The Rhodium-Catalyzed Carbonylation of Linear Primary Alcohols

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Abstract: The results of a comprehensive kinetic, spectroscopic, and analytical study into the rhodium-catalyzed carbonylation of primary linear alcohols (R = Me, Et, and *n*-Pr) are reported. In all cases, the reaction rate is first order in both [Rh] and added [HI] and independent of CO pressure. The only rhodium species observed under catalytic conditions was $RhI_2(CO)_2^-$. The rates of carbonylation of the alcohols decreased in the order MeOH > EtOH > *n*-Pr with relative rates at 170 °C of 21:1:0.47. Apparent activation parameters have been determined. All the data are consistent with the rate-determining step being nucleophilic attack by the rhodium anion on the corresponding alkyl iodide, in agreement with the previous interpretation of the methanol system. Important information was also obtained regarding the stability of the intermediate rhodium alkyl species. Carbonylation of *n*-PrOH gave a mixture of the two isomeric product butyric acids, the composition of which depended on the CO pressure. The isobutyric acid appears to arise from the isomerization of the initially formed *n*-alkyl species, and the pressure dependence of this process suggests that loss of CO from the alkyldicarbonylrhodium(III) species is competitive with the migratory insertion reaction which forms the analogous monocarbonyl acyl species observed previously.

The carbonylation of methanol to acetic acid with a homogeneous iodide-promoted rhodium-catalyst system is now an industrially important process.[1,2] On a molecular level, this process is well understood to involve the rate-determining nucleophilic attack on alkyl iodide by the anion $RhI_2(CO)_2^-$.[3] Recently, several studies on EtOH[4,5] and *i*-PrOH[6] have been reported, in which the data were interpreted in terms of the same general mechanism. One of these, the carbonylation of *i*-PrOH,[6] exhibited, what appeared to be, anomalous behavior for simple S_N2 reactivity. In order to establish more confidently the "expected" reactivity pattern for this process, we initiated detailed studies into the carbonylations of MeOH, EtOH, and *n*-PrOH. Our investigations into the carbonylation of *i*-PrOH will be presented separately.[7]

Experimental Section

Unless otherwise stated, the chemicals were reagent grade and were used as supplied. Ethanol was added as ethyl acetate. Iodide was added as aqueous hydriodic acid (55–58%). Ethanol-d_6 (Cambridge Isotope Laboratories), D_2O, and acetic acid-d_4 (MSD Isotopes) were used as supplied. The dimer [RhCl(1,5-cyclooctadiene)]$_2$ ([RhCl(COD)]$_2$) was prepared by literature methods.[8]

The reactor, infrared cell, and experimental procedures used in this study have been described previously,[9] with the following exceptions. The reactor was equipped with a double charge pot connected in series. The lower pot was charged with [RhCl(CO)$_2$]$_2$,[10] generated in situ from [RhCl(COD)]$_2$,[11] dissolved in CH_3COOH (10 mL). The upper pot was charged with CH_3COOH (18 mL). The remaining components were added to the reactor proper (total solution volume = 100.0 mL). After the pressure was checked, the autoclave was heated to the desired temperature. The reaction was initiated by consecutively injecting the catalyst and rinse solutions, and adding CO until the desired pressure was attained. In this way, induction periods were minimized and linear rates were observed within 5–10 min. Gas samples were taken at the end of each kinetic run and analyzed on a Carle 1196-Series Six (Application 196-A) gas chromatograph. The final reaction solutions were analyzed on an HP 5730A GLC equipped with an HP 5705A TC detector, and

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(6) Hjortkjaer, J.; Jorgensen, J. C. E. *J. Chem. Soc., Perkin Trans. 2* **1978,** 763.
(7) Dekleva, T. W.; Forster, D. *J. Am. Chem. Soc.,* following paper in this issue.
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(11) [RhCl(1,5 norbornadiene)]$_2$ did not react with CO sufficiently fast to allow it to be used as a catalyst precursor.

interfaced with an HP 18625A A/D converter. Analyses of the MeOH and EtOH samples employed a 1.0-m Porapak T column, although the temperature programs were different for each system: MeOH, temperature programmed from 100 to 170 °C at 16 °C/min; EtOH, temperature programmed from 80 to 170 °C at 16 °C/min. The samples in the *n*-PrOH system were analyzed on a 10-m fused silica open tubular AT 1000 column, temperature programmed from 80 to 250 °C at 4 °C/min (iso/n ratio), and a 6 ft Chromosorb 101 column, programmed from 160 °C (4 min) to 240 °C at 15 °C/min. When required, deuterium contents were determined by GC/MS analysis by electron ionization (EI, 70 eV) and/or chemical ionization (CI, CH_4, ca. 2 eV) techniques in the following ways: alkyl iodides by EI with M^+ and (M − I)$^+$ peaks; EtCOOH by EI with M^+ peak; *i*-PrCOOH by CI with (M + I)$^+$ peak and by EI with M^+ and (M − COOH)$^+$ peak; *i*-PrCOOH by CI with (M + 1)$^+$ peak and EI with (M − Me)$^+$ peak. The errors in measurement are estimated to be ±8%.

Results

The products of the carbonylations of MeOH, EtOH, and *n*-PrOH were found to be, as expected, MeCOOH, EtCOOH, and PrCOOH (a mixture of isomers), respectively. In addition, product solutions contained water, the corresponding alkyl iodides, alcohols, and alkyl acetates, as well as the esters of the starting alcohols and product acids. In the *n*-PrOH study, there was no evidence for any *i*-PrOH, or isopropylbutyrates, and only trace levels of *i*-PrI. Gas analyses of the final reaction mixtures showed trace levels of H_2 and CO_2 in all cases, C_2H_4 and C_2H_6 in the EtOH reactions, and C_3H_6 and C_3H_8 in the *n*-PrOH reactions. Generally, the final gas mixtures contained greater than 98% CO. The results of our kinetic investigations are presented in Tables I–III, Supplemental Material. Over the temperature ranges investigated, the carbonylations of EtOH and *n*-PrOH exhibited a rate expression identical with that found previously for MeOH[1,3] (eq 1). Analyses of the liquid in the methanol and ethanol systems

$$\text{rate} = -d(CO)/dt = k[CO]^0[Rh]^1[HI]^1_{added} \qquad (1)$$

indicated essentially quantitative conversion of the added HI to the corresponding alkyl iodide. In the *n*-PrOH system, the same quantifying measurements were not made, although the linear relationship between [HI]$_{added}$ and *n*-PrI was determined. By analogy with the methanol and ethanol systems, and the known reactivities of HI with primary alcohols, we assume that the reaction to form the *n*-PrI is essentially quantitative in this case also. This reduces eq 1 to eq 2. Arrhenius plots for the respective systems are given in Figure 1, and the calculated activation parameters are listed in Table IV.
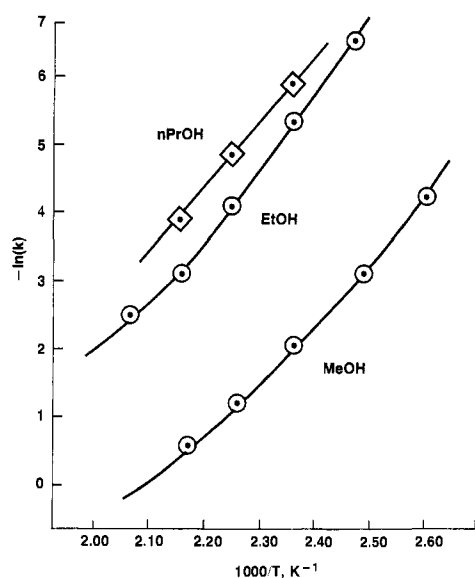
$$\text{rate} = k[Rh]^1[RI]^1 \qquad (2)$$

In all cases, the only rhodium-containing species observed in the infrared spectra, obtained from solutions at operating con-

Table IV. Relative Rate Data and Activation Parameters for the Carbonylation of Linear Primary Alcohols (ROH), Calculated from the Data in Tables I–III

compd R =	E, kJ mol^{-1} (kcal mol^{-1})	ΔH^*, kJ mol^{-1} (kcal mol^{-1})	ΔS^*, J mol^{-1} K^{-1} (cal mol^{-1} K^{-1})	rel rate, 170 °C	S_N2 displacement rate for organic halides[13]
Me	67.1 (16.0)	63.6 (15.2)	−116 (−27.7)	21	30
Et	80.1 (19.1)	76.4 (18.2)	−111 (−26.4)	1	1
n-Pr	83.1 (19.9)	79.5 (19.0)	−109 (−26.1)	0.47	0.4

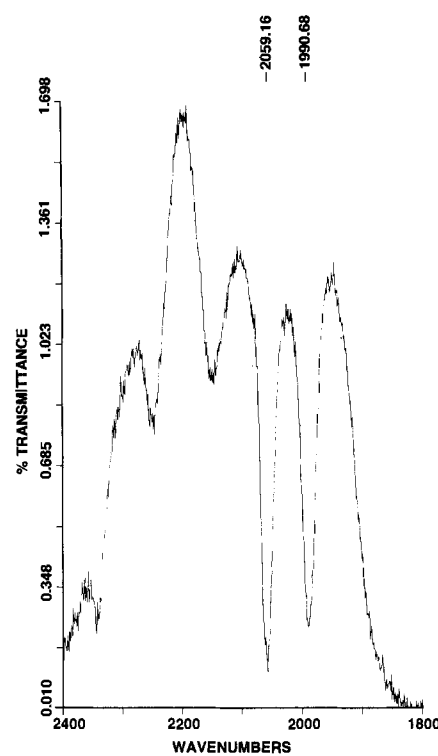**Figure 1.** Arrhenius plots for the carbonylations of the primary alcohols studied in this work.

ditions, was $RhI_2(CO)_2$ (Figure 2).

Carbonylation of EtOH-d_5 at 170 °C and 28.9 atm showed no kinetic isotope effect. Mass spectral analyses of the components in the recovered solution showed that some protic exchange had occurred. However, the extent of deuteration found in the product, EtCOOH (80% d_5, 20% d_4), was essentially identical with that found in the EtI (77% d_5, 23% d_4). A similar comparative experiment with n-PrOH in CD_3COOD/D_2O at 170 °C and 19.4 atm showed no solvent isotope effect; again the mass spectral analyses of the recovered compounds showed the same levels of incorporated deuterium in the recovered n-PrI (97% H_7, 3% H_6), n-PrCOOH (90% H_7, 10% H_6), and i-PrCOOH (89% H_7, 11% H_6). Finally, carbonylation of n-PrOH yielded a mixture of n- and isobutyric acids. Although the absolute rate was independent of CO pressure, the product distribution was not. As P_{CO}^{-1} approached zero, so did the amount of isobutyric acid (Figure 3).

Discussion

The spectroscopic and kinetic results are all entirely consistent with the rate-determining S_N2 displacement of I$^-$ from the corresponding alkyl iodides by $RhI_2(CO)_2^-$. The absence of any measureable rate differences with deuterium, either in the substrate (EtOH) or in the solvent (n-PrOH), is consistent with S_N2-type reactivity.[12] In fact, the relative rate data are remarkably similar to those found for organic nucleophiles.[13] It appears that the rhodium anion is much less sterically demanding than other transition-metal complexes, which, in some cases, exhibit much greater differences in rate with the same alkyl iodide substrates.[14]

The discovery, in the n-PrOH system, that the amount of isobutyric acid, but not the overall reaction rate, varied inversely with CO pressure was rather unexpected. Since the composite

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Figure 2. Representative in situ spectrum obtained during the carbonylation of normal alcohols; this spectrum was obtained during the carbonylation of ethanol at 170 °C and 31 atm.
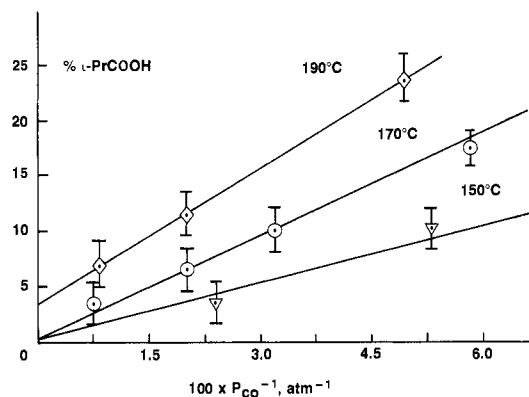
Figure 3. Variation of product distribution with CO pressure in the carbonylation of 1-propanol (data from Table III).

data suggest that the n-alkyl species is formed initially (from oxidative addition of n-PrI), it appears that isomerization to the isoalkyl species occurs after the rate-determining step, but on the same time scale as the trapping of the rhodium–acyl species by CO (the reversibility of the CO insertion reaction has been demonstrated previously in the methanol system,[3] and it is probably operative in this system also). In view of the inhibition by CO of this isomerization process, the most realistic explanation is that, in addition to the previously observed migratory insertion to form the monocarbonyl acyl species, the initially formed alkyldicarbonylrhodium(III) species can also become stabilized by dis-

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J. Am. Chem. Soc., Vol. 107, No. 12, 1985 3567

Scheme I. Proposed Reaction and Rearrangements for the
Production of Isomeric Mixtures during the Carbonylation
of 1-Propanol
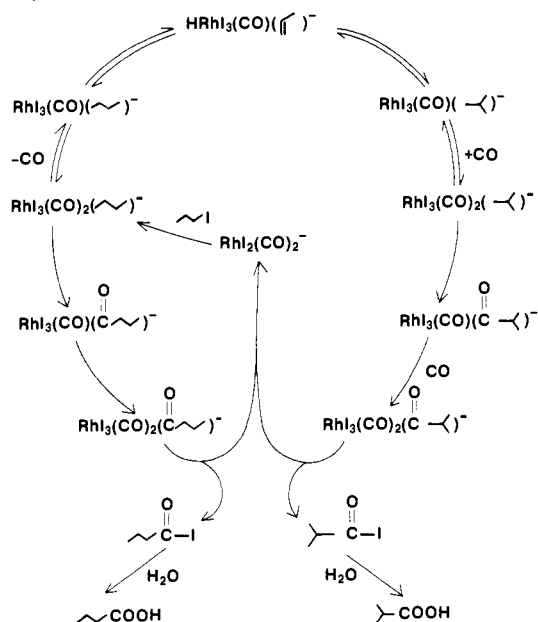
sociating a CO ligand. At the lower CO pressures, this latter mechanism becomes relatively more important. Once CO dissociates, the coordinatively unsaturated rhodium undergoes facile β-hydride elimination to yield an intermediate hydrido–olefin complex, which then can reinsert to form eventually either isomeric product (Scheme I). An analogous process likely occurs in the EtOH system as well, though in this latter system the reinsertion gives an indistinguishable ethyl species. The retention of isotopic integrity in the product acids with respect to the corresponding alkyl iodides, in both the EtOH and *n*-PrOH systems, indicates that the exchange of the Rh(III)–H (or Rh–D) with solvent D^+ (or H^+) is slow relative to the rearrangement processes. It also tends to rule out a significant hydrocarboxylation contribution involving free HI (or DI) and olefin,[15] at least at 170 °C.[16] The apparent positive intercept in Figure 3 for the *n*-PrOH data at 190 °C may suggest an increasing contribution of such a pathway at the higher temperatures.

There is good internal consistency in the apparent activation parameters of the three systems in this work (Table IV). The values for the activation energies (67–83 kJ/mol, 16–20 kcal/mol) are also in good agreement with those found in reactions between organic anions and neutral substrates in polar media (typically[17] 71–83 kJ/mol, 17–20 kcal/mol). Other workers have reported slightly lower values in studies encompassing different temperature ranges (typically[4,6,18] 50 °C higher than in this present study). One must recognize that, to obtain rigorously correct parameters, it is necessary to account for the vaporizations and liquid thermal expansions of the systems, both of which were expected to be significant at the temperatures involved. In order to account for these errors, we systematically measured the vapor pressures and liquid-phase compositions for each system as a function of tem-

perature, over the ranges used to determine the activation parameters. Quite surprisingly, there was essentially no variation in the mol % alkyl iodide (or any other component) over the range examined. There was only a slight diminution in the mol % RI in the liquid phase at elevated temperatures with respect to the mol % in the total system. For example, in separate experiments in which the overall mol % of EtI was 2.4, the measured liquid-phase composition of EtI from 130 to 210 °C was 2.0 ± 0.1 mol % (81% of total; similarly for MeI, 75%, and *n*-PrI, 93%). The vapor-pressure data also suggest that the actual extent of vaporization was small. For example, a reaction mixture (100 mL) containing H_2O (0.563 mol), EtI (0.050 mol), EtOAc (0.250 mol), and HOAc (1.133 mol) exhibited a vapor pressure of ca. 8.3 atm at 210 °C. Assuming ideal behavior, this pressure corresponds to ca. 0.09 mol, or ca. 5% of the total.

Since preferential vaporization of the alkyl iodide would not appear to be the reason for the slight curvatures in Figure 1, we favor, as a possible explanation, the liquid thermal expansion over the temperature ranges tested. While it was not possible to measure either the densities or the volumes of the liquid phases under the operating conditions, we note that the densities of pure acetic acid and the corresponding acetate esters, mixtures of which constituted at least 80% of the total volume in every case, decrease by 20% over the temperature range 110–210 °C.[19] Assuming that the total solution behaves similarly, it is reasonable to expect that increasing the temperature of the solution would increase the effective solution volume, thereby decreasing the [Rh] and [RI] (even if the mol % of RI remains constant). Since the rate was found to be first order in both of these reagents, the measured rate of a solution-phase reaction would be expected to decrease, relative to the actual intrinsic rate, with increasing temperature. A non-linear Arrhenius plot might, then, be expected, rather than anomalous. Calculations of activation parameters based on data derived from systems exhibiting significant thermal expansions would yield activation energy and enthalpy values which are artificially low, relative to the intrinsic values. This error would be more acute at higher temperatures and would also depend on the total composition of the system. Such a rationale would explain the differences in reported activation parameters, and it suggests that the real values are still slightly higher than those given here.

Conclusions

The carbonylations of these primary alcohols by the iodide-promoted rhodium-catalyst system exhibit all of the properties expected for simple nucleophilic displacement reactions. The mechanism proposed for the methanol system appears to be valid for other primary alcohols. In addition, the data suggest that CO dissociation from the alkyldicarbonylrhodium(III) intermediate is competitive with migratory insertion. The hydrido–olefin which results from the facile β-hydride elimination of the coordinately unsaturated alkyl monocarbonyl rhodium(III) complex is stable with respect to solvent (H^+, D^+) exchange.

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

(16) We successfully minimized the formation of alkenes in these systems by operating at much lower temperatures than other workers.[4,6,18] However, we noted that, at least in the EtOH system, there was a measureable reaction at 210 °C with pressures less than 95 atm., even in the absence of rhodium catalyst. The data in Table II reflect only the contribution of rate attributable to the rhodium-catalyzed reaction. The nature of this background reaction was not examined.

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