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THE HYDROGENATION OF STYRENES BY HYDRIDOCOBALT TETRACARBONYL

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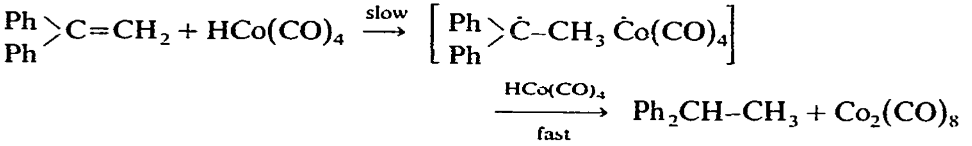
Summary

The rates of hydrogenation of several styrene derivatives by stoichiometric hydridocobalt tetracarbonyl [$HCo(CO)_4$] were measured and compared. The relative rates are discussed in terms of conjugative and steric effects on the geminate radical pair mechanism. An improved method for determining $HCo(CO)_4$ concentration is described.

Introduction

The hydroformylation of alkenes by hydridocobalt tetracarbonyl [$HCo(CO)_4$] is usually accompanied by some hydrogenation, as well [1]. Under high pressure catalytic conditions, the alkane is usually a minor product [1,2]. Many phenyl and carboxyl conjugated alkenes, however, often give large, or even major, amounts of the hydrogenation product [1–3]. Under stoichiometric conditions, hydrogenation products may be exclusive [1,3,4]. Also, the rate of hydrogenation is often very fast for conjugated alkenes, such as 1,1-diphenylethylene and 9-methylenefluorene under mild stoichiometric conditions [4–6].

The mechanism for the stoichiometric hydrogenation of these diphenylethylenes has been proposed to follow the scheme shown:



$$\begin{matrix}\mathrm{Ph}\\ \mathrm{Ph}\end{matrix}\!\!>\!\mathrm{C{=}CH_2 + HCo(CO)_4} \xrightarrow{\mathrm{slow}} \left[\begin{matrix}\mathrm{Ph}\\ \mathrm{Ph}\end{matrix}\!\!>\!\dot{\mathrm{C}}\mathrm{{-}CH_3}\ \dot{\mathrm{C}}\mathrm{o(CO)_4}\right] \xrightarrow[\mathrm{fast}]{\mathrm{HCo(CO)_4}} \mathrm{Ph_2CH{-}CH_3 + Co_2(CO)_8} \qquad (1)$$

This geminate-pair mechanism, originally proposed for 1,1-diphenylethylene on the basis of kinetic data [4], and by analogy to that for the similar $HMn(CO)_5$ reaction [7], has recently been confirmed by CIDNP techniques [6,8].

Under oxo reaction conditions, $HCo(CO)_4$ catalyzes the hydroformylation and hydrogenation of substituted styrene compounds such that 20–70% of the products

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are substituted ethyl benzenes [9]. Under mild, stoichiometric conditions (one atm. CO, 0°C), the major products were found to be ethylbenzenes [3].

Both the hydrogenation and hydroformylation reactions appear to be subject to steric effects. Alkyl substituents bound to either the α- or β-position of styrene have a pronounced effect on the yield and regioselectivity of the reactions of styrene derivatives [1–3,9]. Steric effects on the hydrogenation of 1,1-diphenylethylene derivatives have also been observed [1,3,6], so that, e.g., 1,1-diphenylpropylene reacts much more slowly than 1,1-diphenylethylene (rel. rate 4.48×10^{-3} to 1.00). This report examines the steric effect on the stoichiometric hydrogenation of substituted styrenes by hydridocobalt tetracarbonyl.

Results and discussion

Shown below are the second order rate constants for the hydrogenation of styrene (Table 1). The mean value of 2.72×10^{-4} l mol^{-1} sec^{-1} gives a relative rate of 0.011 compared to 1,1-diphenylethylene [3]. The rate constant for α-methylstyrene is 5.75×10^{-4} l mol^{-1} sec^{-1} at 0°C under CO in CH_2Cl_2, giving a relative rate of 2.11 and 0.024 compared to styrene and 1,1-diphenylethylene, respectively [3].

The rates measured under nitrogen atmosphere and with added $Co_2(CO)_8$ were somewhat slower than those employing freshly prepared $HCo(CO)_4$ under a CO atmosphere. These reflect the slow decomposition of $HCo(CO)_4$, which is augmented by the absence of CO and the presence of $Co_2(CO)_8$ [1]. This parallel decomposition lowers the effective concentration of $HCo(CO)_4$ and this is reflected in the somewhat lower rate constants. These results illustrate the need to perform kinetic measurements with fresh $HCo(CO)_4$ and to use initial rate techniques to minimize the $Co_2(CO)_8$ which is formed as a by-product of hydrogenation, hydroformylation, and air oxidation reactions [1].

Under the reaction conditions employed, hydroformylation products were formed only in minor amounts, ranging from less than 1% for 1-methyleneindane, α-methylstyrene, and 2′,4′-dimethylstyrene up to approximately one fourth the hydrogenation product for styrene and α-ethylstyrene. For styrene, the aldehydes produced were

TABLE 1

RATE OF HYDROGENATION OF STYRENE AT 0°C [a]

$[Styrene]_0 \times 10^2$	$[HCo(CO)_4]_0 \times 10^2$	rate$_0$ [b] (mol l^{-1} sec^{-1})$\times 10^7$	k (l mol^{-1} sec^{-1})$\times 10^4$
4.35	3.16	3.85	2.71
4.35	8.86	10.4	2.71
4.35	8.66	10.3	2.73
4.35	13.8	15.9	2.66
8.70	6.70	15.7	2.69
4.35	7.89	8.40	2.50 [c]
4.35	8.66	8.85	2.35 [d]

[a] Under one atmosphere CO in CH_2Cl_2; k values ±5%; determined for the rate of formation of ethyl benzene. [b] Initial rate for the first 1–4% hydrogenation reaction. [c] Under one atmosphere N_2 in CH_2Cl_2. [d] Twenty mg $Co_2(CO)_8$ present initially.

distributed between two isomers in ratios of 60/40 up to 85/15 (see ref. 2 for very similar aldehyde ratios). The rate constants reported are for the rate of formation of the hydrogenation product only.

Styrene was hydrogenated at several temperatures between 0°C and room temperature. The enthalpy and entropy of activation were found to be 17.1 ± 0.2 kcal/mol and -12 ± 2 eu, respectively. These values compare closely to those for 1,1-diphenylethylene: 17.0 ± 0.3 kcal/mol and -10 ± 2 eu [4].

1,1-Diphenylethylene exhibits an inverse isotope effect which is characteristic for metal-hydride addition reactions in which the hydrogen is essentially completely transferred at the transition state of the slow step [4]. This evidence supports the geminate-pair view of the reaction for which the transition state complex resembles the geminate pair:

$$\mathrm{Ph_2C{=}CH_2 + HCo(CO)_4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{intermediate}] \xrightarrow[\text{fast}]{k_2} \mathrm{Ph_2CHCH_3} \qquad (2)$$

where $k_1 < k_2 \leqslant k_{-1}$

Styrene and α-methylstyrene were similarly reduced by $DCo(CO)_4$, yielding a faster rate than with $HCo(CO)_4$ as shown in Table 2. The inverse isotope effects of 0.66 and 0.68 for styrene and α-methylstyrene are only slightly larger than that previously reported for 1,1-diphenylethylene [4].

2-Vinylnaphthalene hydrogenated faster than styrene. Increasing the degree of conjugation has the expected result on rate, as previously discussed [1,3,4].

The steric effects on this reaction may be evaluated from Table 3. It can be seen that an α-alkyl group does not always have a retarding effect on the rate of hydrogenation, since $k(\alpha\text{-Me})/k(\text{sty}) = 2.11$. However, this rate enhancement is negated by increasing the size of the α-alkyl group, such that $k(\alpha\text{-Et})/k(\text{sty}) = 1.01$. As observed previously, a β-alkyl group greatly retards the reaction ($k(\beta\text{-R})/k(\text{sty}) < 0.01$) [1,3]. A similar dramatic steric effect may be observed by comparing the rates for styrene, 4′-methylstyrene, 2′,4′-dimethylstyrene, and 2′,4′,6′-trimethylstyrene in Table 3.

As expected [3], a *para*-methyl substituent produces little effect on the rate of reaction. The 2,4-dimethyl homologue is (surprisingly) faster than styrene, similar to the effect of an α-methyl substituent. However, the trimethyl compound is very slow, suggesting interference of the two *ortho*-methyl groups in the hydrogen abstraction process and/or in conjugation and stabilization of the geminate pair produced.

TABLE 2

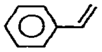
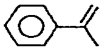
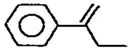
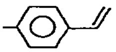
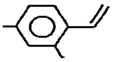
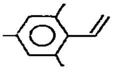
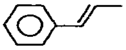
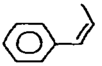
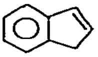
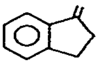
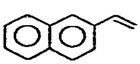
ISOTOPE EFFECT FOR STYRENE AND α-METHYLSTYRENE[a]

$[\mathrm{PhCR{=}CH_2}]_0 \times 10^2$	$[\mathrm{DCo(CO)_4}]_0 \times 10^2$	$k(\mathrm{l\ mol^{-1}\ sec^{-1}}) \times 10^4$	k_H/k_D[b]
Styrene 4.35	8.39	4.11	0.66
α-Methylstyrene 3.85	8.39	8.46	0.68
1,1-Diphenylethylene 2.83	10.2	4.17	0.58[c]

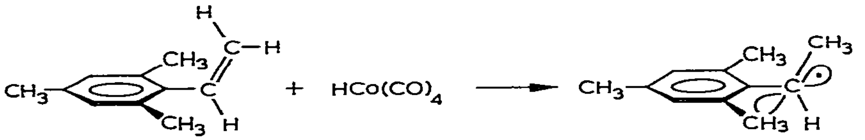
[a] At 0°C in CH_2Cl_2 under 1 atmosphere of CO. [b] ±0.03. [c] from ref. 4.

TABLE 3

RATE OF HYDROGENATION OF ALKYL STYRENES AT 0°C [a]

Compound	$[\text{R-Styr}]_0 \times 10^2$	$[HCo(CO)_4]_0 \times 10^2$	k ($l\ mol^{-1}\ sec^{-1}$)$\times 10^4$	k_{rel} [b]
	4.35	8.86	2.72	(1.00)
	3.85	8.71	5.75	2.11
	3.44	8.86	2.74	1.01
	3.86	6.22	2.54	0.93
	3.22	6.22	5.76	2.12
	3.11	8.60	⩽ 0.02	⩽ 0.01 [c]
	3.85	6.80	⩽ 0.02	⩽ 0.01 [c,d]
	3.85	6.80	⩽ 0.02	⩽ 0.01 [c,d]
	3.90	6.80	⩽ 0.02	⩽ 0.01 [c,d]
	3.45	8.80	⩽ 0.02	⩽ 0.01 [c]
	3.85	7.18	10.9	4.00

[a] Under one atmosphere CO, in CH_2Cl_2; k values ±5%. [b] Relative to styrene. [c] Appreciable reaction within one hour only above 0°C. [d] From ref. 3.



(3)

The styrene compounds reported appear to behave very similarly to their diphenyl homologues in all kinetic respects, except that they react somewhat more slowly.

The rapid rate of hydrogenation of 1,1-diphenylethylene at room temperature [3,4] makes this compound useful as a quantitative reagent for determining $HCo(CO)_4$

concentration. Used as a quenching reagent at 50–100% excess, 1,1-diphenylethylene reacts with all the $HCo(CO)_4$, and the ratio of the excess alkene to the sole hydrogenation product can be determined routinely by gas chromatography. This obviates the need to titrate with aqueous NaOH, which must be stirred rapidly at room temperature during the back-titration with standardized HCl. Even if the titration is performed under CO, this technique does not always give precise results, and the slight darkening of the solution during titration suggests that some decomposition may occur. The quench/GLC method is a rapid, simple technique, which also allows for analysis at the kineticist convenience. However, due to the synergistic rate enhancement by diphenylethylene with some compounds [3], this technique was used here only for determining initial $HCo(CO)_4$ concentration, when no styrenes were present.

Experimental

$HCo(CO)_4$ was prepared immediately before use. Employing the method previously described [4,10], about 13 ml of a 0.06–0.09 *M* solution of $HCo(CO)_4$ in CH_2Cl_2 was prepared. Immediately before a kinetic experiment, one (1.00) ml of this solution was then removed by pipette and 20.0 μl of 1,1-diphenylethylene was added, producing a very dark solution in about one minute. The solution was stored in a capped vial for about 1 h, then shaken with one ml of 10% aqueous ethylene diamine (to remove $Co_2(CO)_8$). After letting stand overnight, the colorless CH_2Cl_2 layer was removed and then dried by filtering through anhydrous Na_2SO_4 or $CaCl_2$. The CH_2Cl_2 solution was then concentrated to about 50–100 μl for multiple GLC analysis on a 3 m 8% Carbowax 20M (Chromosorb W) column at 195°C. Resolution of 1,1-diphenylethene from its hydrogenation product is routine and the peak area ratios may then be converted into initial concentrations of $HCo(CO)_4$. When compared to the more demanding aqueous titration method [10], the quench/GLC method was found to give very similar results (usually 1–5% higher).

Kinetics were performed as previously described [3,4]. $DCo(CO)_4$ preparation and isotope effects were obtained as previously described [3,4].

Styrene, α-methylstyrene, and 2-vinylnaphthalene were purchased from Aldrich Chemical Co. and used without further purification. 1,1-Diphenylethylene, 1-methylene indane, 4′-methyl-, 2′,4′-dimethyl-, 2′,4′,6′-trimethyl- and α-ethyl styrene were prepared via the Wittig reaction from the appropriate carbonyl compound. These were purified by elution from F-20 alumina with petroleum ether or hexane.

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