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Laser Photolysis Study of Dirhenium Decacarbonyl: Evidence for a Nonradical Primary Process

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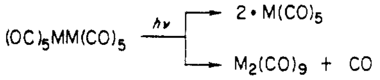
The photochemistry of $Re_2(CO)_{10}$ in cyclohexane was investigated by nanosecond laser flash photolysis (355-nm excitation). Experimental results verified that there are two photodissociation processes: one the well-known metal–metal bond scission to produce $\cdot Re(CO)_5$ and the other the newly found nonhomolytic process of dissociative CO loss. The CO dissociation process is more dominant in the photolysis of $Re_2(CO)_{10}$ than in that of $Mn_2(CO)_{10}$.

Introduction

It is now believed that the photoexcitation of $Mn_2(CO)_{10}$ in hydrocarbons may result in two primary processes: homolytic metal–metal bond cleavage to give $\cdot Mn(CO)_5$ (eq 1) and dissociative CO loss without homolytic metal–metal bond cleavage to produce $Mn_2(CO)_9$ (eq 2).[2-5] Use of IR spectroscopic detection has revealed that presence of a bridging CO in the transient $Mn_2(CO)_9$ in 77 K matrices[6] and also in hydrocarbon solutions,[7] and the semibridging of CO was established in a low-temperature matrix polarization study.[8]



$$(OC)_5MM(CO)_5 \xrightarrow{h\nu} 2\cdot M(CO)_5 \quad (1)$$

$$(OC)_5MM(CO)_5 \xrightarrow{h\nu} M_2(CO)_9 + CO \quad (2)$$

There is, however, no information on the primary photochemical processes of $Re_2(CO)_{10}$ in solution, other than process 1.[9-11] It was of interest to determine whether a second process in addition to bond homoloysis (1) is occurring in the photolysis of $Re_2(CO)_{10}$.

We report here evidence for the existence of a second process involving dissociative CO loss in the photolysis of $Re_2(CO)_{10}$ in solution. Interestingly, the occurrence of such a second primary process in the photolysis of $Mn_2(CO)_{10}$ and $Re(CO)_{10}$ in gas phase has been reported recently.[12]

Experimental Section

$Re_2(CO)_{10}$ was purchased from Strem Chemicals, Inc., and was used without further purification. Cyclohexane stored on K–Na alloy was added to sample compartments in vacuo. Then, CO or Ar was admitted through a side arm with a Teflon stopcock after the sample cells had been hermetically sealed. The concentrations of $[Re_2(CO)_{10}]$ sample solutions were approximately 1.0×10^{-2} mol dm^{-3}.

The third harmonic of a Nd:YAG laser (1.5 mJ, 5-ns pulse duration) was used as the nanosecond excitation light source. For the decay kinetics study of the absorbance change at 500 nm, a pulsed Xe lamp (350 W) was used as the monitoring light source. The excitation light beam was aligned perpendicularly to the monitoring light path (l_{eff} = 0.3 cm) at the desired wavelength. In order to observe the time dependence of the absorbance change at 430 nm, a CW Xe lamp was used as the monitoring light source. The excitation light beam was aligned coaxially with the monitoring light path (l_{eff} = 0.1 cm) at the desired wavelength.

Results and Discussion

Time-resolved absorption spectra were observed for intermediates following $Re_2(CO)_{10}$ photolysis in cyclohexane under 1 atm of Ar after 355-nm excitation. The spectra at 0.5, 3.0, and 30 μs after excitation are shown in Figure 1. The observed transient absorption spectrum which is shown by curve 1 in Figure 1 is composed of two components. One absorption band with λ_{max} around 550 nm disappears within 20 μs. The absorption spectrum of the longer lived component[13] with λ_{max} at 420 nm extends to longer than 600 nm.

The absorption band (λ_{max} = 550 nm) is attributed to $\cdot Re(CO)_5$ on the basis of the absorption spectrum,[10] its decay kinetics, and efficient quenching with CCl_4. The time dependence of the absorbance $(A(t))$ at 500 nm follows second-order kinetics as shown in Figure 2, which gives the observed value $k_3/\epsilon_{500}l_{eff} = (1.5 \pm 0.2) \times 10^{-7}\ s^{-1}$; k_3 and ϵ_{500} are the rate constant for the recombination reaction (3) and the molar extinction coefficient of $\cdot Re(CO)_5$ at 500 nm, respectively.

$$2\ \cdot Re(CO)_5 \xrightarrow{k_3} Re_2(CO)_{10} \quad (3)$$

By use of the reported value, $\epsilon_{500} = 800\ mol^{-1}\ dm^3\ cm^{-1}$ in ethanol,[10] k_3 is determined to be $(3.6 \pm 0.5) \times 10^9\ mol^{-1}\ dm^3\ s^{-1}$. This is in good agreement with the reported values of $3.7 \times 10^9\ mol^{-1}\ dm^3\ s^{-1}$ in hexane[9a] and $5.4 \times 10^9\ mol^{-1}\ dm^3\ s^{-1}$ in ethanol.[10]

When CCl_4 (1.67×10^{-2} mol dm^{-3}) is added to the solution, the decay becomes faster and follows pseudo-

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(13) The long-lived transient and its observed reaction with excess CO during the flash photolysis of $Re_2(CO)_{10}$ in isooctane have been noted in the ref 10.

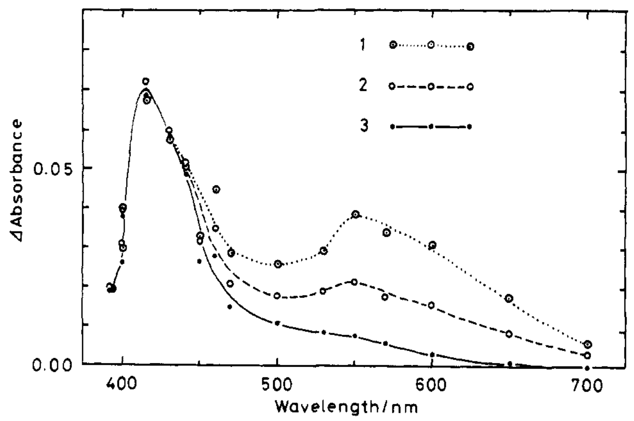

Figure 1. Transient absorption spectra of $Re_2(CO)_{10}$ in cyclohexane: (1) curve 1, 0.5 μs; (2) curve 2, 3.0 μs: and (3) curve 3, 30 μs after 355-nm excitation.

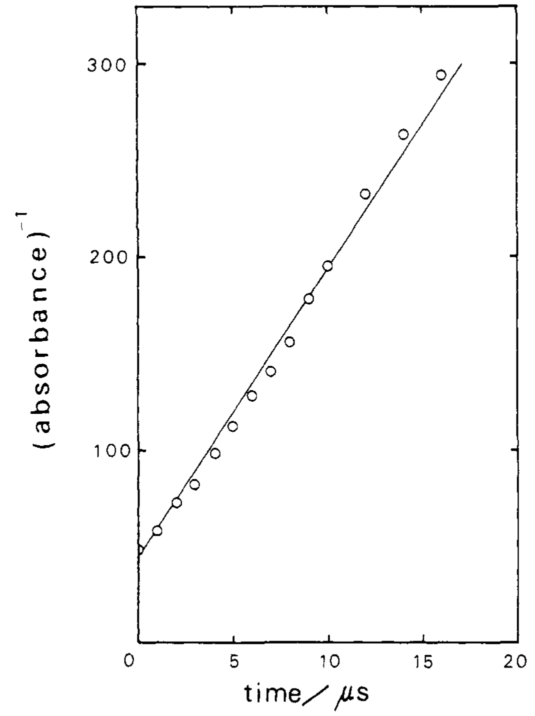

Figure 2. Time dependence of absorbance of $Re_2(CO)_{10}$ in cyclohexane at 500 nm under 1 atm of Ar after 355-nm excitation.

first-order kinetics. The rate constant for the reaction of $\cdot Re(CO)_5$ with CCl_4 (k_{CCl_4}) is estimated to be 5.8×10^7 mol^{-1} dm^3 s^{-1}. This agrees closely with the reported values 3.9×10^7 mol^{-1} dm^3 s^{-1} in ethanol[10] and 4.9×10^7 mol^{-1} dm^3 s^{-1} in cyclohexane.[9c]

The other transient species with a λ_{max} at 420 nm has a longer lifetime ($\tau \sim 30$ ms) under 1 atm of Ar, and the decay of the absorbance at 430 nm follows second-order kinetics down to more than 70% decrease as shown in Figure 3. The rate constant for the second-order reaction (k'_2) was obtained as $(1.3 \pm 0.5) \times 10^3$ s^{-1}. When 1 atm of CO is admitted, the decay rate of the absorbance at 430 nm increases and the decay follows pseudo-first-order kinetics with a rate constant (k'_{obsd}(430 nm)) of $(4.4 \pm 0.4) \times 10^2$ s^{-1} as shown in Figure 4. Addition of CCl_4 to the Ar-filled system affects neither the absorbance change nor the decay rate of the absorption band around 430 nm. These facts clearly show that the second transient absorption can be attributed to a dirhenium species, $Re_2(CO)_9$, formed via a nonradical path similar to the CO dissociation process observed in the $Mn_2(CO)_{10}$ system. From the observed pseudo-first-order and the second-order rate constants (k'_{obsd}(430 nm)) and k'_2 ($= k_4/\epsilon_{430}l_{eff}$)), the second-order rate constant (k_4) for reaction 4 was estimated to be 4.4×10^4 mol^{-1} dm^3 s^{-1} on the assumption that the concentration of CO in cyclohexane at 1 atm of CO pressure is 1×10^{-2} mol dm^{-3}.[14] The rate constant for the

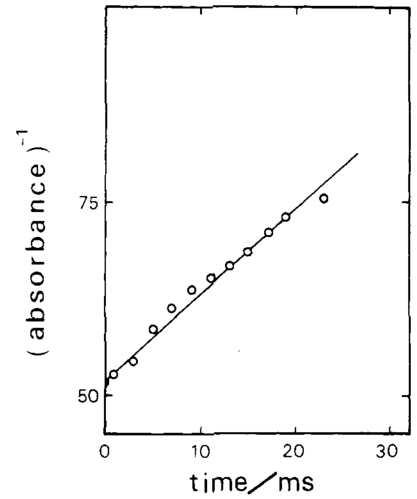

Figure 3. Time dependence of absorbance of $Re_2(CO)_{10}$ in cyclohexane at 430 nm under 1 atm of Ar after 355-nm excitation.

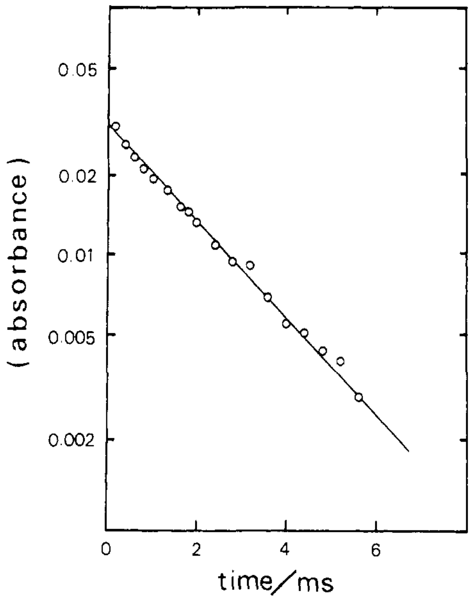

Figure 4. Time dependence of absorbance of $Re_2(CO)_{10}$ in cyclohexane at 430 nm under 1 atm of CO after 355-nm excitation.

$$Re_2(CO)_9 + CO \xrightarrow{k_4} Re_2(CO)_{10} \qquad (4)$$

recombination of $Re_2(CO)_9$ with CO is 1 order of magnitude smaller than that for $Mn_2(CO)_9$, 4.2×10^5 mol^{-1} dm^3 s^{-1}.[15]

With the use of the estimated k_4, ϵ_{430} was evaluated as 340 ± 150 mol^{-1} dm^3 cm^{-1}. The quantum yield ratio between the two reaction processes (1) and (2), Y_1/Y_2, also was estimated as 0.13 at 355-nm excitation based on ϵ_{430} and ϵ_{500} estimated in the previous paper.[10] The Y_1/Y_2 value for $Re_2(CO)_{10}$ indicates that the CO dissociation process is a much more dominant process over metal–metal bond homolysis compared with the $Mn_2(CO)_{10}$ system, in which Y_1/Y_2 at 355-nm excitation is 1.1 ± 0.2.[5,16]

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Although there is no clear explanation for the slower reaction of $Re_2(CO)_9$ with CO compared with that of $Mn_2(CO)_9$ at present, it may show a semibridging of CO also in $Re_2(Co)_9$, as in $Mn_2(CO)_9$.[8] This deserves further study by other techniques such as IR spectroscopy. The present study shows that the nonradical process (2) is important in the photolysis of $Re_2(CO)_{10}$ in hydrocarbon.

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Registry No. $Re_2(CO)_{10}$, 14285-68-8; $Re(CO)_5$, 53796-42-2; CO, 630-08-0; cyclohexane, 110-82-7.

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[16] Y_1/Y_2 was estimated to be 0.74 ± 15^5 on the assumption that the molar extinction coefficient of $\cdot Mn(CO)_5$ at 830 nm is equal to that of $Mn_2(CO)_9$ at 500 nm. (a) Kobayashi, T.; Ohtani, H.; Noda, H.; Teratani, S.; Yamazaki, H.; Yasufuku, K., submitted for publication in *Organometallics.*

Thermolytic Behavior of Some 1-Oxa-Substituted 1-(Trimethylsilyl)cyclopropanes

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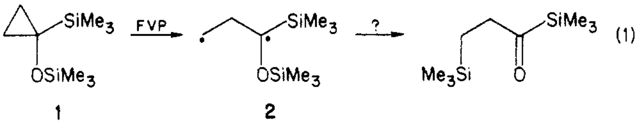
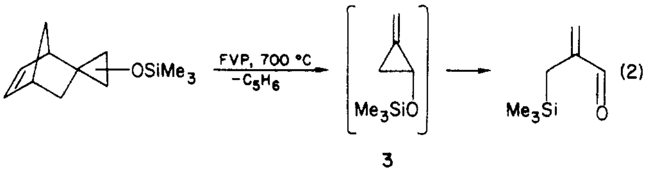
The flash vacuum pyrolysis (FVP) of 1-(trimethylsiloxy)-1-(trimethylsilyl)cyclopropane at 625 °C afforded mostly hexamethyldisiloxane and *cis*- and *trans*-1-(trimethylsiloxy)-3-(trimethylsilyl)propene. Evidence is presented supporting the intermediacy of 3-(trimethylsiloxy)-3-(trimethylsilyl)propene in this process. The thermolytic behavior of both 1-methyl-1-(trimethylsiloxy)cyclopropane and 1-ethoxy-1-(trimethylsilyl)cyclopropane shows similarities to that above, but FVP of 1-acetoxy-1-(trimethylsilyl)cyclopropane affords 3-acetoxy-2-(trimethylsilyl)propene by an alternate process.

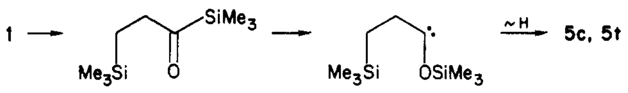
An interest in acylsilane chemistry led us to investigate the flash vacuum pyrolysis (FVP) of 1-(trimethylsiloxy)-1-(trimethylsilyl)cyclopropane (1) as a possible route to β-silylacylsilanes (eq 1). By way of analogy, Bloch and Denis have proposed[1] that a similar O to C transfer of a silyl group occurs within a species such as **3**, where ring opening is possibly facilitated by the intermediacy of a trimethylenemethane (eq 2). Although these same authors reported that other siloxycyclopropanes were stable under these conditions, our ready access to **1**[2] and the possibility that an α-silyl group would lend additional stability[3] to the trimethylene species **2** encouraged our efforts.



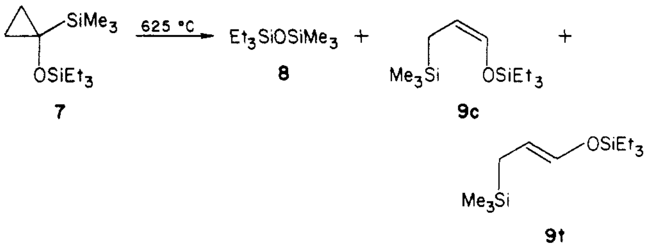


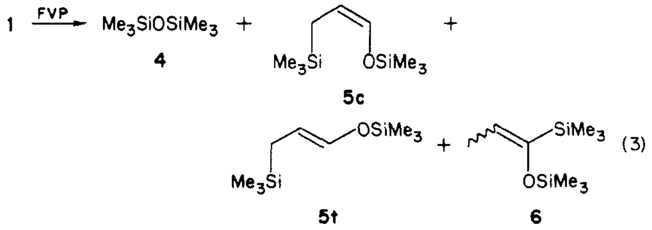
Thermolysis of **1** did indeed lead to reorganized products. Thus, FVP at 600 °C converted 90% of **1** to a mixture consisting almost entirely[4] of **4**, **5c**, **5t**, and **6** (37:45:15:4 mole ratio). At 625 °C, total conversion occurred to these same products in a 29:48:20:3 ratio (eq 3).

Scheme I



Scheme II





The formation of **4** might reasonably be attributed to a geminal elimination[5] within **1** producing cyclo-

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