Coordination and Adsorption of Acetylene in the Poly[(vinylcyclopentadienyl)manganese] Membrane

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ABSTRACT: A copolymer of (vinylcyclopentadienyl)dicarbonylmanganese (CpMn) and octyl methacrylate forms its acetylene-coordinated complex reversibly and stably in the solvent-free membrane state. Kinetic and equilibrium constants of the acetylene coordination to the CpMn residue in the copolymer membrane are determined spectroscopically in situ. The acetylene coordination parameters are much smaller than those of the corresponding nitrogen coordination. Acetylene transport for the membrane is expected to be selectively augmented due to the coordination of acetylene to the fixed CpMn. However, acetylene transport behavior is in accordance with total immobilization of acetylene on the CpMn residue in the acetylene permeation through the membrane.

Introduction

A polymer containing a metal complex to which a gaseous molecule coordinates specifically would be of great interest as a specific adsorbent or a transport membrane.[1,2] Recently, we reported highly selective adsorption and transport of molecular oxygen through polymer membranes containing a cobalt porphyrin complex and a Schiff base complex as the fixed oxygen carrier in which oxygen coordinates to the complex residue rapidly and reversibly even in the solvent-free solid state.[3] This selective oxygen permeation was successfully explained by a dual-mode model[4,5] of facilitated transport (Scheme I).

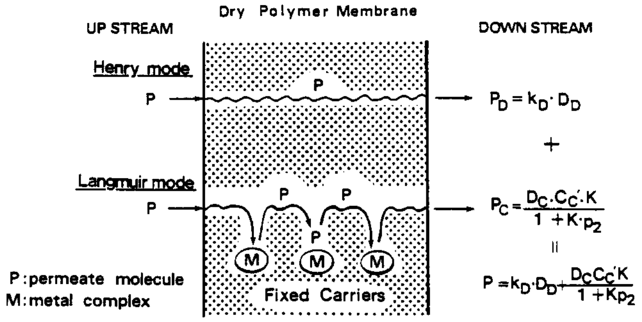
The similar facilitated transport was observed for nitrogen through the dry membrane of poly[(vinylcyclopentadienyl)manganese].[6] In this membrane molecular nitrogen coordinated to the cyclopentadienylmanganese residue in the polymer rapidly and reversibly. A predominant feature of this polymeric nitrogen-coordinated complex is its extraordinarily high stability under air atmosphere as compared with the corresponding low molecular analogous complex, which indicates effects of the polymer matrix to retard irreversible degradation of the metal complex or a dimerization reaction of the metal complex.

An organometallic polymer to which molecular acetylene coordinates reversibly and rapidly is expected to adsorb and transport acetylene selectively. We prepared a transparent and flexible polymer membrane from poly[vinylcyclopentadienylmanganese-*co*-(octyl methacrylate)] (Scheme II), which has one unsaturated coordination site even in the solid membrane state. In this paper, we describe stable and reversible coordination of acetylene to the cyclopentadienylmanganese residue of the polymer in the solvent-free solid state and selective adsorption and transport of acetylene in the membrane.

Experimental Section

Materials. 1,2- and 1,3-isomers (molar ratio ca. 2/8) of tricarbonyl(methylvinylcyclopentadienyl)manganese were synthesized as in the literature.[7] A copolymer of tricarbonyl(methylvinylcyclopentadienyl)manganese and octyl methacrylate was prepared by radical copolymerization in benzene solution using azobis(isobutyronitrile) as an initiator at 60 °C for 3 h after three alternate freeze–thaw degassing cycles. The copolymer was purified by two reprecipitations from benzene to methanol. Content of the CpMn residue and weight-average molecular weight of the copolymer were determined as 14.2 mol % and 2.0 × 10^5 by elemental analysis and gel-permeation chromatography (with tetrahydrofuran as the solvent and polystyrene as a standard).

Scheme I



A benzene solution of the copolymer was carefully cast on a Teflon plate under argon atmosphere and then dried in vacuo, to yield a transparent and flexible membrane with a thickness of ca. 60 μm (λ_{max} 327 nm; IR ν_{CO} 2018, 1930 cm^{-1}). The membrane prepared was irradiated with UV light (a 32-W low-pressure mercury lamp) for 1 h under an absolute argon atmosphere at room temperature. Tricarbonyl CpMn complex was converted to the corresponding dicarbonyl CpMn complex (λ_{max} 320 nm; IR ν_{CO} 1865 cm^{-1}).

Spectroscopic Measurement. Reversible acetylene coordination to the CpMn residue in the membrane was observed to be accompanied by a spectral change in the visible absorption (using a high-sensitivity spectrophotometer, Shimazu UV2100). Flash photolysis measurement was carried out with a pulse and laser flash spectrophotometer equipped with a kinetic data processer (UNISOKU FR-2000). The laser flash was applied perpendicularly to the light path of the spectrophotometer, and the membrane was placed at the crossing of the laser flash and the light path and at 45° to both. The rapid absorption change was recorded with a contact-type photomultiplier to cancel the noise caused by scattered light. Rate parameters for acetylene binding and dissociation were calculated by pseudo-first-order kinetics. The concentration of acetylene in the membrane was calculated by using the solubility coefficient of acetylene determined by permeation measurement.

Permeation Measurement. The acetylene permeation coefficient for various upstream gas pressures was measured with a low-vacuum permeation apparatus in a chamber with stable thermostating (Rika Seiki Inc., Model K-315 N-03). The pressure on the upstream side was maintained essentially constant. The pressure on the downstream side was kept at a very small value (10^{-3} mmHg) in comparison with the upstream side by using a explosion-protected pump. The pressures on the upstream and downstream sides were detected by using a Baratron absolute pressure gauge (MKS Instruments Inc.). The acetylene permeation coefficient was calculated from the slope of the steady-

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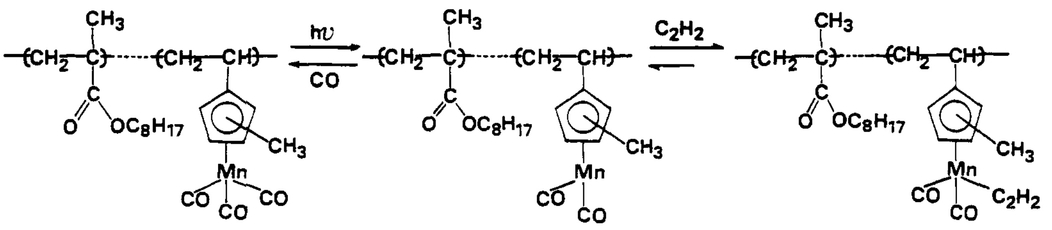
Scheme II



state straight line of the permeation curve. The induction period, θ, i.e., the time for the un-steady-state permeation in the early stage, was also measured to calculate the permeation parameters.

Results and Discussion

Acetylene Coordination to the CpMn Residue in the Membrane. The CpMn residue formed by UV irradiation has one unsaturated coordination site in the solvent-free solid state and can bind acetylene reversibly. On exposure to acetylene atmosphere, the membrane showed a strong IR absorption peak $\nu_{C\equiv C}$ at 1740 cm^{-1} assigned to a side-on-type coordinated acetylene.[8] When the membrane was allowed to stand under argon at 60 °C for a day, the IR absorption peak disappeared due to release of the coordinated acetylene and the evolved amount of acetylene was determined by means of gas chromatography.[9] The acetylene coordinated to the CpMn residue in the polymer containing 14 wt % CpMn was estimated to have a gravity of 80 μg/g of polymer (acetylene pressure $p_2(C_2H_2)$ = 760 mmHg) at 45 °C, which is more than 5 times larger than that of physically dissolved acetylene. This IR spectral change occurred rapidly; e.g., for a 5-μm-thick membrane the acetylene coordination equilibrium was established within a few minutes after exposure of the membrane to acetylene or in vacuo at 25 °C. These results suggest that this polymer has potential to be applied as a selective adsorbent of acetylene. For example, the adsorption ratio [acetylene]/[ethane] into the membrane after exposure of the membrane for 10 min at 25 °C to the 1/1 gas mixture of acetylene and ethane at 760 mmHg was 4.6. A control datum for activated carbon was 0.59.

Although the acetylene-coordinated complex was relatively stable even under air atmosphere at room temperature, the intensity of $\nu_{C\equiv C}$ of the coordinated acetylene decreased very slowly with time under air atmosphere. The lifetime (τ, half-time) was estimated to be 33 h from the decreased slope (first-order kinetics) in the absorption intensity of $\nu_{C\equiv C}$. This was in contrast with that of the corresponding low molecular weight analogue of the acetylene coordinated CpMn complex; the latter was formed only below 0 °C for a few minutes and was rapidly and irreversibly converted to the μ-carboxy dinuclear species ($\nu_{(C=O)bridge}$ 1777 cm^{-1}) and/or the manganese carbene species ($\nu_{C=C}$ 1650–1500 cm^{-1}). The polymeric acetylene complex was very stable because of effects of the polymer matrix to prevent irreversible degradation of CpMn or a dimerization reaction of CpMn.

The acetylene coordination in response to $p_2(C_2H_2)$ was also observed by the spectral change in the UV–visible absorption (Figure 1): λ_{max} (acetylene free) 327 nm; λ_{max} (C_2H_2/Mn = 1/1 adduct) 320 nm; isosbestic points 330, 348 nm. Photodissociation and recombination of the coordination acetylene from and to CpMn in the polymer membrane were successfully observed by pulse and flash spectroscopy in situ. The monitoring wavelength of the recombination reaction after the flash photolysis was set at 320 nm because of its largest change in absorbance, which agreed with the absorption maximum of the acetylene-coordinated complex. A typical example of the time course of absorbance increase is shown in Figure 2. The acetylene binding and dissociation rate constants (k_{on} and k_{off}) were estimated by pseudo-first-order kinetics and are given in Table I, with the reference data for the coordination of tetrahydrofuran (THF) and nitrogen to the same CpMn complex in the polymer.[6] The acetylene coordination equilibrium constant (K) and enthalpy and entropy change for the acetylene coordination were calculated from the temperature dependence (5–35 °C) of K and are given also in Table I.

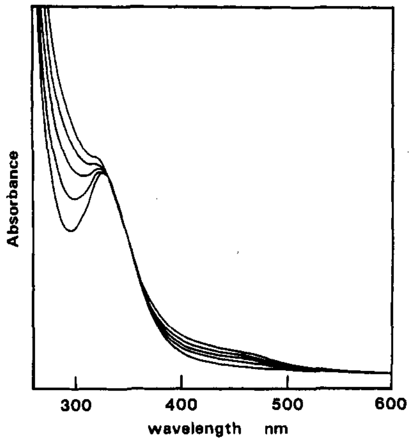


Figure 1. Visible absorption spectral change for the CpMn membrane under acetylene atmosphere.

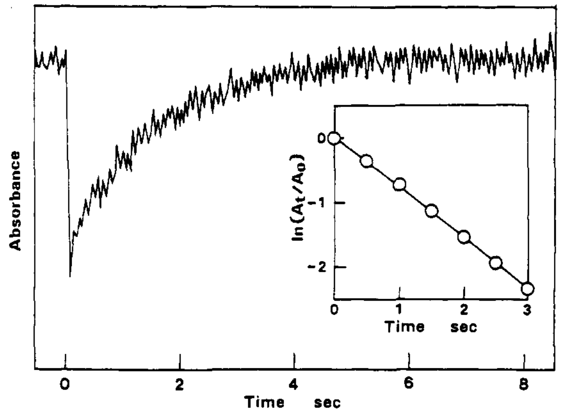


Figure 2. Laser flash photolysis of the acetylene-coordinated complex in the CpMn membrane and approximation to pseudo-first-order kinetics at 25 °C.

The K value for the acetylene coordination to CpMn is ca. 1/40 as large as that for the nitrogen coordination. Although the larger enthalpy gain (more negative ΔH value) suggests a stronger bond between C_2H_2 and Mn in comparison with the N_2–Mn bond, a much more negative entropy change through the acetylene coordination contributes to the smaller K value. The larger entropy decrease in the coordination step for the more bulky acetylene molecule reduces the coordination equilibrium constant in comparison with the coordination of the smaller nitrogen molecule.

Table I
Ligand Coordination Equilibrium (K) and Rate Constants (k_{on}, k_{off}) and Enthalpy (ΔH) and Entropy Change (ΔS) for Ligand Coordination to the CpMn Residue in the Membrane

ligand	physical state	$10^{-2}K$, M^{-1}	ΔH, kJ mol^{-1}	ΔS, J K^{-1} mol^{-1}	$10^{-5}k_{on}$, M^{-1} s^{-1}	$10^{-3}k_{off}$, s^{-1}	ref
THF	THF solution, 0 °C	8.3	*a*	*a*	61	7.4	6
N_2	membrane, 20 °C	9.8	−45	−146	2.9	0.3	6
C_2H_2	membrane, 25 °C	0.26	−64	−209	0.000 24	0.000 94	this work

[a] The $CpMn(CO)_2$ complex was degraded in solution even at 0 °C.

The k_{on} and k_{off} values for the acetylene coordination were 3 orders smaller than those for nitrogen. This k_{on} value for acetylene is 10^6 times smaller than that reported for the oxygen coordination to iron porphyrin.[10] The small k_{on} value means an organometallic character for the acetylene coordination, in comparison with ligand substitution labile, Werner type inorganic complexes.[11]

Acetylene Permeation in the CpMn Membrane. The CpMn complex residue in the membrane selectively sorbs acetylene as mentioned above. The acetylene sorption was described by the sum of Henry's law sorption to the polymer matrix and additional Langmuir sorption to the CpMn residue. If the acetylene coordination ability in the CpMn membrane corresponds to acetylene transport, the transport is expected to be accelerated by the additional Langmuir mode in addition to the Henry mode. This dual-mode transport theory is represented as follows:[4,5]

$$P = k_D D_D + C_C' K D_C/(1 + K p_2) \qquad (1)$$

Here P is the permeability coefficient, k_D is the solubility coefficient for Henry's law, D_D and D_C are the diffusion coefficients for the Henry-type physical permeation and for the Langmuir-type penetrant permeation via the fixed CpMn residues, K is the acetylene coordination equilibrium constant, C_C' is the saturated amount of the acetylene coordinated to the CpMn residue or the concentration of CpMn, and p_2 is upstream pressure.

Acetylene permeation–time curves through the membrane contain an induction period (θ) before establishing a steady-state straight line. θ for the CpMn membrane is also governed by both the Henry and Langmuir modes.

$$6D_D\theta/l^2 = [1 + R[f_0(y) + FRf_1(y) + (FR)^2f_2(y)] + FRf_3(y) + (FR)^2f_4(y)]/[1 + FR/(1 + y)]^3 \qquad (2)$$

$$f_0(y) = \frac{6}{y^3}\left[\frac{y^2}{2} + y - (1 + y)\ln(1 + y)\right]$$

$$f_1(y) = \frac{6}{y^3}\left[\frac{y}{2} - \frac{3y}{2(1 + y)} + \frac{\ln(1 + y)}{(1 + y)}\right]$$

$$f_2(y) = \frac{6}{y^3}\left[\frac{1}{6} - \frac{1}{2(1 + y)} + \frac{1}{2(1 + y)^2} - \frac{1}{6(1 + y)^3}\right]$$

$$f_3(y) = \frac{6}{y^3}\left[-\frac{3}{2}y + \frac{y}{2(1 + y)} + (1 + y)\ln(1 + y)\right]$$

$$f_4(y) = \frac{6}{y^3}\left[\frac{1}{2} - \frac{1}{2(1 + y)^2} - \frac{\ln(1 + y)}{(1 + y)}\right]$$

Here F is defined as D_C/D_D, R is defined as KC_C'/k_D, $y = Kp_2$, and l is the thickness of the membrane.

Figure 3 shows the effect of upstream acetylene pressure on acetylene permeation. θ for the acetylene permeation depends on $p_2(C_2H_2)$, which indicates that acetylene clearly interacts with the CpMn complex residue. The $\theta_{C_2H_2}$ and $p_2(C_2H_2)$ dependencies of $\theta_{C_2H_2}$ increase with decreasing temperature. These $\theta_{C_2H_2}$ and $p_2(C_2H_2)$ dependencies of $\theta_{C_2H_2}$ are influenced by the acetylene-binding constants to CpMn and are enhanced at lower temperature, because the K value increases and the k_{off} value decreases with a decrease in temperature.

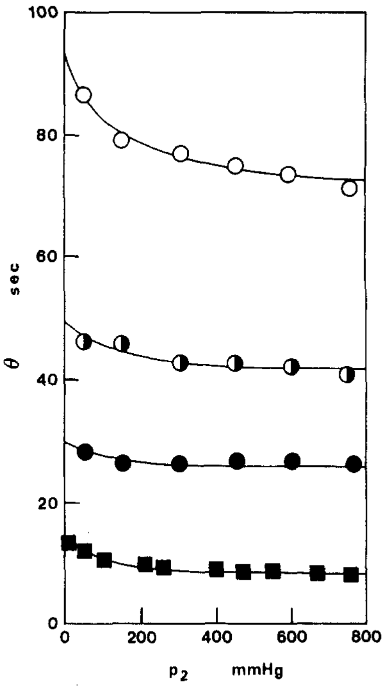


Figure 3. Effect of upstream gas pressure (p_2) on induction period (θ) for the permeation of acetylene (○) and nitrogen (□) in the CpMn membrane: (○) 25 °C, (◑) 35 °C, and (●) 45 °C.

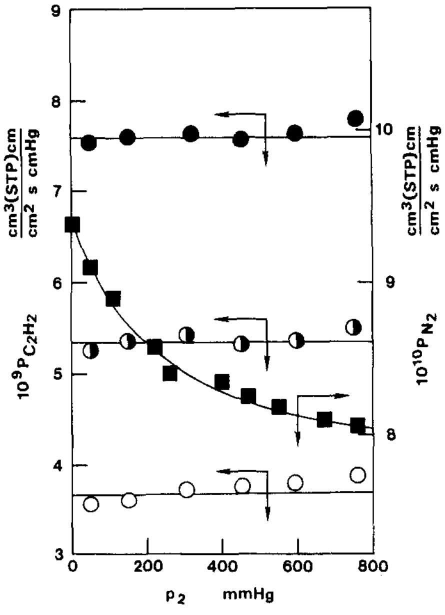


Figure 4. Effect of upstream gas pressure (p_2) on acetylene (○) and nitrogen (□) permeability coefficients for the CpMn membrane: (○) 25 °C, (◑) 35 °C, and (●) 45 °C.

On the other hand, although the acetylene permeability coefficient ($P_{C_2H_2}$) is larger than that of nitrogen, $P_{C_2H_2}$ is independent of $p_2(C_2H_2)$, as shown in Figure 4. That is, acetylene is totally immobilized onto the CpMn residue

Table II
Dual-Mode Transport Parameters for the CpMn Membrane

ligand	T, °C	$10^7 D_D$[a]	$10^7 D_C$[a]	$10^3 k_D$[b]	C_C'[c]
N_2	45	19	7.0	0.30	0.1
C_2H_2	25	2.3	0	16	0.4
	35	3.6	0	15	0.4
	45	5.4	0	14	0.4

[a] $cm^2\ s^{-1}$. [b] cm^3 (STP) $cm^{-3}\ cmHg^{-1}$. [c] cm^3 (STP) cm^{-3}.

in the polymer. The acetylene transport is not facilitated. In a previous paper,[6] we reported facilitated transport of molecular nitrogen through this polymeric CpMn membrane. The acetylene binding and dissociation rate constants (k_{on} and k_{off}) given in Table I are much smaller than those of nitrogen. Thus the acetylene coordination to the CpMn residue does not contribute to the acetylene transport because the k_{off} value for the coordinated acetylene is very small. This means that the diffusion coefficient for the Langmuir mode via the fixed CpMn residue, D_C, is close to zero and acetylene coordinated to the CpMn residue is apparently immobilized. When D_C is approximated at zero, eqs 1 and 2 are converted into (3) and (4).

$$P = k_D D_D \tag{3}$$

$$6D_D\theta/l^2 = 1 + Rf_0(y) \tag{4}$$

The acetylene permeation parameters are calculated by eqs 3 and 4 and are given in Table II. The saturated amount of acetylene coordinated to the CpMn residue is independent of temperature, which supports the validity of the calculation. Values were calculated by using eq 2 and the obtained parameters and are given in Figure 3 as the solid lines. The experimental plots for θ agreed with the solid lines in Figure 3, which quantitatively indicates the total immobilization of acetylene to the CpMn residue in the membrane.

Poly[(vinylcyclopentadienyl)manganese-*co*-(octyl methacrylate)] reversibly and stably forms its acetylene-coordinated complex even under open air atmosphere and acts as a selective adsorbent of acetylene. Acetylene transport is not facilitated, as has been expected by kinetic constants determined spectroscopically for the smaller acetylene binding and dissociation to and from the cyclopentadienylmanganese residue in the membrane.

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Registry No. (CpMn)(octyl methacrylate), 133472-82-9; nitrogen (copolymer), 7727-37-9; acetylene, 74-86-2.