

References

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Kinetic Studies on the Reaction of the Heterobimetallic Anion, (OC)₅CrMn(CO)₅⁻M⁺ (M⁺=Na⁺, PPN⁺) with CH₃I

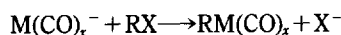
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The reaction of the heterobimetallic anion, (OC)₅CrMn(CO)₅⁻M⁺ (M⁺=Na⁺, PPN⁺) with CH₃I was proven to be overall 1st order with respect to [(OC)₅CrMn(CO)₅⁻]. This reaction mechanism may be described in terms of the consecutive reaction pathway in which Cr(CO)₅(THF) may be an important intermediate, leading to the corresponding products such as MeMn(CO)₅ and ICr(CO)₅⁻, accordingly. The counterion effect on this reaction was also elucidated.

Introduction

The displacement of X⁻ from RX (RX=organic halides) by anionic transition metal carbonylates usually follows a second order rate law, reaction rate= $k_2[M(CO)_x]^- [RX]$.



For the last two decades many chemists have studied the effects of ion pairing on the structure and reactivity of transition metal organic salts.¹

Particularly much effort has been directed to the mononuclear carbonylates such as HFe(CO)₄⁻², Mn(CO)₅⁻³, Co(CO)₄⁻⁴, CpMo(CO)₃⁻⁵, and CpW(CO)₃⁻⁶. For alkyl halides a "normal" counterion effect was observed; the less associated the anion is with its cation, the greater is its nucleophilicity. However, an "inverse" counterion effect was detected in the reactions of Co(CO)₄⁻, Mn(CO)₅⁻, and CpMn(CO)₃⁻ with the activated organic halides such as benzyl halides or allyl halides.⁷ In such cases, tight ion pairs were observed to enhance the corresponding reaction rates.

For several years we tried to understand the reactions using the anionic heterobimetallics such as L(CO)₄CrMn(CO)₄ L⁻M⁺ (M⁺=Na⁺, PPN⁺ (bis-(triphenylphosphoranylidene) ammonium ion); L=CO, PR₃).^{8,9} In this paper, we would like to elucidate the counterion effect on the reaction of the heterobimetallic anion, (OC)₅CrMn(CO)₄⁻M⁺ (M⁺=Na⁺, PPN⁺)

with methyl iodide.

Experimental

An inert-atmosphere glove box and Schlenk line and high-vacuum techniques were employed for most of sample transfers and manipulations. Infrared spectra were recorded on Perkin-Elmer 238B spectrophotometer. The temperature was controlled with Haake A81 thermostat. Most of weighing and transfers of compounds were done under an Ar atmosphere in the glove box (Vacuum Atmosphere Co.).

Photoreactions were performed using a 450 watt Hg vapor lamp covering a rather broad range of UV-VIS wavelengths. Solvents were distilled under N₂ atmosphere from appropriate drying and O₂ scavenging agents: tetrahydrofuran (THF) and toluene, Na⁰/benzophenone/diglyme; methylene chloride, P₂O₅; acetonitrile, CaH₂ followed by P₂O₅; ethanol, Mg⁰/I₂. All reagents were purchased from ordinary vendors and used as received without further purification.

Preparation of PPN⁺CrMn(CO)₁₀⁻. The following modification of the preparation of this complex in the literature¹⁰ was utilized to give good yields of the complex. To Na⁺Mn(CO)₅ (4.5 mmol) was added the THF solution (150 ml) of Cr(CO)₅(THF) (4.5 mmol) freshly prepared from the photolytic reaction. This solution was stirred for more than 3 hr at room temperature. This reaction solution was then passed through a Celite column and concentrated to about 1/4 of its initial volume under vacuum. Hexane (50 ml) was

* PPN⁺ = bis(triphenylphosphoranylidene)ammonium ion

added and oil was separated. The oily product was washed with hexane several times and then THF (50 ml) was added so as to get a homogeneous solution. PPN⁺Cl⁻ (4.5 mmol) dissolved in CH₂Cl₂ (5 ml) was slowly added at room temperature over the course of 3 hr. A yellow precipitate formed on the bottom. The mother liquor was again passed through a Celite column and transfer *via* cannula to another Schlenk flask. This product solution was concentrated under vacuum until there formed a sudden yellow precipitate. The product yield was 1.83 g (43.5%). ν (CO) IR (THF) 2063 (w), 1988 (m), 1950 (s), 1923 (w, sh), 1894 (m), 1862 (m).¹⁰

Preparation of M(CO)₅THF (M=Cr). A degassed THF (100 ml) solution of M(CO)₆ (0.05 mmol) was photolyzed under a UV lamp (450 W Hg Hanovia Lamp) for one hour. The product solution is orange colored. ν (CO) IR (THF) Cr(CO)₅ (THF) 2074 (w), 1938 (s), 1894 (m).¹¹

Reaction of CrMn(CO)₁₀⁻ with CH₃I. Usually 10 ml of THF was added to the mixture PPN⁺CrMn(CO)₁₀⁻ (0.05 mmol) and a 20-fold excess of CH₃I in a 10 ml vol. flask *via* cannula at ambient temperature. This THF solution was shaken for a few minutes prior to being kept in a water bath set at a specific temperature. This reaction was monitored by ν (CO) IR spectroscopy. Rates of reaction were observed by following the decrease in absorption of the intense CO band (1950 cm⁻¹) of the reactant which does not overlap with the band of products. Pseudo first order reaction conditions using at least a 20-fold excess of CH₃I were employed where appropriate. Rate constants were calculated using a linear least squares program for the first order rate plots of $\ln(A_t - A_\infty)$ vs. time, where A_t is the absorbance at time t and A_∞ is the absorbance at time infinity. Usually seven or more ν (CO) IR spectra were obtained for each k_{obs} . Products CH₃Mn(CO)₅,¹³ and ICr(CO)₅⁻¹⁴ were identified by their ν (CO) IR spectra as compared with previously isolated compounds characterized in our laboratories. CH₃Mn(CO)₅, ν (CO) IR (THF) 2103, 2001, 1981; PPN⁺ICr(CO)₅⁻, ν (CO) IR (THF) 2046, 1914, 1850; Na⁺ICr(CO)₅⁻, ν (CO) IR (THF) 2042, 1915, 1856.

Results and Discussion

Reactions of PPN⁺CrMn(CO)₁₀⁻ with PR₃. The heterobimetallic anion, (OC)₅CrMn(CO)₅⁻ was prepared by the ligand substitution of labile Cr(CO)₅(THF) with Mn(CO)₅⁻ in the THF at ambient temperature in high yields. This synthetic approach appears to be very efficient compared with either the procedure through the high temperature thermal displacement of CO from Cr(CO)₆ by Mn(CO)₅⁻¹⁰ or that by the metal exchange reaction¹² (Mn₂(CO)₁₀ + Cr₂(CO)₁₀²⁻). This anionic heterobimetallic compound, (OC)₅CrMn(CO)₅⁻ was tried to react with 20 fold excess of PR₃ under the pseudo 1st order conditions to yield Mn(CO)₅⁻, Cr(CO)₅PR₃ (major), and Cr(CO)₄(PR₃)₂ (minor) almost quantitatively. Kinetic study shows that this reaction was overall of 1st order with respect to [(OC)₅CrMn(CO)₅⁻]. The activation parameters ($\Delta H^\ddagger = 27.24$ kcal/mol; $\Delta S^\ddagger = 58.7$ e.u.) suggested a dissociative reaction mechanism in which the cleavage of Cr-Mn bond is likely to be the rate determining step. This dissociative character was further supported by the fact that neither electronic nor steric factor of the incoming ligand showed any change in the reaction rate.⁸ However, with one PR₃ ligand substitution either Mn or Cr moiety could lead to

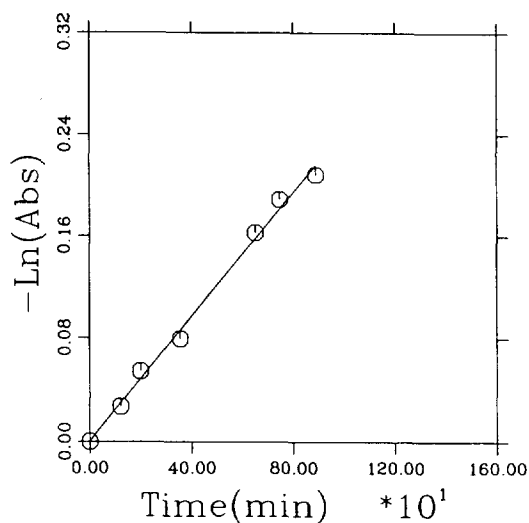


Figure 1. Pseudo 1st order plot of the reaction of PPN⁺CrMn(CO)₁₀⁻ (5.0 mM) with CH₃I (100 mM) in THF at 34°C.

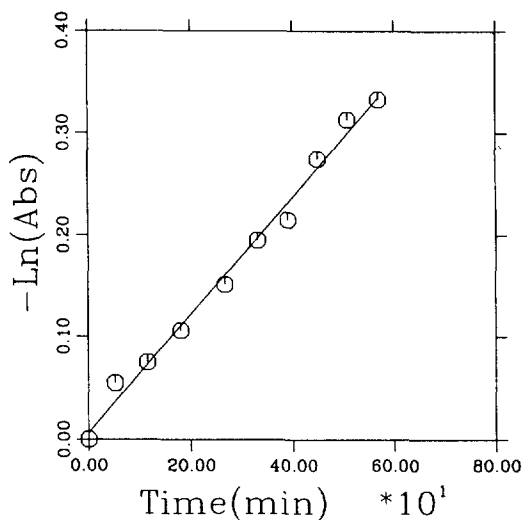


Figure 2. Pseudo 1st order plot of the reaction of Na⁺CrMn(CO)₁₀⁻ (5.0 mM) with CH₃I (100 mM) in THF at 34°C.

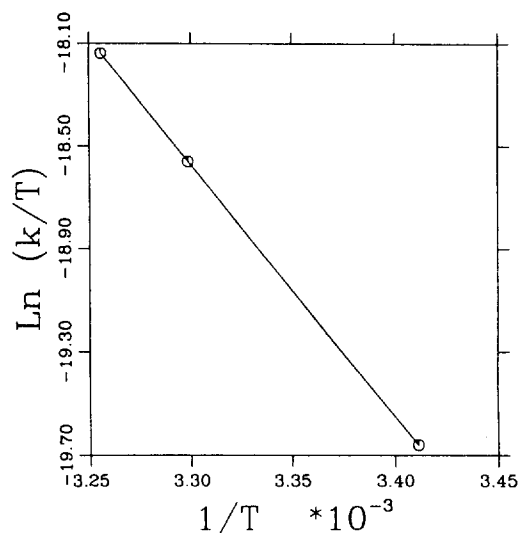
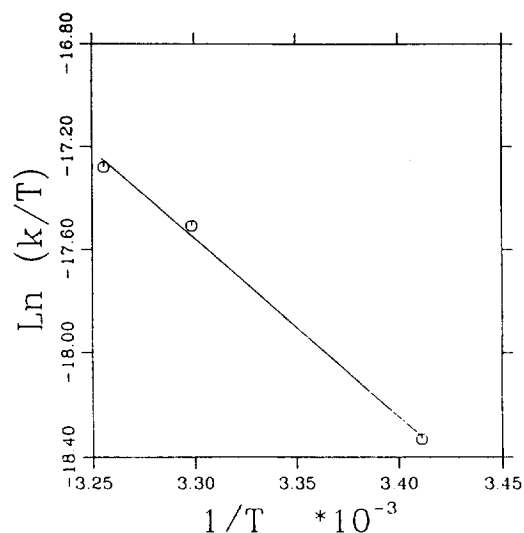
a drastic change in the mechanism. In this case, the electronic nature of the incoming ligand (PR₃) seems to be a dominant factor in determining the reaction rate of [(OC)₅CrMn(CO)₄PR₃]⁻ PPN⁺. Since PR₃ is regarded as a better σ -donor than CO, Mn(CO)₄PR₃⁻ is more basic toward the Lewis acid, Cr(CO)₅(THF) than the all CO analogue, Mn(CO)₅⁻. This enhanced basicity probably produces a stronger Mn-Cr bond than in the all-CO analogue, (OC)₅CrMn(CO)₅⁻. This greater electron density at Mn-Cr bond could preferentially cause the initial Cr-CO bond cleavage by the incoming ligand, PR₃, leading to the product, Cr(CO)₄(PR₃)₂ and Mn(CO)₄PR₃⁻. This reaction turned out to be of the 2nd order.⁹

$$\text{rate} = k_2[(\text{OC})_5\text{CrMn}(\text{CO})_4\text{PR}_3^-][\text{PR}_3].$$

Reaction of (OC)₅CrMn(CO)₅⁻ with CH₃I. Reactions of (OC)₅CrMn(CO)₅⁻ typically with a 20-fold excess of CH₃I were performed in THF and monitored by the IR carbonyl stretching vibration peak change.

Table 1. The Relationship between CH₃I Concentrations and the Rates (k_{obs}) of the Reaction of PPN⁺CrMn(CO)₁₀⁻ in THF at 30°C

Conc. [CrMn(CO) ₁₀ ⁻] M(×10 ³)	Conc. [CH ₃ I] M(×10 ³)	$K_{obs} \times 10^6, s^{-1}$
5.0	75	2.28 ± 0.14
5.0	100	2.64 ± 0.06
5.0	300	2.78 ± 0.12

**Figure 3.** Eyring plot for the reaction of PPN⁺CrMn(CO)₁₀⁻ (5.0 mM) with CH₃I (100 mM) in THF.**Figure 4.** Eyring plot for the reaction of Na⁺CrMn(CO)₁₀⁻ (5.0 mM) with CH₃I (100 mM) in THF.

The reaction of (OC)₅CrMn(CO)₅⁻ with CH₃I nearly quantitatively afforded Mn(CO)₅CH₃ and ICr(CO)₅⁻. As is shown in Figure 1 and 2, this reaction follows a first order dependence on [(OC)₅CrMn(CO)₅⁻]. The rate law is given by Eq. (1), as is evidenced by Table 1.

$$\text{rate} = k_1[(OC)_5CrMn(CO)_5^-] \quad (1)$$

Table 2. The Relationship between CH₃I Concentrations and the Rates (k_{obs}) of the Reaction of Na⁺CrMn(CO)₁₀⁻ in THF at 30°C

Conc. [CrMn(CO) ₁₀ ⁻] M(×10 ³)	Conc. [CH ₃ I] M(×10 ³)	$K_{obs} \times 10^6, s^{-1}$
5.0	75	7.57 ± 0.55
5.0	100	7.55 ± 0.14
5.0	300	7.86 ± 0.43

Table 3. Temperature Dependence of Kinetic Data for the Reaction of PPN⁺CrMn(CO)₁₀⁻ with CH₃I in THF

Conc. [CrMn(CO) ₁₀ ⁻] M(×10 ³)	Conc. [CH ₃ I] M(×10 ³)	Temp. (°C)	$K_{obs} \times 10^6, s^{-1}$
5.0	100	20	0.85 ± 0.10
5.0	100	30	2.64 ± 0.06
5.0	100	34	4.07 ± 0.25

Table 4. Temperature Dependence of Kinetic Data for the Reaction of Na⁺CrMn(CO)₁₀⁻ with CH₃I in THF

Conc. [CrMn(CO) ₁₀ ⁻] M(×10 ³)	Conc. [CH ₃ I] M(×10 ³)	Temp. (°C)	$K_{obs} \times 10^6, s^{-1}$
5.0	100	20	3.26 ± 0.15
5.0	100	30	7.55 ± 0.14
5.0	100	34	9.61 ± 0.32

Determination of the Activation Parameters for the Reaction of CrMn(CO)₁₀⁻M⁺ (M⁺=Na⁺, PPN⁺) with CH₃I in THF. The first order rate constants, k_1 were measured for this reaction as a function of temperature and the activation parameters were calculated from the Eyring plot (Figure 3, 4). The activation parameters of $\Delta H^\ddagger = 19.4 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -20.0 \pm 1.1$ e.u. with PPN⁺ salt suggest that rather associative character of the reactants may be involved in the rate determining step. This surprising result repeated with Na⁺ salt, too ($\Delta H^\ddagger = 13.7 \pm 0.9$ kcal/mol and $\Delta S^\ddagger = 37.0 \pm 0.4$ e.u.). In this case, Na⁺ may play a positive role at the rate determining step, leading to an increase in reaction rate. Usually more than two fold increase in reaction rates were observed for Na⁺ salt compared with those of PPN⁺ salt (Table 2).

This reaction was also observed to be temperature dependent (Table 3 and 4).

Solvent Effect on the Reaction Rate. Solvents such as toluene, THF, CH₃CN were utilized to determine the solvent dependence on the rates. In case of PPN⁺ salt, almost no change in rates was observed in the variation of solvent polarity ($\epsilon = 36.2$ to 2.4). However, for Na⁺ salt, about two times increase in rate was observed in both THF and CH₃CN compared with that in toluene. The decrease in rate in case of toluene may be related to the thermal stability of the possible intermediate, Cr(CO)₅L (L=solvent). Those coordinating solvents such as THF and CH₃CN may effectively stabilize the Lewis acid moiety Cr(CO)₅ by providing electron

Table 5. Solvent Dependence of Kinetic Data for the Reaction of $M^+CrMn(CO)_{10}^-$ ($M^+ = Na^+, PPN^+$) with CH_3I at $34^\circ C^a$

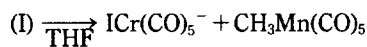
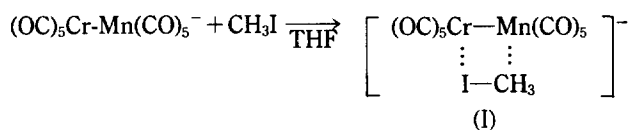
Complex	Solvent(ϵ) ^b	$k_{obs} \times 10^6, s^{-1}$
$PPN^+CrMn(CO)_{10}^-$	toluene (2.4)	4.80 ± 0.65
	THF (7.3)	4.07 ± 0.25
	CH_3CN (36.2)	4.97 ± 0.39
$Na^+CrMn(CO)_{10}^-$	toluene (2.4)	5.24 ± 0.58
	THF (7.3)	9.61 ± 0.32
	CH_3CN (36.2)	9.36 ± 0.59

^a $[CrMn(CO)_{10}^-] = 5.0$ mM; $[CH_3I] = 100$ mM. ^bMeasured at $25^\circ C$.

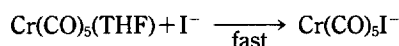
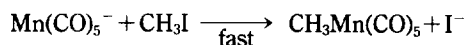
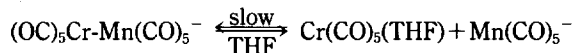
pair (Table 5). This situation can be further described in more detail later in the mechanistic considerations.

Mechanistic Considerations. Based on the kinetic data so far obtained, two reaction pathways (A and B) were proposed:

(A) Concerted Reaction Pathway



(B) Consecutive Reaction Pathway



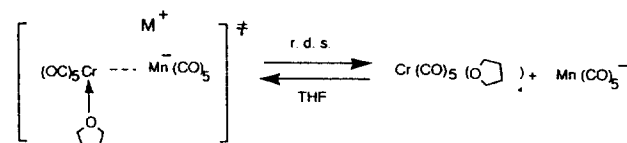
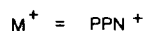
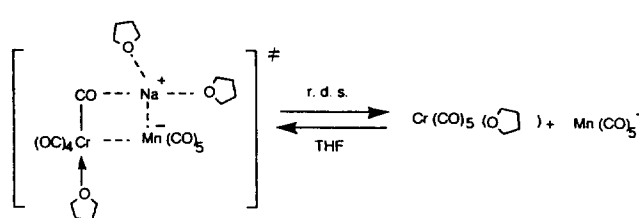
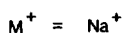
The proposed concerted reaction pathway seems to be apparently plausible. However, the fact that this reaction is overall of 1st order dependence with respect to $[(OC)_5CrMn(CO)_5^-]$ may rule out this possibility even though the negative entropy unit of activation may in part support this mechanism. It took several hours to finish this reaction in THF at the elevated temperatures ($20-34^\circ C$); however, $Mn(CO)_5^-$ reacted with CH_3I to produce $CH_3Mn(CO)_5$ and I^- within several minutes.

$Cr(CO)_5(THF)$, prepared from the photochemical reaction of $Cr(CO)_6$ in THF, was also observed to react very fast with I^- to yield $ICr(CO)_5^-$. The reaction of $(OC)_5CrMn(CO)_5^-$ with PR_3 was also proven to be overall of 1st order with respect to $[(OC)_5CrMn(CO)_5^-]$. These kinetic evidences could drive us to propose the consecutive reaction pathway. THF solvent molecules in this reaction mechanism may aggregate around the Cr-Mn bond at rate determining step so as to coordinate $Cr(CO)_5$ moiety to yield $Cr(CO)_5(THF)$ where the Cr-Mn bond is moderately loosened, as evidenced by the negative entropy change of activation (Table 6). $Cr(CO)_5(THF)$ can survive for hours under the N_2 atmosphere. Therefore, it could be a quite stable intermediate in the reaction. In this case the coordinating solvent could effectively stabilize the $16e^-$ species, $Cr(CO)_5$ moiety, thereby, leading

Table 6. Activation Parameters from the Reaction of $M^+CrMn(CO)_{10}^-$ ($M^+ = Na^+, PPN^+$) with CH_3I in THF^a

Complex	Activation parameters
$PPN^+CrMn(CO)_{10}^-$	$\Delta H^\ddagger = 19.4 \pm 0.3$ kcal/mol
	$\Delta S^\ddagger = -20.0 \pm 1.1$ e.u.
$Na^+CrMn(CO)_{10}^-$	$\Delta H^\ddagger = 13.7 \pm 0.9$ kcal/mol
	$\Delta S^\ddagger = -37.0 \pm 0.4$ e.u.

^a $[CrMn(CO)_{10}^-] = 5.0$ mM; $[CH_3I] = 100$ mM

**Figure 5.****Figure 6.**

to the corresponding products, such as $CH_3Mn(CO)_5$ and $ICr(CO)_5^-$.

Counterion Effect on Reaction Rates. It is obvious that bulky cation such as PPN^+ can hardly penetrate the coordination sphere of $(OC)_5CrMn(CO)_5^-$; Therefore, there would be no apparent interaction between the two ions. This situation may help us to believe that there is some electron density buildup on Cr-Mn bond though much of it may be drained out into the carbonyl bonds through $d\pi-p\pi^*$ back donation. This electron density localized on Cr-Mn bond may in part hinder the approach of the solvent molecule such as THF. However, in case of $Na^+(OC)_5CrMn(CO)_5^-$ reaction with CH_3I , Na^+ may interact with Cr-Mn bond so that the electron density on the Cr-Mn bond may be shifted in some degree to the Lewis acid, Na^+ . Therefore, the Cr-Mn bond may be somewhat weakened so that an increase in rate could be expected. The sodium cation may possibly interact with both the coordinated carbonyl ligand and the THF molecules (Figure 5 and 6). This phenomenon could also be evidenced by the even larger negative entropy change of activation ($\Delta S^\ddagger = -37.0 \pm 0.4$ e.u.) compared with that ($\Delta S^\ddagger = -20.0 \pm 1.1$ e.u.) in PPN^+ salt (Table 5 and 6).

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Study of Nonstoichiometry and Physical Properties of the $\text{Ca}_x\text{Eu}_{1-x}\text{FeO}_{3-y}$ System

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A series of samples of the $\text{Ca}_x\text{Eu}_{1-x}\text{FeO}_{3-y}$ ($x=0.00, 0.25, 0.50, 0.75,$ and 1.00) system has been prepared at $1,250^\circ\text{C}$ under an atmospheric air pressure. X-ray diffraction analysis of the solid solution assigns the structure of the compositions of $x=0.00, 0.25, 0.50,$ and 0.75 to the orthoferrite-type orthorhombic system, and that of $x=1.00$ to the brownmillerite-type orthorhombic one. The mole ratios of Fe^{4+} ion in the solid solutions or τ values were determined by the Mohr's salt analysis and nonstoichiometric chemical formulas of the system were formulated from $x, \tau,$ and y values. From the result of the Mössbauer spectroscopy, the coordination and magnetic property of the iron ion are discussed. The electrical conductivities are measured as a function of temperature. The activation energy is minimum at the composition of $x=0.25$. The conduction mechanism can be explained by the hopping of electrons between the mixed valences of Fe^{3+} and Fe^{4+} ions.

Introduction

Perovskite-type compounds,¹⁻⁷ ABO_3 , have been extensively studied because of their unique and applicable properties due to the mixed valence state of B ion and oxygen vacancy. The properties can be controlled by the substitution of lower valence metals such as $\text{Ca}^{2+}, \text{Sr}^{2+},$ and Ba^{2+} in place of higher one, Ln^{3+} , as well as the heating temperature and oxygen pressure maintained during the synthesis.

The orthoferrites⁸ have the formula of RFeO_3 where R is rare earth metals. The ferrite has the distorted perovskite structure in which the iron environment retains essentially octahedral but an octahedral chain along a c -axis has the form of zigzagging. The degree of zigzagging is determined to a large extent by the size of R ion. The larger the R ion, the more the chain stretches, the degree of zigzagging decreases. The substitution of larger alkaline earth metal in place of rare earth metal accelerates the phenomenon. The compositions of $x=0.50$ and 0.25 in the $\text{Sr}_x\text{La}_{1-x}\text{FeO}_{3-y}$ and $\text{Ba}_x\text{La}_{1-x}\text{FeO}_{3-y}$ systems^{6,9} have the ideal cubic perovskite structure in which Fe-O-Fe angle is 180° . In these systems, the valence state of Fe ion changes partly from

the trivalent to the tetravalent state with increasing Sr^{2+} or Ba^{2+} ion content and the electrical conductivity increases. The magnetic ordering temperature decreases with increasing x value, which is explained by the superexchange model.¹⁰

In the study of defect model for perovskite oxides, Roosmalen *et al.*¹¹ have suggested that in the SrMnO_{3-y} , the Mn^{3+} ions are coordinated trigonal bipyramidally and octahedrally, while the structure for SrFeO_{3-y} consists of tetragonally and octahedrally coordinated iron ions. Grenier *et al.*¹² have investigated the Mössbauer resonance effect on the $\text{Ca}_2\text{La}_{1-2y}\text{FeO}_{3-y}$ system in which the ratios of six and four coordinated iron ions increase with y value, while the variation of Néel temperature is not significant on the contrary, in $\text{Sr}_x\text{La}_{1-x}\text{FeO}_{3-y}$ and $\text{Ba}_x\text{La}_{1-x}\text{FeO}_{3-y}$ systems.

The CaFeO_3 ^{13,14} prepared only under higher oxygen partial pressure, has the crystal structure distorted slightly from cubic system and the charge disproportionation of Fe^{4+} ion into Fe^{3+} and Fe^{5+} ions occurs at the liquid helium temperature. The $\text{CaFeO}_{2.5}$ system^{15,16}, however, has the brownmillerite-type orthorhombic structure in which the oxygen vacancy ordering along $[101]$ strings occurs in every other (010) plane and a slight shift of the iron atoms in these planes