

Kinetic Studies on Dimer (CrMn(CO)₁₀)⁻ DisruptionsYong Kwang Park, In Sup Han, and Tae Sung Huh*¹

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A kinetic study of the heterobimetallic dimer disruption of PPN⁺CrMn(CO)₁₀⁻ by ligand L (L = CO, PR₃) is described. The rate was determined in several aprotic solvents. The results indicated that the reaction of PPN⁺CrMn(CO)₁₀⁻ with PR₃ is of first order with respect to [PPN⁺CrMn(CO)₁₀⁻] and the heterolytic Cr-Mn bond dissociation energy is approximately 27 kcal/mol.

Introduction

Heterobimetallic complexes can be prepared either by homolytic cleavage of dimer followed by recombination, Lewis acid-base adduct formation, or binuclear reductive elimination¹. Heterobimetallic complexes have a donor-acceptor metal-metal bond in which two electrons from the electron-rich metal moiety are donated to the other electron-deficient metal moiety. Thus, this electron-deficient transition metal group will satisfy the 18 electron rule². Some heterobimetallic hydrides such as HFeM(CO)₉⁻ (M = Cr, W) tend to undergo a thermal degradation to produce HFe(CO)₄⁻ and M(CO)₅ fragments (M = Cr, W). In that case the hydride is retained on the Fe metal. The M(CO)₅ fragments eventually decomposes to become M(CO)₆.³ This heterobimetallic reacts with HM(CO)₅⁻ to give HFe(CO)₄⁻ and μ-HM₂(CO)₁₀⁻. The heterobimetallic anion MnCr(CO)₁₀⁻, originally prepared and characterized by Graham and Anders⁴, is isoelectronic with the homobimetallic Mn₂(CO)₁₀ and Cr₂(CO)₁₀²⁻. Graham assumed that negative charge resides on Cr(CO)₅ moiety of CrMn(CO)₁₀⁻. This assignment was accepted by others.⁵⁻⁸ However, in analogy with the HFeCr(CO)₉⁻ anion it might be argued that the typically anionic fragment Mn(CO)₅⁻ will retain much of the negative charge. Therefore it is of importance and interest to see the implication of the thermal chemistry involving the donor-acceptor metal-metal bond cleavage. Thus a kinetic study of either PR₃ or CO promoted dimer disruption reaction of CrMn(CO)₁₀⁻ has been carried out.

Experimental

An inert-atmosphere glove box and Schlenk line and/or high-vacuum techniques were employed for most of sample transfers and sample manipulations. Infrared spectra were recorded on either an IBM FTIR/32, IBM FTIR/85, or Perkin-Elmer 238B spectrophotometer. ¹³C nuclear magnetic resonance spectra were recorded on the Varian XL200 MHz spectrometer. Reaction temperature control was achieved with either Haake A81 or Precision R20 thermostat. Most of weighing and transfers of compounds were done under an Ar atmosphere in the glove box (HE-63-P 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 from appropriate

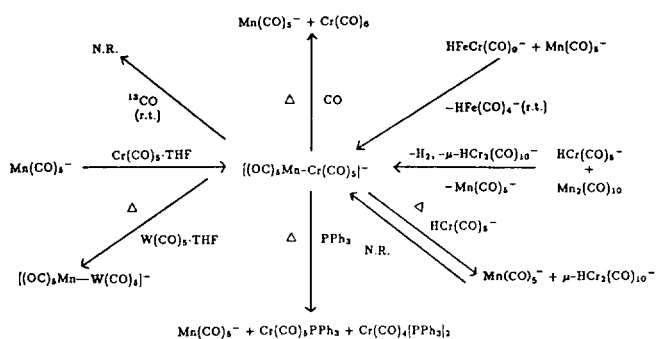
drying and O₂ scavenging agents: tetrahydrofuran (THF) and toluene, Na⁹/benzophenone/diglyme; methylene chloride, P₂O₅; acetonitrile, CaH₂ followed by P₂O₅; ethanol, Mg⁹/I₂.¹⁰ Common reagents were purchased from ordinary vendors and used as received without further purification.

Preparation of PPN⁺CrMn(CO)₁₀⁻. There is an alternative procedure for the preparation of CrMn(CO)₁₀⁻ in the literature.⁹ The following is, however, a synthesis of higher yield. To Na⁺Mn(CO)₅⁻ (4.5 mmol) was added the THF solution (150 ml) of Cr(CO)₅THF (4.5 mmol) freshly prepared from the photolytic reaction.¹¹ 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 added and an oil 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 and also a white precipitate formed on the bottom. The mother liquor was again passed through a celite column and transferred *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) 1988(m), 1950(s), 1923(w, sh), 1984(m), 1826(m).⁴

Preparations of M(CO)₅THF (M = Cr, W)¹¹. 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)₅THF, 1938(s), 1984(m); W(CO)₅THF, 1936(s), 1895(m).

Reaction of PPN⁺CrMn(CO)₁₀⁻ with PR₃ (R = C₆H₅, OCH₃, C₂H₅). Usually 10 ml of THF was added to the mixture of PPN⁺CrMn(CO)₁₀⁻ (0.05 mmol) and a 20-fold excess of PR₃ in a 10 ml vol. flask *via* cannula at ambient temperature. This THF solution was shaken for a few min prior to being kept in a thermostatted 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 (1990 cm⁻¹) of the reactant which is not overlapped with the band of the products. Pseudo first order reaction conditions using at least a 10-fold excess of PR₃ 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_∞) vs. time, there A_t is the absorbance at time *t* and A_∞ is the absorbance at time in-

*PPH⁺ = bis(triphenylphosphine) iminium cation.



finity. Ten or more $\nu(\text{CO})$ IR spectra were obtained for each k_{obs} . Products were identified by their $\nu(\text{CO})$ IR spectra as compared with previously isolated compounds characterized in our laboratories.

Attempted $^{13}\text{C}/^{12}\text{C}$ Exchange in $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$. A THF solution (10 ml) of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ (0.05 mmol) was prepared in a 100 ml vol. Schlenk flask tightly rubber septumed. This flask was then degassed by freeze-thaw cycles. Upon completion of degassing, 90% ^{13}C (Prochem, B.O.C. Ltd., London) was admitted to a slightly positive pressure and was kept stirring at ambient temperature for 66 hr. No apparent change in $\nu(\text{CO})$ IR spectra was observed.

Reaction of Anionic Dimer ($\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$) with CO. THF solution (10 ml) of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ (0.05 mmol) was prepared in a tightly rubber-septumed 100 ml vol. Schlenk flask. CO was bubbled through the reaction mixture solution *via* cannula. This container was then placed in a thermostated bath at 50 °C for more than 3 hr and this reaction was monitored by $\nu(\text{CO})$ IR spectroscopy.

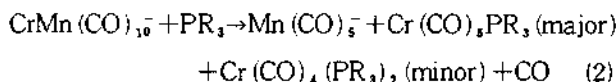
Thermal Reaction of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ with $\text{PPN}^+\text{HCr}(\text{CO})_5^-$. A THF solution (10 ml) of $\text{Cr}(\text{CO})_5\text{THF}$ (0.10 mmol) was added to $\text{PPN}^+\text{Mn}(\text{CO})_5^-$ (0.10 mmol) in a tightly septumed 100 ml vol. Schlenk flask *via* cannula. This solution was then stirred at ambient temperature for about 2 hr and was confirmed by $\nu(\text{CO})$ IR spectra to have $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$. A THF solution (10 ml) of $\text{PPN}^+\text{HCr}(\text{CO})_5^-$ (0.10 mmol) was added to the reaction mixture solution. After attaching a water-cooling condenser to the Schlenk flask, this solution was placed in a silicone oil bath set at 80 °C for more than 4 hr. This reaction was monitored both by $\nu(\text{CO})$ IR spectroscopy and ^1H -NMR.

Results and Discussion

A. Reaction of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$. The heterobimetallic anion $\text{CrMn}(\text{CO})_{10}^-$ was first prepared by Graham and Anders⁴ through the high temperature thermal displacement of CO from $\text{Cr}(\text{CO})_6$ by $\text{Mn}(\text{CO})_5^-$. This heterobimetallic complex was also made by the metal exchange reaction route ($\text{Mn}_2(\text{CO})_{10} + \text{Cr}_2(\text{CO})_{10}^{2-}$) of Ruff⁹; however, both synthetic approaches are of lower yield than the synthesis of $\text{CrMn}(\text{CO})_{10}^-$ through the reaction of $\text{Mn}(\text{CO})_5^-$ with $\text{Cr}(\text{CO})_5\text{THF}$ in THF at ambient temperature.

A summary of the reactions which were explored for the mixed metal anion $\text{CrMn}(\text{CO})_{10}^-$ are found in Scheme 1. Three synthetic routes are found therein: (1) Reaction of $\text{Mn}(\text{CO})_5^-$ with $\text{Cr}(\text{CO})_5\text{THF}$ (the synthesis of choice) in THF at

ambient temperature produced $\text{CrMn}(\text{CO})_{10}^-$ ($t_{1/2} \sim 10$ min). (2) $\text{CrMn}(\text{CO})_{10}^-$ and $\text{HFeCr}(\text{CO})_9^-$ were also obtained from the metal exchange reaction of $\text{HFeCr}(\text{CO})_9^-$ with $\text{Mn}(\text{CO})_5^-$ in THF at room temperature for about three hours. (3) $\text{HCr}(\text{CO})_5^-$ reacts with $\text{Mn}_2(\text{CO})_{10}$ to yield $\text{CrMn}(\text{CO})_{10}^-$ (10~20%) as a minor product in addition to $\mu\text{-HCr}_2(\text{CO})_{10}^-$, $\text{Mn}(\text{CO})_5^-$, and H_2 gas at room temperature in THF. Another example of metal exchange reaction was observed in the reaction of $\text{CrMn}(\text{CO})_{10}^-$ with $\text{HCr}(\text{CO})_5^-$ in THF reflux for hours to produce $\mu\text{-HCr}_2(\text{CO})_{10}^-$ and $\text{Mn}(\text{CO})_5^-$. However, the reverse reaction did not occur under the same condition. Therefore $\text{CrMn}(\text{CO})_{10}^-$ seems more robust than $\text{HFeCr}(\text{CO})_9^-$ but less stable than $\mu\text{-HCr}_2(\text{CO})_{10}^-$. It is very interesting that this heterobimetallic species $\text{CrMn}(\text{CO})_{10}^-$ undergoes a metal exchange with $\text{W}(\text{CO})_5\text{THF}$ to yield $\text{W}(\text{CO})_5\text{Mn}(\text{CO})_{10}^-$ (ca. 10~15% yield) in THF at 50 °C for 3 hours. But the reverse reaction ($\text{WMn}(\text{CO})_{10}^-$ with $\text{Cr}(\text{CO})_5\text{THF}$) did not occur at the same conditions (in THF at 50 °C for 3 hr). This reaction was monitored by $\nu(\text{CO})$ IR. Arndt observed a similar result ($\text{HFeW}(\text{CO})_9^-$) from the reaction of $\text{HFeCr}(\text{CO})_9^-$ with $\text{W}(\text{CO})_5\text{THF}$ in THF at ambient temperature on time of mixing.³ Though $\text{CrMn}(\text{CO})_{10}^-$ seems moderately robust, this heterobimetallic complex is slowly disrupted at elevated temperature by either CO or PR_3 ($\text{PR}_3 = \text{PPh}_3, \text{P}(\text{OCH}_2)_3, \text{P}(\text{C}_2\text{H}_5)_3$) (Eq. 1, 2).



^{13}C (2~3 fold excess) was mixed with $\text{CrMn}(\text{CO})_{10}^-$ in THF at ambient temperature for days; however, no disruption by ^{13}C was observed. Neither was there CO ligand exchange. $\text{PPN}^+\text{Mn}(\text{CO})_5^-$ reacted with $\text{W}(^{13}\text{C})_5\text{THF}$ in THF and then was monitored by ^{13}C -NMR in $d^6\text{-THF}/d^8\text{-THF}$ (1:1 vol. ratio). $\text{PPN}^+\text{WMn}(\text{CO})_{10}^-$ was also prepared in the same way and ^{13}C -NMR spectrum for $\text{PPN}^+\text{WMn}(\text{CO})_{10}^-$ was run for spectral comparison. $\text{PPN}^+\text{WMn}(\text{CO})_{10}^-$ has four singlets (δ 207.1 ppm (peak ratio 4), 205.7(1), 202.0(1), 200.6(4)); The former two peaks may correspond to CO's of $\text{Mn}(\text{CO})_5$ moiety (207.1 ppm (4); 4 CO's equatorial to $\text{Mn}(\text{CO})_5$ moiety, 205.7(1) 1 CO axial to $\text{Mn}(\text{CO})_5$ moiety). The latter two may correspond in the same reason to CO's of $\text{W}(\text{CO})_5$ moiety. However, $\text{PPN}^+\text{WMn}(\text{CO})_5(^{13}\text{C})_5^-$ showed two similar-sized broad peaks (205.3, 199 ppm). If the ^{13}C 's on W ($^{13}\text{C})_5$ moiety did not exchange ^{12}C with $\text{Mn}(\text{CO})_5$ moiety in $\text{PPN}^+\text{WMn}(\text{CO})_5(^{13}\text{C})_5^-$, the peaks for ^{13}C 's of W ($^{13}\text{C})_5$ moiety would be much larger than those for CO's of $\text{Mn}(\text{CO})_5$ moiety due to the ^{13}C natural abundance in W ($^{13}\text{C})_5$ moiety. Therefore, there seems to be a scrambling between ^{13}C and ^{12}C in this heterobimetallic complex.

B. Reactions of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ with PR_3 ($\text{R} = \text{C}_6\text{H}_5, \text{OCH}_3, \text{C}_2\text{H}_5$). Reactions of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ with typically a 20-fold excess of PR_3 were performed in THF and monitored with time by $\nu(\text{CO})$ IR. This reaction of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ with PR_3 produced $\text{PPN}^+\text{Mn}(\text{CO})_5^-$ and $\text{Cr}(\text{CO})_5\text{PR}_3$; $\text{Cr}(\text{CO})_4(\text{PR}_3)_2$ was observed in less amount as a minor product at high temperature (for example, up to 20%, $\text{Cr}(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$; 65 °C). As is shown in Figure 1. The reaction follows a first order dependence on $[\text{CrMn}(\text{CO})_{10}^-]$ and there is no dependence of reaction rate on $[\text{PR}_3]$. The

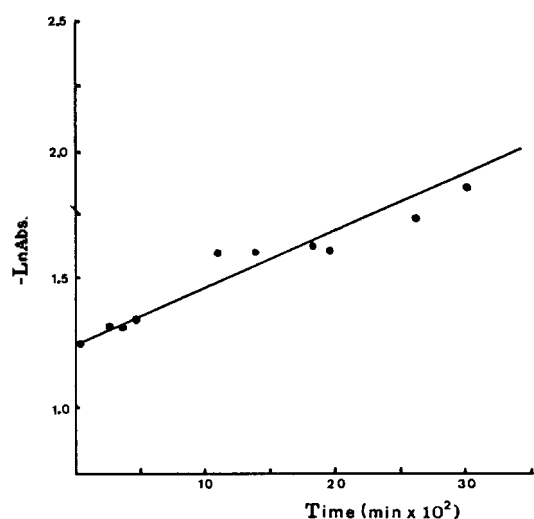


Figure 1. Pseudo-first plot of the reaction of PPN⁺CrMn(CO)₁₀⁻ with P(C₆H₅)₃ (20 fold excess) in THF at 40.0°C.

Table 1. The Relationship Between P(C₆H₅)₃ Concentrations and the Reaction Rate (*k*_{obs}) of the Reaction of PPN⁺CrMn(CO)₁₀⁻ with P(C₆H₅)₃ in THF at 40°C

Conc. [CrMn(CO) ₁₀ ⁻] M (× 10 ³)	Conc. (P(C ₆ H ₅) ₃) M (× 10 ³)	<i>k</i> _{obs} × 10 ⁶
5.0	25	3.1 ± 0.1
5.0	50	3.2 ± 0.8
5.0	100	3.3 ± 0.3
5.0	200	2.8 ± 0.3
5.0	300	3.1 ± 0.3

rate law is given by Eq. 3, as is evidenced by Table 1.

$$\text{Rate} = k_1 [\text{CrMn(CO)}_{10}^-] \quad (3)$$

C. Determination of the Activation Parameters for the Reaction of PPN⁺CrMn(CO)₁₀⁻ with P(C₆H₅)₃ in THF. The first order rate constants, *k*₁, were measured for the reaction of PPN⁺CrMn(CO)₁₀⁻ with P(C₆H₅)₃ in THF as a function of temperature and the activation parameters were calculated from Arrhenius plot is given in Figure 2. The activation parameters of $\Delta H^\ddagger = 27 \pm 2$ kcal/mol and $\Delta S^\ddagger = 59 \pm 4$ e.u. suggest that either a metal-metal bond or metal-carbonyl bond is breaking at the rate-determining step. PPN⁺Mn(CO)₅⁻ (0.05 mmol) was added to the THF solution of PPN⁺CrMn(CO)₁₀⁻ (0.05 mmol) and 20 fold excess of P(C₆H₅)₃ at 65°C. The *k*_{obs} for this reaction was $(6.8 \pm 0.6) \times 10^{-5}$ s⁻¹ compared to *k*_{obs} $(7.7 \pm 1.0) \times 10^{-5}$ s⁻¹ for the same reaction under the same conditions without adding PPN⁺Mn(CO)₅⁻. This slight difference in rates may be within the experimental error range; therefore, there seems to be no clear rate decrease caused by adding Mn(CO)₅⁻ to the reaction solution of CrMn(CO)₁₀⁻ and P(C₆H₅)₃. Since PPh₃ is a more effective competitor for Cr(CO)₅ than Mn(CO)₅⁻, this result is inconclusive to Mn-Cr reversible bond cleavage.

D. Ligand Effect on the Reaction Rate. As shown in Table 1, the reaction rates were independent of P(C₆H₅)₃ concentrations at a [P(C₆H₅)₃]/[CrMn(CO)₁₀⁻] ratio greater than 5 or more. There is almost no change within experimen-

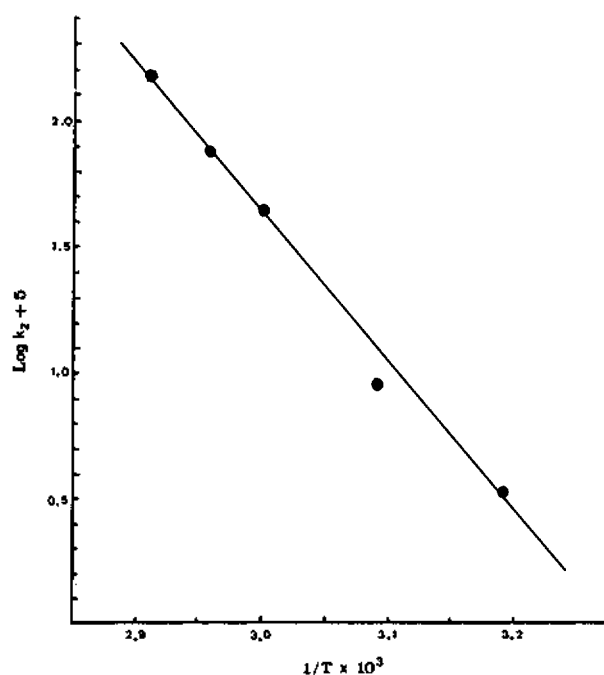


Figure 2. Arrhenius plot for the reaction of PPN⁺CrMn(CO)₁₀⁻ with P(C₆H₅)₃ (20-fold excess) in THF.

Table 2. Temperature Dependence of Kinetic Data for the Reaction of PPN⁺CrMn(CO)₁₀⁻ with 20 Fold Excess of P(C₆H₅)₃^b in THF

Temp. (°C)	<i>k</i> _{obs} ^c × 10 ⁶ , M ⁻¹ s ⁻¹ ^b	Activation energy parameters ^b
40	3.3 ± 0.3	
50	9.0 ± 0.5	
60	44 ± 8	$\Delta H^\ddagger = 27 \pm 2$ (kcal/mol)
60	39 ± 4	$\Delta S^\ddagger = 59 \pm 4$ (e.u.)
65	77 ± 10	
70	152 ± 10	
70	147 ± 11	

^a[PPN⁺CrMn(CO)₁₀⁻]; 5.0 mmol. ^b[P(C₆H₅)₃]; 100 mmol. ^cConfidence limits at 90%.

tal errors in the reaction rates (*k*_{obs} = 4×10^{-5} M⁻¹ s⁻¹) with changes in ligand (PR₃; R = C₆H₅, OCH₃, C₂H₅) at 60°C. That is to say, neither sigma donation effect nor pi accepting effect of these ligands effects the reaction rate. This result firmly establishes the dissociative character of the rate determining step.

E. Solvent Effect on the Reaction Rate. Several solvents such as CH₃CN, C₂H₅OH, THF, C₆H₅CH₃ were used to determine the solvent effect on the rate of the reaction of PPN⁺CrMn(CO)₁₀⁻ with a 20-fold excess of P(C₆H₅)₃ at 65°C. Table 3 shows clearly that polar solvent activates this reaction. Polar solvent may assist in Cr-Mn bond breaking by good solvation. Therefore, the nonpolar or non-coordinating solvent toluene is found to be the least-effective one of these solvents as expected in this respect.

In conclusion, the reaction of CrMn(CO)₁₀⁻ with PR₃ is of first order with respect to [PPN⁺CrMn(CO)₁₀⁻]. ΔH^\ddagger values of 25 to 30 kcal/mol are typical of M-CO dissociation processes. Nevertheless if a M-CO dissociation was applicable

Table 3. Solvent Dependence of Kinetic Data for Reaction of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ with 20 Fold Excess of $\text{P}(\text{C}_6\text{H}_5)_3$ in THF at 60°C

Solvent	Dielectric Const.*	$k_{obs} \times 10^5$
CH_3CN	36.2	30.2 ± 0.6
EtOH	24.3	14 ± 2
THF	7.3	8 ± 1
$\text{C}_6\text{H}_5\text{CH}_3$	2.4	6 ± 1

*Measured at 25°C.

here one would expect neutral disubstituted product $\text{Cr}(\text{CO})_4(\text{PR}_3)_2$ to dominate. This was not the result; in fact only 20% of the disubstituted product was obtained at 65°C. The product distribution (major $\text{Cr}(\text{CO})_5\text{PR}_3$ and $\text{PPN}^+\text{Mn}(\text{CO})_5^-$; minor $\text{Cr}(\text{CO})_4(\text{PR}_3)_2$) may suggest the corresponding bond strength comparisons ($\text{Cr}-\text{Mn} < \text{Cr}-\text{CO} < \text{Mn}-\text{CO}$). This comparison of bond strength may be related to the electron density located on each metal center. In fact, it is assumed that more electron density is located on the Mn than Cr in $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$; therefore, the more electron density on Mn would lead to the stronger Mn-CO bond than the Cr-CO bond. The electron density on Mn moiety of $\text{PPN}^+\text{CrMn}(\text{CO})_{10}^-$ eventually returns to the $\text{Mn}(\text{CO})_5^-$ on the disruption by PR_3 . This result may be inconsistent with Graham's observation that negative charge resides on $\text{Cr}(\text{CO})_5$ moiety of $\text{CrMn}(\text{CO})_{10}^-$.⁴ The observation that there was no depression in reaction rate upon adding $\text{Mn}(\text{CO})_5^-$ (equimolar amount of $\text{CrMn}(\text{CO})_{10}^-$) to the reaction solution may be ascribed to the result ($\text{W}(\text{CO})_5\text{PPh}_3$ (~90%) and $\text{WMn}(\text{CO})_{10}^-$ (~10%)) of the previous competition reaction of $\text{Mn}(\text{CO})_5^-$ and 20 fold excess of PPh_3 with $\text{W}(\text{CO})_5^-$ in THF at 22°C. From these re-

sults it is assumed that metal-metal bond cleavage is involved in the rate-determining step and therefore the heterolytic Cr-Mn bond dissociation energy may be approximately 27 kcal/mol.

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Excitation Mechanism of Fluorescent Polycyclic Aromatic Amines and Polycyclic Aromatic Hydrocarbons in Peroxyoxalate Chemiluminescence Reactions

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The excitation mechanism of polycyclic aromatic amines (amino-PAHs) and polycyclic aromatic hydrocarbons (PAHs) for the chemiluminescence arising from the reaction between oxalate ester, bis(2,4,6-trichlorophenyl)oxalate (TCPO) or bis(2,4-dinitrophenyl)oxalate (DNPO) and hydrogen peroxide has been studied in terms of the excitation efficiencies to singlet excitation energies and the oxidative half-wave potentials. As a result of the study, the excitations of both amino-PAHs and PAHs appear to involve the charge transfer type of energy transfer. However the chemiluminescence efficiency corrected for fluorescence quantum yield of the amino-PAHs are varied more sensitively to the oxidative half-wave potential than that of PAHs possibly due to the large difference in solvation energy between the compounds and their ions.

Introduction

During the past years after the discovery of peroxyoxalate chemiluminescence (POCL), much attention has been focused on developing efficient chemical light source as a cold light.^{1,2} Recently, the excellent sensitivity of POCL as a detection of fluorescent compounds has been utilized for

chemical analysis by high-performance liquid chromatography (HPLC).³⁻⁷

Some researchers studied that various PAHs having emission spanning the visible-infrared spectrum could be excited by the intermediate(s) produced from a reaction between aryl oxalate ester and hydrogen peroxide.⁸⁻¹⁰ Ryan *et al.* reported that fluorescers with low excitation energy ap-