similarity between the uncorrected relative abundances of the $[NO(N_2O_3)_n]^+$ clusters formed in both methods.

Conclusion

In addition to producing simple fragment and molecular ions, presumably by the standard collision cascade mechanism, the bombardment of molecular solids held at cryogenic temperatures with the heavier rare gas (and possibly other) ions promises to become a source of a rich variety of simple and complicated cluster ions for further investigation. In some cases the composition of the solvating unit in the cluster ions reflects faithfully the molecular composition of the solid (H_2O,[7] N_2,[9] CO,[9] rare gases[1]). In the case of the nitrogen oxides studied here, the solvating units are significantly different from the neutral components of the molecular solid, showing that a deep-seated chemical rearrangement occurs.

The results can be summarized as follows: (i) The spectra depend sensitively on molecular structure of the solid and not only its stoichiometry. (ii) A single primary ion impact can cause the formation of a large number of chemically transformed species in a single secondary cluster ion. (iii) The relative abundance of higher cluster ions increases with the primary ion momentum. (iv) There are characteristic differences in the secondary ion kinetic energy distributions of the molecular and the fragment ions on the one hand and the cluster ions on the other hand.

We propose tentatively that the cluster formation involves the following events. Upon ion bombardment with the heavier rare gas ions pieces of the matrix originating in the damage track, containing several reactive centers, and resembling charged droplets of liquid are lifted from the solid substrate. They undergo chemical transformations due to these reactive centers before, during, and after the departure from the surface. Finally, they lose excess heat by shaking off the less polarizable molecules and stabilize into their final form in a time shorter than 100 μs.

At this time, we cannot exclude other mechanisms, but those we have been able to think of so far appear less probable to us (e.g., the abundance of oxygen relative to nitrogen atoms in the cluster ions from N_2O and NO could be caused by preferential orientation of the molecules on the surface of the solid). Additional experiments of a more quantitative nature are clearly needed to elucidate the matter.

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Registry No. N_2O, 10024-97-2; NO, 10102-43-9; N_2O_3, 10544-73-7; N_2O_4, 10544-72-6.

Fast Reaction Studies of Rhenium Carbonyl Complexes: The Pentacarbonylrhenium(0) Radical

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Abstract: The $Re(CO)_5\cdot$ radical has been generated in the pulse radiolysis of a variety of organorhenium compounds in ethanol solution as well as in the flash photolysis of $Re_2(CO)_{10}$ in isooctane solution. This radical exhibits an optical absorption band in the visible region with a maximum at 535 nm and a molar extinction coefficient, in ethanol, of ϵ_{535} 1000 ± 100 M^{-1} cm^{-1}. Absolute rate constants were determined for the reactions of the solvated electron, in ethanol, with $Re(CO)_5Br$ (6.7×10^9), $Re(CO)_5SO_2CH_3$ (6.6×10^9), and $Re_2(CO)_{10}$ (7.8×10^9 M^{-1} s^{-1}). Rate constants were also obtained for the reactions of $Re(CO)_5\cdot$ and of $Mn(CO)_5\cdot$ in abstracting a chlorine atom from carbon tetrachloride in ethanol solution. The values, at 22 °C, are 3.9×10^7 and 6.1×10^5 M^{-1} s^{-1}, respectively, indicating a 65-fold higher reactivity for the pentacarbonylrhenium radical as compared with the pentacarbonylmanganese radical in this abstraction reaction. The rate constant for the recombination reaction of $Re(CO)_5\cdot$ radicals in isooctane was found to be $2k_7 = 5.4 \times 10^9$ M^{-1} s^{-1}.

In a recent paper(2) concerned with the application of pulse radiolysis in fast reaction studies of organotransition-metal transients, we reported some physical and chemical properties of $Mn(CO)_5\cdot$. The present work extends these investigations to the congeneric $Re(CO)_5\cdot$ radical and also includes some complementary results obtained by flash photolysis.

The radical $Re(CO)_5\cdot$ was first detected by mass spectrometry.[3] It was subsequently generated photochemically from $Re_2(CO)_{10}$ and trapped as $Re(CO)_5X$ by the use of organic halides.[4,5] A recent molecular beam study[6] has demonstrated that photodissociation of $Re_2(CO)_{10}$ in the gas phase results in the formation of $Re(CO)_5\cdot$ with no loss of CO. This radical was also prepared by the reaction of Re with CO in a matrix and shown by infrared spectroscopy to have a square-pyramidal C_{4v} structure.[7]

Reported here are our pulse radiolysis studies of solutions of $Re(CO)_5X$ (X = Cl, Br, I), $Re(CO)_5SO_2CH_3$, $ReMn(CO)_{10}$, and $Re_2(CO)_{10}$, as well as a flash photolysis study of $Re_2(CO)_{10}$. The $Re(CO)_5\cdot$ radical was generated, and its optical absorption spectrum, which has heretofore not been reported, was recorded. The absolute rate constants for some of its reactions as well as those of $Mn(CO)_5\cdot$ were determined.

Experimental Section

The apparatus in use with a Varian V-7715A electron linear accelerator has been described previously.[8-10] The 4-MeV electrons with a

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(1) (a) The Ohio State University. (b) The University of Saskatchewan.

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pulse duration of 200–1000 ns were used for this work. The dose per pulse was in the range of (1–5) × 10^{17} eV/g, giving an initial e_{sol}^- concentration of about 5 μM for a 1000-ns pulse length. The 2-cm quartz irradiation cell was constructed so it could be filled in the absence of air, and a syringe technique, described elsewhere,[11] was employed for filling the cell. All solutions were deaerated by using argon gas (99.999%), and experiments were performed at 22 °C. A double pass of the analyzing beam was utilized.

$Re_2(CO)_{10}$ was purchased from Pressure Chemical Co., and $Mn_2(CO)_{10}$ was purchased from Strem Chemicals, Inc. All of the other rhenium and manganese carbonyl complexes were prepared by published procedures.[12-14] The compounds were purified by sublimation and stored in the dark at 10 °C generally under an argon atmosphere. Infrared and ultraviolet spectra of these compounds were found to be in good agreement with reported spectra.[5,12,14-19] The stability of the compounds dissolved in ethanol was checked by UV spectra and found to be satisfactory for the time intervals required for the experimental work. All other chemicals and gases used were of reagent quality. The ethanol utilized for all the solutions was specially provided by U.S. Industrial Chemicals Co. and could be 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. The half-life of the e_{sol}^- in this deaerated ethanol ranged from 1 to 5 μs depending on the dose, and the decay of the e_{sol}^- closely approximated first-order kinetics. However, the first-order rate constant did increase with increasing dose. Both this and the range of half-lives are in agreement with previously reported results.[20,21]

The flash photolysis experiments were done with an air-filled flash lamp (pressure ca. 1 torr) described elsewhere,[22] across which 200 J could be dissipated to produce a flash with a 90% rise time and fall time of about 20 μs. The flash tube was surrounded by a Pyrex sleeve in order to restrict the radiation to wavelengths above about 280 nm. A cylindrical suprasil reaction vessel with a 10-cm optical path was mounted parallel to the flash lamp.

Isooctane (Fisher certified grade), used as the solvent, was purified by standard procedures.[23] All solutions were deaerated, and the solution in the reaction cell was changed after each flash. In those instances where the solutions contained added CO (Matheson research grade carbon monoxide of 99.99% minimum purity), the pressure of CO over the solutions was maintained at 180 torr above atmospheric pressure.

Results and Discussion

The information on the properties of the pentacarbonylrhenium radical, $Re(CO)_5\cdot$, developed in our current investigations, consists of the optical absorption spectrum and several kinetic parameters. Among these are the rate constants for its formation by dissociative attachment of solvated electrons to a number of different precursor compounds in ethanol, the rate constant for its dimerization reaction in isooctane, and its reactivity in abstracting a chlorine atom from carbon tetrachloride in ethanol solution. The larger part of the data were obtained with the pulse radiolysis technique, as in our earlier work[2] on $Mn(CO)_5\cdot$, but important information was also obtained from flash photolysis experiments. The solvent used in the pulse radiolysis was ethanol, whereas isooctane was the solvent in the flash photolysis.

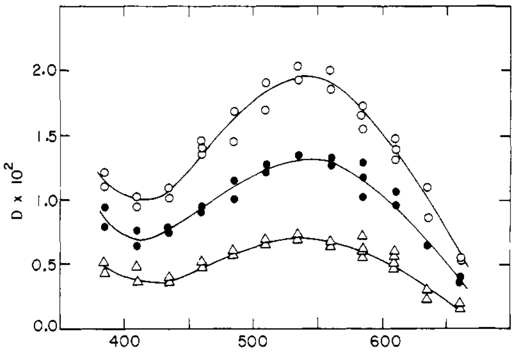

Figure 1. Optical absorption band of the $Re(CO)_5\cdot$ radical in a deaerated ethanol solution of 350 μM $Re(CO)_5I$ at *t* = 3, 7, and 15 μs after the electron pulse.

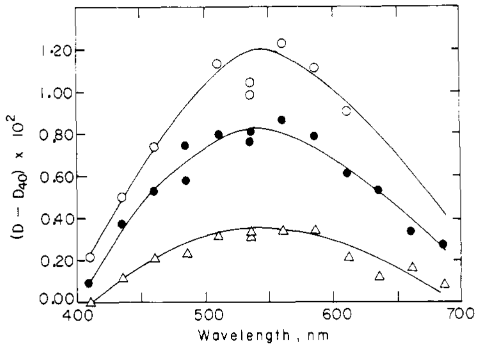

Figure 2. Absorption spectrum of $Re(CO)_5\cdot$ as a difference spectrum in a deaerated ethanol solution of 330 μM $ReMn(CO)_{10}$ at *t* = 4, 7, and 15 μs after the electron pulse.

The transient optical absorption in the pulse radiolysis was produced by the reducing action of the solvated electron:

$$e_{sol}^- + Re(CO)_5X \rightarrow Re(CO)_5\cdot + X^- \qquad (1)$$

The direct photolysis of dirheniumdecacarbonyl was the primary process in the flash photolysis:

$$Re_2(CO)_{10} + h\nu \rightarrow 2Re(CO)_5\cdot \qquad (2)$$

Optical Absorption Spectra. Pulse irradiation of deaerated ethanol solutions (250–400 μM) of a number of different precursor compounds, namely, $Re(CO)_5X$ (X = Cl, Br, I), $Re(CO)_5SO_2CH_3$, and $ReMn(CO)_{10}$, produced a common transient absorption band over the wavelength range 410–630 nm with its absorption maximum at 535 nm. Figure 1 shows this absorption band in a solution of $Re(CO)_5I$, at times of 3, 7, and 15 μs after the electron pulse. In contrast to our previous observations[2] on $Mn(CO)_5I$, there appears to be no detectable iodine abstraction reaction of $Re(CO)_5I$ with $CH_3\dot{C}HOH$, formed from the solvent, to yield additional $Re(CO)_5\cdot$ in a slower process. As the absorption band decays, no change in the shape of the band or in its λ_{max} is occurring. This is a fairly clear indication that this 535-nm band is to be ascribed to a single optically absorbing species. The same optical absorption band (same λ_{max} and same WHM) was obtained with all three halide compounds and with the sulfinato pentacarbonyl complex, thus supporting its identification as $Re(CO)_5\cdot$.

In the case of $ReMn(CO)_{10}$, a longer lived absorbing species was also obtained along with the 535-nm band and overlapping with it. The 535-nm band was obtained as a difference spectrum. Since the 535-nm band had decayed almost completely in a time of 40 μs after the pulse, the difference spectrum was obtained by subtracting the optical density at 40 μs from the optical density at 4, 7, and 15 μs. The resulting difference spectrum is shown in Figure 2. Again it is the same absorption band formed in solutions of the other four compounds. No absorption band at 830 nm,[2] corresponding to $Mn(CO)_5\cdot$, was observed in this solution. Apparently the dissociative attachment of e_{sol}^- to the mixed metal decacarbonyl produces the radical $Re(CO)_5\cdot$ and the anion

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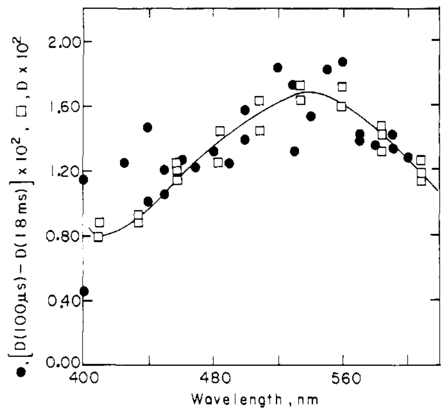

Figure 3. Optical absorption band of $Re(CO)_5\cdot$ obtained by flash photolysis (●) of 120 µM $Re_2(CO)_{10}$ with 0.01 M CO in isooctane and by pulse radiolysis (□) of a deaerated ethanol solution of 350 µM $Re(CO)_5I$ at t = 3 µs after the electron pulse. Data for $Re(CO)_5I$ are normalized to flash photolysis data at 535 nm.

$Mn(CO)_5^-$, which does not absorb in the visible region;[24] the nature of the longer lived species is not obvious.

In all the foregoing solutions, no stable absorbing product was observed in the region 410–620 nm. Saturation of the ethanol solutions with N_2O, an effective scavenger of the solvated electron, eliminated the transient absorbing species as was to be expected since they were formed by the reducing action of e_{sol}^- as indicated in reaction 1.

Pulse irradiation of an ethanol solution of the two compounds $Mn(CO)_5Br$ (280 µM) and $Re(CO)_5Br$ (370 µM), produced an optical absorption in the UV which revealed the presence of $Mn_2(CO)_{10}$ but not $Re_2(CO)_{10}$. Pulse irradiation of a deaerated tetrahydrofuran solution of 330 µM $Re(CO)_5Br$ also showed an absorption band at 535 nm along with a stronger peak at 415 nm.

Further evidence for the identification of the 535-nm band with $Re(CO)_5\cdot$ was obtained in the flash photolysis, monitored at $\lambda > 400$ nm, of solutions of $Re_2(CO)_{10}$ (120 µM) in isooctane. These experiments were carried out with and without CO present. The transient absorption observed in the wavelength range 400–610 nm has an absorption maximum at 535–540 nm, obtained as a difference spectrum since there was an additional long-lived transient absorbing near 400 nm. The rate of decay of this additional species was sufficiently slow relative to that of $Re(CO)_5\cdot$ so that its contribution to the absorption spectrum could be treated as a constant residual in obtaining the difference spectrum. Absorption in the region around 400 nm was diminished by the presence of CO. The absorption spectrum is in reasonably good agreement with the results of the pulse radiolysis experiments, as shown in Figure 3. The flash photolysis spectrum shown in this figure was obtained with CO present (0.01 M).

The absorption of $Re(CO)_5\cdot$ at 535 nm may be compared with the band at 830 nm for $Mn(CO)_5\cdot$. Recently, Poliakoff and Turner[25] determined the electronic absorption spectrum of $Mn(CO)_5\cdot$ in solid CO matrices at 10–20 K. Two absorptions were observed, a low intensity band at 798 nm, presumably corresponding to the band we reported[2] at 830 nm in solution, and a more intense absorption at 331 nm. In view of these findings, it seems likely that $Re(CO)_5\cdot$, which is isoelectronic and isostructural with $Mn(CO)_5\cdot$, also has an absorption band in the UV. However, readings in this spectral region would be difficult to obtain because of the overlapping absorption of the precursor rhenium pentacarbonyls.

Pulse radiolysis of solutions of $Re_2(CO)_{10}$ in ethanol, on the other hand, showed no formation of the 535-nm absorption band. The absorption spectrum which was observed showed a major peak at 415 nm and a weak, narrow peak at 515 nm as discerned from the difference spectrum. We conclude from the absence of the 535-nm band that the electron attachment to the decacarbonyl is nondissociative (eq 3). $Re_2(CO)_{10}^-\cdot$ has been observed in ESR

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

experiments[26] on γ-irradiated $Re_2(CO)_{10}$ at 77 K. The radical anion formed in reaction 3 is very likely protonated in a reaction in which the solvent, ethanol, is the proton donor (eq 4). Such

$$Re_2(CO)_{10}^-\cdot + C_2H_5OH \rightarrow HRe_2(CO)_{10} + C_2H_5O^- \tag{4}$$

a reaction is analogous to the protonation, by ethanol, of various aromatic radical ions reported[27] some years ago. $HRe_2(CO)_{10}$ represents the species formed in the protonation. It may very well be unstable, probably decomposing to one or more of the known, stable rhenium carbonyl hydrides. The failure of the decacarbonyldirhenium anion to dissociate, in contrast with the ready dissociation[2] of the decacarbonyldimanganese radical anion (eq 5), may be understood on the basis of different bond strength of

$$Mn_2(CO)_{10}^-\cdot \rightarrow Mn(CO)_5\cdot + Mn(CO)_5^- \tag{5}$$

the metal–metal bond in the two compounds. The Re–Re bond in $Re_2(CO)_{10}$ is stronger[6,28-31] than the Mn–Mn bond in $Mn_2(CO)_{10}$.

Reaction Rate Constants. Absolute rate constants were obtained for several reactions which are relevant here. These include (a) the attachment reaction of the solvated electron in ethanol to several precursor compounds, (b) the recombination reaction of $Re(CO)_5\cdot$ in isooctane solution, and (c) the abstraction of Cl from CCl_4 in ethanol, by both $Re(CO)_5\cdot$ and $Mn(CO)_5\cdot$, which show a substantial difference in reactivity.

The rate constants for the electron attachment to the precursor compounds, $k_{e_s^-}$, were obtained under pseudo-first-order conditions, i.e., where $[\text{compound}]_0 >> [e_{sol}^-]_0$. The observed rate constant, k_{obsd}, for the decay of the solvated electron (first order in all cases), was corrected for the concurrent first-order decay of the electron in the absence of precursor compound, $k'_{e_s^-}$, by the use of eq 6.

$$k_{e_s^-} = \frac{k_{obsd} - k'_{e_s^-}}{[\text{compound}]} \tag{6}$$

The following values were obtained, in ethanol solution.

compd	k, $10^{-9} M^{-1} s^{-1}$
$Re(CO)_5Br$	6.7
$Re(CO)_5SO_2CH_3$	6.6
$Re_2(CO)_{10}$	7.8

The experimental uncertainty in these values is less than ±10%. The correction for $k'_{e_s^-}$ amounts to about 20%. The rate constants for the three compounds are essentially the same and are very near the diffusion-limited value. These rate constants for attachment of e_{sol}^- also represent, in the case of $Re(CO)_5Br$ and $Re(CO)_5SO_2CH_3$, the rate constants for formation of $Re(CO)_5\cdot$, since the anion dissociation is so fast.

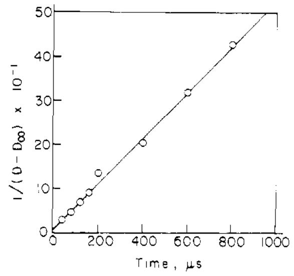

Figure 4. Second-order kinetic plot for decay of transient at 550 nm obtained from flash photolysis of 120 µM $Re_2(CO)_{10}$ with 0.01 M CO in isooctane.

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The rate constant for the recombination reaction (eq 7), in isooctane solution, can be obtained from the data of the flash photolysis of $Re_2(CO)_{10}$. The decay kinetics of the 535-nm band

$$Re(CO)_5\cdot + Re(CO)_5\cdot \rightarrow Re_2(CO)_{10} \qquad (7)$$

follow a second-order rate law as may be seen in Figure 4 which shows a plot of $1/(D_t - D_\infty)$ (D being the optical density) against time. The rate constant, $2k_7 = 5.4 \times 10^9$ M^{-1} s^{-1}, was obtained from $2k = (\text{slope})\epsilon_{535}l$, where ϵ_{535} is the molar extinction coefficient of $Re(CO)_5\cdot$ at 535 nm, l = 10 cm is the length of the optical path, and the slope is from data such as plotted in Figure 4. The value of the rate constant was independent of wavelength (470–590 nm) and was not substantially altered by the presence of CO. The molar extinction coefficient of the rhenium pentacarbonyl radical at the maximum, ϵ_{535} 1000 ± 100 M^{-1} cm^{-1}, was obtained by pulse radiolysis and is based on ϵ 15 000 M^{-1} cm^{-1} at 700 nm for e_{sol}^- in ethanol.[32] The fraction of the initial concentration of e_{sol}^- scavenged by the precursor compound was obtained from

$$\frac{k_{e_s^-}[\text{compound}]}{k_{e_s^-}[\text{compound}] + k'_{e_s^-}} \qquad (8)$$

Where $k_{e_s^-}$ and $k'_{e_s^-}$ are defined in eq 6. This fraction amounted to 0.80 in the pertinent experiments.

The decay kinetics of the 535-nm absorption band in the pulse radiolysis of ethanol solutions did not follow a second-order rate law but was of mixed order, indicating a more complex chemistry than was seen in isooctane solution or that observed for the $Mn(CO)_5\cdot$ radical in ethanol solution. Two factors may be responsible. The α-hydrogen in ethanol may be abstracted more readily than the hydrogen in isooctane judging from the rate constants[33] for abstraction of hydrogen by hydroxyl radical from ethanol and from methanol (1.8×10^9 and 8×10^8, respectively). Secondly, the $Re(CO)_5\cdot$ radical is considerably more reactive than $Mn(CO)_5\cdot$, as is evident from our determination of the rate constants for their reaction with carbon tetrachloride. The hydrogen abstraction reaction would contribute a first-order component to the decay of $Re(CO)_5\cdot$, while the possible reaction of $Re(CO)_5\cdot$ with the α-ethanol radical, $CH_3\dot{C}HOH$, which is formed in the radiolysis of ethanol itself, would contribute a second-order component. It is noteworthy in this context that our attempts to observe the presence of $Re_2(CO)_{10}$ by means of its optical absorption band at 275 and 310 nm failed to reveal the presence of this compound. However, an absorption band at 270 nm was observed, which may indicate the presence of $HRe(CO)_5$.[17,34] It should be added that small amounts of $Re_2(CO)_{10}$ could escape detection by UV spectra because the absorption bands of the precursor compounds and the 270-nm product overlap those of $Re_2(CO)_{10}$. It was not possible to characterize the product(s) by infrared methods. The IR absorptions of the precursor compounds and possible products ($Re_2(CO)_{10}$ and $HRe(CO)_5$) all occur in approximately the same region. The overlapping bands do not allow detection of a product which exists in micromolar amounts, and the signal to noise ratio for such low concentrations is poor. In addition the determination of IR spectra in ethanol is difficult because the observed bands are broad.

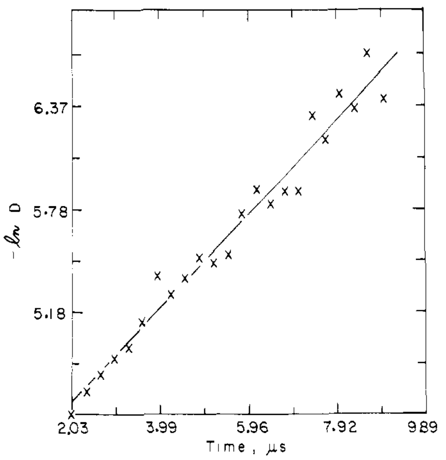

Figure 5. First-order kinetic plot for reaction of $Re(CO)_5\cdot$ with CCl_4. The deaerated ethanol solution was 5.7 mM $Re(CO)_5SO_2CH_3$ and 4.0 mM CCl_4.

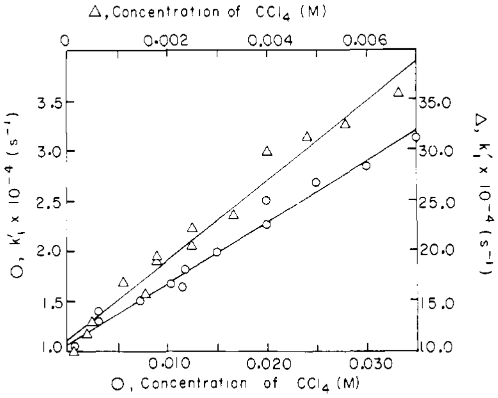

Figure 6. Pseudo first order rate constants for the reactions of $Re(CO)_5\cdot$ (Δ) and $Mn(CO)_5\cdot$ (O) with CCl_4 as a function of CCl_4 concentration.

The reactivity of both $Re(CO)_5\cdot$ and $Mn(CO)_5\cdot$ with carbon tetrachloride in solution was investigated by using $Re(CO)_5Br$, $Re(CO)_5I$, $Re(CO)_5SO_2CH_3$, and $Mn(CO)_5SO_2CH_3$ as precursor compounds. The latter two compounds are considerably more soluble in ethanol than the halides and were used in experiments involving higher concentrations of CCl_4. The decay of the pentacarbonyl radicals in reactions 9 and 10 was found to fit a

$$Re(CO)_5\cdot + CCl_4 \rightarrow Re(CO)_5Cl + CCl_3 \qquad (9)$$

$$Mn(CO)_5\cdot + CCl_4 \rightarrow Mn(CO)_5Cl + CCl_3 \qquad (10)$$

first-order rate law as may be seen in Figure 5. The pseudo-first-order rate constants obtained were then plotted against the concentration of CCl_4, as in Figure 6, and the rate constants were obtained from the slope of the line. The values are

$$k_{Re} = (3.9 \pm 0.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{Mn} = (6.1 \pm 0.8) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

The pentacarbonylrhenium radical is thus 65-fold more reactive in this Cl-abstraction reaction than is the corresponding manganese radical. The presence of the product $Re(CO)_5Cl$ was established by the observation of its absorption bands at 342 and 318 nm. The yield of the chloride was 0.9 molecule/100 eV, and the initial yield of the radical, $Re(CO)_5\cdot$, was also 0.9 molecule/100 eV, indicating good material balance, within the experimental uncertainty, for reaction 9. Fox and Poë[35] have determined the ratio of the rate constants for dimerization of $Mn(CO)_5$ and for reaction 10 in cyclohexane. Abrahamson and Wrighton,[36] by means of competition kinetics based on product analysis in benzene solution, determined approximate rate constant ratios for reaction with carbon tetrachloride. From their data, we obtain

$$\frac{k_{Mn}}{k_{Re}} = \left(\frac{k_{Mn}}{k_W}\frac{k_W}{k_{Re}}\right) < \frac{0.13}{0.54} = 0.24$$

Our values for these rate constants, in ethanol solution, are in agreement with regard to the order of the reactivities, but they reveal a much larger effect, namely, $k_{Mn}/k_{Re} = 0.016$, than is

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indicated by the upper limit of 0.24.

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Registry No. $Re(CO)_5\cdot$, 15684-00-1; $Re_2(CO)_{10}$, 14285-68-8; $ReMn(CO)_{10}$, 14693-30-2; $Re(CO)_5Br$, 14220-21-4; $Re(CO)_5Cl$, 14099-01-5; $Re(CO)_5I$, 13821-00-6; $Re(CO)_5SO_2CH_3$, 37988-72-0; $Mn(CO)_5\cdot$, 15651-51-1; CCl_4, 56-23-5.

Hydrogenation of Alkylzirconium(IV) Complexes: Heterolytic Activation of Hydrogen by a "Homogeneous" Metal Alkyl

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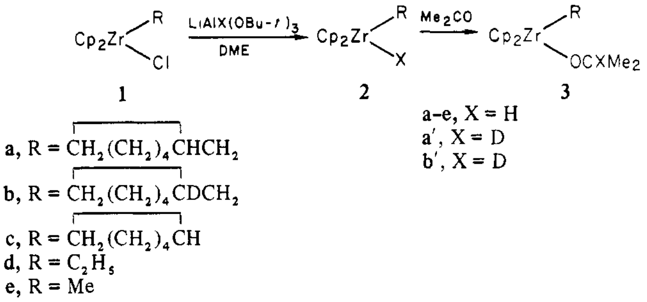
Abstract: Bis(η^2-cyclopentadienyl)zirconium(IV) alkyl chlorides and hydrides have been prepared and characterized. Hydrogenation of these species yields the corresponding alkane and zirconium hydride complexes, Cp_2ZrHCl and Cp_2ZrH_2, respectively. Deuterium labeling experiments suggest that these d^0 complexes activate H_2 by heterolytic attack on that molecule. Qualitative rates for hydrogenation of a series of complexes were $Cp_2Zr(R)H > Cp_2Zr(R)Cl \simeq Cp_2ZrR_2 > [(Cp_2ZrCl)_2(\mu\text{-OCHR})] > Cp_2Zr(COR)Cl$. This rate trend is the same as that for carbonylation and suggests a conceptual link between mechanisms for hydrogenation and carbonylation of these unsaturated complexes. A possible relationship is noted between heterolytic activation and oxidative addition of H_2 to transition-metal species.

The development of novel systems for activation of hydrogen continues to be an active area of research:[1,2] an understanding of elementary processes effecting this transformation may ultimately allow the design of catalysts for the selective reduction of "difficult" substrates such as carbon monoxide. One interesting approach to the design of such systems would be to utilize a transition-metal complex which can react directly with H_2 to give "hydridic" hydride ligands (where "hydridic" is defined as the ability of that ligand to reduce a carbonyl group to give the corresponding metal alkoxide).[3] Whereas most transition-metal hydrides are neutral or weakly acidic,[4] group 4a metal hydrides have reactivity patterns which are similar to those of boron or aluminum hydrides.[3,5] Perhaps because of this property, CO is stoichiometrically reduced to methane by $Cp_2Ti(CO)_2$ under H_2,[6] to methanol precursors by systems based on Zr(IV),[7-9] and to a mixture of precursors of linear aliphatic alcohols, promoted by $Cp_2ZrCl_2\cdot 3(i\text{-Bu})_2AlH$.[8] Although simple CO reduction systems based on group 4A metals are unlikely to be catalytic because of the strength of the metal-oxygen bond,[10] stoichiometric processes based on them are instructive examples which can suggest directions for further investigation: a knowledge of mechanisms for H_2 activation by group 4 transition-metal complexes is important to a general understanding of stoichiometric reductions using hydrides of this class.

Scheme I



Catalytic hydrogenation of olefins using Zr(IV) (d^0) species Cp_2ZrH_2,[11] $Cp_2Zr(H)Cl$,[11] and $Cp_2ZrCl_2\cdot(i\text{-Bu})_3Al$[12] has been demonstrated. In these reactions intermediary low-oxidation-state complexes of Zr have been assumed to be responsible for H_2 activation. Indeed, complexes of Zr(II)[7a-c,13] are known to oxidatively add H_2 to generate the corresponding Zr(IV) dihydrides. To better define mechanisms by which Zr(IV) complexes react with H_2, we have studied hydrogenation of alkylbis(η^5-cyclopentadienyl)zirconium(IV) complexes which are likely intermediates in the Cp_2ZrHX-catalyzed (X = Cl or H) hydrogenation of olefins. Our results suggest that mechanisms for hydrogenation and carbonylation of alkylzirconium(IV) hydrides are related and imply that a pathway previously unacknowledged in the hydrogenation chemistry of transition-metal alkyls (one other than

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