text{OH}$  groups and the corresponding values of  $\delta$  are  $\delta(^1\text{H}) = 7$  ppm and  $\delta(^{15}\text{N}) = 43$  ppm. These results prove that the  $\text{OH}$  dissociation reaction is complete in the presence of  $\text{NH}_3$ .

### III. 2. 3 *Silica gel (8, 10)*

The case of silica gel is slightly more difficult but more interesting. As in the previous case the position of the signal detected for  $^1\text{H}$  and  $^{15}\text{N}$  depends on the  $\text{NH}_3$  concentration, the exchange reactions and the  $\text{OH}$  dissociation. But it has been shown that at relatively low coverage,  $\text{NH}_3$  adsorption occurs only by reaction.<sup>9)</sup> The corresponding chemical shifts of  $^1\text{H}$  and  $^{15}\text{N}$  can then be used to characterize the  $\text{OH}$  dissociation constant  $\alpha$  in the presence of ammonia ( $\alpha = 0.15$ ) and to calculate  $\delta_{\text{H}}(\text{OH}) \sim 2$  ppm (not directly measurable).

### III. 2. 4 *Brönsted acidity*

The Brönsted acid strength depends on the polarization of the  $\text{OH}$  bond and therefore on the electronic environment of  $^1\text{H}$  which is determined by its screening constant. Consequently the chemical shift can be considered as a measure of the Brönsted acidity. This seems to be particularly interesting for acid catalysts for which it is impossible to define characteristic acidity value akin to  $\text{pK}$  values for homogeneous media. It is then possible to obtain a single acidity scale for all systems homogeneous and heterogeneous.

## N.M.R. Chemical Shifts and Reactivity of Solid Surfaces

	ethanol	silica gel	silica-alumina	HY zeolite	HCOOH
$\delta_{\text{C(SON)}}$ ppm (Reference: gas TMS)	0.5	2	4-5	8	11

## III. 2. 5 Silica gel + pyridine + HCl

Gay<sup>10</sup> proposed a method based on the same principles to determine the surface concentration of the acidic OH group of a solid. He studied the <sup>13</sup>C chemical shift of pyridine adsorbed on a silica gel (containing a monolayer of Si-OH groups) in the presence of an increasing amount of HCl. The results show a linear dependence of the shift of each <sup>13</sup>C in the adsorbed phase on the ratio HCl/pyridine up to a value of unity.

Above this value the shift no longer varies. This behavior expresses the variation of the relative concentrations of pyridine molecules and pyridinium ions formed in reaction (a)



In our opinion this method for determining the concentration of acidic OH groups is easily applicable in the case of very strong acidity *i. e.* when reaction *a* is complete. If this not the case, the dissociation coefficient of the

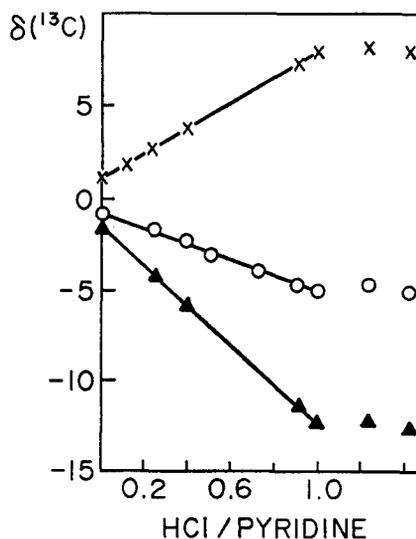


Fig. 2. <sup>13</sup>C chemical shifts with respect to liquid pyridine (corrected) as a function of HCl/pyridine ratio. (X) C-2; (O) C-3; ( $\Delta$ ) C-4. Positive shifts are to higher field.

OH groups in the presence of pyridine must be taken into account. This coefficient can be determined studying another nuclear spin such as  $^{15}\text{N}$ .

#### IV. Paramagnetic Systems

##### IV.1 Theory

The unpaired electronic spin distribution in paramagnetic systems is more conventionally studied by ESR than by NMR. Relative advantages and disadvantages of the two techniques are summarized in table 1.<sup>12)</sup> In fact these techniques are more complementary than competitive.

TABLE 1. Comparison of NMR and ESR in heterogeneous paramagnetic systems

	N. M. R.	E. S. R.
detection of the signal at $T > 25^\circ\text{C}$	often detectable $T_{1e} \leq 10^{-11}$ sec	often undetectable $T_{1e} > 10^{-9}$ sec
detection of the coupling	possible even if the nuclear spin concentration is low	impossible if the nuclear spin concentration is not high enough
magnitude of $A$	appropriate theory required	directly available
sign of $A$ and $\rho$	directly determined	not available
intepretation of $A$ in terms of MO containing spin	very complex theory requi- red. Both $\sigma$ and $\pi$ MO must be involved	MO easily characterized

In their conferences on ESR<sup>13)</sup> Meriaudeau and Ben Taarit have already defined the different types of interaction between the spin  $S$  of the unpaired electron and that of the nucleus  $I$ , as well as the different characteristic values; in particular, in the case of Fermi-contact interaction;

-The coupling constant

$$a = \frac{8\pi}{3} \gamma_N \hbar g_e \beta |\psi(0)|^2 \quad (15)$$

where  $|\psi(0)|^2$  is the probability of finding the electron within the nucleus;

-the spin density

$$\rho = \frac{a}{K_e} \quad (16)$$

where  $K_e$  is the coupling constant when the  $ns$  orbital is singly occupied;

-the contact shift of a nucleus  $i$

$$\delta_i = -a_i \frac{\gamma_e}{\gamma_N} \frac{g_e \beta S(S+1)}{3 kT} \quad (17)$$

*N. M. R. Chemical Shifts and Reactivity of Solid Surfaces*

Then the basic problem becomes that of electron correlation in the system studied and in particular that of the spin polarization. Electron correlation arises from Coulomb repulsion and spin exchange effects. For a free electron in an applied magnetic field  $H_0$ , the spin  $S_z = -1/2$  (positive spin density) has its magnetic moment parallel to the applied field and has lower energy than the spin  $S_z = 1/2$ . However, electron correlation can cause the  $S_z = 1/2$  spin state to be energetically favored over  $S_z = -1/2$  in certain regions of space within a molecule, giving rise to negative spin density.

Correlation has a negligible effect on electron distribution within a molecule, which is primarily responsible for the chemical properties of the complex, but may be the dominant effect in the distribution of unpaired spin, which is primarily responsible for the character of the magnetic resonance.

In ref. (12) can be found a detailed account of the different possible cases of spin polarization; in particular when there is a spin density in a  $\pi$ -system.

#### IV. 2 Examples

IV. 2. 1. Kazansky *et al.*<sup>7)</sup> have applied the previous method to the study of the adsorption of various molecules such as olefines, cycloalkanes, Benzene, *etc.*, on paramagnetic centers supported on aerosil. The physical model is very close to that which is used in the chemistry of complex compounds in solution: on entry into the coordination sphere of a paramagnetic ion, a spin density can arise in the nuclei of the adsorbed molecule as a result of contact interaction which leads to a shift in the spectral components. Dipole-dipole interaction may be another source of paramagnetic shifts.<sup>13)</sup>

For example, the NMR spectrum (at  $-50^\circ\text{C}$ ) of ethylene adsorbed on  $\text{Ni}^{2+}$  (trigonal coordinated) supported on silica consists of one line shifted upfield with respect to the spectrum of the same molecule condensed in pores of the adsorbent. The surface complexes formed can be classified as "strong" as is indicated by the linear dependence of the shift on the reciprocal of adsorption. The negative spin density detected on the proton is easily explained by spin polarization in the C-H  $\sigma$  bond, induced by a positive spin density transferred into the  $\pi$ -orbital of the molecule by for-

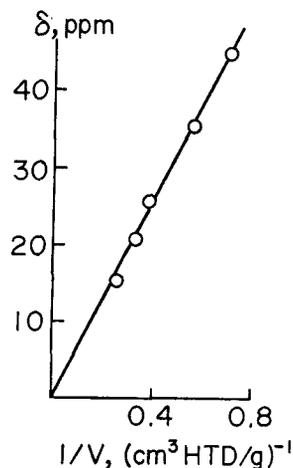


Fig. 3. Dependence of shift of NMR line of ethylene adsorbed on aerosil containing  $\text{Ni}^{2+}$  ions into high field on reciprocal adsorption.

mation of a complex with the metal ion. This example is a simple case which does not offer many alternatives for interpretation.

IV. 2. 2. However in more complicated cases, in order to deduce the mechanism of ligand-metal bond formation, one has to be able to interpret correctly the mechanism of spin correlation, which causes the measured spin densities. Such an interpretation very often requires

- measurement of the spin densities of all the nuclei,
- calculation of the MO's of the complexes formed, the most sophisticated quantum mechanical methods being used to take account of the effects of electron correlation.

The two following examples  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  in solution are particularly convincing. In such octahedral complexes, the two  $a_1$ -MO of water and  $\text{NH}_3$  molecules are  $\sigma$ -donors while the  $b_1$  and  $b_2$ -MO may be used for  $\pi$  donation.<sup>14</sup> But  $\text{Ni}^{2+}$  has filled  $t_{2g}$ - $d$  orbitals and the unpaired-electrons are confined to  $\sigma$ -type orbitals

$$\begin{array}{ll} \text{H}_2\text{O} & \begin{array}{l} 2 \ a_1 = 0.85 (2s) + 0.13 (2p_z) + 0.18 (h_a + h_b) \quad E = -1.40 \text{ ua} \\ 3 \ a_1 = -0.50 (2s) + 0.80 (2p_z) + 0.30 (h_a + h_b) \quad E = -0.48 \text{ ua} \end{array} \\ \text{NH}_3 & \begin{array}{l} 2 \ a'_1 = 0.70 (2s) + 0.15 (2p_z) + 0.15 (h_a + h_b) \quad E = -1.1 \text{ ua} \\ 3 \ a'_1 = 0.40 (2s) - 0.90 (2p_z) - 0.12 (h_a + h_b) \quad E = -0.37 \text{ ua} \end{array} \end{array}$$

a) All these  $\sigma$  MO's contain some hydrogen  $1s$  character. Thus, unpaired spin density is directly transferred from the metal  $d$  orbital to the hydrogen  $1s$  orbital by  $\sigma$  bond formation. This must lead to a downfield chemical shift. The difference of the positive spin density thus transferred in each of the complexes must depend on only the energy difference of the  $a_1$ -MO and the difference in the  $1s(\text{H})$  character of MO.

It is seen that in the present case these differences are not very great.

b) This mechanism of direct transfer of positive spin density is counterbalanced by spin polarization along the  $\sigma$ -NH bond, which shifts the  $^1\text{H}$  signal upfield.

One could expect to have similar proton chemical shifts in the two complexes. The experimental result is quite different since  $\delta^1\text{H}(\text{H}_2\text{O}) = 8.7$  ppm (downfield) and  $\delta^1\text{H}(\text{NH}_3) = -120$  ppm (upfield).

This difference in behavior is retained when the complexes are situated in the super-cages of Y-zeolites. For example, in  $\text{NaNi Y}$ ,  $\delta(^1\text{H})$   $[\text{Ni}^{2+}(\text{H}_2\text{O})_6]^{2+}$  is about 14 ppm instead of 8 ppm in solution. This difference can be explained easily by a slight variation in the angle between the OH bond and the axis of the complex.<sup>15</sup>

*N.M.R. Chemical Shifts and Reactivity of Solid Surfaces*

IV.2.3. We now give a simple example to show why NMR is interesting in the study of heterogeneous catalysis. It concerns the decomposition of formic acid on titanium dioxide. (This decomposition is a test

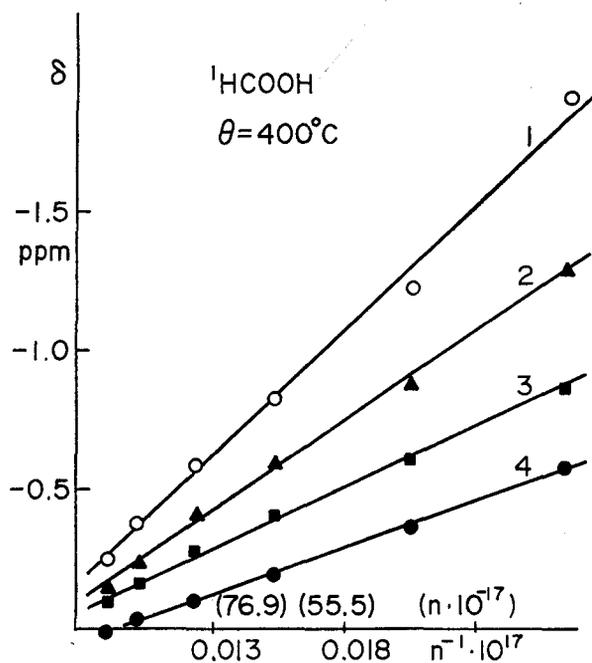


Fig. 4.  $\delta(^1\text{H})$  against reciprocal adsorption. Sample temperatures: 1: 300 K; 2: 320 K; 3: 340 K; 4: 358 K.

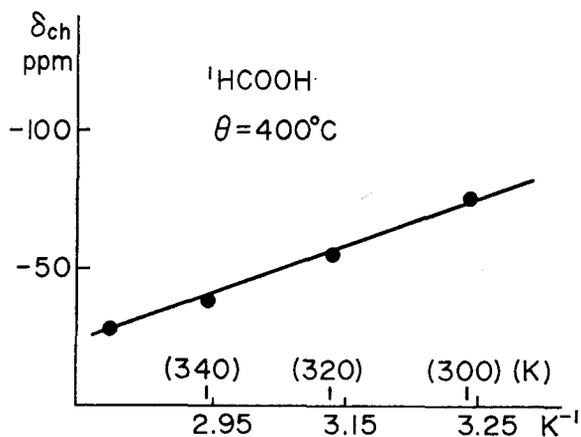


Fig. 5. Calculated  $\delta_{\text{ch}}$  of chemisorbed molecules vs.  $T^{-1}$ .

J. FRAISSARD

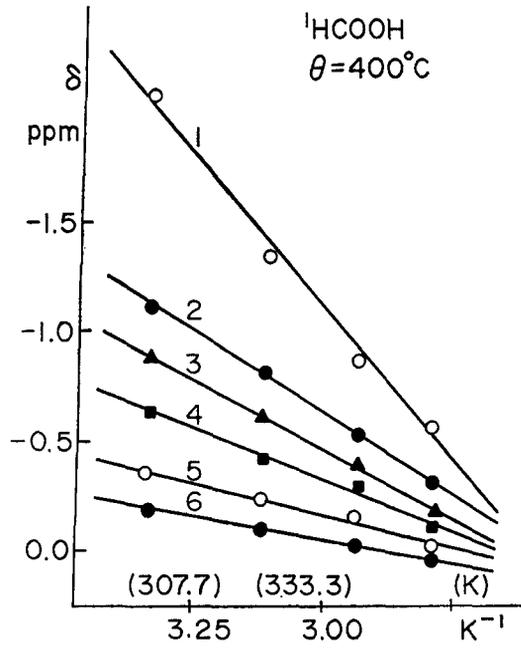


Fig. 6.  $\delta({}^1\text{H})$  vs. reciprocal temperature.

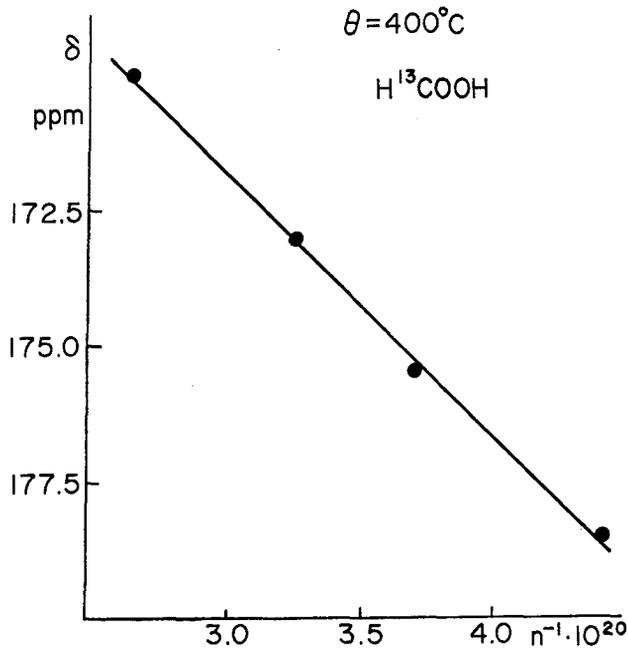


Fig. 7.  $\delta({}^{13}\text{C})$  against reciprocal adsorption.

*N. M. R. Chemical Shifts and Reactivity of Solid Surfaces*

reaction much used in the study of dehydrogenation or dehydration reactions).

It is known that, by vacuum treatment at different temperatures  $\theta$ , electron-donor centers are released or created at the  $\text{TiO}_2$ -surface.<sup>16)</sup> For example, above 250°C, oxygen vacancies are created and at the same time  $\text{Ti}^{3+}$  ions which can be essayed by the now-classical method of adsorbing an electron-acceptor such as TCNE, and detecting the  $\text{TCNE}^-$  signal by ESR.<sup>17)</sup> The decomposition of formic acid is almost exclusively a dehydration and the corresponding rate constant is observed to vary with  $\theta$  in exactly the same way as the number of donor centers; the latter can therefore be assumed to play an important role in the catalysis reaction.<sup>10)</sup> It can be shown moreover that  $\text{HCOOH}$  and  $\text{Ti}^{3+}$  interact since the  $\text{Ti}^{3+}$  ESR signal is shifted when the acid is adsorbed.<sup>18)</sup>

It is not possible however to detect any hyperfine coupling since the natural  $^{13}\text{C}$  and  $^{17}\text{O}$  concentrations are really too small. In fact the final results show that even with a sufficiently high concentration of these nuclear spins the components due to electron-nucleus coupling could not be resolved, the  $\text{Ti}^{3+}$  ESR signal of the  $\text{Ti}^{3+}-\text{HCOOH}$  complex being too broad.

The NMR signal of the OH group proton of chemisorbed acid is very broad and practically undetectable. We have therefore studied the signal of the CH group  $^1\text{H}$  and  $^{13}\text{C}$  atoms. We report the results obtained for a sample treated under vacuum at 400°C. (Fig. 4-7).

Experiments were carried out at high surface coverage. The number  $n$  of adsorbed molecules is

$$3.10^{18} < n = [\text{HCOOH}]_{\text{ads}}/\text{m}^2 < 11.10^{18}$$

For comparison the number  $E$  of electron-donor centers is

$$(E) = (\text{Ti}^{3+}) = 10.75 \cdot 10^{18} \text{ spin/m}^2$$

The existence of a unique signal for both  $^1\text{H}$  and  $^{13}\text{C}$  shows that chemically and physically adsorbed molecules exchange rapidly. The observed shifts  $\delta(^1\text{H})$  and  $\delta(^{13}\text{C})$  (relative to the gas phase) are linear functions of  $\left(\frac{1}{n}\right)_{T < 300\text{K}}$  and of  $\left(\frac{1}{T}\right)_n$ . These variations show that the chemisorbed molecules interact strongly with paramagnetic centers. So, according to eq. (7)

$$\delta = \frac{S}{n} \delta_{\text{ch}}$$

$S$  = number of chemisorption sites per  $\text{m}^2$

$\delta_{\text{ch}}$  = chemical shift of a nucleus of the chemisorbed molecule.

J. FRAISSARD

Assuming that the only paramagnetic electron centers are the electron-donor centers essayed by ESR ( $E=S$ ) it is possible to calculate  $\delta_{\text{ch}}$ :

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

$$\delta_{\text{ch}}(^{13}\text{C}) = 2934 \pm 25 \text{ ppm (downfield)}$$

Whence the hyperfine coupling constants are:

$$a_{\text{H}} = -2.85 \text{ MHz or } -1.019 \text{ gauss}$$

$$a_{^{13}\text{C}} = +37.30 \text{ MHz or } +13.33 \text{ gauss}$$

We have checked that these chemical shifts are due simply to Fermi-contact interaction.

We suppose firstly that the chemisorbed HCOOH molecule is *planar*. The previous results can only be explained as follows; by formation of a ( $\text{Ti}^{3+} - \text{HCOOH}$ )  $\pi$ -complex, positive spin density  $\rho_{\pi}$  is directly transferred in the  $\pi$ -system of the molecule. By spin polarization along the  $\sigma$ -bond, this density near carbon,  $\rho_{\pi, \text{C}}$  induces a spin density, positive on  $^{13}\text{C}$  and, consequently, negative on  $^1\text{H}$ . From the equation (12)

$$a_{\text{H}} = -22 \cdot \rho_{\pi, \text{C}}$$

the spin density (and in this case the electron charge density) in the  $\pi$  orbital near the carbon is  $\rho_{\pi, \text{C}} = 4.10^{-2}$ .

However, when the C atom is  $sp^2$  hybridized (planar) and the electron spin densities, positive and negative on C and H respectively, are due to spin polarization along the CH  $\sigma$ -bond induced by a  $\pi$  spin density, the coupling constants  $|a_{\text{C}}|$  and  $|a_{\text{H}}|$  are of the same order of magnitude. To explain the large value of  $|a_{\text{C}}|$  compared to  $|a_{\text{H}}|$  it must be assumed that part of the positive spin density on C is directly transferred into the  $2s$  orbital; consequently, after adsorption, the  $(\text{HCOOH})^{\ominus}$  entity is no longer planar. The deviation relative to the plane perpendicular to the  $\pi$  plane can be calculated from (19)

$$a_{\text{C}}(\theta) = [a_{\text{C}}(0) + 1190 (2 \tan^2 \theta)] \rho_{\pi, \text{C}}$$

where  $a(\theta)$  is the real coupling constant and  $a(0)$  is that corresponding to the theoretical planar structure.

$$\text{whence } \theta \sim 5^\circ.$$

We see therefore that the structure of the chemisorbed complex can be completely defined by NMR, whereas this was impossible by ESR.

We should like to point out that we have confirmed the above interpretation by theoretical studies.

### Conclusion

By means of a few examples we think we have demonstrated in this paper the interest of NMR in the study of gas-solid interactions. Due to lack of space we have restricted our discussion to dia- and para-magnetic solids. We could also have shown its interest in the area of metal catalysts.

Despite early difficulties in this field there is no doubt that NMR becomes increasingly a prime method for the study of the surface properties of solids and of heterogeneous catalyst mechanisms.

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