NMR Studies of Simple Molecules on Metal Surfaces

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In recent years, improvements in the sensitivity of nuclear magnetic resonance have made it possible to detect progressively smaller numbers of nuclei. Experiments and studies previously thought to be impractical can now be undertaken, for example, the study of phenomena at surfaces. Nuclear magnetic resonance has been applied to study simple molecules (carbon monoxide, acetylene, and ethylene) adsorbed on metal surfaces (ruthenium, rhodium, palladium, osmium, iridium, and platinum). The metals, in the form of clusters 10 to 50 angstroms in diameter, supported on alumina, are typical of real catalysts. The experiments provide information about the bonding of the molecules to the metal, the structures the molecules assume after adsorption, the motion of molecules on the surface, the breakup of molecules induced by heating, and the products of such breakup.

ONE OF THE MOST ACTIVE AREAS OF RESEARCH TODAY IS the study of metal surfaces. While a broad range of scientific questions in physics and chemistry underlie this activity, much of the research is motivated by a desire to understand the fundamentals of catalysis, and involves the nine group VIII elements of the periodic table (iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum), which play such an important role in catalysis. One of the key issues in catalysis is specificity. For example, Sinfelt found, in the hydrogenolysis of ethane to produce methane ($C_2H_6 + H_2 \rightarrow 2CH_4$), that the group IB metals (copper, silver, and gold) are orders of magnitude less active than the least active of the group VIII metals (*1*). Moreover, there is a variation of eight orders of magnitude in activity among the group VIII metals themselves (*1*). Although ethane hydrogenolysis is not a desired reaction in a practical sense, its great sensitivity to the nature of the metal makes it a good candidate for probing the fundamental question of catalytic specificity. Indeed, a study of this reaction led Sinfelt to the ideas for bimetallic cluster catalysts (*2*) that actually suppress this reaction. As a result of this suppression, a metal can be made more selective for reactions of greater value, such as reactions for making aromatic hydrocarbons.

The study of surfaces has proceeded on two fronts. The first, made possible by the development of ultrahigh-vacuum techniques, involves the study of oriented single crystals. The other front is based on studies of real catalysts. For a variety of reasons, real catalysts consist of small metal particles, typically 10 Å in diameter, attached to a support, spongelike in structure, such as certain forms of Al_2O_3 (alumina) or SiO_2 (silica). Since the experimental methods appropriate to one type of sample (for example, single crystals) often cannot be used for the other, most researchers work on only one of the two fronts. The newcomer to the field is rapidly made aware of the passion with which many workers adhere to their particular front.

Among the many forms of spectroscopy used, magnetic resonance (in particular nuclear magnetic resonance, NMR) was until recently conspicuous by its absence. One naturally wonders why a technique that has played an important role in the study of chemistry and solid-state physics is not used. The reason is that NMR signals from surfaces are weak. As a result of the many developments in magnetic resonance techniques in recent years, NMR studies of samples containing 10^{18} to 10^{20} nuclei have now become possible. A surface area of 1 cm^2, typical of single crystal studies, has about 10^{15} atom sites. On the other hand, 1 g of a real catalyst may contain 1 to 10 m^2 of metal surface, presenting 10^{19} to 10^{20} atom sites.

Thus the NMR sensitivity limits us to working with small particles. For the best results from resonance techniques, it would be advantageous to work with oriented single crystals: their spectra would be simpler and yield more information. NMR studies of such samples may become feasible under specialized conditions (for example, very low temperatures) but to our knowledge no such studies have been published. On the other hand, NMR allows us to undertake detailed microscopic investigations of the real catalysts themselves, in some cases at pressures or temperatures typical of catalytic reactions.

In 1981, Duncan and Dybowski (*3*) reviewed NMR studies of surfaces (including surfaces of nonmetals), pointing out that at that time, most published studies involved molecules that are weakly bound to the surfaces, so-called physisorbed species. For catalysis, molecules that form chemical bonds with the surface, so-called chemisorbed species, are of interest. Subsequently, there has been strong focus on chemisorbed molecules.

For example, Duncan, Yates, and Vaughan (*4*) did pioneering studies of carbon monoxide (CO) enriched in ^{13}C chemisorbed on a catalyst of rhodium supported on alumina. Subsequently, Duncan, Winslow, and Bell (*5*) used NMR to study the reaction of CO with H_2 to produce CH_4. In particular, they observed and identified various carbon-containing species on the surface. Tirendi, Mills, and Dybowski (*6*) studied benzene and cyclohexane adsorbed on platinum, and Decanio *et al.* (*7*) studied the hydrogenation of benzene to cyclohexane on alumina-supported rhodium catalysts. Hydrogen on

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platinum has been investigated by a number of workers (*8–11*). Gay (*12*) has introduced a method for producing narrow NMR lines, so-called magic angle spinning, for catalytic studies. The work on metal surfaces since the review of Dybowski and Duncan has been recently reviewed (*13*). There has also been extensive work on a related problem, catalysis on zeolites, recently reviewed by Pfeiffer (*14, 15*).

We have been applying NMR to the study of samples containing small particles of ruthenium, rhodium, palladium, osmium, iridium, and platinum. (Iron, cobalt, and nickel are ferromagnets and thus are expected to give NMR lines too broad to observe.) One can consider studies of two kinds of nuclei: (i) those of the metal and (ii) those of adsorbed molecules. The first studies from our group with our colleagues Rhodes, Stokes, and Makowka were investigations of the ^{195}Pt resonance in platinum particles. Rhodes, Stokes, and our group (*16*) studied how the local spin susceptibility of the conduction electrons varies as one approaches the metal surface. Makowka and co-workers used a double-resonance technique involving ^{195}Pt and the ^{13}C nucleus of adsorbed CO to detect the ^{195}Pt NMR of the surface layer of platinum atoms (*17*).

We now describe our work on the simple adsorbed molecules CO, acetylene (C_2H_2), and ethylene (C_2H_4). We find that NMR provides information about the bonding of the molecules to the metal, lets us determine the structure that the molecules assume after adsorption, enables us to detect and measure motion of the molecules on the surface, and permits us to follow details of the breakup of the molecules induced by heating.

Special Features of the NMR of Adsorbed Species

It is useful, in thinking about our experiments, to keep the following picture in mind. Metal crystallites or clusters with sizes in the range of 10 to 50 Å frequently approximate regular polyhedra, for example, cuboctahedra (*18*). A cuboctahedron has eight (111) faces, hexagonal in shape, and six (100) faces, square in shape. The surface area is composed of 80% (111) faces and 20% (100) faces. Since the metal particles have crystalline faces, we expect adsorption sites similar to those seen on single crystals. A given kind of molecule (for example, CO) adsorbs at certain characteristic sites, normally a function of the degree of coverage. At a coverage of 50%, CO adsorbs in equal amounts at two types of sites on a Pt (111) face. These sites are called linear and bridged, and correspond to the possibility of a CO bonding to a single platinum atom or a pair of platinum atoms, respectively.

In platinum carbonyl molecules [for example, $Pt_{19}(CO)_{22}$], the ^{13}C NMR spectra of bridged and linear CO differ as a result of the phenomenon called the "chemical shift" (*19*). For ^{13}C it is conventional to measure shifts relative to the ^{13}C resonance of tetramethylsilane [$(CH_3)_4Si$], conventionally abbreviated TMS. Typical ^{13}C shifts of diamagnetic molecules cover a total range of some 250 ppm. The ^{13}CO resonance in platinum carbonyls occurs at 167 ppm for linear sites and 228 ppm for bridge sites downfield from TMS (*19*). The chemical shift depends in general on the orientation of the molecular axes with respect to the static field. In liquids, this anisotropy averages to zero under the rapid molecular tumbling, the lines are narrow, and small chemical shift differences can be detected. In our samples, all orientations of the surfaces are equally probable. Consequently, when the molecules are at rest, the chemical shift anisotropy broadens the NMR line. For ^{13}C, this broadening amounts to several hundred parts per million, whereas ^{1}H chemical shifts cover a range of about 15 ppm.

The fact that the metal cluster has a static magnetic susceptibility leads to another line-broadening mechanism comparable in size for some metals to ^{13}C chemical shift anisotropy and much larger usually than the chemical shift anisotropy for protons. Application of the static magnetic field induces a magnetization of the metal, which in turn produces a magnetic field that acts on the adsorbed molecules in addition to the applied static field. Since this extra magnetic field has different values at different points on the surface of the metal cluster, it broadens the NMR line of nuclei in a molecule adsorbed on the cluster surface. The broadening is of the order $4\pi\chi/3$, where χ is the magnetic susceptibility of the metal. Some values for $4\pi\chi/3$ are 268 ppm for palladium, 93 ppm for platinum, 56 ppm for rhodium, and 5 ppm for osmium.

We observed the magnetic resonance by the so-called spin echo method (*20, 21*). We applied two radio-frequency pulses separated by a time τ, and recorded the spin echo that occurred near 2τ. The area under the spin echo curve gave the NMR absorption at the frequency of the radio-frequency field and was proportional to the number of nuclei whose resonance is at that frequency. This method enables one to map the shape of very broad, asymmetric NMR lines reliably by measuring spin echoes at different line positions. A useful feature of the echo is that its peak height is unaffected by the effects of static field inhomogeneities such as those arising from chemical shifts or the magnetic susceptibility of the metal. Thus, the signal at the peak of the echo stands as though those broadening effects did not exist. Additionally, by plotting the echo amplitude as a function of τ, one can observe how other interactions (such as the ^{13}C–^{13}C coupling in C_2H_2) affect the echo signal.

The size of the NMR signal one gets depends on various factors: number and type of nucleus, strength of the static magnetic field, temperature, and so forth. Typical samples weigh about 1 g, contain 5 to 10% metal by weight, and have from 10 to 85% of the metal atoms on the surface. Take a 1-g sample where 75% of the platinum atoms are on the surface of the particles, with ^{13}CO adsorbed to full coverage (one CO for two surface platinum atoms): at a temperature of 77 K, a single spin echo signal has a signal-to-noise ratio of 5. If one drops the coverage or the surface area, the signal drops in proportion, and one must then average the signal over many echoes. A decrease in surface area by a factor of ten would require 10^2 echoes to get back to the original signal-to-noise ratio. One can also increase the signal by lowering the temperature to the liquid helium region (signal strength is inversely proportional to the temperature).

Bonding of Molecules to the Metal

We have found that we get information about the electronic properties of the bonding of atoms or molecules to the metal surface from two NMR measurements: (i) the spin-lattice relaxation time, T_1, and (ii) the shift of the NMR line position. We illustrate with data for ^{13}CO adsorbed on metal surfaces. The data reveal the mixing of the molecular wave functions of the CO molecule with the wave functions of the conduction electrons in the metal. To some extent the molecule takes on a metallic character when adsorbed on the surface. Such mixing is a central feature of many theories (*22*) of the adsorption bonds, but we know of no experimental method other than NMR that directly measures the degree of mixing.

Spin-lattice relaxation is the process whereby nuclei achieve their net thermal equilibrium polarization in the applied static field. For this process to take place, the nuclei must be coupled to some thermal reservoir, conventionally termed the "lattice," with which they can exchange energy. Measurements of the temperature dependence of the relaxation rate often allow one to determine the fundamental processes that make the energy transfer between the spins and the lattice possible.

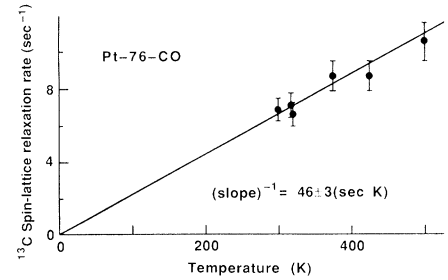

Fig. 1. ^{13}CO spin-lattice relaxation rate, $1/T_1$, versus temperature, θ, for 76% dispersion platinum fully covered with ^{13}CO. The fact that the rate is proportional to θ shows that the relaxation is via the conduction electrons. [Reprinted from (*23*) with permission of the American Institute of Physics]

Figure 1 shows data obtained by Rudaz, Ansermet, P.-K. Wang, Slichter, and Sinfelt (*23*) of the relaxation rate, $1/T_1$, of ^{13}CO on platinum versus the absolute temperature, θ. The notation "Pt-76-CO" means that the metal is platinum; that the particle size is such that, on average, 76% of the platinum atoms are on the surface (the fraction of metal atoms on the surface, called the "dispersion" of the sample, has been determined by the method of chemisorption); and that the surface has been covered with a monolayer of chemisorbed CO to the maximum extent. These data and data presented later from work at temperatures above 300 K were made possible by use of a high-temperature NMR probe developed in our lab by Ansermet.

The relaxation time at 300 K is about 150 msec, much faster than ^{13}C in carbonyl molecules (*24*). Figure 1 shows that the relaxation rate, $1/T_1$, is proportional to the temperature, $1/T_1 \propto \theta$. Such a temperature dependence is characteristic of nuclei in metals. In a metal, only the conduction electrons in the tail of the Fermi distribution (those least inhibited by the Pauli exclusion principle from exchanging energy) can relax nuclei. The number of such electrons is proportional to the temperature. Such a temperature dependence is thus the hallmark of relaxation by conduction electrons. Shore (*25*) has measured T_1 for CO on ruthenium and palladium, and Z. Wang (*26*) has measured T_1 for CO on rhodium, osmium, and iridium. At 77 K, the resulting times are all rather similar, so that, though we have not as yet done detailed temperature-dependence studies, we expect the conduction electron mechanism to account for all.

Ansermet (*27*), P.-K. Wang, and Slichter have jointly investigated detailed models of the relaxation. Following Obata (*28*), they consider the mechanisms of magnetic coupling of the ^{13}C nucleus with the conduction electron orbital and spin magnetization. In analyzing these mechanisms, there are two possibilities. The first is that the conduction electrons are confined to the platinum atoms. The second is that the conduction electrons are able to leak onto the CO molecule. Even if the leakage is small, it enables the conduction electrons to get much closer to the ^{13}C nucleus, and thereby to couple strongly. If we assume, as did Ansermet, P.-K. Wang, and Slichter, that the electrons are solely on the platinum atoms, then the relaxation rates are much longer than found experimentally. In order to account for the experimental relaxation times, the conduction electrons must get onto the carbon atom itself. To express the leakage phenomena mathematically, they mix the molecular wave functions with the metallic ones. Measurements of T_1 yield the mixing coefficients.

Another manifestation of this mixing is in the ^{13}CO line position. Figure 2 shows typical spin echo line-shape data from our group [rhodium, osmium, iridium and platinum data by Z. Wang (*26*); ruthenium and palladium data by Shore (*25*)]. The plot gives line positions relative to the resonance of the reference compound TMS. To help guide the eye, least squares fits to Gaussian line shapes (normalized to equal areas) are shown. (Of course, the real shape is not necessarily Gaussian.) CO on palladium metal is thought to be predominantly bridge-bonded (*29*). The line at 540 ppm is to our knowledge the world's record for ^{13}C shifts downfield, and is 310 ppm downfield from typical bridge-bonded CO (230 ppm). What can cause such a large shift? From analysis of a similar though smaller shift for ^{13}CO on platinum, Rudaz, Ansermet, P.-K. Wang, and others (*23*) proposed that such a shift might arise from the presence of the conduction electrons on the ^{13}C atom. In metals, the polarization of the magnetic moments of the conduction electrons gives rise to a shift in the metal NMR line called the Knight shift after its discoverer (*30*). They proposed that the ^{13}CO shift is indeed a Knight shift. The proposal can be tested by measuring the ^{13}C spin-lattice relaxation time. Many years ago, Korringa (*31*) showed that the coupling mechanism between the nucleus and the conduction electron which produces a Knight shift also provides a mechanism for spin-lattice relaxation. He showed how from knowledge of the Knight shift one can predict the associated T_1. Attributing the extra 310-ppm shift of CO on palladium to a Knight shift, his theory leads to a predicted T_1 of 0.57 second at 77 K, close to the value 0.45 second measured by Shore (*25*). We thus confirm another sign of the mixing of the CO wave functions with those of the metal.

Structure of Simple Molecules

The use of high-resolution NMR in liquids to determine the structure of molecules has advanced to a method of great sophistication and power. The study of molecular structures on surfaces has, however, come nowhere near this level of power since, as remarked earlier, the spectra are not high-resolution spectra. Nevertheless, structures can be determined for simple molecules. The method is based on measuring the nuclear magnetic dipole coupling between

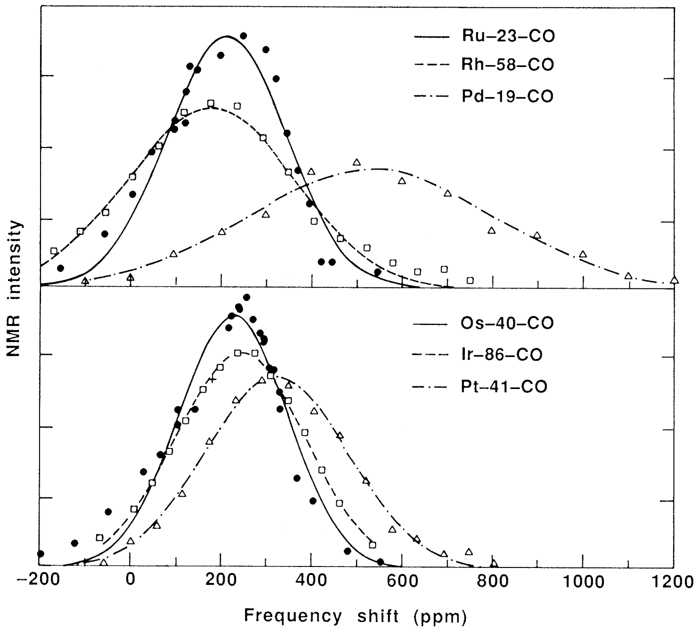

Fig. 2. ^{13}CO NMR line shapes at 77 K: NMR absorption versus frequency shift δ relative to TMS (positive numbers represent higher frequency): upper, ●, Ru; □, Rh; △, Pd; lower, ●, Os; □, Ir; △, Pt. The various lines are the Gaussian curves that best fit the data, centered at the average shift of the data. The shift for CO on palladium is the largest shift known for ^{13}C. The notation Pt-41-CO means 41% dispersion platinum coated with CO. [From Shore (*25*) and Z. Wang (*26*) reprinted from (*13*) with permission of *Annual Reviews*]

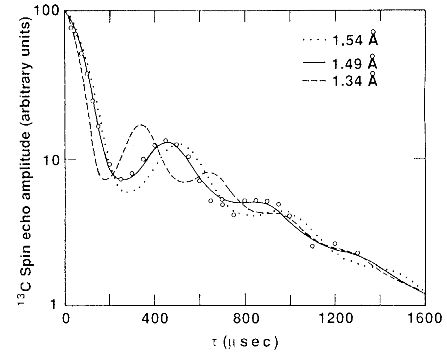

Fig. 3. Ethylene bond length determination by ^{13}C spin echo: Spin echo amplitude versus the time, τ, between echo pulses. The oscillation arises from ^{13}C–^{13}C nuclear dipolar coupling between carbon pairs in given molecules. Theoretical fits are for different bond lengths. [Reprinted from (*34*) with permission from the American Chemical Society]

nuclei in the molecule. Its historical roots are the pioneering studies by Pake (*32*) of the water molecule in gypsum and by Gutowsky *et al.* (*33*) of hydrocarbons that show how the dipolar coupling gives NMR line shapes that are distinct for H–H pairs, H–H–H triples, and groups of four coupled hydrogen atoms. The spectrum of a pair of protons, for example, consists of two closely spaced absorption lines, the so-called "Pake doublet," arising because a given hydrogen atom has a neighbor whose spin can point either up or down. Thus the neighbor contributes a magnetic field that either aids or opposes the applied field, giving rise to two resonance positions.

Ethylene on platinum, osmium, or iridium. The use of NMR to determine structures can be illustrated by the work of P.-K. Wang *et al.* (*34*), who determined the structure of C_2H_4 adsorbed on platinum, osmium, and iridium at room temperature. Although it was known (*35*) that on single crystal (111) faces the molecule sheds one hydrogen atom, becoming a CCH_3 molecule, the structure had not been determined on small particles. P.-K. Wang *et al.* (*34*) studied molecules in which the carbon was enriched to 90% with ^{13}C. The dipole coupling between the carbon nuclei in a pair should give rise to a Pake doublet in the line shape. However, it is concealed by the broadening caused by the chemical shift anisotropy and the metal susceptibility. They used spin echoes to eliminate the effects of chemical shift anisotropy, metal susceptibility, and ^{13}C–^{1}H coupling. Figure 3 shows the envelope of the ^{13}C echo signal versus the time, τ, between pulses. The envelope displays two components, a single exponential decay and an oscillatory component that also decays exponentially. The single exponential arises from ^{13}C nuclei that have no ^{13}C neighbor, either because they belong to a ^{13}C–^{12}C pair or because they belong to a C_2H_4 molecule in which the C–C bond broke on adsorption. The oscillatory component arises from the dipolar coupling between ^{13}C nuclei in ^{13}C–^{13}C pairs. (This oscillation is, in fact, the Fourier transform of the Pake doublet.) Since the strength of the coupling is inversely proportional to the cube of the distance between the ^{13}C nuclei, one can deduce the C–C bond length by measuring the period of the oscillations. P.-K. Wang *et al.* (*34*) find a bond length of 1.49 ± 0.02 Å. The results and the fit with a bond length of 1.49 Å as well as predictions for a single-bond length of 1.54 Å and a double-bond length of 1.34 Å are also shown in Fig. 3.

The fact that the C–C bond is close to a single bond suggests that the structure is a CH_2CH_2, a $CHCH_3$, or a CCH_3 species. P.-K. Wang *et al.* (*34*) used ^{13}C–^{1}H double resonance to investigate these possibilities. Their method, called spin echo double resonance (SEDOR), involves applying a third radio-frequency pulse, tuned to the ^{1}H NMR, in addition to the two pulses that produce the ^{13}C spin echo (*21*). If the ^{1}H atom were left alone, the ^{13}C–^{1}H dipolar coupling would produce a static magnetic field broadening of the ^{13}C resonance, which would be refocused by the echo pulses. Because of the ^{13}C–^{1}H nuclear dipolar coupling, flipping the ^{1}H nucleus changes the precession frequency of the ^{13}C nucleus and thereby interferes with the formation of the echo. One can destroy the echo of a ^{13}C that is bonded to a ^{1}H atom in this manner.

Since the CH_2CH_2 and $CHCH_3$ molecules have a hydrogen atom bonded to every carbon, one should be able to destroy the entire ^{13}C signal by flipping protons. We call the fraction of the echo destroyed by SEDOR the SEDOR fraction. Thus for CH_2CH_2 and $CHCH_3$ the SEDOR fraction at long times is expected to approach 1, whereas it is expected to approach 0.5 for CCH_3 for which only half of the carbon atoms are bonded to hydrogen atoms. Figure 4 shows the SEDOR fraction for this case. Several theoretical curves are shown. One corresponds to CCH_3 in which the orientation of the CH_3 group is fixed in time. A second assumes a CCH_3 molecule with the CH_3 group rotating rapidly on the NMR time scale about the C–C bond. The third assumes a $CHCH_3$ molecule in which the CH_3 is in rapid rotation. The data at 77 K fit the solid theoretical line, a CCH_3 species in which the CH_3 group is rotating rapidly. Within experimental error, P.-K. Wang *et al.* (*34*) found the same C–C bond length for C_2H_4 adsorbed on osmium and iridium.

Structure of acetylene. P.-K. Wang *et al.* (*36, 37*) have also determined the structure of C_2H_2 adsorbed on platinum, osmium, and iridium. In this case the structure was still a subject of controversy for single crystals (*38*). In samples enriched in ^{13}C, they measured the C–C bond length as 1.44 ± 0.02 Å, midway between typical single bonds (1.54 Å) and double bonds (1.34 Å). To determine what fraction of the ^{13}C atoms were bonded to hydrogen atoms, they used ^{13}C-^{1}H SEDOR. Various species have been proposed to result from adsorbing C_2H_2 on metals: HCCH, CCH, CCH_2, and CCH_3 among others. In general, one expects a mixture of more than one species. Best fits to the SEDOR data allowed three possibilities: 75% CCH_2 and 25% HCCH; or 50% CCH_3 and 50% CCH; or 100% CCH. To distinguish between the possibilities, they noted that the first possibility contains hydrogen atoms in a CH_2 group, the second, hydrogen atoms in a CH_3 group, and the third, hydrogen atoms only in a CH group. They were led to try to "count" the hydrogen atoms in close proximity by an NMR technique called "multiple-quantum coherence." This ingenious concept, first introduced by Hatanaka and co-workers (*39*), has been brilliantly developed by several other groups among which are Wokaun and Ernst (*40*), Warren and Pines (*41*), and Bodenhausen and the Volds (*42*). Roughly speaking, two-quantum coherence involves flipping two spins simultaneously via the coupling between them, and three-quantum coherence involves flipping three spins. P.-K. Wang *et al.* (*37*) demonstrated a strong two-quantum coherence, but negligible three-quantum coherence, which enabled them to conclude that C_2H_2 on platinum clusters was 75% CCH_2, 25% HCCH.

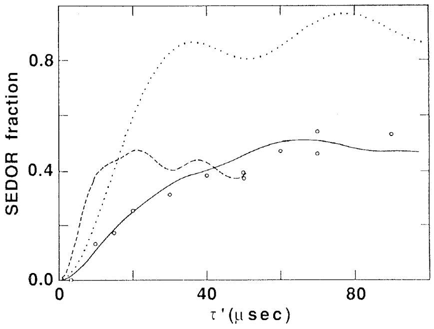

Fig. 4. Bonding of hydrogen atoms to carbon in ethylene: The fractional destruction of the ^{13}C spin echo produced by flipping ^{1}H nuclei in a SEDOR experiment versus the time, τ', of application of the ^{1}H pulse. Data at 77 K. Solid line: CCH_3 species with rapid CH_3 rotation about the C–C axis; dashed line: CCH_3 without CH_3 rotation; dotted line: $CHCH_3$ with rotating CH_3. [Reprinted from (*34*) with permission from the American Chemical Society]

Observation of Chemical Reactions and Reaction Products

One's ability to use NMR to determine simple molecular structures can be extended to follow changes in structure such as those that occur in chemical reactions. We have used NMR to follow the breaking of C–C and C–H bonds resulting from heating C_2H_2 and C_2H_4 adsorbed on platinum, osmium, and iridium.

The C–C scission is revealed by its effect on the ^{13}C spin echo envelope. As we have remarked, the oscillatory component of the echo envelope arises from the coupling between ^{13}C nuclei that are bonded to each other. When some C–C bonds break, the intensity of the oscillatory decay decreases, and the intensity of the nonoscillatory decay increases.

Data of P.-K. Wang, Ansermet, and co-workers for the CCH_3 molecule on platinum produced by adsorbing C_2H_4 are shown in Fig. 5 (*43*). The NMR spectra of Fig. 5 were all measured at 77 K, but between NMR observations the sample was annealed in an oven for 3 hours at progressively higher temperatures. As the annealing temperature was increased, the amplitude of the oscillatory component decreased, showing that C–C bonds are breaking. The solid lines of Fig. 5 are theoretical fits from which one can deduce the fraction of oscillatory component, hence the fraction of C–C bonds broken at each temperature. Figure 6 shows the fraction of C–C bonds broken versus annealing temperature. From these data, assuming an exponential reaction rate with a frequency prefactor ν_0 of 10^{13} per second, one finds a barrier energy $E = 36$ kcal/mol. Since a change by a factor of ten in ν_0 changes E by only 2 kcal/mol, one can conclude the barrier for C–C rupture is close to 36 kcal/mol. The fact that the oscillation frequency of the slow beat (Fig. 5) does not change with progressive annealing shows that the C–C bond length is not changing, hence that the molecules retain their hydrogen up to the point of C–C bond scission. P.-K. Wang *et al.* (*44*) found similar results for both C_2H_4 and C_2H_2 on iridium. All three systems have similar barrier energies.

In contrast, P.-K. Wang *et al.* (*44*) have shown that there is substantial loss of hydrogen from C_2H_2 on platinum C–C scission. In ^{13}C–^1H spin echo double-resonance studies, the SEDOR fraction after it has been annealed to 490 K is 50 to 60% of its value before annealing, although most of the C–C bonds are still intact at this annealing temperature. Thus there is a substantial loss of hydrogen before the C–C bonds break. The spin echo data suggest that there is more than one bond length present. Therefore, one expects a mixture of two or more species (for example, 25% C_2 and 75% CCH or 60% C_2 and 40% HCCH after annealing at 490 K). The exact configurations are not yet known.

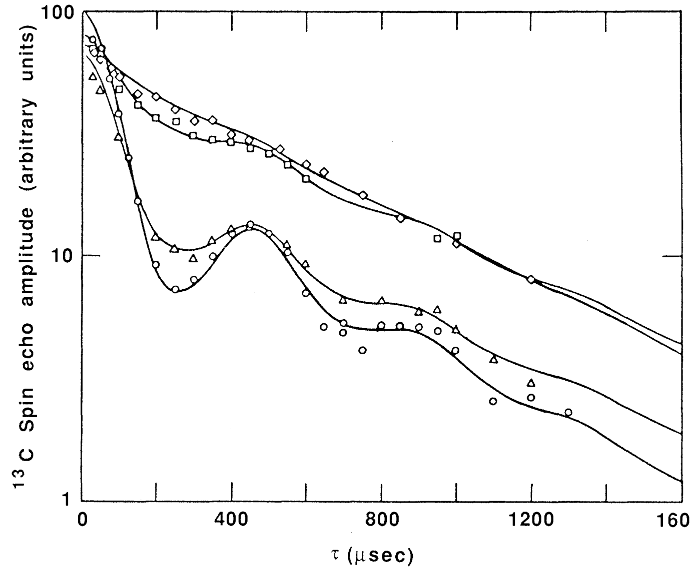

Fig. 5. The scission of C–C bonds produced by annealing ethylene on platinum: ^{13}CO spin echo amplitude versus time, τ, between echo pulses measured at 77 K after annealing periods of 3 hours at various temperatures (◇, 479 K; □, 453 K; △, 391 K; ○, room temperature). The decrease in the size of the oscillation on annealing shows the breaking of bonds to neighboring ^{13}C atoms. [Reprinted from (*34*) with permission from the American Chemical Society]

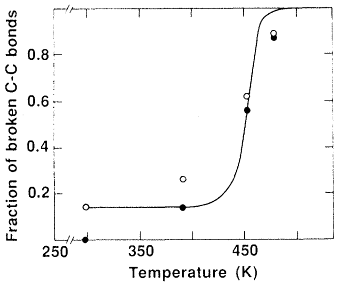

Fig. 6. Fraction of C–C bonds broken for ethylene on platinum versus annealing temperature. ○, Raw data; ●, data with a small correction, solid curve is theoretical fit for 36 kcal/mol activation energy. [Reprinted from (*34*) with permission from the American Chemical Society]

Identification of Isolated Carbon Atoms

P.-K. Wang with Ansermet and others (*43*) have studied the reaction products resulting from the breaking up of all the C–C bonds of C_2H_2 and C_2H_4 chemisorbed on platinum annealed to 690 K. In this section we show that a major conclusion is that one product is isolated carbon atoms, and in the next section we show that the atoms are highly mobile. Adsorbed carbon atoms have long been thought to play a crucial role in metal-catalyzed reactions such as the synthesis of hydrocarbons from CO and H_2 gas (Fischer-Tropsch synthesis). Our results confirm an earlier study of Duncan, Winslow, and Bell (*5*) who studied the methanation reaction on ruthenium catalysts. They found a ^{13}C resonance at a shift 380 ppm downfield from TMS. They concluded that such a large shift arose from isolated carbon atoms either at an interstitial position or on the surface.

P.-K. Wang, Ansermet, and co-workers (*43*) studied the ^{13}C NMR line shape at 77 K of platinum coated with C_2H_2 at 300 K before and after it was annealed at 690 K. They found that a broad line centered at about 100 ppm downfield from TMS before annealing was transformed into a narrow line that was close to 0 ppm and a broad line that peaked near 320 ppm downfield from TMS. Since the narrow line was at the position of CH_4, and since its position and width were similar to those of condensed CH_4 at 77 K, which is narrowed by rapid internal motion, they concluded that CH_4 is one product of the annealing. The broad line at 320 ppm arose from a ^{13}C species that was immobile at 77 K, since it showed the typical broadening of about 400 ppm that arises from the platinum susceptibility and from the anisotropy of the ^{13}C chemical shift (in the next section, we discuss the effect of motion). By ^{13}C-^1H spin echo double resonance, P.-K. Wang, Ansermet, and our group (*43*) showed that over 85% of the ^{13}C in the broad line does not have hydrogen atoms attached. From the ^{13}C spin echo decay they showed that the nearest C–C distance must be more than 3 Å, and thus that the carbon atoms are not bonded to one another. Hence, the resonance arises from isolated carbon atoms. They showed that the carbon atoms are bonded to the metal by demonstrating the "conduction electron signature" in the temperature dependence of the ^{13}C spin-lattice relaxation ($1/T_1 \propto \theta$) (Fig. 7) for temperatures from 300 to 450 K. Above 450 K the T_1 shortens because of diffusion of the carbon atoms on the surface, as we discuss below.

Motion on the Surface

Diffusion of atoms or molecules on metal surfaces is revealed in several independent ways with NMR. Here we describe how the motion is seen through motional narrowing of the line width, and through its effect on the spin-lattice relaxation time.

Diffusion of carbon atoms on platinum. P.-K. Wang, Ansermet, and others (*43*) found that the NMR line of isolated carbon atoms on platinum has a width of about 400 ppm at 77 K. The width arises because the NMR frequency of an adsorbed nucleus depends on the orientation of the crystal face on which it is adsorbed relative to the applied field (through the chemical shift anisotropy) and also on its position on the particle surface through the particle magnetization arising from the platinum susceptibility. At higher temperatures, as the nuclei diffuse on the surface, their resonance frequency changes with position on the particle surface. When the motion becomes sufficiently rapid, the NMR line narrows. This phenomenon, well-known in magnetic resonance, is called "motional narrowing."

Figure 8 shows the logarithm of the line width of the ^{13}C atom NMR as a function of the inverse of the temperature. We see a strong narrowing occurring between room temperature and about 350 K from the low-temperature (rigid lattice) value of 400 ppm to a plateau at the higher temperature of 60 ppm. P.-K. Wang, Ansermet, and other members of our group (*43*) suggest that the plateau arises either because the particle is not a sufficiently symmetrical polyhedron or because the carbon atoms are excluded from the face of the polyhedron in contact with the alumina support. By analysis of the temperature dependence of the line width, they find an activation energy for diffusion of about 7 kcal/mol. As we see in the next section, this is about half that of a CO molecule on platinum (*26*). As the temperature is raised further, above 430 K, the line narrows from its plateau. This further narrowing implies that the carbon atoms can move from one metal cluster to another. We do not yet know the mechanism. Diffusion on the surface of the alumina or gaseous transport are two possibilities.

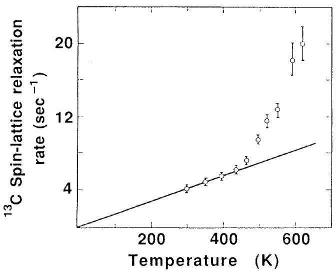

Fig. 7. Carbon atoms on platinum: ^{13}C spin-lattice relaxation rate ($1/T_1$) versus temperature, θ. The linear dependence on θ up to 450 K shows the atoms are attached to the metal. The rapid rise from $\theta > 450$ K is due to diffusion of the carbon atoms. [Reprinted from (*43*) with permission from the American Institute of Physics]

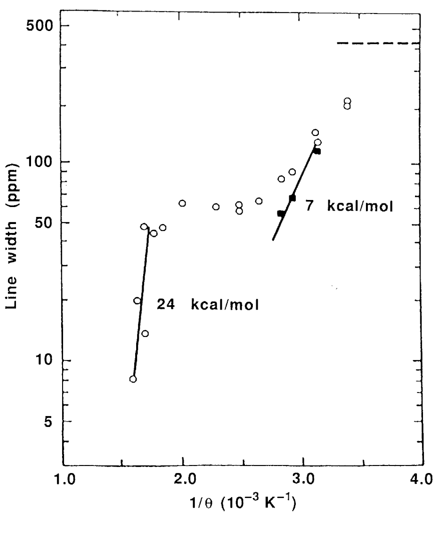

Fig. 8. Motion of carbon atoms as revealed by NMR line width: logarithm of the line width versus the inverse of the temperature ($1/\theta$) showing line narrowing as one warms from the lowest temperatures (activation energy, 7 kcal/mol), a plateau (at 60 ppm) for intermediate temperatures, and a further narrowing above about 560 K as the atoms go between different metal clusters. [Reprinted from (*43*) with permission from the American Institute of Physics]

Table 1. Gas kinetic (*1*) and NMR barrier energies. [From (*13*) with permission from *Annual Reviews*]

Element	Surface species undergoing C–C scission	Activation energy (kcal/mol)
	Gas kinetics	
Os	C_2H_2	35
Ir	C_2H_2	36
Pt	C_2	54
	NMR study of acetylene	
Os	CCH_2, HCCH	37
Ir	CCH_2, HCCH	37
Pt	C_2 and others*	53

*Includes other combinations, such as CCH.

A second manifestation of motion is its effect on T_1. Analysis of the rapid increase of $1/T_1$ for $\theta > 450$ K seen in Fig. 7 yields a diffusion energy of 7 kcal/mol in agreement with the value deduced from motional narrowing.

Diffusion of CO on platinum and other metals. We have used similar methods to study the diffusion of CO on the metals. Ansermet's (*27*) value of 13 kcal/mol for the barrier energy on platinum agrees reasonably with the 14 to 15 kcal/mol found by Lewis and Gomer (*45*) using field emission microscopy. For CO on palladium, Shore finds the barrier is only 6 kcal/mol (*25*).

Relating NMR Results to Catalysis

The results we have presented show that NMR can yield a variety of data important to understanding fundamental processes involved in surface chemistry. In this section, we show a close connection to studies of catalysis.

In his studies of the systematic kinetics of C_2H_6 hydrogenolysis, Sinfelt (*1*) investigated how the rate of production of CH_4 depended on the partial pressures of C_2H_6 and H_2 and on the temperature. He concluded that hydrogenolysis proceeded through a chemisorbed species C_2H_x, with $x = 2$ for osmium and iridium. However, he concluded $x = 0$ for platinum. The rate-limiting step in producing CH_4 was the breaking of the C–C bond of the species C_2H_x. By studying the temperature dependence of the reaction rate, he deduced a barrier height for breaking the C–C bond. His results for osmium, iridium, and platinum are summarized in Table 1.

The NMR results for C_2H_2 give direct support for these ideas. The pertinent data are also summarized in Table 1. Sinfelt's results are equivalent to saying that C_2H_6 rapidly becomes C_2H_2 on osmium and iridium, and goes past C_2H_2 to C_2 on platinum. We therefore review our NMR results for C_2H_2. The NMR data give an activation energy of 37 kcal/mol for the breaking of the C–C bond on osmium and iridium, close to the values found by Sinfelt (35 kcal/mol for osmium, 36 kcal/mol for iridium). As we remarked earlier, for C_2H_2 on osmium or iridium, the NMR data show that the C–H bonds remain intact until the C–C bond breaks. On the other hand, NMR shows that C_2H_2 on platinum begins to lose hydrogen atoms at temperatures for which the C–C bonds are largely intact. For platinum, we find a barrier energy of 53 kcal/mol by NMR, close to the 54 kcal/mol deduced by Sinfelt from reaction rates. It is evident that the two techniques are ways of analyzing the same process, and that NMR is verifying the details deduced more indirectly by Sinfelt.

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Interpreting Interpersonal Behavior: The Effects of Expectancies

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Attempts to understand the personal characteristics of others, in interactions with them, are complicated by the fact that one tends to find what one expects. This happens not only because processing of information is selective, but also because expectancies cause one to act in ways that elicit behavior interpretable as confirming those expectancies, even when the expectancies might have been mistaken. Studies provide ample evidence of such self-fulfilling prophecies in social interaction and are beginning to spell out the crucial steps in the process for confirming expectancies. Such studies help link the psychology of first impressions to the psychology of long-term relationships by showing how expectancies are sustained or modified through behavioral sequences that are partially determined by initial expectancies.

THE PROCESS OF PERCEIVING OR UNDERSTANDING ANOTHER person in the course of interacting with that person is the subject of this article. How do we come to know the motives and traits of those around us—those who compose our social world and who mediate our fate in that world? We rarely if ever confront others without some expectations about how they should behave. How are these expectancies integrated with new behavioral information to create our evolving impression about what kind of person the other is? We are not passive observers of our respective social worlds, but active forces in the shaping of those worlds. To an important extent we create our own social reality by influencing the behavior we observe in others. To the extent that we fail to take account of our participation in this creation process, we inevitably misread the significance of the behavior we see and erroneously attribute personal dispositions to others to account for actions that can be otherwise explained.

In 1968, Rosenthal and Jacobson (*1*) reported an experiment in which teachers were led to expect that certain of their first to sixth grade students would "bloom" academically. Although the designated students were randomly chosen, subsequent testing revealed that in fact they did better than the students who were not designated in that way. Though this study aroused considerable controversy and was criticized on a variety of methodological grounds, subsequent research has generally supported the conclusions drawn. The Rosenthal and Jacobson findings were important not merely in showing

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