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The Kinetics of Reduction of Palladium(IV) by 3-Thiomorpholinone

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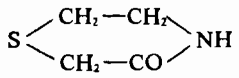
Kinetic investigation on redox reaction of the complex $[PdCl_6]^{2-}$ *with 3-thiomorpholinone by pH measurements is reported. The* $[PdCl_6]^{2-}$ *complex undergoes reduction with formation, in aqueous solution, of the final compound* trans–$[Pd(OH)_2T_2]$ (T = *3-thiomorpholinone). The kinetic process is more complicated than the similar reduction of platinum(IV) to platinum(II) by the same ligand and proceeds by some different steps. The first step is the hydrolysis equilibrium of* $[PdCl_6]^{2-}$ *with* $[PdCl_5OH]^{2-}$ *followed, in our interpretation, by a substitution reaction of T to the hydroxyl ion with formation of the complex* $[PdCl_5T]^-$ *and then, by some hydrolysis and substitution steps, of the complex* $[PdCl_3T_2OH]$. *The latter reacts with the ligand with reduction to* trans–$[PdCl_2T_2]$ *and, by two additional hydrolytic stages, to* trans–$[Pd(OH)_2T_2]$. *pH measurements carried out in KCl* 3 M, *in* $NaClO_4$ *0.1* M, *at 20, 25, 30, 35 and 40°C, lead one to propose this interpretation; the values of the rate constants are reported for hydrolysis equilibrium, the first substitution of T and the reduction stage, which steps are supposed to be slow; the corresponding activation parameters are also reported. The rate constants for the reduction step are independent of the ionic strength. The results are correlated to the coordinating properties of the ligand T.*

Introduction

In previous works (1, 2) we studied platinum and palladium compounds with 3-thiomorpholinone (T)



The diamagnetic, crystalline compounds *trans*–$[PdCl_2T_2]$, $[PtCl_2T_2]$, $[PdBr_2T_2]$ and $[PtBr_2T_2]$ were separated out in the solid state, the first two being yellow and the remainder orange. The formation of the compounds $[PdBr_2T_2]$, $[PtCl_2T_2]$ and $[PtBr_2T_2]$ is quantitative and may be followed by means of H.F. or conductometric titrations. The presence of an equivalent point for the molar ratio 1:1 in the titration of $[PtBr_4]^{2-}$ with T and a subsequent polarographic study of this system revealed the formation of the monosubstituted compound $K[PtBr_3T]$ as a transient intermediate. Spectrophotometric examination in the UV-Visible region of the system formed by $[PdCl_4]^{2-}$ and T, carried out using the method of continuous variations, led to the conclusion that immediately after the mixing of the reagents the predominant species in solution is the relatively soluble compound $[PdCl_2T_2]$ which reacts with the excess of $[PdCl_4]^{2-}$ present to be transformed into $[PdCl_3T]^-$ following a second order mechanism ($k = 2.34\times10^{-1}$ min^{-1} at 25°C). pH and conductivity measurements show that tin aqueous solution the compound $[PdCl_2T_2]$ hydrolyses quantitatively to *trans*–$[Pd(OH)_2T_2]$ producing two moles of HCl titratable with NaOH.

The compounds $[PdCl_2T_2]$ and $[PtCl_2T_2]$ may also be prepared in the solid state starting from the compounds $Na_2[PdCl_6]$ and $Na_2[PtCl_6]$ and working at high concentrations with evident reduction of the metal. In this case, three moles of ligand are consumed for each mole of compounds produced, one in the reduction step and the other two in the formation of the compound.

The reaction between $Na_2[PtCl_6]$ and T occurs with an increase in the acidity of the solution following a second order rate law ($k = 5.52\times10^{-2}$ sec^{-1} at 25°C). The following reaction mechanism has been proposed:

$$[PtCl_6]^{2-}+T+H_2O \xrightarrow{slow} [PtCl_4]^{2-}+T{=}O+2H^++2Cl^-$$

$$[PtCl_4]^{2-}+2T \xrightarrow{fast} [PtCl_2T_2]+2Cl^-$$

The kinetic study of the reduction of palladium(IV) by reaction with T leading to the compound $[PdCl_2T_2]$ (or its hydrolysis products) is the aim of the present investigation.

IR spectrophotometric measurements carried out on all the compounds obtained allowed us to establish that the chloride compounds prepared starting from the complexes $[MCl_6]^{2-}$ and $[MCl_4]^{2-}$ (M = Pd, Pt) are the same. Furthermore, examination of the absorbance bands present in the range 1,000-200 cm^{-1} reveals that to this class of compounds may be attributed a square planar structure with a *trans* configuration in which the ligand is bonded to the metal by a strong M–S bond.[2]

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(1) D. De Filippo and C. Preti, *Gazz. Chim. It.*, *98*, 64 (1968).
(2) D. De Filippo and C. Preti, *Inorg. Chim. Acta*, *3*, 287 (1969).

Experimental Section

Materials. The salt $Na_2[PdCl_6]$ was obtained from $(NH_4)_2[PdCl_6]$ (purity 99,9%, Fluka) by reaction with the stoichiometric quantity of NaOH and subsequent repeated crystallisations on drierite *in vacuo.* The 3-thiomorpholinone (supplied by Aldrich) was purified by extraction with ether and recrystallisation. Samples of $NaClO_4$, KCl and NaCl (supplied by C. Erba, CGS) were used to adjust the ionic strength and the concentration of chloride ion. The solutions were prepared with double-distilled water ($\chi_{25} = 2.3 \times 10^{-6}$ ohm^{-1} cm^{-1}).

Apparatus. The kinetics were followed by means of pH measurements, performed using a DAT 2002 digital pH meter and a glass electrode (ref: Ag/AgCl), which results in a degree of precision of ± 0.005 pH units. The readings were recorded by hand and, simultaneously, with a Bausch and Lomb recorder, in which a timer is incorporated for the calibration of the time axes. The solutions were thermostated at the required temperature with a degree of accuracy of ±0.05°C.

Measurements. In performing the measurements solutions of $Na_2[PdCl_6]$ $10^{-3}\,M$ were used, for which the solvents were solutions of $NaClO_4$ 0.1 *M*, KCl 3 *M* or solutions of different ionic strength (μ ranging between 2.25×10^{-3} and 0.9), or also solutions with a constant ionic strength ($\mu = 2.7$) and a concentration of chloride ion ranging between 0.45 and 2.7 *M*, the latter solutions being obtained by means of suitable mixtures of NaCl and $NaClO_4$. The solutions of T, pre-thermostated at the same temperature, were in the same solvent and had concentrations of 0.1, 0.2 or 1 *M* in order to minimize the concentration changes resulting from the mixing of the reagents. Some typical results of the measurements in $NaClO_4$ 0.1 *M* and KCl 3 *M*, carried out at 20, 25, 30, 35 and 40°C with continuous and vigorous magnetic stirring are reported in Figure 1; the experimental measurements at different values of μ or $[Cl^-]$ are not shown.

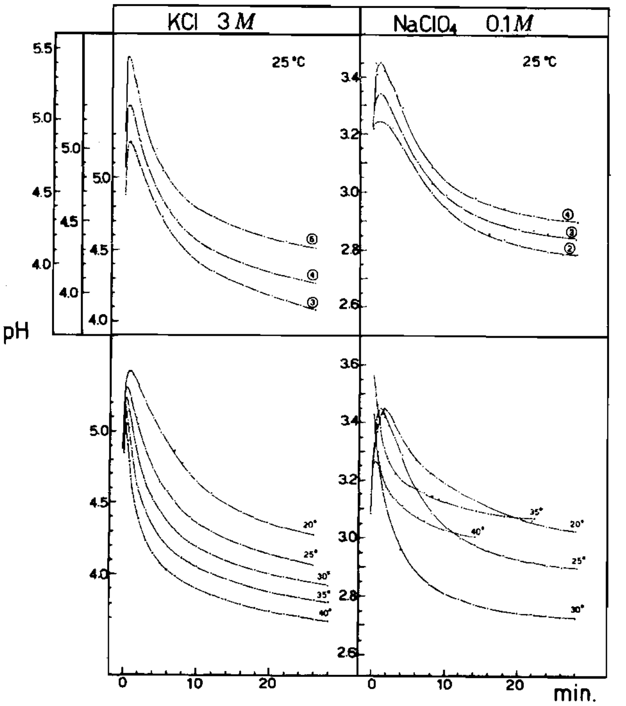

Figure 1. On the top of the figure is shown dependence on concentration of ligand (molar ratios $[PdCl_6^{2-}]:[T]$ = (2) 1:2; (3) 1:3; (4) 1:4; (6) 1:6); on the bottom, is shown dependence on temperature for the molar ratio $[PdCl_6^{2-}]$: [T] = 1:4.

Results and Discussion

The pH of the $10^{-3}\,M$ solutions of $[PdCl_6]^{2-}$ is very close to 3 in $NaClO_4$ 0.1 *M* while it is close to 5 in KCl 3 *M*. This shows that, in aqueous solution, the salt undergoes the process of base hydrolysis

$$[PdCl_6]^{2-} + H_2O \rightleftarrows [PdCl_5OH]^{2-} + H^+ + Cl^-$$

which is almost complete in the absence of chloride ion but can be made to withdraw to the left in an excess of this ion. The pK_h values, calculated at the various temperatures, are reported in Table I. The agreement obtained in these two extreme conditions is relatively good, and the differences are likely to be only due to the different ionic strength of the solution.

Table I. Values of pK_h for the equilibrium $[PdCl_6]^{2-} + H_2O \rightleftarrows [PdCl_5OH]^{2-} + HCl$

t°C	($NaClO_4$ 0.1 *M*)	(KCl 3 *M*)
20	6.39	6.28
25	6.53	6.31
30	6.53	6.33
35	6.44	6.27
40	6.32	6.19

The pH/time plots (Figure 1) show an initial relatively fast rising curve, corresponding to a decrease in the acidity of the solutions, and followed, after a maximum value of pH has been reached within 1 - 2 mins., by a falling curve, corresponding to an acidity increase. The reaction mixture reach the final pH within 20 - 30 mins depending on the temperature and ratios between the reagents.

The maximum value of pH attained in the course of the reactions is a function of the concentration of T. It is therefore quite evident that after the mixing of the reagents, a rather complicated reaction takes place in which there are at least two slow steps, the first of which brings about a decrease in the acidity of the solution, while the second causes an increase. The process depends on the initial hydrolysis equilibrium of the salt $Na_2[PdCl_6]$.

The first slow step, whose rate is a function of the concentration of the ligand and the temperature, may be identified as the substitution of T at the hydroxyl ion according to the scheme

$$[PdCl_5OH]^{2-} + T \longrightarrow [PdCl_5T]^- + OH^-$$

thus justifying the decrease in the acidity of the solution.

The strong M—S bond established labilizes the ligand *trans* to it thus favouring new steps of hydrolysis and substitution. As far as the second slow step is concerned we propose that this can be ascribed, as has already been demonstrated for platinum, to the reduction of the metal, leading to the compound *trans*-$[PdCl_2T_2]$; the latter is subsequently quickly hydrolised, as has been shown in a previous paper (2) by means of pH and conductivity measurements, to the compound *trans*-$[Pd(OH)_2T_2]$, which is the final product of the reaction in question.

A detailed model of this mechanism is seen in Figure 2.

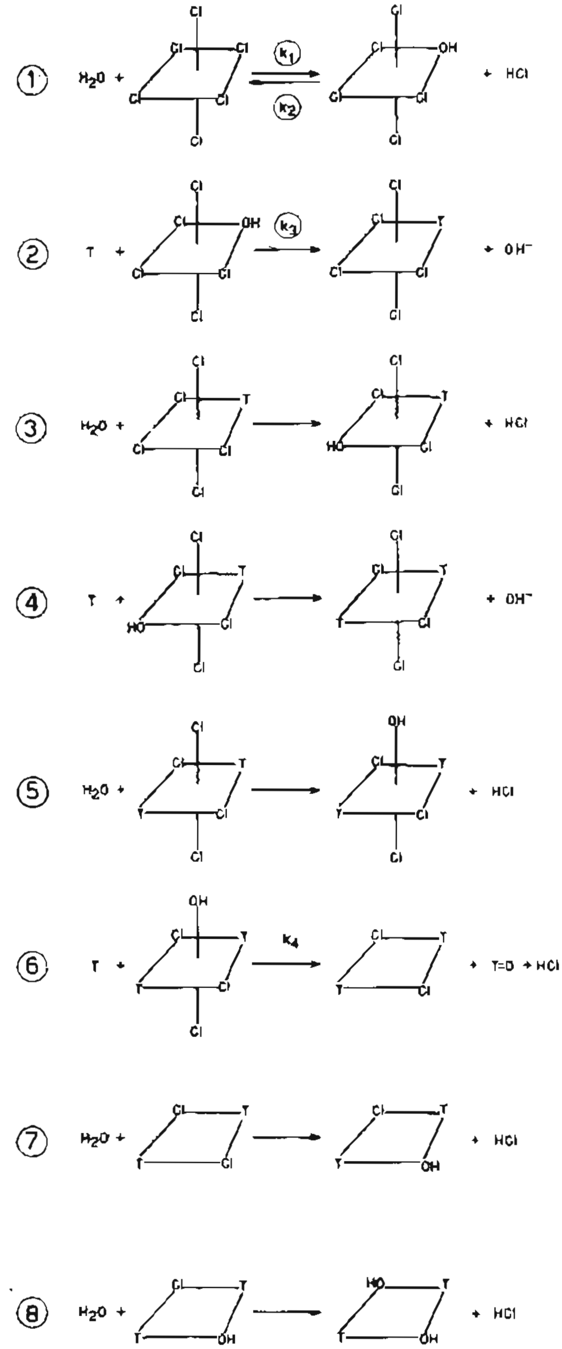

Figure 2. Model of mechanism.

In order to collate the experimental data according to the proposed interpretation the following rate and stoichiometric equations apply:

$$-\frac{d[PdCl_6^{2-}]}{dt} = k_1[PdCl_6^{2-}]- k_2[Cl^-][H^+][PdCl_5OH^{2-}] \qquad (1)$$

$$\frac{d[PdCl_5OH^{2-}]}{dt} = k_1[PdCl_6^{2-}]- k_2[Cl^-][H^+][PdCl_5OH^{2-}]-k_3[T][PdCl_5OH^{2-}] \qquad (2)$$

$$\frac{d[PdCl_3T_2OH]}{dt} = k_3[T][PdCl_5OH^{2-}]- k_4[T][PdCl_3T_2OH] \qquad (3)$$

$$\frac{d[Pd(OH)_2T_2]}{dt} = k_4[T][PdCl_3T_2OH] \qquad (4)$$

$$[PdCl_6^{2-}] = [PdCl_6^{2-}]_0-([PdCl_5OH^{2-}]+ [PdCl_3T_2OH]+[Pd(OH)_2T_2]) \qquad (5)$$

$$[T] = [T]_0-(2[PdCl_3T_2OH]+3[Pd(OH)_2T_2]) \qquad (6)$$

$$[Cl^-] = [Cl^-]_0+[PdCl_5OH^{2-}]+ 3[PdCl_3T_2OH]+6[Pd(OH)_2T_2] \qquad (7)$$

$$[H^+] = [PdCl_5OH^{2-}]+[PdCl_3T_2OH]+3[Pd(OH)_2T_2] \qquad (8)$$

$$k_1/k_2 = K_h \qquad (9)$$

All the other processes (from $[PdCl_5T]^-$ to $[PdCl_3T_2OH]$ and from *trans*-$[PdCl_2T_2]$ to *trans*-$[Pd(OH)_2T_2]$) are considered to be much faster than those in question and therefore without influence on the kinetic behaviour of the reaction.

Taking the measurements carried out in KCl 3 *M* as a basis, it may be hypothesized that the species $[PdCl_5OH]^{2-}$ and $[PdCl_3T_2OH]$ attain a stationary state condition some instants after the mixing of the reagents. The initial hydrolysis equilibrium is repressed almost completely due to the effect of the high concentration of chloride ion (3,000 : 1) so that the non-hydrolysed species, $[PdCl_6]^{2-}$, predominates over the product of hydrolysis, $[PdCl_5OH]^{2-}$, by about 100: 1 (pH$\simeq$5). It may be contended, therefore, that the concentration of $[PdCl_5OH]^{2-}$ remains constant for a certain time starting some instants after the mixing of the reagents, even if it is obvious from a simple qualitative examination of the experimental data that $k_3 \gg k_4$. By analogy it may be hypothesized that the concentration of $[PdCl_3T_2OH]$ also remains constants for a certain period of time. The expression (3) and (4) may therefore be equated to zero, while the equations (5 - 8) may be written in the form:

$$[PdCl_6^{2-}] \simeq [PdCl_6^{2-}]_0-[Pd(OH)_2T_2] \qquad (5')$$

$$[T] \simeq [T]_0-3[Pd(OH)_2T_2] \qquad (6')$$

$$[Cl^-] \simeq 3 \qquad (7')$$

$$[H^+] \simeq 3[Pd(OH)_2T_2] \qquad (8')$$

Table II.

	t°C	k [a] l . mole⁻¹ sec⁻¹	ΔH* Kcal . mole⁻¹	ΔS* e.u.	
$PdCl_6^{2-} + H_2O \longrightarrow PdCl_5OH^{2-} + HCl$	20	2.08×10^{-5}	22.7	2	$\ln(k_1 \times 10^5) = 40.88 - \frac{23.35}{RT}$
	25	4.26			
	30	6.46			
	35	15.84			
	40	31.82			
$PdCl_5OH^{2-} + HCl \longrightarrow PdCl_6^{2-} + H_2O$	20	4.02×10^3	21.1	21	$\ln(k_2 \times 10^{-3}) = 38.75 - \frac{21.71}{RT}$
	25	8.82			
	30	12.29			
	35	29.56			
	40	49.31			
$PdCl_5OH^{2-} + T \longrightarrow PdCl_5T^- + OH^-$	20	6.70×10^{-4}	12.7	−16	$\ln(k_3 \times 10^4) = 24.58 - \frac{13.25}{RT}$
	25	9.81			
	30	13.64			
	35	19.23			
	40	27.18			
$PdCl_3T_2OH + T \longrightarrow PdCl_2T_2 + T{=}O + HCl$	20	2.53×10^{-6}	18.3	−21	$\ln(k_4[F] \times 10^6) = 33.55 - \frac{18.94}{RT}$
	25	4.70			
	30	7.88 [b]			
	35	13.24			
	40	15.76			

[a] From measurements in KCl 3 *M*; each value is the average of the results of four runs. [b] $k_4[F]$, where [F] is the concentration of $[PdCl_3T_2OH]$.

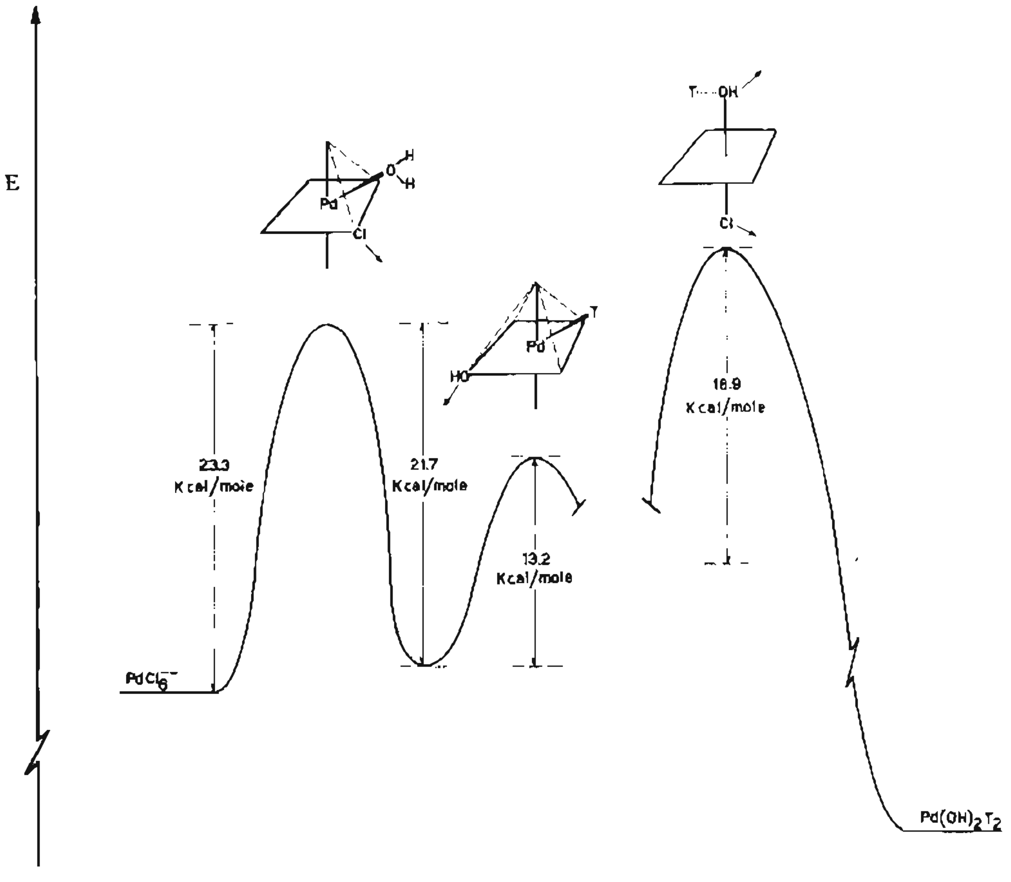

Figure 3. Energetic profile of reaction.

Working on this hypothesis a special programme for an IBM 1620 computer was used. It was hypothesized that the stationary state was reached at a point in time coincident with the maximum pH value. From this value a first concentration of the species $[PdCl_5OH]^{2-}$ was calculated, and from this first approximation *k* values were obtained. Starting with these *k* values it was possible to obtain a further value of $[PdCl_5OH^{2-}]$ which was used in the calculation of new *k* values for the subsequent short time interval, and so on. This procedure shows that *k* values and $[PdCl_5OH^{2-}]$ are constant for a large interval of time. The average k_1, k_2, k_3 and k_4 $[PdCl_3T_2OH]$ values are reported in Table II.

From the *k* values plotted against 1/T, are calculated the values of ΔE_{act} reported in Figure 3 which reproduces the energy profile of the reaction. The ΔH* and ΔS* activation values were calculated (3) and are

Kynoch Press, Birmingham, England, 1965, Vol. 3, Table 3.3.1 A.

reported in Table II. By treating the experimental data obtained from the runs carried out at constant ionic strength ($\mu = 2.7$) and at varying concentration of chloride ion in the same way, it is possible to see that the k_3 and $k_4[PdCl_3T_2OH]$ values are a linear function of $[Cl^-]$ in the interval of 0.45 - 2.7 (Figure 4).

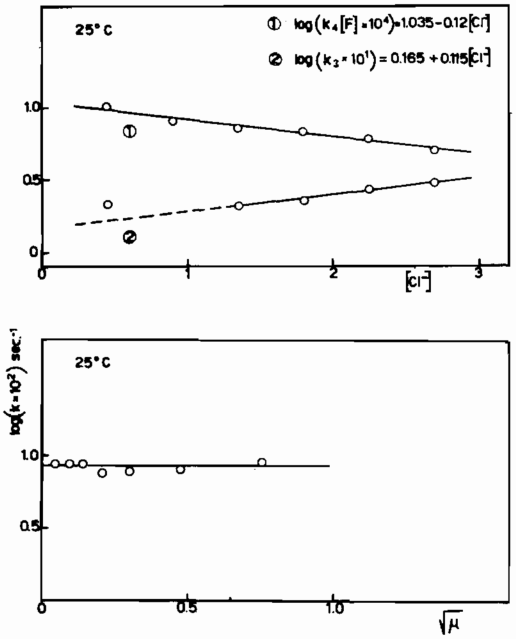

Figure 4. On the top of the picture is reported a correlation between k's and $[Cl^-]$ ($F = PdCl_3T_2OH$) from measurements in KCl 3 M; below, a correlation between k and $\sqrt{\mu}$ in $NaClO_4$.

In the case of the experimental measurements carried out in $NaClO_4$ 0.1 M it is not possible to postulate the hypothesis of the stationary state, at least as far as the species $[PdCl_5OH]^{2-}$ is concerned. From the measurements in KCl 3 M the result was in fact $k_3 \gg k_4[PdCl_3T_2OH]$; furthermore, since the chloride ion concentration is not buffered, the hydrolysis equilibrium is completely shifted towards the hydrolyzed species, the concentration of which will decrease rapidly in the course of the second step of the reaction. It can then be proposed that, after some time, this step can be considered practically complete and that the progress of the reaction is due only to the reduction process (stage 6). With this rather rough approximation values of k_4 were calculated, the logarithms of which are reported against 1/T in Figure 5. The ΔE_{act} thus calculated turned out to be 18.3 Kcal/moles, that is to say, in good agreement with the value of 18.9 Kcal/moles deduced from the measurements in KCl 3 M and with different calculation approximations.

When the measurements performed at different values of ionic strength were collated in the same way it was found that the $\ln k_4$ values are independent of $\sqrt{\mu}$ (Figure 4), at least as far as the solutions with the lower ionic strength are concerned. This result confirms that a molecular species, *i.e.* the ligand, participates in the elementary act of the slow process, as postulated (Figure 2).

The overall results of the calculation are in good agreement with the proposed mechanism.

It is therefore interesting to point out that substitution of thiomorpholinone at the chloride ion occurs indirectly as the result of a step of base hydrolysis.

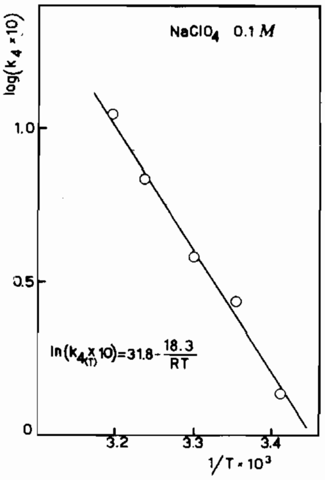

Figure 5. Correlation between k_4 and 1/T.

As is obvious from Figure 3, the substitution reaction of the ligand to the hydroxyl ion involves a noticeably lower activation energy (13.2 Kcal/moles) than does hydrolysis (23.3) or reduction (18.9). This result is in agreement with the experimental data. On working at the higher temperatures (35 or 40°C) and with higher concentrations of ligand a rising pH curve is, in fact, no longer recorded, as the process has almost become instantaneous.

The effect of neutral ligands on the oxidising power of platinum complexes, like *trans*–$[PtX_4L_2]$, is reported.[4] It was found that this oxidising power increases with the increase in the π-acceptor ability of the ligand and decreases with the increase in the ligand's σ-donor ability. The qualitative series $S > N > P$ was proposed, in which, as far as sulphur is concerned, those compounds were studied where L represents a thioether. 3-thiomorpholinone is comparable to these, where it may be proposed the results obtained for platinum to be extended to compounds of palladium.

A final observation is that the rate constant for the reduction step, calculated, even if only in an approximate manner, from the measurements in $NaClO_4$ 0.1 M, is 5 times greater for palladium (27.2×10^{-2} sec^{-1} at 25°C) than that obtained with previous measurements for the corresponding compound of platinum (5.52×10^{-2} sec^{-1} at 25°C). This finding is also in agreement with the general observation that palladium compounds are always distinctly more reactive than the corresponding compounds of platinum.

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(3) A. A. Frost and R. G. Pearson, Kinetics and Mechanism, 2nd edition J. Wiley and Sons Inc., 1963, p. 98-101.

(4) A. Peloso G. Dolcetti, and R. Ettorre, *Inorg. Chim. Acta, 1,* 403 (1967).