Studies into the Mechanism of the Rhodium-Catalyzed Carbonylation of Isopropyl Alcohol

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Abstract: The carbonylation of isopropyl alcohol with the rhodium/HI catalyst system has been extensively investigated at 170 °C in an acetic acid/water solvent system. The reaction rate was inhibited by CO pressure, was first order in rhodium, and was less than first order in HI. The product ratio of isobutyric acid to n-butyric acid (iso/n) increased from ca. 0.7 to ca. 1.6 as the CO pressure increased from 14.6 to 205 atm, but it was essentially independent of [Rh] or [HI]. Addition of propylene at $P(CO) = 140$ atm caused a large increase in rate and enhanced the relative rate of formation of the n-isomer. Carbonylation of deuterium-labeled isopropyl alcohol gave evidence for both α and β secondary kinetic isotope effects (KIEs); these were essentially independent of pressure and were found to be KIE(T) = 2.2 (±0.15), KIE(iso) = 2.0 (±0.1), and KIE(n) = 2.6 (±0.1). Because of the differences in the KIE(iso) and KIE(n), substitution of deuterium (in the β position of i-PrOH/i-PrI) caused preferential formation of the isoproduct. Significant (though not exclusive) retention of deuterium was observed in all cases. Addition of iodide to the system had a slight accelerating effect on the rate but little effect on the product distribution. While it has not yet been possible to unambiguously determine all of the pathways involved, it appears that a hydrocarboxylation pathway (Rh-H/olefin) is a major contributor to the total reaction, at least under certain conditions. A second route involving an electron-transfer mechanism is suggested to explain the retention of deuterium at rates too fast to be attributed simply to a nucleophilic displacement reaction.

The iodide-promoted rhodium-catalyzed carbonylation of alcohols has been the subject of considerable interest recently.[1-6] We were especially interested in a report by Hjortkjaer and Jorgensen concerning the carbonylation of isopropyl alcohol (i-PrOH).[5] While proposing an S_N2 pathway for this reaction, they noted that their data were not entirely consistent with such a mechanism. In particular, the dependence on HI concentration was non-first order and the activation parameters were very different from what they had observed in other systems.[3,4] In addition, we noted that the absolute rate for the carbonylation of this secondary alcohol was 7 times faster than that for EtOH.[4] The presence of significant quantities of propylene suggested to us that some contribution of the reaction may be arising from an extremely efficient olefin/hydride pathway.[7] Accordingly, we have undertaken a more thorough investigation into the mechanisms of rhodium–iodide catalyzed alcohol carbonylations. The results of our studies with primary alcohols are given in the previous article.[8]

Experimental Section

The methods for obtaining the kinetic and infrared spectral data have been described previously.[8,9] Kinetic data were reproducible within 5%. Because of difficulties in resetting the temperature sensor to exactly 170 °C for the iodide studies, there is a discrepancy in the absolute rate measurement for this set of experiments (cf. Tables I–III).

In the experiments with added propylene, the gas (Matheson C.P.) was added through the vent line as a static charge at room temperature. The final pressure was calculated from the ideal gas law by using the measured pressure at the desired temperature. After heating, the runs were done as previously described. Because the experiments were conducted in this way, there was significant contribution to the measured rate due to propylene consumption, especially at the higher levels of propylene.

The products of the reactions were analyzed with instrumentation described previously,[8] employing a 1.0-m Porapak T column, temperature programmed to operate at 160 °C for 8 min after injection and then increasing at 16 °C/min to 190 °C. This iso/n ratio was taken to be the ratio of integrated areas of the (isopropylisobutyrate + isobutyric acid)/(isopropyl-n-butyrate + n-butyric acid). In contrast to the report of Hjortkjaer,[5] there was no evidence whatsoever for any n-propylbutyrates. This column did not allow separation of the isopropyl acetate from the isopropyl iodide, but this could be achieved (when necessary) with a Chromosorb 101 column (6 ft × 1/2 in.), temperature programmed from 120 to 240 °C at 10 °C/min. In all cases, the n-PrI/i-PrI ratio was much less than 5%, typically 1–2%, at the end of the reactions.

Diethylcarbitol (bis(2-ethoxyethyl) ether, Kodak) was vacuum distilled from LiAlH4 prior to use. n-Butylcarbitol (diethyleneglycol monobutyl ether, Fisher), acetone (Fisher reagent), acetone-d_6 (MSD, 99.9 atom % D), LiAlH4 (Aldrich), and LiAlD4 (MSD, 99 atom % D) were used as supplied. The deuterium-labeled isopropyl alcohols were either used as supplied (i-PrOD-d_8 was obtained from Cambridge Isotope Laboratories, 99%) or were prepared batch-wise (α-d_1 and β-d_6 i-PrOH) with the implied method of V. J. Shiner.[10] Yields were typically 70%, based on initial acetone. Mass spectral analyses using chemical ionization (CI, CH4, 2 eV) gave base peaks at (M - OH)+: d_8-i-PrOD (m/e 50, $C_3D_7^+$); H_7-i-PrOH (m/e 43, $C_3H_7^+$); α-d_1-i-PrOH (m/e 44, $C_3H_6D^+$); β-d_6-i-PrOH (m/e 49, $C_3D_6H^+$). Using electron ionization (EI, 70 eV) gave base peaks at (M - CH3/CD3)+: d_7-i-PrOH (m/e 49, $C_2D_4HO^+$); α-d_1-i-PrOH (m/e 46, $C_2H_4DO^+$); β-d_6-i-PrOH (m/e 48, $C_2D_3H_2O^+$).

The isotopic purities of the isopropyl alcohol, isopropyl iodide, isobutyric acid, and n-butyric acids at the end of each carbonylation run were determined, when necessary, by GC/MS (Porapak T column) with both EI and CI by using the following respective peaks: i-PrI by EI with M+ and (M - I)+ peaks; i-PrCOOH by CI with (M + 1)+ peak and EI with M+ and (M - COOH)+ peaks; n-PrCOOH by CI with (M + 1)+ peak and EI with (M - Me)+ peak. These peaks were determined to be suitable for determining deuterium composition by comparing the mass spectra of (CH3)2CHI (generated in situ in all protic media), (CH3)2C-HCOOH (generated in situ in all protic media), (CD3)2CDCOOH (MSD, 98.7 atom % D), CH3CH2CH2COOH (generated in situ in all protic media), and CD3CD2CD2COOH (MSD, 98.7% atom D) under the same conditions.

Results

Infrared Spectroscopy. In situ spectra of the reaction mixtures at 170 °C were measured under the following conditions: (a) $P(T)$ = 14.6 atm, [Rh] = 1.01 × 10^{-2} M, [HI] = 0.50 M; (b) $P(T)$ = 22.1 atm, [Rh] = 1.50 × 10^{-2} M, [HI] = 0.50 M, d_8-i-PrOD; (c) $P(T)$ = 24.2 atm, [Rh] = 1.01 × 10^{-2} M, [HI] = 1.00 M, [NaI] = 1.0 M. In all cases, the only rhodium species observed was $(RhI_2(CO)_2)^-$ (ν(CO) at 2060 and 1988 cm^{-1}).[11] The relative

(1) Roth, J. F.; Craddock, J. H.; Hershman, A.; Paulik, F. E. *Chem. Technol.* 1971, 600.

(2) Forster, D. *J. Am. Chem. Soc.* 1976, 98, 846.

(3) Hjortkjaer, J.; Jensen, V. W. *Ind. Eng. Chem., Prod. Res. Dev.* 1976, 15, 46.

(4) Hjortkjaer, J.; Jorgensen, J. C. *J. Mol. Catal.* 1978, 4, 199.

(5) Hjortkjaer, J.; Jorgensen, J. C. *J. Chem. Soc., Perkin Trans. 2* 1978, 763.

(6) Dake, S. B.; Kohle, D. S.; Chaudhari, R. V. *J. Mol. Catal.* 1984, 24, 99.

(7) For example, see: Forster, D.; Hershman, A.; Morris, D. F. *Catal. Rev.-Sci. Eng.* 1981, 23 (1 and 2), 89.

(8) Dekleva, T. W.; Forster, D. *J. Am. Chem. Soc.*, preceding paper in this issue.

(9) Forster, D. *J. Chem. Soc., Dalton Trans.* 1979, 1639.

(10) Shiner, V. J., Jr. *J. Am. Chem. Soc.* 1952, 74, 5285. See also: Nystrom, R. F.; Yanko, W. H.; Brown, W. G. *J. Am. Chem. Soc.* 1948, 70, 441.
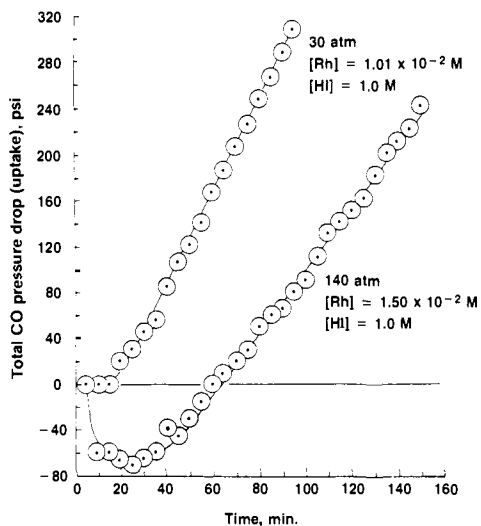
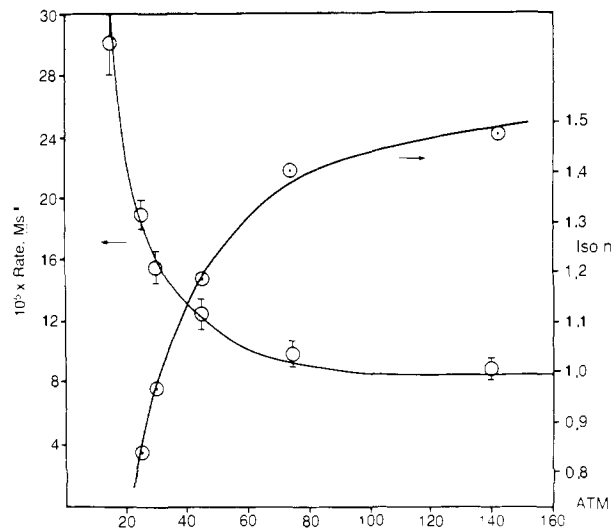Figure 1. Representative reaction profiles for the carbonylation of isopropyl alcohol.

Figure 2. Effect of CO pressure on the rate and product distribution for the carbonylation of isopropyl alcohol at 170 °C: [Rh] = 1.01 × 10⁻² M; [HI] = 0.50 M (data from Table I).

peak intensities suggest that there was no other detectable rhodium species with accidentally degenerate ν(CO)'s. Since raising the CO pressure would presumably favor formation of the anionic Rh(I) species even more, experiments at higher pressures were not attempted, and it is concluded that the rhodium exists mainly as this species under all the conditions investigated.

Interpretation of the Reaction Profiles. The bases of the kinetic studies in this i-PrOH system are the uptake rate data presented in Tables I–IV.

During the course of this study, it was observed that the shape of the reaction profile (CO uptake vs. time) was dependent on CO pressure (Figure 1). At lower pressures, the apparent slight induction period observed could be attributed to the time necessary for the temperature to equilibrate after injecting the catalyst and rinse solutions, as well as the time necessary to generate the active catalyst. At higher pressures (e.g., 137.1 atm), there was significant gas evolution in the early stages of the reaction. Blank experiments (no rhodium) showed this same gas evolution at both 24.2 and 139.8 atm. Analyses of the gas phases indicated that this was due to formation of propylene (Table I, lines 1 and 2). Since the levels of propylene in the final gas mixtures were much lower when the reaction mixtures contained rhodium (especially at lower pressures), it appears that the propylene was consumed in the catalytic cycle. At lower pressures, the consumption of propylene apparently was competitive with its generation, so the latter did not manifest itself in the reaction profile. At higher pressures, where the reaction (gas consumption) was much slower, the gas uptake could not compete with the propylene evolution, and the reaction showed an overall evolution, until the (higher) "steady-state" concentration of propylene was reached.

Under all conditions, the gas uptake eventually became linear with time, and it was this portion of the reaction profile that was used to determine the rate of reaction.

Experiments at 46.6 and 139.8 atm indicated that the product (iso/n) distribution is essentially invariant with time (±4%; e.g., Table I, lines 23–25, footnotes e–g).

Kinetic Data. The rate of carbonylation of i-PrOH exhibited an inverse dependence on CO pressure (Figures 2 and 3), was first order with respect to [Rh], and was less than first order in [HI] (analyses for half-order and first- to zero-order dependences gave equally good plots—Figures 4 and 5). It is important to note the variability of propylene partial pressures (which can be estimated from the final gas compositions in Tables I–IV). Within a given total pressure, the measured final levels of propylene decreased with increasing [Rh] and [HI]. The absolute levels of propylene also increased with increases in total pressure, and so P(CO). Generally, in the absence of added propylene, higher
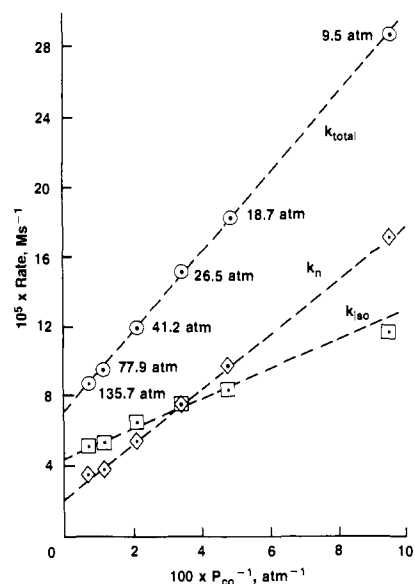
Figure 3. Plots of k_{total}, k_{iso}, and k_n as a function of P_{CO}^{-1} at 170 °C: [Rh] = 1.01 × 10⁻²M and [HI] = 0.50 M (from Table I, where, for example, k_{iso} = (% iso)(k_{total})/(100)).

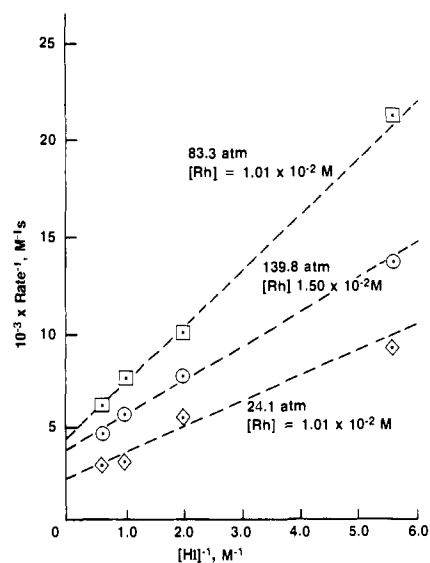Figure 4. Inverse plot for the dependence of rate on [HI] (Table I).

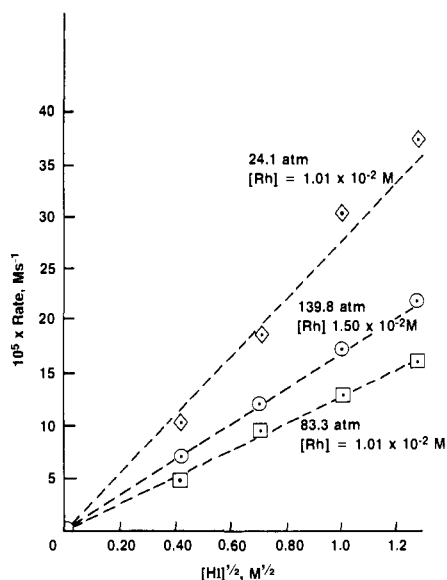(11) Forster, D. *Inorg. Chem.* **1969**, *8*, 2556.

Figure 5. Dependence of rate on $[HI]^{1/2}$ (Table I).

reaction rates were accompanied by lower levels of propylene. Addition of external propylene at $P(CO) = 137.1$ atm had the effects of eliminating the induction period, accelerating the rate, and favoring the relative rate of formation of the n-butyric acid (decrease in iso/n ratio). Addition of iodide salts had a slight accelerating effect on the rate, but it did little to affect the iso/n ratio of the products.

Effect of Selective Deuteration of the Substrate i-PrOH. Unlike the EtOH and n-PrOH systems,[8] the i-PrOH system showed marked kinetic isotope effects (KIE's). The $k(H_7)/k(d_7) = 2.2$ ($\pm$ 0.15) at 170 °C (tables I and IV) was essentially invariant with pressure. Is is also interesting to note that the KIE's of the observed rate constants, k(iso) and k(n) (contribution of rate which gives iso and n products, respectively), are also constant with pressure, but differ significantly from one another (KIE(iso) = 2.0, KIE(n) = 2.6). The data suggest either (i) a single pathway, (ii) a mechanism with several pathways with different isotope effects whose relative contributions to the total rate do not vary over the pressure range investigated, or (iii) a mechanism with several pathways, each of which exhibits similar isotope effects. By carbonylating the α-d_1 and β-d_6 isopropyl alcohols, it was possible to determine the relative contributions of α- and β-effects.[12] The data which address this question are given in Table IV; these suggest that at lower pressures (23.5 atm), the total KIE arises solely from β-substitution, while at higher pressures (139.8 atm), the total KIE is a composite value, with a measureable α-effect. These suggest the presence of more than one pathway. Although the values quoted convey a greater degree of accuracy than is perhaps actually possible, their internal consistency (KIE(total) = KIE(α) $\times$ KIE(β)) suggests this degree of accuracy is, at least in part, justified.
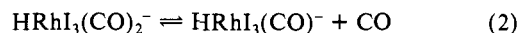
Mass spectral analyses of the final reaction solutions in these labeling studies also gave some very important information. First, during the rigors of the experiment, there was significant H/D scrambling in the substrate alcohol and i-PrI (Table V). This was also observed in the EtOH and n-PrOH systems[8] and corrections for it can be made. This may suggest that the observed KIE's are lower than the "pure" intrinsic values, because of "dilution" of the substrate with respect to deuterium content, but since the calculated isotope effect of each deuterium is less than 1.1, the errors involved will be small. Since the α-deuterium is retained throughout the carbonylations, the scrambling only involves the β-deuterons, and is probably caused either by reversible deprotonation at this site or, more likely, reversible loss of DI (replacement by HI is preferred simply by availability).

Examination of the final isotopic composition of the product acids indicated that there was a significant retention of deuterium atoms in the reaction (Table V). This is especially so in the i-PrCOOH, where there is upward of 70% full retention at the higher pressures. There is ca. 30% retention in the n-PrCOOH. (Since we are dealing with different initial compositions, percent retention is defined to be the ratio of percent of acid to percent of i-PrI, where percent of acid and percent of i-PrI refer only to the normalized amount of the respective compound recovered at the end of the run which contained the maximum number of available deuterons. For example, when starting with β-d_6-i-PrOH, % retention = % d_6-acid/% d_6-i-PrI. This definition is subject to errors in the measurements of the mass spectral intensity data, but it provides at least a semiquantitative description, sufficiently accurate for the present discussion.) Again, since α-d_1 is completely retained, any loss of deuterium in the product must be occurring at the expense of the β-deuterons in i-PrI; this is in addition to the normal exchange rate (scrambling) discussed previously. The actual values for percent of retention may be intrinsically slightly higher, since the substrates with lower deuterium content react marginally faster, thereby enriching the product with higher protic species.

Discussion

The rhodium/HI catalyzed carbonylation of i-PrOH has been examined kinetically, spectroscopically, and by using isotopically labeled precursors, and the reults indicate a mechanism which is significantly more complicated than those involved in the carbonylations of the linear alcohols. In the latter reactions, the simple kinetics (first order with respect to both rhodium and HI (alkyl iodide), independent of CO), relative rate data, absence of any measureable kinetic isotope effects, and retention of isotopic integrity all strongly suggested the mechanism involving rate-determining nucleophilic attack by $RhI_2(CO)_2^-$ on the alkyl iodides. By contrast, the carbonylation of i-PrOH showed much more complicated kinetic behavior, measureable kinetic isotope effects, relative rate data totally inconsistent with S_N2 reactivity, and only partial retention (i.e., significant loss) of isotopic integrity. Hjortkjaer[5] previously studied this system and concluded that the S_N2 mechanism was operative here also. On the basis of our present data, it is concluded that if the S_N2 reaction is occurring, and if relative rate data have any validity in this system, its contribution to the total is small (vide infra).

The only species observed in these studies was the $RhI_2(CO)_2^-$ anion. Despite this observation, it is unlikely that this species was the active catalyst for the greater part of the reaction. The inverse dependence on CO suggests that there is a preequilibrium involving dissociation of this ligand initiated by the addition of another species (spontaneous CO loss is unlikely under these conditions). This initiator is probably HI (eq 1 and 2). Although the added HI exists predominantly as i-PrI, free HI is in equilibrium with this and added H_2O (eq 3). The $HMI_3(CO)_2^-$ species (eq 1 and

$$RhI_2(CO)_2^- + HI \rightleftharpoons HRhI_3(CO)_2^- \qquad (1)$$

$$HRhI_3(CO)_2^- \rightleftharpoons HRhI_3(CO)^- + CO \qquad (2)$$

$$i\text{-PrI} + H_2O \rightleftharpoons i\text{-PrOH} + HI \qquad (3)$$

2) has been isolated from $MI_2(CO)_2^-$ in the isoelectronic M = Ir case,[9] and it is not unreasonable to expect the same chemistry with M = Rh. Unlike the Rh–alkyl intermediate proposed (but never observed) in the mechanisms of the linear alcohols, the dicarbonylrhodium hydride cannot be stabilized by a migratory insertion reaction. Instead, it seems quite reasonable that this instability is relieved by dissociating a CO ligand, as invoked in the n-PrOH system.[8] The chemistry given in eq 2 and 3 is probably the same as that observed in the water-gas-shift reaction studied by Forster and Singleton et al.,[13] in which the oxidation

(12) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; John Wiley & Sons: New York, 1980.

(13) (a) Singleton, T. C.; Park, L. J.; Price, J. L.; Forster, D., Division of Petroleum Chemistry, Joint Meeting of the American Chemical Society and Chemical Society of Japan, Honolulu, April, 1979. (b) Forster, D.; Singleton, T. C. *J. Mol. Catal.* **1982**, *17*, 299 and references cited therein.

of $RhI_2(CO)_2^-$ by HI (at low acidity) was inhibited by CO.

The proposed hydride was also believed to be the active species in the hydrocarboxylation of ethylene by this catalyst system.[7] In view of the levels of propylene which develop in the absence of catalyst, it seems certain that at least part of the butyric acid formation occurs by way of a Rh-H/olefin pathway. While it was not possible to determine the magnitude of this contribution, it is certainly not the sole route. In particular, this is shown by the retention of isotopic integrity when deuterated substrates are used. Under the conditions of the experiments, the D^+/H^+ ratio was 0.13 when starting with d_8-i-PrOH and 0.00 when using the other deuterated substrates; the amounts of DI (Rh-D) would be small or insignificant with respect to the HI (Rh-H) present. Formation of the olefin is accompanied by β-deuterium loss; this would be replaced by the hydride in the hydrocarboxylation reaction, so this route would be expected to give $(n - 1)$ β-deuteriums for an (n) β-deuterated substrate, even assuming no reversibility in the insertion.

Another argument against the singularity of the hydrocarboxylation pathway comes from the variation in product distribution. In contrast to the findings of Hjortkjaer and Jorgensen,[5] we found that the product distribution depended only on CO pressure (the more complicated behavior described by the previous study likely was the result of the same pressure dependence, though unrecognized at the time). A similar dependence of product distribution on CO pressure also has been observed in the carbonylation of n-PrOH.[8] In this latter case, the extrapolation to infinite CO pressure gave consistent evidence as to the nature of the initially formed alkyl species. A similar analysis with the data in this i-PrOH system suggested that the initial alkyl species was actually a mixture of isomers (ca. 65% isoalkyl). This was not altogether surprising, in view of the fact that a hydrido-olefin pathway had already been identified as a likely pathway. The factors which govern the kinetic preferences of olefin insertion reactions are not well understood so it was entirely plausible that the formation of the isoalkyl could be favored in a sterically nondemanding environment. To test this possibility, several experiments were conducted at $P(CO) = 140$ atm. Addition of external propylene was expected to enhance the relative contribution of the hydrido-olefin path. If this were the only pathway available, then, it was expected that the product distribution would remain the same. However, since reactions with added propylene yielded mainly n-butyric acid, under conditions where isomerization was believed to be minimal, it is concluded that the insertion reaction yields mainly the normal isomer (this finding is consistent with those of Roe,[14] whose NMR studies indicated that insertion of the hydride of $HRh(C_3H_6)(P(i$-$Pr)_3)_2$ into the propylene ligand favored the formation of the normal isomer by 2-to-1). As the reaction yielded mainly isobutyric acid in the absence of added propylene, it is concluded that at least one other pathway, leading to favored formation of the iso isomer, acts in conjunction with the hydrido-olefin pathway.

The results of the deuterium-labeling experiments suggest that this second path also results in retention of isotopic integrity. Some contribution of the total retention may be accounted for by an S_N2 pathway, similar to that invoked for primary alcohols. However, relative rate data would predict a much lower rate than is seen. It is improper to directly compare the rate data of EtOH with those of this system because of the different overall rate expression; but by assuming that there is a contribution of S_N2 reactivity to the latter, relative rate data can be used to determine its probable contribution. Assuming i-PrOH:EtOH = 0.02,[15] the contribution to the i-PrOH system at [Rh] = 15 mM, [HI] = 1.0M, and 170 °C is estimated to be 4.6×10^{-6} M s^{-1}. Even at 140 atm, where this pathway would make its greatest relative contribution, this represents 4.6/176, or 2.6% of the total reactivity. Another way of looking at this problem takes advantage of the results of the labeling studies. An S_N2 pathway would be expected
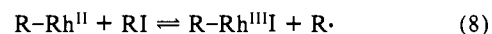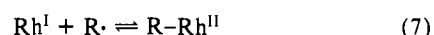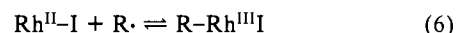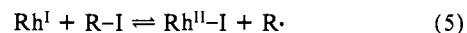
to show a negligible kinetic isotope effect.[12] If this latter point is correct, then, the contribution of S_N2 reactivity is the same as the rate of formation of the d_7-iso- and n-butyric acids (eq 4).

$$\text{rate}(S_N2) = k(\text{iso}) \times (\% \text{ retention iso}) + k(n) \times (\% \text{ retention } n) \quad (4)$$

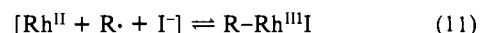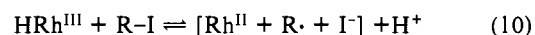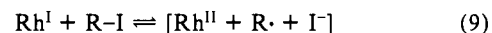Tables I and V list the relevant data. The calculations give $k(S_N2)$ = 3.77×10^{-5} M s^{-1} at 23.5 atm (46% n), 3.25×10^{-5} M s^{-1} at 83.4 atm (22% n), and 3.51×10^{-5} M s^{-1} at 139.8 atm (23% n). Taking the mean value of 3.51×10^{-5} M s^{-1}, one may calculate the relative rate with respect to EtOH under the same conditions ([Rh] = 10 mM; [HI] = 0.50 M) to be 3.51/8.0 = 0.44. This value is 22 times larger than that expected for organic analogues[15] and comparable to the experimentally determined relative rate for n-Pr:Et = 0.47.[8] While the differences in the relative rates for primary and secondary substituents may be subject to some variance, the differences in S_N2 reactivities for these substrates with transition-metal complexes are usually even greater (e.g., Collman and McLaury found a rate difference of 300 on going from n-BuI to i-PrI, using a bulky rhodium nucleophile).[16,17] This is, in part, due to the larger size of the transition-metal complexes, compared with organic nucleophiles. It may be argued that the $RhI_2(CO)_2^-$ is relatively sterically undemanding, based on the adherence to expected behavior for the primary alcohol systems.[8] However, the insignificant difference in the relative rates of n-PrOH and i-PrOH is still inconsistent with the latter being solely by way of an S_N2 mechanism.

One other possibility, initially suggested to explain the isotope effects, retention of isotopic integrity, and half-order dependence in HI, involved ionization of i-PrI to allyl cation and iodide, the former being captured by the anionic rhodium catalyst in the rate-determining step.[18] This possibility can be discarded, in view of fact that the addition of free iodide actually increased the rate. This rate acceleration was probably due to a salt effect.[19]

In order to rationalize the high observed rates (of retention), a reaction involving radical intermediates is suggested. It is now widely recognized that reactions of secondary and even some primary alkyl halides, particularly iodides, with transition-metal centers often proceed by competitive radical chain or radical cage mechanisms, especially when the halides are poorer S_N2 substrates.[16] Reaction sequences involving initiation either by halide abstraction (eq 5-8) or electron-transfer (eq 9-11) mechanisms to generate the required rhodium(III)-alkyl species can be envisioned in the present case. Several metallate anions[20] and hydrido-d_6 anions[21] have been shown to react with alkyl halides by electron-transfer mechanisms, and it is not unreasonable to expect the same type of chemistry here.[22]

$$Rh^I + R\text{-}I \rightleftharpoons Rh^{II}\text{-}I + R\cdot \quad (5)$$

$$Rh^{II}\text{-}I + R\cdot \rightleftharpoons R\text{-}Rh^{III}I \quad (6)$$

$$Rh^I + R\cdot \rightleftharpoons R\text{-}Rh^{II} \quad (7)$$

$$R\text{-}Rh^{II} + RI \rightleftharpoons R\text{-}Rh^{III}I + R\cdot \quad (8)$$

or

$$Rh^I + R\text{-}I \rightleftharpoons [Rh^{II} + R\cdot + I^-] \quad (9)$$

$$HRh^{III} + R\text{-}I \rightleftharpoons [Rh^{II} + R\cdot + I^-] + H^+ \quad (10)$$

$$[Rh^{II} + R\cdot + I^-] \rightleftharpoons R\text{-}Rh^{III}I \quad (11)$$

(14) Roe, D. C., du Pont Central Research, personal communication.
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Unfortunately, in the present system, while reaction schemes involving radical intermediates are well precedented for stoichiometric reactions and wholly consistent with all of the available data for this catalytic system, the definitive experiments to test this postulate are inaccessible. The rigorous experimental conditions tend to preclude the use of radical initiators or inhibitors. Similarly, the efficiency of the hydrocarboxylation chemistry involved rules out the use of substrates whose radical derivatives rearrange at near diffusion-controlled bimolecular reaction rates, since such precursors generally contain and take advantage of internal olefinic moieties, which would be preferentially consumed. To avoid these problems and determine more directly the possible intermediacy of radicals, future work will focus on the stoichio-

metric reaction between $RhI_2(CO)_2^-$ and i-PrI (and other secondary iodides) under milder conditions.

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Effect of Aryloxide Ancillary Ligands on the Chemistry of Molybdenum–Molybdenum and Tungsten–Tungsten Multiple Metal–Metal Bonds[†][1]

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Abstract: The effect of aryloxide ancillary ligands on the chemistry of Mo_2 and W_2 dinuclear compounds has been investigated by reaction of the compounds $M_2(NMe_2)_6$ (M = Mo and W) and $Mo_2(O$-t-$Pr)_6$ with a variety of phenols. The sterically less demanding ligands 4-methylphenol ($HOAr$-4-Me) and 3,5-dimethylphenol ($HOAr$-3,5-Me_2) react with $Mo_2(NMe_2)_6$ to give salt complexes $[Me_2NH_2][Mo_2(OAr)_7(HNMe_2)_2]$ in good yields. A single-crystal diffraction study shows the anion obtained by using 4-methylphenol to contain a confacial bioctahedral arrangement of ligands in the $Mo_2O_7N_2$ core, with a metal–metal distance of 2.601 Å. Both complexes are slightly paramagnetic in solution at 30 °C, μ = 0.8–0.9 μ_β by Evans' method. However, relatively sharp contact shifted ^1H NMR spectra are present at 30 °C for both complexes, and in the case of the 4-methylphenoxo derivative, the temperature dependence of the 4-methyl groups indicates that the electrons on the molybdenum atoms are antiferromagnetically coupled. An estimate of the exchange integral, J, gave a value between 230 and 290 cm^{-1}. Using $W_2(NMe_2)_6$ instead of $Mo_2(NMe_2)_6$ in the reaction yields only the simple amine adducts $W_2(OAr$-4-Me$)_6(HNMe_2)_2$ and $W_2(OAr$-3,5-$Me_2)_6(HNMe_2)_2$. Addition of only 4 equiv of 3,5-dimethylphenol to $Mo_2(NMe_2)_6$ in the presence of a large excess of $HNMe_2$ leads to the formation of a reduced, Mo_2^{4+}-containing species $Mo_2(OAr$-3,5-$Me_2)_4(HNMe_2)_4$ as a blue crystalline solid in good yield. Ligand exchange with trimethylphosphine gives the emerald green $Mo_2(OAr$-3,5-$Me_2)_4(PMe_3)_4$. The pathway of the reduction is uncertain, but from the reaction mixture an oxidized species $Mo_2(OAr$-3,5-$Me_2)_6(NMe_2)(HNMe_2)_2$ was isolated and structurally characterized. The Mo_2^{7+} core is surrounded by a confacial bioctahedral arrangement of ligands with a bridging dimethylamido group. The Mo–Mo distance of 2.41 Å is consistent with the presence of a bond of order 2.5. Electrochemical one-electron oxidation of the quadruply bonded $Mo_2(OAr$-3,5-$Me_2)_4(PMe_3)_4$ leads to the monocation containing an Mo_2^{5+} core with a formal bond order of 3.5. EPR measurements show the resulting unpaired electron coupled to the four PMe_3 nuclei. Crystal data for $[Mo_2(OAr$-4-Me$)_7(HNMe_2)_2]\cdot n$-hexane at −163 °C are as follows: a = 14.677 (6) Å, b = 16.62 (7) Å, c = 14.402 (6) Å, α = 115.78 (2)°, β = 107.67 (2)°, γ = 77.82 (2)°, Z = 2, d_{calcd} = 1.281 g cm^{-3} in space group $P\bar{1}$. Crystal data for $Mo_2(OAr$-3,5-$Me_2)_6(NMe_2)(HNMe_2)_2$ at −140 °C are as follows: 29.281 (6) Å, b = 12.071 (4) Å, c = 14.653 (8) Å, β = 92.57 (3)°, Z = 4, d_{cald} = 1.350 g cm^{-3} in space group $P2_1/n$.

Over the past 20 years, the study of multiple metal–metal bonding has developed rapidly and is presently an important area of inorganic chemistry.[2] Initial endeavors centered mainly on the isolation and characterization of compounds that contained

strong metal–metal interactions, but more recently the potential uses of these highly reactive functional groups has been a major focus of research.[3,4] Catalytic cycles in which the electrons initially contained in the metal–metal bond are used have been proposed and, in at least one case, realized.[5] Another major aspect

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is prevented in the last digit of the numbering: e.g., III → 3 and 13.)

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