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THE STOICHIOMETRIC HYDROGENATION OF 1,1-DIPHENYLETHYLENE WITH HYDRIDOCOBALT TETRACARBONYL; DIFFERENCES FROM THE HYDROFORMYLATION REACTION

Jerome A. Roth* and Milton Orchin**
Department of Chemistry, University of Cincinnati,
Cincinnati, Ohio 45221

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Summary

The kinetics of the stoichiometric hydrogenation of 1,1-diphenylethylene with $HCo(CO)_4$ is cleanly second order, permitting a determination of the activation parameters. The rate is unaffected by the atmosphere over the reaction and is enhanced by substituting $DCo(CO)_4$ for $HCo(CO)_4$. These results contrast sharply with those secured in the hydroformylation of 1-alkenes and thus dual mechanistic pathways are available for the reaction of $HCo(CO)_4$ with unsaturated systems. It is very possible that the stoichiometric hydrogenation of 1,1-diphenylethylene involves a geminate free radical pair but definitive proof is still lacking.

Introduction

Much of our knowledge concerning the mechanism of cobalt-catalyzed hydroformylation of 1-alkenes has been secured from studies on stoichiometric hydroformylations,

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*Present address, Chemistry Department, Northern Michigan University, Marquette, MI 49855.

**To whom correspondence concerning this paper should be addressed.

using $HCo(CO)_4$ to furnish all the additional hydrogen required for the aldehydes produced by the reaction. The mechanism of such hydroformylations is very complex, involving perhaps six or seven equilibria prior to product formation [1,2,3]. These stoichiometric studies have revealed that hydroformylations of 1-alkenes are characterized by: (a) pseudo first order kinetics; (b) the formation and intermediacy of σ-complexes and π-complexes of both alkyl- and acylcobalt with varying molar quantities of ligated CO; (c) relatively poor (35-60%) yields of isolable products; (d) a high degree of sensitivity to the presence of an atmosphere of CO; (e) deuterium isotope effects close to 1.0 when using $DCo(CO)_4$; and (f) the formation of only small quantities of saturated hydrocarbons [1,2,3]. We wish to report here on the stoichiometric reaction between $HCo(CO)_4$ and 1,1-diphenylethylene ($Ph_2C{=}CH_2$, 1), a reaction which we find to differ remarkably with respect to all the above features which characterize the hydroformylation reaction.

Results and Discussion

The reaction between 1,1-diphenylethylene and hydridocobalt tetracarbonyl proceeds rapidly and exclusively by hydrogenation:

$$Ph_2C{=}CH_2 + 2HCo(CO)_4 \longrightarrow Ph_2CHCH_3 + Co_2(CO)_8$$

In all the rate studies reported here, except for those conducted at very low temperatures, the reaction was carried to completion and a quantitative yield of 1,1-diphenylethane was obtained. The progress of the reaction was determined by periodic removal of aliquots, quenching with triphenylphosphine [4,5], and analyzing the aliquots by gas chromatography. The results of five typical

TABLE 1

Rate of Hydrogenation of 1,1-Diphenylethylene at 0°C.[a]

$[HCo(CO)_4]_o \times 10^2$ [b]	$[Ph_2C{=}CH_2]_o \times 10^2$	Ph_2CHCH_3 % [c]	rate$_o$ [d] (mol $l^{-1}sec^{-1}$) $\times 10^5$	k[e] (l mol^{-1} sec^{-1}) $\times 10^2$
6.55	2.83	100	4.47	2.42
5.60	2.83	99.0	4.02	2.50
12.9	2.83	100	11.3	3.1
2.64	2.83	46.7	1.83	2.45
5.58	1.42	100	2.36	2.13

[a] At one atmosphere CO in CH_2Cl_2.

[b] Initial concentration determined titrametrically.

[c] Determined by glc.

[d] Initial rate of disappearance of 1,1-diphenylethene.

[e] ± 0.15

experiments are given in Table 1. The reaction conforms to the second-order rate expression:

$$\frac{-d[Ph_2C{=}CH_2]}{dt} = k[Ph_2C{=}CH_2]\ [HCo(CO)_4]$$

From rate measurement at 23°, 0°, and -23°C (Table 2), values of $\Delta H^{\ddagger}=17.0\pm0.3$ kcal/mole, and $\Delta S^{\ddagger}=-10 \pm 2$ eu were calculated.

The stoichiometric hydroformylation of alkenes is highly sensitive to even very small changes in the partial pressure of CO; there is a substantial enhancement of rate when hydroformylations are conducted under nitrogen, or other inert

TABLE 2

Effect of Temperature and Atmosphere on the Rate of Hydrogenation of 1,1-Diphenylethylene [a]

$[HCo(CO)_4]_o \times 10^2$ [b]	$[Ph_2C{=}CH_2]_o \times 10^2$	T(°C)	Gas[c]	rate$_o$ ($mol\ l^{-1} sec^{-1}$) $\times 10^5$	k[d] ($l\ mol^{-1} sec^{-1}$) $\times 10^2$
6.55	2.83	0.0	CO	4.47	2.42
6.55	2.83	0.0	N_2	4.10	2.21
4.10	2.83	23.0	CO	20.3	17.5
3.17	2.83	-23[e]	CO	0.161	0.112

[a] In CH_2Cl_2.

[b] Determined titrametrically.

[c] One atmosphere of gas; solvent purged at least 15 min. with same gas before run commenced.

[d] ±5%

[e] Dry-ice/CCl_4 bath.

gases, accompanied by decreased yields of aldehydes and dramatically increased isomerization of the 1-alkene [5]. In the case of 1, however, the reaction is essentially unaffected by conducting it under nitrogen rather than under CO, as the data in Table 2 show. Clearly, the reaction does not require that 1 displace a coordinated CO on cobalt, as is the case with 1-alkenes. Accordingly, it appears that π-complexation either does not occur or is kinetically unimportant during the hydrogenation of 1.

In previous studies on the stoichiometric hydroformylation of cyclopentene [6], and the decomposition of $HCo(CO)_4$ [6,7], it was shown that, under CO, there is an induction period in the reaction and that this induction period can be eliminated (for reasons not clearly understood) by adding $Co_2(CO)_8$ to the reaction mixture. Figure 1 shows the typical behavior exhibited by 1-hexene. Under CO, an induction period is observed, but the rate is subsequently very similar to that under CO with $Co_2(CO)_8$ added at the start of the reaction. The reaction of $\underset{\sim}{1}$ with $HCo(CO)_4$ shows no such induction period; the presence of $Co_2(CO)_8$ does not affect the rate. Figure 1 also shows the amazingly rapid catalytic isomerization of 1-hexene with $HCo(CO)_4$ under N_2, a phenomenon previously reported in detail in a study of 4-methyl-1-pentene [5]. This figure also shows, as expected, that

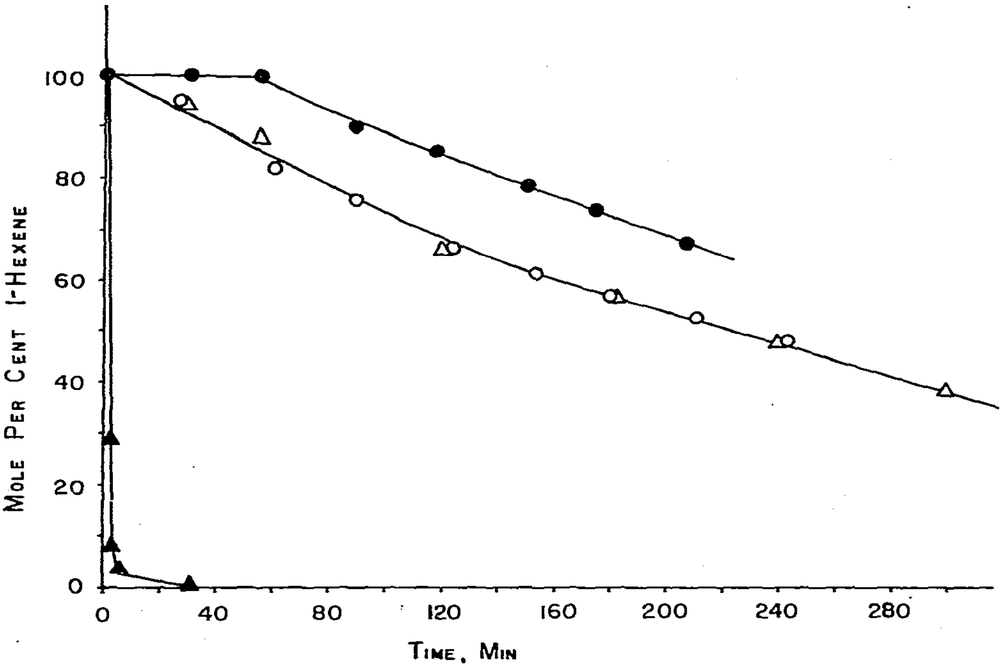

Fig. 1: Disappearance of 1-hexene at 22°C under various conditions: ●, under CO; ○, under CO, $Co_2(CO)_8$ added; △, $DCo(CO)_4$, under CO, $Co_2(CO)_8$ added; ▲, under N_2.

there is essentially no isotope effect in the stoichiometric hydroformylation of 1-hexene.

Although solvent effects on the catalytic hydroformylation reaction have been studied [8], there is relatively little information on the effects of solvent on the stoichiometric hydroformylation reaction. We have examined the effects of various solvent systems on the stoichiometric hydrogenation of **1** and obtained the results shown in Table 3. Although

TABLE 3

Effect of Solvent on the Rate of Hydrogenation of 1,1-Diphenylethylene at 0°C [a]

$[HCo(CO)_4]_o \times 10^2$	$[Ph_2C{=}CH_2]_o \times 10^2$	Solvent[b]	k^c $(l\ mol^{-1} sec^{-1}) \times 10^2$
5.60	2.83	CH_2Cl_2	2.50
5.6	2.83	hexane	2.72
6.85	2.83	$CHCl_3$	2.28
4.32	2.83	THF[d]	1.80
6.76	2.83	acetone[d]	2.28
6.16	2.83	acetonitrile[d]	1.93
6.04	2.83	acetone/water (77/23)[d]	0.289
6.65	2.83	CH_2Cl_2/EtOH (99.5/0.5)	2.43
5.65	2.83	CH_2Cl_2/EtOH (90/10)	2.98
5.65	2.83	CH_2Cl_2/EtOH (80/20)	2.80
10.5	2.83	CH_2Cl_2/EtOH (50/50)	0.562
8.69	2.83	EtOH (100)[d]	0.123
5.5	2.83	N-Methylpyrrolidone	no reaction

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[a] Under one atmosphere CO.

[b] For mixed solvents, numbers refer to volume percent.

[c] ±5% of value shown.

[d] Yield of diphenylethane substantially less than theoretical.

most of the aprotic solvents give approximately the same rate, the results are difficult to interpret. The reduced rates observed with solvent containing a high proportion of ethanol, and with aqueous systems, may be due to solvation and/or ionization of $HCo(CO)_4$ in such media [9]. Using the highly polar, non-protic N-methylpyrrolidone as solvent, no reaction is observed. Apparently, this solvent completely deprotonates the $HCo(CO)_4$ [10], making the latter unavailable as a reducing agent.

With respect to the mechanism of the reaction, the evidence is consistent with the overall scheme shown in equation (1).

$$Ph_2C{=}CH_2 + HCo(CO)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{complex}] \xrightarrow[k_2]{HCo(CO)_4} Ph_2CHCH_3 + Co_2(CO)_8 \qquad (1)$$

The structure of the complex is obviously of critical importance.

It has been suggested that the observed hydrogenation of polynuclear hydrocarbons under catalytic oxo conditions proceeds by a radical mechanism [11]. Radical intermediates have previously been suggested [12] as intermediates in the reduction of α,β-unsaturated substrates achieved with $[HCo(CN)_5]^{3-}$, although the reduction of 1 in this system is quite slow [13]. More recently, convincing NMR evidence (CIDNP) has been published in a particularly insightful paper, showing that the reduction of α-methylstyrene by $HMn(CO)_5$ proceeds by a mechanism involving a free radical geminate pair [14]. If such a mechanism were applicable to our stoichiometric reduction, the [complex] in equation (1) may be the geminate radical pair $Ph_2\dot{C}CH_3$, $\cdot Co(CO)_4$.

The reduction of 1 with $DCo(CO)_4$ resulted in a pronounced inverse isotope effect (Table 4). While such isotope effects

TABLE 4

Isotope Effect Due to $DCo(CO)_4$ on the Rate of Hydrogenation of 1,1-Diphenylethylene at 0°C.

$[HCo(CO)_4]_o \times 10^2$	$[Ph_2C{=}CH_2]_o \times 10^2$	Solvent	$k(l\ mol^{-1}sec^{-1}) \times 10^2$	k_H/k_D [a]
5.60	2.83	hexane	4.20	0.59
5.60	2.83	hexane	4.25	0.58
5.6	2.83	CH_2Cl_2	4.32	0.58

[a] ± 0.04

are relatively rare, they have also been observed in the related system with $HMn(CO)_5$ [14]. Such an effect [15] may be taken to indicate that the transition state in the rate determining step closely resembles the structure of the intermediate, with the C-D bond largely formed.

We have conducted experiments [16] in an ESR cavity under a variety of conditions and were unable to detect a paramagnetic signal. Even when the reaction is conducted in the presence of a tenfold stoichiometric excess of 1, a quantitative yield of 2 is obtained, and all the excess olefin is recovered; no polymer is formed. Also, performing the reaction in the presence of methyl methacrylate (as solvent) failed to initiate the polymerization of the ester. Attempts to spin trap radicals with phenyl t-butyl nitrone and 2-nitroso-2-methylpropane also proved negative. One would expect that the necessity of combining two $\cdot Co(CO)_4$ species (to form $Co_2(CO)_8$) would provide an opportunity to intercept or spectrally observe such radicals. However,

TABLE 5

Deuterium Exchange with and Addition to 1,1-Diphenylethylene

$[DCo(CO)_4]_0 \times 10^2$	$[Ph_2C{=}CH_2]_0 \times 10^2$	Solvent	Ph_2CHCH_3 %	Ave. No. D		
				$=CH_2$[a]	CH[b]	CH_3[c]
20	2.83	CH_2Cl_2	100	---	0.82	1.71
5.6	2.83	CH_2Cl_2	~100	---	0.49	1.51
5.60	2.83	hexane	~100	---	0.51	1.45
~13	11.2	hexane	57.2	0.56	0.55	1.12
~8	11.2	hexane	37.2	0.28	0.43	1.04

[a] Methylene group of 1; values ±0.03.

[b] Methine group of 2; values ±0.03.

[c] Methyl group of 2; values ±0.05.

the crucial (and perhaps definitive) NMR (CIDNP) experiments remain to be successfully performed with $HCo(CO)_4$ in order to demonstrate existence of the geminate radical pair.

The hydrogenation of 1 with $DCo(CO)_4$ at various concentrations (Table 5) provides some information on the relative values of the rate constants in Equation (1). With a 3.5 to 1 stoichiometric ratio of $DCo(CO)_4$ to 1, 82% of the methine hydrogen and 57% of the methyl hydrogen in 2 are derived from $DCo(CO)_4$. At the other extreme, with only a 0.36 to 1 stoichiometric ratio initially present (and all of the $DCo(CO)_4$ ultimately consumed) about 45% of the methine and 35% of the methyl hydrogen are derived from

$DCo(CO)_4$, and 14% of the original methylidene hydrogens are exchanged. These data suggest that in Equation (1), $k_{-1} \geqq k_2 \gtrsim k_1$.

Conclusions

The work presented here indicates that at least two kinds of mechanisms may be operative during the reaction of $HCo(CO)_4$ with carbon-carbon double bonds. Those substrates such as 1,1-diphenylethylene that readily undergo hydrogenation may very well do so by a non-chain geminate pair radical mechanism, but those that undergo hydroformylation such as 1-alkenes proceed by the $\pi \rightarrow \sigma$ complex sequence. Essentially the same suggestion has been advanced elsewhere [11]. The substrates that lead to both hydrogenation and hydroformylation may be proceeding by both mechanisms simultaneously [11,20,21], and such cases need to be re-examined and new examples sought to determine the contribution each mechanism makes to a particular reaction.

EXPERIMENTAL

Materials and Equipment

1,1-Diphenylethylene was purchased from Aldrich Chemical Company, and was found to be greater than 99% pure by gas chromatography. 1-Hexene was also from Aldrich and was used directly.

Methylene chloride was purchased from Matheson, Coleman, and Bell and was dried by distillation from P_2O_5. Tetrahydrofuran was also obtained from MC&B and was dried by filtering through P_2O_5. Other solvents were used without further purification.

Dicobalt octacarbonyl was prepared in a stirred autoclave as previously described [17].

Gas chromatographic analyses were performed with an F&M Model 700 with katharometer detector. The following columns were used: 1) for 1,1-diphenylethylene, a 1/4" x 15' 10% SE-30 on Chromosorb W at 190°C under flowing helium; 2) for 1-hexene, a 1/4" x 15' 20% carbowax 20M on Chromosorb W at 67°C under flowing helium.

Rate of Hydrogenation of 1,1-Diphenylethylene. Because of its slow decomposition above 0°C, $HCo(CO)_4$ was prepared immediately prior to each kinetic run. The pyridine-H_2SO_4 method [10] was usually used and the gas phase $HCo(CO)_4$ passed through a short column of P_2O_5 and then directly into about 13 ml of solvent at -78°C, under flowing CO (10 cc/min). Typically, 0.25g $Co_2(CO)_8$ yields a 13 ml solution of about 0.06 M. The exact concentration was obtained by removing a 2.00 ml aliquot at 0°C, adding it to 5.00 ml of 0.1 M NaOH and back-titrating to the phenolphthalein end point with 0.01 HCl [18]. Of the remaining solution, 10.0 ml was removed by pipette and transferred to a 50 ml, CO purged round-bottom flask immersed in a water or ice-bath. After 15 minutes (to allow for temperature equilibration) the reaction was commenced by syringing 50.0 ml of 1,1-diphenylethylene into the thermostated solution. At convenient intervals, the flask was opened (under flowing CO) and 1.00 ml samples removed and quenched with 0.5 ml of 1 M PPh_3 in ethyl ether. After precipitation and coagulation (ca 1hr) of cobalt complexes, the solution was filtered through glass wool, and analyzed by glc. 1-Hexene was treated in exactly the same way. For experiments under nitrogen, the solvents and glassware were purged for 15-30 minutes at 0°C before commencing the reaction. For experiments with $DCo(CO)_4$, the $HCo(CO)_4$ solution was prepared in the usual way, then shaken with 5.00 ml D_2O, the mixture cooled in dry-ice/acetone, and the

$DCo(CO)_4$ solution removed and its concentration determined. Alternatively, hexane solutions of $DCo(CO)_4$ can be prepared directly with $Co_2(CO)_8$, DMF, and 20% DCl [19].

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