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Influence of Basicity and Steric Hindrance on the Reactivity of Amines toward Tetrachloroaurate(III) Ion

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The kinetics of the reactions $[AuCl_4]^- + am \rightarrow [Au(am)Cl_3] + Cl^-$ where am is pyridine or a substituted pyridine have been followed in methanol at 25°. A linear free energy relationship is observed between the second-order rate constants and the basicity of the entering groups. Steric hindrance due to the presence of one or two methyl groups in α position decreases the reactivity, and the effects of methyl groups are additive. Comparison with the reverse reactions and with the calculated equilibrium constants shows that the free energy variations arising from steric perturbations in the transition state and in the complexes containing the amine are very similar, so that these effects can be detected kinetically only in the forward reactions. Comparison with a neutral platinum(II) substrate shows that the role of basicity in determining reactivity is greater in gold(III) complexes.

Introduction

Although a very large number of papers have been published on the relationship between basicity and nucleophilicity with respect to organic substrates[1] and on the effect of steric hindrance upon this, little is known about analogous relationships in the nucleophilic substitution reactions on square-planar transition metal complexes.

It has been shown[2] that steric hindrance arising from the presence of *ortho*-substituted aryl ligands in square-planar Ni(II), Pd(II), and Pt(II) complexes markedly decreases the rates of their reaction. In a recent paper[3] we have reported kinetic data on the nucleophilic displacement by amines of the coordinated chloride in a neutral platinum(II) substrate

$$[Pt(bipy)Cl_2] + am \longrightarrow [Pt(bipy)(am)Cl]^+ + Cl^-$$

The kinetics were followed in methanol at 25° and a linear free energy relationship was obtained by plotting log k_2 *vs.* pK_a of the entering amine. The reactivity decreases when one or two methyl groups are present in α- and α,α'-substituted pyridines. The effect of steric hindrance in decreasing reactivity was found to be additive. The small slope of the straight line in the diagram log k_2 *vs.* pK_a (0.06) was related to the relatively small influence of basicity in determining reactivity at "soft" reaction centers.

The replacement of amines in a series of neutral gold(III) complexes[4] has been studied in methanol at 25° and a linear free energy relationship was found by plotting log k_2/k_1 *vs.* the pK_a of the leaving amine when the entering nucleophile was an essentially σ-bonded one, such as Cl^-

$$[Au(am)Cl_3] + Cl^- \longrightarrow [AuCl_4]^- + am$$

An interesting observation was that, whereas a steric effect is clearly evident in the nucleophilic attack of amines on the platinum(II) complex and whereas sterically hindered platinum(II) substrates show a relatively small reactivity,[2,5] there is no indication of steric hindrance effects when amines are leaving groups in the reactions of gold(III) complexes.

In the present paper we report the kinetics of the displacement of chloride ion in $[AuCl_4]^-$ by amines

$$[AuCl_4]^- + am \longrightarrow [Au(am)Cl_3] + Cl^-$$

These are the reverse reactions of those reported in the previous work on Au(III) complexes.[4] It is now possible to discuss the steric effects and also to make a first comparison of the relationship between reactivity and basicity in Pt(II) and Au(III) complexes.

Results

The change in the ultraviolet spectrum of a methanolic solution originally containing chloroauric acid and an excess of amine shows that the reaction is exactly the opposite of that observed following the displacement of coordinated amine by chloride.[4] The same isosbestic points are observed and the final spectra correspond exactly to those of the starting materials in the reverse reaction, $[Au(am)Cl_3]$. The reactions were carried out in the presence of a large excess of amine so that the amount consumed by coordination and protonation from the chloroauric acid was negligible compared to the total amount present. In this way the kinetics were of first-order form. In addition, sufficient amine was present to force the equilibrium

$$[AuCl_4]^- + am \rightleftharpoons [Au(am)Cl_3] + Cl^-$$

far enough over to the right to ignore the reverse reaction. The rate constants were obtained from the optical density of the reaction mixture at various times, in the range 315–350 mμ, by the method previously reported;[3] the strong ultraviolet absorbance of pyridines prevented the possibility of following the reactions at shorter wavelengths.

The dependence of the observed rate constant upon the concentration of the entering amine, am, can be expressed by the relationship

$$k_{obsd} = k_1 + k_2[am]$$

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[1] R. F. Hudson and R. J. Withey, *J. Chem. Soc.*, 3513 (1964), and references therein.

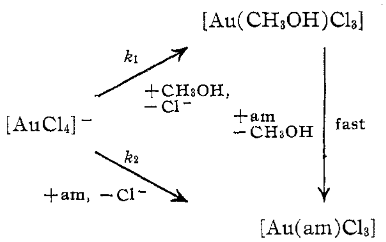
[2] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).

[3] L. Cattalini, A. Orio, and A. Doni, *Inorg. Chem.*, **5**, 1517 (1966).

[4] L. Cattalini and M. L. Tobe, *ibid.*, **5**, 1145 (1966).

[5] F. Basolo and W. H. Baddley, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

which now appears to be a general kinetic expression for nucleophilic substitutions in planar complexes of d^8 transition metal ions.[6] The first-order rate constants (k_1) are independent of the nature of the nucleophile am, so that even here one can accept the reaction scheme usually adopted for nucleophilic substitutions in planar substrates:



In fact, some observations on samples of $NaAuCl_4$ that had been allowed to reach equilibrium in methanol show that the reactions

$$[Au(CH_3OH)Cl_3] + am \longrightarrow [Au(am)Cl_3] + CH_3OH$$

are fast in comparison with the processes controlled by the specific rate constants k_1 and k_2.

The results are summarized in Table I, together with the second-order rate constants of the reverse processes that are listed here as k_{-2} and with the calculated equilibrium constants, K $(= k_2/k_{-2})$. The value of k_1, which is not reported in Table I, is $(4 \pm 0.5) \times 10^{-3}$ sec^{-1} for all of the reactions studied; in fact, the reaction scheme requires that k_1 must be independent of the nature of the entering amine. The low accuracy of k_1 is due to the fact that the process controlled by the k_2 is, by far, the most important one. In Figure 1 log k_2 is plotted against the pK_a of the entering amine. As in the case of the substrate $[Pt(bipy)Cl_2]$,[3] linear free energy relationships are obtained for amines having the same form of hindrance.

TABLE I

SECOND-ORDER RATE CONSTANTS AND EQUILIBRIUM CONSTANTS FOR THE REACTIONS BETWEEN AMINES AND CHLOROAURATE ANION IN METHANOL AT 25°

Amine	pK_a[a]	k_2, M^{-1} sec^{-1}	k_{-2}, M^{-1} sec^{-1}	K
3-Cyanopyridine	1.39	0.5	. . .	. . .
4-Cyanopyridine	1.90	0.565	. . .	. . .
3-Chloropyridine	2.84	0.69	. . .	. . .
Pyridine	5.17	1.6	0.417[b]	3.84
3-Methylpyridine	5.68	2.0	0.195[b]	10.2
4-Methylpyridine	6.02	2.1	0.096[b]	21.9
3,5-Dimethylpyridine	6.34	2.5	0.090[b]	27.8
3,4-Dimethylpyridine	6.50	2.9	. . .	. . .
2-Methylpyridine	6.10	0.227	0.095	2.39
2,4-Dimethylpyridine	6.99	0.325	0.023	12.6
2,6-Dimethylpyridine	6.75	0.030	0.039[b]	0.77
2,4,6-Trimethylpyridine	7.48	0.0365	0.0095	3.80

[a] The values of pK_a are for the conjugate acid to the amine in water. [b] Data from ref 4.

In order to obtain the values reported in Table I, the amine concentration was varied over a tenfold range for any one reaction. The range 5×10^{-3} to 5×10^{-2} M was covered for the faster reactions and 5×10^{-2} to 5×10^{-1} M for the slower ones. The concentration of the complex was in the range 5×10^{-5} to 5×10^{-4} M.

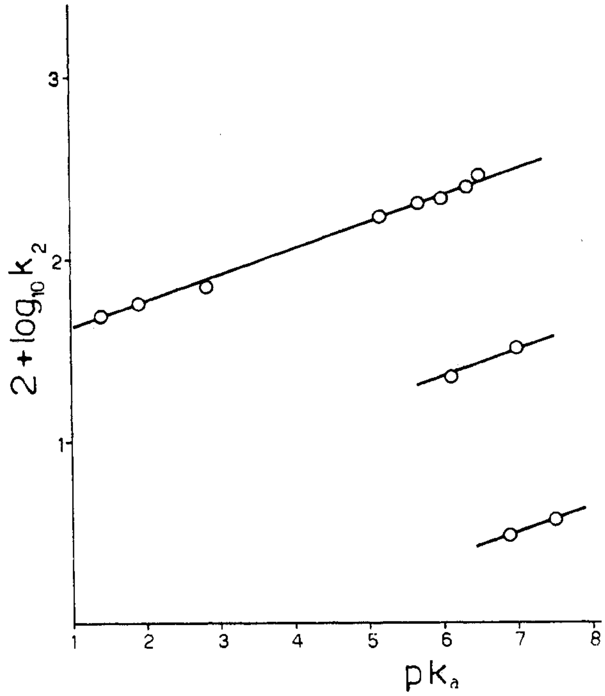


Figure 1.—Plot of log k_2 vs. pK_a for reactions of replacement of one chloride by substituted pyridines in $[AuCl_4]^-$ in methanol at 25°: upper line, pyridines without steric hindrance; central line, pyridines with one α-methyl group; lower line, pyridines with two α-methyl groups.

Discussion

Two different points must be taken into account in this discussion. The first is to correlate the kinetic data obtained in this work (k_2) with that of the reverse reaction (k_{-2}), in order to explain the different influence of steric hindrance on the reactivity and equilibrium, and the second is to compare the linear free energy relationship obtained in the case of $[AuCl_4]^-$ with that obtained, under the same conditions, with $[Pt(bipy)Cl_2]$.

Basolo, *et al.*,[2,5] have shown that steric hindrance in square-planar platinum(II) complexes leads to a decrease in reactivity, sometimes quite drastically. In our case the experimental data, as they appear in Figure 1, show that steric hindrance effects are clearly present in the reactions where the amines are entering groups

$$[AuCl_4]^- + am \longrightarrow [Au(am)Cl_3] + Cl^-$$

whereas there are no effects (either accelerating or retarding) upon the reverse reaction.

These results can be explained by realizing first that, according to the principle of microscopic reversibility, the transition states for the forward and reverse reactions will be identical. If the steric hindrance of the substituted amine in the neutral complex $[Au(am)Cl_3]$ is the same as in the transition state, the rate of displacement of the amine ligand will show no effects due to steric hindrance whereas the rate of entry of the amine

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(6) U. Belluco, L. Cattalini, and A. Turco, *J. Am. Chem. Soc.*, **86**, 226 (1964), and references therein.

into the unhindered $[AuCl_4]^-$ will obviously show this effect. This is represented diagrammatically in Figure 2, where, for comparison purposes, the energy profiles along the reaction coordinate of

$$[AuCl_4]^- + \text{pyridine} \longrightarrow [Au(\text{pyridine})Cl_3] + Cl^-$$

$$[AuCl_4]^- + \text{2,6-dimethylpyridine} \rightleftharpoons [Au(\text{2,6-dimethylpyridine})Cl_3] + Cl^-$$

are drawn superimposed except for the steric hindrance effect. A simple curve has been drawn even though the presence of a five-coordinate intermediate is not unlikely; this added complication will affect the diagram but not the argument. The requirement that the steric hindrance in $[Au(am)Cl_3]$ and in the *quasi*-trigonal-bipyramidal transition state $[Au(am)Cl_4]^-$ are similar can only be met if the Au–N bond is nearly fully formed in the transition state and is not greatly changed from that in $[Au(am)Cl_3]$. The geometry of the square plane and of the trigonal bipyramid (Figure 2) indicates that the interaction of the methyl groups with the *cis*-chlorine atoms, which provides most of the steric hindrance, does not change to any marked extent in going from the planar complex to the transition state.

The effect of steric hindrance can be discussed in a more quantitative fashion by making use of the rate constants k_2 and k_{-2}. The equilibrium constants, K, reported in Table I are obtained from the ratio k_2/k_{-2}; this appears to be the most convenient method of measuring these equilibrium constants, since, unless the amine and chloride are both present in sufficient excess, there will be extensive solvolysis of the complexes thereby making measurements on the equilibrium mixtures impossible. As one might expect, the tendency for the amine to coordinate to the gold atom increases with the increasing basicity. The presence of α substituents on the pyridine reduces the stability of the resultant complex (Figure 3). It is possible, by using the data in Figures 1 and 3, to separate the effects of basicity and steric hindrance, both in rate and equilibrium constants. The separations $\Delta \log k_2$ and $\Delta \log K$ can be regarded as the steric effects arising from the introduction of the methyl groups in the α position, without any interference from the basicity change that might accompany this introduction. From these differences we have calculated the differences of free energy of activation $\Delta(\Delta F^*)$ and of formation of the complexes $\Delta(\Delta F)$. These are respectively 1.34 (1.32) and 1.36 (1.36) kcal/mole for the change: α substitution → one α-CH_3 group and one α-CH_3 group → two α-CH_3 groups. The values of $\Delta(\Delta F)$ are given in parentheses.

The slopes of the lines in Figure 1 can be used as a measure of the dependence of the reactivity upon the basicity of the entering amine. A comparison of the kinetic behavior of the complexes $[Pt(bipy)Cl_2]$ and $[AuCl_4]^-$ in their reactions with amines shows that the slope of the plot $\log k_2$ against pK_a is greater in the case of gold(III) (0.15) than in the case of platinum(II) (0.06), even though the gold complex is anionic. Discussion in terms of the total ionic charge can be misleading because we must remember that the central atom is changed from Pt(II) to Au(III) and the effective nuclear charge as experienced by the entering and

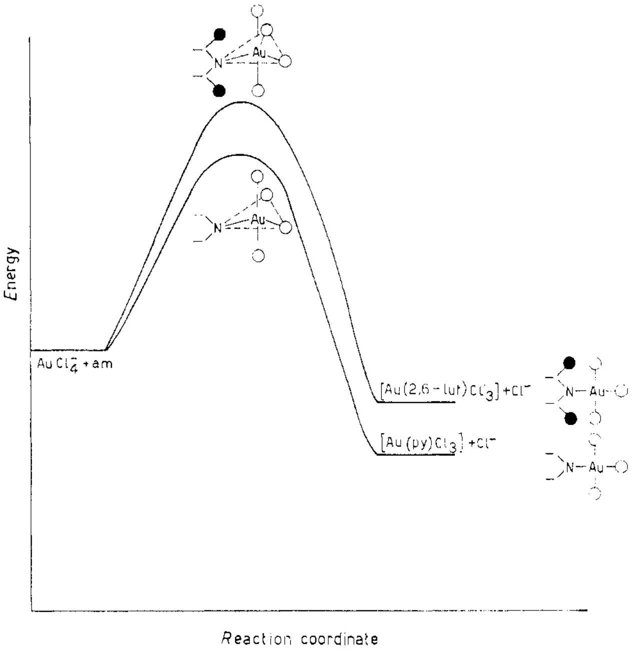

Figure 2.—Energy profile along the reaction coordinate for the substitution of one chloride in $[AuCl_4]^-$ by pyridine and 2,6-dimethylpyridine and for the reverse reaction.

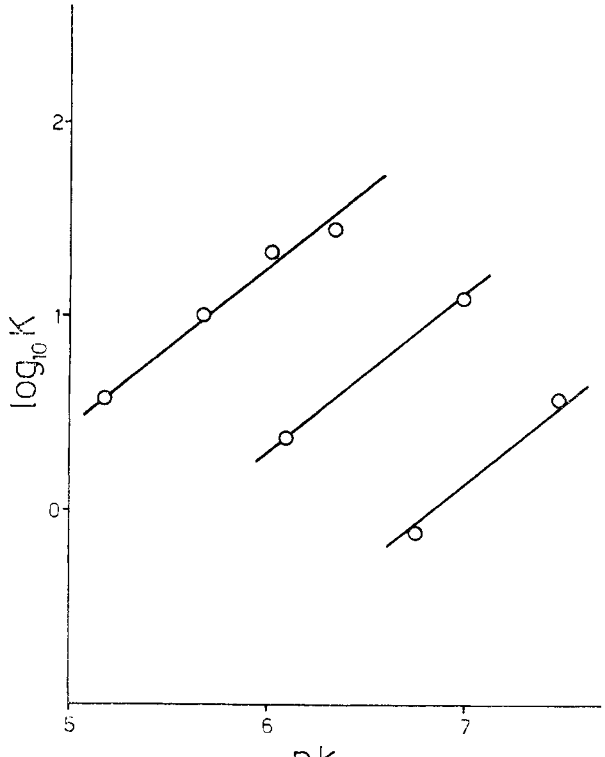

Figure 3.—Plot of log K *vs.* pK_a for the equilibria between substituted pyridines and $[AuCl_4]^-$ in methanol at 25°: upper line, pyridines without steric hindrance; central line, pyridines with one α-methyl group; lower line, pyridines with two α-methyl groups.

leaving groups is likely to be higher for Au(III) than Pt(II) irrespective of the number of chloride ions coordinated. If, as suggested by Basolo,[7] the main driving force for the reactions of gold(III) complexes is bond formation in the transition state, one must expect that the reactivity as well as the dependence of reactivity upon the basicity of the entering amine increases in going from Pt(II) to Au(III) complexes. The increase in reactivity, expressed as log (k_2^{Au}/k_2^{Pt}), is 2.15 for the weakest base, 4-cyanopyridine, and increases to 2.58 for the strongest base compared, 3,5-dimethylpyridine. At the same time the increase in the slope of the plot of log k_2 *vs.* pK_a is 2.75. Further investigations will be necessary in order to estimate the effect of the total charge of the complex upon the relationship between reactivity and basicity.

Experimental Section

Chloroauric acid was prepared starting from metallic gold with the usual method described in the literature. Methanolic solutions of $H[AuCl_4]$ follow Beer's law and no appreciable solvolysis is observed during the time necessary to follow the kinetics. Commercial pyridines were purified by distillation over potassium hydroxide pellets. Anhydrous methanol was prepared by distillation over $Mg(OCH_3)_2$. The products $[Au(am)Cl_3]$ were identified from the ultraviolet spectrum.[4]

Kinetics.—Methanolic solutions of chloroauric acid and of the amine were thermostated and mixed in the cell which was placed in the thermostated compartment of the spectrophotometer. The measurements were made by using a Optica-CF4 recording spectrophotometer, by scanning the near-ultraviolet spectrum from time to time in the course of the reaction. Some kinetic runs were made several times under the same conditions, and the rate constants were generally reproducible to better than 5%.

Acknowledgments.—We thank Professor A. Turco and Dr. M. L. Tobe for helpful and stimulating discussions.

[7] F. Basolo, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 92.

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Cyanide Complexes of Copper with Ammonia and Ethylenediamine[1]

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Complex cyanides of copper(I) are susceptible to oxidation by oxygen in the presence of ammonia or ethylenediamine if the $CN^-:Cu(I)$ ratio is less than 3. The stable products contain Cu(II) and Cu(I) in the ratio of 1:2. This was shown by stoichiometric analysis, by titration with NH_2OH_2Cl, and by magnetic susceptibility measurement. Crystalline samples of $Cu_3(NH_3)_4(CN)_4$ and $Cu_3(en)_2(CN)_4$ were prepared. Measurements of infrared and visible absorption spectra show that the N base is coordinated to Cu(II) as is also the Cu(I) cyano anion. In aqueous solution the cation–anion association persists for the ethylenediamine case. It dissociates on dilution, however. For the ammonia species, dissociation is complete even in saturated solution.

The formation of coordination compounds containing the cyanide ion is of great interest because of the possibility of π-bond formation between the metal ion and the ligand.[2] This possibility, along with the relative ease of observation of the C–N stretching frequency, has led to the use of cyanide ligands in investigations of mixed-ligand complexes. In some cases it has been found that the C–N frequency is sensitive to changes in the other ligands of a mixed (square-planar) complex.[3] An attempt to obtain information about this type of effect in a mixed-ligand complex with tetrahedral coordination involved an investigation of mixed complex formation with copper(I) cyanides.[4] It was found however that instead of mixed complex formation with copper(I), in the presence of N donors and air, the copper(I) was oxidized to a copper(II) species. Copper(I) cyanides are otherwise very stable toward oxidation of the metal (reaction with oxygen occurs at slightly elevated temperatures with the formation of copper(I) cyanate). The possibility of mixed complex formation with the copper(II) species exists. As stable complexes containing cyanide bound to copper(II) are unusual, it was thought that the oxidation and the product were deserving of further study. Infrared and visible spectroscopy provides information about the bonding in the copper(II) species, and the results with ammonia and with ethylenediamine (en) are presented here.

Experimental Section

Preparation of $Cu_3(NH_3)_4(CN)_4$. (a) From Copper(I) Cyanide.—Copper(I) cyanide was prepared by the method of Barber.[5] Sodium cyanide (0.25 mole) was dissolved in water (50 ml) and copper(I) cyanide (0.139 mole) was dissolved in the resulting solution. A 40% aqueous ammonia solution (20 ml) was added to the solution and a deep blue color formed within a few seconds, spreading downward from the exposed surface. The mixture was left for 48 hr to allow some of the ammonia

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(1) This work was supported by Grant G.P. 2643 from the National Science Foundation and presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(2) W. P. Griffith, *Quart. Rev.* (London), **16**, 188 (1962).

(3) J. M. Smith, L. M. Jones, L. K. Kressin, and R. A. Penneman, *Inorg. Chem.*, **4**, 369 (1965).

(4) D. Cooper and R. A. Plane, *ibid.*, **5**, 16 (1966).

(5) H. J. Barber, *J. Chem. Soc.*, 125 (1924).