^{95}Mo T_1 Measurements of $Mo(CO)_6$ Encapsulated in Na–Y Zeolite

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On the basis of ^{95}Mo T_1 measurements made on samples of $Mo(CO)_6$ encapsulated in dried Na–Y zeolite over the temperature range 223–323 K, it is confirmed that $Mo(CO)_6$ experiences significant rotational freedom in the 13-Å zeolite supercages. In addition, it is found that the activation energy for rotation is about 40 ± 4 kJ mol^{-1}, and the ambient temperature rotational correlation time, τ_c, is approximately 3 orders of magnitude longer than is τ_c in solution.

There has been considerable interest in recent years in the species formed on the sorption of metal carbonyl complexes on oxide surfaces such as silica, alumina, and zeolites.[1] Techniques utilized to date to investigate these interesting systems include infrared, Raman, ESR, and NMR spectroscopy, temperature programmed decomposition (TPD), analysis of gaseous products, EXAFS and X-ray structure determinations, adsorption studies, and elemental analyses. A wealth of information exists concerning the nature both of the initially formed, physisorbed molecular carbonyl species and of a variety of chemisorbed subcarbonyl and fully decarbonylated species formed on the thermal decarbonylation of the physisorbed compounds.[1]

Of considerable importance in this context are the species formed on encapsulation of molybdenum hexacarbonyl, $Mo(CO)_6$, in the supercages of faujasitic zeolites, both because of the very interesting butadiene hydrogenation catalysts which result[2a] and because of the possibility of synthesizing new and interesting materials on encapsulating this and similar compounds in zeolite cavities.[2b] In addition, recent work has shown that the 13-Å-diameter supercage lattices of Y-type zeolites can activate $Mo(CO)_6$ to very novel CO substitution reactions.[2c]

It is well established, on the basis of a number of IR, TPD, and ^{23}Na NMR investigations,[4] that sorption of $Mo(CO)_6$ into, for instance, the supercages of Na–Y zeolite at ambient temperatures results in retention of the structural integrity of the $Mo(CO)_6$. The latter binds loosely to the sodium ions in the zeolite supercages of Na–Y via either electrostatic interactions or a Lewis acid–Lewis base type of interaction, species of the types $\{(OC)_5MoCO\cdots Na^+\}$ and $\{(OC)_4Mo(CO)_2\cdots(Na^+)_2\}$ having been postulated.[2c,4c,e,f] Heating above ~350 K results in thermal decomposition and stepwise decarbonylation,[4a–c] but a detailed consensus on the IR spectra of the initially encapsulated compound and on both the IR spectra and the stoichiometries of the products of thermal decomposition seems to be lacking at present,[4] perhaps because of subtle differences in the modes of preparations of the zeolites used in different studies.

Although a coordinative interaction between a sodium ion and a carbonyl lone pair would presumably be weak, there has been presented as yet surprisingly little information concerning either the strength of the presumed $(OC)_5MoCO\cdots Na^+$ interactions or of the mobility of the $Mo(CO)_6$ in the zeolite lattice. However, non-MAS ^{13}CO NMR spectra of $Mo(CO)_6$ sorbed onto alumina[5] and zeolite[6] surfaces often exhibit reasonably narrow CO ^{13}C resonances, implying that the sorbed $Mo(CO)_6$ molecules may tumble freely. Indeed, NMR spectroscopy has in recent years found numerous applications in the study of small molecules sorbed onto the surfaces of solids,[7] and it seemed likely that utilization of ^{13}C and ^{95}Mo relaxation time measurements in particular should be very informative concerning the dynamic motions of $Mo(CO)_6$ in a zeolite lattice. Detailed studies of ^{95}Mo T_1s of a variety organomolybdenum compounds in solution have been reported previously,[8] and we now present the results of a variable-temperature investigation of ^{95}Mo T_1s of $Mo(CO)_6$ in Na–Y zeolite.

Experimental Section

Sample of $Mo(CO)_6$ (Strem Chemicals) in Na–Y zeolite (Strem Chemicals: powdered form, dried at 500 °C in air) were prepared by drawing excess sublimed $Mo(CO)_6$ through a sample of the zeolite at 298 K with a dynamic vacuum. Sorption was monitored by periodically removing small amounts of the zeolite under nitrogen and obtaining IR

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spectra (Nujol mulls, Bruker IFS-85 FTIR spectrometer) in the CO stretching region. After about 10–12 h, the spectra had ceased changing, and the products were pumped on for a further 6–8 h at 298 K in order to remove any $Mo(CO)_6$ which might have been adhering to the zeolite surfaces. The resulting pale yellowish materials exhibited CO stretching bands at $\sim$2120 cm^{-1} (very weak) and $\sim$1987 cm^{-1} (very strong, broad), the IR spectra being very similar to those reported elsewhere for similar materials.[4]

NMR spectra were run on zeolite samples sealed in 10-mm NMR tubes under nitrogen. Prior to measurements of the T_1s, ^{95}Mo NMR spectra of the zeolite samples were run at 298 K on a Bruker AM-400 NMR spectrometer (9.395 T) at 26.06 MHz; typically 500–1000 transients were collected with a pulse width of 30° and a relaxation delay of 0.300 ms. The T_1 measurements were made over the temperature range 223–323 K, utilizing the conventional inversion–recovery (180°–t–90°–acquire) sequence and 11 values of t in the range 1 μs–1 s.[9a,b] Using Bruker software, time and intensity data were computer fitted to a three-parameter equation of the form $S_t = S_\infty[1 - B\exp(-t/T_1)]$ to give the best values of S_∞, B, and T_1.

Results and Discussion

Sorption of $Mo(CO)_6$ into dried Na–Y zeolite at ambient temperature resulted in a product similar in its appearance and IR spectra to similar materials reported elsewhere.[4] The sorption experiment was designed to result in saturation loading (two $Mo(CO)_6$ moieties per zeolite supercage[4a]) in order to maximize the signal to noise ratios of the NMR spectra. The ^{95}Mo NMR spectra of the samples used exhibited single resonances similar in chemical shift to that of $Mo(CO)_6$ in $CDCl_3$ solution,[8f] although the room temperature line widths of the sorbed materials were considerably greater, $\sim$150 Hz compared with 0.3 Hz.

The rate of quadrupolar relaxation of a ^{95}Mo nucleus in an isotropically tumbling molecule is described by the general equation (1).[9c] Here T_1 is the spin-lattice relaxation time, I = $^5/_2$, $e^2q_{zz}Q/h$ is the quadrupole coupling constant, η is the asymmetry parameter of q_{zz}, the electric field gradient, and τ_c is the rotational correlation time.

$$\text{rate of relaxation} = T_1^{-1} = \frac{3\pi^2}{50}\frac{(2I+3)}{I^2(2I-1)} \times \left(\frac{e^2q_{zz}Q}{h}\right)^2\left(1+\frac{\eta^2}{3}\right)\left(\frac{\tau_c}{1+\omega^2\tau_c^2}+\frac{4\tau_c}{1+4\omega^2\tau_c^2}\right) \quad (1)$$

When $\omega^2\tau_c^2 \ll 1$ (the extreme narrowing regime, as in low viscosity, liquid solutions), the correlation time term in brackets reduces to $5\tau_c$ and eq 1 reduces to eq 2.[8,9d] Under these condition, $T_1 = T_2$ and both are inversely proportional to τ_c.

$$T_1^{-1} = \frac{3\pi^2}{10}\frac{(2I+3)}{I^2(2I-1)}\left(\frac{e^2q_{zz}Q}{h}\right)\left(1+\frac{\eta^2}{3}\right)\tau_c \quad (2)$$

When $\omega^2\tau_c^2 \gg 1$ (the slow motion regime, as in many solids), the correlation time term reduces to $2/\omega^2\tau_c$, $T_1 > T_2$, and T_1 is proportional to $\omega^2\tau_c^1$. Thus, on passing from the slow motion to the extreme narrowing regime by increasing the temperature of a sample, T_1 can be expected to decrease, pass through a minimum, and then increase. The minimum in T_1 occurs when $\omega\tau_c = 0.62$.[9e]

Since I and Q are fixed, ^{95}Mo spin–lattice relaxation times in solution depend largely on the electric field gradient q_{zz} and the correlation time τ_c. In the case of $Mo(CO)_6$, an octahedral compound for which the electric field should be very small, it has been found that quadrupolar relaxation in both solution and the solid states is wholly a result of a small, static electric field gradient undergoing isotropic tumbling.[8a] If Na–Y-encapsulated $Mo(CO)_6$ behaves as in solution, sufficient averaged molecular rotational motion would occur that the rate of relaxation of the ^{95}Mo nucleus of $Mo(CO)_6$ would be dominated by the quadrupolar mechanism. Assuming both that the zeolite-encapsulated $Mo(CO)_6$ retains considerable rotational freedom and that the above-mentioned assumptions concerning the magnitude of the electric field gradient pertain, then measurements of the ^{95}Mo relaxation times of Na–Y-sorbed $Mo(CO)_6$ should give information concerning the rotational motion of this interesting molecule. Furthermore, ^{95}Mo T_1 data should be much less ambiguous than would the complementary ^{13}C data, which would be complicated by chemical shift anisotropy effects.[6c,9]

Table I. ^{95}Mo Relaxation Times and Line Widths of $Mo(CO)_6$ in Na–Y Zeolite

temp (K)	T_1 (ms)	$\Delta\nu_{1/2}$ (Hz)	$\Delta\nu_{1/2}$(nat) (Hz)	T_2 (ms)
223	1760	400	0.2	0.8
248	146	200	2	1.6
273	70	170	5	1.9
298	22	150	15	2.3
323	49	130	7	2.6

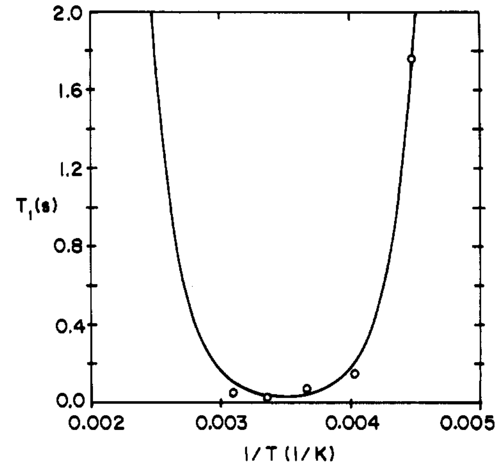

Figure 1. Plot of the experimental T_1 values. The solid curve indicates the best fit values of E_a and A calculated using eqs 1 and 3.

A series of T_1 measurements was made over 223–323 K, a temperature range limited by serious line broadening at the lower temperatures and the onset of thermal decomposition at higher temperatures.[4a–c] The results of these experiments are listed in Table I, along with estimates of T_2 based on the resonance line widths, $\Delta\nu_{1/2}$, corrected for "natural" line widths calculated from T_1. Errors in T_1 measurements and line width estimates are believed to be about 10%.

As can be seen, the T_1 values do not increase with increasing temperature, in accord with eq 2, but rather decrease significantly as the temperature increases from 223 to 298 K. Also inconsistent with eq 2, the T_1 values are in all cases significantly greater than the corresponding T_2 values, although several of the latter are of low accuracy because of errors in estimates of $\Delta\nu_{1/2}$ at the lower temperatures. Thus, although the T_1 values are comparable with those of many molybdenum complexes in solution, where the extreme narrowing regime described by eq 2 is believed to apply,[8] such is not the case for $Mo(CO)_6$ in Na–Y zeolite. Instead, it is clear that the slow motion regime has been encountered over the lower temperatures, at least, one in which the correlation time τ_c is comparable with or exceeds the Larmor frequency, ω.[9] The spin–lattice relaxation behavior is then better described by the general expression, eq 1.

That this interpretation is reasonable is shown in Figure 1, where the curved line shows the dependence of ln T_1 vs T^{-1}, calculated utilizing eq 1 and assuming that the correlation time

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obeys the Arrhenius equation:[9e]

$$\tau_c = A \exp(-E_a/RT) \quad (3)$$

A least-squares, nonlinear regression program was used to fit the experimental data, also shown, to eq 1, the parameters varied being the activation energy for reorientation, E_a, and the preexponential term, A. The "best fit" values of these parameters are $E_a = 40 \pm 4$ kJ mol^{-1} and $A = 2.2 \pm 0.1 \times 10^{-16}$ s, while the minimum in T_1 was found to occur at about 286 K.[10] Since $\omega = 0.16 \times 10^9$ rad s^{-1}, then $\tau_c \approx 4 \times 10^{-9}$ s, a value 3 orders of magnitude longer than that reported for $Mo(CO)_6$ in chloroform solution at a comparable temperature.[8a] Thus $Mo(CO)_6$ does exhibit rotational mobility in Na–Y zeolite, albeit considerably less than in solution, either because of the above-mentioned weak, attractive interactions with one or more carbonyl groups of the $Mo(CO)_6$ to the extraframework sodium ions or, perhaps, because of the relatively restricted environment of the rigid zeolite crystal lattice.

Primary evidence for the sorbed species has been provided by the observed CO stretching absorptions at about 2120 and 1960–1980 cm^{-1}, which have been respectively assigned[4] to the ν_1 (A_{1g}, at 2120.7 cm^{-1} for gaseous $Mo(CO)_6$:[11] IR inactive in O_h symmetry but allowed because weak interactions with the zeolite reduce the overall symmetry) and ν_6 (T_{1u}, at 2000.3 cm^{-1} for gaseous $Mo(CO)_6$[11]: IR active) normal modes of $Mo(CO)_6$. To date, however, few high-resolution IR studies of Na–Y zeolite-sorbed $Mo(CO)_6$ have been reported, and those that have do not agree in detail.[4b,e] The spectra are rather more complicated than anticipated, suggesting that $Mo(CO)_6$ may exist in more than one environment within the Na–Y crystal lattice and/or in a site of lower symmetry. Clear understanding of this and related systems must await more extensive low-temperature, high-resolution IR experiments, as well as variable-temperature and field ^{13}C and metal nuclei relaxation time measurements.

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