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Further Pulse Radiolysis Studies of Decacarbonyldimanganese(0) and Decacarbonyldirhenium(0). Temperature and Solvent Effects

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Abstract

Pulse radiolysis of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in alcohol and isooctane solutions over the temperature ranges −43 to 22 °C (for $Mn_2(CO)_{10}$) and 22 to 106 °C (for $Re_2(CO)_{10}$) has been investigated. At room temperature, $Mn_2(CO)_{10}$ affords the $Mn(CO)_5\cdot$ radical in both ethanol and methanol. However, at −27 (in ethanol) and −37 °C (in methanol), a transient is generated that exhibits an absorption band with a maximum at 700 nm and a molar extinction coefficient, in ethanol, of ϵ_{700} 10,120 ± 150 M^{-1} cm^{-1}. This species decays by first-order kinetics with a rate constant of $k = 1.1 \times 10^5$ s^{-1}, and has been tentatively formulated as a product of protonation of $Mn_2(CO)_{10}^{\cdot-}$ by the solvent. Pulse irradiation of $Re_2(CO)_{10}$ in ethanol solution up to 60 °C, and in 1-butanol solution up to 106 °C, produces what appears to be the corresponding protonated dirhenium species, but no detectable $Re(CO)_5\cdot$ radical. By way of contrast, both $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ yield their respective pentacarbonyl radicals on pulse irradiation in isooctane solution. The values of E_a for the reactions of $Mn(CO)_5\cdot$ and $Re(CO)_5\cdot$ with CCl_4 and for the coupling reaction of $Mn(CO)_5\cdot$, all in ethanol solution, were found to be 2.8, 2.5, and 2.1 kcal/mol, respectively.

Introduction

Previous work in this laboratory showed that pulse radiolysis of ethanol solutions of $Mn_2(CO)_{10}$ at room temperature generates the $Mn(CO)_5\cdot$ radical [1]. In contrast, pulse radiolysis of ethanol solutions of $Re_2(CO)_{10}$ at room temperature affords a dirhenium species, possibly $HRe_2(CO)_{10}$, but no detectable $Re(CO)_5\cdot$ radical [2]. However, $Re(CO)_5\cdot$ was produced by pulse irradiation of ethanol solutions of $Re(CO)_5X$ (X = Cl, Br, and I), $Re(CO)_5SO_2CH_3$, and $ReMn(CO)_{10}$, and by flash photolysis of an isooctane solution of $Re_2(CO)_{10}$ [2]. In this paper we report further pulse radiolytic studies of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. These studies were undertaken to explore possible effects of solvent and temperature on the previously observed different behaviors of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.

Experimental

The apparatus in use with a Varian V-7715A electron linear accelerator has been described previously [3–5]. The 3–4 MeV electrons with a pulse duration of 200–1000 ns were used for this work. The dose for a 1000 ns pulse was found to be 1.7×10^{18} eV/g in water by thiocyanate dosimetry. It is linear with pulse width and is slightly lower in the solvents utilized, e.g., *ca.* 5×10^{17} eV/g for a 1000 ns pulse in ethanol. The 2 cm quartz irradiation cell was constructed so it could be filled in the absence of air, and a syringe technique, described elsewhere [6], was employed for filling the cell. All solutions were deaerated by using argon gas (99.999%). A double pass of the analyzing beam was utilized.

For the temperature dependence work, the quartz irradiation cell was mounted in a thermal isolation chamber (TIC). The TIC was constructed of a clear, cross-linked, plastic polycarbonate, Lexan, chosen for its resistance to radiation and ability to withstand temperature changes. Quartz windows were used for the double light pass, and the irradiation window was of double Mylar construction. A ceramic heating unit, connected to an RFL Industries, Inc. temperature controller (Model 76T-1) permitted the temperature to be raised above room temperature by heating air passed over the heating coils before it entered the TIC. For lower temperatures, nitrogen gas was passed through liquid nitrogen and then through the heating unit. Thermocouples, attached with epoxy to the quartz irradiation cell, were connected to the controller and to a digital temperature readout instrument, which was an Omega Model

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410A Trendicator with a copper–constantan thermocouple having a 0.1 °C resolution and ±0.2 °C accuracy. The thermocouples attached to the cell were calibrated against thermocouples inserted in an ethanol solution in the cell. The flow of air or nitrogen gas used to heat or cool the solutions in the irradiation cell was directed onto the cell and equilibrated temperatures were obtained within 3–5 min. A hinged door on the TIC allowed for adjustments in the position of the cell and enclosed mirror.

$Re_2(CO)_{10}$ was purchased from Pressure Chemical Co., and $Mn_2(CO)_{10}$ was purchased from Strem Chemicals, Inc. The S-sulfinatopentacarbonyl complexes $M(CO)_5SO_2CH_3$ where M = Mn and Re were prepared by published procedures [7]. The compounds were purified by sublimation and stored in the dark at 10 °C generally under an argon atmosphere. The stability of the compounds was checked by UV spectra and found to be satisfactory for the time intervals required for the experimental work.

1-Butanol and methanol were high purity solvents purchased from Burdick and Jackson Laboratories, Inc. The spectrophotometric grade (99+% pure) isooctane was purchased from Aldrich Chemical Co. It was refluxed over P_2O_5 for 2 h and distilled. Ethanol was provided by U.S. Industrial Chemical Co. and was used as received. An analysis (furnished by USIC) showed the impurity levels to be very low: water was 0.005 vol%, isopropyl alcohol was 20 ppm, sec-butyl alcohol was 14 ppm, and all other impurities were less than 5 ppm.

Results and Discussion

Previous work in this laboratory showed that pulse irradiation of a deaerated ethanol solution of $Mn_2(CO)_{10}$ at 20 °C produced a transient which was characterized as the $Mn(CO)_5\cdot$ radical [1]. The transient had an optical absorption band with λ_{max} 830 nm and a molar extinction coefficient of 800 ± 80 M^{-1} cm^{-1}. It was generated by the reducing action of the solvated electron:

$$e_{sol}^- + Mn_2(CO)_{10} \rightarrow Mn_2(CO)_{10}^{\cdot -} \quad (1)$$

$$Mn_2(CO)_{10}^{\cdot -} \rightarrow Mn(CO)_5\cdot + Mn(CO)_5^- \quad (2)$$

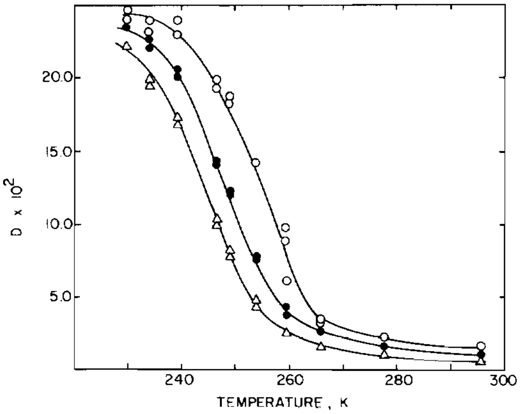

Fig. 1. Optical density at 700 nm of a pulse-irradiated, deaerated ethanol solution of 340 μM $Mn_2(CO)_{10}$ as a function of temperature from −43.5 to 22.0 °C at t = 3, 6, and 10 μs after the electron pulse.

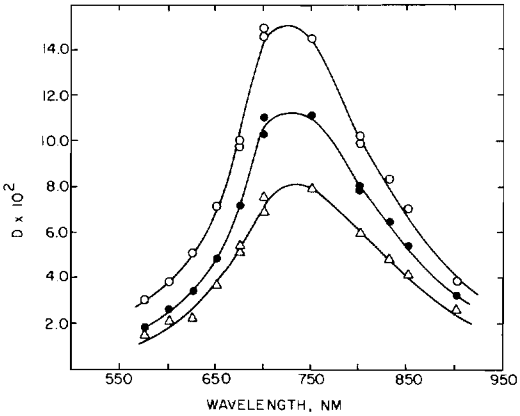

Fig. 2. Absorption spectrum obtained by pulse irradiation of a deaerated ethanol solution of 350 μM $Mn_2(CO)_{10}$ at −26.9 °C at t = 3, 6, and 10 μs after the electron pulse.

We now found that lowering the temperature of a pulse-irradiated 350 μM solution of $Mn_2(CO)_{10}$ produced a remarkable change in the optical absorption spectrum. As the temperature was lowered, the intensity of the band with λ_{max} 830 nm decreased and that of a new absorption band with λ_{max} 700 nm increased. This is illustrated in Fig. 1 with a plot of optical density at 700 nm as a function of temperature from −43 to 22 °C. Figure 2 shows the 700 nm absorption band of the low-temperature species at −26.9 °C. The molar extinction coefficient of this species at the maximum was found to be 10,120 ± 150 M^{-1} cm^{-1} based on ϵ 15,000 M^{-1} cm^{-1} at 700 nm for e_{sol}^- in ethanol [8]. The decay of the 700 nm absorption band obeyed first-order kinetics as shown in Fig. 3, with $k = 1.1 \times 10^5$ s^{-1}. The rate was invariant with wavelength (790–900 nm) and was independent of dose (500 and 1000 ns). The first-order kinetics for the decay of the 700 nm species contrast with a second-order rate law for the decay of the 830 nm band of $Mn(CO)_5\cdot$ at room temperature [1]. It is evident that the 700 nm species is not $Mn(CO)_5\cdot$ and that cleavage of the Mn–Mn bond is not occurring during pulse irradiation of $Mn_2(CO)_{10}$ at −27 °C.

Pulse irradiation of a deaerated 12.0 mM solution of $Mn(CO)_5SO_2CH_3$ in ethanol produced the 830 nm absorption band of $Mn(CO)_5\cdot$ at both 20.3 and −30.5 °C. As expected, the 700 nm band was not

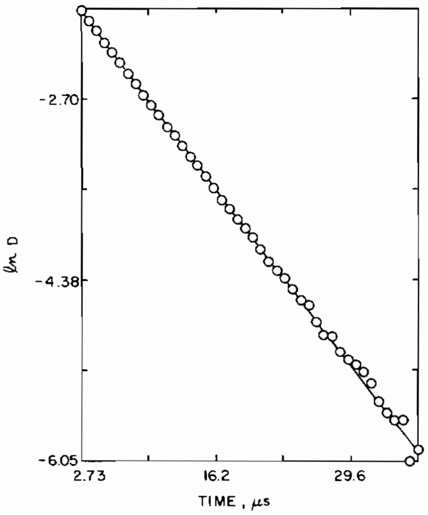

Fig. 3. First-order kinetic plot for decay of the 700 nm species at −26.9 °C. The deaerated ethanol solution was 350 μM $Mn_2(CO)_{10}$.

observed. Pulse radiolysis of a 350 μM solution of $Mn_2(CO)_{10}$ in the aprotic solvent isooctane at −32.6 °C also did not result in the appearance of the 700 nm band. Rather, the absorption of the $Mn(CO)_5\cdot$ radical, shifted slightly to *ca.* 820 nm, was observed. However, pulse irradiation of a 350 μM solution of $Mn_2(CO)_{10}$ in methanol produced the same kind of change in optical absorption on lowering the temperature as did pulse irradiation of the corresponding solution in ethanol, but at somewhat lower temperatures. Accordingly, the 700-nm band was observed at −36.5 °C. At 19 °C, only the 830-nm band of $Mn(CO)_5\cdot$ was discernible.

We have previously reported that pulse irradiation of ethanol solutions of $Re_2(CO)_{10}$ at 22 °C resulted in the appearance of a major absorption band at 415 nm and a weaker one at 515 nm [2]. The $Re(CO)_5\cdot$ radical, which absorbs at 535 nm, was not detected. We concluded that the electron attachment to $Re_2(CO)_{10}$, unlike the electron attachment to $Mn_2(CO)_{10}$, is nondissociative at room temperature (eqn. (3)):

$$e_{sol}^- + Re_2(CO)_{10} \rightarrow Re_2(CO)_{10}^{\cdot -} \qquad (3)$$

The reports that the Re–Re bond in $Re_2(CO)_{10}$ is stronger than the Mn–Mn bond in $Mn_2(CO)_{10}$ [9] are relevant to these observations. In the present work, pulse irradiation studies of $Re_2(CO)_{10}$ were extended to higher temperatures and to other solvents with a view to ascertaining whether the electron attachment to $Re_2(CO)_{10}$ becomes dissociative under any of these conditions. We found that pulse radiolysis of a 390 μM solution of $Re_2(CO)_{10}$ in ethanol at 60 °C furnished the same result as at 22 °C. Likewise, pulse irradiation of a 330 μM solution of $Re_2(CO)_{10}$ in 1-butanol at temperatures up to 106 °C gave similar results showing no apparent dissociation of the Re–Re bond. In contrast, Re–Re bond cleavage was observed following pulse irradiation of a 1.1 mM solution of $Re_2(CO)_{10}$ in isooctane at 20 °C (eqn. (4)):

$$Re_2(CO)_{10}^{\cdot -} \rightarrow Re(CO)_5\cdot + Re(CO)_5^- \qquad (4)$$

Figure 4 shows the absorption spectrum of the $Re(CO)_5\cdot$ radical, obtained as a difference spectrum since a long-lived transient absorbing at 400 nm was also produced. The 400 nm species was observed, along with $Re(CO)_5\cdot$, in the flash photolysis study of $Re_2(CO)_{10}$ in isooctane as well [2].

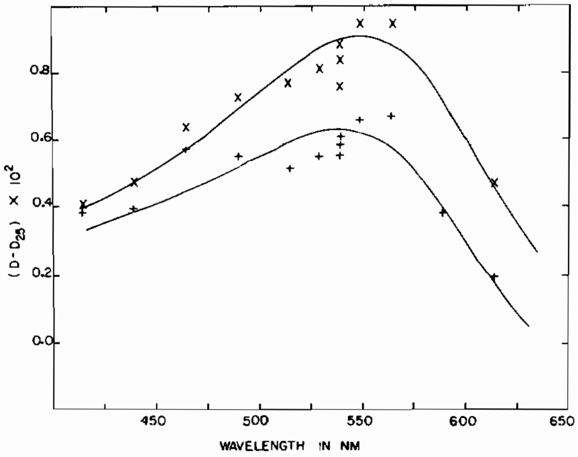

Fig. 4. Optical absorption band of the $Re(CO)_5\cdot$ radical as a difference spectrum in a deaerated isooctane solution of 1.1 mM $Re_2(CO)_{10}$ at t = 3 and 5 μs after the electron pulse.

The nondissociative electron attachment to $Re_2(CO)_{10}$ over the temperature range 22–106 °C, and to $Mn_2(CO)_{10}$ at low temperatures, may be rationalized by protonation of the radical anions $Re_2(CO)_{10}^{\cdot -}$ and $Mn_2(CO)_{10}^{\cdot -}$, respectively, by the alcohol solvent (eqns. (5) and (6)):*

$$Re_2(CO)_{10}^{\cdot -} + ROH \rightarrow HRe_2(CO)_{10} + RO^- \qquad (5)$$

$$Mn_2(CO)_{10}^{\cdot -} + ROH \rightarrow HMn_2(CO)_{10} + RO^- \qquad (6)$$

This proposal receives support from the observed formation of $Re(CO)_5\cdot$ and $Mn(CO)_5\cdot$ when the pulse irradiation is carried out in isooctane solution.

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*It is possible that the presumed dinuclear radical anions undergoing protonation are nonacarbonyls, such as $Re_2(CO)_9^{\cdot -}$ [10], or related species.

TABLE I. Experimental Conditions and the Arrhenius Parameters for Reactions (8)–(10).

Reaction	Temperature range (℃)	E_a (kcal/mol)	A (M^{-1} s^{-1})
8[a]	−18.3 to 59.3	2.8 ± 0.3	$(1.2 \pm 0.4) \times 10^8$
9[b]	−9.8 to 60.4	2.5 ± 0.4	$(2.8 \pm 0.5) \times 10^9$
10	−20.8 to 41.2	2.1 ± 0.4	$(3.0 \pm 0.4) \times 10^{10}$

[a] 10.0 to 52.6 mM $Mn(CO)_5SO_2CH_3$, 3 to 33 mM CCl_4. [b] 2.0 mM $Re(CO)_5SO_2CH_3$, 500 μM CCl_4.

Recently, rate constants have been measured for the protonation of several mononuclear and polynuclear metal carbonyl hydride anions by methanol at 25 ℃ (eqn. (7)) [11]:

$$H_{x-1}M_y(CO)_z^- + CH_3OH \longrightarrow H_xM_y(CO)_z + CH_3O^- \quad (7)$$

The values were found to fall in the range 2×10^{-2} to 25 s^{-1}. In our study, the rate constant for the presumed protonation of $Mn_2(CO)_{10}^{\cdot -}$ by ethanol must be substantially larger than the reported values for reaction (7) in order that the dissociation in eqn. (2) be suppressed. Both $HMn_2(CO)_{10}$ and $HRe_2(CO)_{10}$ represent 35-electron species; they are therefore expected to be unstable, probably decomposing to one or more of the known stable manganese and rhenium carbonyl hydrides.

The temperature dependence of three reactions of the pentacarbonyl radicals was investigated in ethanol solution. These reactions are (a) the abstraction of chlorine from CCl_4 by $Mn(CO)_5\cdot$ (eqn. (8)), (b) the abstraction of chlorine from CCl_4 by $Re(CO)_5\cdot$ (eqn. (9)), and (c) the coupling of $Mn(CO)_5\cdot$ (eqn. (10)):

$$Mn(CO)_5\cdot + CCl_4 \longrightarrow Mn(CO)_5Cl + CCl_3\cdot \quad (8)$$

$$Re(CO)_5\cdot + CCl_4 \longrightarrow Re(CO)_5Cl + CCl_3\cdot \quad (9)$$

$$Mn(CO)_5\cdot + Mn(CO)_5\cdot \longrightarrow Mn_2(CO)_{10} \quad (10)$$

Reaction conditions and the values of activation energy, E_a, and the pre-exponential factor, A, in the Arrhenius equation, $k = Ae^{-E_a/RT}$ are set out in Table I.

The decay of $Mn(CO)_5\cdot$ and $Re(CO)_5\cdot$ according to eqns. (8) and (9) was studied with $[CCl_4] \gg [Mn(CO)_5\cdot]$ and $[Re(CO)_5\cdot]$. As reported previously [2], under this condition, a first-order rate law was obtained. Plotting pseudo first-order rate constants against the concentration of CCl_4, as shown in Fig. 5 for $Mn(CO)_5\cdot$, yielded the rate constants from the slope of the lines. The values for reaction (8) are given in Table II. Figure 6 shows the temperature dependence of the rate constant for reaction (8). From this plot, the values of E_a and A

TABLE II. Rate Constants for Reaction of $Mn(CO)_5\cdot$ with CCl_4 in Ethanol at −18.3 to 59.3 ℃.

Temperature (℃)	$k \times 10^{-5}$ (M^{-1} s^{-1})
−18.3 ± 1.5	5.0
−3.7 ± 2.0	6.9
19.9 ± 1.1	10.9
39.0 ± 1.3	14.8
59.3 ± 1.9	16.8

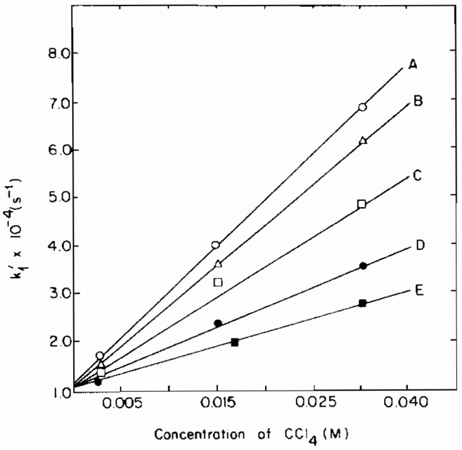

Fig. 5. Pseudo first-order rate constants for the reaction of $Mn(CO)_5\cdot$ with CCl_4 as a function of CCl_4 concentration at different temperatures (A) 59.3, (B) 39.0, (C) 19.9, (D) −3.7, and (E) −18.3 ℃.

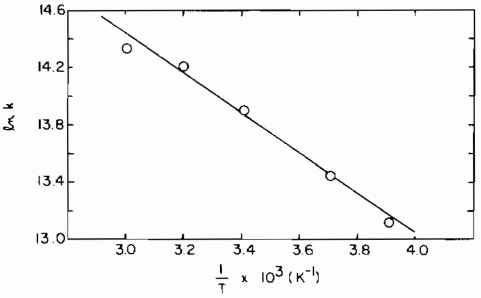

Fig. 6. Arrhenius plot showing the temperature dependence of the rate constant for the reaction of $Mn(CO)_5\cdot$ with CCl_4.

were determined. For reaction (9), it was not possible to obtain data over a wide range of CCl_4 concentration, since CCl_4 scavenges the solvated electron and thus reduces the amount of $Re(CO)_5\cdot$ generated. This introduces considerable error in the data collected at higher concentrations of CCl_4 owing to poor signal to noise ratio.

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