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THE STOICHIOMETRIC HYDROGENATION OF SUBSTITUTED PHENYL ALKENES BY HYDRIDOCOBALT TETRACARBONYL

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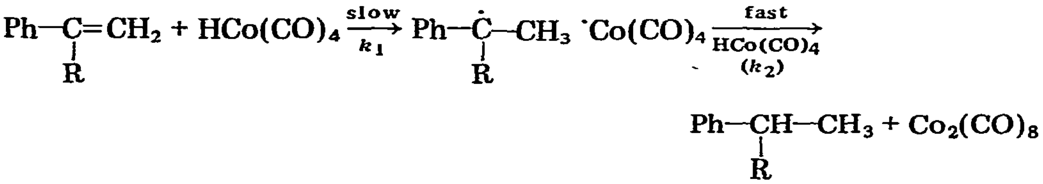
Summary

The relative rates of hydrogenation of a series of styrenes, phenylpropenes, 1,1-diphenylethylenes, and 1,1-diphenylpropenes were measured. Compared to 1,1-diphenylethylene ($k_2 = 2.42 \times 10^{-2}$ l mol^{-1} sec^{-1}), 1,1-diphenylpropene and styrene have relative rates of 0.0045 and 0.011 respectively. The effect of 4-chloro and 4-methoxy substituents on both styrene and diphenylethylene is slightly rate enhancing. An unusual kinetic dependence occurs with mixtures of alkenes.

Introduction

It has recently been reported [1,2] that the facile hydrogenation of 1,1-diphenylethylene and 9-methylidenefluorene by stoichiometric $HCo(CO)_4$ may be due to a geminate-pair free-radical pathway. The evidence supporting this proposed mechanism is primarily kinetic: (1) simple second-order kinetics, first order in alkene and first order in $HCo(CO)_4$, (2) inverse k_H/k_D isotope effect of about 0.5, (3) lack of a significant solvent effect, (4) lack of CO dependence, and (5) 100% rapid hydrogenation under very mild conditions (0° C/1 atm. CO) [1,2]. Also, the proposed mechanism is very similar to that for $HMn(CO)_5$ hydrogenation, wherein the involvement of radical species has been successfully demonstrated by CIDNP techniques [3]. All of these results contrast with the well-known hydroformylation of alkenes [4,5]. Our further studies with substituents are consistent with the geminate-pair model and two-step addition reaction mechanism.



$$\mathrm{Ph{-}}\underset{\mathrm{R}}{\mathrm{C}}\mathrm{{=}CH_2} + \mathrm{HCo(CO)_4} \xrightarrow[k_1]{\text{slow}} \mathrm{Ph{-}}\underset{\mathrm{R}}{\dot{\mathrm{C}}}\mathrm{{-}CH_3}\ {}^{\cdot}\mathrm{Co(CO)_4} \xrightarrow[\mathrm{HCo(CO)_4}\ (k_2)]{\text{fast}} \mathrm{Ph{-}}\underset{\mathrm{R}}{\mathrm{CH}}\mathrm{{-}CH_3} + \mathrm{Co_2(CO)_8} \quad (1)$$

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In addition, however, we have also observed a synergistic rate enhancement when alkenes are mixed and we feel that this may be due to a rapid post-equilibrium.

Results and discussion

The rate of hydrogenation of 1,1-diphenylethylene (I), its 4-methoxy (Ia) and 4-chloro (Ib) derivatives, 1,1-diphenylpropene (II) and 1,1-diphenylcyclopropane (III) were measured and compared (Table 1). Also styrene (IV), and its 4-methoxy (IVa), 4-chloro (IVb) and α-methyl (V) derivatives, *trans*-phenylpropene (VI), *cis*-phenylpropene (VII), and indene (VIII) were reduced by stoichiometric $HCo(CO)_4$ and the rates measured and compared (Table 2). Substituent groups other than alkyl, alkoxy, and chloro were not attempted, since nucleophilic ones (as with vinyl pyridine) reacted directly with $HCo(CO)_4$, and unsaturated ones (as with nitro) were sometimes reduced.

Styrene followed second order kinetics and no induction period or CO dependence was found under our experimental conditions. This is the same behavior reported previously for diphenylethylene and contrasts sharply with that of 1-hexene [1] and other 1-alkenes.

The relative rates indicate a modest influence on the rate of reaction when CH_3O and Cl are *para* to the vinyl group, suggesting that the reaction is nonionic in the slow step. β-Methyl substituents have a pronounced rate reduction effect, as has been previously reported [2], such that 1,1-diphenylpropene (II) is at least 200 times slower than diphenylethylene (I). A similar retardation was found for *trans*- and *cis*-phenylpropene (VI and VII) and indene (VIII) compared to styrene (IV). However, an α-methyl substituent has little effect on the rate (compare V to IV). The effect of phenyl groups can be clearly seen by comparing I and IV; the effect of conjugation has been dramatically demonstrated previously [1,2]. Cyclopropyl does not ring-open under the reaction conditions, although several transition metal complexes catalyze this reaction [6] (see compound III).

An unusual feature of the reaction is the rate enhancement caused by mixing compounds (Table 3). 1,1-Diphenylpropene (II) independently hydrogenates more than 200 times slower than diphenylethylene (I), but when I and II are

TABLE 1

RELATIVE RATES OF HYDROGENATION OF DIPHENYLETHYLENES

Compound	Relative rate ^{a}
1,1-Diphenylethylene (I)	(1.00)
4-Methoxydiphenylethylene (Ia)	1.78
4-Chlorodiphenylethylene (Ib)	1.24
1,1-Diphenylpropene (II)	4.48×10^{-3}
1,1-Diphenylcyclopropane (III)	0.00
Styrene (IV)	1.12×10^{-2}
α-Methylstyrene (V)	3.65×10^{-2}

^{a} $k_2 = 2.42 \times 10^{-2}$ mol^{-1} s^{-1}, in CH_2Cl_2 at 0°C under 1 atm CO; relative rate values are ±5%.

TABLE 2

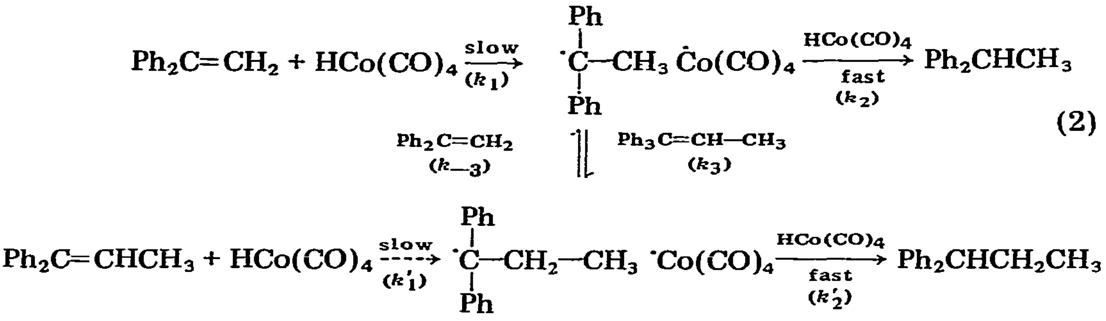
RELATIVE RATES OF HYDROGENATION OF STYRENES

Compound	Relative rate [a]
Styrene (IV)	(1.00) [a]
4-Methoxystyrene (IVa)	12.8
4-Chlorostyrene (IVb)	1.52
α-Methylstyrene (V)	2.10
trans-Phenylpropene (VI)	0.00 [b]
cis-Phenylpropene (VII)	0.00 [b]
Indene (VIII)	0.00 [b]

[a] $k_2 = 2.72 \times 10^{-4}$ l mol^{-1} s^{-1}, in CH_2Cl_2 at 0°C under 1 atm. CO; values ±5%. [b] Appreciable reaction within two hours only at 25°C.

mixed, II reacts nearly half as fast as I and the rate of the mixture overall is initially about the same as for I alone. This rate enhancement was observed for several other compounds as well; for compounds which had similar independent rates, little change was observed (compare I and Ia).

If the slow step in reaction 1 is the formation of the geminate pair, the retarding effect of a β-methyl group can be understood as a steric effect on the orientation of the two reagents. However, it is difficult to imagine how the presence of diphenylethylene might reduce or eliminate this effect, unless the rate enhancement occurs as a result of providing an alternate path to the geminate pair. An equilibrium after the slow step satisfies this scheme:



$$Ph_2C{=}CH_2 + HCo(CO)_4 \xrightarrow[(k_1)]{slow} {}^{\cdot}C(Ph)_2{-}CH_3\ \dot{C}o(CO)_4 \xrightarrow[fast\ (k_2)]{HCo(CO)_4} Ph_2CHCH_3$$

$$Ph_2C{=}CH_2\ (k_{-3}) \rightleftharpoons Ph_3C{=}CH{-}CH_3\ (k_3) \qquad (2)$$

$$Ph_2C{=}CHCH_3 + HCo(CO)_4 \xrightarrow[(k'_1)]{slow} {}^{\cdot}C(Ph)_2{-}CH_2{-}CH_3\ {}^{\cdot}Co(CO)_4 \xrightarrow[fast\ (k'_2)]{HCo(CO)_4} Ph_2CHCH_2CH_3$$

TABLE 3

COMPETITIVE RATES OF HYDROGENATION BY $HCo(CO)_4$

Compounds	Rel. rate [a]	Comp. rel. rate [b]
Diphenylethylene (I)	(1.00)	(1.00)
and diphenylpropene (II)	4.48×10^{-3}	4.3×10^{-1}
Diphenylethylene (I)	(1.00)	(1.00)
and 4-methoxydiphenylethylene (Ia)	1.78	1.38
Diphenylethylene (I)	(1.00)	(1.00)
and styrene (IV)	1.12×10^{-2}	5.4×10^{-2}
Diphenylethylene (I)	(1.00)	(1.00)
and anthracene	1×10^{-3}	5.0×10^{-2}

[a] Compared to diphenylethylene with $k_2 = 2.42 \times 10^{-2}$ l mol^{-1} s^{-1}; rates measured independently; values ±5%. [b] Competitive rates relative to the rate for diphenylethylene for equimolar amounts of alkenes; values ±7%.

In this proposed scheme, diphenylpropene must displace diphenylethylene from the solvent cage geminate pair rapidly. The competitive rate ratio value in Table 3 would then reflect the relative stability of the two similar geminate pairs, rather than differences in their rate of formation, provided that k_3 and $k_{-3} >> k_1$, k_2 and k'_2, whereas the independent rates reflect the differences between k_1 and k'_1. This scheme also explains the facile exchange and deuterium scrambling of diphenylethylene when reduced with $DCo(CO)_4$, previously reported [1], and the scrambling of deuterium during the reduction of α-methylstyrene [7,8].

Experimental

$HCo(CO)_4$ was prepared immediately before each kinetic experiment and the concentration in CH_2Cl_2 determined titrametrically, as previously described [1]. Kinetic runs were initiated by addition of the alkene of interest, samples were periodically quenched with excess ethylene diamine, as reported [1,2]. After standing for at least one hour, the quenched samples were filtered, dried, and concentrated for gas chromatographic analysis.

Gas chromatography was performed with a Varian Model 1700 katharometer gas chromatograph fitted with a 3 m X 6 mm (o.d.) column packed with 8% Carbowax 20M on Chromosorb W (60/80 mesh). This method allowed for routine analysis of 0.1% reaction.

Phenylalkenes styrene, *cis*- and *trans*-phenylpropene, α-methylstyrene, and indene were purchased from Aldrich Chemical Co. and used without further purification. The remaining phenylalkenes were prepared by well-known methods (Grignard/dehydration or Wittig [8]) and used after column chromatographic purification (F-20 alumina, hexane/benzene/ethyl ether) until near 100% pure.

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References

1 J.A. Roth and M. Orchin, J. Organometal. Chem., 182 (1979) 299.
2 T.E. Nalesnik and M. Orchin, J. Organometal. Chem., 199 (1980) 265.
3 R.L. Sweany and J. Halpern, J. Amer. Chem. Soc., 99 (1977) 8335.
4 B.R. James, Homogeneous Hydrogenation, Wiley, New York, NY, 1973.
5 M. Orchin and W. Rupilius, Catal. Rev., 6 (1972) 85.
6 K.C. Bishop, Chem. Rev., 76 (1976) 461.
7 C. Botteghi, M. Branca, M. Marchetti and A. Saka, J. Organometal. Chem., 161 (1978) 197.
8 R. Lai and E. Ucciani, J. Mol. Catal., 4 (1978) 401.