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EFFECT OF SOLVENT VISCOSITY ON THE REACTION OF STYRENES WITH $HCo(CO)_4$ AND CO

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Summary

Changing the solvent from octane to Nujol in the reaction of styrenes with $HCo(CO)_4$ and CO only slightly decreases the overall rates but significantly enhances carbonylation at the expense of hydrogenation. This effect provides further support for the view that a geminate radical pair is an intermediate in the reaction.

Introduction

Kinetic evidence suggests that the reaction of $HCo(CO)_4$ and styrene proceeds through rate-determining formation of a geminate radical pair which is the common intermediate in formation of both ethylbenzene and (under CO) of α-phenylpropionyl tetracarbonyl. Escape of the α-phenylethyl radical from the radical pair (k_e) followed by a rapid hydrogen atom abstraction from $HCo(CO)_4$ leads to ethylbenzene, whereas α-phenylpropionylcobalt carbonyl is the product of recombination (k_c) and CO insertion [1]:

$$\mathrm{PhCH{=}CH_2} + \mathrm{HCo(CO)_4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Ph\dot{C}HCH_3,\dot{C}o(CO)_4}]$$

$$\begin{tikzcd}[column sep=small] & \mathrm{Ph\dot{C}HCH_3} \arrow[r, "\mathrm{HCo(CO)_4}"] & \mathrm{PhCH_2CH_3} \\ {[\mathrm{Ph\dot{C}HCH_3,\dot{C}o(CO)_4}]} \arrow[ur, "k_e"] \arrow[dr, "k_c"'] & & \\ & \mathrm{PhCH(CH_3)Co(CO)_4} \arrow[r, "\mathrm{CO}"] & \mathrm{PhCH(CH_3)COCo(CO)_4} \end{tikzcd}$$

$$k_{CO} = \frac{k_c \cdot k_1}{k_{-1} + k_e + k_c}; \quad k_H = \frac{k_e \cdot k_1}{k_{-1} + k_e + k_c}$$

If this idea is correct, then the viscosity of the solvent should affect the ratio of escape and recombination products.

Results and discussion

Experiments were performed with styrene and two α-substituted styrenes in n-octane and Nujol as solvent. Higher rates of CO absorption and larger CO

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TABLE 1

INITIAL CO ABSORPTION RATES (r_{CO}) AND THE MAXIMUM OF CO UPTAKE IN THE REACTION OF $HCo(CO)_4$ WITH α-SUBSTITUTED STYRENES $PhCR{=}CH_2$ UNDER CO IN n-OCTANE AND IN NUJOL [a]

Temperature (°C)	R	Solvent	$r_{CO} \cdot 10^6$ ($M \cdot s^{-1}$)	$\frac{\text{mol CO}^{b}}{\text{mol HCo(CO)}_4}$
15	H	n-octane	17.4	0.46
15	H	n-octane	34.2 [c]	0.48 [c]
15	H	Nujol	19.3	0.65
15	H	Nujol	41.8 [c]	0.71 [c]
10	H	n-octane	11.3	0.49
10	H	Nujol	13.9	0.69
10	Me	n-octane	5.5	0.02
10	Me	Nujol	9.5	0.15
10	Ph	n-octane	– [d]	0.00
10	Ph	Nujol	2.1	0.03

[a] Initial concentrations: $[HCo(CO)_4]$ 0.0297 *M*, [olefin] 0.200 *M*, $P_{total} = 984 \pm 10$ mbar. [b] The observed maximum CO uptake. [c] With $DCo(CO)_4$. [d] Not detectable.

up-takes at the end of the reaction were observed in Nujol (Table 1). In Nujol carbonylation was achieved even with olefins which were found to undergo exclusively hydrogenation with $HCo(CO)_4$ at 0°C in CH_2Cl_2 [2].

Since the rate of the reaction of $HCo(CO)_4$ with styrene [1], 1,1-diphenylethylene [2] and α-methylstyrene [3] was found to be independent of the CO concentration, the lower solubility of CO in Nujol [4] compared to heptane [5] cannot account for the observed enhanced CO uptake. Most likely the higher viscosity of the Nujol retards the escape from the radical pair and increases the probability of recombination within the solvent cage.

In an attempt to obtain more information about the factors which influence the formation of hydrogenated and carbonylated products, we extended our investigations to ring-substituted styrene derivatives. The reactions are effectively first order in $HCo(CO)_4$ and styrene, and the rate constants, which are not affected by CO and $Co_2(CO)_8$ [1], were obtained at 15°C by measuring the initial rates of CO uptake and the ratio of ethylbenzenes formed at the end of the reaction from a 1/1 mixture of substituted and unsubstituted styrenes (competition experiments). The results compiled in Table 2 show that: (a) the effect of solvent viscosity on carbonylation is the same as that for α-substituted styrenes, and (b) almost all the ring substituents are favorable for both carbonylation and hydrogenation. Thus only for the 4-MeO, 4-Me, 3-Me and H substituents was there a correlation of the Hammett σ values with log relative rates, and the slope $\rho = -1.0$ is practically the same both for carbonylation and hydrogenation. This means that these substituents affect only the rate-determining step but not the subsequent fast transformations of the intermediate radical pair. The magnitude of the observed ρ value is similar to that commonly found for radical reactions [6]. The 4-Cl and 3-Cl substituents do not fit this correlation.

It is remarkable that despite the possible steric hindrance, in the reaction with

TABLE 2

THE REACTION OF RING-SUBSTITUTED STYRENES $RC_6H_4CH{=}CH_2$ WITH $HCo(CO)_4$ UNDER CO AT 15°C[a]

R	Solvent Nujol		Solvent n-octane			
	$k_{CO} \times 10^3$ $(M^{-1}\ s^{-1})$[b]	$\frac{\text{mol CO}}{\text{mol } HCo(CO)_4}$	$k_{CO} \times 10^3$ $(M^{-1}\ s^{-1})$[b]	$\frac{\text{mol CO}}{\text{mol } HCo(CO)_4}$	$\frac{RC_6H_4C_2H_5}{C_6H_5C_2H_5}$[c]	$k_H \times 10^3$ $(M^{-1}\ s^{-1})$[d]
H	3.25	0.65	2.92[1]	0.46	(1.00)	1.63
2-Me	6.96	0.73	4.91	0.41	2.60	
3-Me	3.73	0.68	3.40	0.45	1.16	
4-Me	4.71	0.70	4.41	0.47	1.53	
4-MeO	6.18	0.68	5.60	0.48	1.96	
3-Cl	3.50	0.68	2.60	0.39	1.22	
4-Cl	4.95	0.71	3.61	0.38	2.37	

[a] [Olefin] 0.200 M, $[HCo(CO)_4]$ 0.0297 M, P_{total} 984 ± 10 mbar. [b] The observed rate constants ($k_{CO} = r_{CO}/[HCo(CO)_4][\text{olefin}]$) calculated from the initial CO absorption rates (r_{CO}). [c] Ratio of ethylbenzenes formed from a 1/1 molar mixture of substituted and unsubstituted styrenes at the end of the reaction after removing $Co_2(CO)_8$ at −78°C and adding pyridine. Determined by quantitative GLC analysis using cumene as internal standard (Hewlett–Packard 5830/A, SE 30 10 m glass capillary column 40°C, 2 ml Ar/min, FID). [d] The observed rate constant ($k_H = r_H/[HCo(CO)_4][\text{styrene}]$) from the initial rate of ethylbenzene formation (r_H), from ref. 1. Rate constants for the hydrogenation reaction at 0°C and in CH_2Cl_2 solvent are also known for styrene and for some substituted styrenes [3,8] which are, however, not in correlation with our data derived from competitive measurements.

TABLE 3

RATE CONSTANTS FOR CARBONYLATION (k_{CO}) AND HYDROGENATION (k_H) OF RING-SUBSTITUTED STYRENES $RC_6H_4CH{=}CH_2$ IN THE REACTION WITH $HCo(CO)_4$ IN n-OCTANE AND IN NUJOL AS SOLVENTS AT 15°C

R	In n-octane $\frac{k_{CO}}{k_H}$[a]	In Nujol $\frac{k_{CO}}{k_H}$[a]	In n-octane $(k_{CO}+k_H)\times 10^3$ $(M^{-1}\ s^{-1})$[b]	In Nujol $(k_{CO}+k_H)\times 10^3$ $(M^{-1}\ s^{-1})$[b]
H	1.70	3.25	4.64	4.25
2-Me	1.39	5.40	8.44	8.25
3-Me	1.64	4.25	5.47	4.61
4-Me	1.77	4.67	6.90	5.72
4-MeO	1.84	4.25	8.64	7.63
3-Cl	1.28	4.25	4.63	4.32
4-Cl	1.23	4.90	6.54	5.96

[a] k_{CO}/k_H was calculated from the observed maximum of CO uptake (see Table 2) neglecting aldehyde formation: $RC_6H_4CH(CH_3)COCo(CO)_4 + HCo(CO)_4 \rightarrow RC_6H_4CH(CH_3)CHO$. Because of the large excess of olefin, however, the error caused by this simplification, as estimated from the infrared spectra of the products (aldehyde $\nu(CO)$), is less than 10%. [b] $k_{CO} + k_H$ was calculated using the values of k_{CO}/k_H and the observed rate constants k_{CO}.

2-methylstyrene the rate of CO absorption and the relative rate of 2-methylethylbenzene formation are higher than those for 4-methylstyrene. A similar *ortho* effect and a small negative ρ constant ($\rho \approx -1.0$) was recently observed for CO insertion into η^5-$C_5H_5Mo(CO)_3CH_2C_6H_4R$ compounds [7].

Although the rate of hydrogenation could not be determined directly when Nujol was used as solvent, the experimental results allow its estimation (Table 3). As can be seen, the increase of k_{CO}/k_H is more significant than that of the directly observed r_{CO} when the viscosity of the solvent is increased. This is caused by a small decrease of the overall reaction rate $k_{CO} + k_H$. The k_{CO}/k_H values therefore reflect even more strikingly the effects of the solvent cage stability on the combination and escape reactions.

The infrared spectra of the reaction mixtures just after CO absorption has stopped show, in addition to ν(CO) bands characteristic of acylcobalt carbonyls, some weak bands characteristic of η^1- and η^3-type [9] benzyl complexes. By comparing the intensities of these bands the relative tendencies to formation of these compounds may be estimated. The sequence for the η^1 compounds was 4-Me > 4-Cl $\geqslant$ 3-Cl $\geqslant$ 4-MeO $\geqslant$ 3-Me > H > 2-Me, and that for η^3 compounds was 4-Me > 4-MeO > 2-Me > 3-Me > H > 4-Cl > 3-Cl.

Finally, it should be noted that the viscosity of the solvent did not change the inverse isotope effect for this reaction (Table 1), which was previously observed [1].

Experimental

Styrene, 2-methylstyrene, α-methylstyrene and n-octane were distilled under carbon monoxide. 1,1-Diphenylethylene (Fluka), 3-methylstyrene (Fluka), 4-methylstyrene (Fluka), 4-chlorostyrene (Fluka), 4-methoxystyrene (EGA) and 3-chlorostyrene (EGA) were used without further purification. Nujol was a highly refined colorless and dry paraffin oil (Mineral Oil Company Komárom, Hungary): D_4^{20} = 0.841 g ml^{-1}, viscosity: 29.9 mm^2 s^{-1} at 20°C and 3.3 mm^2 s^{-1} at 100°C, freezing point: −18°C; it was degassed in vacuum and saturated with carbon monoxide.

The initial rate of CO absorption and the maximum of CO uptake were measured in a thermostatted gasometric apparatus. The reaction was started by injecting 2.0 mmol of the olefin into the vigorously stirred (at 900 revolutions per min by a gas-tight mechanical stirrer) and thermostatted solutions of $HCo(CO)_4$. These solutions were prepared for each run by mixing the solvent with 0.297 mmol of a 0.634 *M* stock solution of $HCo(CO)_4$ (or $DCo(CO)_4$) in n-octane [1].

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