11 June 1982, Volume 216, Number 4551 **SCIENCE**

Nuclear Magnetic Resonance at High Pressure

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Our understanding of the liquid state has lagged far behind our basic knowledge of the solid and gas states. While there exists an ideal crystal lattice model for solids and an ideal gas model for gases, no such simple ideal model is available for liquids. This lag is due to the inherent complexity of liquids (*1*): they have neither the rigid geometric structure of solids nor the complete randomness of gases. In recent years, there has been significant progress toward a better understanding of the liquid state based on both theoretical and experimental work. In particular, studies in which pressure has been used as an experimental variable have contributed in a major way to the recent advances in our knowledge of liquids.

Summary. Nuclear magnetic resonance relaxation measurements at high pressure provide unique information about the microscopic behavior of liquids. This article presents the principles of this technique; illustrates its usefulness by several specific examples of studies of molecular liquids, water, and supercritical dense fluids; and indicates the promising future of high-resolution nuclear magnetic resonance spectroscopy at high pressure with examples of studies of chemical exchange and homogeneous catalytic processes.

During the past two decades the field of research at high pressure (*2*) has undergone rapid growth and significantly affected diverse areas of chemistry and physics. Aided by new developments in instrumentation, relaxation measurements have become an indispensable tool in studying motions and interactions at the atomic and molecular level. In view of my own expertise, I focus here on the recent progress in nuclear magnetic resonance (NMR) relaxation techniques to investigate molecular motions and interactions in liquids at high pressures. The vast majority of NMR studies have used temperature as the only experimental variable, with pressure left constant, usually at the atmospheric value. The first NMR study at high pressure was carried out by Benedek and Purcell (*3*); the early, very limited, work has been reviewed by Benedek (*4*) and the more recent activity has been discussed by Jonas (*5*).

Considering the fact that NMR spectroscopy at ambient conditions has been applied to a wide spectrum of problems in chemistry and physics, it is not surprising to find that high-pressure NMR techniques have also had many applications. In this article, I shall discuss the results of several specific NMR relaxation measurements on liquids at high pressures to illustrate the range of problems that can be studied by this approach. Since liquids are relatively compressible, the maximum pressure usually used is 10 kilobars (*6*); such pressures only change intermolecular distances. In contrast, to change the molecular electronic structure of a specific material (*7*), pressures in excess of 30 kbar have to be used.

Information Content of NMR Relaxation Measurements

It is well known that an NMR signal from magnetic nuclei in liquids can provide detailed information about the nature and the rate of molecular motions. During the NMR relaxation experiment, after the spin magnetization is changed from its equilibrium value by a specific radio-frequency pulse, one determines the time constant of its return to equilibrium. This time constant, the spin-lattice relaxation time, T_1, is the time needed to reach thermal equilibrium between the spins and the lattice (*8*). The lattice is the collection of atoms of molecules that constitute the sample. Depending on the specific nucleus and the specific liquid system, nuclei can relax by different mechanisms.

The dipolar, quadrupolar, and spin-rotation interaction mechanisms represent the main relaxation modes observed in studies of the dynamics of liquids. The relaxation process occurs through fluctuating magnetic and electric fields (for quadrupolar nuclei). Since these fluctuating fields have their origin in motions of the molecules in the liquid, the measured relaxation times provide information about molecular motions. Using well-known theoretical expressions, one can analyze the experimental spin-lattice relaxation times and determine the correlation times for the appropriate motion. Physically, a correlation time represents the average time the molecule needs to lose memory of its initial position, orientation, or angular momentum. The information content of the NMR relaxation experiments is very high. For example, by measuring the relaxation of nuclei at different parts of a molecule, one can learn how fast the molecule rotates about its different axes.

In addition, one can learn from the NMR experiments about diffusion—a

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0036-8075/82/0611-1179$01.00/0

fundamental transport property of a liquid. The NMR spin-echo method (*8*) is a reliable technique for measuring the self-diffusion coefficients in liquids and is particularly adaptable for experiments on liquids at high pressures.

Reason for Measurements at High Pressures

The use of pressure as an experimental variable in an NMR relaxation experiment leads to some added complexity in instrumentation; however, the information to be gained from this technique fully justifies its use. There are several fundamental reasons for performing experiments on liquids at high pressures.

In most NMR studies of liquids only the temperature has been varied in spite of the fact that the use of pressure provides another dimension over which to investigate the liquid system. It is important to realize that changing temperature at constant pressure affects molecular motions in two distinct ways: not only is the average kinetic energy of the molecule changed, but there is always an accompanying change in the average volume available for the motion of the molecule. Only by using both pressure and temperature as variables in an NMR experiment can one separate the effects of density and temperature on molecular motions. Due to the close packing of molecules in a liquid, even a small change in density can produce a considerable change in the molecular dynamics of the system; therefore, in order to test rigorously a theoretical model of a liquid, or a model of a specific dynamic process in a liquid, one must perform isochoric, isothermal, and isobaric experiments. As an illustration of the importance of separating the effects of density and temperature on molecular motions, Fig. 1 shows the temperature dependence of the self-diffusion coefficient, D, in liquid tetramethylsilane (TMS) at constant density and at constant pressure (*5*). The dramatic difference in the temperature dependence of D at constant pressure or at constant density is readily apparent.

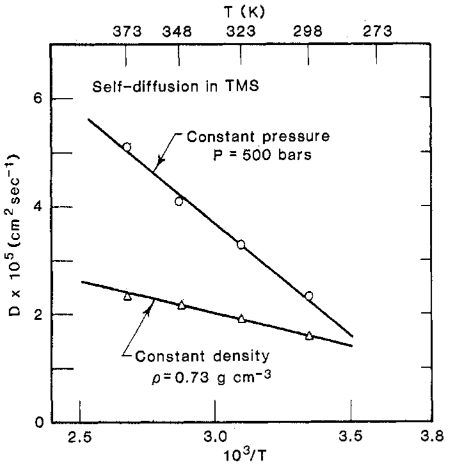
In addition, the use of pressure enables one to extend the measurement range on liquids well above the normal boiling point and allows the study of supercritical dense fluids. As an example, Fig. 2 shows the NMR proton T_1 in water (*9*) measured both in the low-temperature ($T < 30°C$) anomalous region and in the high-temperature ($T > 400°C$) supercritical region. The temperature and density dependence of the proton T_1 as shown in Fig. 2 is typical for the case where two relaxation mechanisms with opposite temperature and density dependence contribute to the observed T_1. At lower temperatures ($T \leq 150°C$) the dipolar mechanism makes the major contribution to proton relaxation, whereas at supercritical temperatures the spin-rotation interaction is the dominant relaxation mechanism.

Yet another reason for the use of high pressure is related to a relatively specialized application. For example, one can take advantage of the specific form of the phase diagram of water and heavy water and perform the relaxation measurements at temperatures below 0°C. At high pressure, even at $-15°C$, water is still a liquid (*10*). In Fig. 3 the shaded area indicates the range of measurements that were possible only when pressure was used as an experimental variable.

Dynamic Structure of Liquids

Recent evidence indicates that many physical properties of liquids may be determined, to a large extent, by the size and shape of the constituent atoms or molecules. In particular, molecular dynamics studies by Alder *et al.* (*11*) have elucidated many aspects of the static and dynamic behavior of hard sphere fluids. This picture of fluids is based on the idea that when the liquid density is high (approximately twice the critical density), the molecules are so closely packed that the forces between particles arise almost exclusively from the harsh short-range repulsive forces between nearest neighbors. The slowly varying attractive forces can be neglected.

On the basis of a successful prediction of the static properties of liquids, we though it worthwhile to find the extent to which their dynamic properties can be explained in terms of hard sphere models. A major problem in this type of analysis, however, is determining which hard sphere system (that is, which hard sphere diameter) to associate with a particular liquid. Fortunately, this hard sphere diameter can be determined from the density dependence of the self-diffusion coefficient under isothermal conditions. The purpose of our systematic studies of diffusion in simple polyatomic molecular liquids such as $Si(CH_3)_4$,



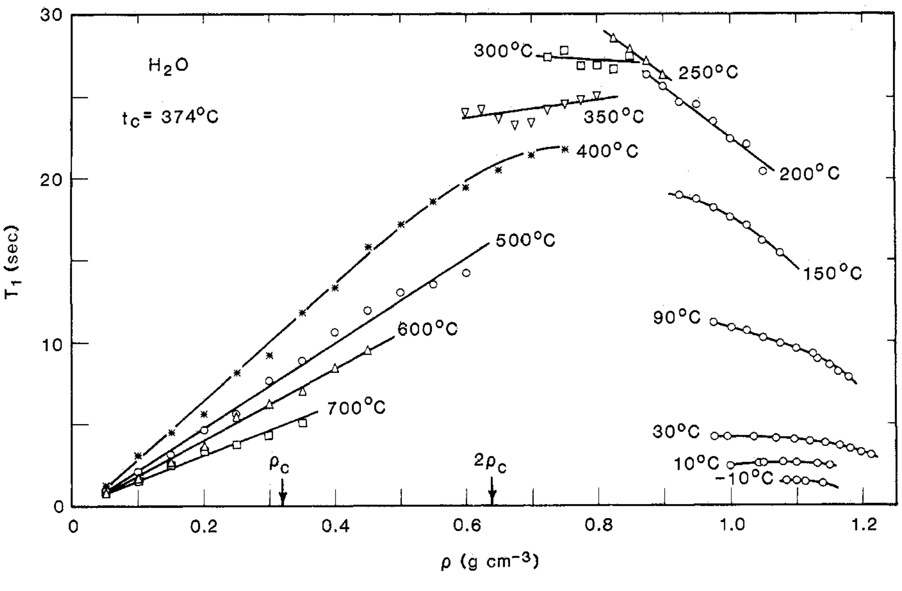


Fig. 1 (left). Temperature dependence of self-diffusion in liquid tetramethylsilane at (○) constant pressure and (△) constant density. Fig. 2 (right). Proton spin-lattice relaxation time, T_1, in water as a function of density over the temperature range $-10°$ to 700°C (*9*).

C_6H_6, SF_6, C_4F_8, and C_6H_{12} was to determine the hard sphere diameter, and then compare the experimental diffusion coefficients to those predicted theoretically with the rough hard sphere (RHS) model of liquids. The RHS model (*12*) takes into account the coupling between the rotational and translational motions of molecules, reflecting the fact that real molecules cannot be represented as smooth hard spheres. From the analysis of the experimental data in terms of the RHS model, we also determined the coupling between the rotational and translational motions of the molecules. We showed that the more pronounced the nonspherical shape of the molecules, the larger the coupling between rotational and translational motions. Our experiments established the limits of applicability of the RHS model (*12*) and showed that for simple molecular liquids composed of molecules approaching a spherical shape this model describes their diffusion behavior well (*13*).

Since our experiments (*5*) provided self-diffusion coefficients and shear viscosities of various liquids over a wide range of temperatures and densities, it was possible to test the validity of the hydrodynamic Stokes-Einstein equation on a molecular scale. This equation states that the product of the diffusion coefficient and the viscosity is a constant related to the diameter of the spherical particle moving through a fluid. Over a wide range of volumes and temperatures, the Stokes-Einstein equation is remarkably accurate.

In contrast to simple molecular liquids, the behavior of water is quite complex (*14*) and it is not surprising that the hard sphere picture is not applicable to this important liquid. During our studies (*5*) of density effects on the dynamic structure of liquids, we observed that the most interesting behavior of various transport and relaxation properties for water and heavy water occurs at temperatures between −15° and 40°C. In normal fluids, compression and increased packing significantly slow down all motions; in water, on the other hand, the T_1, self-diffusion coefficients, and fluidity go through a maximum with initial compression, and only with further increases in pressure is motional freedom restricted. It is interesting to note that even the average residence time of a proton on a water molecule shows this anomalous behavior with compression at temperatures below 40°C (*15*).

The general effect of pressure and temperature on the dynamic properties of water is illustrated in Fig. 4, which shows the effect of pressure on self-diffusion in liquid heavy water in the temperature range −15° to 200°C. Analogous plots can be drawn for any dynamic property of D_2O or H_2O.

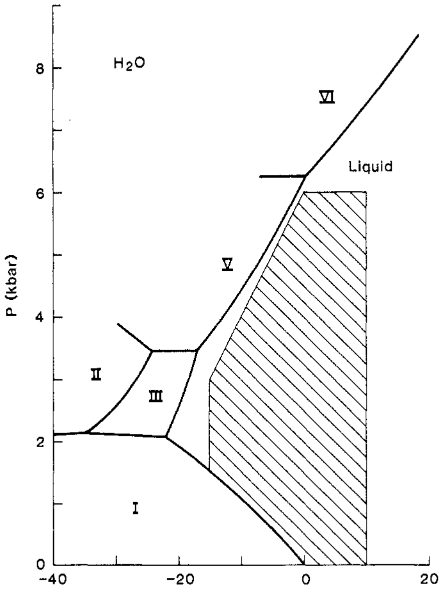


Fig. 3. Phase diagram for water. Roman numerals denote various ice modifications and the shaded area indicates the experimental range covered (*10*).

The anomalous motional behavior of water molecules with initial compression can be qualitatively interpreted in terms of a simple physical picture (*16*) based on changes in the random hydrogen-bond network. The characteristic structural feature of liquid water is the local tetrahedral environment of each molecule, beyond which there is a randomized imperfect space-filling network of hydrogen-bonded molecules. By compressing liquid water in the selected low-temperature range, we affect the hydrogen-bond network and gradually go from optimal tetrahedral order toward a more compact packing arrangement. There is a competition in water between the tendency of strongly directional forces to build an open, hydrogen-bond network and the tendency for external pressure to pack the molecules together more efficiently. Since the process for self-diffusion, shear viscosity, and reorientation of the water molecules necessitates the breaking and reforming of hydrogen bonds, one can expect that it will be easier to break an already bent hydrogen bond than an undistorted one. Initial compression, therefore, increases motional freedom, and only further compression slows down all the dynamic processes because of a more compact packing of the water molecules. Under high compression the repulsive hard core interactions begin to compete strongly with the directional forces that are responsible for the open structure of water at low pressures and low temperatures.

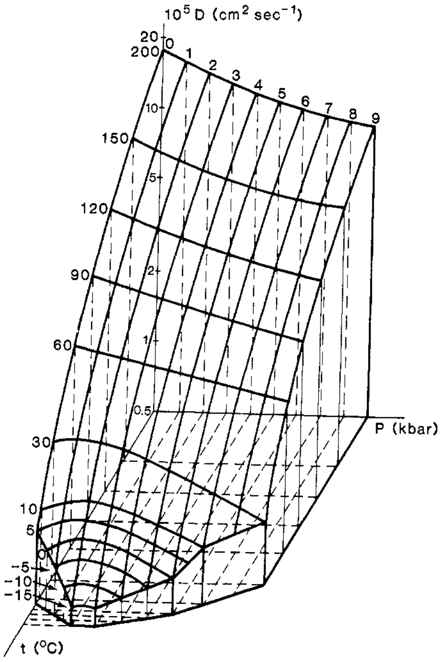


Fig. 4. Self-diffusion relief map as a function of temperature and pressure in liquid D_2O (*5*).

Supercritical Dense Fluids

Supercritical dense fluids are gases compressed to densities comparable to typical liquid densities. These fluids are of interest because their properties are quite unusual and they are becoming increasingly important in various chemical separation processes (*2*).

The NMR relaxation measurements of nuclei relaxed by the spin-rotation interaction mechanism provide unique information about the behavior of the angular velocity of molecules in a liquid. Since the angular momentum correlation time, τ_J, is directly related to the collision frequency in liquids, the measurement of τ_J by NMR is of great interest. In order to obtain valid results, one has to select systems and experimental conditions under which the spin-rotation mechanism dominates over other relaxation mechanisms; otherwise, separation of the contributions due to different relaxation mechanisms is quite difficult and very often leads to ambiguous results. Fortunately, the spin-rotation relaxation mechanism becomes stronger with increasing temperature while the contribution of other relaxation mechanisms diminishes. Thus τ_J studies are uniquely suited for NMR investigations of the dynamic behavior of supercritical dense fluids.

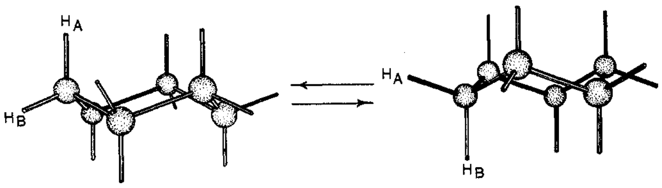


Fig. 5. Schematic diagram for conformational isomerization of cyclohexane.

On the basis of our experiments on simple polyatomic molecular fluids outlined in the preceding section, we concluded that the RHS model (*12*) describes well the behavior of angular velocity in liquids for densities larger than twice the critical density ($\rho > 2\rho_c$). The fact that we worked at supercritical temperatures and could easily extend the measurements to low densities allowed us to test the theoretical assumption that the RHS model (*12*) is valid only for $\rho > 2\rho_c$. For CF_4 and binary mixtures of CF_4 and Ar and Ne, we measured (*5*) the fluorine NMR relaxation times over a density range extending from the dilute gas region to the dense fluid for which $\rho > 2\rho_c$. We found a breakdown of the RHS model at lower densities, which may be attributed to the increased importance of the intermolecular attractive forces. At higher densities, the long-range attractive forces are negligible because of the "screening" of the slowly varying attractive potential by the short-range, quickly varying repulsive forces. At lower densities this screening is less effective and the attractive forces can no longer be neglected.

In view of the anomalous properties of water at low temperatures, it is not surprising to find that supercritical dense water (compressed supercritical steam) has a number of truly remarkable properties. Franck (*17*) found that supercritical dense water exhibits complete miscibility with nonpolar liquids, dissociates electrolytes into ions of high mobility, and dissolves complex compounds of heavy metals.

Our measurements of the self-diffusion coefficient in compressed supercritical water (*18*) compared well to theoretical predictions based on a dilute polar gas model, with a Stockmayer potential for the evaluation of collision integrals and a temperature-dependent hard sphere diameter. The product of density and D was of independent density under isothermal conditions, which indicated that two-body collisions dominate the diffusion behavior. This finding was in agreement with our results on proton relaxation (*9*) in compressed supercritical water, which were also analyzed by assuming that two-body collisions govern the spin-rotation interaction mechanism. This relatively simple behavior is in agreement with the conclusion reached in our experiments at low temperatures, that water begins to behave more like a "normal" fluid with high compression at high temperatures.

Applications of Multinuclear High-Resolution NMR at High Pressures

The large majority of NMR applications in chemistry deal with liquids in which the NMR lines are narrowed by motional averaging to a natural line width of the order of 0.1 to 1 hertz. High-resolution NMR spectra of complex molecules in the liquid phase usually exhibit a great deal of structure and yield a wealth of information about the molecule. I include a discussion of some of the applications of multinuclear high-resolution Fourier transform (FT) NMR spectroscopy at high pressure because this recently developed technique shows great promise in the study of chemical exchange and of homogeneous catalytic processes.

Inorganic systems are currently the main subjects of NMR studies on the effects of pressure on chemical exchange processes. Mehrbach and co-workers (*19*) have concentrated on the elucidation of the mechanism of solvent exchange on metal ions and ligand exchange on transition metal coordination compounds. In addition to many proton NMR studies, Mehrbach and co-workers (*20*) used ^{17}O NMR to investigate water exchange on divalent and trivalent metal ions.

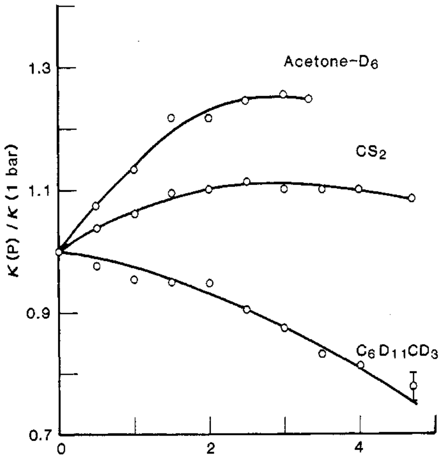


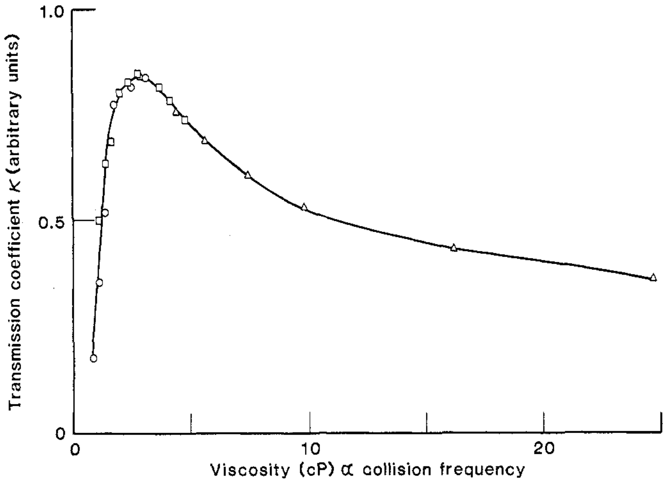
Fig. 6. Reduced transmission coefficient κ as a function of pressure and solvent for conformational isomerization of cyclohexane at 225 K.

In our laboratory we employed newly developed instrumentation to investigate the conformational isomerization of cyclohexane (*21*) (see Fig. 5) in several solvents under high pressure, with the goal of testing the stochastic models of isomerization reactions. These models (*22*) propose that there are dynamic effects on isomerization because the reaction coordinate is coupled to the surrounding medium. This leads to the dependence of the transmission coefficient κ on the "collision frequency," α, which in the absence of electrostatic effects reflects the actual coupling of the reaction coordinate to the surrounding medium. In classical transition state theory (TST) (*23*) κ is assumed to be unity and independent of thermodynamic state. The stochastic models introduce κ in

$$k(\Delta t) = \kappa k_{\mathrm{TST}} \qquad (1)$$

where $k(\Delta t)$ is the observed isomerization rate and k_{TST} represents the rate as defined in the classical TST. The stochastic theory (*22*) predicts that with weak coupling (the inertial regime) an increase in pressure will lead to an increase in the isomerization rate, whereas with strong coupling (the diffusive regime) the increase in pressure will decrease the isomerization rate. Between the inertial and diffusive regimes there is a nonmonotonic transition.

Since cyclohexane has no dipole moment the coupling to the surrounding medium is given by the collision frequency, which is proportional to the shear viscosity, η, of the solvents. This was our rationale for selecting the three solvents used in our study (*21*)—η(acetone-d_6) < η(carbon disulfide) < η(methylcyclohexane-d_{14})—which enabled us to cover the different regions of the κ-α dependence in measurements of the pressure dependence of the isomerization rate of cyclohexane. A good representation of our results is shown in Fig. 6, which gives the normalized transmission coefficient $\kappa(P)/\kappa(1\ \mathrm{bar})$ as a function of pressure, P, for the three solvents studied. In the acetone and CS_2 solvents cyclohexane is in the low coupling region, whereas in deuterated methylcyclohexane (high viscosity) the strong coupling region is reached where κ decreases with increasing pressure. A direct correlation of κ with viscosity, as shown in Fig. 7, also demonstrates the



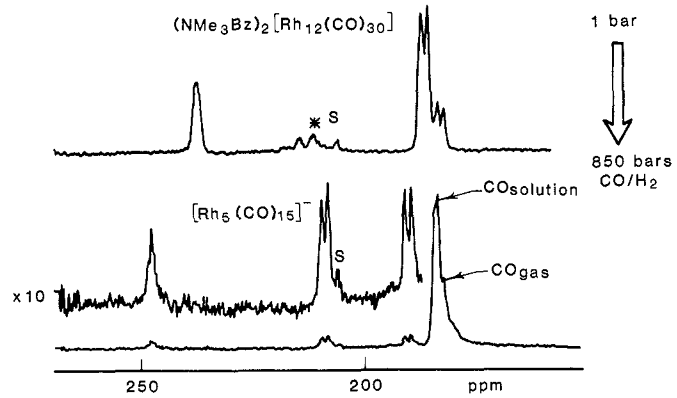


Fig. 7 (left). Relation between transmission coefficient κ and viscosity η (η proportional to collision frequency) for conformational inversion of cyclohexane at 225 K. Solvents: (○) acetone-d_6; (□) carbon disulfide; and (△) methylcyclohexane-d_{14}. Fig. 8 (right). Carbon-13 NMR spectra at 45.2 MHz in a high-pressure probe: $(NMe_3C_6H_4CH_2)_2Rh_{12}(CO)_{30}$ at −40°C in $(CD_3)_2CO$ and after pressurization (850 bars) with CO and H_2 (2.1:1; 13.7 percent ^{13}CO) at −32.8°C. The letter *S* denotes solvent and the asterisk denotes impurity $[Rh_6(CO)_{15}]^{2-}$.

nonmonotonic dependence of κ on the reduced collision frequency. Our results represented experimental proof of the theoretical predictions of stochastic models by showing a nonmonotonic transition between the inertial and diffusive regimes of isomerization reactions.

The use of high-resolution multinuclear FT NMR spectroscopy at high pressures to study homogeneous catalytic processes, under conditions of pressure and temperature actually used during an industrial process, is another example of the applications of this novel technique. Because of the ready availability of CO and H_2 from coal, we witness an increased research effort in the area of catalytic synthesis based on CO and H_2. For example, there is evidence that transition metal carbonyl cluster compounds are involved in the homogeneous catalytic synthesis of ethylene glycol (*24*). However, these catalytic reactions require reasonably high pressures and temperatures and, so far, have been monitored only by infrared spectroscopy. Although useful information was obtained in this way, it was generally not possible to obtain unambiguous structural identification and exchange information, which are of importance in establishing reactivity patterns of intermediates that are present under these conditions. The NMR technique can provide this type of information, which is essential for understanding the mechanism of these catalytic processes.

Because of the involvement of the $[Rh_{12}(CO)_{30}]^{2-}$ cluster in the catalytic synthesis of ethylene glycol from synthesis gas, it was of interest to examine this reaction by high-resolution ^{13}C NMR spectroscopy at a high pressure of CO and in the presence of H_2. In a collaborative effort with Heaton (*25*) we recently measured the ^{13}C spectra of rhodium carbonyl clusters under a high pressure of CO and H_2. The main result of our experiments is presented in Fig. 8, which shows schematically the formation of the pentanuclear cluster under these conditions. Pressurization of solutions of $[Rh_{12}(CO)_{30}]^{2-}$ with CO showed that $[Rh_5(CO)_{15}]^-$ is formed quantitatively and that below 298 K further fragmentation does not occur on pressurization up to 1 kbar with CO and H_2. Variable-temperature measurements on $[Rh_5(CO)_{15}]^-$ showed that the rate of inter-exchange of carbonyls with CO at high pressure is slow on the NMR time scale and that at room temperature all the carbonyls, except the three bridging the Rh_3 equatorial plane, undergo intraexchange. Thus, high-pressure, high-resolution NMR studies make it possible to investigate the mechanism of many homogeneous catalytic processes of industrial interest.

Technological Relevance

Aside from the basic research value of NMR measurements at high pressure, the technological relevance of such work is evident in the application of high-resolution FT NMR at high pressure to the study of homogeneous catalytic processes. Several other aspects of our NMR work bear directly on specific problems in applied fields. For example, a detailed understanding, at the molecular level, of the dynamic processes and intermolecular interactions in supercritical dense fluids will aid in the development of new, highly selective extraction and separation procedures with supercritical fluids (*2*) as the solvent medium. The work on supercritical compressed steam is relevant to energy-related problems, and the extension of these studies to more complex systems, such as H_2O-CO_2-electrolytes, should be of great interest to geochemists and geophysicists.

In a general sense, a better understanding of the liquid state of matter will have a far-reaching impact on technology. Since most engineering materials are in liquid form at some stage of their fabrication or production, more information about this intermediate state may lead to the development of better engineering materials. Experiments at very high pressures and temperatures should provide valuable new information on the behavior of materials under extreme conditions. The increasing demands of modern technology for materials that perform better under extreme operating conditions are well recognized. One could list a number of additional technological areas which will benefit from the results obtained by the NMR studies of liquids at high pressure. For example, new information on liquids at the atomic and molecular level will help workers in the applied field of lubrication.

Concluding Remarks

Several of these examples of NMR relaxation studies at high pressure demonstrate that only by using pressure as an experimental variable can one obtain detailed information about molecular motions and interactions in liquids. Only by performing isobaric, isochoric, and isothermal experiments can one obtain valid data for rigorously testing current theoretical models of liquids or for establishing a firm experimental basis for the development of new theoretical models. This general conclusion is equally valid for other experimental techniques, such as neutron scattering, x-ray diffraction, and light scattering, which are used to investigate the dynamic structure of liquids. We have demonstrated the value of high-pressure experiments through laser Raman scattering studies of liquids (*26*).

Judging from the history of high-resolution NMR (*27*), which in the past 30 years has become an indispensable tool in diverse areas of chemistry, one can foresee increased activity in the field of high-resolution FT NMR at high pressure. Commercial availability of the equipment for NMR measurements at high pressure will be critical for the rapid development of this field. Although only a few high-resolution NMR–high-pressure experiments on systems of biochemical interest have been reported so far (*28*), rapid growth of this specific area would be expected in view of the increasing use of NMR in solving biochemical problems. Finally, because many disordered systems, including some polymers, are readily compressible, new applications of high-pressure NMR should emerge in this research direction as well.

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29. This article is based on work supported by the National Science Foundation under grant NSF CHE 79-12-801142,0, by the Air Force Office of Scientific Research under grant US AFOSR 81-0010, and by the Department of Energy under contract DE-AC02-76ER01198. I would like to express my thanks to A. Jonas and H. G. Drickamer for helpful criticism.