Inorg. Chem. **1988**, *27*, 3147-3151

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Reactions of the 17-Electron Bis(dimethylglyoximato)(triphenylphosphine)rhodium(II) Radical

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Received May 26, 1988

The indicated metal-centered radical arises from the laser-flash photolysis of the dinuclear complex $[\mathrm{Rh(dmgH)_2PPh_3}]_2$. In the absence of other reagents the radical (which shows an absorption maximum at 580 nm, $\epsilon = 2 \times 10^3$ L mol^{-1} cm^{-1}) dimerizes rapidly, with $k_D = 2.3 \times 10^8$ L mol^{-1} s^{-1} in 95% ethanol. The metal-centered radical reacts rapidly with O_2, $k = 1.4 \times 10^9$ L mol^{-1} s^{-1}, with the first step assigned to the formation of a 1:1 oxygen adduct. This reaction ultimately yields hydrogen peroxide. The reactions between $\mathrm{Rh(dmgH)_2PPh_3}$ and a wide range of alkyl halides have also been studied. The rate constants k_{RX} span a wide range, from $\sim 4 \times 10^2$ ($CHCl_3$) to 9×10^8 (CBr_4). There is an approximate correlation between log k_{RX} and the carbon–halogen bond dissociation energy. A correlation is also found with the half-wave potential for the reaction $RX + e^- \rightarrow R^\bullet + X^-$. The mechanism of the reactions with alkyl halides is discussed, and it seems probable that these reactions proceed by halogen atom abstraction.

Introduction

X-ray diffraction[1] has established that rhodium(II) rhodoxime[2] exists as a dimer, $[\mathrm{Rh(dmgH)_2PPh_3}]_2$. In this compound the monomeric halves are linked by a rhodium–rhodium single bond. Irradiation into the principal visible absorption band of the rhodium dimer, which is characterized by a strong absorption maximum at 452 nm ($\epsilon = 5 \times 10^4$ M^{-1} cm^{-1}), produces the transient monomeric Rh(II) unit, a reactive, 17-electron species.

The rhodium(II) radical undergoes rapid dimerization,[3] a facile process by which the parent rhodium dimer is recovered. The photodissociation and recombination are represented by eq 1.

$$[\mathrm{Rh(dmgH)_2PPh_3}]_2 \overset{h\nu}{\rightleftarrows} 2\mathrm{Rh(dmgH)_2PPh_3} \qquad (1)$$

Alkyl halides react with the rhodium(II) radical by halogen atom abstraction (eq 2).[4] $\mathrm{Co(dmgH)_2L}$ complexes, which show no tendency to dimerize, react similarly with alkyl halides.[5]

$$\mathrm{Rh(dmgH)_2PPh_3} + \mathrm{RX} \rightarrow \mathrm{XRh(dmgH)_2PPh_3} + \mathrm{R}^\bullet \qquad (2)$$

The only prior information on the kinetics and mechanism of this reaction comes from our report[4] of indirect determinations. Those data relied on the ratio of products (dimeric rhodoxime: halorhodoxime) obtained when an alkylrhodoxime was flash irradiated in the presence of a given concentration of alkyl halide. The duration of the flashlamp pulse was ca. 100 μs, too slow to permit a direct, time-resolved study of the kinetics. In addition, the product ratio method was highly imprecise, especially since the two pathways by which $\mathrm{Rh(dmgH)_2PPh_3}$ reacts have different kinetic orders, second order (dimerization) and pseudo first order (RX reaction), and thus vary in relative contribution with time.

We have therefore returned to this system, now to measure directly the rates of the alkyl halide reactions. A much faster photodissociation system was used, in the form of a flashlamp-pumped dye laser that has a pulse width of 600 ns, thus permitting the monitoring of the time course of the reactions represented by eq 2. One of our objectives was to learn the extent to which the rates are governed by two pertinent variables, the carbon-halogen bond energy, D(C–X), versus the electrode potential for the reduction of alkyl halides ($RX + e^- \rightarrow R^\bullet + X^-$). The same issues have been addressed in several studies of a rhenium(0) carbonyl radical[6-9] that also abstracts a halogen atom from alkyl halides. We have also studied the dimerization reaction of $\mathrm{Rh(dmgH)_2PPh_3}$ and its reaction with O_2.

Experimental Section

Reagents. $\mathrm{ClRh(dmgH)_2PPh_3}$ was prepared by the literature method.[10] The rhodium dimer $[\mathrm{Rh(dmgH)_2PPh_3}]_2$ was prepared from the chloro complex by borohydride reduction, yielding a hydridorhodoxime that decomposes to the dimer upon addition of hydrochloric acid, as described previously.[11]

Kinetics. All kinetics measurements were carried out by laser flash photolysis on the system described earlier.[12] The laser dye Coumarin 504, which gives an intensity maximum at 499 nm, was used. The kinetics of the reactions between $\mathrm{Rh(dmgH)_2PPh_3}$ and RX were monitored at 580 or 590 nm, where the rhodium radical absorbs. The alkyl halide concentrations were maintained in pseudo-first-order excess. The solvent was 95% ethanol, except in a few instances where benzene was employed. Oxygen was removed from all solutions, except when the O_2 reaction was being studied, by purging with argon. Kinetic measurements were carried out at 23 ± 1 °C.

Hydrocarbon products were determined by gas chromatography on a VZ-10 column at 50 °C by use of a Hewlett-Packard instrument, Model 5790A. Air-free solutions containing $[\mathrm{Rh(dmgH)_2PPh_3}]_2$ and the desired alkyl halide were placed in a 1-cm spectrophotometer cell. This sample was subjected to 14–18 laser shots. Portions of the gas phase above the solution were injected for the GC analysis.

Hydrogen Peroxide Analysis. A solution of $[\mathrm{Rh(dmgH)_2PPh_3}]_2$ in air-saturated ethanol (1 mL) was placed in a standard 1-cm UV cell. This was subjected to eight laser shots. Concentrated sulfuric acid (0.1 mL) was added, the solution purged with argon to remove dissolved oxygen, and then aqueous potassium iodide (1 mL, 0.02 M) added. The extent and rate of formation of I_3^- were monitored at 350 nm.

Results

Visible Spectrum of the $\mathrm{Rh(dmgH)_2PPh_3}$ Radical. A series of experiments was performed in which a solution of ca. 3×10^{-5} M $[\mathrm{Rh(dmgH)_2PPh_3}]_2$ in 95% ethanol was pulsed with the 499-nm laser excitation light. The resulting absorbance changes were monitored as a function of time at selected single wavelengths. The absorbance–time traces above 530 nm showed a rapid rise in absorbance after the flash, followed by a second-order decay that came to a final absorbance that equaled that measured before the flash. The visible absorption spectrum of the transient $\mathrm{Rh(dmgH)_2PPh_3}$ radical is shown in Figure 1 over the region 530–680 nm.

An estimate of the molar absorptivity of monomeric $\mathrm{Rh(dmgH)_2PPh_3}$ was obtained by comparing the absorbance changes at 452 and 580 nm observed on flashing. If it is assumed that at 452 nm the only absorbing species is the dimer, then the initial concentration of the metal radical can be calculated from the decrease in absorbance at 452 nm on flashing. By this procedure a value $\epsilon_{580} = 2.0 \times 10^3$ L mol^{-1} cm^{-1} was obtained for $\mathrm{Rh(dmgH)_2PPh_3}$.

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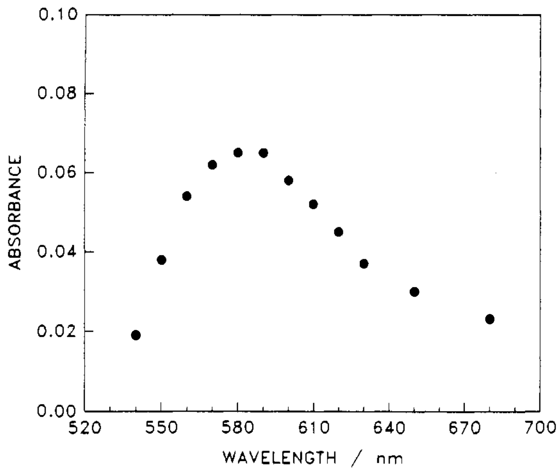


Figure 1. Visible spectrum of the $Rh(dmgH)_2PPh_3$ radicals in 95% ethanol. $\epsilon_{580} = 2.0 \times 10^3$ L mol^{-1} cm^{-1}.

Dimerization of the $Rh(dmgH)_2PPh_3$ Radical. Second-order rate constants for dimerization (k_D) were measured from the absorbance–time trace recorded by the digital oscilloscope at monitoring wavelengths of 452 and 580 nm. The rate constant is defined as $-d[M]/dt = 2d[D]/dt = 2k_D[M]^2$, where M and D are the respective concentrations of monomer and dimer. Second-order rate constants were calculated according to eq 3,

$$A_t = A_\infty + \frac{A_0 - A_\infty}{1 + 2[M]_0 k_D t} = A_\infty + \frac{A_0 - A_\infty}{1 + \dfrac{2(A_0 - A_\infty)}{\Delta\epsilon l} k_D t} \qquad (3)$$

in which A_t, A_0, and A_∞ are the absorbance values at time t, at the start, and at the end of the reaction, and $\Delta\epsilon = \epsilon_M - \epsilon_D/2$.

The value $k_D = 1.03 \times 10^8$ L mol^{-1} s^{-1} was obtained at 580 nm, and $k_D = 9.6 \times 10^6$ L mol^{-1} s^{-1} at 452 nm in ethanol; $k_D = 1.10 \times 10^8$ L mol^{-1} s^{-1} evaluated in benzene at 590 nm. Kinetic data were also obtained on solutions containing a small concentration of free PPh_3, 2×10^{-4} to 1.6×10^{-3} M. The value $k_D = 1.4 \pm 0.1 \times 10^8$ L mol^{-1} s^{-1} was obtained at 580 nm, and $k_D = 2.3 \pm 0.2 \times 10^8$ L mol^{-1} s^{-1} was obtained at 452 nm. The value of k_D was independent of $[PPh_3]$ over the range indicated. Kinetic solutions for the experiments with O_2 and alkyl halides also contained added PPh_3.

Reaction with Oxygen. Solutions of the dimer were kept oxygen-free to prevent the unwanted reaction of the monomeric radical with oxygen. The rate constant for the O_2 reaction was measured directly by adding a small volume of O_2-saturated ethanol (7.8×10^{-3} M O_2) to a larger volume of the parent dimer, also in ethanol. When the solution was flashed with the laser the disappearance of the monomer followed pseudo-first-order kinetics at 580 nm. From these data we obtained the second-order rate constant $k_4 = k_{obsd}/[O_2] = 1.4 \times 10^9$ M^{-1} s^{-1}.

We presume the O_2 reaction occurs as written in eq 4, by analogy with the reaction between O_2 and isoelectronic cobalt(II) macrocycles. The rhodium(III)–superoxo complex so formed can then disproportionate to yield oxygen and hydrogen peroxide.

$$O_2 + Rh(dmgH)_2PPh_3 \xrightarrow{k_4} O_2Rh(dmgH)_2PPh_3 \qquad (4)$$

An analysis for hydrogen peroxide in the product solution was carried out. A 1-mL reaction solution containing 2.9×10^{-5} M $[Rh(dmgH)_2PPh_3]_2$ and 1.6 mM O_2 was pulsed with the laser several times, at which point all of the dimeric complex had disappeared. The peroxide formed was determined by following the oxidation of iodide ions to I_3^- after acidification. The reaction produced 1.9×10^{-5} M H_2O_2.

An attempt was also made to learn if free superoxide ions are formed in the course of reaction 4. Tetranitromethane was used, since it undergoes a characteristic reaction with $O_2^{\bullet-}$. This was not feasible, however, since $[Rh(dmgH)_2PPh_3]_2$ reacts directly with $C(NO_2)_4$, giving nitroform anion, $C(NO_2)_3^-$, as one of the products.

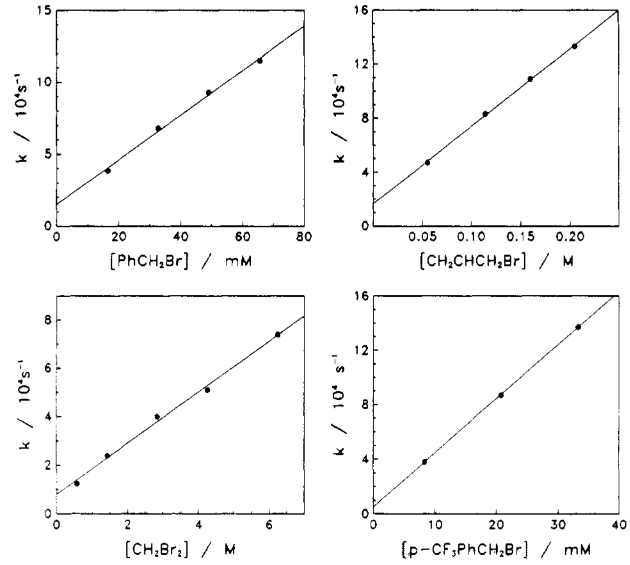


Figure 2. Plots of observed first-order rate constants versus concentration of benzyl bromide, allyl bromide, dibromomethane, and 4-(trifluoromethyl)benzyl bromide in 95% ethanol.

Table I. Reaction of $Rh(dmgH)_2PPh_3$ with Alkyl Halides[a]

alkyl halide	k_{RX}, L mol^{-1} s^{-1}	D(C–X),[b] kJ mol^{-1}	$E_{1/2}$,[c] V
CCl_4	2.0×10^6	285	−0.78
$CHCl_3$	$\sim 4 \times 10^2$		
CBr_4	$\sim 9 \times 10^8$	208	−0.30
$CHBr_3$	3.5×10^7	232	−0.64
CH_2Br_2	1.05×10^4	249	−1.48
$CH_2{=}CHCH_2Br$	5.7×10^5	230	−1.29
CH_2BrCH_2Br	5×10^3	255	−1.52
$CH_3CHBrCH_3$	*d*	285	
CH_3I	7×10^4	235	−1.63
CH_3CH_2I	4.2×10^4[e]	224	−1.67
$CH_3CH_2CH_2I$	1.8×10^4	224	
CH_3CHICH_3	5.1×10^5	222	
p-$MePhCH_2Br$	7.8×10^5		
$PhCH_2Br$	1.6×10^6	211	−1.34
p-$BrPhCH_2Br$	8.7×10^5		−1.24
m-$BrPhCH_2Br$	2.0×10^6		−1.14
p-CF_3PhCH_2Br	4.0×10^6		
p-NO_2PhCH_2Br	3.7×10^6		−0.59

[a] In 95% ethanol and 4×10^{-4} M triphenylphosphine. [b] C–X bond dissociation energies.[16] [c] Half-wave potentials for reduction of alkyl halides measured in 75% dioxane/25% water against SCE. $E_{1/2}$ values for the substituted benzyl bromides were measured in DMF against Ag/AgBr. These were normalized to the other values by comparison of values measured in both systems.[18] [d] Reaction too slow to measure, $k < \sim 4 \times 10^2$. [e] The rate constant in benzene is 2.7×10^4 L mol^{-1} s^{-1}.

Reaction with Alkyl Halides. The reactions of the $Rh(dmgH)_2PPh_3$ with a wide range of alkyl halides were studied. Excess organic halide was added to a solution of the rhodium dimer, which was then pulsed with the laser. The timed decay in absorbance was monitored at either 580 or 590 nm, and it followed pseudo-first-order kinetics. Second-order rate constants, k_{RX}, were obtained from the slopes of the plots of k_{obsd} against the concentration of alkyl halide. Four typical plots are shown in Figure 2. All of the plots show small positive intercepts. These are due, at least in part, to the competing dimerization of $Rh(dmgH)_2PPh_3$, as expressed by eq 5. In some cases the intercepts appear larger than expected due to experimental error. Values of k_{RX} are presented in Table I.

$$-d[Rh(dmgH)_2PPh_3]/dt = 2k_D[Rh(dmgH)_2PPh_3]^2 + k_{RX}[Rh(dmgH)_2PPh_3][RX] \qquad (5)$$

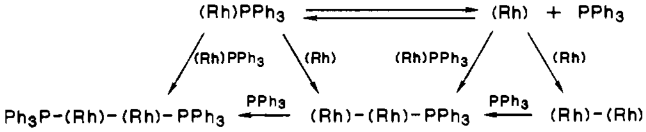
The identity of the rhodium product under the reaction conditions was investigated. A solution of $[Rh(dmgH)_2PPh_3]_2$ and tetrachloromethane was repeatedly flashed with 499-nm laser

Table II. Gas Chromatography Results for Reaction of $Rh(dmgH)_2PPh_3$ with Alkyl Halides

alkyl halide[a]	solvent	% product gases CH_4	C_2H_6	C_2H_4
EtI (0.35)	EtOH		91	9
MeI (0.46)	EtOH	100		
EtI (0.35)	C_6H_6		50	50
EtI (12.4)	EtI		48	52

[a] The concentration (M) is given in parentheses.

Scheme I



pulses until the dimer was absent. The UV/visible spectrum of the product solution had an absorption peak at 270 nm, and closely resembled that of $ClRh(dmgH)_2PPh_3$. A separately prepared sample[10] of $ClRh(dmgH)_2PPh_3$ had a peak at 272 nm, with a molar absorptivity at this wavelength of 2.1×10^4 M^{-1} cm^{-1}. A similar experiment using tribromomethane in place of tetrachloromethane gave a product solution with a peak at 277 nm, presumably due to $BrRh(dmgH)_2PPh_3$.

The gaseous organic products were investigated with gas chromatography. Four experiments were performed in which ethanol, benzene, and iodoethane were used as solvents and iodoethane and iodomethane were used as the alkyl halide reactants. The results are summarized in Table II. In particular, it should be noted that butane was not detected in any of the experiments.

Discussion

Dimerization. Addition of triphenylphosphine results in values of k_D for the dimerization reaction that are independent of $[PPh_3]$ over the range studied but are larger than in runs with no added PPh_3. With added PPh_3, the values are constant within reasonable experimental error at each wavelength, although the average value at 452 nm ($k_D = 2.3 \times 10^8$ L mol^{-1} s^{-1}) is higher than that at 580 nm (1.4×10^8 L mol^{-1} s^{-1}). The reliability of these rate constants depends upon the reliability of the molar absorptivities used to calculate the initial concentration of the rhodium radical immediately following the laser pulse. The molar absorptivity of the rhodium dimer at 452 nm was measured directly, whereas that for the monomer at 580 nm was based upon the assumption that the monomeric radical does not absorb significantly at 452 nm. If that assumption is incorrect and the monomer does indeed absorb significantly at this wavelength, then the calculated value of ϵ_{580} would be in error (higher than its true value), and the apparent values of k_D obtained at both wavelengths would be affected. This could account for the fact that the values of k_D obtained at 452 and 580 nm with added triphenylphosphine are not in exact agreement.

The greatest discrepancy in rate constants was obtained in experiments with no added triphenylphosphine, where $k_D = 1.03 \times 10^8$ L mol^{-1} s^{-1} was determined at 580 nm, but when measured at 452 nm, $k_D = 9.6 \times 10^6$ L mol^{-1} s^{-1}. This large difference suggests the involvement of one or more intermediates in the dimerization reaction. Dissociation of the $Rh(dmgH)_2PPh_3$ monomer into $Rh(dmgH)_2$ and PPh_3 is the obvious first step in any reaction scheme designed to explain the kinetic effect of added PPh_3. The presence of these two species of monomers leads to three different species as the immediate product of dimerization. This is illustrated in Scheme I.

Experiments with and without added triphenylphosphine gave similar values for the apparent molar absorptivity of rhodium monomer, implying that $Rh(dmgH)_2PPh_3$ and $Rh(dmgH)_2$ have approximately equal molar absorptivities at 580 nm. It has been observed[13] that $[Rh(dmgH)_2py]_2$ lacks the strong 452-nm absorption characteristic of the phosphine complex. This suggests that $[Rh(dmgH)_2]_2$, the dimeric species with no coordinated PPh_3, would not absorb significantly at 452 nm. This could be the intermediate needed to explain the observed results.

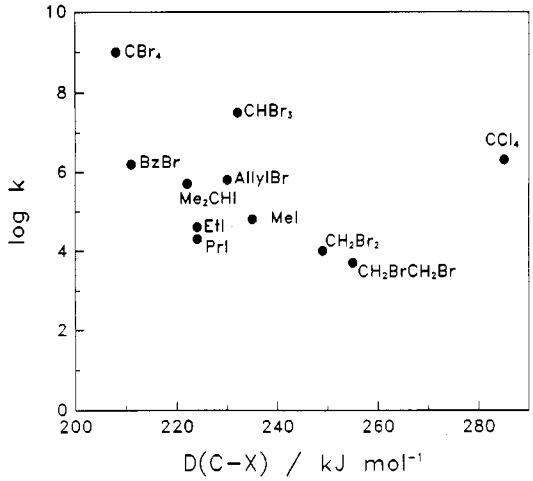


Figure 3. Plot of log k for reaction of alkyl halides with $Rh(dmgH)_2PPh_3$ versus C–X bond dissociation energy of alkyl halides.

With no added triphenylphosphine, $Rh(dmgH)_2$ is the major monomeric rhodium species present in solution. The data at 580 nm suggest this species dimerizes at a slightly lower rate than $Rh(dmgH)_2PPh_3$. The results at 452 nm, where the formation of the dimer was monitored, gave a much lower value for the rate constant labeled k_D. This is reasonable, since it is not dimerization that was observed in this case; it is the reaction of triphenylphosphine with the nonabsorbing dimeric species $[Rh(dmgH)_2]_2$.

Halogen Atom Abstraction. The second-order rate constants for the reaction of $Rh(dmgH)_2PPh_3$ with the alkyl halides range from $\sim 4 \times 10^2$ L mol^{-1} s^{-1} for trichloromethane to 9×10^8 for tetrabromomethane. The competing dimerization reaction of $Rh(dmgH)_2PPh_3$ prevents slower reactions from being studied. At the other end of the scale, rate constants greater than 10^9 L mol^{-1} s^{-1} give reactions that are too fast to follow. The reactivity order for the alkyl halides is I > Br > Cl. The magnitude of these differences is large: $k(CBr_4)/k(CCl_4) \simeq 5 \times 10^2$; $k(CHBr_3)/k(CHCl_3) \simeq 9 \times 10^4$. When bromide is compared with iodide, $k = 5.1 \times 10^5$ L mol^{-1} s^{-1} for 2-iodopropane, but the reaction with 2-bromopropane is too slow to measure ($< \sim 4 \times 10^2$ L mol^{-1} s^{-1}). These reactivity differences are indicative of a halogen abstraction mechanism (eq 6) that typically[14] shows a great sensitivity to the

$$M + RX \rightarrow [M^{+}\text{---}X^{-}\text{---}R] \rightarrow MX + R^{\bullet} \qquad (6)$$

nature of the halogen in the alkyl halide. In contrast, an outer-sphere electron-transfer mechanism (eq 7) has a much smaller halogen dependence,[15] $k_{RI}/k_{RBr} \sim k_{RBr}/k_{RCl} \sim 1\text{–}10$.

$$M + RX \rightarrow [M^{+} + RX^{\bullet -}] \rightarrow M^{+} + R^{\bullet} + X^{-} \qquad (7)$$

The rate constants for the halogen atom transfer, k_{RX}, and the bond dissociation energy for the alkyl halides may be correlated. The available bond dissociation energies[16] are listed in Table I, and a plot of log k_{RX} versus bond dissociation energy is given in Figure 3. There does appear to be a trend toward lower rate constants at higher bond energies, but the quantitative correlation is very poor.

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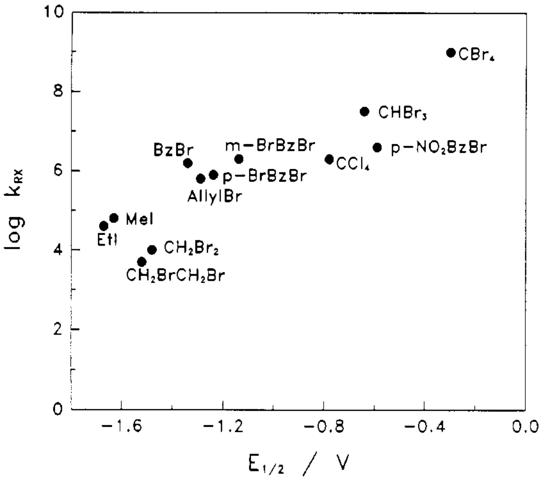


Figure 4. Plot of log k for reaction of alkyl halides with $Rh(dmgH)_2PPh_3$ versus half-wave potentials for irreversible reduction of alkyl halides.

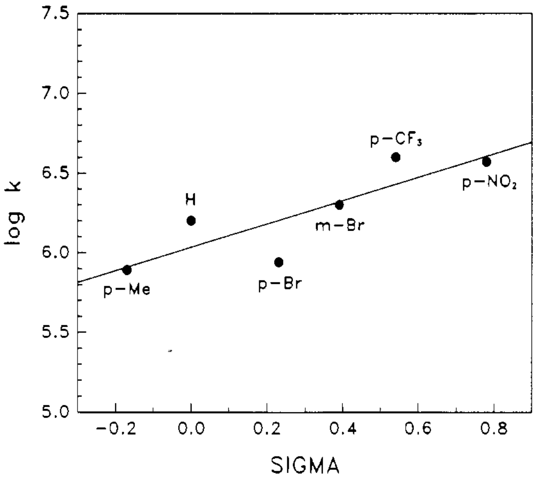


Figure 5. Hammett free energy relationship plot of log k_x versus σ_x for reaction of $Rh(dmgH)_2PPh_3$ with a series of substituted benzyl bromides.

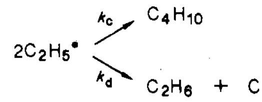
An alternative approach is to use the half-wave reduction potentials, $E_{1/2}$, of the alkyl halides instead of bond dissociation energies. These $E_{1/2}$ values are irreversible; reduction of alkyl halides leads directly to halide ion and alkyl radical formation by a concerted electron-transfer–bond-breaking process.[17] The available $E_{1/2}$ values[18] are listed in Table I, and a plot of log k_{RX} versus $E_{1/2}$ is given in Figure 4. The correlation is approximately linear for the reactions studied; the alkyl halides with the most negative $E_{1/2}$ values show the lowest reactivity.

The data shown in Figure 4 could be fitted to a free energy relationship, such as the Rehm–Weller equation,[19] or the Agmon–Levine equation.[20] These relationships have been applied to halogen atom transfer to rhenium(0) carbonyl radicals.[9] Such an exercise would be difficult to justify for the present results. A much better correlation of rate constants with $E_{1/2}$ values would be needed to obtain a meaningful fit to one of the free energy relationships. Also, since electron transfer to alkyl halides is an irreversible process, the parameters obtained from such a fit would not be quantitatively accurate.[21]

The alkyl halides used in the present study include a series of substituted benzyl bromides. A plot of the Hammett free energy relationship, log $(k_x/k_H) = \rho\sigma_x$, is shown in Figure 5. There is a small rate-enhancing effect of electron-withdrawing groups; the slope of this plot gives $\rho = 0.73$. The positive value of ρ indicates a buildup of negative charge at the benzylic carbon in the transition state, i.e., a movement of electron density from the rhodium center to the bromine atom. This is consistent with the halogen abstraction mechanism (eq 6).

Product Distributions. The UV/visible spectrum of the product solution with tetrachloromethane confirms that the only significant rhodium product is the chloro–rhodium complex, $ClRh(dmgH)_2PPh_3$. This again confirms the mechanism to be halogen abstraction, since the inorganic rhodoximes are substitutionally inert.

The non-rhodium product in a halogen abstraction reaction is the alkyl radical; the fate of this radical can be deduced from the gas chromatography results. Ethyl radicals undergo two self-reactions, combination and disproportionation,[22] to give a mixture of butane, ethane, and ethene as products (eq 8).



$$2C_2H_5^{\bullet} \xrightarrow{k_c} C_4H_{10} \qquad 2C_2H_5^{\bullet} \xrightarrow{k_d} C_2H_6 + C_2H_4 \tag{8}$$

In ethanol solution k_d/k_c is expected to be ~0.18, and in benzene solution $k_d/k_c \sim 0.17$. In the present study no butane was detected, indicating that the self-reaction was not occurring to any significant extent. The ethyl radical must therefore be undergoing a more rapid competing reaction. The only possible self-reaction for the methyl radicals is the combination reaction forming ethane. The reaction with iodomethane yielded no ethane, indicating again that the self-reaction is not important under the present reaction conditions. For the reactions in which ethanol is the solvent, the obvious contender as the competing reaction is abstraction of an α-hydrogen from ethanol (eq 9 and 10). The

$$C_2H_5^{\bullet} + CH_3CH_2OH \rightarrow C_2H_6 + CH_3\dot{C}HOH \tag{9}$$

$$CH_3^{\bullet} + CH_3CH_2OH \rightarrow CH_4 + CH_3\dot{C}HOH \tag{10}$$

α-hydroxyalkyl radical can undergo a self-reaction or reduce another alkyl radical. Thus hydrogen abstraction from ethanol can account for the observed major products. Calculations using a second-order rate constant[23] of 6×10^2 L mol^{-1} s^{-1} for reactions 9 and 10 show that the reaction of the alkyl radicals with ethanol is expected to win out over the self-reactions. Where iodoethane is used as solvent, the likely reaction of the ethyl radical is abstraction of a hydrogen from the iodoethane (eq 11). The iodoalkyl radical formed loses iodine giving ethene (eq 12). This scheme

$$C_2H_5^{\bullet} + C_2H_5I \rightarrow C_2H_6 + C_2H_4I^{\bullet} \tag{11}$$

$$C_2H_4I^{\bullet} \rightarrow C_2H_4 + I^{\bullet} \tag{12}$$

correctly predicts the observed 1:1 ethane:ethene product ratio. Calculations using a second-order rate constant[24] of 1.2×10^3 L mol^{-1} s^{-1} for reaction 11 confirm this result. The products obtained in benzene are the most difficult ones to explain. The 1:1 ethane:ethene product ratio is consistent with abstraction of hydrogen from iodoethane, but the latter is present at a concentration of only 0.35 M. In order for this reaction to predominate over the ethyl radical self-reaction, a rate constant of greater than 10^4 L mol^{-1} s^{-1} is needed for reaction 11.

Oxygen. The reaction of $Rh(dmgH)_2PPh_3$ with molecular oxygen is presumed to take place by the formation of a 1:1 adduct, as represented by eq 4. This $O_2Rh(dmgH)_2PPh_3$ species may well

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(23) Measured for $^{\bullet}CH_3 + CH_3CH_2OH$: "Rate Constants for Reactions of Aliphatic Carbon-Centered Radicals in Aqueous Solution"; NSRDS-NBS70; U.S. Government Printing Office: Washington, DC, 1982.

(24) Measured for the reaction $^{\bullet}CH_3 + C_2H_5CN$.[23]

dissociate to a Rh(III) complex and superoxide ions, which in turn form hydrogen peroxide by disproportionation, as shown by eq 13.[25] In that case, 1 mol of the original rhodium dimer reacts to give 1 mol of hydrogen peroxide.

$$O_2Rh(dmgH)_2PPh_3 \rightarrow Rh(dmgH)_2PPh_3^+ + O_2^{\bullet-} \xrightarrow{ROH/H_2O} \tfrac{1}{2}(H_2O_2 + O_2) \quad (13)$$

Acknowledgment is made to the National Science Foundation for support under Grant CHE-84-18084. Some of this work was accomplished with the facilities of Ames Laboratory, operated by Iowa State University for the U.S. Department of Energy under Contract W-7405-Eng-82.

Registry No. Rh(dmgH)$_2$PPh$_3$, 21057-94-3; CCl$_4$, 56-23-5; CHCl$_3$, 67-66-3; CBr$_4$, 558-13-4; CHBr$_3$, 75-25-2; CH$_2$Br$_2$, 74-95-3; CH$_2$CHCH$_2$Br, 106-95-6; CH$_2$BrCH$_2$Br, 106-93-4; CH$_3$I, 74-88-4; CH$_3$CH$_2$I, 75-03-6; CH$_3$CH$_2$CH$_2$I, 107-08-4; CH$_3$CHICH$_3$, 75-30-9; *p*-MePhCH$_2$Br, 104-81-4; PhCH$_2$Br, 100-39-0; *p*-BrPhCH$_2$Br, 589-15-1; *m*-BrPhCH$_2$Br, 823-78-9; *p*-CF$_3$PhCH$_2$Br, 402-49-3; *m*-CF$_3$PhCH$_2$Br, 100-11-8.

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(25) We discount a possible reaction between the superoxo complex and additional Rh(dmgH)$_2$PPh$_3$, because (as pointed out by a reviewer) such a reaction, in competition with eq 4, would require an impossibly high bimolecular rate constant.

Contribution from the Corporate Science and Technology Center and Corporate Research Services Department, Air Products and Chemicals, Inc., Allentown, Pennsylvania 18195

Synthesis and Characterization of *trans*-(PMe$_3$)$_2$PtHCl and an Investigation of Its Role in Olefin Hydration Catalysis

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Received March 11, 1988

Analytically pure *trans*-(PMe$_3$)$_2$PtHCl was synthesized and examined for its ability to catalyze the anti-Markovnikov hydration of terminal olefins. Although this catalyst has been reported to give high selectivities to primary alcohols, our attempts to hydrate 1-hexene in a basic aqueous medium in the presence of a phase-transfer agent or surfactant and pure *trans*-(PMe$_3$)$_2$PtHCl failed to yield any alcohol products. In addition, spectroscopic studies failed to confirm nucleophilic attack of hydroxide ion on coordinated olefins in this system. Instead, the predominant reaction under a variety of conditions was olefin isomerization.

Introduction

The catalytic hydration of terminal olefins to primary alcohols would be an important route to industrially useful alcohols. In a recent report, Jensen and Trogler[1] claimed the direct anti-Markovnikov hydration of terminal olefins using a soluble platinum catalyst. This would represent a revolutionary improvement over current methods of manufacturing primary alcohols[2] and has received a great deal of attention.[3] The published results claim that *trans*-(PMe$_3$)$_2$PtHCl in a 1:1 mixture of 0.4 M aqueous NaOH and 1-hexene forms a species that, at 60 °C and in the presence of benzyltrimethylammonium chloride, catalyzes selective hydration to 1-hexanol.

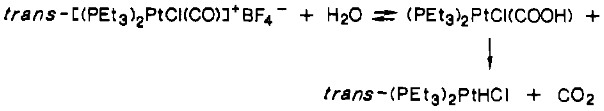
Efforts in our laboratories to reproduce this catalysis have been unsuccessful. In this paper, we provide details of our attempts to effect the claimed catalysis and also present some interesting spectroscopic results observed during our studies.

Our work was initially hampered by the fact that literature methods for the preparation of *trans*-(PMe$_3$)$_2$PtHCl do not yield analytically pure material or fail to provide any information on analytical purity. For example, *trans*-(PMe$_3$)$_2$PtHCl was first prepared by Chatt and Shaw in 1962 via the reduction of *cis*-(PMe$_3$)$_2$PtCl$_2$ with aqueous hydrazine.[4] Their material was impure, and it was unstable during further purification attempts. We have confirmed these observations.

In 1984, Flood and Statler synthesized high yields of *trans*-(PMe$_3$)$_2$PtHCl by thermally decomposing platinum alkyl complexes.[5] Although we have no reason to doubt the purity of their material, the synthesis requires a multistep procedure and no analytical data were published. Finally, Trogler's group has synthesized the complex by sodium naphthalide reduction of *cis*-(PMe$_3$)$_2$PtCl$_2$ under an atmosphere of H$_2$ and has determined its structure by X-ray crystallography.[6] Again, however, no analytical data on the bulk material were reported. Our efforts to synthesize active catalyst by this method gave catalytically inactive material that was difficult to purify. Because of the possibility that our inability to reproduce the reported catalysis was due to our use of impure material, one of our primary goals was to prepare analytically pure *trans*-(PMe$_3$)$_2$PtHCl.

Results and Discussion

Preparation of Analytically Pure *trans*-(PMe$_3$)$_2$PtHCl. Our first synthetic route (eq 1) was modeled after a procedure used by Catellani and Halpern for preparing *trans*-(PEt$_3$)$_2$PtHCl.[7] Because the cationic complex for the analogous trimethylphosphine complex was unknown, this complex was first prepared according to eq 2. The complex was characterized by IR, ^{1}H NMR (Table I), and ^{31}P NMR spectroscopy (Table II) and by elemental analysis.


$$\begin{tikzcd} trans\text{-}[(PEt_3)_2PtCl(CO)]^+BF_4^- + H_2O \arrow[r, shift left] & (PEt_3)_2PtCl(COOH) + H^+ \arrow[l, shift left] \arrow[d] \\ & trans\text{-}(PEt_3)_2PtHCl + CO_2 \end{tikzcd} \quad (1)$$

$$cis\text{-}(PMe_3)_2PtCl_2 + NH_4PF_6 + CO \rightarrow trans\text{-}[(PMe_3)_2Pt(CO)Cl]^+PF_6^- + NH_4Cl \quad (2)$$

The carbonyl complex was dissolved in acetone, and an excess of water was added. Extraction of the solution with ether yielded a solid that was spectroscopically verified as *trans*-(PMe$_3$)$_2$PtHCl, but only in trace amounts. Problems were also encountered because of the low stability of the hydride in water–acetone solution. For these reasons, we investigated alternative synthetic approaches.

We found that the best way to synthesize *trans*-(PMe$_3$)$_2$PtHCl was by a modification of the methanolic NaBH$_4$ reduction used

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