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Kinetics and Equilibria for the Acid Hydrolysis of Dichloro(ethylenediamine)platinum(II)

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The specific rate constants and the equilibrium quotients for the successive replacement of chloride ligands by water in aqueous solutions of $Pt(en)Cl_2$ have been evaluated at 15°, 25° and 35° and an ionic strength of 0.318 M. *For the reaction:*

$$Pt(en)Cl_2+H_2O\rightarrow Pt(en)Cl(H_2O)^{+}+Cl^{-}$$

the equilibrium quotient, K_1, *is* $2.19\pm0.11\times10^{-3}$ M *at 25°,* $\Delta H°$ *is* 4 ± 1 *kcal/mol,* k_1 *is* $3.4\pm0.4\times10^{-5}$ s^{-1}, ΔH^* *is* 20 ± 2 *kcal/mol. For the reaction:*

$$Pt(en)Cl(H_2O)^{+}+H_2O\rightarrow Pt(en)(H_2O)_2^{2+}+Cl^{-}$$

the equilibrium quotient, K_2, *is* $1.43\pm0.11\times10^{-4}$ M, *at 25°,* $\Delta H°$ *is* -1 ± 2 *kcal/mol,* k_2 *is* $4.4\pm0.6\times10^{-5}$ s^{-1}, ΔH^* *is* 8 ± 3 *kcal/mol.*

Introduction

This study represents an extension of studies in this Laboratory upon the kinetics and equilibria for the replacement reactions for halide ligands of square-planar platinum(II) complexes which have been reviewed recently.[1] With the two nitrogen to platinum bonds from the chelating ethylenediamine molecule occupying *cis* positions it is of special interest to compare the behavior of thic complex with that of the *cis*-dichlorodiammineplatinum(II).[2]

The replacement of chloride ligands in $Pt(en)Cl_2$ is expected to take place in a stepwise fashion according to the reactions in equations (1) and (2) which also designate the relevant equilibrium quotients and the rate constants.

$$Pt(en)Cl_2+H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Pt(en)(H_2O)Cl^{+}+Cl^{-}, \qquad K_1 \quad (1)$$

$$Pt(en)(H_2O)Cl^{+}+H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Pt(en)(H_2O)_2^{2+}+Cl^{-} \qquad K_2 \quad (2)$$

Banerjea, Basolo, and Pearson[3] and more recently Panasyuk and Malashok[4] have studied the rate of the first acid hydrolysis (k_1) by a technique in which the chloride released was titrated by silver nitrate with a Ag: AqCl indicator electrode.

Experimental Section

Materials. $Pt(en)Cl_2$ was prepared from K_2PtCl_4 by the method of Basolo Bailar and Tarr.[5] *Anal.* Found: Pt, 59.41; C, 7.38; H, 2.48; N, 8.28; Cl, 21.89. Calcd. for $Pt(en)Cl_2$: Pt, 59.82; C, 7.37; H, 2.47; N, 8.59; Al, 21.74.

Activation analyses have indicated that the iridium content of the platinum was less than 0.030 ppm. The ethylenediamine used for the preparation was freshly distilled (B.P. 116.5-117°C).

All other chemicals were analytical reagent grade which were certified to meet A.C.S. Standards. Water was drawn from the Laboratory distilled water tap, redistilled from alkaline permanganate and again redistilled through a fractionating column.

Equipment. Acid-base titrations and pH-stat studies were conducted with a Radiometer SBR2c/ABU1c/TTA3 automatic recording titrator apparatus in conjunction with either a 2.500 mℓ burette with an accuracy of 2.5 μℓ+0.5% or a 0.250 mℓ burette with an accuracy of 1 μℓ+0.7%. The titration vessel was designed for temperature control from ±0.05° at 25° to ±0.08° at 35°. An atmosphere of Grade A nitrogen was maintained over the vessel.

The ultraviolet spectra and absorbance measurements were recorded by means of a Cary Model 14 recording spectrophotometer with a H_2-arc lamp. Water-jacketed spectrophotometer cells had silica windows of optical quality. Absorbance were measured with respect to a base line which had been recorded with the appropriate reference solution in both the sample and reference cells.

Stopped flow experiments utilized a Durrum Gibson stopped-flow spectrophotometer in conjunction with a Tektronix Type 564 storage oscilloscope.

Procedures. The aquo ligands of platinum(II) complexes are sufficiently acidic that one proton for each complexed H_2O molecule can be titrated with an endpoint between pH of 8 and 9. The concentration of the aquo ligands in solutions which had reached equi-

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[1] D.S. Martin, Jr., *Inorg. Chim. Acta Reviews*, *1*, 87 (1967).

[2] J.W. Reishus and D.S. Martin, Jr., *J. Am. Chem. Soc.*, *83*, 2457 (1961).

[3] D. Banerjea, F. Basolo, and R.G. Pearson, *J. Am. Chem. Soc.*, *79*, 4055 (1957).

[4] V.D. Panasyuk and N.F. Malashok, *Zhur. Neorg. Khim.*, *14*, 1006 (1968).

[5] F. Basolo, J.C. Bailar, and B.R. Tarr, *J. Am. Chem. Socs.*, *75*, 2433 (1950).

librium with respect to reactions (1) and (2) were therefore determined by potentiometric titrations. Ionic strength was maintained at 0.318 *M* by the presence of $NaClO_4$. The NaOH solutions were standardized by titrating solutions of the primary standard, potassium acid phthalate, at concentrations in the range of the equilibrium solutions . Solutions of Pt(en)Cl_2 were aged approximately 36 hours before a series of titrations which extended over another 25 to 30 hour period to assure that the titer of the solutions was not changing. The use of the automatic titrator permitted the attainment of the endpoints within 1 minute. Rapid titrations are essential since the titration disturbs the equilibrium so more extensive aquation of the substrate will occur. A number of titrations at one half the addition rate of titrant were in good agreement with others so it can be concluded that negligible aquation occurred during the actual titration period. Such titrations were, of course, much more convenient than the old technique without automated equipment in which a fresh sample was drawn for each point on the titration curve.

The kinetics for the aquation of Pt(en)Cl_2 were studied both spectrophotometrically and by the pH stat tecnique. The spectrum of Pt(en)Cl_2, which is included in Figure 2, was obtained for a solution in which a weighed quantity of the compound was dissolved in a 0.318 *M* solution of KCl. The high chloride concentration served to suppress the aquation of the neutral complex. The spectrum of Pt(en)Cl_2 had a peak with a molar absorbtivity of 230 ± 2 cm^{-1} M^{-1} at 300 nm. Since a weighed sample of Pt(en)Cl_2 did not all dissolve rapidly, solutions for kinetics experiments were prepared by shaking an excess of the solid in a 0.318 *M* $NaClO_4$ solution for 15 sec and then filtering off the undissolved residue. Samples of the filtrate were pipetted into the spectrophotometer cell or into the titration vessel. The concentration of the complex in the solutions was subsequently determined by adding KCl and recording the absorbance at 300 nm. In the spectrophotometric method the spectrum of the solution was recorded periodically. For the pH-stat method the addition of standard NaOH solution necessary to maintain the pH of the solution at a constant value was recorded. The pH values were selected higher than the endpoint of the titrations for the equilibrium solutions and were in the region 9.0 to 9.5.

The replacement of the first aquo ligand in Pt(en)$(H_2O)_2^{2+}$ by chloride was studied by the stopped-flow technique. Solution of Pt(en)Cl_2 which had equilibrated with respect to reactions (1) and (2) were injected into the cuvette togeher with the chloride solution. The absorbance was recorded for 285 nm which is an isosbestic point for the Pt(en)Cl_2 and the Pt(en)$(H_2O)^+$ species so there would be no contribution to the absorbance from the addition of the second chloride. Two sweeps of the 10 cm oscilloscope trace at 0.5 cm/sec were recorded. The half-times of the pseudo first order process were obtained from the photographs of the sweeps.

The replacement of the aquo ligand in Pt(en)$(H_2O)Cl^+$ was sufficiently slow to follow by conventional technique. To the solution of Pt(en)Cl_2, equilibrated with respect to reactions (1) and (2), was added the chloride solution. The mixed solution was quickly transfered to the jacketed spectrophotometer cells but by this time any Pt(en)$(H_2O)_2^{2+}$ was completely converted to Pt(en)$(H_2O)Cl^+$. The increase in absorbance at 300 nm was recorded. Some experiments were performed with $HClO_4$ in the cell to establish the independence of pH in the pH range 1 to 5.

Results and Discussion

Aquation Equilibria. In the titration of equilibrium solutions, if one proton per aquo ligand is neutralized, the titer, *T*, of the solution is given by the expression:

$$T = [\mathrm{Pt(en)(H_2O)Cl^+}] + 2[\mathrm{Pt(en)(H_2O)_2^{2+}}] \qquad (3)$$

The equilibrium quotients for reactions (1) and (2) are related to *T* by the equation:[6]

$$T^3 + K_1T^2 + (K_1K_2 - aK_1)T - 2aK_1K_2 = 0 \qquad (4)$$

were a = initial concentration of Pt(en)Cl_2 which was dissolved.

The results of the titration experiments are presented in Table I. The concentration range for *a* was limited by the solubility of the complex and by the dilution at which the titrations could be conducted with suitable accuracy. Values of the quotients, K_1 and K_2, were computed by a least squares procedure which minimized the quantity, S,

$$S = \Sigma w_i (T_{i-obsd} - T_{i-calcd})^2 \qquad (5)$$

The weights w_i were taken as $1/\sigma_i^2$ where σ_i is the standard deviation for the $T_{i\text{-}obsd}$. The values of $T_{i\text{-}calcd}$ from the set of constants K_1 and K_2 are also included in Table I. A plot of the values of T_i *vs* *a* for 25° is shown in Figure 1 where the curve is the calculated value for the function *T*. At high dilutions, as can be seen in Figure 1, the ratio *T/a* was greater than 1.0. Hence the second aquation process, reac-

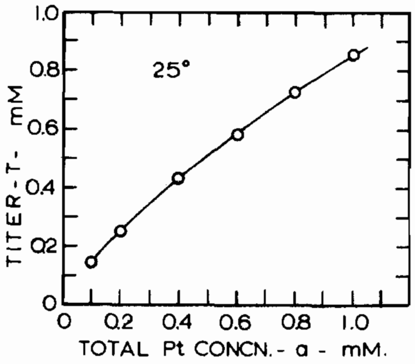

Figure 1. The equilibrium titer for the neutralization of ligand protons *versus* the total concentration of the platinum complexes.

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807 (1961).
(6) C.I. Sanders and D.S. Martin, Jr., *J. Am. Chem. Soc.*, 83,

Table I. Titration Data for the Aquation Equilibrium Quotients of $Pt(en)Cl_2$, K_1 and K_2 for Ionic Strength at 0.318 *M*. Each Titer is the Average for Ten Titrations.

Total Pt—*a* m*M*	Equilibrium Titer—*T* Obsd	Calcd
	25°C	
0.1002	0.145±.002	0.1456
.2004	0.257±.002	.2562
.4008	0.440±.004	.4435
.6011	0.609±.004	.6066
.8015	0.754±.003	.7544
1.0019	0.891±.005	.8909
	30°C	
0.1006	0.147±.002	0.1470
.2012	0.258±.001	.2576
.4024	0.439±.003	.4419
.6036	0.599±.004	.6003
.8048	0.743±.004	.7424
1.0060	0.874±.004	.8728
	35°C	
0.1002	0.146±.002	0.1455
.2002	0.255±.003	.2545
.4003	0.436±.003	.4357
.6005	0.588±.004	.5909
.8006	0.729±.006	.7299
1.0008	0.859±.005	.8572

Table II. Equilibrium Quotients for the Aquation Reactions of $Pt(en)Cl_2$. Ionic Strength = 0.318 *M*.

Temp.	$K_1 \times 10^3$ *M*	$K_2 \times 10^4$ *M*
25°	2.19±0.11	1.43±0.11
30°	2.33±0.09	1.48±0.05
35°	2.76±0.05	1.38±0.05
$\Delta H°$ (kcal/mol)	4 ±1	—1 ±2

tion (2), occurred to a significant extent. The determinations of K_1 and K_2 are in Table II with the indicated values of $\Delta H°$. The small values of $\Delta H°$ are fairly typical of the aquation reactions of chloride ligands in the platinum(II) complexes.

The absorption spectrum of $Pt(en)Cl_2$ was available from freshly prepared solutions of $Pt(en)Cl_2$ which agreed with the equilibrium spectra in 0.318 *M*. KCl where the fraction of complexes in the $Pt(en)Cl_2$ form was greater than 99 per cent. In addition, the spectrum of $Pt(en)(H_2O)_2^{2+}$ was available from the initial scans when $HClO_4$ was added to the solutions of $Pt(en)(OH)_2$ that had been formed by the reaction between $Pt(en)Cl_2$ and NaOH. For an equilibrium solution the absorbance, *A*, is given by the equation

$$A/\ell = \varepsilon_0[Pt(en)Cl_2] + \varepsilon_1[Pt(en)(H_2O)Cl^+] + \varepsilon_2[Pt(en)(H_2O)_2^{2+}] \qquad (6)$$

where the ε's are the molar absorptivities for the indicated species and ℓ is the cell length.

Since ε_0 and ε_2 were available as functions of wave length, the molar absorbtivity,, ε_1, could be calculated from *a*, K_1 and K_2 for the equilibrium solutions in which $Pt(en)(H_2O)Cl^+$ was the major species. The spectra of the three complexes are plotted in Figure 2.

The spectrum of $Pt(en)Cl_2$ resembles that of *cis*-$Pt(NH_3)_2Cl_2$ with the location of the bands although the absorption is somewhat more intense for the ethylenediamine complex. Accordingly, the peak at 300 nm (33,300 cm^{-1}) is attributed[7] to the transition $^1B_2 \leftarrow {}^1A_1$ ($\sigma^* - d_{xy} \leftarrow d_{x^2-y^2}$) as originally for *cis*-$Pt(NH_3)_2Cl_2$ by Chatt, Gamlen and Orgel.[8] In the replacement of chloride by H_2O in the complex there is a shift of the band to higher energies, consistent with the higher "ligand field" of H_2O over chloride.

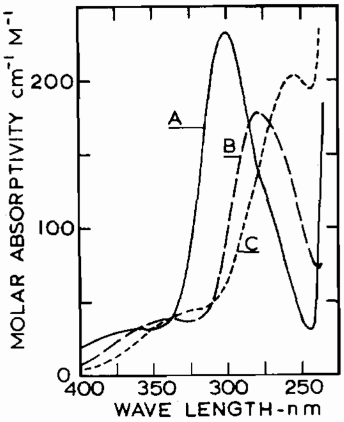

Figure 2. The absorption spectra for the complexes. A) $Pt(en)Cl_2$. B) $Pt(en)(H_2O)Cl^+$. C) $Pt(en)(H_2O)_2^{2+}$.

Kinetics. The kinetics for the aquation of $Pt(en)Cl_2$, reaction (1), was determined from both the spectrophotometric and pH-stat method. In each case the initial slope method was used. From plots of absorbance at 300 nm (the wave length where ε_0 is a maximum) *vs* time, the rate constant k_1 was calculated by means of the expression,

$$k_1 = (dA/dt)_{t=0}/a(\varepsilon_1 - \varepsilon_0)\ell \qquad (7)$$

From the pH-stat experiment k_1 was calculated by means of the equation

$$k_1 = (dV_{NaOH}/dt)_{t=0}M_{NaOH}/aV_{soln} \qquad (8)$$

This method requires that the second order replacement of chloride by $OH^- \ll$ than the replacement of chloride by H_2O, and that the formation of the hydroxo complex results from the rapid neutralization of the aquo ligand in the basic solution. The two methods were in substantial agreement and the results are included with the rate constants in Table III.

In the stopped flow experiments to measure the replacement of the first H_2O ligand in $Pt(en)(H_2O)_2^{2+}$ by chloride, Guggenheim plots[9] were prepared from the difference in the two sweeps on the oscilloscope trace. The pseudo first order rate constants were determined for experiments with 0.0795 *M* chloride at 30° and 35° and for 0.1590 *M* chloride at 25°, 30°, and 35°. The concentration of the complex varied

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[7] D.S. Martin, L.D. Hunter, R. Kroening, and R.F. Coley, *J. Am. Chem. Soc.*, *93*, 5433 (1971).

[8] J. Chatt, G.A. Gamlen, and L.E. Orgel, *J. Chem. Soc.*, 486 (1958).

[9] E.A. Guggenheim, *Phil. Mag.*, *2*, 538 (1926).

Table III. Rate Constants for the Reversible Aquation Reactions of $Pt(en)Cl_2$. Ionic Strength of 0.318 M.

Temp.	$k_1 \times 10^5$ s^{-1}	$k_{-1} \times 10^2$ s^{-1} M^{-1}	$k_2{}^a \times 10^5$ s^{-1}	$k_{-2} \times 10$ s^{-1} M^{-1}
25°C	3.4 ± 0.4	1.54 ± .03	4.4 ± 0.7	3.1 ± 0.4
30°C	6.2 ± 1.7	2.53 ± 0.05	6.2 ± 0.5	4.2 ± .30
35°C	11 ± 0.4	4.01 ± 0.09	7.3 ± 0.9	5.2 ± 0.65
ΔH^* (kcal/mol)	20.4 ± 2.5	17.5 ± .7	8.1 ± 4	9. ± 3
ΔS^* (25°) (cal/mol deg)	—10 ± 8	—8 ± 2	—50 ± 10	—31 ± 10

^{a} Calculated from k_{-2} and K_{-2}.

from 0.3 to 0.5 mM. The determinations are also included in Table III. The indicated values of k_2 calculated from k_{-2} and K_2 are also given in Table III.

Upon the addition of chloride ion to the solutions of $Pt(en)(H_2O)_2^{2+}$ the replacement of the first chloride was substantially complete in a few seconds. The replacement of the second chloride was followed by conventional spectrophotometry. The system is predicted to approach equilibrium in accordance with the equation:

$$-d[Pt(en)(H_2O)Cl^+]/dt = k_{-1}[Cl^-][Pt(en)(H_2O)Cl^+] - k_1(a - [Pt(en)(H_2O)Cl^+]. \quad (9)$$

Solution of this rate equation yields:

$$\ln(A_\infty - A)/(A_\infty - A_o) = -(k_1 + k_{-1}[Cl])t = -t/\tau, \quad (10)$$

where $-1/\tau$ is the slope of the linear plot of ℓn $(A_\infty\text{-}A)/(A_\infty\text{-}A_o)$ *vs* t. From this slope,

$$k_{-1} = (1/\tau - k_1)/[Cl^-]. \quad (11)$$

The values for k_{-1} are also included in Table III. The ratio, k_1/k_{-1}, agree very satisfactorily with the values of K_1 from the titrations of equilibrium solutions. Although the uncertainties in the rate constants introduce rather large uncertainties in the activation enthalpies, it seems apparent that the first aquation process has a considerably higher enthalpy barrier than the second. The much lower activation enthalpy of the second aquation is nearly offset by its very large negative entropy. The comparison of the $Pt(en)Cl_2$ with the *cis*-$Pt(NH_3)_2Cl_2$ is especially interesting because of the similarity of bonding about the platinum atoms. The rate constant, k_1, for $Pt(en)Cl_2$ at 25° is 35% higher than the corresponding constant for $Pt(NH_3)_2Cl_2$. The rigidity of the ring would appear therefore to provide a moderate but definite enhancement for the attack by a water molecule along the axis normal to the plane of ligand bonds and the formation of the trigonal bipyramid coordination figure in the transition state. The equilibrium quotient, K_1 for the formation of the mono-aquo species for $Pt(en)Cl_2$ is only 0.66 as great as for *cis*-$Pt(NH_3)_2Cl_2$.

Earlier Panasyuk and Malashok[4] reported a value of 4.93×10^{-5} s^{-1} for k_1 at 25°C. This value was for an a of 0.5 mM and an ionic strength of 0.01 M. Their value was in moderate agreement with Banerjea, Basolo, and Pearson,[3] who reported 5.4×10^{-5} s^{-1}, but it was 45% higher than our value in Table III. The dependence of a rate constant upon ionic strength is expected to be related through the activity coefficients by the equation.[10]

$$k(\mu) = k^\circ \gamma_A \gamma_B / \gamma_{\neq} \quad (12)$$

where: k° is a rate constant at zero ionic strength, $\gamma_A\gamma_B$ represents the product of the reactants' activity coefficients, $\gamma_{\neq}$ is the activity coefficient for the transition complex.

According to Debye Huckel theory for electrolytes the γ's depend upon the large of the species and the ionic strength of the solution. Since aquation proceeds through a transition state in which the ionic charge of the transition complex is the same as the substrate species, only slight ionic strength effects are predicted. Hence the disagreement of the k_1 in the present work with the value Panashyuk and Malashok can not be attributed to an ionic strength effect. In their treatment of the kinetics they measured the appearance of chloride by titrations with $AgNO_3$ and a Ag-AgCl indicator electrode. The concentration of chloride in a system with no added chloride corresponds to our T variable. They plotted the logarithm of the function, $([Cl]_\infty - [Cl])/[Cl]_\infty$ *vs* time from between values of 0.90 and 0.45 and evaluated their k_1 from a straight line fitted to their points. A similar experimental technique was apparently also used by Banerjea, Basolo, and Pearson.

The four rate constants for reactions 1 and 2 were calculated for 25° and an ionic strength of 0.1 from the values in Table III with the use of equation (12). For each of the rate constants

$$\begin{aligned} k_1 &= k_1{}^0 \gamma_0{}^2/\gamma_0 \\ k_{-1} &= k^0{}_{-1}\gamma_1{}^2/\gamma_0 \\ k_2 &= k^0{}_2\gamma_1\gamma_0/\gamma_1 \\ k_{-2} &= k^0{}_{-2}\gamma_0\gamma_1/\gamma_1 \end{aligned} \quad (13)$$

were γ_0, γ_1, and γ_2 are for species with ionic changes of 0, ±1 or ±2 respectively.

The activity coefficient, γ_0, was taken as 1, γ_1 was taken from $\gamma\pm$ for hydrochloric acid in KCl,[11] and $\gamma_2/\gamma_1{}^2$ was set equal to $\gamma_{C_2O_4{}^{2-}}/\gamma_{HC_2O_4{}^-}\gamma_{Cl^-}$ from the potentiometric determination by Pinching and Bates[12] for the second ionization constant of oxalic acid. The indicated values for the rate constants at 25°, μ =

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(10) A.A. Frost and R.G. Pearson, « Kinetics and Mechanism », John Wiley and Sons, Inc., New York, 1953, p. 138.

(11) H.S. Harned and R.W. Ehlers, *J. Am. Chem. Soc.*, *55*, 2179 (1935).

(12) G.D. Pinching and R.G. Bates, *J. Research, Natl. Bur. Standards*, *40*, 405 (1948).

0.01 M are: $k_1 = 3.4 \times 10^{-5}$ s^{-1}, $k_{-1} = 2.4 \times 10^{-2}$ s^{-1} M^{-1}, $k_2 = 4.4 \times 10^{-5}$ s^{-1}, $k_{-2} = 5.5 \times 10^{-1}$ s^{-1} M^{-1}. With these constants the equilibrium state for $a = 0.5$ mM was calculated to be: $[Pt(en)(H_2O)Cl^+]$ = 0.33 mM; $[Pt(en)(H_2O)_2^+]$ = 0.060 mM, and T = 0.45 mM. The value of T/a is calculated to be 0,9 which gives the illusion that only a single aquation occurs which is nearly complete. The concentration of each species in an aquating system, $a = 0.5$ mM, was computed by a numerical integration of the differential rate equations by means of Runge-Kutta method[13] with the IBM 360-65 computer of the Iowa State Computer Center. A plot of the computed log $(1\text{-}T/T_\infty)$ is presented as the solid curve in Figure 3. This curve has a small but important curvature. The slope $d\ell n(1-T/T_\infty)/dt$ at zero time is k_1 or 3.4×10^{-5} s^{-1}. However, the dashed line in Figure 3 is drawn to intersect the curve at 0.90 and 0.45. It can be seen that the deviations of this line from the curve are not large and that an apparent good fit of data to a stranght line would be possible. The slope of the dashed line is 5.0×10^{-5} s^{-1}, very close to the reported value of Panasyuk and N. F. Malashok; and their data does appear to be in good agreement with the description of the system in the present work. Thus it appears necessary to consider the successive aquation steps as well as the approach to an equilibrium state in evaluating the rate constants to describe the kinetics system.

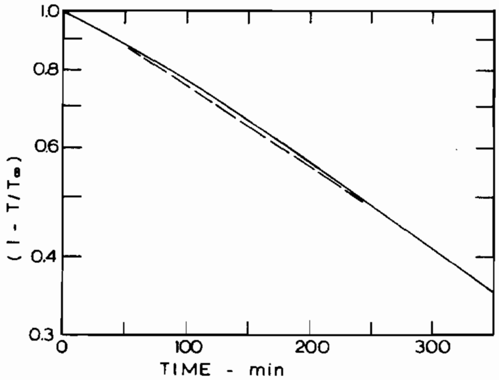

Figure 3. A plot of the function log $(1-T/T\infty)$ for an a of 0.5 mM, Ionic Strength of 0.01 M and 25°C as calculated from the rate constants in this paper with corrections for ionic strength. The straight dashed line connects the points for $1-T/T\infty$ of 0.90 and 0.45.

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(13) J.B. Scarborough, « Numerical Mathematical Analysis » 4th Ed., Johns Hopkins Press. Martimore, MD, 1958, pp. 314-319.