Preliminary communication

ABSOLUTE RATE CONSTANTS FOR THE COORDINATION OF OLEFINS TO A TRANSIENT COORDINATIVELY UNSATURATED COBALT COMPLEX

SHIGERO OISHI, NORIKO KIHARA and AKERI HOSAKA

Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229 (Japan)

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Summary

Absolute second-order rate constants for the coordination of diethyl phenylphosphonite and various olefins to a transient coordinatively unsaturated cobalt complex, i.e. hydridotris(diethyl phenylphosphonite)cobalt(I), have been measured in cyclohexane at 23°C using laser flash photolysis techniques. The rate constants have been found to depend markedly on the structures of the olefins, e.g. 1.2×10^8 and 6.5×10^4 M^{-1} s^{-1} for 1-hexene and tetramethylethylene, respectively. The mechanism of photochemical double-bond migration catalyzed by the transient is discussed on the basis of these rate constants.

The nitrogen laser pulse excitation of hydridotetrakis(diethyl phenylphosphonite)cobalt(I) ($HCoP_4$) was found to generate a transient coordinatively unsaturated species ($HCoP_3$) with a quantum yield of almost 1.0 [1]. Furthermore, in the mechanism of photo-isomerization of allylbenzene to β-methylstyrene with an analogous cobalt complex, the species maintaining the catalytic cycle was suggested to be a coordinatively unsaturated species [2].

We describe here the results of a laser flash photolysis study concerning the coordination of diethyl phenylphosphonite (P) and various olefins to $HCoP_3$, which corresponds to the primary step of the catalytic photo-isomerization of olefins. As far as we know, this is the first case of measurement of the absolute rate constants for the coordination of olefins to a metal complex, although many equilibrium constants have been reported in the case of nickel [3—5], rhodium [6,7], palladium [8], silver [9], iridium [10], and platinum [11].

Cyclohexane solutions of $HCoP_4$ (0.6 mM) were deaerated by bubbling argon through the solutions, and then subjected to pulsed-laser photolysis at 23°C, using a nitrogen laser (pulse width 5 ns, 4 mJ/pulse) for excitation. A right-angle optical system was employed for the excitation-analysis set-up and the volume

analyzed was confirmed to be completely covered by the excitation beam [12].

A transient species (λ_{max} 580 nm, ϵ 1.7 $\times$ 10^3 M^{-1} cm^{-1}) was identified as a coordinatively unsaturated species ($HCoP_3$), the decay trace of which was consistent with second-order reaction kinetics according to the re-coordination of P to $HCoP_3$ [1]. In the time region in which the re-coordination can be ignored, namely, 5 μs per full scale of a storage scope, the addition of P or olefins has been found to bring about a new decay as shown in Fig. 1, which could be analyzed with pseudo-first-order reaction kinetics. Although the life time of the transient was extremely shortened by the addition of P or olefins, the transient spectra were the same as those in the case of $HCoP_4$ alone; moreover, the UV and visible absorption spectra of $HCoP_4$ were independent of the presence of P or olefins. It can, therefore, be concluded that the decay in this time region is due to the coordination of additional P or olefins to the transient $HCoP_3$.
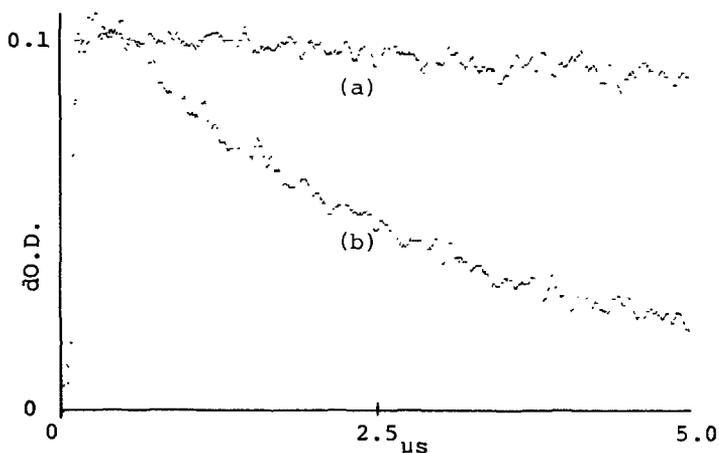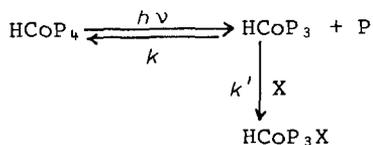

Fig. 1. Typical reaction trace at 580 nm for transient $HCoP_3$ generated by laser pulse excitation from $HCoP_4$ alone in cyclohexane (0.6 mM) (a) and in the presence of additional P (3.0 mM) (b).

SCHEME 1

Equation 1 can be derived from Scheme 1. The first term in eq. 1 can be ignored in this time region, as stated above, and the pseudo-first-order rate constant corresponds to k''. From the plots of k'' versus the concentrations of P or olefins (e.g. Fig. 2), the absolute second-order rate constants k' have been obtained (Table 1).

$$-\frac{d[HCoP_3]}{dt} = k[HCoP_3][P] + k'[HCoP_3][X]$$

$$= k[HCoP_3]^2 + k''[HCoP_3] \tag{1}$$

$$(k'' = k'[X])$$

k" ×10⁻⁵/s⁻¹

9.6

4.8

0

0   3.2   6.4

[X] /mM
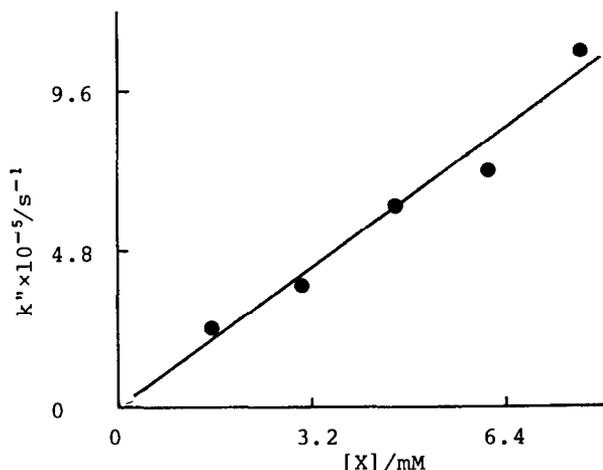
Fig. 2. Least-squares plots for pseudo-first-order rate constants k'' versus the concentration of allylbenzene [X].
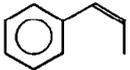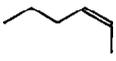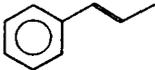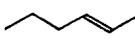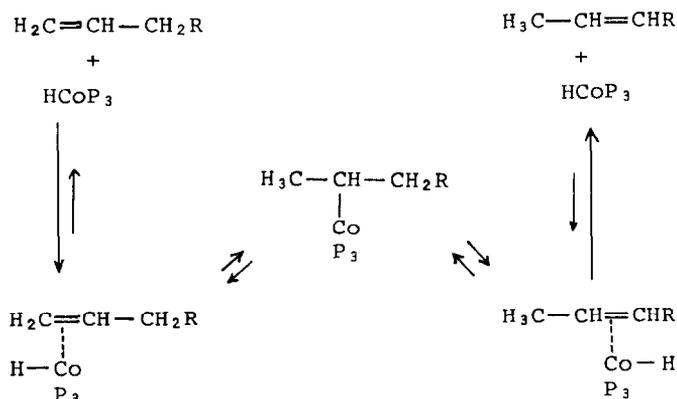
TABLE 1

SECOND ORDER RATE CONSTANTS FOR COORDINATION $(M^{-1}\ s^{-1})^a$
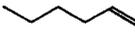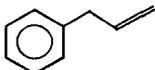
P Ph(OEt)₂	1.4×10^8 [b]	(1-pentene)	1.2×10^8 [b]
(allylbenzene)	1.3×10^8	(2-methyl-1-butene)	1.5×10^7
(cis-β-methylstyrene)	2.4×10^7	(cis-2-pentene)	2.5×10^7
(trans-β-methylstyrene)	1.6×10^6	(trans-2-pentene)	2.4×10^6
(2-methyl-2-butene)	6.5×10^4	(cyclohexene)	1.9×10^7

^{a} In cyclohexane, at 23°C. ^{b} Ref. 1.

Although the second-order rate constants for P and allylbenzene are almost identical, the photo-isomerization of allylbenzene to β-methylstyrene using HCoP₄ has been shown to be completely prevented by the addition of P [2]. This indicates that the rate-determining step of the double-bond migration corresponds to a later step than the coordination of an olefin, probably the insertion of an olefin into the hydrido-cobalt bond (Scheme 2). In other words, competition is actually taking place between the coordination of P to HCoP₃, leading to thermally unreactive HCoP₄, and the rate-determining step. The coordination of an olefin to HCoP₃ does not render a stable complex, i.e. the dissociation is also fast. This can be explained by assuming that the stabilization originating from both a donating and a back-donating bond in the case of P is far greater than that in the case of an olefin [13].

$$H_2C = CH - CH_2R \qquad\qquad H_3C - CH = CHR$$

$$+ \qquad\qquad\qquad\qquad +$$

$$HCoP_3 \qquad\qquad\qquad\qquad HCoP_3$$

$$H_3C - CH - CH_2R$$
$$|$$
$$Co$$
$$P_3$$

$$H_2C = CH - CH_2R \qquad\qquad H_3C - CH = CHR$$
$$| \qquad\qquad\qquad\qquad\qquad |$$
$$H - Co \qquad\qquad\qquad\qquad Co - H$$
$$P_3 \qquad\qquad\qquad\qquad\qquad P_3$$

SCHEME 2

The second-order rate constants for the coordination of olefins have been found to decrease in the order terminal, *cis*-, and *trans*-olefins, by one order of magnitude each, and it is noticeable that k' for tetramethylethylene is far smaller than that for 1-hexene, namely, by a factor of 5×10^{-4}. These facts suggest severe steric requirements for the coordination of olefins to $HCoP_3$. It can, therefore, be concluded that the isomerization of a terminal olefin to an internal olefin is favorable not only thermodynamically but also in the sense of steric requirements for the coordination of olefins to a transient catalyst species.

References

1 S. Oishi, K. Tajime, A. Hosaka and I. Shiojima, J. Chem. Soc. Chem. Commun., (1984) 607.
2 M. Onishi, K. Hirai, M. Matsuda and T. Fukunaga, Chem. Lett., (1983) 261.
3 T. Yamamoto, A. Yamamoto and S. Ikeda, J. Am. Chem. Soc., 93 (1971) 3360.
4 C.A. Tolman, J. Am. Chem. Soc., 96 (1974) 2780.
5 S.D. Ittel, Inorg. Chem., 16 (1977) 2589.
6 R. Cramer, J. Am. Chem. Soc., 89 (1967) 4621.
7 V. Schurig and E. Gil-Av, J. Chem. Soc. Chem. Commun., (1971) 650.
8 H. Kurosawa, T. Majima and N. Asada, J. Am. Chem. Soc., 102 (1980) 6996.
9 T. Fueno, O. Kajimoto and J. Furukawa, Bull. Chem. Soc. Jpn., 41 (1968) 782.
10 L. Vaska, Acc. Chem. Res., 1 (1968) 335.
11 J.R. Joy and M. Orchin, J. Am. Chem. Soc., 81 (1959) 305.
12 M. Bazin and T.W. Ebbesen, Photochem. Photobiol., 37 (1983) 675.
13 Cf., for example, F.A. Cotton and G.W. Wilkinson, "Advanced Inorganic Chemistry, 3rd edit., Wiley-Interscience, New York, 1972, pp. 719—721.