

Equilibrium and High-Pressure Kinetic Study of Formation and Proton-Assisted Aquation of Monodentate Acetate, Propionate, and Glycolate Complexes of Palladium(II) in Aqueous Solution

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Kinetics and equilibria for reversible formation of 1:1 monodentate complexes between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and acetic, propionic, and glycolic acid (RCOOH) according to the equation $\text{Pd}(\text{H}_2\text{O})_4^{2+} + \text{RCOOH} \rightleftharpoons \text{Pd}(\text{H}_2\text{O})_3\text{OOCR}^+ + \text{H}_3\text{O}^+$ (k_1, k_{-1}) have been studied as a function of temperature and pressure in an aqueous medium with $0.60 \leq [\text{H}^+] \leq 1.00$ M, $[\text{RCOOH}]/[\text{H}^+] \leq 1.0$, and ionic strength 1.00 M. Stability constants β_1 for the formation of acetate, propionate, and glycolate complexes are $(2.19 \pm 0.09) \times 10^4$, $(2.10 \pm 0.24) \times 10^4$, and $(6.4 \pm 0.1) \times 10^3$ M⁻¹, respectively, at 25 °C and for a 1.00 M perchlorate medium. The rate expression, $k_{\text{obsd}} = k_1[\text{RCOOH}] + k_{-1}[\text{H}^+]$, indicates that reaction between palladium and carboxylate anions is negligible under the experimental conditions used. Values for $k_1/\text{M}^{-1} \text{s}^{-1}$, $k_{-1}/\text{M}^{-1} \text{s}^{-1}$, $\Delta H_1^\ddagger/\text{kJ mol}^{-1}$, $\Delta H_{-1}^\ddagger/\text{kJ mol}^{-1}$, $\Delta S_1^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$, $\Delta S_{-1}^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$, $\Delta V_1^\ddagger/\text{cm}^3 \text{mol}^{-1}$, and $\Delta V_{-1}^\ddagger/\text{cm}^3 \text{mol}^{-1}$ at 25.0 °C are 19.3 ± 0.6 , 32.8 ± 0.2 , 52.5 ± 0.4 , 57.5 ± 0.4 , -44 ± 1 , -23 ± 1 , -8.1 ± 0.3 , and -1.7 ± 0.2 for acetic acid; 12.0 ± 1.1 , 26.4 ± 0.3 , 55.3 ± 0.6 , 56.8 ± 0.3 , -32 ± 2 , -34 ± 1 , -8.9 ± 0.8 , and -1.7 ± 0.2 for propionic acid; and 21.1 ± 0.3 , 13.7 ± 0.1 , 53.6 ± 0.4 , 59.2 ± 0.6 , -40 ± 1 , -25 ± 2 , -3.4 ± 0.2 , and -2.3 ± 0.2 for glycolic acid. There is no relation between formation rate constants and $\text{p}K_a$ for these carboxylic acids. The nucleophilic properties of the carboxylic acids toward palladium(II) are similar to those of water molecules. A trigonal bipyramidal transition state stabilized by hydrogen bonding between the entering carboxylic acid and the leaving aqua ligand or (equivalent) between the entering oxonium ion and the leaving carboxylate ligand is suggested. Negative entropies, volumes of activation, and volume profiles support a strong contribution from bond making in the activation process.

Introduction

Palladium(II) acetate was first prepared by Wilkinson and co-workers, who suggested a trimeric structure.¹ Crystallographic studies of Pd(II) carboxylates have verified the structure $\text{Pd}_3(\text{OOCR})_6$, with $\text{R} = \text{CH}_3$, C_2H_5 , $\text{C}(\text{CH}_3)_3$, and $2,4,6\text{-C}_6\text{H}_2(\text{CH}_3)_3$, and with bridging carboxylates.^{2–4} Palladium(II) carboxylates, in particular the acetate, have been extensively used as catalysts in a great variety of organic reactions,^{5–7} and as a starting material for preparation of other compounds.⁸ The kinetics for the splitting of $\text{Pd}_3(\text{OOCCH}_3)_6$

by acetate⁹ in acetic acid and by *N,N*-dimethylbenzylamine and its derivatives¹⁰ in chloroform have been studied.

There are few investigations of reactions between square planar Pd(II) centers and carboxylic acids/carboxylates in aqueous solution so far, including only equilibria between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and acetic acid,¹¹ formation of mixed ligand complexes, $\text{Pd}(\text{dien})\text{OOCR}^+$ from PdCl_4^{2-} , diethylenetriamine (dien), and carboxylates;¹² and kinetics for complex formation and aquation of $\text{Pd}(\text{Me}_3\text{dien})(\text{H}_2\text{O})^{2+}$ and $\text{Pd}(\text{Et}_3\text{dien})(\text{H}_2\text{O})^{2+}$ with oxalate.¹³ We here describe studies of equilibria and kinetics for complex formation between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and acetic, propionic, and glycolic acids, with the aim to elucidate the reaction mechanism. Kinetics for complex formation between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and halides^{14,15} and with nucleophiles containing nitrogen¹⁶ and sulfur^{17,18} donors have been investigated earlier. High-pressure kinetic studies of complex formation between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and Me_2SO ,¹⁷ MeCN ,¹⁶ and thioethers¹⁸ as well as water exchange on $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ ¹⁹ have provided further indications of a mechanism dominated by bond making in these systems.

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- (1) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.
- (2) Skapski, A. C.; Smart, M. L.; *J. Chem. Soc., Chem. Commun.* **1970**, 658.
- (3) Cotton, F. A.; Han, S. *Rev. Chim. Miner.* **1983**, *20*, 496.
- (4) Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Schwotzer, W. *Polyhedron* **1988**, *7*, 615.
- (5) (a) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146 and references therein. (b) Henry, P. M. *Palladium Catalysed Oxidation of Hydrocarbons*; D. Reidel Publishing Company: Dordrecht, Holland, 1980. (c) Negishi, E.-I. *Acc. Chem. Res.* **1982**, *15*, 340. (d) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, 1985. (e) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
- (6) For recent literature, see: (a) Benhaddou, R.; Czernecki, S.; Ville, G. *J. Org. Chem.* **1992**, *57*, 4612. (b) Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009. (c) Denmark, S. E.; Schnute, M. E. *J. Org. Chem.* **1995**, *60*, 1013. (d) Yoshizaki, H.; Satoh, H.; Sato, Y.; Nukui, S.; Shibasaki, M.; Mori, M. *J. Org. Chem.* **1995**, *60*, 2016.
- (7) Kao, L.-C.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991**, *113*, 700.
- (8) (a) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *222*, 155. (b) Garcia-Ruano, J. L.; Lopez-Solera, I.; Masaguer, J. R. Navarro-Ranninger, C.; Rodriguez, J. H.; Martinez-Carrera, S. *Organometallics* **1992**, *11*, 3013.

(9) Pandey, R. N.; Henry, P. M. *Can. J. Chem.* **1974**, *52*, 1241.

(10) Ryabov, A. D.; Sakodinskaya, I. K.; Yatsimirskii, A. K. *J. Chem. Soc., Dalton Trans.* **1985**, 2629.

(11) Yatsimirskii, A. K.; Berezin, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, *7*, 1490.

(12) Shoukry, M. M.; Khairy, E. M.; Saeed, A. *J. Coord. Chem.* **1988**, *17*, 305.

(13) Pienaar, J. J.; Kotowski, M.; van Eldik, R. *Inorg. Chem.* **1989**, *28*, 373.

(14) Elding, L. I. *Inorg. Chim. Acta* **1972**, *6*, 683.

(15) Elding, L. I.; Olsson, L.-F. *Inorg. Chim. Acta* **1986**, *117*, 9.

(16) Hellquist, B.; Elding, L. I.; Ducommun, Y. *Inorg. Chem.* **1988**, *27*, 3620.

(17) Ducommun, Y.; Merbach, A. E.; Hellquist, B.; Elding, L. I. *Inorg. Chem.* **1987**, *26*, 1759.

(18) Elmroth, S.; Bugarcic, Z.; Elding, L. I. *Inorg. Chem.* **1992**, *31*, 3551.

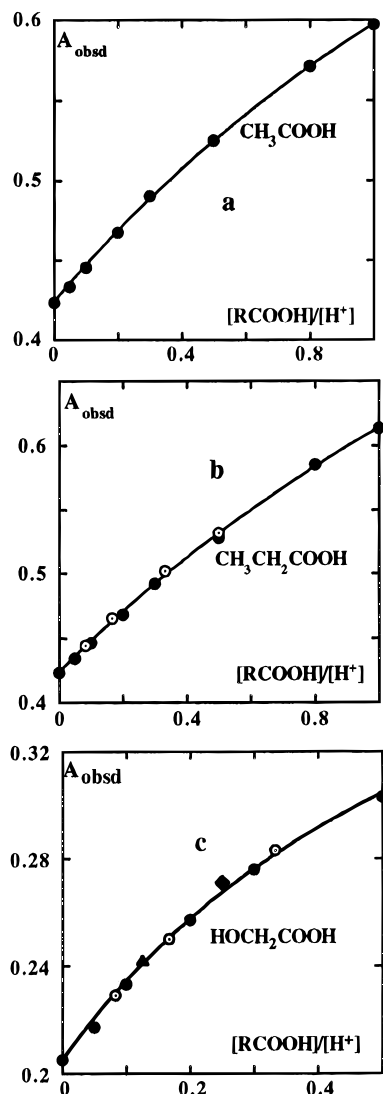


Figure 1. Absorbances of equilibrated solutions as a function of $[\text{RCOOH}]/[\text{H}^+]$ for the reactions with (a) acetic, (b) propionic, and (c) glycolic acid at 25 °C and 400 nm. Hydrogen ion concentrations are 0.40 M (\blacklozenge), 0.60 M (\odot), 0.80 M (\blacktriangle), and 1.00 M (\bullet). The solid curves represent a nonlinear least-squares fit of eq 3 to the experimental data.

Experimental Section

Chemicals and Solutions. Stock solutions of tetraaquapalladium(II) perchlorate (ca. 50 mM) in 1.00 M perchloric acid were prepared from palladium sponge (Johnson and Matthey, Spec. Pure) as described previously.²⁰ Concentrations were determined spectrophotometrically from the absorbance at 380 nm ($\epsilon^{380} = 82.8 \text{ M}^{-1} \text{ cm}^{-1}$).²⁰ Stock solutions of 1.000 and 2.000 M perchloric acid were prepared from concentrated perchloric acid (Merck, p.a.), and stock solutions of 1.00 M NaClO_4 were prepared from solid sodium perchlorate, $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Merck, p.a.). Acetic acid (Janssen, 99.5%), propionic acid (Janssen, 99.5%), and glycolic acid (Janssen, 99%) were used directly without further purification. The 500 mL stock solutions of 1.00 M carboxylic acid in 1.00 M perchloric acid were prepared by dissolving weighed samples in 250 mL of 2.00 M perchloric acid, which were then diluted to the required concentrations with water. The ionic strength was adjusted to 1.00 M with 1.00 M perchloric acid and 1.00 M sodium perchlorate. Water was doubly distilled from quartz.

Apparatus. UV–visible spectra were recorded on a Milton Roy 3000 diode-array spectrophotometer with thermostated 1.00 cm quartz Suprasil cells. The kinetics were followed at ambient pressure by use

of a modified Durrum–Gibson stopped-flow spectrophotometer and at elevated pressures by use of a Hi-Tech high-pressure stopped-flow spectrophotometer, HPSF-56, equipped with a digital pressure indicator.²¹ Kinetic data were evaluated using the OLIS nonlinear least-squares-minimizing kinetic program Model 4000 Data System Stopped-Flow Version 9.04.²²

Equilibrium Measurements. Spectra between 250 and 500 nm of equilibrated solutions of 5.6 mM $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ with different total concentrations of carboxylic acid were recorded at 25.0 °C. They were stable for at least 24 h. Data are given in Tables SI–SIII of the supporting information.

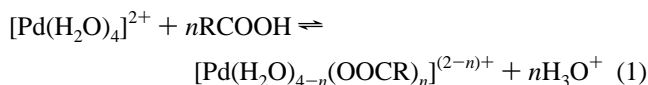
Kinetic Measurements. Reactions were initiated by mixing equal volumes of $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and carboxylic acid solution directly in the stopped-flow instruments. They were monitored as an absorbance increase between 235 and 260 nm under pseudo-first-order conditions with carboxylic acid in at least 40-fold excess. All kinetic runs could be described by single exponentials, and no subsequent reactions were observed. The observed pseudo-first-order rate constants, k_{obsd} , at ambient pressure were calculated as average values from five to seven independent runs. Data are given in Tables SIV–SVI in the supporting information and are summarized in Figures 3 and 4 below.

The pressure dependencies of the observed rate constants were studied at 25.0 °C in the interval of 0.1–150 MPa with $[\text{H}^+] = 1.00 \text{ M}$ and with $1.7 \leq [\text{Pd}(\text{II})]_{\text{tot}} \leq 5.6 \text{ mM}$. Kinetic data are given in Tables SVII–SIX in the supporting information and are summarized below in Figure 5.

Protolysis Data. Protolysis constants K_a and partial molar volume changes, ΔV_a , for protolysis of the carboxylic acids used have been determined under different conditions. The data used in the present calculations were as follows: for acetic acid, $\text{p}K_a = 4.57 \pm 0.04^{23a}$ at 25 °C and $\mu = 1.0 \text{ M}$, $\Delta V_a = -11.3 \text{ cm}^3 \text{ mol}^{-1}$ ²⁴ at 25 °C and $\mu = 0.50 \text{ M}$; for propionic acid, $\text{p}K_a = 4.67 \pm 0.01^{23b}$ at 25 °C and $\mu = 1.0 \text{ M}$, $\Delta V_a = -13.0 \text{ cm}^3 \text{ mol}^{-1}$ ²⁴ at 25 °C and $\mu = 0.50 \text{ M}$; for glycolic acid, $\text{p}K_a = 3.62 \pm 0.01^{23c}$ at 25 °C and $\mu = 1.0 \text{ M}$, $\Delta V_a = -11.8 \text{ cm}^3 \text{ mol}^{-1}$ ²⁵ at 25 °C and $\mu = 0.50 \text{ M}$. The protolysis constant for $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ is estimated to $\text{p}K_h = 3.0$ at 25 °C and $\mu = 1.00 \text{ M}$.²⁶

Results

Equilibrium Studies. In the pH region used, the carboxylic acids are the dominant species, whereas the concentrations of the carboxylate anions are small. Hence, the equilibria for reactions between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and acetic or propionic acid can be described by eq 1.



The equilibrium constants are defined by eq 2, if only one complex is assumed to be formed for $[\text{RCOOH}]/[\text{H}^+] \leq 1.0$, i.e. $n = 1$. The observed absorbances of equilibrated solutions,

$$K_1 = \frac{[\text{Pd}(\text{H}_2\text{O})_3\text{OOCR}^+][\text{H}^+]}{[\text{Pd}(\text{H}_2\text{O})_4^{2+}][\text{RCOOH}]} \quad (2)$$

A_{obsd} , as functions of the total concentration of palladium, $[\text{Pd}(\text{II})]_{\text{tot}}$, and of the total concentration of carboxylic acid, $[\text{RCOOH}]$, are expressed by eq 3, where A_0 denotes the

$$A_{\text{obsd}} = (A_0 + \epsilon_1 l [\text{Pd}(\text{II})]_{\text{tot}} K_1 [\text{RCOOH}]/[\text{H}^+]) / (1 + K_1 [\text{RCOOH}]/[\text{H}^+]) \quad (3)$$

absorbance at $[\text{RCOOH}] = 0$, l is the path length, and ϵ_1 is the molar absorptivity of the complex formed. The measurements

(21) A development of the high-pressure bomb described by Nichols, P. J.; Ducommun, Y.; Merbach, A. E. *Inorg. Chem.* **1983**, *22*, 3993.

(22) OLIS kinetic-fitting program, OLIS Inc., Jefferson, GA 30549, USA.

(23) (a) Martell, A. E.; Smith, R. M. *Critical Stability Constants; Other Organic Ligands*; Plenum: New York, 1977; Vol. 3, p 3. (b) Reference 23a, p 8. (c) Reference 23a, p 24.

(24) Høiland, H. J. *Chem. Soc., Faraday Trans. 1* **1974**, *70*, 1180.

(19) Helm, L.; Elding, L. I.; Merbach, A. E. *Helv. Chim. Acta* **1984**, *67*, 1453.

(20) Elding, L. I. *Inorg. Chim. Acta* **1972**, *6*, 647.

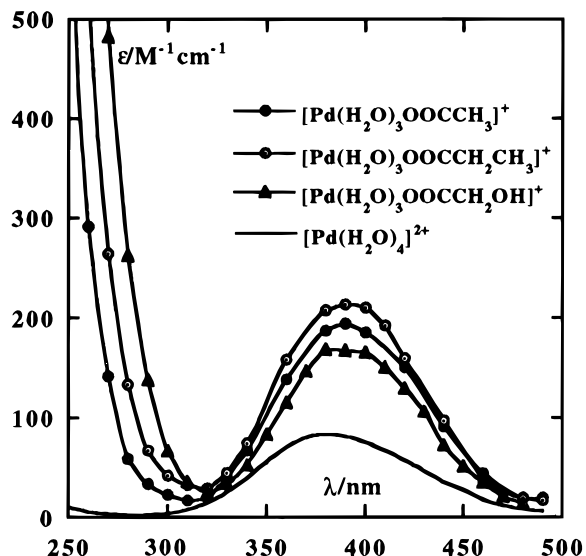
Table 1. Equilibrium Constants and Molar Absorption Coefficients for the Reactions between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and Carboxylic Acids at 25 °C

RCOOH	λ/nm	K_1	$\epsilon_1/\text{M}^{-1}\text{cm}^{-1}$
acetic acid	260	0.45 ± 0.02	291 ± 7
	280	0.57 ± 0.12	59 ± 8
	300	0.34 ± 0.05	23 ± 3
	340	0.35 ± 0.03	67 ± 12
	360	0.41 ± 0.04	138 ± 6
	380	0.41 ± 0.03	187 ± 6
	400	0.40 ± 0.03	185 ± 7
	420	0.33 ± 0.04	153 ± 9
	440	0.32 ± 0.06	91 ± 8
	460	0.34 ± 0.07	44 ± 4
	av	0.40 ± 0.08	
propionic acid	260	0.40 ± 0.04	510 ± 40
	280	0.48 ± 0.07	133 ± 15
	300	0.42 ± 0.12	42 ± 8
	340	0.33 ± 0.09	74 ± 7
	360	0.31 ± 0.04	158 ± 8
	380	0.33 ± 0.05	207 ± 11
	400	0.34 ± 0.04	210 ± 9
	420	0.35 ± 0.04	159 ± 10
	440	0.34 ± 0.08	97 ± 12
	460	0.61 ± 0.15	38 ± 4
	av	0.39 ± 0.09	
glycolic acid	260	1.13 ± 0.03	770 ± 14
	280	1.20 ± 0.05	262 ± 8
	300	1.28 ± 0.07	67 ± 2
	340	1.95 ± 0.58	52 ± 6
	360	1.67 ± 0.44	115 ± 8
	380	1.35 ± 0.08	168 ± 10
	400	1.36 ± 0.17	165 ± 8
	420	1.29 ± 0.19	129 ± 8
	440	1.82 ± 0.28	72 ± 4
	460	1.61 ± 0.44	35 ± 6
	av	1.47 ± 0.26	

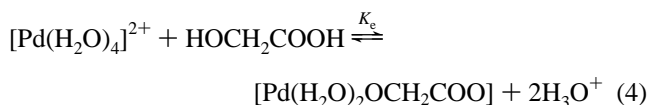
were analyzed by means of a nonlinear least-squares method. Figure 1 shows fits of the data at 400 nm, according to eq 3 with K_1 and ϵ_1 as adjustable parameters for the reactions of acetic, propionic, and glycolic acid. Similar good fits were obtained for the data collected at the other wavelengths used and gave the equilibrium constants and molar absorptivities listed in Table 1.

Analysis was also carried out assuming that higher complexes, $[\text{Pd}(\text{H}_2\text{O})_{4-n}(\text{OOCR})_n]^{(2-n)+}$, $n = 2-4$, are formed for $[\text{RCOOH}]/[\text{H}^+] \leq 1.0$. That assumption gave no improvement of the curve fit and no meaningful values for K_n and ϵ_n . Therefore, the equilibrium of eq 1 with $n = 1$ is sufficient to describe the reactions of $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ with these carboxylic acids under the present experimental conditions, although complexes $[\text{Pd}(\text{H}_2\text{O})_{4-n}(\text{OOCCH}_3)_n]^{(2-n)+}$, $n = 1-3$, have been reported for $[\text{CH}_3\text{COOH}]/[\text{H}^+] \leq 33.6$.¹¹ The independence of the K_1 values on the wavelength and the good agreement between the values of K_1 derived from equilibrium and kinetic measurements (*cf.* data in Table 2 below) further support the assumption of only one complex being formed. Polynuclear complex formation can also be excluded, since the observed rate constants (*vide infra*) are independent of the total concentration of palladium(II).

In the reaction with glycolic acid, there are three possibilities for complex formation even if only a 1:1 complex is formed. (i) The first possibility is formation of a monodentate complex as described above and illustrated in Figure 1c. (ii) Another possibility is formation of a chelate as in the reaction between

**Figure 2.** Calculated absorption spectra of palladium monodentate carboxylate complexes together with the spectrum of $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$.

$\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and glycolic acid,²⁷ according to eq 4.



The measured absorbance corresponding to eq 4 can be derived as eq 5 with $K_a \ll [\text{H}^+]$ and $K_h \ll [\text{H}^+]$. Plots according to eq

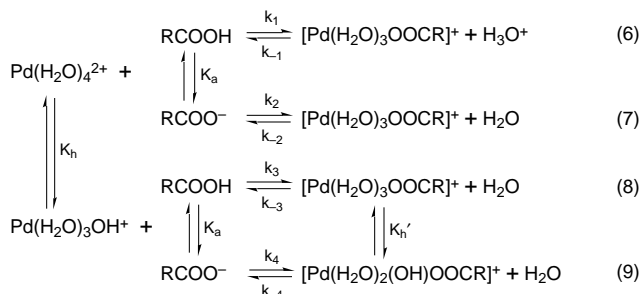
$$A_{\text{obsd}} = (A_0 + \epsilon l [\text{Pd}(\text{II})]_{\text{tot}} K_{\text{el}} [\text{HOCH}_2\text{COOH}]/[\text{H}^+]^2) / (1 + K_c [\text{HOCH}_2\text{COOH}]/[\text{H}^+]^2) \quad (5)$$

5 of A_{obsd} as a function of $[\text{HOCH}_2\text{COOH}]/[\text{H}^+]^2$ gave bad fits, eliminating this alternative. (iii) Alternatively, $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ forms a chelate with glycolic acid without deprotonation of the α -OH. In such a case, the expression for the measured absorbance as functions of $[\text{HOCH}_2\text{COOH}]$ and $[\text{H}^+]$ is identical to eq 3.

Calculated spectra of the 1:1 complexes formed are shown in Figure 2. The close similarities between these spectra support the assumption of a monodentate complex being formed also for glycolic acid, *i.e.* alternative (i) above. This is further supported by the derived stability constants, *vide infra*.

Kinetics. Taking into account the protolysis of the incoming ligands and $\text{Pd}(\text{H}_2\text{O})_4^{2+}$, the simplest mechanism for the present system is described by Scheme 1, including reactions 6–9.

Scheme 1



For reaction with excess carboxylic acid, the observed pseudo-first-order rate constants can be derived as eq 10 with K_a , K_h , and $K_h' \ll [\text{H}^+]$.

(25) Høiland, H.; Vikingstad, E. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 2007.

(26) Shi, T.; Elding, L. I. Unpublished results.

(27) Mentasti, E. *Inorg. Chem.* **1979**, *18*, 1512.

$$k_{\text{obsd}} = \{k_1 + (k_2K_a + k_3K_h)/[H^+] + k_4K_aK_h/[H^+]^2\} \times [\text{RCOOH}] + k_{-1}[H^+] + k_{-2} + k_{-3} + k_{-4}K_h'/[H^+] \quad (10)$$

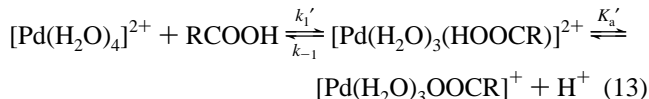
Plots of k_{obsd} vs $[\text{RCOOH}]$ for $[H^+] = 0.60, 0.80,$ and 1.00 M at 25.0 °C result in parallel straight lines for each carboxylic acid, *cf.* Figure 3, indicating that there is no significant contribution to k_{obsd} from the forward reactions of eqs 7–9, *i.e.* terms containing $k_2, k_3,$ and k_4 . Further, the ratios of intercept/ $[H^+]$ are constant, and $k_{\text{obsd}}/[H^+]$ plotted against $[\text{RCOOH}]/[H^+]$ gives excellent straight lines, *cf.* Figure 4. These observations imply that the terms of $k_{-2}, k_{-3},$ and k_4 in eq 10 do not contribute to the overall kinetics and can also be neglected. Therefore, reactions 7–9 are negligible for the present experimental conditions and Scheme 1 can be reduced to eq 6. Then, eq 10 can be simplified to eq 11, which can be further rearranged as eq 12.

$$k_{\text{obsd}} = k_1[\text{RCOOH}] + k_{-1}[H^+] \quad (11)$$

$$k_{\text{obsd}}/[H^+] = k_1[\text{RCOOH}]/[H^+] + k_{-1} \quad (12)$$

The k_1 and k_{-1} values were evaluated by a least-squares fit of eq 12 to the data in Figure 4. The temperature dependencies of those rate constants allowed for the calculations of enthalpies and entropies of activation by use of Eyring's equation. Rate constants, equilibrium constants, $K_1 = k_1/k_{-1}$, and activation parameters derived from these experiments are summarized in Table 2.

If the coordinated carboxylate ligands are assumed to be significantly protonated in the pH region used, eq 6 transforms to 13.



In that case, k_{obsd} can be rephrased as eq 14. The good linear

$$k_{\text{obsd}}/[H^+] = k_1[\text{RCOOH}]/[H^+] + k_{-1}'/(K_a' + [H^+]) \quad (14)$$

plots in Figure 4 of $k_{\text{obsd}}/[H^+]$ vs $[\text{RCOOH}]/[H^+]$ at 25 °C and different $[H^+]$ for each particular carboxylic acid display a common intercept, indicating that the term $k_{-1}'/(K_a' + [H^+])$ in eq 14 is independent of $[H^+]$. This means that $K_a' \gg [H^+]$ and $k_{-1}'/K_a' = k_{-1}$ (*cf.* eqs 12 and 14). In other words, the presence of protonated carboxylic acid ligands coordinated to palladium(II) can be neglected for the present experimental conditions.

In order to determine volumes of activation for the forward and reverse reactions, k_{obsd} was determined as a function of $[\text{RCOOH}]$ for constant $[H^+] = 1.00$ M at ambient pressure and at 25, 50, 75, 100, 125, and 150 MPa. Data are given in Tables SVII–SIX in the supporting information. Values of k_1 and k_{-1} were evaluated by a least-squares fit of eq 11 to the experimental data for each pressure. Plots of $\ln k_1$ and $\ln k_{-1}$ vs pressure are given in Figure 5. Volumes of activation for forward (ΔV_1^\ddagger) and reverse (ΔV_{-1}^\ddagger) reactions were calculated by fitting eq 15 to these data with k_0 and ΔV^\ddagger as adjustable parameters, and with k_0 denoting the values of the rate constants (k_1 and k_{-1} , respectively) at ambient pressure. No significant pressure dependence of the volumes of activation was observed.

$$\ln k = \ln k_0 - \Delta V^\ddagger P/RT \quad (15)$$

Activation volumes and partial molar reaction volumes calcu-

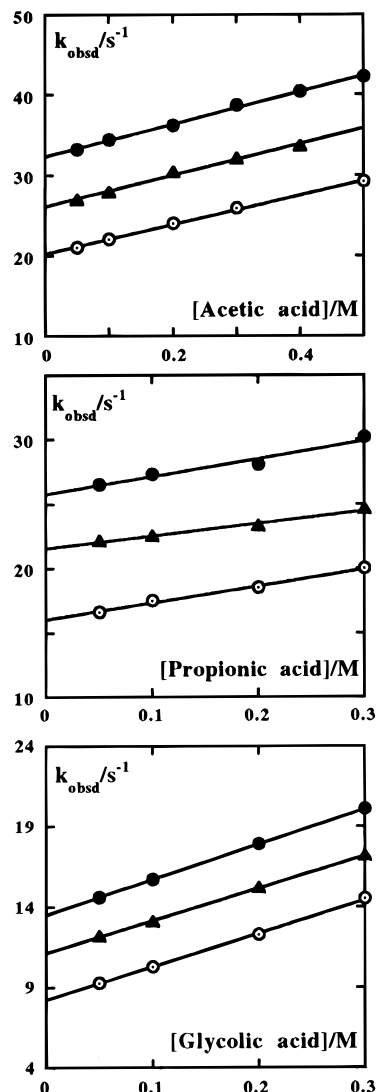


Figure 3. Plots according to eq 10 of k_{obsd} vs excess concentration of carboxylic acid at different hydrogen ion concentrations at 25 °C. $[H^+] = 0.60$ M (\circ), 0.80 M (\blacktriangle), 1.00 M (\bullet).

lated as $\Delta V_1^\ddagger = \Delta V_1^\ddagger - \Delta V_{-1}^\ddagger$ are also listed in Table 2. The resultant volume profiles are depicted in Figure 6.

Discussion

Stability Constants. Stability constants β_1 for the monodentate palladium complexes calculated as $\beta_1 = K_1/K_a$ are given in Table 3 together with data for nickel(II) carboxylate complexes. Glycolate occasionally forms a chelate with metal ions without deprotonation of the α -OH group. This is the case for nickel(II) glycolate.^{28–32} Accordingly, the stability constant of the nickel(II) glycolate complex is considerably larger than that of nickel(II) acetate. In contrast, the stability constant for palladium(II) glycolate is significantly smaller than that for

(28) Nakamoto, K.; McCarthy, P. J.; Miniatis, B. *Spectrochim. Acta* **1965**, *21*, 379.

(29) (a) Evans, W. P.; Monk, C. B. *J. Chem. Soc.* **1954**, 550. (b) Grabaric, B.; Filipovic, I. *Croat. Chem. Acta* **1970**, *42*, 479. (c) Filipovic, I.; Matusinovic, T.; Mayer, B.; Piljac, I.; Bach-Dragutinovic, B.; Bujak, A. *Croat. Chem. Acta* **1970**, *42*, 541.

(30) Hoffmann, H. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 432.

(31) Harada, S.; Okue, Y.; Kan, H.; Yasunaga, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 769.

(32) Inoue, T.; Sugahara, K.; Kojima, K.; Shimozawa, R. *Inorg. Chem.* **1983**, *22*, 3977.

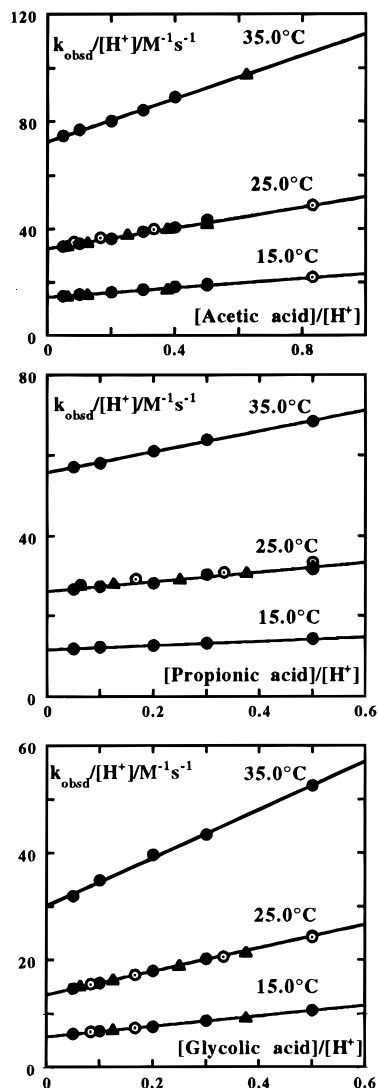


Figure 4. $k_{\text{obsd}}/[\text{H}^+]$ as a function of $[\text{RCOOH}]/[\text{H}^+]$ according to eq 12. Hydrogen ion concentrations are 0.60 M (\odot), 0.80 M (\blacktriangle), and 1.00 M (\bullet).

Table 2. Rate Constants, Equilibrium Constants, and Activation Parameters for Reactions of $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ with Carboxylic Acids at 1.00 M Ionic Strength

	acetic	propionic	glycolic
$k_1^{298}/\text{M}^{-1} \text{s}^{-1}$	19.3 ± 0.6	12.0 ± 1.1	21.1 ± 0.3
$k_{-1}^{298}/\text{M}^{-1} \text{s}^{-1}$	32.8 ± 0.2	26.4 ± 0.3	13.7 ± 0.1
K_1^{288a}	0.63 ± 0.01	0.45 ± 0.02	1.70 ± 0.05
K_1^{298a}	0.59 ± 0.02	0.45 ± 0.05	1.54 ± 0.03
K_1^{308a}	0.54 ± 0.02	0.47 ± 0.02	1.47 ± 0.06
K_1^{298b}	0.40 ± 0.08	0.39 ± 0.06	1.47 ± 0.26
$\Delta H_1^\ddagger/\text{kJ mol}^{-1}$	52.5 ± 0.4	55.3 ± 0.6	53.6 ± 0.4
$\Delta S_1^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$	-44 ± 1	-32 ± 2	-40 ± 1
$\Delta H_{-1}^\ddagger/\text{kJ mol}^{-1}$	57.5 ± 0.4	56.8 ± 0.3	59.2 ± 0.6
$\Delta S_{-1}^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$	-23 ± 1	-34 ± 1	-25 ± 2
$\Delta H_1^\circ/\text{kJ mol}^{-1}$	-5.0 ± 0.8	-1.5 ± 0.9	-5.6 ± 1.0
$\Delta S_1^\circ/\text{J K}^{-1} \text{mol}^{-1}$	-21 ± 2	2 ± 3	-15 ± 3
$\Delta V_1^\ddagger/\text{cm}^3 \text{mol}^{-1}$	-8.1 ± 0.3	-8.9 ± 0.8	-3.4 ± 0.2
$\Delta V_{-1}^\ddagger/\text{cm}^3 \text{mol}^{-1}$	-1.7 ± 0.2	-1.7 ± 0.2	-2.3 ± 0.2
$\Delta V_1^\circ/\text{cm}^3 \text{mol}^{-1c}$	-6.4 ± 0.5	-7.2 ± 1.0	-1.1 ± 0.4

^a Calculated as k_1/k_{-1} . ^b Average values in Table 1. ^c Calculated as $\Delta V_1^\ddagger - \Delta V_{-1}^\ddagger$.

palladium(II) acetate, which further supports the assumption of formation of a monodentate complex, as discussed above in connection with the absorption spectra. In general, however, the palladium(II) carboxylate complexes are between 2 and 3 orders of magnitude stronger than those of nickel(II).

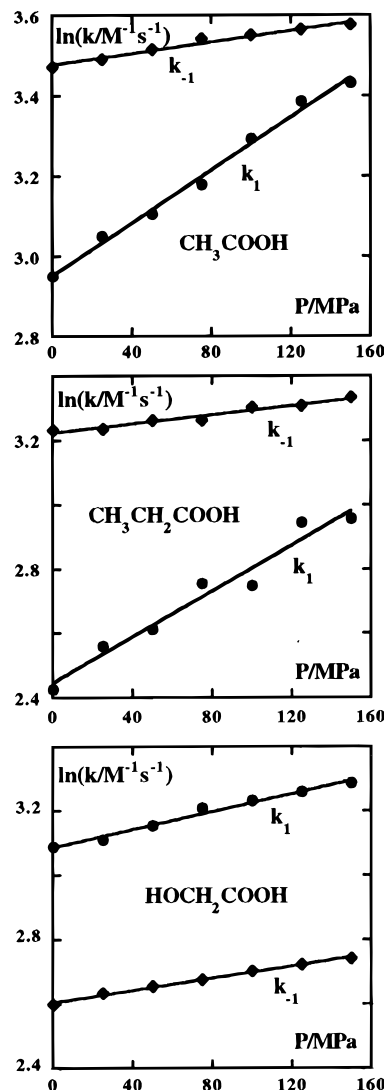


Figure 5. Pressure dependence of forward and reverse rate constants for reaction 6 at 25 °C according to eq 15.

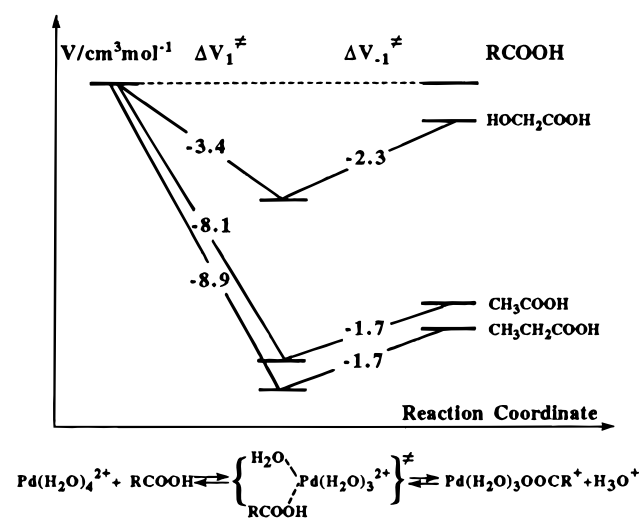


Figure 6. Volume profiles for complex formation between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and acetic, propionic, and glycolic acids, reaction 6.

Reaction Volumes. The partial molar reaction volumes of reaction 6 were calculated as $\Delta V_1^\circ = \Delta V_1^\ddagger - \Delta V_{-1}^\ddagger$, cf. Table 2. By use of the partial molar volumes ΔV_a for protolysis of acetic,²⁴ propionic,²⁴ and glycolic acid,²⁵ volumes for reactions of $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ with the carboxylate anions were derived from

Table 3. Stability Constants and Partial Molar Reaction Volumes for Complex Formation between $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ and Carboxylate Anions at 25 °C and $\mu = 1.00$ M

	acetate	propionate	glycolate
$\beta_1^{\text{Pd}}/\text{M}^{-1}$	$(2.19 \pm 0.09) \times 10^4$ ^a	$(2.10 \pm 0.24) \times 10^4$ ^a	$(6.4 \pm 0.1) \times 10^3$ ^a
$\beta_1^{\text{Ni}}/\text{M}^{-1}$	8.5 ^b	49 ± 2 ^c	100 ± 10 ^d
$\Delta V_{\text{Pd}}/\text{cm}^3 \text{ mol}^{-1}$	4.9 ± 0.5 ^e	5.8 ± 1.0 ^e	10.7 ± 0.4 ^e
$\Delta V_{\text{Ni}}/\text{cm}^3 \text{ mol}^{-1}$	8.0 ± 1.5 ^b		17.3 ± 1.0 ^f

^a This work ^b Reference 33, $\mu = 0.10$ M. ^c Reference 29c, $\mu \approx 0$.
^d Reference 30, $\mu = 2.0$ M. ^e Calculated from this work and refs 24 and 25. ^f Reference 32, 20 °C, and $\mu \approx 0$.

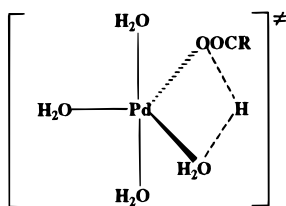
eq 16. They are listed in Table 3 together with volumes for

$$\Delta V_{\text{Pd}} = \Delta V_1^\ddagger - \Delta V_{\text{a}} \quad (16)$$

the reactions of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$. The partial molar volume changes for reaction with Ni(II) are significantly more positive than those for reaction with Pd(II). This arises mainly from a smaller release of electrostriction in the case of palladium, having a larger ionic radius. For the reaction of Ni(II) with glycolate, the formation of a chelate and the release of two water molecules are expected to make a significant contribution to the large positive reaction volume observed, as compared to the monodentate palladium(II) glycolate.

Kinetics. Formation rate constants for reactions of acetic and glycolic acid with Pd(II) remain virtually the same in spite of the variation of $\text{p}K_{\text{a}}$ from 3.62 to 4.57. On the other hand, $\text{p}K_{\text{a}}$ for propionic acid is similar to that of acetic acid, but the rate constant is slightly smaller. It seems that there is no obvious correlation between rate constants and protolysis constants of these carboxylic acids.

The experimental rate expression, eq 11, indicates that the transition state of reaction 6 involves a proton.³⁴ The transfer of the proton from the entering carboxylic acid to the leaving water molecule (forward reaction 6) or from the incoming oxonium ion to the leaving carboxylate (reverse reaction 6) is assumed to take place through a transition state of the following type, stabilized by hydrogen bonding:



Similar transition states have been proposed for the reaction of $\text{B}(\text{OH})_3$ with chromotropic acid³⁵ and for reactions of Fe-

(33) Amari, T.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1988**, *27*, 3368.

(34) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill Publishing Company: New York, 1995; Chapter 6.

(35) Ishihara, K.; Mouri, Y.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1991**, *30*, 2356.

$(\text{H}_2\text{O})_6^{3+}$ with hydroxamic acids.³⁶ It appears that the substitution of the carboxylic acids into the coordination sphere of the Pd(II) complex exhibits similarities with the water exchange on $\text{Pd}(\text{H}_2\text{O})_4^{2+}$,¹⁹ although a proton is involved in the carboxylic acid reactions. For instance, values of ΔH_1^\ddagger , $\Delta H_{\text{ex}}^\ddagger$, and ΔS_1^\ddagger , $\Delta S_{\text{ex}}^\ddagger$ are similar (second-order rate constant for water exchange and corresponding activation parameters are as follows: $k_{\text{ex}} = 41 \text{ M}^{-1} \text{ s}^{-1}$, $\Delta H_{\text{ex}}^\ddagger = 50 \text{ kJ mol}^{-1}$, and $\Delta S_{\text{ex}}^\ddagger = -48 \text{ J K}^{-1} \text{ mol}^{-1}$).¹⁹ It follows that the properties of the carboxylic acids as nucleophiles for palladium(II) are not too different from those of a water molecule.

Volumes of Activation. Volumes of activation are composed of one intrinsic contribution due to bond making or breaking in the activation process, and one solvational term: $\Delta V^\ddagger = \Delta V_{\text{intr}}^\ddagger + \Delta V_{\text{solv}}^\ddagger$.³⁷ The observed volumes of activation for the forward processes in the present systems reflect primarily intrinsic changes, since there is no net change in ionic charge in the activation process. All values are negative, corresponding to an overall contraction as expected for a process dominated by bond making. The much less negative value of ΔV_1^\ddagger observed for glycolic acid as compared to that of the other two acids studied is most likely due to solvational changes in the activation process related to the pending α -OH group.

It is noteworthy that the activation volumes ΔV_{-1}^\ddagger for displacement of carboxylate anions by oxonium ion are almost identical within experimental errors and independent of the nature of the leaving ligand. Moreover, they are very similar to the activation volumes reported earlier for displacement of Me_2SO ($-1.7 \text{ cm}^3 \text{ mol}^{-1}$),¹⁷ acetonitrile ($-1.5 \text{ cm}^3 \text{ mol}^{-1}$),¹⁶ and water ($-2.2 \text{ cm}^3 \text{ mol}^{-1}$)¹⁹ by water in analogous palladium(II) complexes. Thus, the difference in partial molar volume between the transition states and the reactants appears to be independent of the nature of the leaving group when water or oxonium ion is the incoming ligand. If bond breaking was important in the activation process, the values of ΔV_{-1}^\ddagger are expected to be modulated depending on the nature of the leaving ligand. Since this is not the case, the present results strongly support our previous suggestion¹⁶ that the activation process in the present systems seems to be strongly dominated by bond making.

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Registry Numbers (supplied by author): $\text{Pd}(\text{H}_2\text{O})_4^{2+}$, 22573-07-5; CH_3COOH , 64-19-7; $\text{CH}_3\text{CH}_2\text{COOH}$, 79-09-4; HOCH_2COOH , 79-14-1.

Supporting Information Available: Absorbances of equilibrated solutions of $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ and acetic, propionic, and glycolic acids (Tables SI–SIII) and observed pseudo-first-order rate constants as a function of temperature (Tables SIV–SVI) and as a function of pressure (Tables SVII–SIX) (9 pages). Ordering information is given on any current masthead page.

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(36) Brink, C. P.; Crumbliss, A. L. *Inorg. Chem.* **1984**, *23*, 4708.

(37) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.