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Preliminary communication

RHODIUM(I) CATALYZED DECOMPOSITION OF FORMIC ACID

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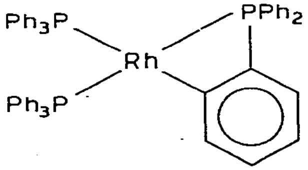
Summary

$Rh(C_6H_4PPh_2)(PPh_3)_2$ catalyzes the decomposition of formic acid to CO_2 and H_2. The initial step is the oxidative addition of formic acid to produce the intermediate $Rh(HCO_2)(PPh_3)_3$, which probably is followed by β-hydride elimination, to produce CO_2 and $RhH(PPh_3)_3$. The latter reacts with formic acid to produce H_2 and to reform $Rh(HCO_2)(PPh_3)_3$.

During the course of an investigation of the reactions of hydroxyl-containing organic substrates with rhodium(I) complexes [1], it was discovered that formic acid cleaves the rhodium—σ-carbon bond of $Rh(C_6H_4PPh_2)(PPh_3)_2$ (I, abbreviated $Rh(P—C)P_2$) [2] and is catalytically decomposed to carbon dioxide and hydrogen by some subsequently formed rhodium complex in solution. These results are presented here because they bear directly on two areas of organometallic chemistry of current interest, carbon dioxide fixation [3] and the water—gas shift reaction [4].



(I)

The reaction of $Rh(P—C)P_2$ in toluene (0.034 M) with formic acid (1.6 M) at 20°C was monitored in a closed volume connected to a manometer. Gases slowly evolved from the dark amber solution at a rate of 1.2×10^{-6} M s^{-1} (this roughly corresponds to two equivalents of gas per equivalent of rhodium per day). The gas was found to contain a non-condensable (at −196°C) component that was identified as hydrogen by mass spectrometry and a condensable component that was identified as carbon dioxide by its IR spectrum. Within experimental error, CO_2 and H_2 are present in equimolar amounts in the evolved gas.

The toluene and remaining formic acid were removed rapidly, under vacuum, from the reaction mixture after seven equivalents of gas (based on rhodium) had been evolved. The solution darkened appreciably as soon as the evolved gases were removed from the closed system. The dark orange residue exhibited IR bands, among others, at 2145w, 1965m, and 1615m(br) cm^{-1}. When the dark orange residue was redissolved in toluene, a mixture of condensable and non-condensable gases again was evolved.

The decomposition of formic acid to carbon dioxide and hydrogen (reaction 1) accounts for the observations described above. The seven equivalents of gas require that 3.5 equivalents of formic acid had decomposed. Thus, the reaction is catalyzed by some rhodium compound in solution. A plot of moles of gas evolved vs. time is linear from 400 min to 2800 min, implying that the catalytic activity was constant over this period and that many more than 3.5 equivalents of formic acid could be decomposed.

$$HCOOH \rightarrow CO_2 + H_2 \qquad \Delta G^0 = -7.9 \text{ kcal mol}^{-1} \tag{1}$$

The activity of Rh(P—C)P_2 as a formic acid decomposition catalyst is compared to other Group VIII catalysts in Table 1. The stoichiometric decomposition of formic acid by certain platinum metal compounds produces (1) metal hydrides plus carbon dioxide [8,9] (e.g., reaction 2), (2) metal formates [9,10] (e.g., reaction 3), and (3) metal carbonyl complexes [11] (reaction 4). The IR band at 1615 cm^{-1} exhibited by the dark orange residue (see above) can be

TABLE 1

DECOMPOSITION OF FORMIC ACID TO HYDROGEN AND CARBON DIOXIDE

Catalyst (conc., mM)	Temp. (°C)	Solvent (conc. of HCOOH, M)	Rate[a] (M sec^{-1})	Ref.
Rh(P—C)P_2 (34)	20	toluene (1.6)	6.0×10^{-7}	[c]
$Pd(HCO_2)_2$ (0.5)	112	acetic acid (1.2)	7.2×10^{-5}	5
$PtCl_2(PBu_3)_2$ (6.1)	118	acetic acid (0.75)	5.6×10^{-6}	6
IrH_2ClP_3 (6.2)	118	acetic acid (0.75)	2.1×10^{-3}	7
Pt(P-i-Pr_3)$_3$ (6.4)	20	acetone/water, 15/1 (0.41)	2.9×10^{-4}	7

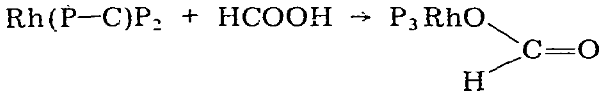
[a] Rate = $-d[HCOOH]/dt$. [b] Lithium acetate (2 M), copper(II) acetate (0.3 M), and oxygen (40 psig) are necessary components in this catalytic reaction. [c] This work.

$$cis\text{-}PtCl_2(PEt_3)_2 + HCOOH \rightarrow trans\text{-}PtHCl(PEt_3)_2 + HCl + CO_2 \tag{2}$$

$$Os(CO)_3P_2 + 2HCOOH \rightarrow Os(HCO_2)_2(CO)_2P_2 + H_2 \tag{3}$$

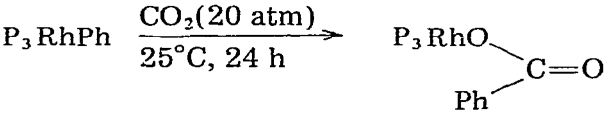
$$RuCl_4^{2-} + HCOOH \rightarrow Ru(CO)(H_2O)Cl_4^{2-} \tag{4}$$

attributed to a monodentate formate ligand (cf. 1630 cm^{-1} for $Os(HCO_2)_2(CO)_2P_2$ [9] and 1615 cm^{-1} for $Ru(HCO_2)_2(CO)_2P_2$ [10]). The complex $Rh(HCO_2)P_3$ probably forms as shown in reaction 5. The assignment of the formate ligand as



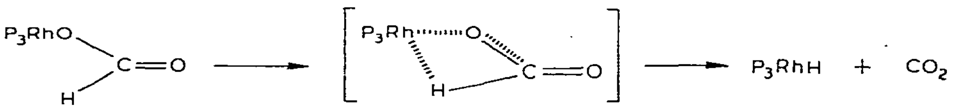
$$Rh(P\text{—}C)P_2 + HCOOH \rightarrow P_3RhOC(=O)H \quad (5)$$

monodentate is reasonable since $Rh(PhCO_2)P_3$, which has been shown to contain a monodentate benzoate ligand by a single crystal X-ray study [12], exhibits a strong IR band at 1608 cm^{-1} [12]. It is significant that the triphosphine benzoate complex is formed by the insertion of carbon dioxide into a rhodium—carbon bond (reaction 6) [12]. Carbon dioxide formation from the $Rh(HCO_2)P_3$ intermediate probably occurs by a reaction analogous to the reverse of reaction 6:



$$P_3RhPh \xrightarrow[25^\circ C,\ 24\ h]{CO_2(20\ atm)} P_3RhOC(=O)Ph \quad (6)$$

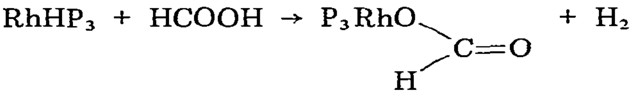
the β-elimination of a hydrogen atom from a monodentate formate ligand to the metal center (reaction 7). This mechanism has been proposed for a number of transition metal systems [13]. The IR band at 1965 cm^{-1} exhibited by the dark orange residue is probably due to coordinated carbon monoxide, although



(7)

there cannot be appreciable amounts of this gas in the non-condensable component of the evolved gases. The band at 2145 cm^{-1} may be due to ν(Rh—H) of $RhHP_4$ (lit. [14] 2140 cm^{-1}). The amount of this compound or of the carbonyl compound present in the dark orange residue, relative to the proposed $Rh(HCO_2)P_3$ intermediate, cannot be realistically estimated with the present data.

The production of hydrogen and the requirement of a closed catalytic cycle imply that formic acid reacts with $RhHP_3$ as shown in reaction 8. Carboxylic



$$RhHP_3 + HCOOH \rightarrow P_3RhOC(=O)H + H_2 \quad (8)$$

acids in general are known to cleave Group VIII metal—hydrogen bonds [15]. Note that the isolation of the formate complex implies that, for this system, the rate-determining step for the decomposition of formic acid is β-elimination. This is interesting because β-elimination from other $RhXP_3$ complexes (X = alkyl [16], alkoxide [1], or amide [17]) is very fast.

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References

1 S.H. Strauss, Ph.D. Dissertation, Northwestern University, Evanston, IL, June, 1979.
2 W. Keim, J. Organometal. Chem., 14 (1968) 179.
3 (a) P. Haynes, L.H. Slaugh and J.F. Kohnle, Tetrahedron Lett., (1970) 365; (b) B. Jesowska-Trzebiatowska and P. Sobota, J. Organometal. Chem., 76 (1974) 43; (c) Y. Inoue, Y. Sasaki and H. Hashimoto, Chem. Commun., (1975) 718; (d) T. Herskovitz and L.J. Guggenberger, J. Amer. Chem. Soc., 98 (1976) 1615; (e) Y. Inoue, H. Izumida, Y. Sasaki and H. Hashimoto, Chem. Lett., (1976) 863; (f) H. Koinuma, H. Kato and H. Hirai, Chem. Lett., (1977) 517.
4 (a) R.M. Laine, R.G. Rinker and P.C. Ford, J. Amer. Chem. Soc., 99 (1977) 252; (b) H.-C. Kang, C.H. Mauldin, T. Cole, W. Slegeir, K. Cann and R. Pettit, J. Amer. Chem. Soc., 99 (1977) 8323; (c) R.B. King, C.C. Frazier, R.M. Hanes and A.D. King, Jr., ibid., 100 (1978) 2925; (d) T. Yoshida, Y. Ueda and S. Otsuka, ibid., 100 (1978) 3942; (e) P.C. Ford, R.G. Rinker, C. Ungermann, R.M. Laine, V. Landis and S.A. Maya, ibid., 100 (1978) 4596.
5 A. Aguilo, J. Catal., 13 (1969) 283.
6 R.S. Coffey, Chem. Commun., (1967) 923.
7 T. Yoshida, Y. Ueda and S. Otsuka, J. Amer. Chem. Soc., 100 (1978) 3941.
8 J. Chatt and B.L. Shaw, J. Chem. Soc., (1962) 5075.
9 K.R. Laing and W.R. Roper, J. Chem. Soc. (A), (1969) 1889.
10 B.F.G. Johnson, R.D. Johnston, J. Lewis and I.B. Williams, J. Chem. Soc. (A), (1971) 689.
11 J. Halpern and A.L.W. Kemp, J. Amer. Chem. Soc., 88 (1966) 5147.
12 I.S. Kolomnikov, A.O. Gusev, T.S. Belopotapova, M.Kh. Grigoryan, T.V. Lysyak, Yu.T. Struchkov and M.E. Volpin, J. Organometal. Chem., 69 (1974) C10.
13 M.E. Volpin and I.S. Kolomnikov, Organometal. Reactions, 5 (1975) 313.
14 K.C. Dewhirst, W. Keim and C.A. Reilly, Inorg. Chem., 7 (1968) 546.
15 S.D. Robinson and M.F. Uttley, J. Chem. Soc. (Dalton), (1973) 1912 and ref. therein.
16 S.H. Strauss and D.F. Shriver, Inorg. Chem., 17 (1978) 3069.
17 S.E. Diamond and F. Mares, J. Organometal. Chem., 142 (1977) C55.