steric repulsions in the adduct. The studies of Tamres, *et al.*,[25] indicate that steric effects are very common in BF_3 adducts. These authors believed F strain was minimal in tetrahydrofuran (THF), and it should also be small in the BF_3–$CH_3C(O)OC_2H_5$ adduct. Using the gas-phase enthalpies of adduct formation of BF_3 with the donors THF, ethyl acetate, and dimethyl ether, we calculate E_A and C_A parameters of 11.6 and 1.98, respectively. These should be regarded as tentative in view of the limited amount of enthalpy data on BF_3 systems in which steric effects can be assumed to be minor. Since two enthalpies are needed to calculate E and C, we have only one check. The parameters reported for diethyl ether were taken for dimethyl ether, since those for the latter have not been evaluated. This assumption is based on the similarity of the E and C values for the analogous methyl- and ethylamines. The reported enthalpy of formation of the BF_3 adduct of diethyl ether is 2 kcal/mol lower than that of dimethyl ether[24] suggesting the likelihood of steric problems in the diethyl ether adduct. The calculated and experimental values are listed in Table III.

TABLE III
CALCULATED AND EXPERIMENTAL ENTHALPIES OF FORMATION OF BF_3 ADDUCTS

Donor	E_B	C_B	$\Delta H°$, kcal/mol Calcd	$\Delta H°$, kcal/mol Exptl
$(CH_3)_2O$[a]	0.65	3.55	−14.6	−13.7
$CH_3C(O)OC_2H_5$	0.83	1.67	13.1	−12.8
$(CH_2)_4O$	0.61	4.69	−16.4	−16.8

[a] E_B and C_B are the $(C_2H_5)_2O$ parameters.

The E_B and C_B parameters for $(C_2H_5)_2S$ when combined with E_A and C_A for BF_3 lead to a calculated enthalpy of −15.2 kcal/mol. This is in contrast with an experimental enthalpy of −2.9 kcal/mol. A tentative explanation that can be offered at present is a steric repulsion of the large sulfur atom and fluorines of BF_3. More thermodynamic data on carefully designed systems are needed before the behavior of BF_3 as an acid can be understood and be incorporated into the correlation with confidence.

Acknowledgment.—The authors wish to thank the National Science Foundation for their generous support of this research through Grant GP-5498.

(25) D. E. McLaughlin, M. Tamres, S. Searles, and S. Nukina, *J. Inorg. Nucl. Chem.*, **17**, 112 (1961).

CONTRIBUTION FROM ISTITUTO DI CHIMICA GENERALE ED INORGANICA, II SEZIONE,
UNIVERSITÀ DI PADOVA, PADUA, ITALY

Nucleophilicity of Thioethers toward Neutral Platinum(II) Complexes

BY L. CATTALINI, M. MARTELLI, AND G. KIRSCHNER

Received February 5, 1968

The kinetics of the nucleophilic displacement of the ligand X from complexes of the type Pt(bipy)(C)X (C, X = Cl, Cl; N_3, Cl; NO_2, Cl; NO_2, NO_2; NO_2, N_3) by thioethers (RSR′) have been measured in methanol at 25°. The results permit the discussion of the effect of the nature of the entering group, of the leaving group, and of the *cis* effect. The rates of these reactions are compared with those of the same substrates with other reagents under the same experimental conditions and the differences are discussed in terms of the different role of the bond-making and bond-breaking aspects of the substitution in the intimate mechanism.

Introduction

The kinetics of ligand displacement in planar complexes of d^8 transition metal ions, particularly platinum(II) derivatives, have been studied extensively in the past few years.[1,2] It was suggested[3] that the intimate mechanism of square-planar substitution corresponds to an association between the substrate and the entering group to produce a labile intermediate of higher coordination number which then dissociates to give the four-coordinate product. There has been indirect evidence to support this hypothesis[4–6] but the only direct kinetic evidence was obtained[7] with a peculiar planar rhodium(I) complex. Therefore, in the majority of the cases, it is still necessary to decide whether the formation of the new bond (increase of coordination) or the breaking of the old one (decrease of coordination) is more important in controlling the rate of the reaction.

In order to elucidate this point we decided to investigate the kinetic behavior of thioethers acting as nucleophiles toward planar complexes, since the sulfur donors are expected to be relatively soft[8] and could favor the formation of relatively stable intermediates when interacting with soft reaction centers, such as platinum(II) complexes. There are data in the literature concerning the reactions of complexes of the type Pt(bipy)(C)X with a variety of reagents, which enable one to discuss (a) the effect of the nature of the leaving

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(1) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

(2) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967.

(3) H. B. Gray, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 103.

(4) U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966); U. Belluco, M. Graziani, M. Nicolini, and P. Rigo, *ibid.*, **6**, 721 (1967).

(5) L. Cattalini, A. Orio, and M. L. Tobe, *J. Am. Chem. Soc.*, **89**, 3130 (1967).

(6) L. Cattalini and M. Martelli, *Gazz. Chim. Ital.*, **97**, 498 (1967).

(7) L. Cattalini, R. Ugo, and A. Orio, *J. Am. Chem. Soc.*, in press.

(8) R. G. Pearson, *ibid.*, **85**, 3533 (1963).

group X[6] and (b) the effect of the anionic ligand, C, *cis* to the leaving group.[9] Therefore, we have studied reactions of the type

$$\mathrm{Pt(bipy)(C)X + RSR' \longrightarrow Pt(bipy)(C)(RSR')^+ + X^-} \quad (1)$$

for five separate complexes and five thioethers. The kinetics were followed under the same experimental conditions (methanol, 25°) and the results are reported and discussed in this paper.

Results

Examination of the changing spectrum of a methanolic solution originally containing the starting complex and the excess thioether shows, through the development of well-defined isosbestic points, that a single-stage process is involved. The final product has been isolated in the case of the reaction of $Pt(bipy)Cl_2$ with $(C_2H_5)_2S$ (see Experimental Section) and the analysis indicates that only one chloride is replaced by $(C_2H_5)_2S$. The spectrum of a pure sample of $Pt(bipy)Cl(C_2H_5)_2S^+$ corresponds exactly to that of the reaction mixture at the end of the reaction and is quite different from the initial spectrum, which is that of the complex $Pt(bipy)Cl_2$.

Although the reaction product has only been isolated and examined in this one case, we have assumed that all of the reactions proceed according to eq 1. Further proof has been obtained in the case of $C_6H_5SCH_2$, where the kinetics have also been followed by conductivity measurements. The initial molar conductivity is very small, as one would expect for a nonionic system, but increases with time in a first-order fashion to reach the value of 89 ohm^{-1} cm^{-1}, which is very close to that of 1:1 electrolyte under these conditions (5×10^{-4} *M*). The use of the conductivity to follow the reaction was necessary in the case of $C_6H_5SCH_3$ at higher concentrations, since the reagent absorbed strongly in the uv region. Some of the kinetic runs were repeated spectrophotometrically and the agreement between the rate constants obtained by the two methods was excellent.

The reactions were carried out in the presence of a large excess of the entering reagent, in order to provide pseudo-first-order conditions. The kinetics were followed spectrophotometrically in the range 270–360 mμ and the rate constants (k_{obsd}) were obtained from the plot of log ($D_t - D_\infty$) *vs.* time, where D_t and D_∞ are the optical densities of the reaction mixture, at a wavelength where there is an adequate variation, at time *t* and at the end of the reaction, respectively. The first-order rate constants obtained in the kinetic runs are summarized in Table I.

Discussion

The second-order rate constants (k_2) for the bimolecular attack by the thioethers were determined from the slope of the plot of k_{obsd} against [RSR′] and are collected in Table II. They permit, in conjunction with data from the literature, discussion of three effects, namely, (i) the nature of the entering reagent, (ii) the nature of the leaving group, and (iii) the nature of the ligand *cis* to the leaving group.

The Effect of the Entering Group.—The logarithm of the second-order rate constants for each of the substrates reacting with the thioethers are plotted, in Figure 1, against the sum of the Taft σ^* values ($-\Sigma\sigma^*$),[10] reported also in Table II, relative to the radicals R and R′ bonded to the sulfur atom. The linear relationship between log k_2 and the inductive effects of R and R′ shows the importance of the σ-donor properties in determining the reactivity. It also implies that steric hindrance effects do not play any significant role in these reactions.

The fact that alkyl and aryl sulfides lie on the same straight line (Figure 1) might be taken as evidence that π interaction between the sulfur and platinum atoms is not important in this situation. This is in accord with other observations relative to the kinetic behavior of thioethers toward complexes of metals other than platinum(II)[11] and also with nonkinetic evidence.[12–14]

With $Pt(bipy)Cl_2$ as substrate it is possible to compare the rates of the reactions with the series of thioethers with those obtained with a series of amines. The kinetics of the processes

$$\mathrm{Pt(bipy)Cl_2 + am \longrightarrow Pt(bipy)(am)Cl^+ + Cl^-}$$

were studied under the same experimental conditions[15] (methanol, 25°) and it was found that the second-order rate constants for amines having the same form of steric hindrance are related to their basicity (pK_a in water as a standard measure of the basicity), by the expression

$$\log k_2 = 0.06(pK_a) + \text{constant} \quad (2)$$

Since Hall has shown[16] that the basicity of amines of the same type can be related to the sum of the Taft σ^* values of the radicals bonded to the nitrogen atom by the equation

$$pK_a = -3.2(\textstyle\sum\sigma^*) + \text{constant} \quad (3)$$

and the difference between the various classes of amines is mainly reflected in the value of the constant, eq 2 can be written in the form

$$\log k_2 = -0.19(\textstyle\sum\sigma^*) + \text{constant} \quad (4)$$

which can be compared with the corresponding expression

$$\log k_2 = -1.23(\textstyle\sum\sigma^*) + \text{constant} \quad (5)$$

for the reactions

$$\mathrm{Pt(bipy)Cl_2 + RSR' \longrightarrow Pt(bipy)Cl(RSR')^+ + Cl^-}$$

It seems reasonable to interpret the greater influence of the inductive effects of radicals bonded to sulfur

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[9] L. Cattalini and M. Martelli, *Inorg. Chim. Acta*, **1**, 189 (1967).

[10] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965.

[11] L. Cattalini, *et al.*, unpublished results.

[12] R. Backhouse, M. E. Foss, and R. S. Nyholm, *J. Chem. Soc.*, 1714 (1957).

[13] G. Dyer and D. W. Meek, *Inorg. Chem.*, **4**, 1398 (1965).

[14] G. Dyer, M. O. Workman, and D. W. Meek, *ibid.*, **6**, 1404 (1967).

[15] L. Cattalini, A. Orio, and A. Doni, *ibid.*, **5**, 1517 (1966).

[16] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5442 (1957).

TABLE I

FIRST-ORDER RATE CONSTANTS (k_{obsd}) FOR PROCESS 1 IN METHANOL AT 25°[a]

Process	RSR′	10^2[RSR′], *M*	10^3k_{obsd}, sec^{-1}
(a) $Pt(bipy)Cl_2 + RSR' \longrightarrow Pt(bipy)Cl(RSR')^+ + Cl^-$	n-$C_4H_9SC_2H_5$	0.88	1.3
		2.2	3.15
		4.4	6.25
		0.5	0.7
	$C_2H_5SC_2H_5$	0.4	0.5
		0.75	1.0
		1.9	2.5
		3.3	4.25
	$C_2H_5SCH_3$	0.58	0.55
		2.9	2.75
		5.8	5.6
	$ClCH_2CH_2SCH_3$	0.9	0.25
		4.5	1.1
		9.0	2.3
	$C_6H_5SCH_3$	1.5	0.21
		1.5	0.215[b]
		2.0	0.3[b]
		7.5	1.1[b]
(b) $Pt(bipy)(NO_2)Cl + RSR' \longrightarrow Pt(bipy)(NO_2)(RSR')^+ + Cl^-$	n-$C_4H_9SC_2H_5$	0.7	2.6
		3.5	12.3
		7.0	25
	$C_2H_5SC_2H_5$	0.25	0.85
		0.5	1.55
		0.75	2.2
		5.0	14.2
	$C_2H_5SCH_3$	2	3.2
		10	16
		20	31.5
	$ClCH_2CH_2SCH_3$	1.13	0.255
		5.65	0.61
		11.3	1.08
	$C_6H_5SCH_3$	3.1	0.24
		3.1	0.23[b]
		15.5	0.53[b]
		23	0.7[b]
		31	0.915[b]
(c) $Pt(bipy)(N_3)Cl + RSR' \longrightarrow Pt(bipy)(N_3)(RSR')^+ + Cl^-$	n-$C_4H_9SC_2H_5$	0.098	0.36
		0.197	0.72
		0.492	1.83
		0.985	3.64
	$C_2H_5SC_2H_5$	0.09	0.28
		0.9	2.9
		0.68	2.25
		0.45	1.49
	$C_2H_5SCH_3$	0.09	0.26
		0.3	0.95
		0.68	2.25
		0.9	2.9
	$ClCH_2CH_2SCH_3$	0.1	0.2
		0.2	0.35
		0.5	1.0
		1.0	1.92
	$C_6H_5SCH_3$	0.1	0.2
		0.1	0.19[b]
		0.255	0.45[b]
		0.53	0.85[b]
		1.06	1.7[b]
(d) $Pt(bipy)(NO_2)_2 + RSR' \longrightarrow Pt(bipy)(NO_2)(RSR')^+ + NO_2^-$	n-$C_4H_9SC_2H_5$	0.07	0.072
		0.175	0.18
		0.35	0.35
		0.7	0.71
	$C_2H_5SC_2H_5$	0.3	0.24
		0.74	0.58
		2.23	1.75
		4.47	3.6
	$C_2H_5SCH_3$	1.0	0.42
		2.6	1.2
		5.2	2.3
		10.4	4.55
	$ClCH_2CH_2SCH_3$	2.4	0.061
		6.0	0.145
		12	0.306
		24	0.615
	$C_6H_5SCH_3$	1.5	0.011
		1.5	0.012[b]
		5.1	0.040[b]
		10.2	0.081[b]
		15.3	0.121[b]
(e) $Pt(bipy)(NO_2)N_3 + RSR' \longrightarrow Pt(bipy)(NO_2)(RSR')^+ + N_3^-$	n-$C_4H_9SC_2H_5$	0.105	0.07
		0.35	0.21
		0.7	0.412
		1.05	0.6
	$C_2H_5SC_2H_5$	0.94	0.38
		2.28	0.95
		4.57	1.75
		9.4	3.81
	$C_2H_5SCH_3$	0.086	0.022
		0.315	0.08
		0.63	0.16
		0.865	0.22
	$ClCH_2CH_2SCH_3$	4.5	0.07
		11.3	0.192
		22.6	0.375
		45.2	0.75
	$C_6H_5SCH_3$	1.0	0.005[b]
		5.0	0.023[b]
		10	0.0455[b]
		20	0.089[b]

[a] The concentration of the substrate in the reaction mixture was always equal to or less than 5×10^{-4} *M*. [b] Data obtained from conductivity measurements.

than that of radicals bonded to nitrogen by considering that the micropolarizability of sulfur is greater than that of nitrogen. Thus, not only do the thioethers promote a higher degree of bond making than amines in the reactions with the "soft" platinum(II) substrate but also the extent is very much more sensitive to the nature of the attached groups R and R′, since their inductive effects are more readily transmitted through the "soft" sulfur. It can be observed that in this case the greater discrimination between thioethers is parallelled by a greater reactivity.

The Effect of the Leaving Group.—The complexes $Pt(bipy)(NO_2)Cl$, $Pt(bipy)(NO_2)N_3$, and $Pt(bipy)(NO_2)_2$ differ from each other only in the nature of the leaving group (Cl, N_3, and NO_2, respectively). The kinetic study of the effect of the leaving group was done by following the kinetics with the nucleophiles Cl^-, Br^-, N_3^-, I^-, and SCN^- [6] and it was shown that,

TABLE II

SECOND-ORDER RATE CONSTANTS, k_2, RELATIVE TO THE REPLACEMENT OF THE LIGAND X FROM THE COMPLEXES Pt(bipy)(C)X IN METHANOL AT 25°, BY THIOETHERS

		10^3k_2, M^{-1} sec^{-1}				
$-\Sigma\sigma^*$	Reagent	C = Cl X = Cl	C = N_3 X = Cl	C = NO_2 X = Cl	C = NO_2 X = NO_2	C = NO_2 X = N_3
0.23	n-$C_4H_9SC_2H_5$	140	365	350	105	59
0.2	$C_2H_5SC_2H_5$	130	330	280	80	41
0.1	$C_2H_5SCH_3$	95	322	158	44.5	25.5
−0.385	$ClCH_2CH_2SCH_3$	25	192	8.15	2.55	1.6
−0.6	$C_6H_5SCH_3$	14	152	2.44	0.79	0.455

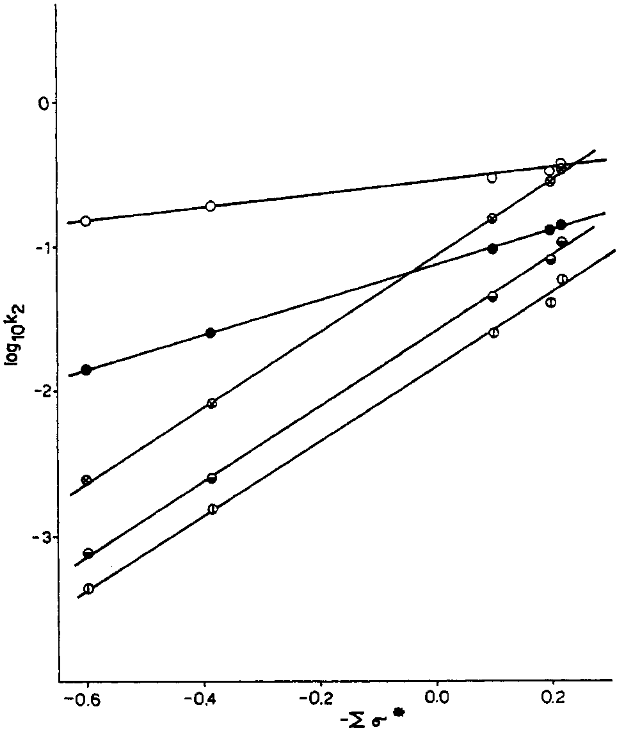

Figure 1.—Plot of log k_2 against $-\Sigma\sigma^*$ (see text) for the reactions $Pt(bipy)(C)X + RSR' \rightarrow Pt(bipy)(C)(RSR')^+ + X^-$: O, C = N_3, X = Cl; ●, C = Cl, X = Cl; ⊗, C = NO_2, X = Cl; ⊖, C = NO_2, X = NO_2; ⦶, C = NO_2, X = N_3.

although the nature of the leaving group influences the reaction rate, it does not affect the discrimination between different entering nucleophiles.

In the reactions with thioethers the same type of relationship is observed, namely, that the ability of the substrate to discriminate between entering groups (now expressed as the slope of the plot of log k_2 against $-\Sigma\sigma^*$) is independent of the nature of the leaving group (Figure 1). There is, however, one significant change, and that is that the reactivity difference for a particular nucleophile is much less sensitive to the nature of the leaving group when the entering group is an S donor. Thus, when $Pt(bipy)(NO_2)X$ reacts with thioethers, the value of k_2 changes with X in the order N_3 (1.0) < (NO_2 (2) < Cl (7) whereas with the anionic nucleophiles mentioned above the order was found to be in the region of N_3 (1.0) < NO_2 (10) < Cl (250).

The *cis* Effect.—The three substrates, $Pt(bipy)Cl_2$, $Pt(bipy)(NO_2)Cl$, and $Pt(bipy)(N_3)Cl$ differ from each other through the nature of the ligands *cis* to the leaving chloride. It has been shown[9] that, as far as the reactions with reagents such as Br^-, N_3^-, I^-, and SCN^- are concerned, the discrimination between various nucleophiles changes with the nature of the *cis* ligand, according to the sequence $N_3 > NO_2 > Cl$. By taking as a reference the complex $Pt(bipy)Cl_2$, the *cis*-effect sequence can be expressed quantitatively: N_3 (1.27) > NO_2 (1.16) > Cl (1.00), where the number in parentheses represents the slope of the linear plot of log k_2 for the complex concerned against log k_2 for the standard with the same nucleophile. However, the data for thioethers do not obey this relationship but lie on different lines whose slopes are in the order: NO_2 (2.22) > Cl (1.00) > N_3 (0.38). The greater influence of the *cis* ligands on the discrimination power of the substrate indicates that the nonparticipating ligands are more important in determining the energetics of the reaction. This could be due to the fact that in this case both the substrate and the incoming reagent are neutral and soft, and therefore a greater covalency can be developed in the platinum–ligand bonds in the transition state. This might explain the change in the sequences reported above since the π interaction in the Pt–NO_2 bond can contribute effectively to the stabilization of the transition state and lead to a greater discrimination, whereas the azide group which is not appreciably biphilic[17] and is a better σ donor than chloride shows the opposite effect.

Conclusions

These observations are consistent with the idea of a nonsynchronous addition mechanism. Once the bond-making and bond-breaking aspects of substitution start to separate, it is possible to consider two extreme types of energy profiles.[18] In one case (A) the higher energy barrier is that of the dissociative step and so the breaking of the bond with the leaving group should exert a powerful influence on the reaction rate, whereas in the other (B) bond formation is the driving force of the reaction and the nature of the replaceable ligand will affect the reaction rate only insofar as it is one of the four nonparticipating ligands. It is not possible yet to locate precisely or even approximately the position of the reaction profile between the limits represented by A and B, respectively, but one can say that for some reason the processes in which the thioethers are entering ligands must be represented by profiles that are more "B-like" than those involving the other reagents. The decreasing importance of the dissociation aspect is reflected in the decrease in sensitivity of rate to the nature of the leaving group, and the greater importance of the associative path is seen in the great sensitivity to the donor properties of the sulfur and the nature of the *cis* ligands. Why thioethers should be so

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(17) L. Cattalini, A. Orio, and M. Nicolini, *J. Am. Chem. Soc.*, **88**, 5734 (1966).

(18) See ref 1, p 47.

peculiar in these respects is not yet clear and research is in progress to investigate the problem further.

Experimental Section

The complexes Pt(bipy)(C)X (C, X = Cl, Cl; N_3, Cl; NO_2, Cl; NO_2, NO_2; NO_2, N_3) were prepared according to the methods reported in the literature.[6,9] The complex [Pt(bipy)Cl-$((C_2H_5)_2S)]NO_3$ was obtained from the dichloro complex. Pt(bipy)Cl_2 (845 mg), dissolved in the minimum amount of dimethylformamide, was treated with 340 mg of $AgNO_3$. After 30 min the solution, separated from AgCl, was treated with 250 ml of benzene. The precipitate was separated and dissolved in the minimum amount of methanol, containing 180 mg of $(C_2H_5)_2S$, and the product was then obtained as a precipitate by adding ether. *Anal.* Calcd for $PtC_{14}ClH_{18}N_3O_3S$: C, 31.15; H, 3.36; N, 7.80; S, 5.94. Found: C, 31.2; H, 3.14; N, 7.7; S, 5.8. The thioethers were commercial products, reagent grade. The methanol was dried by distillation over $Mg(OCH_3)_2$.

Kinetics.—The complexes obey Beer's law and are stable in methanol. Known volumes of methanolic solutions of the substrate and reagent were brought separately to 25° and mixed in the thermostated cell of a double-beam recording spectrophotometer, Optica CF4. The reactions were followed by measuring the changes in optical density in the ultraviolet region of the spectrum over a period of time. Conductivity measurements were carried out by means of an LKB 3216B conductivity bridge.

Acknowledgments.—We thank Dr. M. L. Tobe for stimulating discussions and the Italian Council for Research (CNR, Rome) for financial support.

CONTRIBUTION FROM ISTITUTO DI CHIMICA GENERALE ED INORGANICA, II SEZIONE,
UNIVERSITÀ DI PADOVA, PADUA, ITALY

The Reactivity of Thioethers toward Neutral Gold(III) Complexes

BY L. CATTALINI, M. MARTELLI, AND G. MARANGONI

Received February 19, 1968

The rates of displacement of amines (am) from complexes of the type $AuCl_3(am)$ by a variety of thioethers have been measured in acetone at 25°. The discrimination of the entering reagent between the various substrates decreases as the reactivity increases, and it reaches a constant value. This is discussed in terms of an increasing importance of the bond-making aspects of the substitution. A comparison of the nucleophilicity of thioethers toward Au(III) and Pt(II) substrates is reported and the part played by steric hindrance is also discussed.

Introduction

In a previous paper[1] the kinetics of the forward and reverse reactions

$$AuCl_3(am) + Bz_2S \rightleftharpoons AuCl_3(Bz_2S) + am$$

(Bz_2S = dibenzyl sulfide, am = pyridine derivatives) were studied in detail for a range of complexes containing amines of different basicity and steric hindrance. Having established the kinetic properties of dibenzyl sulfide, it was then desirable to study the nucleophilicity of other thioethers toward gold(III) substrates, in order to attempt to correlate the reactivity with nonkinetic properties and to clarify the role of steric hindrance. Furthermore, a set of data concerning the nucleophilicity of thioethers toward platinum(II) substrates is now available[2] and it is therefore possible to compare the data of thioethers reacting on the isoelectronic substrates of the two d^8 transition metal ions.

In this paper we report the kinetics of replacement of amines from a series of complexes of the type $AuCl_3$(am), by various thioethers, RSR′. The systematic study of the changing of both the entering and the leaving groups requires a relatively large amount of kinetic data, but it does enable us to compare not only the reaction rates but also the ability of each reagent to discriminate between substrates containing different replaceable amines.

Results

The progress of the reaction was examined spectrophotometrically and the course of the reaction was much the same as was reported previously[1] for the reactions with dibenzyl sulfide. Since the reactions were carried out in the presence of an excess of thioethers, reduction may be likely. The change of optical density with time at 340 mμ takes places in two stages. In the first the absorbance increases from that of the amino to that of the sulfide complex, as experienced in the case of $(C_2H_5)_2S$ by comparison of the spectrum with that of an original sample of $AuCl_3((C_2H_5)_2S)$. In the second step, which is much slower, there is a decrease of optical density. The complex $AuCl_3((C_2H_5)_2S)$ can be obtained, in almost quantitative yield, by carrying out the reaction in more concentrated solution (preparative conditions) and using equimolar quantities of $AuCl_3$(am) and $(C_2H_5)_2S$, when the least basic amines are displaced, as previously reported for the entry of dibenzyl sulfide. The first stage therefore corresponds to the replacement of the coordinated amine by $(C_2H_5)_2S$ (or Bz_2S) and we assume it is the same also for the other thioethers. The second stage corresponds to the reduction from Au(III) to Au(I), and the stoichiometry and mechanism of the reaction are under investigation.

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(1) L. Cattalini, G. Marangoni, and M. Martelli, *Inorg. Chem.*, **7**, 1145 (1968).

(2) L. Cattalini, M. Martelli, and G. Kirschner, *ibid.*, **7**, 1488 (1968).