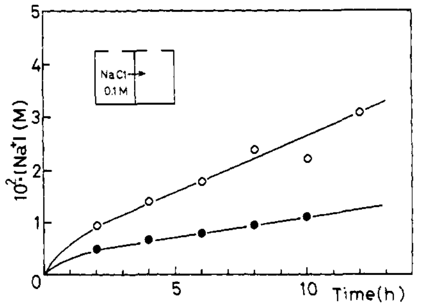

Figure 2. Changes in the concentration of Na^+ ion on the right side of the hydrolyzed membrane at 31.0 °C. Initial concentration of Na^+ ion on the left side, 0.1 M. (○) At pH 7; (●) at pH 3. A diaphragm cell that consisted of two detachable parts with the volume of 50 mL was used. Concentration of Na^+ ion transported was measured by atomic absorption photometry.

hydrolysis CD spectrum showed a positive curve centered at 226 nm, which represents that poly(β-benzyl L-aspartate) chains (branch) in the membrane take mainly left-handed α-helix, in a similar manner to homopolymer of β-benzyl L-aspartate in the solid state.[11]

When the hydrolyzed film[12] was fitted in a quartz cell (path length, 10 mm) filled with an aqueous solution of HCl (pH 3), CD spectrum still exhibited a positive curve centered at 222 nm, but of lower intensity than that of the film before hydrolysis. Relative maximum value of ellipticity at pH 3 of hydrolyzed film was 20% of that before hydrolysis. The positive peak at 222 nm indicates the formation of left-handed α-helix in contrast with the fact that poly(L-aspartic acid) forms right-handed α-helix in acidic aqueous solution like other polypeptides from L-amino acid.[13]

When the hydrolyzed film was immersed in an aqueous solution of NaOH (pH 9), a pronounced decrease in the intensity of the CD spectrum (from 20% to 3%, as the relative maximum value to that before hydrolysis) was observed, indicating the transformation from ordered to random coil form of the poly(amino acid) chain in the film. This behavior is fully reversible; upon lowering the pH (from 9 to 3) the same CD curve as the starting reappeared immediately.

A preliminary experiment of Na^+ ion transport across the hydrolyzed membrane[14] was carried out. As shown in Figure 2, Na^+ ion was found to permeate through the hydrolyzed membrane prepared from the graft copolymer. Transfer of water due to the osmotic pressure was also observed. On the other hand, Na^+ ion did not permeate through the membrane from the homopolymer of butyl methacrylate that was subjected to the same hydrolyzing condition. The graft copolymer that was not treated with the hydrolyzing solution was also impermeable for Na^+ ion. From these results, it is considered that continuous phases of poly(L-aspartic acid) domain are formed in the membrane and function as permeating pathways, or "transmembrane channels", for Na^+ ion. Under acidic condition (pH 3), the transport rate of Na^+ ion decreased significantly compared with that under neutral condition (pH 7), which is considered to be ascribed, at least partly, to the pH-induced conformational change of the poly(L-aspartic acid) domain.

Thus, the membrane from butyl methacrylate–L-aspartic acid graft copolymer may be regarded as a good model of biomembrane; the transmembrane polypeptide domain undergoes the pH-dependent reversible conformational change, with impermeable poly(butyl methacrylate) domain as the stable matrix.

Registry No. Poly(β-benzyl L-aspartate) (homopolymer), 25248-99-1; poly(β-benzyl L-aspartate) (SRU), 25736-41-8.

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(11) Kondo, Y.; Iizuka, E.; Oka, A.; Hayakawa, T. *Polymer* **1977**, *18*, 111.

(12) Hydrolysis was carried out by immersing the polymer-coated quartz plate into a water–methanol–2-propanol (1:2:2, by volume) mixed solvent containing 5 wt. % NaOH for 16 h.

(13) Brahms, J.; Spach, G. *Nature (London)* **1963**, *200*, 72.

(14) The graft copolymer used in the transport experiment was that having the degree of branching of 16 mol % and $\overline{DP}_n$ of the branch of 10, 0.12 g of which was blended with 0.15 g of homopolymer of butyl methacrylate (M_r 40000) in order to reinforce the membrane. The mixture (0.27 g) was dissolved in chloroform (10 mL) and was cast on a Teflon-brand plate (diameter, 5 cm). The membrane (ca. 0.2 mm thick) obtained by solvent evaporation was fixed vertically in the center of a diaphragm cell. Hydrolysis of the membrane was performed by filling the both sides of the cell with a NaOH solution[12] for 16 h.

Direct Evidence for Bridge–Terminal Carbonyl Exchange in Solid Dicobalt Octacarbonyl by Variable-Temperature Magic Angle Spinning ^{13}C NMR Spectroscopy

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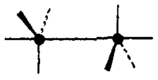
Structural problems in metal carbonyl chemistry have historically been difficult to solve. Perhaps the best documented example is the solid-state structure of $Fe_3(CO)_{12}$.[2-4] High-resolution solid-state ^{13}C NMR spectroscopy has contributed further to the understanding of this molecule by elucidating a fluxional process in the solid state.[5] In general, high-resolution NMR spectroscopy of solids has proven to be an important tool for characterizing solid-state dynamics.[6,7]

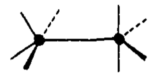
For dicobalt octacarbonyl, previous structural investigations have dealt mainly with the solution structure. In a series of elegant papers, several research groups demonstrated, by infrared[8-10] and Raman[11] spectroscopy, the presence of three isomers for $Co_2(CO)_8$ in solution and in frozen matrices, Ia–c. One of these, Ia, represents the molecular structure as determined by X-ray crystallography.[12] In solution, these isomers interconvert rapidly, resulting in the exchange of bridging and terminal carbonyl ligands.

Ia

Ib



Ic



Previously, one of us had reported the observation of a single resonance in the high-resolution ^{13}C NMR spectrum of solid $Co_2(CO)_8$ at room temperature.[13] The implied dynamic behavior,

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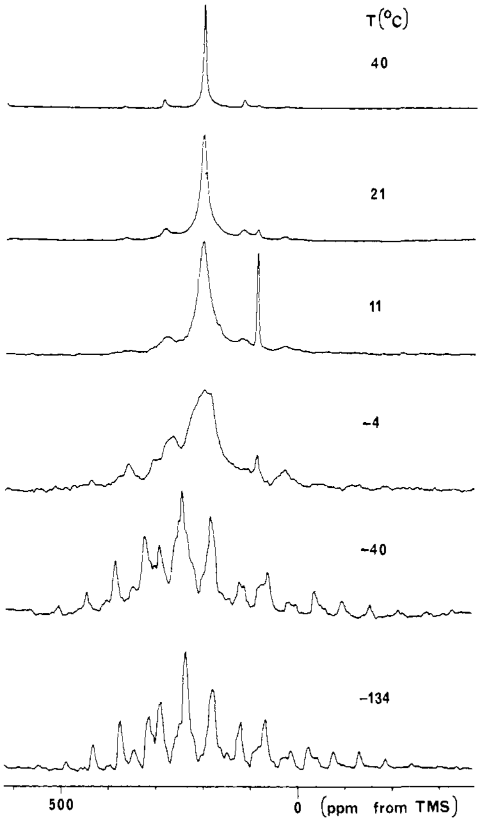

Figure 1. Magic angle spinning variable-temperature ^{13}C NMR spectra of $Co_2(CO)_8$. The ^{13}C frequency was 50 MHz. The spinning speeds varied from 3200 Hz at 40 °C to 2500 Hz at -134 °C. Proton irradiation was used only in the 11 °C spectrum to obtain a Delrin reference peak (89 ppm). Some residual Delrin signal is apparent in the high-temperature spectra even in the absence of proton decoupling. Each spectrum is the result of 64 scans with a 1-s pulse delay.

i.e., rapid bridge–terminal carbonyl exchange in the solid state, has now been confirmed by variable-temperature magic angle spinning ^{13}C NMR spectroscopy.[14] Figure 1 shows a set of spectra obtained for $Co_2(CO)_8$ as a function of temperature over the range -134 to 40 °C. Figure 2 compares the spectrum obtained at -41 °C using a simple $\pi/2$ carbon pulse sequence vs. the spectrum at the same temperature using the TOSS[15,16] (total suppression of sidebands) sequence.

At high temperature, the spectra consist of a single resonance, which generates an increasingly complex pattern as the temperature is lowered. In general, this is due to the fact that line narrowing caused by the internal averaging due to motion or site exchange occurs readily at high temperature. As the temperature is reduced, the rate of these processes is slowed and the resultant line broadening occurs. When the temperature is reduced further, the spectra are split into spinning sideband patterns in which the center peaks are surrounded by a series of sidebands spaced at intervals equal to the spinning speed in hertz. Each line in the low-temperature spectra reveals the homogeneous (i.e., T2*) line width, while the width of the sideband pattern is representative of the inhomogeneous interactions (CSA and dipolar coupling) that are averaged by spinning. The large intensity of the sidebands relative to the center bands indicates that the spin rate used was much less than the static (inhomogeneous) line width.[17] At least two progressions of spinning sidebands (corresponding to bridging and terminal carbonyls) are responsible for the complex pattern observed at -134 °C. Additional structure in the spectrum may be due to the fact that all of the bridging carbonyls are not equivalent and all of the terminal carbonyls are not equivalent.

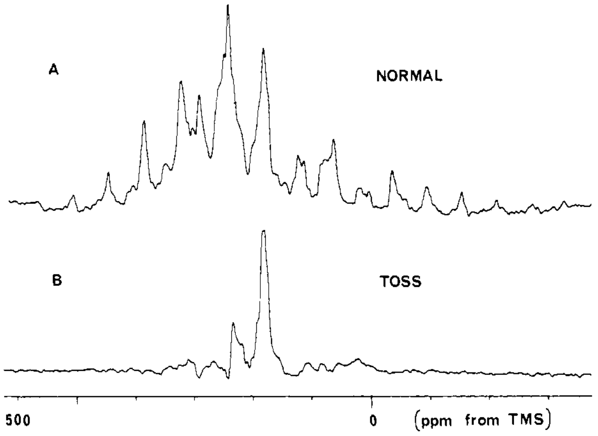

Figure 2. A comparison of the spectrum recorded at -41 °C with a normal single pulse sequence (A) and the spectrum as obtained with the TOSS pulse sequence (B).

Spinning sideband free spectra, obtained with the TOSS technique, were used to isolate the isotropic peaks in the low-temperature spectrum obtained at -41 °C. The low-temperature TOSS spectrum reveals the presence of two carbonyl peaks centered at 182 and 234 ppm. These chemical shifts are consistent with assignments made previously for terminal and bridging carbonyl carbons, respectively, in other metal carbonyl complexes in solution.[18] Their relative integrated areas were found to be approximately 4:1. This is significantly different from the ratio of 3:1 expected for the complex containing two bridging and six terminal carbonyls. However, it is not unreasonable to obtain a quantitative error of this magnitude when the TOSS experiment is applied in the slow spinning regime.[15]

If the line broadening observed from 40 to -4 °C is assumed to be a result of bridge–terminal carbonyl exchange, then an activation energy calculation is straightforward.[19] A lower limit of 11.7 ± 0.6 $kcal/mol^{-1}$[20] can thus be placed on the activation energy for bridge–terminal exchange.

Any proposed mechanism for bridge–terminal exchange must be consistent with the observed crystal structure. Crystallographically, two independent pairs of molecules are observed per unit cell.[12] These lie on a mirror plane bisecting the Co–Co bond. Importantly, there is no disorder in the structure. In the absence of disorder, carbonyl ligands can only exchange between crystallographically observed sites. Such an exchange must be cyclic in order to preserve unit occupancy of carbonyl sites; for example, on one cobalt, a sequence $B \rightarrow T' \rightarrow T'' \rightarrow T''' \rightarrow B$ may take place (B = bridging carbonyl, T = terminal carbonyl).

The observed fluxional behavior reported here for solid $Co_2(CO)_8$ is unprecedented. For example, the closely related molecule, $Fe_2(CO)_9$, does not undergo bridge–terminal exchange in the solid state.[13] Also, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, which undergoes rapid bridge–terminal exchange in solution, is static in the solid state.[13]

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(14) The variable-temperature magic angle spinning experiments were performed on a wide-bore (89 mm) JEOL FX-200 equipped with a Chemagnetics VT/MAS solid-state probe system. The probe uses a double-bearing rotor design in which the stator and bearing are controlled with separate gas regulators. For low-temperature work, the driving gas is passed through a coil immersed in liquid nitrogen and raised to the desired temperature with an external heater attached to a VT controller. The gas lines and sample chamber are insulated within the probe and the cold gas is exhausted out of the top of an insulated tube. The temperature was measured with a Pt resistance sensor placed at the inlet to the sample chamber. The accuracy of the temperature regulation was approximately ±2 °C. Delrin rotors with 0.7-cm^3 sample volume were used with spinning speeds from 3200 to 2500 Hz over the entire temperature range.

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(20) The limiting line width at high temperature was assumed to be equal to that imposed by the static field inhomogeneities (~5 Hz). Three points in the temperature range 21–40 °C that satisfy the fast-exchange limit criteria[19] were used to calculate the activation energy.

Carbonyl exchange in solid $Fe_3(CO)_{12}$ is a result of rotation of the Fe_3 triangle while the carbonyl ligands remain fixed in the crystal lattice.[5,21] Several cyclooctatetraene derivatives of metal carbonyls, e.g., $(COT)_2Ru_3(CO)_4$, have been investigated by solid-state NMR.[22,23] Exchange in these molecules involves motion of the cyclooctatetraene ring. In other systems where chemical exchange occurs in the solid state, the motion is restricted to a small group, e.g., proton jumping in tropolone[7] and naphthazarin-B.[24]

In the nondegenerate Cope rearrangement recently described for solid semibullvalene, the bond-breaking and -forming steps require very little movement of atomic positions.[25] The bond-breaking and -forming steps in $Co_2(CO)_8$ require carbonyl groups to move ~3 Å at a jump.

Further mechanistic studies on carbonyl exchange in $Co_2(CO)_8$ and its derivatives are under way.

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Registry No. Dicobalt octacarbonyl, 10210-68-1.

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Photoinduced Electron-Transfer Reactions. Evidence for Two Different Radical Cations of Hexamethyl(Dewar benzene)

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The photosensitized conversion of hexamethylbicyclo[2.2.0]-hexa-2,5-diene [hexamethyl(Dewar benzene) (**1**)] to hexamethylbenzene (**2**) is well established. In nonpolar solvents, **1** quenches the fluorescence of aromatic hydrocarbons and undergoes isomerization to **2**. This conversion is accompanied by a dual exciplex fluorescence.[1] In polar solvents, **1** is converted to **2** with quantum efficiencies far greater than unity.[2] These results were explained by invoking a radical ion chain reaction initiated by electron transfer from **1** to the photosensitizer. This mechanism requires a highly efficient ring opening of the intermediate cation and raises serious questions as to whether a radical cation of **1** can be an energy minimum. Indeed, a recent nanosecond spectroscopic study failed to reveal any evidence for a radical cation other than the hexamethylbenzene cation.[3]

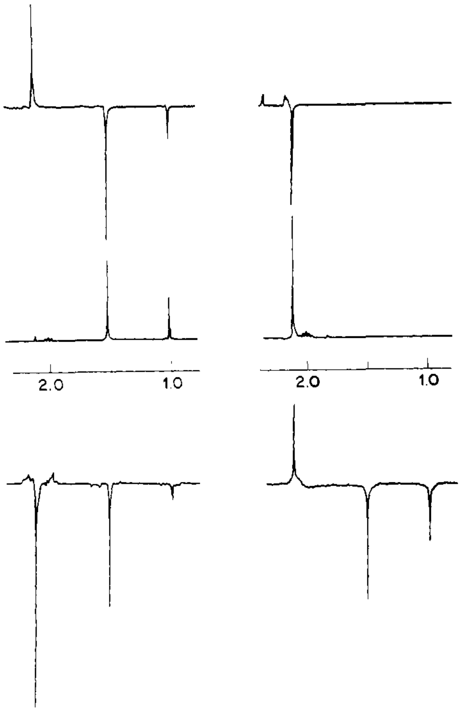

Figure 1. Top: ^1H NMR spectra (90 MHz) observed during UV irradiation of 0.02 M solutions of chloranil in acetone-d_6 containing 0.02 M hexamethyl(Dewar benzene) (left) or hexamethylbenzene (right). Center: ^1H NMR spectra of the same solutions in the dark. Bottom: ^1H NMR spectra observed during UV irradiation of a 0.02 M solution of hexamethyl(Dewar benzene) in acetone-d_6 containing 0.005 M anthraquinone (left) and of a 0.005 M solution of hexamethyl(Dewar benzene) in acetone-d_6 containing 0.02 M acetophenone (right).

Scheme I[a]

$$^3A^* + D \rightarrow {}^3\overline{A^-D^+} \tag{1}$$

$$^3\overline{A^-D^+} \rightleftarrows {}^1\overline{A^-D^+} \tag{2}$$

$$^1\overline{A^-D^+} \rightarrow A + D^{\dagger} \tag{3}$$

$$^{1,3}\overline{A^-D^+} \rightarrow {}^2A^- + {}^2D^+ \tag{4}$$

$$^2D^+ \rightarrow {}^2B^+ \tag{5}$$

$$^2B^+ + D \rightarrow B^{\ddagger} + {}^2D^+ \tag{6}$$

[a] *denotes an excited state; A, D, and B represent the acceptor, hexamethyl(Dewar benzene), and hexamethylbenzene; dagger and double dagger represent nuclear spin polarization of opposite sign.

Previous experience in many systems[4-8] suggested that the CIDNP technique is well suited to probe the existence of such a cation and to elucidate its structure. Accordingly, we have studied the photoreactions of strong electron acceptors (e.g., chloranil) with **1** and have examined the nuclear spin polarization effects induced in these reactions: the two methyl signals of **1** appeared in emission whereas the single methyl signal of **2** showed enhanced absorption (Figure 1, top left).

These results can be explained by a mechanism involving electron transfer from **1** to photoexcited (triplet) chloranil (eq 1, Scheme I). The resulting radical ion pair may undergo hyperfine-induced intersystem crossing (eq 2) and recombination (eq 3) or may suffer separation by diffusion (eq 4) and ring opening (eq 5). In essence, the competition between the electron spin dependent reaction (eq 3) and the electron spin independent process (eq 4) causes the generation of nuclear spin polarization

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