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# Time-Resolved Infrared Studies of Gas-Phase Coordinatively Unsaturated Photofragments $(\eta^5-C_5H_5)Mn(CO)_x$ (x = 2 and 1)

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Time-resolved infrared spectroscopy is used to study the coordinatively unsaturated species  $(\eta^5-C_5H_5)Mn(CO)_x$  (x = 2 and 1) generated by 266- and 355-nm laser photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$  in the gas phase.  $(\eta^5-C_5H_5)Mn(CO)$  is the predominant photoproduct upon 266-nm photolysis while both  $(\eta^5-C_5H_5)Mn(CO)$  and  $(\eta^5-C_5H_5)Mn(CO)_2$  are produced upon 355-nm photolysis. IR spectra in the region of 1820-2033 cm<sup>-1</sup> are assigned for the coordinatively unsaturated species ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>x</sub> and found to be in major disagreement with those obtained in condensed phases. The rate constants for the reactions of  $(\eta^5-C_5H_5)Mn(CO)_2$  and  $(\eta^5-C_5H_5)Mn(CO)$  with CO are determined to be  $(5.9 \pm 0.4) \times 10^{11}$  and  $(6.7 \pm 0.2) \times 10^{12}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, respectively. The rate constant for the reaction of  $(\eta^5 - C_5 H_5)Mn(CO)$  with CO is on the order of 1/10 gas kinetic while the corresponding value for  $(\eta^5 - C_5 H_5)Mn(CO)_2$  is over an order of magnitude smaller. The magnitudes of the rate constants for the reactions of  $(\eta^5 - C_5 H_5)Mn(CO)_x$  with CO are compared with those of  $(\eta^6 - C_6 H_6)Cr(CO)_x$  previously observed and are discussed in terms of the change of spin states of these reactions. In addition, it is found that the presence of rare gas Q (Q = Ar, He, and Xe) has remarkable influence on the kinetic behavior of  $(\eta^5-C_5H_5)Mn(CO)_2$ , implying the formation of rare-gas complexes  $(\eta^5 - C_5 H_5) Mn(CO)_2 Q$  in the gas phase.

#### I. Introduction

Coordinatively unsaturated transition-metal carbonyl compounds are of primary importance in the elucidation of mechanisms of various systems.<sup>1</sup> Several techniques have been developed toward the identification and characterization of these short-lived, highly reactive species.<sup>2-4</sup> Flash photolysis with time-resolved IR spectroscopy is regarded as a powerful technique in studying the structure and reactivity of coordinatively unsaturated metal carbonyl species in both solution and the gas phases.<sup>3,4</sup> Application of this technique in the gas phase is particularly useful since gas-phase studies offer the opportunity to provide the detailed information of the structure and reactivity of these species free from the disturbance of host matrix or solvent molecules.<sup>4</sup>

An extraordinarily rich chemistry is currently developing around the coordinatively unsaturated fragment  $(\eta^5-C_5H_5)Mn(CO)_2$ .<sup>5</sup>

There has been a large body of experimental investigations<sup>6-14</sup> as well as theoretical calculations<sup>15,16</sup> concerning this species.  $(\eta^5-C_5H_5)Mn(CO)_2$  was first postulated as an intermediate in the photochemical substitution of  $(\eta^5-C_5H_5)Mn(CO)_3$ .<sup>6</sup> It has since been generated and characterized following UV photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$  in low-temperature rare-gas matrices<sup>7,8</sup> and frozen hydrocarbon glasses.<sup>9-11</sup> The more highly unsaturated species  $(\eta^5-C_5H_5)Mn(CO)$  has also been observed upon prolonged UV photolysis of  $(\eta^5 - C_5 H_5) Mn(CO)_3$  in hydrocarbon glasses.<sup>10</sup> More recent time-resolved studies of UV flash photolysis of  $(\eta^5 - C_5 H_5) Mn(CO)_3$  in alkane solution at room temperature provided the structure and kinetic information of the solvated species  $(\eta^5-C_5H_5)Mn(CO)_2 \cdot S$  (S = solvent).<sup>12,13</sup> It was found that in *n*-heptane solution the rate constant for the reaction of  $(\eta^5$ - $C_{5}H_{5}$ )Mn(CO)<sub>2</sub>·S with CO is about 10 times smaller than the corresponding value for the reaction of  $Cr(CO)_5$  with CO in cyclohexane solution.12,13

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Figure 1. Transient IR absorption spectra obtained (a) 1.4  $\mu$ s following 266-nm photolysis of ( $\eta^5$ -C<sub>3</sub>H<sub>3</sub>)Mn(CO)<sub>3</sub> in the presence of 4.0 Torr of Ar and (b) 1.8  $\mu$ s following 355-nm photolysis of ( $\eta^5$ -C<sub>3</sub>H<sub>3</sub>)Mn(CO)<sub>3</sub> in the presence of 3.0 Torr of Ar.

The coordinatively unsaturated species  $(\eta^5-C_5H_5)Mn(CO)_x (x = 2 \text{ and } 1)$  has been less studied in the gas phase. This paper, using time-resolved IR absorption spectroscopy, is aimed to study the IR spectra in CO stretching region and reactivity of the gas-phase  $(\eta^5-C_5H_5)Mn(CO)_x$  generated upon UV laser photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$ . Both photofragments are identified by examining the temporal behavior of the IR absorptions observed. The IR spectra of  $(\eta^5-C_5H_5)Mn(CO)_x$  obtained in this study are compared with those previously obtained in condensed phases and found to be in major disagreement. The rate constants for the reactions of  $(\eta^5-C_5H_5)Mn(CO)_x$  with CO are measured in the presence of various buffer gases.

## **II.** Experimental Section

The time-resolved IR absorption apparatus used in this study has been described in detail elsewhere.<sup>17</sup> Briefly, a mixture of ~5-50 mTorr of  $(\eta^5-C_5H_5)Mn(CO)_3$  in buffer gas (He, Ar, or Xe) and/or CO was photolyzed with a frequency tripled (355 nm) or quadrupled (266 nm) Nd:YAG (Quanta Ray) laser operating at ca. 3 Hz. The laser pulse width is about 5 ns, and fluences of 2-5 mJ/cm<sup>2</sup> were typically employed. The formation of products was monitored by the output of a liquid nitrogen-cooled line-tunable CW CO laser (2033-1820-cm<sup>-1</sup> tuning range at ~4-cm<sup>-1</sup> spectral resolution). The CO laser beam, after passing through the gas cell coaxially with respect to the UV laser beam, was directed to a liquid nitrogen-cooled InSb detector. The output of the detector was amplified, digitized, and sent to a personal computer for signal averaging, storage, and manipulation. Generally, data were obtained by averaging 30-100 kinetic traces. Time-resolved IR absorption spectra were constructed from a series of kinetic traces at different probe wavelengths. The measured rise time of the overall detection system in this study is about 0.5

Two different types of gas cells were available for each experiment. For generating time-resolved spectra a flow cell was used. In the studies involving detailed kinetics a static cell was employed.  $(\eta^5-C_5H_5)Mn(CO)_3$  was introduced directly into the gas cell as a solid or by equilibration of the cells with the contents of a tube containing solid  $(\eta^5-C_5H_5)Mn(CO)_3$ .  $(\eta^5-C_5H_5)Mn(CO)_3$ , was obtained from Aldrich Chemical Co. and was sublimed in situ before use. He (99.999% purity), Ar (99.999% purity), and Xe (99.99% purity) were obtained from Beijing Oxygen Co., and CO (99.98% purity) was obtained from Beijing Analytical Instrument Co. and used without further purification.

#### III. Results

**Spectra.** The transient IR absorption spectra obtained following 266- and 355-nm laser photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$  in the gas phase are shown in Figure 1. The times of the spectra are selected to maximize the extent of rovibrational relaxation of the



**Figure 2.** Time-resolved IR spectra following 266-nm photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$  in the presence of 0.9 Torr of CO and 3.3 Torr of Ar. The spectra a were taken at 1.0- $\mu$ s intervals in the range of 1.1-5.1  $\mu$ s. The spectra b were taken at 11- $\mu$ s intervals in the range of 6-50  $\mu$ s. An up arrow indicates absorption increasing and a down arrow shows absorption decreasing with time.

"hot" nascent fragments, while also minimizing the extent of secondary, bimolecular reactions of the fragments. The spectra show that one or more fragments are formed upon 266- and 355-nm laser photolysis. The negative band at 1965 cm<sup>-1</sup> represents the photodepletion of the parent molecules.  $(\eta^5-C_5H_5)$ -Mn(CO)<sub>3</sub> has two IR absorptions at ~1965 (E mode) and ~2040  $cm^{-1}$  (A<sub>1</sub> mode) in the gas phase. This negative band is assigned to the E mode of  $(\eta^5 - C_5H_5)Mn(CO)_3$ . The A<sub>1</sub> mode of  $(\eta^5 - C_5H_5)Mn(CO)_3$ .  $C_5H_5$ )Mn(CO)<sub>3</sub> lies outside the tuning range of the CO probe laser at the present configuration. The positive bands in Figure 1 represent the photoproduction of primary fragments. Comparison of Figure 1, a and b, shows that the distribution of photoproducts upon 266- and 355-nm laser photolysis is different. The 266-nm photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$  leads to the formation of a single band at  $\sim 1948$  cm<sup>-1</sup>, while 355-nm photolysis results in the formation of the 1948-cm<sup>-1</sup> band as well as two other bands at  $\sim 1874$  and  $\sim 2021$  cm<sup>-1</sup>. The band at 1948 cm<sup>-1</sup> is assigned to the CO-stretching mode of  $(\eta^5-C_5H_5)Mn(CO)$  and the bands at 1874 and 2021 cm<sup>-1</sup> are assigned to the  $B_1$  and  $A_1$  CO-stretching modes of  $(\eta^5-C_5H_5)Mn(CO)_2$ , respectively. In addition, note a weak broad absorption over 2010 cm<sup>-1</sup> upon 266-nm photolysis (Figure 1a). It is assigned to the absorption of hot CO ( $\nu = 2$  or 3) ejected upon 266-nm photolysis. These assignments are principally based on the kinetic behavior of these bands as well as that of the parent in the presence of added CO.

Figure 2 shows time-resolved IR spectra obtained following 266-nm laser photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$  in the presence of 0.9 Torr of CO and 3.3 Torr of Ar buffer gas. At earlier times (not illustrated), the temporal behavior of the spectra is similar to that observed without CO: together with a decrease in the absorption of the parent at 1965 cm<sup>-1</sup>, two absorptions grow in at 1948 and over 2010 cm<sup>-1</sup>. In the middle-time region (Figure 2a), the absorption at 1948 cm<sup>-1</sup> decays concomitant with the growth of two new absorptions at 1874 and 2021 cm<sup>-1</sup>. In turn (Figure 2b), these two new absorptions decay accompanied by a matching recovery of the parent. For clarity, Figure 3 displays the single-frequency time evolution of IR absorptions (kinetic traces) taken at 1948, 1874, 2021, and 1965 cm<sup>-1</sup> in the presence of added CO. It demonstrates clearly the temporal behaviors of these bands described above. Although the 2021-cm<sup>-1</sup> band is affected by the primarily formed band over 2010 cm<sup>-1</sup> which is best assigned as the absorption of hot CO, its formation can be concluded from the CO-pressure dependence of this band. For comparison, Figure 3 also shows the time evolution of IR signal at 2021  $\text{cm}^{-1}$  in the absence of added CO. In the absence of added CO, the absorption over 2010 cm<sup>-1</sup> remained almost unchanged over the time scale of  $\sim 20 \ \mu s$ . In the presence of added CO, the band at 2021 cm<sup>-1</sup> shows CO-pressure dependent growth and



30

 $(\mu s)$ 

40

50

**Figure 3.** Single-frequency time-resolved IR absorption signals obtained upon 266-nm photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$ . The pressures of CO and Ar are the same as in Figure 2. For comparison, signal taken at 2021 cm<sup>-1</sup> in the absence of added CO (under otherwise identical conditions) (...) is also displayed which shows the "net" absorption of "hot" CO.

20

Time

10

ntensity (a.u.)

decay superimposing over the "background" of hot CO absorption.<sup>18</sup> [In Figure 2b and Figure 3, the growth of a weak absorption at 1948 cm<sup>-1</sup> at later times and incomplete recovery of the parent can also be observed. This is due to the binuclear-formation reaction of the photofragment ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub> with the parent (see below) and can be suppressed completely by adding sufficient CO.<sup>19</sup>] The above observations are consistent with the primary fragment sequentially adding two CO ligands to reform the parent ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>3</sub>. This identifies the primary fragment absorbing at 1948 cm<sup>-1</sup> as ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO) and associates the intermediate 1874- and 2021-cm<sup>-1</sup> absorptions with ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub>.

Detailed examination of temporal evolution of the spectra observed upon 355-nm photolysis supports above assignments. As mentioned above, 355-nm photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$  leads to the formation of three absorption bands at 1874, 2021, and 1948 cm<sup>-1</sup> (Figure 1b). In the presence of added CO, the bands at 1874 and 2021 cm<sup>-1</sup> return to the baseline at the same rate as does the parent band over a range of added CO pressures of 2–20 Torr, while the band at 1948 cm<sup>-1</sup> returns to the baseline faster. In addition, in the presence of N<sub>2</sub> (or H<sub>2</sub>), the bands at 1874 and 2021 cm<sup>-1</sup> decay at the same rate accompanied by the growth of two new bands at 1948 and 1997 cm<sup>-1</sup> (or 1948 and 2003 cm<sup>-1</sup>), which can be assigned as molecular nitrogen (or hydrogen) complex  $(\eta^5-C_5H_5)Mn(CO)_2(N_2)$  (or  $(\eta^5-C_5H_5)Mn(CO)_2(H_2)$ ).<sup>20</sup> These behaviors link the absorptions at 1874 and 2021 cm<sup>-1</sup> with  $(\eta^5-C_5H_5)Mn(CO)_2$  and 1948 cm<sup>-1</sup> with  $(\eta^5-C_5H_5)Mn(CO)^{21}$ 

The relative degree of internal excitation possessed by metal carbonyl photofragments is usually a useful aid in assigning transient absorption bands observed upon UV photolysis.<sup>22-24</sup> The photofragment that has lost only one CO on the photolysis is expected to be more internally excited than those that have lost two or more CO ligands. As internally excited molecules are deactivated by collision, their absorption bands narrow and shift to higher energy. More internal excitation and more shift to higher energy with time are observed for the bands at 1874 and 2021 cm<sup>-1</sup> relative to the band at 1948 cm<sup>-1</sup> (see Figure 4). This observation is consistent with the above assignments that the bands at 1874 and 2021 cm<sup>-1</sup> are ascribed to  $(\eta^5-C_5H_5)Mn(CO)_2$  and the band at 1948 cm<sup>-1</sup> to  $(\eta^5-C_5H_5)Mn(CO)$ .

The production of  $(\eta^5-C_5H_5)Mn$  species upon 266- and 355-nm photolysis is possible since this species is undetectable with our technique. However, detailed kinetic measurements show that, in the presence of added CO, the decay of  $(\eta^5-C_5H_5)Mn(CO)$  can be well fit to a single-exponential function with a rate corresponding to the growth of  $(\eta^5-C_5H_5)Mn(CO)_2$ . In addition, the rate for the reaction of  $(\eta^5-C_5H_5)Mn(CO)$  with CO is on the order of 1/10 gas kinetic (see Kinetics), a typical value for the reactions



Zheng et al.

Figure 4. Time-resolved IR spectra following 355-nm photolysis of  $(\eta^5-C_3H_3)Mn(CO)_3$  in the presence of 3 Torr of Ar. The spectra was taken at 0.6- $\mu$ s intervals in the range of 0.2-2.6  $\mu$ s. An up arrow indicates absorption increasing and a down arrow indicates absorption decreasing with time.



**Figure 5.** Time-resolved IR spectra following 355-nm photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$  in the presence of 3 Torr of Ar. The spectra was taken at 25-µs intervals in the range of 3.6-103.6 µs. An up arrow indicates absorption increasing and a down arrow indicates decreasing with time.

of most coordinatively unsaturated metal carbonyls with CO. We thus infer that no significant amount of  $(\pi^5-C_5H_5)Mn$  is formed. The loss or hapticity change of  $C_5H_5$  ring is also an insignificant process which will be discussed in detail in the Section IV.

Gas-phase coordinatively unsaturated metal carbonyl species are well-known to react very rapidly with their parents to form binuclear complexes.<sup>22-24</sup> Some evidence for the existence of binuclear-formation reaction upon 355-nm photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$  is displayed in the time-resolved spectra of Figure 5. These spectra illustrate that, in the absence of added CO, as the bands at 1874 and 2021 cm<sup>-1</sup> ascribed to  $(\eta^5-C_5H_5)Mn(CO)_2$ decrease, a new absorption with lifetime >1 ms grows in at 1948 cm<sup>-1</sup> overlapping with the absorption of  $(\eta^5-C_5H_5)Mn(CO)$ . On the same time scale, secondary depletion of the parent occurs. Since both  $(\eta^5-C_5H_5)Mn(CO)_2$  and  $(\eta^5-C_5H_5)Mn(CO)$  are formed upon 355-nm photolysis, these transient behaviors indicate the presence of reaction of the type

$$(\eta^{5}-C_{5}H_{5})Mn(CO)_{2} + (\eta^{5}-C_{5}H_{5})Mn(CO)_{3} \rightarrow (C_{5}H_{5})_{2}Mn_{2}(CO)_{5}$$
 (1)

or

$$(\eta^{5}-C_{5}H_{5})Mn(CO) + (\eta^{5}-C_{5}H_{5})Mn(CO)_{3} \rightarrow (C_{5}H_{5})_{2}Mn_{2}(CO)_{4}$$
 (2)

This assignment is based on the assumption of retention of all CO

ligands by the binuclear products. Upon 266-nm photolysis, however, no evidence for binuclear-formation reaction is found where  $(\eta^5 - C_5 H_5) Mn(CO)$  is the predominant product. We thus believe that the reaction of  $(\eta^5 - C_5 H_5) Mn(CO)_2$  with the parent is the most important process upon 355-nm photolysis, and the long-lived absorption at 1948 cm<sup>-1</sup> is attributed to the gas-phase  $(C_5H_5)_2Mn_2(CO)_5$ . The formation of  $(C_5H_5)_2Mn_2(CO)_5$  has also been observed upon UV laser photolysis of  $(\eta^5 - C_5 H_5) Mn(CO)_3$ in alkane solution at room temperature.<sup>12</sup> The IR absorption bands reported for  $(C_5H_5)_2Mn_2(CO)_5$  in *n*-heptane solution include one CO-bridge vibration absorption at 1777 cm<sup>-1</sup> and four CO-terminal vibration absorptions at 1993, 1955, 1934, and 1907  $cm^{-1}$ . The gas-phase absorption band at 1948 cm<sup>-1</sup> may correspond to the 1934-cm<sup>-1</sup> solution band. The corresponding gas-phase absorptions of three solution bands at 1993, 1955, and 1907  $cm^{-1}$ , expected to set within our probe range, are not observed in our experiment, presumably due to the weakness of these absorptions or overlap with the other absorptions.

The formation of  $(C_5H_5)_2Mn_2(CO)_5$  can still be observed even in the conditions that the concentration of CO is 3 orders of magnitude greater than that of  $(\eta^5-C_5H_5)Mn(CO)_3$ . Since the rate constant for the reaction of  $(\eta^5-C_5H_5)Mn(CO)_2$  with CO is  $(5.9 \pm 0.4) \times 10^{11}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> (see below), this indicates that the rate constant for reaction 1 approaches the gas kinetic value. The rapid reactions of coordinatively unsaturated species with their parents are often observed in other metal carbonyl systems.<sup>22-24</sup>

**Kinetics.** The kinetic scheme upon 266- and 355-nm laser photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$  in the presence of added CO can be described as

$$(\eta^5 - C_5 H_5) \operatorname{Mn}(\operatorname{CO}) + \operatorname{CO} \xrightarrow{k_{12}} (\eta^5 - C_5 H_5) \operatorname{Mn}(\operatorname{CO})_2$$
 (3)

$$(\eta^5 - C_5 H_5) Mn(CO)_2 + CO \xrightarrow{k_{23}} (\eta^5 - C_5 H_5) Mn(CO)_3$$
 (4)

$$(\eta^{5}-C_{5}H_{5})Mn(CO)_{2} + (\eta^{5}-C_{5}H_{5})Mn(CO)_{3} \xrightarrow{\kappa_{p}} (C_{5}H_{5})_{2}Mn_{2}(CO)_{5} (5)$$

This kinetic scheme is similar to that for the  $(\eta^6-C_6H_6)Cr(CO)_x$ system<sup>17</sup> and, under the conditions of  $k_{23}[CO] \gg k_p[(\eta^5-C_5H_5)-Mn(CO)_3]$ , by omitting eq 5, the predicted time dependences of  $[(\eta^5-C_5H_5)Mn(CO)_x]$  (x = 1-3) are given by

$$[(\eta^{5} - C_{5}H_{5})Mn(CO)] = [A]_{0} \exp(-k'_{12}t)$$
(6)

$$[(\eta^{5} - C_{5}H_{5})Mn(CO)_{2}] = \frac{k'_{12}[A]_{0}}{k'_{23} - k'_{12}} \exp(-k'_{12}t) + \left( [B]_{0} - \frac{k'_{12}[A]_{0}}{k'_{23} - k'_{12}} \right) \exp(-k'_{23}t)$$
(7)

$$[(\eta^{5} - C_{5}H_{5})Mn(CO)_{3}] = [A]_{0} + [B]_{0} + [C]_{0} - \frac{k'_{23}[A]_{0}}{k'_{23} - k'_{12}} \exp(-k'_{12}t) - \left( [B]_{0} - \frac{k'_{12}[A]_{0}}{k'_{23} - k'_{12}} \right) \exp(-k'_{23}t)$$
(8)

where  $k'_{12} = k_{12}[CO]$ ,  $k'_{23} = k_{23}[CO]$ , and  $[A]_0$ ,  $[B]_0$ , and  $[C]_0$ are the initial concentrations of  $(\eta^5 - C_5H_5)Mn(CO)$ ,  $(\eta^5 - C_5H_5) - Mn(CO)_2$ , and  $(\eta^5 - C_5H_5)Mn(CO)_3$ , respectively.

It is apparent that  $[(\eta^5-C_5H_5)Mn(CO)]$  will undergo singleexponential decay with a rate of  $k'_{12}$ , while for  $[(\eta^5-C_5H_5)Mn(CO)_2]$  and  $[(\eta^5-C_5H_5)Mn(CO)_3]$  the time-evolution processes will follow double exponential. However, upon 266-nm photolysis  $([B_0] = 0)$ , since  $k'_{23} < (1/10)k'_{12}$  (see below), the earlier-time evolution of  $[(\eta^5-C_5H_5)Mn(CO)_2]$  is expected to be dominated by a single-exponential rise with a rate of  $k'_{12}$ . Single-exponential fits are made to the decay of  $(\eta^5-C_5H_5)Mn(CO)$  absorption and the rise of  $(\eta^5-C_5H_5)Mn(CO)_2$  absorptions following 266-nm photolysis. All sets of the data obtained show, within experimental error, the same linear dependence on [CO]. Figure 6 shows the CO-pressure dependence of the decay rate of  $[(\eta^5-C_5H_5)Mn(CO)]$ , monitored at 1948 cm<sup>-1</sup>, and the rise rate of  $[(\eta^5-C_5H_5)Mn(CO)_2]$ , monitored at 1874 cm<sup>-1</sup>, following 266-nm photolysis.<sup>25</sup> The slope of the line leads to a rate constant for the reaction of  $(\eta^5-C_5H_5)Mn(CO)$  with CO,  $k_{12}$ , as  $(6.7 \pm 0.2) \times 10^{12}$  cm<sup>3</sup> mol<sup>-1</sup>



**Figure 6.** CO-pressure dependence of the pseudo-first-order decay rate of  $(\eta^5-C_5H_5)Mn(CO)$  and rise rate of  $(\eta^5-C_5H_5)Mn(CO)_2$  observed upon 266-nm photolysis of  $(\eta^5-C_5H_5)Mn(CO)_3$  on the addition of CO and 30 Torr of Ar. The decay of  $(\eta^5-C_5H_5)Mn(CO)$  was monitored at 1948 cm<sup>-1</sup> (**■**) and the rise of  $(\eta^5-C_5H_5)Mn(CO)_2$  at 1874 cm<sup>-1</sup> (**●**). For clarity, only representative error bars are indicated explicitly.



Figure 7. CO-pressure dependence of the decay rate of  $(\eta^5-C_5H_3)Mn(CO)_2$  and recovery rate of  $(\eta^5-C_5H_3)Mn(CO)_3$  observed upon 355-nm photolysis of  $(\eta^5-C_5H_3)Mn(CO)_3$  in the absence of buffer gas (circle) and in the presence of 30 Torr of Ar (square). The decay of  $(\eta^5-C_5H_3)Mn(CO)_2$  was monitored at 1874 cm<sup>-1</sup> (open symbols) and the recovery of  $(\eta^5-C_5H_3)Mn(CO)_3$  at 1965 cm<sup>-1</sup>) (filled symbols). Only representative error bars are indicated.

 $s^{-1}$ . This value is superimposable at Ar pressure of 10-40 Torr, indicating that it is a high-pressure-limited rate constant. This rate constant is on the order of 1/10 gas kinetic collision frequency. In addition, the presence of different buffer gas (He, Ar, and Xe) does not affect this rate constant.

Although the decay of  $[(\eta^5-C_5H_5)Mn(CO)_2]$  and the recovery of  $[(\eta^5-C_5H_5)Mn(CO)_3]$  upon both 266- and 355-nm photolysis follow double exponential, at longer time both processes are expected to approach single exponential with a rate of  $k'_{23}$  (the smaller of  $k'_{12}$  and  $k'_{23}$ ). Single-exponential fits are made to the tails of the decay of  $[(\eta^5-C_5H_5)Mn(CO)_2]$  and the recovery of the parent at a series of CO pressures upon both 266- and 355-nm photolysis. All sets of the data obtained show, within experimental error, the same linear dependence on [CO]. Figure 7 shows two sets of the data measured for the decay of  $[(\eta^5 - C_5 H_5)Mn(CO)_2]$ and the recovery of  $[(\eta^5-C_5H_5)Mn(CO)_3]$  following 355-nm photolysis. The slope of the line gives the rate constant for the reaction of  $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub> with CO,  $k_{23}$ , as (5.9 ± 0.4) ×  $10^{11}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. Due to the possibility of coordination of rare gas to  $(\eta^5-C_5H_5)Mn(CO)_2$  (see below), this value is measured in the absence of buffer gas. The single-line dependence of the decay and recovery rates on [CO] indicates that the reactions are in the

TABLE I: Frequencies (cm<sup>-1</sup>) and Relative Intensities of CO Stretching Bands of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>x</sub> and ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)Cr(CO)<sub>x</sub>

		argon matrix <sup>a</sup>	glasses		n-heptane	
	assign.		MCH/IP <sup>b</sup>	MCH <sup>c</sup>	solution	gas phase <sup>e</sup>
$(\eta^5 - C_5 H_5) Mn(CO)_2$	<b>A</b> <sub>1</sub>	1972.0 (1.0)	1955 (1.0)	1950 (1.0)	1964 (1.0)	2021 (1.0)
	B <sub>1</sub>	1903.2 (1.40)	1886 (1.4)	1880 (1.1)	1895 (1.05)	1874 (1.6)
$(\eta^{5}-C_{5}H_{5})Mn(CO)$			1857		. ,	1948
$(\eta^{6}-C_{6}H_{6})Cr(CO)_{2}$	$\mathbf{A}_{1}$	1937.5 (1.0)√				1981 (1.0)8
	B	1885.0 (1.55)√				1917 (1.5)8
$(\eta^6-C_6H_6)Cr(CO)$						1985 <sup>8</sup>

<sup>a</sup>References 7 and 16. <sup>b</sup>Methylcyclohexane-isopentane (4:1) glass (77 K), ref 10. <sup>c</sup>Methylcyclohexane glass (100 K), ref 11. <sup>d</sup>References 12 and 13. <sup>c</sup>This work. <sup>f</sup>Relative intensity data at CH<sub>4</sub> matrix, ref 16. <sup>g</sup>Reference 17.

high-pressure limits. This is confirmed by the observation that the rate constant obtained in the presence of 10-50 Torr of He is the same within experimental uncertainty as in the absence of buffer gas [The coordination of He to  $(\eta^5-C_5H_5)Mn(CO)_2$  is negligible. See below]. This rate constant is over 10 times smaller than the corresponding values for  $(\pi^5-C_5H_5)Mn(CO)$  and Cr- $(CO)_5$ , <sup>22b,23a,24d</sup> The values of  $k_{23}$  measured over the temperature range of 296-335 K are within experimental error of one another, indicating that the reaction of  $(\eta^5-C_5H_5)Mn(CO)_2$  with CO has a negligible activation barrier. Kinetic measurements taken in the presence of  $N_2$  and  $H_2$  show<sup>20</sup> that the rate constants for the reactions of  $(\eta^5-C_5H_5)Mn(CO)_2$  with N<sub>2</sub> and H<sub>2</sub> are on the same order as that for the reaction of  $(\eta^5-C_5H_5)Mn(CO)_2$  with CO. Both of them are also temperature independent. Previous workers<sup>12,13</sup> have reported that the rate constant for the reaction of the solvated species  $(\eta^5 - C_5 H_5) Mn(CO)_2 \cdot S$  (S = solvent) with CO in *n*-heptane solution at room temperature is 10 times smaller than the corresponding value for Cr(CO)<sub>5</sub>-S in cyclohexane. The lower reactivity of  $(\eta^5 - C_5 H_5) Mn(CO)_2 \cdot S$  could be a result of the stronger interaction of Mn center with the solvent molecule, since for the reaction of solvated species, the breaking of the M-S bond is a significant factor in determining the overall rate of reaction.<sup>13</sup> However, thermochemical studies have suggested<sup>14</sup> that the Mn...n-heptane interaction is 8-9 kcal mol<sup>-1</sup>, similar to 10 kcal mol<sup>-1</sup> of Cr...alkane interaction. This indicates that the lower reactivity of  $(\eta^5 - C_5 H_5) Mn(CO)_2 \cdot S$  with CO in alkane solution is due, at least in part, to the intrinsically lower reactivity of  $(\eta^5-C_5H_5)Mn(CO)_2$  with CO.

## IV. Discussion

Band Assignments. As already mentioned in the Introduction, the coordinatively unsaturated species  $(\eta^5-C_5H_5)Mn(CO)_2$  has received extensive studies in low-temperature rare-gas matrices, frozen glasses, and alkane solution. The more highly unsaturated species  $(\eta^5 - C_5 H_5) Mn(CO)$  has also been observed in frozen glasses. The IR absorption frequencies and relative intensities in CO stretching region for  $(\eta^5 - C_5 H_5) Mn(CO)_x$  and the closely related species  $(\eta^6 - C_6 H_6) Cr(CO)_x$  in condensed phases as well as in the gas phase are gathered in Table I. The positions of IR absorption bands of  $(\eta^5 - C_5 H_5) Mn(CO)_2$  in condensed phases are all in good agreement taking into account the general shifts in different media. The positions of IR absorption bands of  $(\eta^5-C_5H_5)Mn(CO)_2$  in the gas phase are, however, in major disagreement with corresponding values in condensed phases. Generally, the coordinatively unsaturated transition-metal carbonyls observed in the gas phase have their IR absorption bands shifted by  $\sim 10-30$  cm<sup>-1</sup> to higher frequencies than those observed in Ar matrix. For  $(\eta^5-C_5H_5)$ - $Mn(CO)_2$ , however, the positions of  $A_1$  and  $B_1$  modes in the gas phase shift by 49 cm<sup>-1</sup> to higher and 29 cm<sup>-1</sup> to lower frequencies than those in Ar matrix, respectively. In addition, the relative intensities of two modes of  $(\eta^5-C_5H_5)Mn(CO)_2$  in the gas phase are also different from those in condensed phases. Although the band intensities can only be roughly compared due to the relatively low resolution of the spectra in this experiment, the intensity ratio of  $B_1$  and  $A_1$  modes can be estimated to be 1.6:1.0. This value is significantly larger than corresponding values in condensed phases although there is already some disagreements in condensed phases (see Table I). The position of CO stretching band of  $(\eta^5-C_5H_5)Mn(CO)$  in the gas phase are also unexpected. It shifts 91 cm<sup>-1</sup> to higher frequency relative to that of  $(n^5-C_5H_5)Mn(CO)$ in hydrocarbon glasses. Furthermore, the gas-phase IR spectra of  $(\eta^5 - C_5 H_5) Mn(CO)_x$  are also incompatible with those of the isostructural species  $(\eta^6 - C_6 H_6) Cr(CO)_x$ , although the overall behavior of the IR spectra of  $(\eta^5-C_5H_5)Mn(CO)_2$  and  $(\eta^6 C_6H_6)Cr(CO)_2$  in condensed phases are qualitatively very similar.<sup>7</sup> Presumably, the structures of  $(\eta^5 - C_5 H_5) Mn(CO)_x$  in condensed phases are distorted significantly by interaction with host matrix or solvent molecules. It is well-known that the structures of matrix-isolated species can be distorted by the interactions with even relatively inert matrix materials.<sup>26</sup> There are also examples where coordinatively unsaturated molecules may show significant differences in structure between matrix and gas phase.<sup>24b</sup> Our primary experiments have shown that the gas-phase  $(\eta^5-C_5H_5)$ - $Mn(CO)_2(n-hexane)$  species absorbs at 1915 and 1978 cm<sup>-1</sup>, in agreement with the positions of absorptions of this species in alkane solutions. However, the shifts in frequency from  $(\eta^5-C_5H_5)Mn^{-1}$  $(CO)_2$  to  $(\eta^5-C_5H_5)Mn(CO)_2(n-hexane)$  are significantly larger than would be expected if the shifts are due merely to interaction of C-H  $\sigma \rightarrow$  metal electron donation.<sup>24e</sup> It seems likely that the geometry change of  $(\eta^5-C_5H_5)Mn(CO)_2$  upon addition of *n*-hexane should also be considered to interpret the larger shifts in frequency.

Although the kinetic arguments behind our assignments are convincing, the IR bands of gas-phase  $(\eta^5-C_5H_5)Mn(CO)_x$  shift so much from condensed-phase bands that one might question that the species being observed are not ground-state  $(\eta^5-C_5H_5)Mn (CO)_x$  at all. For a polyene complex, the number of polyene carbons bound to metal can change during chemical reactions (so called "hapticity change"). In the present case, there may be the possibility of, for example,  $\eta^5 \rightarrow \eta^3$ -C<sub>5</sub>H<sub>5</sub> or other form of "ring slippage" accompanying the dissociation of CO upon UV photolysis. However, as mentioned in the Results, in the presence of sufficient CO ([CO]  $\gg$  [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>3</sub>]) all bands observed can return to the baseline completely and no new strong absorption appears. [This observation also excludes the possibility of loss of  $C_5H_5$  ring at high efficiency.] Furthermore, the species we assigned as  $(\eta^5-C_5H_5)Mn(CO)_2$  reacts with N<sub>2</sub> leading to the formation of stable compound  $(\eta^5-C_5H_5)Mn(CO)_2(N_2)$  with its own distinctive and known IR bands. We thus conclude that the species being observed are indeed  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> complexes. There may also be the possibility that the  $(\eta^5 - C_5 H_5) Mn(CO)_x$  being observed are electronically excited species.<sup>27</sup> Since  $(\eta^5-C_5H_5)Mn(CO)_2$  are observed both as a primary product upon 355-nm photolysis and as a secondary product via the reaction of  $(\eta^5-C_5H_5)Mn(CO)$  with CO in the presence of various pressures of buffer gases (3-50 Torr of He or Ar), it is unlikely that  $(\eta^5 - C_5 H_5) Mn(CO)_2$  is in the excited state. In addition, as the lifetime of  $(\eta^5-C_5H_5)Mn(CO)$ is not affected by changes in buffer gas pressure, it is unlikely that this species is in an excited state since an excited electronic state would be expected to be readily collisionally quenched by rare gas. An assignment to an excited state of  $(\eta^5-C_5H_5)Mn(CO)$ is also unlikely due to energy considerations. The average Mn-CO bond energy in  $(\eta^5-C_5H_5)Mn(CO)_3$  was estimated to be ~30 kcal mol<sup>-1</sup> (ref 28) and the first Mn-CO bond dissociation energy to be 55 kcal mol<sup>-1</sup> (ref 14). As a result, upon 355-nm (80 kcal mol<sup>-1</sup>) photolysis, formation of  $(\eta^5-C_5H_5)Mn(CO)$  would lead to little excess energy disposing on  $(\eta^5 - C_5 H_5) Mn(CO)$  and two CO ligands ejected. Thus, it is unlikely that the excited state of  $(\eta^5-C_5H_5)Mn(CO)$  is formed in any significant amount. From

the above discussion, we believe that the species being observed are ground-state  $(\eta^5-C_5H_5)Mn(CO)_x$ .

Kinetics. We have previously reported that the rate constant for the reaction of  $(\eta^6 - C_6 H_6)Cr(CO)$  with CO is considerably smaller than the corresponding value for the reaction of  $(\eta^{\circ})$  $C_6H_6)Cr(CO)_2$  with CO.<sup>17</sup> By contrast, as mentioned above, the rate constant for the reaction of  $(\eta^5-C_5H_5)Mn(CO)$  with CO is significantly larger than the corresponding value for the reaction of  $(\eta^5 - C_5 H_5) Mn(CO)_2$  (Table II). Since both of the reactions of  $(\eta^5 - C_5H_5)Mn(CO)_2$  and  $(\eta^6 - C_6H_6)Cr(CO)$  with CO are temperature independent, smaller preexponential factors are responsible for the slowness in the observed recombination rates. It is unlikely that the major factor in slowness of the recombination rates for these two reactions is due to the change in geometry, since the geometric changes on the reactions of  $(\eta^5 - C_5H_5)Mn$ - $(CO)_2$  and  $(\eta^6-C_6H_6)Cr(CO)$  with CO cannot be severely different from those occurring on the reactions of  $(\eta^5-C_5H_5)Cr(CO)_2$  and  $(\eta^6-C_6H_6)Mn(CO)$ , respectively. This argument is compatible with the fact that no geometric dependence of rate constants for the reactions of coordinatively unsaturated metal carbonyls has been reported. In the  $Fe(CO)_5$  system, it has been found that the change of spin state is a major factor in determining the magnitude of the rate constant for reaction of coordinatively unsaturated species and that the rate constant for the spin-disallowed process is significantly smaller than the corresponding value for the spin-allowed process.<sup>22a,e,f</sup> For example, the rate constant for the reaction of  $Fe(CO)_4$  with  $CO^{22a}$  is almost 3 orders of magnitude smaller than those of the typical addition reactions of coordinatively unsaturated species. This reaction is known to be spin-disallowed reaction going from triplet  $Fe(CO)_4$  to singlet  $Fe(CO)_5$ . From the above discussion, it seems likely that the reactions of  $(\eta^5 - C_5 H_5) Mn(CO)_2$  and  $(\eta^6 - C_6 H_6) Cr(CO)$  with CO are also spin-disallowed. Unfortunately, to our knowledge there has been no report concerning the spin multiplicity of electronic ground states of  $(\eta^5 - C_5 H_5) Mn(CO)_x$  and  $(\eta^6 - C_6 H_6) Cr(CO)_x$ . In the case of  $Fe(CO)_4$ , there are good Jahn-Teller arguments for the distorted geometry and triplet ground state.<sup>29</sup> However, these arguments do not apply in  $(\eta^5 - C_5 H_5) Mn(CO)_x$  and  $(\eta^6 - C_6 H_6)$ - $Cr(CO)_x$  as they have much lower symmetry. Weitz and Ryther have recently reported that the rate constant for the reaction of triplet  $Fe(CO)_4$  with triplet ground-state  $O_2$  is more than 50 times larger than that for the reaction of  $Fe(CO)_4$  with  $CO.^{22f}$  This implies that the magnitude of rate constant for reaction with triplet  $O_2$  may be used, to some extent, as a probe for the spin multiplicity of unsaturated organometallic species. We obtained a rate constant for the reaction of  $(\eta^5 - C_5 H_5) Mn(CO)_2$  with  $O_2$  which is 3 times as large as the corresponding value for the reaction with CO. Attempts to measure the rate constant for the reaction of  $(\eta^6-C_6H_6)Cr(CO)$  with O<sub>2</sub> were unsuccessful because the parent  $(\eta^6-C_6H_6)Cr(CO)_3$  decomposes significantly at the experimentally used temperature ( $\sim$ 350 K) in the presence of O<sub>2</sub>. The larger rate constant for the reaction of  $(\eta^5 - C_5 H_5) Mn(CO)_2$  with  $O_2$  than with CO seems to favor triplet  $(\eta^5-C_5H_5)Mn(CO)_2$ . However, we also found that singlet  $W(CO)_5$  reacts with triplet  $O_2$  having a rate constant virtually identical with that for the reaction of  $W(CO)_5$  with CO. Further work is valuable to determine whether the major factor is the change of spin states in the slowness of recombination rates of  $(\eta^5 - C_5 H_5) Mn(CO)_2$  and  $(\eta^6 - C_6 H_6) Cr(CO)$ .

The coordination of rare gas to coordinatively unsaturated metal carbonyl centers has been the subject of many studies.<sup>30-36</sup> The low-temperature rare-gas matrix studies of Turner and Perutz<sup>30</sup> showed the formation of  $M(CO)_5 \cdot Q$  (M = Cr, Mo, or W; Q =rare gas) in low-temperature matrices with a weak M–Q bond. Studies of Poliakoff and co-workers<sup>31</sup> in low-temperature rare-gas solution provided the first IR spectroscopic evidence for the formation of  $Cr(CO)_5 \cdot Xe$  in liquid Xe and Kr at 173 K following UV photolysis of  $Cr(CO)_6$ . More recently, Bergman and Moore and their co-workers<sup>32</sup> obtained the kinetic evidence for the formation of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Rh(CO)·Q (Q = Xe and Kr) in liquid Xe (242 K) and Kr (153–193 K) following UV photolysis of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Rh(CO)<sub>2</sub>. Ab initio calculations<sup>33</sup> also suggested that the interaction between the pentacarbonyls M(CO)<sub>5</sub> and a rare gas

TABLE II:	<b>Rate Constants</b>	for Reactions	of Some C	oordinatively
Unsaturated	Metal Carbonyl	Species with	CO in the	Gas Phase

	spin allowed	rate constant $(10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$
$(\eta^5 - C_5 H_5) Mn(CO)_2 + CO$	?	0.06 <sup>a</sup>
$(\eta^{5}-C_{s}H_{s})Mn(CO) + CO$	Y	0.674
$(\eta^{6}-C_{6}H_{6})Cr(CO)_{2} + CO$	Y	0.63
$(\eta^6 - C_6 H_6) Cr(CO) + CO$	?	0.14 <sup>b</sup>
Fe(CO)₄ + CO	Ν	0.003°
$Cr(CO)_5 + CO$	Y	1.5, <sup>d</sup> 2.2, <sup>e</sup> 2.4 <sup>f</sup>

<sup>a</sup>This work. <sup>b</sup>Reference 17. <sup>c</sup>Reference 22a. <sup>d</sup>Reference 22b. <sup>c</sup>Reference 23a. <sup>f</sup>Reference 24d.

Q is attractive at the level of the dispersion energy and the stabilization energy is estimated as high as 8-10 kcal mol<sup>-1</sup> for  $Mo(CO)_{5}Kr$ . The formation of a rare-gas complex in the gas phase at room temperature has also received considerable attention.<sup>22-24,35,36</sup> To investigate the possibility of the formation of such complex in the gas phase, we have measured the reaction kinetics of  $(\eta^5 - C_5 H_5)Mn(CO)_x$  in the presence of He, Ar, and Xe. We find that the rate constant for the reaction of  $(\eta^5-C_5H_5)$ -Mn(CO) with CO in the presence of different buffer gases is the same within experimental error. However, the rate constant for the reaction of  $(\eta^5-C_5H_5)Mn(CO)_2$  with CO is different in the presence of different buffer gases. A set of the data, which shows the CO-pressure dependence of the rates of decay of the absorptions of  $(\eta^5 - C_5 H_5) Mn(CO)_2$  and recovery of the parent in the presence of 30 Torr of Ar buffer gas, is displayed in Figure 7. It is apparent that the presence of Ar adds complexity into the reaction kinetics of  $(\eta^5 - C_5 H_5) Mn(CO)_2$ . This behavior can be interpreted by assuming that the rate constant measured in the presence of buffer gas is for the reaction

$$(\eta^{5} - C_{5}H_{5})Mn(CO)_{2}Q + CO \rightarrow (\eta^{5} - C_{5}H_{5})Mn(CO)_{3} + Q \quad (9)$$

That is, Q does coordinate to  $(\eta^5-C_5H_5)Mn(CO)_2$ . Interestingly, the effects of He and Xe on kinetic behavior of  $(\eta^5-C_5H_5)Mn(CO)_2$ are not as marked as Ar. The rate constant measured in the presence of 30–60 Torr of He is virtually the same within experimental error as in the absence of buffer gas, while the rate constant measured in the presence of 30 Torr of Xe is only slightly smaller.<sup>37</sup> Presumably, He has too high an ionization potential, whereas Xe is too bulky.<sup>33</sup> Further studies including detailed kinetic analysis are in progress.

## V. Conclusions

Time-resolved IR absorption spectra have been obtained for the gas-phase coordinatively unsaturated species  $(\eta^5 - C_5 H_5)$  Mn- $(CO)_x$  (x = 2 and 1) generated upon 266- and 355-nm laser photolysis of  $(\eta^5 - C_5 H_5)Mn(CO)_3$ . The IR absorption bands observed in this study for  $(\eta^5 - C_5 H_5) Mn(CO)_x$  are in major disagreement with those observed in condensed phases. The rate constants for the reactions of  $(\eta^5 - C_5 H_5) Mn(CO)_x$  with CO have also been obtained and are listed in Table II along with corresponding values for  $(\eta^6 - C_6 H_6) Cr(CO)_x$  and related species. The rate constants for the reactions of  $(\eta^5-C_5H_5)Mn(CO)$  and  $(\eta^6 C_6H_6)Cr(CO)_2$  with CO are on the same order of magnitude as those for spin-allowed reactions of coordinatively unsaturated metal carbonyl species, while the rate constants for the reactions of  $(\eta^5-C_5\dot{H}_5)\dot{M}n(CO)_2$  and  $(\eta^6-C_6H_6)Cr(CO)$  with CO are an order of magnitude smaller.  $(\eta^5 - C_5 H_5) Mn(CO)_3$  and  $(\eta^6 - C_6 H_6) Cr(CO)_3$ provide other two good systems to test the generality of the hypothesis that the change of spin state is a major factor in determining the magnitude of the rate constants for reactions of coordinatively unsaturated organometallic species.

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# Selectivity of Alkyl Radical Formation from Branched Alkanes Studied by Electron Spin Resonance and Electron Spin Echo Spectroscopy

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Electron spin resonance and electron spin echo measurements of alkyl radicals generated from branched alkanes by  $\gamma$ -irradiation have been carried out to elucidate the mechanism of selective alkyl radical formation in low-temperature solids. Alkyl radicals generated at 77 K are primary and penultimate secondary radicals. The primary radicals are generated from alkane radical cations and excited alkanes. Hydrogen atoms and the primary radicals selectively abstract hydrogen atoms on the penultimate secondary carbon atoms of nearby alkanes. Primary C-H hydrogen atoms are not abstracted because of their high activation energy. Tertiary radicals and secondary radicals other than the penultimate one are not generated either by hydrogen abstraction or from excited or ionized molecules, since the motion of carbon atoms assisting the detachment of a C-H hydrogen atom is impeded by alkyl chains attached to the C-H carbon atom. In contrast to the reaction in the glassy solids, the selectivity of radical formation in liquids simply follows the order of C-H bond dissociation energy.

#### Introduction

Irradiation of organic molecules by UV light or ionizing radiation causes the formation of free radicals. Since the energy of radiation is much higher than bond dissociation energies, several types of radicals are expected to be formed by random scission of chemical bonds. However, this is not usually the case. Major radicals formed in condensed media are those generated by the scission of a C-H bond.<sup>1,2</sup> Although the C-C bond is weaker than the C-H bond, radicals formed by the scission of the C-C bond are seldom observed because of the cage effect; large radical fragments cannot escape a solvent cage and recombine with each other. On the other hand, hydrogen atoms are small enough to escape the solvent cage.

Alkyl radicals are known to be generated by three reaction processes, C-H bond rapture of excited molecules, proton transfer of radical cations, and C-H hydrogen abstraction, as