JOURNAL OF CATALYSIS 75, 219–224 (1982)

The Dependence of the Line Shifts in NMR Spectra of Adsorbed Molecules on Surface Coverage with Complex Formation; ^{13}C-NMR Study of the Interaction of Acetone with OH Groups of a Silica Gel

V. YU. BOROVKOV, A. V. ZAIKO, AND V. B. KAZANSKY

N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow, USSR

AND

W. K. HALL

Department of Chemistry, University of Wisconsin, Milwaukee, Wisconsin 53201

Received October 21, 1980; revised November 6, 1981

Equations for the dependence of observed line shifts in NMR spectra of adsorbates on surface coverage under conditions of fast exchange between physisorbed and chemisorbed molecules are derived. These equations were used to explain ^{13}C-NMR data for adsorption of acetone on the surface of the silica gel. The real chemical shifts of $^{13}C{=}O$ in spectra from acetone when coordinated by OH groups, the equilibrium constants for complex formation, and the concentrations of surface hydroxyl groups were determined experimentally.

INTRODUCTION

NMR data for the interaction of adsorbed molecules with the surfaces of solids suggest that in adsorbate–adsorbent systems fast exchange between physisorbed and chemisorbed molecules occurs (*1*) in a way analogous to ligand exchange into the coordination spheres of complexes in solution. The analogy of phenomena taking place in complex formation on solid surfaces and in solutions suggests the possibility, in principle, for the use of experimental approaches for the determination of chemical shifts in the NMR spectra of coordinated molecules, equilibrium constants, and heats of complex formation for heterogeneous systems. The fruitfulness of such an approach in the extreme case where the number of surface active sites was considerably less than the number of adsorbed molecules was demonstrated earlier by us using, for example, the interaciton of saturated hydrocarbons with surface bivalent cobalt ions supported on aerosil (*2*). In particular, it was shown that the dependencies of the line shifts in the NMR spectra of adsorbates on surface coverage and temperature provided a means to determine equilibrium constants and heats of surface complex formation.

Interaction of adsorbed molecules with diamagnetic surface sites gives rise to rather small line shifts in NMR spectra. For protons their values range within 1 to 2 ppm; (*3*); for ^{13}C-NMR they do not usually exceed 10 ppm (*4*). That is why for the study of such interactions, adsorbents with high concentrations of uniform active centers for complex formation are commonly used, e.g., the surface hydroxyls of silica (*5*) and silica–alumina (*6*), or various base-exchange cations in zeolites (*7*). In this connection it is worthwhile to consider theoretically the problem of the dependence of the observed line shifts in NMR spectra of adsorbed molecules on surface coverage in order to evaluate from experimental data the parameters characterizing the complex formation on the solid surface at arbitrary concentrations of active sites.

0021-9517/82/060219-06$02.00/0

In the present work the equations for the dependence of observed line shifts in NMR spectra on surface coverage under the conditions of fast exchange between physisorbed and coordinated molecules are derived. Using as an example the interaction of acetone molecules with hydroxyl groups of silica gel, the real values of the chemical shifts in the NMR spectra of coordinated molecules, equilibrium constants for complex formation, and concentrations of surface OH groups were determined experimentally.

THEORY

The averaged values of the shifts in NMR spectra of adsorbates (δ) for the fast exchange between physisorbed and coordinated molecules can be written as (*8*)

$$\delta = \rho_c \delta_c, \qquad (1)$$

where δ_c is the line shift in the spectrum of coordinated molecules relative to the position of the corresponding line in the spectrum of physisorbed molecules and ρ_c is the mole fraction of coordinated molecules. As follows from (*8*) δ_c should be considered as a mean quantity from three principal values of chemical shift tensor, i.e., $\delta_c = \frac{1}{3}(\delta_{xx} + \delta_{yy} + \delta_{zz})$. ρ_c can be evaluated by considering the thermodynamic equilibrium of formation and decomposition of surface complexes without taking into account the gas phase (*2*).

Two models[1] can be used for the description of this equilibrium:

Model 1. The probability of decomposition of the surface complex is determined by its stability constant only:

$$\mathrm{M} + \mathrm{A} \overset{K_g}{\rightleftarrows} [\mathrm{MA}], \qquad (2)$$

where M is an unoccupied active center on the surface, A is a physisorbed molecule, and [MA] is a surface complex, K_g is the equilibrium constant for complex formation.

Model 2. The decomposition of the surface complex will proceed only if there is next to it an empty site for physical adsorption. In such a case the equilibrium in the system can be written in the form

$$\mathrm{M} + \mathrm{A} \overset{K_L}{\rightleftarrows} [\mathrm{MA}] + \sqcup, \qquad (3)$$

where $\sqcup$ denotes a neighboring empty site for physical adsorption and K_L is the equilibrium constant for this process.

Let us take into consideration the following parameters: let V be the total number of adsorbed molecules, n the number of surface sites active in complex formation, and N the number of centers for physical adsorption.

Expressing the concentration of the quantities in (2) and (3) in terms of the parameters introduced we can write (see Appendix, part (a))

$$\frac{\Delta}{1-\Delta} + K_g V \Delta = K_g n \qquad \text{for Model 1,} \quad (4)$$

$$\frac{\Delta}{1-\Delta} + \frac{K_L - 1}{N} V\Delta = K_L \frac{n}{N} \qquad \text{for Model 2.} \quad (5)$$

The value Δ, introduced in (4) and (5) is equal to the ratio of observed chemical shift to that for the coordinated molecules ($\Delta = \delta/\delta_c$). Equations (4) and (5) describe the dependence of the experimentally observed shifts of the lines over the full range of surface coverages for arbitrary concentrations of active surface centers. From these expressions it follows that a decrease of surface coverage does not lead to the value of observed shift being equal to the real shift for coordinated molecules, but to

---

[1] These models describe the thermodynamics of the equilibrium between coordinated and physisorbed molecules and do not necessarily reflect, completely, the exchange processes between adsorbed molecules. Besides the thermal decomposition of the surface complexes, exchange may occur by substitution of coordinated molecules by physisorbed molecules in a way which does not influence the thermodynamic equilibrium in the adsorbate–adsorbent system (*8*).

some maximum value:

$$\Delta_m = \frac{\delta_m}{\delta_c} = \frac{K_g n}{1 + K_g n} \quad \text{for Model 1} \quad (6)$$

and

$$\Delta_m = \frac{\delta_m}{\delta_c} = \frac{K_L(n/N)}{1 + K_L(n/N)} \quad \text{for Model 2.} \quad (7)$$

The significant disadvantage of Eqs. (4) and (5) is the presence of the value Δ which cannot be determined experimentally as the real line shifts in NMR spectra of coordinated molecules usually are not known. In order to transform them into forms suitable for treatment of experimental data we take into consideration a new value Δ', determined as the ratio of the observed shift to the shift δ_m which can be found by extrapolation of the measured shift to infinitely small surface coverage

$$\Delta' = \frac{\delta}{\delta_m}. \quad (8)$$

Using the obvious correlation $\Delta = \Delta'\Delta_m$ and taking into account (6) and (7) the expressions (4) and (5) are easily transformed to the forms (Appendix, part (b))

$$\frac{V\Delta'^2}{1 - \Delta'} = \frac{1}{\Delta_m} \cdot \frac{(V\Delta')}{1 - \Delta'} - \frac{n}{\Delta_m^2} \quad \text{for Model 1,} \quad (9)$$

$$\frac{V\Delta'^2}{1 - \Delta'} = \frac{1}{\Delta_m} \frac{(V\Delta')}{(1 - \Delta')} - \frac{K_L}{K_L - 1} \cdot \frac{n}{\Delta_m^2} \quad \text{for Model 2.} \quad (10)$$

As is seen from Eqs. (9) and (10) (or Fig. 2 where $V\Delta'^2/(1 - \Delta')$ is plotted vs $V\Delta'/(1 - \Delta')$) it is possible to determine from the slope the value $\Delta_m = \delta_m/\delta_c$ and hence the real shift of the line in the NMR spectra of coordinated molecules. It is important to note that the value δ_c, determined from this plot does not depend on the model used for characterization of the equilibrium on the surface. Obviously the criterion for the choice of one of these two models for the description of the equilibrium on the surface of solids is the deviation of the value $K_L/(K_L - 1)$ [Eq. (10)] from unity. This value, generally speaking, can be evaluated from the experimental data. We will illustrate this possibility using, as an example, the results of an investigation by means of ^{13}C-NMR of the adsorption of acetone on the surface of silica gel.

EXPERIMENTAL

In our work "Davison" silica gel was used which had a specific surface area of 750 m^2/g and a mean pore diameter of 22 Å. Samples of silica gel (about 1 g) were placed into glass ampoules with an o.d. of 10 mm and then heated *in vacuo* at 500°C and pressure of 10^{-4} Torr for about 6 (sample S-6) and 50 (sample S-50) h before cooling.

Acetone vapor was adsorbed at room temperature using a conventional vacuum system. The acetone was purified from traces of oxygen by the pump–freeze–thaw method. The adsorption, V, was measured by a pressure decrease in a calibrated volume joined with the sample. In the first experiments, acetone having the carbonyl carbon enriched to 95% ^{13}C was used. Later ones were performed using ordinary acetone.

^{13}C-NMR spectra were recorded at room temperature using a CFT-20 "Varian" spectrometer with an operating frequency of 22 MHz. The shifts of the line for the C=O group of adsorbed acetone were measured relative to the position of this line in the spectrum of liquid acetone. Corrections for the bulk magnetic susceptibility of the samples were made. The accuracy of shift determination in all runs was better than ±0.2 ppm.

RESULTS AND DISCUSSION

The line of the carbonyl group in the ^{13}C-NMR spectra of acetone adsorbed on silica gel was shifted to lower fields relative to the position of this line in the spectrum of liquid. Moreover, the value of observed shift depended upon the amount adsorbed.

In Fig. 1 the dependencies of the experimentally detected shifts on the amount of adsorbed acetone for the samples S-6 (upper curve) and S-50 (lower curve) are shown. From this plot it was possible, with rather high accuracy, to define the value δ_m corresponding to the largest value of the observed shift which is achieved at infinitely small surface coverages. For the samples S-6 and S-50, δ_m is equal to about 10.0 and 8.5 ppm, respectively.

In Fig. 2 the same experimental data are plotted in coordinates $V\Delta'^2/(1 - \Delta')$ vs $V\Delta'/(1 - \Delta')$ where ($\Delta' = \delta/\delta_m$). The linear character of these dependencies evidences the validity of application of Eq. (9) or (10) for the description of acetone complex formation on the silica gel surface. The slopes of the straight lines which are equal to 1.15 for sample S-6 and 1.25 for S-50 correspond to the values of the shift for the C=O line in the NMR spectra of coordinated acetone of 11.5 and 10.5 ppm. The mean value of the shift is 11 ppm and is close to the value of 11.9 ppm, found in Ref. (*4*).

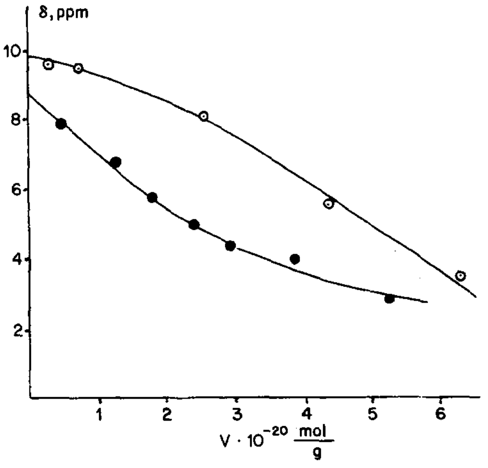

FIG. 1. The dependence of ^{13}C-NMR line shifts of the carbonyl carbon to lower fields upon the amount adsorbed for acetone on silica gel surface. The upper curve is for Davison S-6 and the lower for S-50 silica gel.

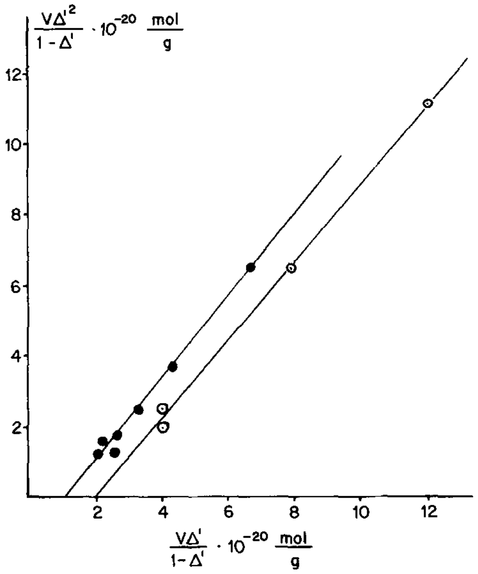

FIG. 2. The dependence of the ^{13}C-NMR carbonyl line shifts upon amount of adsorbed acetone plotted in the coordinates $V\Delta'^2/(1 - \Delta')$ vs $V\Delta'/(1 - \Delta')$.

The centers active in complex formation of acetone on silica gel surfaces resulting in the chemical shift in the NMR spectra of adsorbed molecules are known to be hydroxyl groups (*4*). It was natural to assume that the different times of thermovacuum treatment of the samples S-6 and S-50 influenced only the concentration of OH groups but did not change the total number of adsorption sites (centers active in complex formation, i.e., surface OH groups plus centers for physisorption). This assumption allowed us to evaluate the parameter $K_L/(K_L - 1)$, and therefore to make a choice of which equation, either (9) or (10), is best suited to fit the data.

It is easy to show that

$$\frac{K_L}{K_L - 1} = \frac{a_1\alpha_2^2 - a_2\alpha_1^2}{\alpha_1\alpha_2(a_1\alpha_2 - a_2\alpha_1)}, \quad (11)$$

where α_1, α_2 are quantitatively equal to the slopes of the straight lines in Fig. 2; a_1, a_2 are the intercepts of these lines with the ordinate axis; the indices 1 and 2 correspond to the data obtained for the samples S-6 and S-50, respectively. A calculation using Eq. (11) gave the value of $K_L/(K_L - 1) = 1 \pm 0.05$. This result suggested that to determine the constants for complex formation between acetone and surface hydroxyls, Eq. (9) should be used.

The concentrations of OH groups for the samples S-6 and S-50 calculated from NMR data were 1.3 ± 0.1 OH/100 Å^2 and 0.8 ± 0.1 OH/100 Å^2, respectively. The constant for complex formation, within the limits of errors, is the same for both samples and equal to $K_g = (6.5 \pm 1.0) \times 10^{-21}$ g/particle. The concentrations of OH groups determined in this work, are in agreement with literature data for silica gel samples undergoing thermovacuum treatment at 500°C (*9*). This fact demonstrates the validity of the approach for the description of the dependencies of line shifts in NMR spectra of adsorbed molecules on surface coverage in complex formation.

As was mentioned above, if Eq. (9) fits the experimental data, the implication is that the parameter $K_L/(K_L - 1)$ is approximately equal to one or that $K_L \gg 1$.

The correlation between the constants K_g and K_L, introduced in (2) and (3), can be approximately written in the form

$$K_L \simeq (K_g \cdot n)\frac{N}{n} = K_g N. \qquad (12)$$

From (12) it follows, that Eq. (9) can generally be used for the description of the shift dependencies on the amount of adsorbed substrate for rather strong complexes ($K_g n > 1$) or when the concentrations of active chemisorption sites are relatively small ($n/N \ll 1$). This is the situation for the complex formation of acetone with OH groups of the samples S-6 and S-50. Indeed, for such complexes $K_g n \approx 5$ and assuming the area of the adsorption site is equal to the landing area for the molecule of acetone (~30 Å^2) we find $N/n \simeq 3$ and consequently the parameter $K_L/(K_L - 1) = 1.07$, is very close to 1.

At higher concentration of surface centers participating in formation of "weak" complexes, it seems reasonable to use Eq. (10) for the treatment of experimental data. This takes into account the influence of the surface coverage on the thermodynamic equilibrium between physisorbed and coordinated molecules.

The results obtained in the present work show that NMR studies coupled with adsorption measurements can be applied to the determination of the real line shifts in NMR spectra of chemisorbed molecules and to the thermodynamics of the formation of the surface complexes. The equations derived for the dependence of the observed shifts on the numbers of molecules adsorbed indicate that the determination of the real shift in NMR spectra of coordinated molecules based on the extrapolation of the values of observed shift to the infinitely small coverages, as suggested in the literature (*4, 6*), can lead to incorrect quantitative conclusions on the character of interaction of adsorbed molecules with the active surface sites.

APPENDIX

(a) To derive Eqs. (4) and (5) let us represent the equilibrium constants of the complex formation in the form

$$K_g = \frac{N_{MA}}{N_A N_M} \quad \text{for Model 1,} \qquad (13)$$

$$K_L = \frac{N_{MA} N_{\sqcup}}{N_A N_M} \quad \text{for Model 2,} \qquad (14)$$

where N_{MA} and N_A are, respectively, the number of complexes and the number of physisorbed molecules on the surface of the sample. N_M and $N_{\sqcup}$ denote the number of empty centers active in complex formation, and the number of empty sites for physisorption, respectively.

Using the parameters introduced in the text one can write

$$\begin{aligned} N_{MA} &= V\Delta, \\ N_A &= V(1 - \Delta), \\ N_M &= n - V\Delta, \\ N_{\sqcup} &= N - V(1 - \Delta). \end{aligned} \qquad (15)$$

Introduction of (15) in (13) and (14) leads to Eqs. (4) and (5).

For example, for Model 2 we have

$$K_L = \frac{V\Delta[N - V(1 - \Delta)]}{V(1 - \Delta)(n - V\Delta)} \qquad (16)$$

or

$$\frac{K_L}{N}(n - V\Delta) = \frac{\Delta}{1 - \Delta} - \frac{V\Delta}{N} \qquad (17)$$

from which Eq. (5) follows.

(b) Equation (4) is easily converted into Eq. (9) by a substitution $\Delta = \Delta'\Delta_m$.

$$\frac{\Delta'\Delta_m}{1 - \Delta'\Delta_m} + K_g V\Delta'\Delta_m = K_g n \qquad (18)$$

or

$$K_g V\Delta'\Delta_m - K_g\Delta'^2\Delta_m^2 = K_g n - \Delta'\Delta_m(1 + K_g n).$$

Taking into account (see Eq. (6))

$$\Delta_m(1 + K_g n) = K_g n \qquad (19)$$

we obtain

$$V\Delta'\Delta_m - V(\Delta'\Delta_m)^2 = n(1 - \Delta') \qquad (20)$$

and hence Eq. (9). The procedure for generating Eq. (10) is similar.

(c) To derive Eq. (11) let us consider the expressions for the slope (α) and interception with the ordinate exis (a) of a straight line, built in coordinates $V\Delta'^2/(1 - \Delta')$ vs $V\Delta'/(1 - \Delta')$, which are given by Eq. (10). Introducing

$$\kappa = \frac{K_L}{K_L - 1} \qquad (21)$$

one can write

$$a = \kappa n \alpha^2. \qquad (22)$$

On the other hand (see Eq. (7)) $\alpha = (1 + K_L n/N)/(K_L n/N)$ and hence

$$K_L \alpha n = N + K_L n = (N + n) + n(K_L - 1). \qquad (23)$$

Combination of Eqs. (22) and (23) gives

$$\frac{a}{\kappa\alpha^2}(\kappa\alpha - 1) = \frac{N + n}{K_L - 1}. \qquad (24)$$

For two samples having an equal number of adsorption centers ($N + n$ = Const) and the same equilibrium constant of the complex formation K_L one finds

$$\frac{a_1}{\alpha_1^2}(\kappa\alpha_1 - 1) = \frac{a_2}{\alpha_2^2}(k\alpha_2 - 1). \qquad (25)$$

Equation (11) immediately follows from this equation.

ACKNOWLEDGMENT

W. K. Hall wishes to acknowledge the financial support of NSF under the US-USSR program (Grant CHE 77-10644).

REFERENCES

1. Kazansky, V. B., and Borovkov, V. Yu., *Kinet. Katal.* **14,** 1093 (1973); Cirillo, A. C., Dereppe, J. M., and Hall, W. K., *J. Catal.* **62,** 379 (1980); Kibby C. L., Borovkov, V. Yu., Kazansky, V. B., and Hall, W. K., *J. Catal.* **46,** 245 (1977).
2. Borovkov, V. Yu., Zhidomirov, G. M., and Kazansky, V. B., *J. Struct. Chem.* (*USSR*) **15,** 547 (1974).
3. Derouane, E. G., Fraissard, J., Fripiat, J. J., and Stone, W. E. E., *Catal. Rev.* **7,** 121 (1972).
4. Gay, I. D., *J. Phys. Chem.* **78,** 38 (1974).
5. Gay, I. D., and Liand, S., *J. Catal.* **44,** 306 (1976).
6. Bonardet, J. L., and Fraissard, J., *J. Magn. Reson.* **22,** 1 (1976).
7. Pfeifer, H., *Phys. Rep.* **26,** 293 (1976).
8. Borovkov, V. Yu., Zhidomirov, G. M., and Kazansky, V. B., *J. Struct. Chem.* (*USSR*) **16,** 308 (1975).
9. Uytterhoeven, J., Sleex, M., and Fripiat, J. J., *Bull. Soc. Chim. Fr.* **6,** 1800 (1965); Hall, W. K., Leftin, H. P., Cheselske, F. J., and O'Reilly, D. E., *J. Catal.* **2,** 506 (1963).