Inorganica Chimica Acta, 30 (1978) 29–34

Catalyzed Substitutions on Cationic Palladium(II) Complexes. III. Mercury(II) Catalyzed Displacement of Coordinated Thiocyanate and Selenocyanate Linkage Isomers

M. CUSUMANO, G. GUGLIELMO and P. MARRICCHI
Istituto di Chimica Fisica, Università di Messina, 98100 Messina, Italy
V. RICEVUTO*
Istituto di Chimica Generale, Università di Messina, 98100 Messina, Italy

Received November 22, 1977

A kinetic study of Hg^{2+} catalyzed solvolysis of linkage isomers $[Pd(AAA)XCN/NCX]^+$ (AAA = 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) and 4-methyl-1,1,7,7-tetraethyldiethylenetriamine ($MeEt_4$dien); X = S, Se) has been carried out in methanol at 25 °C. The kinetic results show that the catalytic efficiency of mercury(II) in removing the thiocyanate or selenocyanate ligands is greater in the Pd–XCN substrates than in the Pd–NCX ones, depending on whether the sulfur or selenium atom on which the attack by Hg^{2+} takes place, is bonded directly to palladium(II). The kinetic data for the isomerization and substitution reactions are also reported.

Introduction

Mercury(II) catalyzed aquation of octahedral systems containing coordinate halides and pseudohalides has been mostly studied to provide models for inner-sphere electron transfer reactions [1–5] and to obtain information about the nature of "five-coordinate" intermediates, [6, 7]. Referring to metal catalysis on square planar complexes of low spin d^8 metal ions recently we published a kinetic study of Hg^{II} and Cd^{II} catalyzed removal of coordinate halides from some sterically hindered palladium(II) complexes [8]. Analogous substrates containing N_3 or NO_2 as leaving groups undergo acid catalysis [9]. As part of a continuing study of the effect of metal ions on the rate and mechanism of solvolytic processes, we whish to report the kinetics of mercury(II) catalyzed solvolysis of substrates of the type $[Pd(AAA)XCN/NCX]^+$ (AAA = 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) and 4-methyl-1,1,7,7-tetraethyldiethylenetriamine ($MeEt_4$dien); X = S, Se) in methanol at 25 °C.

Experimental

Preparation of Complexes

$[Pd(Et_4dien)SCN]PF_6$, $[Pd(Et_4dien)SeCN]BPh_4$, $[Pd(Et_4dien)NCSe]BPh_4$ were prepared by following essentially the same procedures described in the literature [10–12].

$[Pd(Et_4dien)NCS]NO_3$ was prepared by reacting $[Pd(Et_4dien)Cl]Cl$ [13] with two equivalents of $AgNO_3$ in methanol under magnetic stirring for 24 hr at room temperature. AgCl was filtered off and the remaining solution was reacted with one equivalent of NaSCN and concentrated under vacuum to a small volume. The mixture, upon cooling, gave the final product which was isolated by filtration and recrystallized from methanol *Anal.* Calc. % for $PdC_{13}H_{29}N_5O_3S$: C = 35.31; H = 6.61; N = 15.84. Found: C = 34.98; H = 6.12; N = 15.26%.

The infrared spectrum of this complex is consistent with an M–NCS linkage showing a broad intense C–N stretching band at 2087 cm^{-1} (Nujol mull) [11, 14].

$[Pd(MeEt_4dien)NCS]PF_6$ was obtained by reacting $[PdMeEt_4dienCl]PF_6$ [13] with one equivalent of $AgNO_3$ in methanol. The solution was stirred for 36 hr at room temperature; after which AgCl was removed and the solution reacted with one equivalent of NaSCN. After concentration, upon cooling the mixture gave the complex $[Pd(MeEt_4dien)NCS]PF_6$ which was isolated by filtration and recristallized from methanol. *Anal.* Calcd. % for $PdC_{14}H_{31}N_4SPF_6$: C = 31.14; H = 5.79; N = 10.38. Found: C = 32.70; H = 5.18; N = 10.12%. The complex exhibits an intense, broad C–N stretching band at 2088 cm^{-1} [14].

All the compounds were characterized through their u.v. [10, 11, 15] and i.r. [10, 11, 14, 16] spectra. The molar conductivities in methanol at 18 °C are in the range 80–100 Ω^{-1} cm^2 mol^{-1} and are

0020-1693/78/0030-0029$2.25

consistent with those of 1:1 electrolytes [17]. We were not able to obtain as pure compounds either the adducts of the complexes with Hg^{++} or the solvolysis products $[Pd(AAA)MeOH]X_2$ ($X = ClO_4$, PF_6 or BPh_4).

The spectral characteristics in the u.v. region of solvo derivatives are identical to those already reported [8, 9, 18]. Standard methanolic solutions of $Hg(ClO_4)_2$ were prepared according to the procedure previously described [8]. Methanol was purified by distillation after heating under reflux over $Mg(OMe)_2$. All other products were reagent grade.

Kinetics

The rates of mercury(II) catalyzed processes as well as the Br^- substitutions were followed by standard spectrophotometric techniques using either an OPTICA CF 4 R recording apparatus or a Beckman D.U. instrument equipped with a Saitron 301 photometer and a Servogor S potentiometric recorder. The reactions were carried out at 25 °C keeping the ionic strength constant at 0.4 *M* by adding $LiClO_4$. In addition a constant excess of perchloric acid (0.1 *M*) was maintained in the kinetics with Hg^{2+}. To provide pseudo-first-order conditions a sufficient excess of reagent was used and the pseudo-first-order rate constants k_{obsd} (s^{-1}) were calculated from the slope of the semilogarithmic plots of $\log(D_T - D_\infty)$ against time. The starting solutions of $[Pd(Et_4dien)SCN]^+$ and $[Pd(Et_4dien)SeCN]^+$ were prepared by dissolving the appropriate amounts in methanol and stored at −20 °C. Fixed volumes of these solutions were thermostatted for about ten minutes and then injected into the reaction cell (under these experimental conditions the degree of isomerization proved to be negligible). Methanol solutions of $[Pd(Et_4dien)NCSe]^+$ were obtained from the corresponding Pd–SeCN linkage isomer and were used once spectrophotometric evidence showed the isomerization had completely taken place.

The Br^- substitution reactions of $[Pd(Et_4dien)SCN]^+$ were tested by the graphical method of Coleman *et al.* [19]. Using the appropriate absorbance matrix it was found that the condition of zero value for any 3 × 3 determinant related to the presence of only two absorbing species was not maintained. It is reasonable (see discussion below) to assume that three absorbing species are involved in these reactions, namely the S-bonded substrate, the N-bonded isomer and the bromide product.

TABLE I. The Mercury(II) Catalyzed Solvolysis of $[Pd(AAA)X]^+$ at 25 °C in Methanol. Dependence of pseudo-first-order rate constants, k_{obsd}, on the metal ion concentration at ionic strength $\mu = 0.4$ *M*.

Complex	$10^3\ [Hg^{2+}]$, *M*	k_{obsd} (s^{-1})
$[Pd(Et_4dien)SCN]^+$	3	2.2×10^{-3}
	5	3.6 "
	5	3.8 "
	6	4.5 "
	7.5	5.4 "
	10	7.25 "
$[Pd(Et_4dien)SeCN]^+$	3	8.0×10^{-2}
	6	16.2 "
	7.5	20.7 "
	9	24.9 "
	10	27.7 "
	12	32.5 "
$[Pd(Et_4dien)NCS]^+$	5	3.53×10^{-2}
	6	3.83 "
	9	3.72 "
	10	3.43 "
	12	3.77 "
	30	3.64 "
	60	3.46 "
	100	3.71 "
$[Pd(Et_4dien)NCSe]^+$	3	8.0×10^{-2}
	6	8.4 "
	9	8.2 "
	12	8.7 "
	15	8.5 "
	30	8.4 "
$[Pd(MeEt_4dien)NCS]^+$	3	1.31×10^{-2}
	5	1.36 "
	9	1.36 "
	10	1.26 "
	12	1.34 "
	30	1.39 "
	60	1.30 "
	100	1.39 "

The contribution of each species to the total absorption at time t can be evaluated by solving equation systems of the type:

$$A_{\lambda_1} = \sum_i \epsilon_{i\lambda_1} \cdot C_i$$

$$A_{\lambda_2} = \sum_i \epsilon_{i\lambda_2} \cdot C_i$$

$$C_{tot} = \sum_i C_i$$

in which A_{λ_1} and A_{λ_2} are the total absorbances at the wavelength λ_1 and λ_2, $\epsilon_{i\lambda_1}$ and $\epsilon_{i\lambda_2}$ the molar extinction coefficients of the i species and C_i the molar concentrations of the i species. C_{tot} is equal to the initial concentration. The rates at which the S-bonded species disappears were determined from the slopes of the linear plots of $\ln C_{Pd-S}$ *vs.* time. The rates of isomerization Pd–XCN → Pd–NCX were measured by following the changes in the optical density at 340 and 350 nm of solutions containing initially the Pd–SCN and Pd–SeCN respectively.

The ionic strength was kept constant (0.4 *M*) using $LiClO_4$. The data gave good linear semiloga-

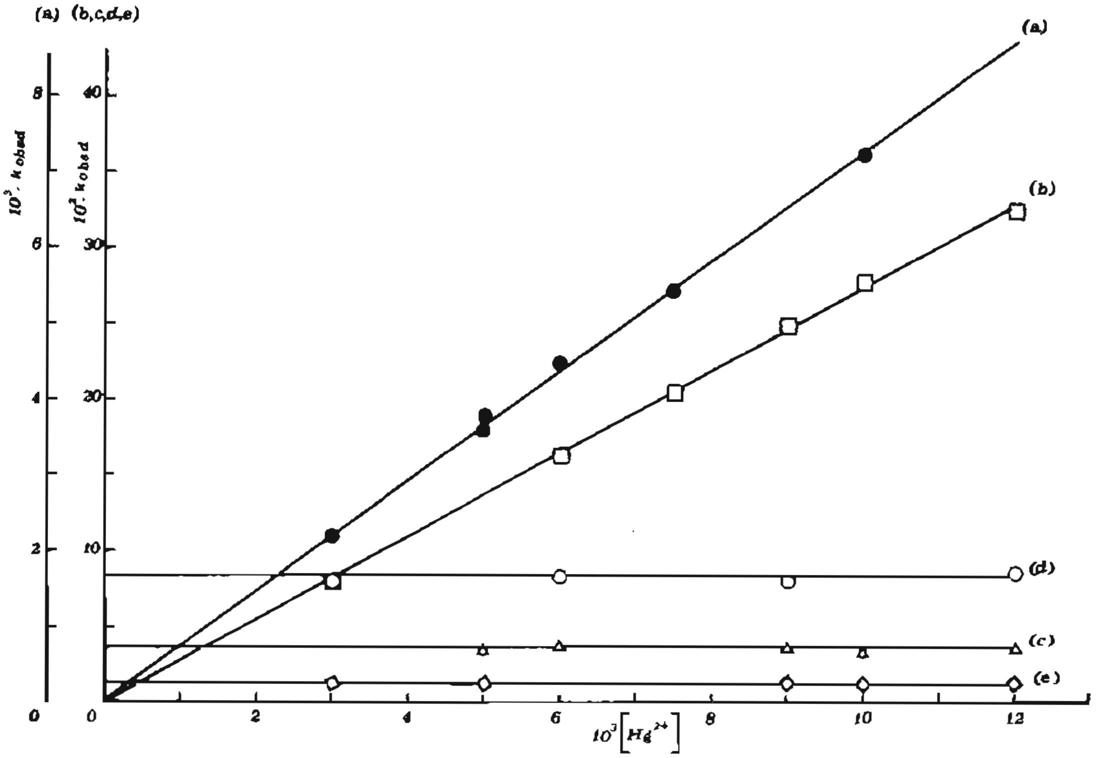


Figure 1. Dependence of pseudo-first-order rate constants, k_{obsd} (s^{-1}), on the concentration of mercury(II) in the reaction $[Pd(AAA)X]^+ + Hg^{2+} + MeOH \rightarrow [Pd(AAA)MeOH]^{++} + HgX^+$ in methanol at 25 °C, $\mu = 0.4$ *M*. a) $[Pd(Et_4dien)SCN]^+$; b) $[Pd(Et_4dien)SeCN]^+$; c) $[Pd(Et_4dien)NCS]^+$; d) $[Pd(Et_4dien)NCSe]^+$; e) $[Pd(MeEt_4dien)NCS]^+$.

rithmic plots from which the first order rate constants k_i (s^{-1}) were estimated.

Results and Discussion

Catalyzed Solvolysis

The values of pseudo-first-order rate constants, k_{obsd} (s^{-1}), for the reactions:

$$[Pd(AAA)XCN/NCS]^+ + Hg^{2+} + MeOH \longrightarrow [Pd(AAA)MeOH]^{++} + HgXCN^+ \qquad (1)$$

(X = S, Se) are recorded in Table I. The kinetic behaviour of these reactions is completely different according to whether the fourth ligand of the complex is coordinated to the central metal ion through the nitrogen or through sulfur or selenium. By adding the Hg^{++} metal ion in solution, the N-bonded substrates undergo an instantaneous change in the u.v. spectrum followed by a slow reaction towards the solvo derivative during which well defined isosbestic points were maintained at 326, 328 and 334 nm for $[Pd(Et_4dien)NCSe]^+$, $[Pd(Et_4dien)NCS]^+$ and $[Pd(MeEt_4dien)NCS]^+$ respectively.

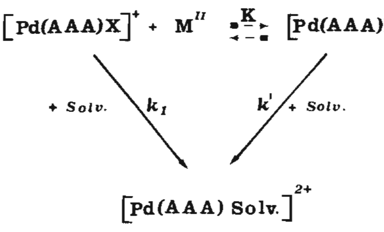
In these cases no dependence on the metal concentration was found (Figure 1) and the rate law is:

$$-d[Complex]/dt = k'[Complex] \qquad (2)$$

On the contrary the Pd–XCN complexes react with a gradual spectral change; the plots of k_{obsd} *vs.* $[Hg^{2+}]$ are straight lines with no intercept (Figure 1) throughout the metal concentration range examined and the rate law is:

$$-d[Complex]/dt = k_{(Hg^{2+})}[Hg^{2+}][Complex] \qquad (3)$$

The catalytic efficiency of Hg^{2+} and Cd^{2+} in the analogous complexes $[Pd(AAA)X]^+$ (X = Cl, Br, I) has been ascribed to the affinity of the metal ions for the coordinate halide [8]. The first-order rate dependence on the metal ion concentration has been rationalized in terms of a mechanism involving the formation of binuclear adducts of the type Pd–X–M, in equilibrium with the substrate. Similarly, the kinetic results for mercury(II) catalyzed displacement of coordinate thiocyanate and selenocyanate linkage isomers can be accounted for by the general reaction scheme:



Scheme 1 X= SCN or NCS; SeCN or NCSe

k_1 and k' are the rate constants for the attack of MeOH on the substrate and the adduct and K is the stability constant for formation of the binuclear adduct. The formation of such adducts has been well established in the reactions of cobalt(III) or chromium(III) bound thiocyanate ion with mercury(II) [5, 20]. Complexes of the type $[CoM(NCS)_4]xL$ (M = Zn(II), Cd(II) or Hg(II)) have been prepared and characterized [21]. The rate-law relative to scheme 1 is:

$$k_{obsd} = \frac{k_1 + k'K[M^{++}]}{1 + K[M^{++}]} \qquad (4)$$

Such an equation allows us to discuss the obtained results for two limiting cases related to the kinetic behaviour of the mercury(II) catalyzed solvolysis of the Pd–NCX and Pd–XCN substrates, in the range of examined metal ion concentration. In the reactions of the Pd–NCS linkages the metal ion can better exert its affinity attacking the free sulfur or selenium of the pseudo-halide coordinated to palladium and the equilibrium in the scheme lies completely on the right. The initial change of absorbance can consequently be associated to the easy formation of the adduct Pd–NCX– – –Hg which collapses to the solvo derivative through the breaking of the Pd–N bond in k' step. Taking into account that the k_1 term is negligible and the product $K[Hg^{2+}] >> 1$, equation [4] reduces to the simpler form $k_{obs} = k'$, equal to expression [2]. If such a mechanism is operative the palladium–nitrogen bond-breaking should not be very dependent on the nature of X (S or Se) bonded to the mercury(II). The values of k' (Table III) of the same order of magnitude are in agreement with this assumption. The Pd–NCX substrates represent the only case in which it is possible to make a comparison of the values k_1 and k' related to the attack of the solvent on the starting substrate and the adduct. Considering the results relative to the two complexes $[Pd(Et_4dien)NCS]^+$ and $[Pd(MeEt_4dien)NCS]^+$, the ratios of spontaneous solvolysis, $k_{1Et_4dien}/k_{1MeEt_4dien}$ as well as that of catalyzed solvolysis, $k'_{Et_4dien}/k'_{MeEt_4dien}$ are about the same being 2.25 and 2.71 respectively. It is of interest to note that these values

TABLE II. Pseudo-first-order Rate Constants, k_{obsd}, for the Reactions $[Pd(AAA)XCN/NCX]^+ + Br^- \rightarrow [Pd(AAA)Br]^+ + XCN^-$ (X = S, Se) in Methanol at 25 °C, μ = 0.4 *M*.

Complex	$10^2[Br^-]$, *M*	$10^5\ k_{obsd}$
$[Pd(Et_4dien)SCN]^+$	1	2.3
	5	3.5
	10	4.8
	25	8.7
	40	12.3
$[Pd(Et_4dien)SeCN]^+$	1	3.4
	5	5.4
	10	8.0
	25	15.9
	40	24.0
$[Pd(Et_4dien)NCS]^+$	1	1.10
	5	1.12
	10	1.09
	40	1.10
$[Pd(Et_4dien)NCSe]^+$	1	3.94
	5	4.05
	10	4.00
	40	4.00
$[Pd(MeEt_4dien)NCS]^+$	1	0.48
	5	0.49
	10	0.48
	40	0.50

parallel those found by Baddley and Basolo [13] in substitution reactions of the same axially blocked halide complexes in which the rate is independent of the reagent concentration. The constancy of the ratios allows us to convalidate the assumption previously made [8] that the two leaving groups -NCS and -NCS-Hg are affected in a completely analogous manner by the replacement of hydrogen of N–H bond with a methyl group in the substrates considered. This indicates that the mechanism of these reactions is not influenced by the nature and size of the leaving group.

As far as the catalyzed solvolysis of non linear [11] Pd–XCN substrates is concerned the equilibrium in the scheme is well over to the left as can be argued by the identity of the spectrum of the starting substrate $[Pd(Et_4dien)SCN]^+$ with that of the reaction mixture at low temperature (the slowest reactions of this series).

Being $K \times [M^{++}] << 1$, equation [4] becomes:

$$k_{obsd} = k_1 + k_{(M^{++})}[M^{++}] \qquad (5)$$

in which $k_{(M^{++})}$ is a composite term given by the product $k' \times K$. As said above the straight lines of Figure 1 for the Pd–XCN complexes are passing through the origin; it means that in these cases the

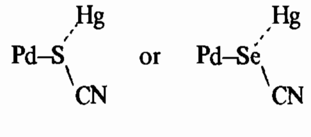
TABLE III. Kinetic Data for Uncatalyzed and Mercury(II) Catalyzed Solvolysis of $[Pd(AAA)XCN/NCX]^+$ in Methanol at 25 °C, $\mu = 0.4$ *M*.[a]

Complex	10^5 k_1 s^{-1}	10^2 k' s^{-1}	$k_{(Hg^{2+})}$ M^{-1} s^{-1}
$[Pd(Et_4dien)NCS]^+$	1.10 ± 0.01	3.64 ± 0.15	–
$[Pd(Et_4dien)NCSe]^+$	4.00 ± 0.00	8.36 ± 0.27	–
$[Pd(MeEt_4dien)NCS]^+$	0.49 ± 0.09	1.34 ± 0.05	–
$[Pd(Et_4dien)SCN]^+$	2.18 ± 0.09	–	0.71 ± 0.02
$[Pd(Et_4dien)SeCN]^+$	2.77 ± 0.06	–	27.60 ± 0.45

[a] Values obtained by least squares treatment.

k_1 value for the spontaneous solvolysis is irrelevant with respect to that referring to metal catalyzed process. The k_1 values 2.18×10^{-5} and 2.77×10^{-5} obtained in the nucleophilic substitution reactions with Br^- of $[Pd(Et_4dien)SCN]^+$ and $[Pd(Et_4dien)SeCN]^+$ respectively, support this assumption. The slopes of straight lines give the values of the rate constants for the mercury-catalyzed solvolysis, $k_{(Hg^{2+})}$, reported in Table III.

The data reveal that the catalytic efficiency of Hg^{2+} in removing the thiocyanate and selenocyanate ligands from the coordination sphere of palladium(II) in the S or Se-bonded complexes is greater than that related to the N-bonded ones. This may be due to the fact that in the Pd–XCN substrates the attack by Hg^{2+} takes place on the sulfur or selenium donor atoms causing a greater labilization of the leaving group. Since the values of specific rate constant for the uncatalyzed solvolytic path for both the substrates $[Pd(Et_4dien)SCN]^+$ and $[Pd(Et_4dien)SeCN]^+$ are about the same, the observed differences in the $k_{(Hg^{2+})}$ values must be attributed to a different stability of the two adducts



leading to the final solvo derivative. In the case of Pd–SeCN complex, because of relief of steric strain and spreading of ethyl groups [22] the bulky Se-atom is less shielded to the attack by Hg^{2+} ion and the formation of the intermediate could be easier. On the basis of the rate law found, an alternative mechanism involving as rate determining step an electrophilic attack by Hg^{2+} cannot be excluded. However the circumstance that a mechanism such as that in the scheme has been proved to be operative in the case of the parent halide compounds [8] and the unmistakable evidence of adduct formation for the N-bonded substrates are clear indications in favour of the pre-equilibrium shown in the general reaction scheme.

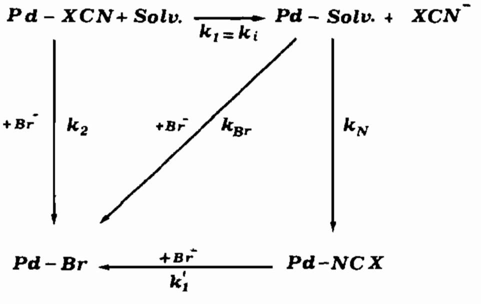
Linkage Isomerization and Nucleophilic Displacement

The nucleophilic substitution reactions of the Pd–XCN complexes with bromide ion follow the rate law $k_{obsd} = k_1 + k_2[Br^-]$, as shown by straight lines obtained when the rate constants (Table II) are plotted against $[Br^-]$. In the case of Pd–NCX substrates the k_2 term disappears and the reactions proceed through the solvolytic path only. The kinetic data of substitution reactions together with those of linkage isomerization are collected in Table IV. The kinetic behaviour of these series of reactions can be explained looking at the following scheme:

TABLE IV. Kinetic Data for the Isomerization and Substitution Reactions of $[Pd(AAA)XCN/NCX]^+$ in Methanol at 25 °C, $\mu = 0.4$ *M*.[a]

Complex	10^5 k_i s^{-1}	10^5 k_1 s^{-1}	10^5 k_2 M^{-1} s^{-1}
$[Pd(Et_4dien)SCN]^+$	2.0	2.18 ± 0.09	25.50 ± 0.41
$[Pd(Et_4dien)SeCN]^+$	3.2	2.77 ± 0.06	52.90 ± 0.3
$[Pd(Et_4dien)NCS]^+$	–	1.10 ± 0.01[b]	0
$[Pd(Et_4dien)NCSe]^+$	–	4.00 ± 0.00[b]	0
$[Pd(MeEt_4dien)NCS]^+$	–	0.49 ± 0.09[b]	0

[a] Values obtained by least squares treatment. [b] Values of k'_1.



Scheme 2

in which a solvento intermediate is formed in the k_1 step, the fate of which will depend on the competition between the re-entry of the ligand through the nitrogen tooth leading to the isomerization and the bromide ion attack in the k_{Br} path. k'_1 is related to the usual solvent assisted substitution mechanism on pseudo-octahedral complexes. The coincidence of the values of k_1 and k_i (see Table IV) indicates quite clearly that the formation of the solvento intermediate is rate limiting both for the solvolysis and isomerization [10, 23]. The accumulation of N-bonded isomer, as argued from the analysis of curves applying the equation systems (see Experimental), decreases with increasing bromide concentration. In the case of the S-bonded substrate the accumulation is favoured since $k'_1 < k_1$ (1.1×10^{-5} s^{-1} *vs.* 2.1×10^{-5} s^{-1} respectively); the contrary occurs for the Se-bonded complex in which $k'_1 > k_1$ (4.0×10^{-5} s^{-1} *vs.* 2.8×10^{-5} s^{-1}). It is interesting to note that the Br^- substitution reactions of the thiocyanate and selenocyanate substrates show a well definite k_2 term.

This is further evidence that the kinetic behaviour of the sterically hindered complexes is not general [13, 18, 22–25] and needs to be reconsidered.

Acknowledgment

This work was supported by the Italian Consiglio Nazionale delle Ricerche (C.N.R.), Rome. The authors wish to thank Dr. R. Romeo for helpful discussions.

References

1 J. P. Candlin and J. Halpern, *Inorg. Chem., 4,* 1086 (1965).
2 J. H. Espenson and S. R. Hubbard, *Inorg. Chem., 5,* 686 (1966).
3 C. Bifano and R. G. Linck, *Inorg. Chem., 7,* 908 (1968).
4 J. P. Birk, *Inorg. Chem., 9,* 735 (1970).
5 L. C. Falk and R. G. Linck, *Inorg. Chem., 10,* 215 (1971).
6 D. A. Buckingam, I. I. Olsen and A. M. Sargeson, *Inorg. Chem., 6,* 1807 (1967).
7 G. E. Dolbear and H. Taube, *Inorg. Chem., 6,* 60 (1967).
8 M. Cusumano, G. Guglielmo, V. Ricevuto, R. Romeo and M. Trozzi, *Inorg. Chim. Acta, 17,* 45 (1976).
9 M. Cusumano, G. Guglielmo, V. Ricevuto, R. Romeo and M. Trozzi, *Inorg. Chim. Acta, 16,* 135 (1976).
10 F. Basolo, W. H. Baddley and K. S. Weidenbaum, *J. Am. Chem. Soc., 88,* 576 (1966).
11 J. L. Burmeister, H. J. Gysling and J. C. Lim, *J. Am. Chem. Soc., 91,* 44 (1969).
12 J. L. Burmeister and J. H. Gysling, *Chem. Comm.,* 543 (1967).
13 W. H. Baddley and F. Basolo, *J. Am. Chem. Soc., 88,* 2944 (1966).
14 J. L. Burmeister, R. L. Hassel, K. A. Johnson and J. C. Lim, *Inorg. Chim. Acta, 9,* 23 (1974).
15 D. J. Hewkin and A. J. Poë, *J. Chem. Soc. A,* 1884 (1967).
16 J. L. Burmeister and J. C. Lim, *Chem. Comm.,* 1346 (1968).
17 W. J. Geary, *Coordination Chem. Rev., 7,* 81 (1971).
18 J. B. Goddard and F. Basolo, *Inorg. Chem., 7,* 936 (1968).
19 J. S. Coleman, L. P. Varga and S. H. Mastin, *Inorg. Chem., 9,* 1015 (1970).
20 M. Orhanovic and N. Sutin, *J. Am. Chem. Soc., 90,* 4286 (1968).
21 P. P. Singh and S. A. Khan, *Inorg. Chim. Acta, 14,* 143 (1975).
22 Karen A. Johnson, J. C. Lim and J. L. Burmeister, *Inorg. Chem., 12,* 124 (1973).
23 R. Roulet and H. B. Gray, *Inorg. Chem., 11,* 2101 (1972).
24 J. B. Goddard and F. Basolo, *Inorg. Chem., 7,* 2457 (1968).
25 D. A. Palmer and H. Kelm, *Inorg. Chim. Acta, 14,* L27 (1975).