It is presumed that vacant coordination sites on the metal are needed in this transfer-hydrogenation, since RuCl$_2$(PPh$_3$)$_3$ lost its high catalytic activity in the presence of excess triphenylphosphine; the complexes which had bidentate ligands also showed little activity.

When tetralin was used as a donor, the hydrogen transfer reaction was not influenced at all by the addition of metal complexes, suggesting that the reaction proceeds instead *via* change transfer complexes. That 1,2-dihydronaphthalene was always detected in the reaction of tetralin shows that this reaction is stepwise and that the driving force for the dehydrogenation of tetralin is not aromatization.

The dehydrogenation of 2,5-dihydrofuran, which has a heteroatom and a double bond, also was not influenced by the addition of metal complexes, and is again presumed to be a noncatalytic reaction.

Experimental Section

Materials. 2-Propanol, tetralin, 2,5-dihydrofuran, and all solvents were purified by distillation. Chloranil was recrystallized from toluene. Duroquinone, chlorotris(triphenylphosphine)rhodium(I),[10] dichlorotris(triphenylphosphine)ruthenium(II),[11] dichlorobis(triphenylphosphine)palladium(II),[12] dichlorobis(tri-*n*-butylphosphine)palladium(II),[13] tetrakis(triphenylphosphine)platinum(0),[14] tetrakis(tri-*p*-tolylphosphine)platinum(0),[14] tetrakis-(tri-*p*-chlorophenylphosphine) platium(0),[14] dichlorobis(triphenylphosphine)platinum (II),[15] dichlorobis(tri-*n*-butylphosphine)nickel(II),[16] dibromobis(tri-*n*-butylphosphine)nickel(II),[16] dichlorobis(triphenylphosphine)nickel(II),[17] dibromobis(triphenylphosphine)nickel(II),[17] dichlorobis(triphenylphosphine)cobalt-(II),[18] 2,2'-bipyridinedichloroiron(II),[19] *o*-phenanthrolinedichloroiron(II),[19] and dibromobis(triphenylphosphine)cobalt(II)[18] were prepared by the methods reported in the literature. PdCl$_2$, MoCl$_5$, RuCl$_3$·H$_2$O, RhCl$_3$·2H$_2$O, Al(OPr^i)$_3$, Ni(acac)$_2$, 1,2-dihydronaphthalene, 2-chloropropane and tetrachlorohydroquinone were purchased and used without purification.

An Example of Dehydrogenation of 2-Propanol. Chloranil (61.5 mg, 0.25 mmol), 2-propanol (19.1 μl at 25°, 0.25 mmol), and NiBr$_2$(PBu$^n_3$)$_2$ (15.6 mg, 0.025 mmol) were put into a Pyrex glass tube which had been sealed at one side. Chlorobenzene was added to make the total volume of the solution 1.0 ml. The tube was sealed under vacuum after two freeze–pump–thaw cycles at 10^{-3} Torr on a vacuum line, using liquid nitrogen. The sealed tube was heated for 2 hr in a silicone oil bath kept at 170 ± 1°. Chloranil and the catalyst dissolved slowly at room temperature but quickly at the elevated temperature. Gc analysis was performed at 100° with a Hitachi Perkin-Elmer instrument equipped

with a flame ionization detector, using a 2 m × 6 mm stainless column packed with 20% Carbowax on Celite 545. As an internal standard 15 μl of *n*-decane was used. By recrystallization of the resulting precipitate from acetone, pure tetrachlorohydroquinone was obtained, ν_{OH} 3350 cm^{-1} (sharp).

The other dehydrogenation reactions of 2-propanol were carried out in a similar way.

An Example of Dehydrogenation of Tetralin. Tetralin (34.1 μl at 25°, 0.25 mmol), chloranil, and NiBr$_2$(PBu$^n_3$)$_2$ were treated as in the reaction of 2-propanol described above, except that the reaction temperature was either 160 or 180°. Gc analysis was carried out at 170° using phenylcyclohexane as an internal standard.

An Example of Dehydrogenation of 2,5-Dihydrofuran. Chloranil, 2,5-dihydrofuran (18.4 μl at 25°, 0.25 mmol), and NiBr$_2$(P-Bu$^n_3$)$_2$ were treated as in the reaction of 2-propanol, except that the reaction temperature was 140°. Gc analysis was carried out at 100°, using a 2 m × 6 mm stainless steel column packed with 10% silicon DC 11 on Diasolid L. As an internal standard 15 μl of *n*-heptane was used.

Registry No.—2-Propanol, 67-63-0; chloranil, 118-75-2; tetralin, 119-64-2; 2,5-dihydrofuran, 1708-29-8.

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HCo(CO)$_4$ and the Hydroformylation Reaction

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The rate of the stoichiometric hydroformylation reaction and the rate of the decomposition of HCo(CO)$_4$ are affected in a strikingly similar manner by the presence of *p*-methoxybenzonitrile. Apparently this results from a common dependence on the concentration of HCo(CO)$_3$, the key intermediate in both reactions.

The stability and reactivity of HCo(CO)$_4$ are key considerations in both the catalytic and the stoichiometric hydroformylation of olefins. The presence of nucleophiles such as tri-*n*-butylphosphine has a substantial effect on the catalytic process,[1] and in a recent paper[2] we have shown that the presence of *p*-methoxybenzonitrile has a profound effect on the course of the stoichiometric reaction. In the present paper, we show that the presence of *p*-methoxybenzonitrile affects the rate of HCo(CO)$_4$ de-

composition in a manner virtually parallel to its effect on the hydroformylation reaction. This parallelism apparently resides in the effect that the nitrile has on the concentration of the key, coordinately unsaturated intermediate, HCo(CO)$_3$, which is in equilibrium with HCo(CO)$_4$.

Experimental Section

A typical reaction was conducted as follows. A toluene solution of HCo(CO)$_4$, prepared and analyzed according to established
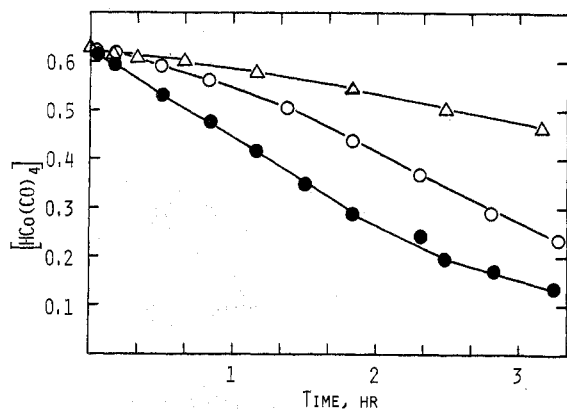
Figure 1. The decomposition of HCo(CO)$_4$ under CO at 25°: △, DCo(CO)$_4$; ○, HCo(CO)$_4$; ●, HCo(CO)$_4$, 0.059 M Co$_2$(CO)$_8$ ($k_H/k_0 = 1.7$).

procedures,[3] was equilibrated for 10 min at the desired reaction temperature under 1 atm of CO and syringed into a stirred toluene solution of p-methoxybenzonitrile, which had been equilibrated for 10 min under the desired reaction conditions. In each experiment, the quantity of toluene was adjusted to maintain the same initial reaction mixture volume in the presence of various amounts of nitrile. The concentration of remaining HCo(CO)$_4$ was determined at appropriate intervals: 1-ml aliquots were withdrawn, quenched by addition to excess 0.1 N NaOH under nitrogen, and back-titrated with 0.02 N HCl to the phenolphthalein end point.

Results

Our previous, unpublished observations[4] that the second-order decomposition of HCo(CO)$_4$ in solution was strongly inhibited by carbon monoxide and exhibited only a small kinetic deuterium isotope effect, as depicted in Figure 1, were essentially corroborated in the publication of Ungvary and Marko.[5] In addition, we found that the presence of as little as 0.1 equiv of Co$_2$(CO)$_8$ per HCo(CO)$_4$ substantially reduced the commonly observed induction period, apparent in Figure 1, and caused a slight rate increase.

During our study of the effect of p-methoxybenzonitrile on the hydroformylation of cyclopentene, we reexamined separately the decomposition of HCo(CO)$_4$ under similar conditions. We found a striking parallelism between the sensitivities of these seemingly dissimilar reactions to the presence of nitrile, as Figure 2 shows. In both instances, the presence of nitrile caused a severe rate reduction under N$_2$ and a significant rate enhancement under CO.

In order to clarify these findings, we examined the dependence of the rate of HCo(CO)$_4$ decomposition on the quantity of p-methoxybenzonitrile under both N$_2$ and CO atmospheres. The results of this study are depicted in Figure 3. Under N$_2$ the presence of as little as 0.1 equiv of nitrile causes a dramatic rate reduction but the effect rapidly diminishes with increasing amounts of nitrile and is even reversed when more than 1 equiv of nitrile is present. Under CO, the presence of small amounts of nitrile causes only a small but reproducible rate decrease; amounts greater than 1 equiv reverse the trend to such an extent that the decomposition becomes faster than in the absence of nitrile.

Discussion

The kinetics of the decomposition of HCo(CO)$_4$ in solution have been shown to be similar to, but more reproducible than, those obtained in the gas phase.[5] The derived rate expression exhibits a second-order dependence on HCo(CO)$_4$ and an inverse dependence on the partial pressure of CO; it is consistent with the mechanism depicted in the left half of Figure 4. The rate-retarding effect of CO
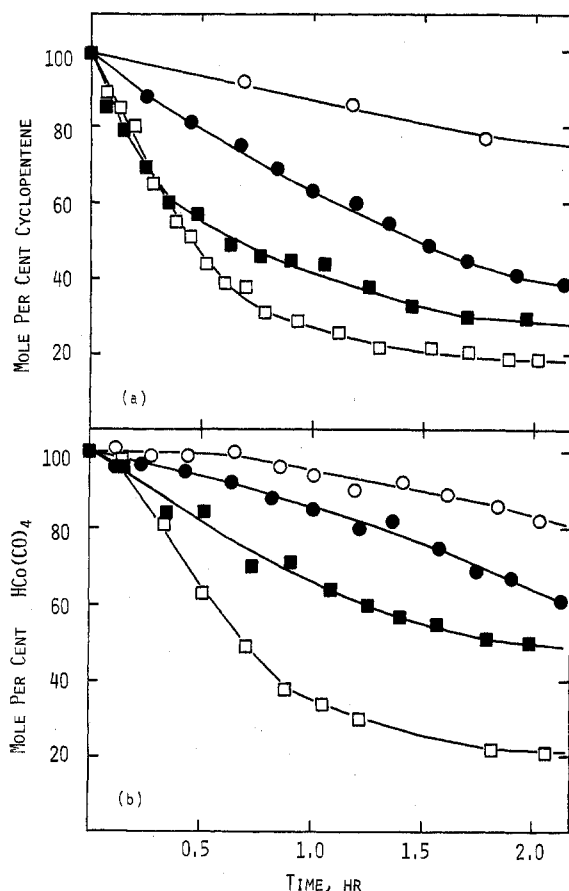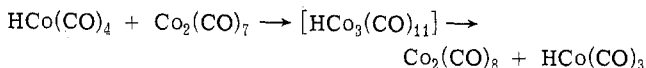

Figure 2. (a) The stoichiometric hydroformylation of cyclopentene ([M]$_0$ = 0.02) with excess HCo(CO)$_4$ ([M]$_0$ = 0.32), ArCN/Co = 1.0, at 30° and (b) the decomposition of HCo(CO)$_4$ ([M]$_0$ = 0.27), ArCN/Co = 1.8, at 30°: ●,○, under CO; ■,□, under N$_2$. Solid and open symbols represent data with and without p-methoxybenzonitrile, respectively.

is attributed to a reduction in the equilibrium concentration of HCo(CO)$_3$. In addition, the decompositions under CO characteristically exhibit substantial induction peri-

$$-\frac{d[\mathrm{HCo(CO)_4}]}{dt} = \frac{k_2 K}{p_{CO}}[\mathrm{HCo(CO)_4}]^2$$

ods; and we suggest that during this initial phase of the decomposition, a reaction occurs, which increases the concentration of HCo(CO)$_3$. The apparent ability of added Co$_2$(CO)$_8$ to reduce these induction periods and the known lability of CO in this complex[6] suggest that HCo(CO)$_4$ may react with Co$_2$(CO)$_7$ to give a trinuclear complex which subsequently dissociates to give Co$_2$(CO)$_8$

$$\mathrm{HCo(CO)_4} + \mathrm{Co_2(CO)_7} \longrightarrow [\mathrm{HCo_3(CO)_{11}}] \longrightarrow$$
$$\mathrm{Co_2(CO)_8} + \mathrm{HCo(CO)_3}$$

and HCo(CO)$_3$. Solvent cage effects such as those discussed previously[2] are consistent with such an irreversible bimolecular reaction giving rise to a higher equilibrium concentration of HCo(CO)$_3$ than the simple reversible dissociation of HCo(CO)$_4$. The possibility that Co$_2$(CO)$_8$ simply absorbs dissolved CO and hence increases the concentration of HCo(CO)$_3$ does not appear likely at atmospheric pressure.[7]

When an additional nucleophile, such as p-methoxybenzonitrile, is introduced into the reaction mixture, the mechanistic scheme is significantly complicated by the possible formation of several nitrile complexes. However, if we assume, as a first approximation, that the reactivity of each nitrile complex is similar to that of its corresponding carbonyl complex, the kinetic consequences are mini-
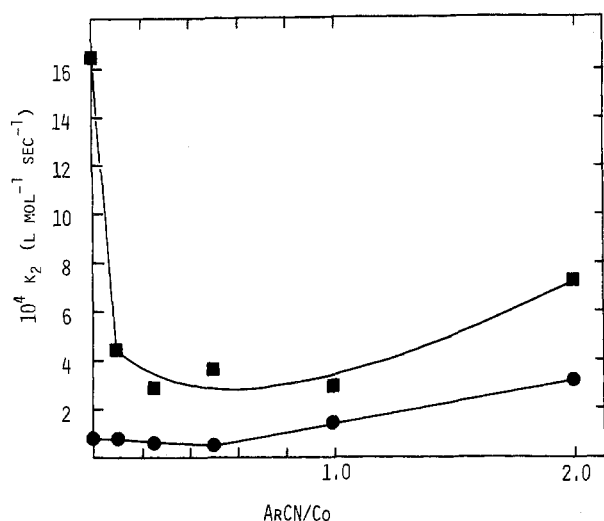
Figure 3. The effect of p-methoxybenzonitrile concentration on the decomposition of HCo(CO)$_4$ ([M]$_0$ = 0.29) at 25° under N$_2$ (■) and under CO (●).
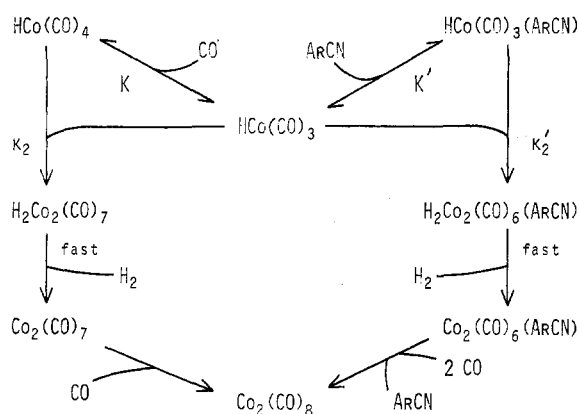

Figure 4. Scheme for the decomposition of HCo(CO)$_4$ with and without p-methoxybenzonitrile, (ArCN).

mal except for the expectation that the formation of HCo(CO)$_3$(ArCN) would reduce the equilibrium concentration of HCo(CO)$_3$ as the scheme on the right of Figure 4 suggests. This expectation is apparently fulfilled, since small amounts of nitrile inhibit the decomposition of HCo(CO)$_4$ under both N$_2$ and CO. However, attempts to confirm the existence of HCo(CO)$_3$(ArCN) by ir and nmr spectroscopy or to trap it with Ni(o-phen)$_3$Cl$_2$[8] failed.

The much larger rate decrease observed under nitrogen can be attributed to the much greater amount of HCo(CO)$_3$ available for complexation of nitrile under N$_2$ as opposed to the few tenths of one per cent[5] available under CO. The fact that the minimum rate of decomposition achieved in the presence of nitrile (1 equiv, 0.288 M) under N$_2$ is much faster than the rate of decomposition in

the absence of nitrile under CO (solubility, 7 × 10^{-3} M in toluene at 1 atm[6]) suggests that, as shown in Figure 4, K' > K. This conclusion is consistent with the suggestion that nitriles are more weakly bound than CO by virtue of their poorer σ-donating and π-accepting properties.[9]

The observation that the rate of decomposition increases with increasing amounts of nitrile after reaching a broad minimum under both N$_2$ and CO remains difficult to explain. At relatively high nitrile concentrations, the proportion of cobalt hydride present as HCo(CO)$_3$(ArCN) may be large and this complex could be somewhat more reactive toward HCo(CO)$_3$ than HCo(CO)$_4$ is, i.e., k_2' > k_2, Figure 4. However, before such a comparison can be made, it would be necessary to know more about the detailed mechanism by which the postulated, but as yet undetected, intermediate H$_2$Co$_2$(CO)$_7$ is formed.

Increasing amounts of nitrile undoubtedly increase the dielectric constant of the reaction medium. However, the dielectric increase can increase the rate of HCo(CO)$_4$ decomposition only if the rate-determining step involves the formation of charged species or a polar transition state. Similar solvent effects have been observed for the conversion of CH$_3$Mn(CO)$_5$ to CH$_3$COMn(CO)$_5$[10] and a variety of oxidative additions to IrCl(CO)(PPh$_3$)$_2$.[11] The small deuterium kinetic isotope effect which we and others have observed is not necessarily inconsistent with the concerted oxidative addition of HCo(CO)$_4$ to HCo(CO)$_3$ which we

$$H\text{----}Co(CO)_4$$
$$\diagdown\alpha\diagup$$
$$H\text{---}Co(CO)_3$$
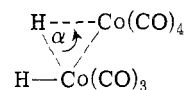
propose as a reasonable rate-determining step. Hydrogen transfers which involve nonlinear (α < 180°) transition states characteristically exhibit small isotope effects,[12] and indeed the oxidative addition of molecular hydrogen to IrCl(CO)(PPh$_3$)$_2$ to give H$_2$IrCl(CO)(PPh$_3$)$_2$ exhibits a k(H$_2$/D$_2$) of only 1.22.[11]

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