

Kinetics and Mechanism of the Base Hydrolysis of Bis(ethylcysteinato)palladium(II)

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Recently Pneumatikakis and Hadjiliadis [1] have described the preparation of a number of solid complexes of palladium(II) and platinum(II) with cysteine (cystOH) and cysteine methyl ester (cystOMe). In the present paper we describe kinetic studies of the base hydrolysis of $[\text{Pd}(\text{cystOEt})_2]^0$.

Experimental

L-Cysteine ethyl ester hydrochloride was purchased from Aldrich and used as received. Potassium tetrachloropalladate(II) was obtained from Alfa. All other chemicals were of Analar grade.

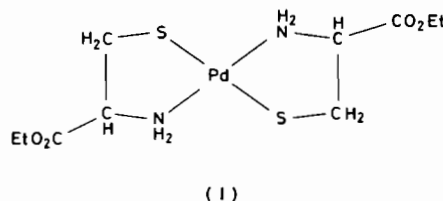
Bis(ethyl cysteinato)palladium(II) was prepared from ethyl cysteinate hydrochloride and K_2PdCl_4 essentially as previously described for the methyl ester [1]. The i.r. spectrum (KBr disc) had νNH , 3250, 3180; $\nu\text{C}=\text{O}$ (ester) 1722; δNH 1560 and $\nu(\text{C}-\text{O})$ 1220 cm^{-1} . *Anal. Calc.* for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}_4\text{S}_2\text{Pd}$: C, 29.82; H, 5.00; N, 6.96; S, 15.92. *Found*: C, 29.66; H, 5.17; N, 6.76; S, 15.81.

The kinetics of hydrolysis of the complex was studied using a Radiometer TTTI automatic titrator used as a pH-stat. The general experimental technique employed has been previously outlined [2]. A high alkalinity glass electrode type G202B was used as indicator electrode. The electrode system was standardised with NBS phosphate buffer (pH 6.86 at 25 °C) and borate buffer (pH 9.18 at 25 °C).

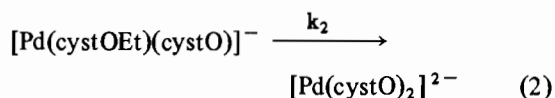
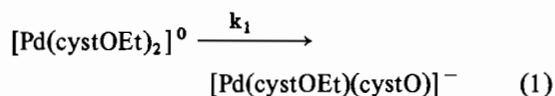
Hydroxide ion concentrations at $I = 0.1 M$ were determined from the pH using $\text{p}K_w = 13.997$ and a value of 0.774 for the activity coefficient of the hydroxide ion. As the complex has limited water solubility it was found convenient to use the following experimental technique. A weighed sample (2×10^{-5} moles) of the complex was added to the reaction vessel followed by 1 cm^3 of N,N-dimethylformamide to dissolve the material. The volume was then made up to 100 cm^3 with KNO_3 solution so that the final ionic strength was 0.1 M . Complete hydrolysis of the complex required two molar equivalents of base. All measurements were carried out at 25 °C.

Results and Discussion

As a result of the strong *trans* influence of the sulphur donor, the complex $[\text{Pd}(\text{cystOEt})_2]^0$ is expected to have the *trans*- N_2S_2 structure shown in (I). The i.r. spectrum of the complex has $\nu(\text{C}=\text{O})$



ester at 1722 cm^{-1} , a value which may be compared with those reported [3] for methyl cysteinate hydrochloride ($\nu\text{CO} = 1735 \text{ cm}^{-1}$) and methyl cysteinate ($\nu\text{CO} = 1730 \text{ cm}^{-1}$). The i.r. data provides good evidence for the validity of structure (I). If the ethoxycarbonyl group rather than the $-\text{NH}_2$ group, was involved in bonding, a substantial decrease in the carbonyl stretching frequency would be observed [3]. Hydrolysis of the complex would be expected to occur in two steps, which could be represented by the eqns. (1) and (2).



Plots of $\log(V_\infty - V_t)$ versus time were all of the type shown in Fig. 1 (V_∞ is the final volume of base consumed and V_t is the volume of base consumed at time t). It is clear that the first hydrolysis step is somewhat slower than the second. Values of $k_1(\text{obs})$ and $k_2(\text{obs})$, the observed first order rate constants at constant pH were obtained from the initial and final slopes of such plots. The rate constants are summarised in Table I.

TABLE I. Kinetic Data at 25 °C and $I = 0.1 M$ (KNO_3).

pH	$10^4[\text{OH}^-]$ (M)	$10^4k_1(\text{obs})$ (s^{-1})	$10^4k_2(\text{obs})$ (s^{-1})
10.14	1.80	3.77	6.77
10.29	2.54	4.10	7.68
10.40	3.28	6.28	9.17
10.62	5.44	10.01	16.95
10.79	8.04	13.47	21.40
10.94	11.36	16.77	25.82

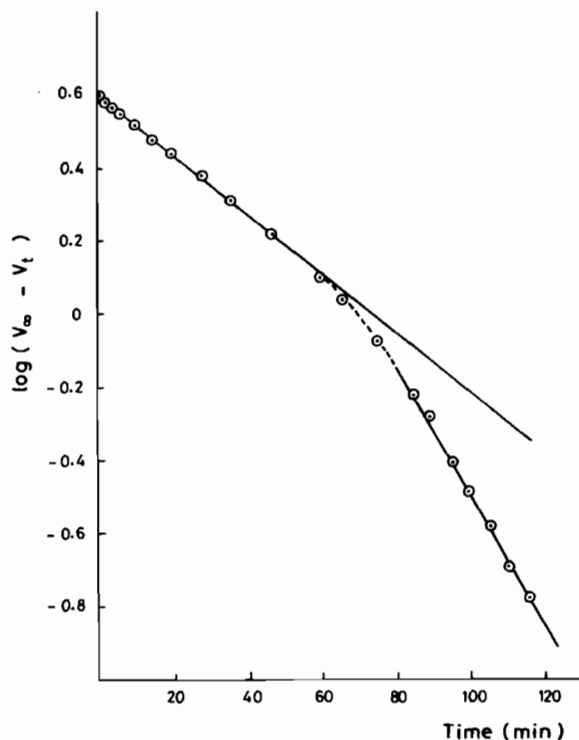


Fig. 1. Plot of $\log (V_{\infty} - V_t)$ for the hydrolysis of $[\text{Pd}(\text{cystOEt})_2]^0$ at pH 10.14 at 25 °C and $I = 0.1 \text{ M}$ (KNO_3).

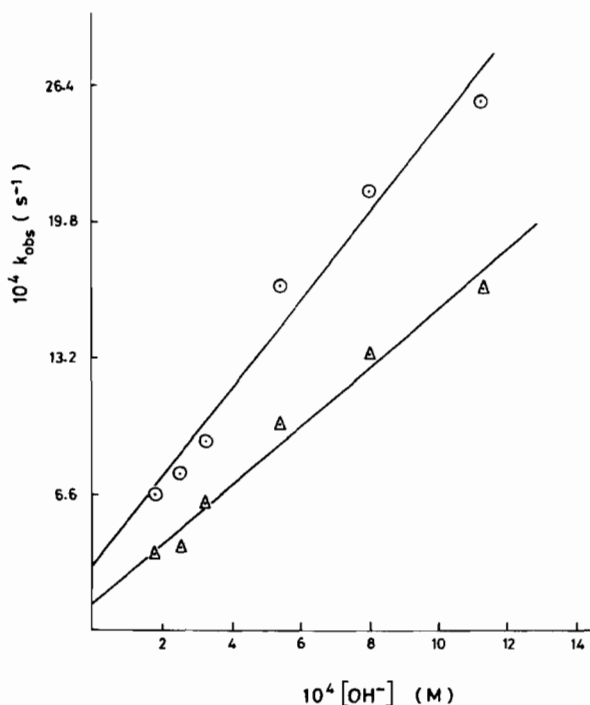
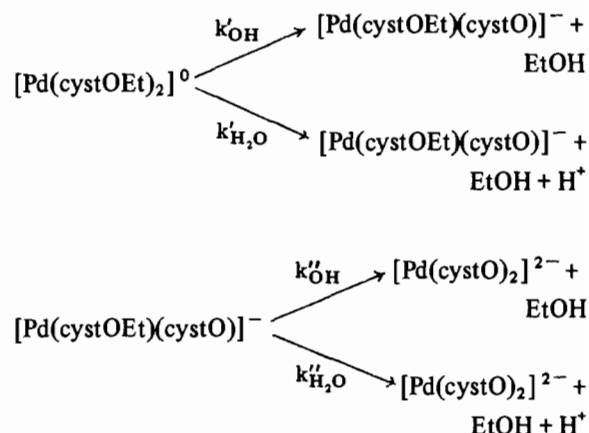


Fig. 2. Plot of $k_1(\text{obs})$ and $k_2(\text{obs})$ versus the hydroxide ion concentration at 25 °C and $I = 0.1 \text{ M}$ (KNO_3) ($k_1(\text{obs}) = \Delta$; $k_2(\text{obs}) = \circ$).

Plots of $k_1(\text{obs})$ and $k_2(\text{obs})$ versus the hydroxide ion concentration are linear with a positive intercept, Fig. 2. This observation indicates both a hydroxide ion and pH-independent hydrolysis pathway. The latter can be assigned to water attack on the complex. Thus the complete kinetic scheme can be summarised,



Values of $k_{\text{H}_2\text{O}}(\text{obs})$ were obtained from the intercept of the plots described above and values of $k_{\text{H}_2\text{O}}$ calculated from the expression $k_{\text{H}_2\text{O}} = k_{\text{H}_2\text{O}}(\text{obs})/[\text{H}_2\text{O}]$ where $[\text{H}_2\text{O}] = 55.5 \text{ M}$. The k_{OH} constants were obtained from the slopes of the plots shown in Fig. 2.

The requisite rate constants are $k'_{\text{OH}} = 1.42 \text{ M}^{-1} \text{ s}^{-1}$, $k'_{\text{H}_2\text{O}} = 2.5 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$, $k''_{\text{OH}} = 2.12 \text{ M}^{-1} \text{ s}^{-1}$ and $k''_{\text{H}_2\text{O}} = 5.7 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$. The ratios $k'_{\text{OH}}/k'_{\text{H}_2\text{O}}$ and $k''_{\text{OH}}/k''_{\text{H}_2\text{O}}$ are 5.7×10^5 and 3.7×10^5 respectively. These values are somewhat lower than ratios previously observed (10^8 – 10^{11}) for the relative nucleophilicities of hydroxide ion and water in metal-ion-promoted ester hydrolysis [4, 6].

For base hydrolysis of the dianion $\text{NH}_2\text{CH}(\text{CO}_2\text{Et})\text{CH}_2\text{S}^-$, the value of k_{OH} is $4.17 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C [5]. Thus the complexed ester anion undergoes base hydrolysis some 2×10^3 to 3×10^3 times faster than the free ligand. These effects are understandable on the basis of structure (1) since direct binding of the ethoxycarbonyl group to the metal centre would be expected to lead to rate accelerations of up to 10^6 . Charge neutralisation in the complex (1) will also lead to accelerated hydroxide ion attack and this appears to be an important consideration in this case.

Acknowledgements

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