J. Am. Chem. Soc. **1989**, *111*, 7175–7179

for the adsorption of the minor component from a solution containing two structurally similar thiols ($HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{11}OH$ in isooctane).[50]

(3) The relationships between the compositions of monolayers and the solutions from which they are adsorbed are nonideal. Monolayers containing comparable amounts of the two components are disfavored relative to monolayers composed largely of a single component. The adsorption isotherms can be understood qualitatively on the assumption of thermodynamic equilibrium between the monolayer and the adsorption solution and consideration of excess enthalpies and entropies of mixing.

(4) The components in the monolayer do not phase-segregate into macroscopic islands. Any clusters that do form are no more than a few tens of angstroms across. It is unlikely, however, that the two components are randomly dispersed throughout the monolayer. There is some evidence for aggregation on a molecular length scale, but it is difficult to derive a detailed picture of the distribution of the two components in the monolayer.

(5) We attempted to model the wettability of the mixed monolayers of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_nCH_3$ by the approach of Fowkes, who employed the geometric mean approximation to estimate the solid–liquid interfacial free energy. Although reasonable agreement was found for hexadecane, bicyclohexyl, and α-bromonaphthalene, there were significant differences between the theoretical predictions and the observed contact angles of water and decane. Fowkes' model applies to planar interfaces in which there is no entropy of mixing between the solid and the liquid. We believe that a detailed model of the wettability of these mixed monolayers will have to incorporate entropy specifically. The relative importance of enthalpic and entropic terms and how best to incorporate entropy into a coherent theory remain unclear.

(6) The variation in hysteresis in the contact angle with the nature of the probe liquid and the structure of the monolayers cannot be explained on the basis of macroscopic heterogeneity, since no such heterogeneity exists in these systems. Hysteresis contains much information about the structure of the surface but, in the absence of a microscopic theory, can only be interpreted through comparison of a number of different systems.

Acknowledgment. We are grateful to our colleagues J. Evall and M. Chaudhury for their valuable suggestions and comments.

Registry No. HD, 544-76-3; Au, 7440-57-5; $HS(CH_2)_{21}CH_3$, 7773-83-3; $HS(CH_2)_{11}CH_3$, 112-55-0; $HS(CH_2)_{15}CH_3$, 2917-26-2; $HS(CH_2)_{11}OH$, 73768-94-2; $HS(CH_2)_{19}OH$, 114896-31-0; decane, 124-18-5; bicyclohexyl, 92-51-3; α-bromonaphthalene, 90-11-9.

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[50] $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{11}OH$ have similar sizes, shapes, and polarizabilities. At low concentrations in isooctane, H bonding does not play an important role.

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Reversible Coordination and Facilitated Transport of Molecular Nitrogen in Poly((vinylcyclopentadienyl)manganese) Membrane

Hiroyuki Nishide, Hiroyoshi Kawakami, Yoshimi Kurimura,[†] and Eishun Tsuchida*

Contribution from the Department of Polymer Chemistry, Waseda University, Tokyo 169, Japan.

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Abstract: Kinetic and equilibrium constants of nitrogen coordination to cyclopentadienylmanganese (CpMn) are spectroscopically determined by using the membrane of the copolymer of (vinylmethylcyclopentadienyl)dicarbonylmanganese and octyl methacrylate. Nitrogen transport through the membrane is selectively augmented due to the rapid and reversible coordination of nitrogen to the fixed CpMn. The facilitated nitrogen-transport behavior is in accordance with a dual-mode transport model to give diffusion coefficients of the penetrant.

Much effort has been expended in studying the selective transport of gaseous molecules through polymeric membranes.[1] Recently we reported highly selective transport of molecular oxygen through polymer membranes containing a (porphinato)cobalt complex as the fixed carrier of oxygen.[2] The key experiment to establish the facilitated oxygen transport involved the proper preparation of a polymer (porphinato)cobalt membrane in which molecular oxygen coordinates to the complex rapidly and reversibly even in the solid state. The permeability ratio of oxygen against nitrogen was greater than 10 through the membrane containing a large amount of the (porphinato)cobalt. This membrane was successfully employed as an oxygen-enriching membrane to separate oxygen from air.[2]

A polymer containing the metal complex to which molecular nitrogen coordinates rapidly and reversibly is expected to transport nitrogen selectively and to show the possibility of a nitrogen-enriching membrane from air. A large number of transition-metal complexes of molecular nitrogen have been synthesized.[3] However, these studies are aimed at nitrogen fixation through the reduction of the nitrogen coordinated to a metal ion, and the nitrogen complexes themselves often undergo degradation under an air atmosphere. Therefore, kinetic and equilibrium profiles of the nitrogen coordination to the metal ion have been receiving surprisingly little attention.

We have reviewed the effects of a polymer matrix to reduce the degradation of a metal complex: an immobilization effect to inhibit a dimerization of metal complexes and an environmental effect to suppress a redox reaction of metal complexes.[4] Here we successfully prepared a transparent and flexible polymer

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[†] Department of Chemistry, Ibaraki University, Mito 310, Japan.

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Scheme I

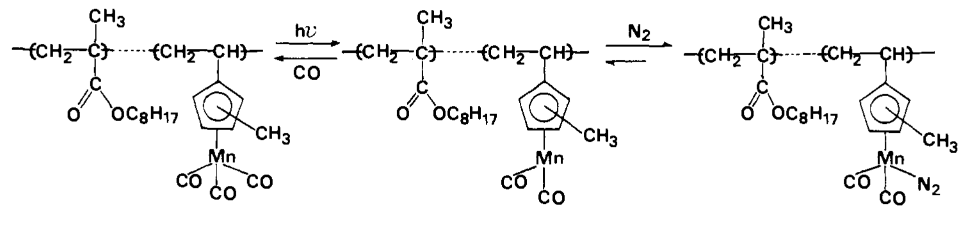

Table I. Ligand-Coordination Rate, Equilibrium Constants, and Thermodynamic Parameters

complex	ligand	physical state	$10^{-2}K$, M^{-1}	$10^{-5}k_{on}$, $M^{-1}\ s^{-1}$	$10^{-3}k_{off}$, s^{-1}	ΔH, $kJ^{-1}\ mol^{-1}$	ΔS, $J\ K^{-1}\ mol^{-1}$	ref
$CpMn(CO)_2$–OMA	THF	THF solution, 0 °C	8.3	61	7.4	*a*	*a*	this work
	N_2	membrane, 20 °C	9.8	2.9	0.3	−45	−146	this work
$CpMn(CO)_2$	THF	THF solution, 0 °C	3.4	18	5.3	*a*	*a*	this work
	N_2	cyclohexane, 22 °C		3.7				8
FePIm	O_2	toluene, 25 °C	23	1060	46	−60	−177	7

[a] The $CpMn(CO)_2$ complexes were gradually degraded at 0 °C, and the temperature dependence of *K* could not be measured even for the THF coordination.

membrane from the copolymer of octyl methacrylate and (vinylmethylcyclopentadienyl)dicarbonylmanganese (Scheme I), which has one unsaturated coordination site even in the solid membrane state to bind nitrogen rapidly and reversibly and through which nitrogen permeation is enhanced. We describe in this paper rapid and reversible coordination of molecular nitrogen to poly((vinylcyclopentadienyl)dicarbonylmanganese) (CpMn) in a solvent-free membrane state and facilitated nitrogen transport through the nitrogen carrier (CpMn) fixed in the membrane.

Results and Discussion

The polymer was synthesized from radical copolymerization of a mixture of 1,2- and 1,3-isomers of tricarbonyl(methylvinylcyclopentadienyl)manganese and octyl methacrylate (Scheme I).[5] Octyl methacrylate was selected as the comonomer of the polymerization because its copolymer yielded a transparent and flexible membrane and because its residue incorporated in the copolymer did not interfere in the subsequent nitrogen coordination. Upon UV irradiation of the membrane in argon atmosphere, the copolymer was converted to the corresponding cyclopentadienyldicarbonylmanganese, whose one unsaturated coordination site is vacant, even in the solid state, and it can bind molecular nitrogen rapidly and reversibly (Scheme I).

On exposure of this membrane to nitrogen atmosphere, the polymer membrane showed a strong IR absorption peak (ν_{N_2}) at 2160 cm^{-1} for $^{14}N_2$ and 2090 cm^{-1} for $^{15}N_2$, assigned to an end-on-type coordinated dinitrogen.[6] The intensity of ν_{N_2} reversibly increased/decreased in response to the partial pressure of nitrogen ($p^2(N_2)$). This ν_{N_2} intensity change occurred very rapidly; for a 10-μm-thick membrane containing 6.4 mol % CpMn, the nitrogen coordination equilibrium was established within 1 min after exposure of the membrane to nitrogen ($p^2(N_2)$ = 760 mmHg) or in vacuo at 25 °C.

The nitrogen coordination in response to $p^2(N_2)$ was also observed by the spectral change in the UV absorption, which exhibited good isosbestic behavior: λ_{max} (nitrogen free) 327 nm, λ_{max} (N_2/Mn = 1/1 adduct) 308 nm. The nitrogen-coordination equilibrium curve was drawn from the spectral change of the membrane (Figure 1a). The curve obeys a typical Langmuir's isotherm from which the binding equilibrium constant ($K = [CpMnN_2]/[CpMn][N_2]$) for the nitrogen coordination can be obtained. The *K* (mmHg^{-1}) obtained was converted to *K* (M^{-1}) by substituting the solubility coefficient of nitrogen in the membrane determined by the nitrogen sorption measurement mentioned later and given in Table I. Thermodynamic parameters for the nitrogen coordination were estimated from the temperature dependence of *K* and are given also in Table I. Control data for the tetrahydrofuran (THF) coordination to the monomeric and polymeric CpMn's were measured in the cooled THF solution (Table I): They support the validity of the nitrogen-coordination measurement for the CpMn polymer. The *K* value for the nitrogen coordination to CpMn is comparable with the *K* values for the THF coordination. *K* and thermodynamic parameters for oxygen coordination to a (porphinato)metal such as [α,α′,α″,α‴-*meso*-tetrakis(*o*-pivalamidophenyl)porphinato]iron(II) 1,2-dimethylimidazole (FePIm) in toluene solution[7] are listed in Table I as references. The *K* value for the nitrogen coordination is a little smaller than that for the oxygen coordination. Both the enthalpy and the entropy change for the nitrogen coordination to CpMn are more positive than those for the oxygen coordination to the (porphinato)iron complex. In comparison with the oxygen co-

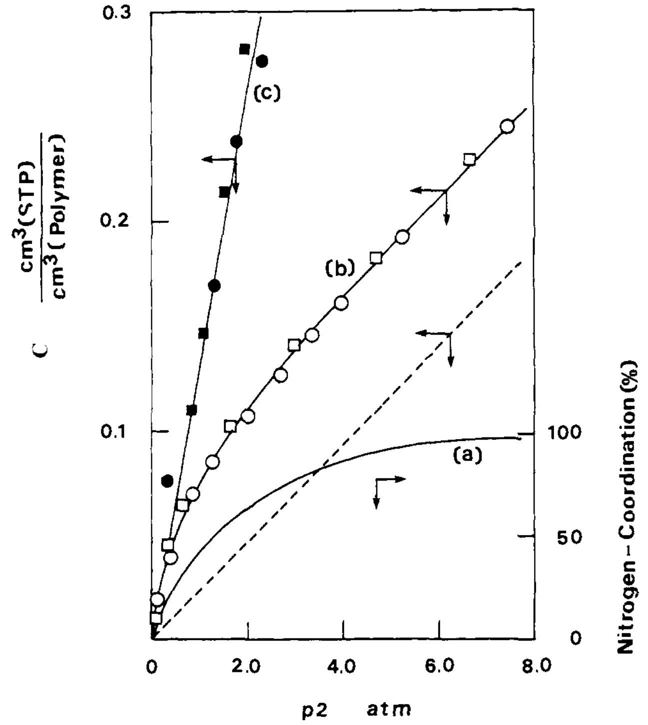

Figure 1. Nitrogen-coordination equilibrium curve monitored by UV spectral change (a) and sorption isotherms for nitrogen (b) and oxygen (c) measured gravimetrically for the $CpMn(CO)_2$–OMA membrane at 45 °C. (---) Sorption isotherm for the nitrogen dissolved physically and described by Henry's law. (○) Sorption, (□) desorption.

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Table II. Dual-Mode Transport Parameters for the $CpMn(CO)_2$–OMA Membrane at 45 °C

membrane[a]	C_C', cm^3 (STP)/cm^3	10^3K,[b] 1/cmHg	k_D, cm^3 (STP)/(cm^3 cmHg)	diffusion coeff, cm^2/s			
				10^7D_{DD}	10^7D_{DC}	10^7D_{CD}	10^8D_{CC}
1	0.05	8.8	3.0	11	2.2	1.5	8.8
2	0.08	9.3	3.0	7.4	1.9	1.2	6.3
3	0.12	9.1	3.3	5.1	1.7	0.69	5.8

[a] See Experimental Section. [b] For example, $K = 9.3 \times 10^{-3}$ $cmHg^{-1}$ is converted to $K = 9.8 \times 10^{-2}$ M^{-1} by substituting $k_D = 3.0$ cm^3 (STP)/(cm^3 cmHg).

ordination, the smaller enthalpy gain in the nitrogen coordination is compensated with the smaller entropy decrease in the immobilization of nitrogen, which provides the relatively large nitrogen-coordination equilibrium constant.

Rapid and reversible nitrogen coordination to the CpMn residue in the membrane was also confirmed by laser flash photolysis of the nitrogen complex. Photodissociation and -recombination of the coordinated nitrogen to and from the CpMn in the membrane was successfully observed: The reaction was completed within 10 ms. It is a surprisingly rapid reaction. The nitrogen-binding and -dissociation rate constants (k_{on} and k_{off}) were estimated by pseudo-first-order kinetics and are given also in Table I with kinetic data for the THF coordination of the CpMn's and for the oxygen coordination of the FePIm. The k_{on} and k_{off} values for the THF coordination of the CpMn polymer in the cooled THF solution are appropriately similar to those of the corresponding monomeric CpMn complex. The k_{on} value with a 10^5 M^{-1} s^{-1} order for the nitrogen coordination means that the organometallic nitrogen coordination is also a rapid reaction, although the rate constants are 10^2 times smaller than those for the oxygen coordination. This k_{on} value determined for the polymer CpMn complex in the membrane state is consistent with the k_{on} value[8] recently reported for the nitrogen-coordinated intermediate of the corresponding manganese complex $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ with time-resolved spectroscopy. One of the advantages of our system is that kinetic and equilibrium constants of the nitrogen coordination can be evaluated in situ spectroscopically: The spectroscopies on organometallic species in a polymer membrane can extend the information about intermediates beyond that already available from low-temperature and/or time-resolved experiments.

Anyhow, the CpMn complex maintains its rapid and reversible binding capability for molecular nitrogen even after immobilization in the dry membrane.

The amounts of nitrogen and oxygen absorbed in the CpMn polymer membrane were determined gravimetrically by using an electromicrobalance which was mounted in a vacuum chamber.[9] A rapid and reversible increase and decrease in weight was established for both nitrogen and oxygen within a few minutes after exposure of the membrane to the atmosphere with a constant nitrogen or oxygen pressure. This also supports the rapid and reversible binding of nitrogen to the polymer membrane.

Figure 1 (b and c) shows sorption isotherms for nitrogen and oxygen in the membrane. The isotherm for oxygen is a linear one, which corresponds to a physical dissolution of oxygen in the membrane. On the other hand, the sorption behavior for nitrogen (Figure 1b) corresponds to a dual-mode sorption;[10] the sorption of nitrogen is equal to the sum of the physical dissolution described by Henry's law and the nitrogen adsorption to the CpMn complex described by the Langmuir isotherm. The dual-mode sorption is represented by

$$\begin{aligned} C &= C_D + C_C \\ &= k_Dp^2 + C_C'Kp^2/(1 + Kp^2) \qquad (1) \end{aligned}$$

Here, C is the total concentration of sorbed nitrogen, C_D is concentration of sorbed nitrogen according to Henry's law, C_C is concentration of sorbed nitrogen according to the Langmuir isotherm, k_D is the solubility coefficient of nitrogen for Henry's law, C_C' is the saturated amount of nitrogen reversibly coordinated to the complex or the concentration of the effective CpMn residue in the membrane, K is nitrogen-coordination equilibrium constant, and p^2 is the atmospheric or upstream nitrogen pressure.

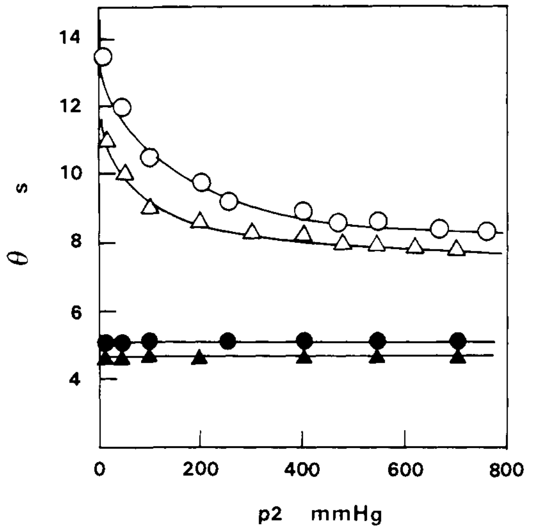

Figure 2. Effect of upstream gas pressure (p^2) on induction period (θ) for the permeation of nitrogen (open symbols) and oxygen (closed symbols) in the $CpMn(CO)_2$–OMA membrane at 45 °C. $C_C' = 0.05$ (△), 0.08 (○) cm^3 (STP)/cm^3.

The sorption isotherm for nitrogen (Figure 1b) was analyzed in terms of this dual-mode sorption model using nonlinear least-squares regression, which gave the parameters k_D, K, and C_C' in Table II. This K value determined gravimetrically is approximately in accordance with that determined spectroscopically and mentioned above (Table I).

Gas permeation–time curves through the membranes contain an induction period (θ) before establishing steady-state straight lines. Figure 2 shows the effect of upstream gas pressure (p^2) on θ for the gas permeation. While θ_{O_2} for the oxygen permeation is short and independent of $p^2(O_2)$, θ_{N_2} for the nitrogen permeation is longer than θ_{O_2} and increases with decreasing $p^2(N_2)$. θ_{N_2} and the $p^2(N_2)$ dependence of θ_{N_2} are enhanced for the membrane with larger C_C'. These facts support a pathway where nitrogen clearly interacts with the CpMn complex in the membrane and where nitrogen diffusivity in the membrane is suppressed by the repeated coordination of molecular nitrogen to the fixed CpMn complexes (carriers).

The effect of p^2 on the permeability coefficient of nitrogen and oxygen (P_{N_2} and P_{O_2}) is shown in Figure 3. P_{N_2} also depends on $p^2(N_2)$ and P_{O_2} is also independent of $p^2(O_2)$, in the same manner as the induction period. This behavior indicates that the CpMn-coordinated or the Langmuir-sorbed nitrogen is not rigidly held to the CpMn complex. This nitrogen can diffuse in the membrane, though, slowly.

These results suggest that the nitrogen transport in the membrane is facilitated and occurs by a dual-mode transport[11] (Henry mode and additive Langmuir mode). The dual-mode transport

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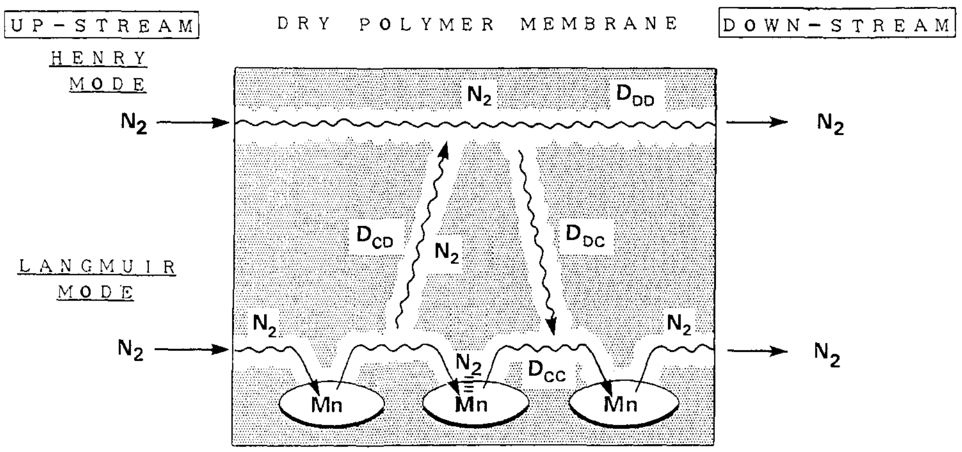
Scheme II



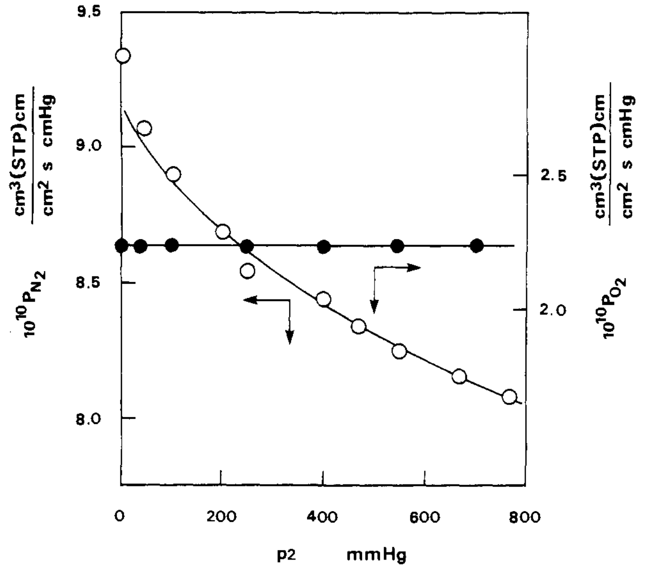


Figure 3. Effect of upstream gas pressure (p^2) on nitrogen (○) and oxygen (●) permeability coefficients for the CpMn(CO)$_2$–OMA membrane at 45 °C. $C_C' = 0.08$ cm^3 (STP)/cm^3. The solid line represents P_{N_2} calculated by eq 2.

of a penetrant in a polymer membrane has been observed for carbon dioxide permeation in glassy polymers.[12] But in those investigations, application of the dual-mode transport model was not rigorously justified since the nature of a microvoid existing in a glassy polymer was not elucidated and the glassy polymer matrix underwent plasticization during the penetrant sorption and transport. On the other hand, the CpMn polymer membranes were in a rubber state at the temperature for the permeation measurement (glass transition temperature were 10 and 21 °C for the membranes containing 18.5 and 32.0 mol % CpMn, respectively). We hereafter verified this facilitated transport or the dual-mode transport using a much simpler system.

The mathematics of the dual-mode transport has been theoretically proposed.[13,14] The facilitated transport behavior in this paper is adequate for an approximate analysis in terms of the following dual-mode transport model (schematically represented in Scheme II):

$$P = k_D D_{DD} + \frac{C_C' K D_{CC}}{1 + Kp^2} + \frac{C_C' K D_{CD} - k_D D_{DC}}{1 + Kp^2} + \frac{2k_D D_{DC}}{Kp^2} \ln (1 + Kp^2) \quad (2)$$

That is, P is equal to the sum of the first term representing the Henry mode attributed to a physical permeation through a polymer matrix, the second term representing the Langmuir mode attributed to a specific sorption (coordination) and diffusion of nitrogen to and through the CpMn complex, and the third term representing the additive Langmuir mode attributed to an exchanging term between the first and second term. Here, D_{DD}, D_{DC}, D_{CD}, and D_{CC} are the diffusion coefficients for the Henry-type physical permeation, for the polymer matrix to the fixed CpMn complex, for the fixed complex to the polymer matrix, and for the jumping between the fixed complexes. The K, C_C', and k_D values determined spectroscopically and gravimetrically are substituted in eq 2; by using these parameters, we could calculate the transport parameters and gave them in Table II. The the P_{N_2} versus $p^2(N_2)$ curve is calculated and drawn as the solid line in Figure 3. The experimental plots agree with the solid line, which supports the facilitated and dual-mode transport of nitrogen in the membrane and a pathway of nitrogen permeation via the fixed complex (carrier).

Table II suggests the following aspects of the facilitated transport. (i) A rapid penetrant exchange between two transport modes is established, as has been expected by the kinetic constants determined spectroscopically for nitrogen binding and dissociation to and from the CpMn fixed in the membrane. (ii) $(D_{CC} + D_{CD})/D_{DD}$ shows that the Langmuir-sorbed or -coordinated nitrogen has one-quarter of the mobility of that due to the Henry mode. (iii) D_{CC}/D_{DD} increases with the fixed CpMn concentration, which suggests a penetrant jumping accompanied by the decrease in the distance between the fixed complexes (carriers).

Experimental Section

Materials. 1,2- and 1,3-isomers (molar ratio ca.2/8) of tricarbonyl(methylvinylcyclopentadienyl)manganese were synthesized as in the literature.[5] ^{13}C NMR (CCl$_4$): δ 13.6, 14.4 (CH$_3$), 101.4, 102.7 (CCH$_3$), 115.0, 115.6 (=CH$_2$), 127.9, 129.4 (CH=vinyl), and 226 (br, 3C:CO), the first of the two peaks always having lower intensity. The polymer was prepared by radical copolymerization with octyl methacrylate in benzene solution using azobis(isobutyronitrile) (1 mol % of the total monomers) as an initiator at 60 °C for 3 h after three alternate freeze–thaw–degassing cycles. The mole fraction of the (vinylcyclopentadienyl)manganese in the feed monomers (1 M) was 7, 20, and 33 mol % for copolymers 1, 2, and 3, respectively. The copolymer was precipitated from methanol, purified by being reprecipitated twice, and dried in vacuo. Yield 45%, 38%, and 34%. The (vinylcyclopentadienyl)manganese residue and weight-average molecular weight of the copolymers were 6.4, 18.5, and 32.0 mol % and 3.5×10^5, 2.0×10^5, and 1.8×10^5 for copolymers 1, 2, and 3, respectively, determined by elemental analysis and gel permeation chromatography (with tetrahydrofuran as the solvent and polystyrene as the standard).

A benzene solution of the copolymer was carefully cast on a Teflon plate under an argon atmosphere, followed by drying in vacuo, to yield a transparent and pale brownish membrane (λ_{max} 327 nm). The transparent membrane was irradiated with UV light (a 32-W low-pressure mercury lamp) for 30–90 min under an absolute argon atmosphere at room temperature. The tricarbonyl CpMn complex was converted to the corresponding CpMn complex (λ_{max} 320 nm; IR ν_{CO} 1870 cm^{-1}).

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Spectroscopic Measurements. The UV absorption spectrum of the membrane was measured with a high-sensitive 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 nitrogen binding and dissociation were calculated by pseudo-first-order kinetics. The concentration of nitrogen in the membrane was calculated using the nitrogen solubility determined by gravimetric measurement.

Gravimetric and Permeation Measurements. The sorption amounts of nitrogen and oxygen in the polymer were measured gravimetrically by using an electromicrobalance (Cahn balance Model 2000) which was mounted in a high-pressure chamber made of stainless steel.[9] The chamber was placed in thermostatically controlled air.

Nitrogen and oxygen permeation coefficients for various upstream gas pressures were measured with a low-vacuum permeation apparatus in the chamber with stable thermostating (Rika Seiki K-315 N-03). The pressures on the upstream and the downstream sides were detected by using a Baratron absolute pressure gauge (MKS Instruments).

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Radical-Scavenging Reactions of Vitamin E and Its Model Compound, 2,2,5,7,8-Pentamethylchroman-6-ol, in a *tert*-Butylperoxyl Radical-Generating System[1]

Mitsuyoshi Matsuo,*,[†] Shigenobu Matsumoto,[†] Yoichi Iitaka,[‡] and Etsuo Niki[§]

Contribution from the Tokyo Metropolitan Institute of Gerontology, 35-2 Sakaecho, Itabashiku, Tokyo 173, Japan, and the Faculty of Pharmaceutical Sciences and the Department of Reaction Chemistry, the Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyoku, Tokyo 113, Japan. *Received October 25, 1988*

Abstract: In a *tert*-butylperoxyl radical-generating system containing di-*tert*-butyl diperoxyoxalate (DBPO) and *tert*-butyl hydroperoxide (BOOH), vitamin E (α-tocopherol: **1**) is converted into 4a,5-epoxy-4a,5-dihydro-8a-hydroperoxy-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6(8a*H*)-one (**2**) and 8a-(*tert*-butyldioxy)-4a,5-epoxy-4a,5-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6(8a*H*)-one (**3**), and its model compound, 2,2,5,7,8-pentamethylchroman-6-ol (**4**), is converted into 4a,5-epoxy-4a,5-dihydro-8a-hydroperoxy-2,2,5,7,8-pentamethylchroman-6(8a*H*)-one (**5**) and 8a-(*tert*-butyldioxy)-4a,5-epoxy-4a,5-dihydro-2,2,5,7,8-pentamethylchroman-6(8a*H*)-one (**6**). The structures of these compounds were deduced on the basis of the spectral data and, in addition, that of **5** was confirmed by X-ray crystallography. The reactions did not proceed under degassed conditions, so the presence of molecular oxygen was suggested to be a requisite for them. In the system without DBPO, **4** gives **5** and **6** in low yields, and without BOOH, **4** gives its dimers (**7a** and **8a**) and trimer (**9a**). Further, it was observed that, in the presence of BOOH, **5** was derived from a hydroperoxide, 8a-hydroperoxy-2,2,5,7,8-pentamethylchroman-6(8a*H*)-one (**10**), and was transformed into **6**. Accordingly, **10** and 8a-hydroperoxy-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6(8a*H*)-one (**11**) may be intermediates of **5** and **2**, respectively, and **5** and **2** may be intermediates of **6** and **3**, respectively. A possible mechanism is shown for the reaction of **1** with the *tert*-butylperoxyl radical (BOO•) under the hydroperoxide-rich conditions. The reaction mechanism is discussed with respect to the chain-breaking reaction of **1** against lipid peroxidation.

Vitamin E, mainly (*R*,*R*,*R*)-α-tocopherol, is a naturally occurring radical scavenger and is considered to act as an efficient chain-breaking antioxidant against lipid peroxidation.[2] Vitamin E activity appears to be related to the retardation of some serious diseases and functional deteriorations,[3] such as cardiovascular diseases, cancer, and aging, which result at least partially from lipid peroxidation. The elucidation of its chain-breaking reactions is very important for the understanding of defense mechanisms in vivo and the development of new treatments against these deteriorative changes.

Kinetic, spin trapping, and product analysis studies of lipid peroxidation show that the chain carrier is the peroxyl radical.[4-6] The accepted mechanism for chain breaking by **1** is outlined as follows:[7,8]

$$\mathrm{TOH} + \mathrm{LOO}^{\bullet} \rightarrow \mathrm{TO}^{\bullet} + \mathrm{LOOH}$$

$$\mathrm{TO}^{\bullet} + \mathrm{LOO}^{\bullet} \rightarrow \text{nonradical products}$$

where **1** is represented by TOH, the peroxyl radical by LOO•, the α-tocopheroxyl radical by TO•, and hydroperoxide **2** by LOOH. The reaction of **1** with the peroxyl radical is the rate-limiting step in the process.[2] Further understanding of the

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[†] Tokyo Metropolitan Institute of Gerontology.

[‡] Faculty of Pharmaceutical Sciences, University of Tokyo.

[§] Faculty of Engineering, University of Tokyo.

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