Kinetics and Mechanism for Reduction of Tetrachloroaurate(III), *trans*-Dicyanodichloroaurate(III), and *trans*-Dicyanodibromoaurate(III) by Sulfite and Hydrogen Sulfite

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Reduction of $[AuCl_4]^-$ and *trans*-$[Au(CN)_2X_2]^-$ (X = Cl, Br) by sulfur(IV) as $SO_2 \cdot nH_2O$, HSO_3^-, and SO_3^{2-} has been studied at 25 °C in aqueous solution with ionic strength 1.0 M and 0 < pH < 2.3 by use of stopped-flow spectrophotometry. Redox takes place directly without initial substitution at the gold(III) centers with stoichiometry Au(III):S(IV) = 1:1 and with Au(I) complexes and HSO_4^- as products. A mechanism with two parallel redox reactions and HSO_3^- and SO_3^{2-} as reductants results in the following respective rate constants for reduction of $[AuCl_4]^-$, *trans*-$[Au(CN)_2Cl_2]^-$, and *trans*-$[Au(CN)_2Br_2]^-$: by HSO_3^-, 35 ± 9, $(1.5 \pm 0.2) \times 10^2$, and $(1.7 \pm 0.2) \times 10^3$ M^{-1} s^{-1}; by SO_3^{2-}, $(6.8 \pm 0.4) \times 10^6$, $(1.6 \pm 0.1) \times 10^7$, and $(1.8 \pm 0.1) \times 10^8$ M^{-1} s^{-1}. Reduction is ca. 10^5 times faster with SO_3^{2-} than with HSO_3^-. A halide-bridged, two-electron transfer in a transition state where the sulfur of the reductant interacts with the halide ligand and which is further stabilized through direct interaction between the positive metal center and the negatively charged oxygen of the sulfite/hydrogen sulfite is proposed. Reduction of *trans*-$[Au(CN)_2Br_2]^-$ is ca. 10 times faster than reduction of *trans*-$[Au(CN)_2Cl_2]^-$, in agreement with bromide being a more efficient bridging ligand for electron transfer. In the case of $[AuCl_4]^-$ and *trans*-$[Au(CN)_2Cl_2]^-$, there is also a parallel solvolytic pathway, with the acid hydrolysis of these complexes being rate-determining for the reduction, with rate constants $(2.4 \pm 0.6) \times 10^{-2}$ and $(5.6 \pm 1.4) \times 10^{-2}$ s^{-1}, respectively. Intermediate formation of sulfite radicals and formation of dithionate as reaction product in the $[AuCl_4]^-$ reaction, as claimed in recent literature, can most likely be ruled out.

Introduction

Previous kinetic studies of reduction of gold(III) complexes by various one-electron reducing nucleophiles Y, such as iodide, thiocyanate, thiosulfate, thiourea, and alkyl sulfides, provide evidence for a common intermolecular reaction mechanism in many of these systems.[1,2] It has been suggested that the rate-determining step is an attack by the nucleophile on a coordinated ligand X, followed by bridged two-electron transfer to the metal and elimination of XY.[1-9] A similar bridge mechanism seems to operate when some gold(III) complexes are reduced by the two-electron reductants $[Pt(CN)_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$.[10,11]

For some combinations of nucleophiles and gold(III) complexes, the approach of Y results in rapid substitution followed by reductive elimination in a subsequent step.[1-9] Thus the mechanism for reduction of many gold(III) complexes can be described as a competition between substitution and redox reactions were the natures of the metal center, the coordinated ligands, and the nucleophile are crucial for the degree of substitution that takes place prior to reduction.[1,2,8]

Reduction of complexes of gold(III) by two-electron reductants has been far less studied. In addition to the bridge mechanism, the possibility of a direct interaction between the reducing nucleophile and the metal center has been discussed in the case of the $[Au(NH_3)_4]^{3+}$—thiosulfate reaction.[3] A recent study of the reaction between $[AuCl_4]^-$ and sulfur(IV), i.e. an equilibrium mixture of $SO_2 \cdot nH_2O$, HSO_3^-, and SO_3^{2-}, claims formation of sulfite radicals and gold(II) intermediates.[12] If this is correct, gold(III) complexes might be efficient as catalysts for the autoxidation of sulfur(IV).

In view of these previous results, and as a continuation of our recent studies of mechanisms of redox reactions involving metal complexes and sulfur(IV) oxo compounds,[13-15] we have studied the reduction of $[AuCl_4]^-$ and *trans*-$[Au(CN)_2X_2]^-$ (X = Cl, Br) by $SO_2 \cdot nH_2O$, HSO_3^-, and SO_3^{2-} in acidic aqueous solution.

Experimental Section

Chemicals and Solutions. *trans*-K[Au(CN)_2Cl_2]·H_2O and *trans*-K[Au(CN)_2Br_2]·3H_2O were synthesized by oxidation of K[Au(CN)_2] (Degussa) as described previously.[2,16] H[AuCl_4]·3H_2O (Degussa) was used as received. Stock solutions of ca. 2 mM Au(III) complex were prepared by dissolving an accurately weighed amount of *trans*-K[Au(CN)_2Cl_2]·H_2O, *trans*-K[Au(CN)_2Br_2]·3H_2O, or H[AuCl_4]·3H_2O, respectively, in an acidic aqueous ionic medium. The solutions were protected from light and not used for more than ca. 1 week.

Stock solutions of ca. 50 mM sulfur(IV) were prepared fresh before each set of experiments by dissolving Na_2SO_3 (Merck p.a.) in an

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oxygen-free acidic ionic medium, continuously flushed with argon. The sulfur(IV) concentrations, determined by iodometric titration,[17] were constant during the course of the experiments. Secondary sulfur(IV) solutions were prepared immediately before use from the stock solutions by dilution with an air-saturated ionic medium. They were not used for more than 1 h. Spectrophotometric measurements of the absorptivity of $SO_2(aq)$ at 278 nm confirmed that the sulfur(IV) concentrations of these solutions were constant during that period of time.

NaBr and NaCl (Merck p.a.) were used to adjust the halide concentration, and $HClO_4$ (Merck 70—72%, p.a.) and HCl (Merck 37%, p.a.) were used to adjust the pH. The ionic strength was 1.0 M in all experiments if nothing else is stated. $NaClO_4$ (Merck p.a.) was used as a supporting electrolyte. Water was doubly distilled from quartz, and argon was used as received from suppliers.

Apparatus. Spectra were recorded by use of a Milton Roy 3000 diode-array spectrophotometer and thermostated 1 cm quartz Suprasil cells. The kinetics was monitored at (25.0 ± 0.1) °C by use of a modified Durrum-Gibson stopped-flow spectrophotometer and an Applied Photophysics Bio Sequential SX-17MV stopped-flow ASVD spectrofluorimeter. Time-resolved spectra were also recorded with the Applied Photophysics instrument. The kinetics was evaluated using on-line least-squares minimizing programs.[18,19] Oxygen concentrations were measured by use of an Orion Research oxygen electrode, Model 97-08, connected to an Orion Research EA 920 expandable ion analyzer.

Equilibria in the Sulfur(IV) System. The equilibria for the sulfur-(IV) system in water can be written as follows: $SO_2 \cdot nH_2O \rightleftharpoons HSO_3^- + H_3O^+ + (n - 2)H_2O$ ($pK_{a1} = 1.37$, $I = 1.0$ M, 25 °C);[20] $HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$ ($pK_{a2} = 6.3$, $I = 1.0$ M, 25 °C);[20] $2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$ ($pK_3 = 1.15$).[21] The presence of $S_2O_5^{2-}$ is negligible under the present experimental conditions, and at pH < 2.5 the predominant species are HSO_3^- and $SO_2 \cdot nH_2O$. Below, S(IV) denotes the equilibrium mixture of $SO_2 \cdot nH_2O$, HSO_3^-, and SO_3^{2-}.

Spectra. Spectra of *trans*-[Au(CN)$_2$X$_2$]$^-$ (X = Cl, Br) and [AuCl$_4$]$^-$ have been published.[5,22,23] The spectrum of an equilibrium solution obtained by mixing equal volumes of 4.2×10^{-5} M *trans*-[Au(CN)$_2$-Cl$_2$]$^-$ and 4×10^{-4} M S(IV) at [H$^+$] = 10 mM, corrected for the absorbance of excess sulfur(IV), compared with a spectrum of 2.0×10^{-5} M [Au(CN)$_2$]$^-$, recorded separately in the same ionic medium, indicates that *trans*-[Au(CN)$_2$Cl$_2$]$^-$ is reduced to [Au(CN)$_2$]$^-$. Similar spectra show that this is true also for *trans*-[Au(CN)$_2$Br$_2$]$^-$. [AuCl$_4$]$^-$ is reduced to [AuCl$_2$]$^-$, which most likely undergoes rapid subsequent substitution to form mixed Au(I) chloro—sulfito complexes. Since Au-(I) complexes are transparent, this substitution could not be observed. A slow increase of absorptivity in the interval 240—320 nm after completion of the redox reaction, observed in both the *trans*-[Au-(CN)$_2$Br$_2$]$^-$ and the *trans*-[Au(CN)$_2$Cl$_2$]$^-$ systems, did not have any influence on the kinetics for the reduction of these complexes and was not studied further.

Figure 1 shows time-resolved spectra recorded after mixing equal volumes of gold(III) and sulfur(IV) solutions, produced by processing kinetic traces, automatically sampled every fifth nanometer with the Applied Photophysics instrument.[19] There is no evidence for any rapid complex formation between the gold(III) complexes and sulfur(IV) prior to reduction. Initial substitution of halide by sulfur(IV) is expected to give spectra with new absorbance peaks, different from those of the reactant gold(III) halide complexes. This is not the case.

Stoichiometry. When *trans*-[Au(CN)$_2$X$_2$]$^-$ (X = Cl, Br) and sulfur-(IV) are mixed in equimolar concentrations at the conditions given in Table 1, reduction of the complex is completed within a few seconds. This is much faster than the very slow autoxidation of sulfur(IV) under the present experimental conditions. The reduction of *trans*-[Au-

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Table 1. Determination of Stoichiometric Coefficients, x^a

complex	$10^5[Au(III)]_0$/M	[H$^+$]/mM	[X$^-$]/mM^b	λ/nm	x^c
trans-[Au(CN)$_2$Cl$_2$]$^-$	4.9	100	10	218	0.92
	4.9	100	10		1.05
	4.9	100	10		1.0
	4.2	10	0		1.17
	4.1	10	10		1.12
trans-[Au(CN)$_2$Br$_2$]$^-$	5.1	100	10	241	0.90
	5.2	30	10		0.98
[AuCl$_4$]$^-$	16	30	1000	315	1.40
	16	30	1000		1.62
	16	10	1000		1.38
	8.2	30	1000		1.27

^{a} Conditions: [S(IV)] < 1×10^{-4} M for *trans*-[Au(CN)$_2$X$_2$]$^-$ and [S(IV)] < 3.2×10^{-4} M for [AuCl$_4$]$^-$, $I = 1.0$ M, room temperature. ^{b} X = Cl, Br. ^{c} x denotes the stoichiometric coefficient defined by eq 1.

$(CN)_2X_2]^-$ (X = Cl, Br) can be represented by reaction 1, where x

$$[Au(CN)_2X_2]^- + xHSO_3^- \rightarrow [Au(CN)_2]^- + 2X^- + P \quad (1)$$
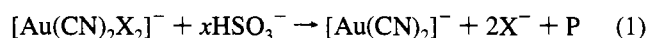
denotes the stoichiometric coefficient and P the oxidized sulfur product. At wavelengths > 215 nm, the absorptivities of HSO_4^-/SO_4^{2-} and $S_2O_6^{2-}$ are negligible. Since these are the only possible final sulfur products, the total absorptivity, A/l, at the 218 and 241 nm maxima for *trans*-[Au(CN)$_2$Cl$_2$]$^-$ and *trans*-[Au(CN)$_2$Br$_2$]$^-$, respectively, can be expressed as eq 2 where $C_{Au} = [Au(CN)_2X_2^-] + [Au(CN)_2^-]$. $\epsilon_{Au(III)}$

$$A/l = (\epsilon_{Au(III)} - \epsilon_{Au(I)})[S(IV)]/x + C_{Au}\epsilon_{Au(III)} \quad (2)$$

and $\epsilon_{Au(I)}$ denote the molar absorptivities of *trans*-[Au(CN)$_2$X$_2$]$^-$ (X = Cl, Br) and [Au(CN)$_2$]$^-$, respectively. Thus, for constant total concentration of gold, A/l is a linear function of [S(IV)] with slope $(\epsilon_{Au(III)} - \epsilon_{Au(I)})/x$ and intercept $C_{Au}\epsilon_{Au(III)}$. The stoichiometry for reduction of *trans*-[Au(CN)$_2$X$_2$]$^-$ (X = Cl, Br) was determined by measuring the absorptivity at the 218 and 241 nm maxima, respectively, of a series of solutions containing a constant gold(III) concentration and increasing sulfur(IV) concentrations. These experiments were repeated at different [H$^+$]. The stoichiometric coefficient was calculated from the slopes of absorbance vs [S(IV)] plots according to eq 2. The molar absorptivities of *trans*-[Au(CN)$_2$X$_2$]$^-$ (X = Cl, Br) at 218 and 241 nm, respectively, were determined by measuring the absorptivity of five metal solutions for each complex. Values of 2.08×10^4 and 2.78×10^4 M^{-1} cm^{-1} for *trans*-[Au(CN)$_2$Cl$_2$]$^-$ and *trans*-[Au(CN)$_2$-Br$_2$]$^-$, respectively, were calculated from the slopes of the linear plots of absorptivity vs [Au(III)]. Similarly, the molar absorptivities of [Au(CN)$_2$]$^-$ were determined to be 2.30×10^3 and 2.38×10^3 M^{-1} cm^{-1} at 218 and 240 nm, respectively. The results are summarized in Table 1. The mean value for x is 1.0 ± 0.1, which implies that the reduction of *trans*-[Au(CN)$_2$X$_2$]$^-$ (X = Cl, Br) by sulfur(IV) is best represented by the overall reaction (3). The stoichiometry for the

$$[Au(CN)_2X_2]^- + HSO_3^- + H_2O \rightarrow$$
$$[Au(CN)_2]^- + 2X^- + HSO_4^- + 2H^+ \quad (3)$$
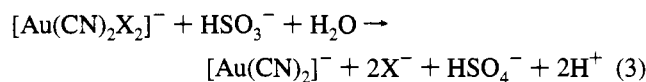
reduction of [AuCl$_4$]$^-$ was determined at the 315 nm maximum where Au(I), S(IV), HSO_4^-/SO_4^{2-} and $S_2O_6^{2-}$ are transparent. Thus, the stoichiometric coefficient can be calculated from plots of absorptivity vs [S(IV)] at constant total concentration of gold, (Table 1). In all four cases, $x > 1$, probably due to irreproducible formation of mixed gold(I)—chloro—sulfito complexes depending on mixing conditions. Sen Gupta et al.[12] reported a stoichiometry of about 1.5 for the same reaction in acidic aqueous solution using an excess of sulfur(IV) and a 0.4 M chloride medium. Also in that case deviation from $x = 1.0$ can most likely be explained by formation of gold(I) sulfito complexes which are strong but transparent at the wavelength used.

Autoxidation. The concentration of dissolved oxygen was measured as a function of time for 1.2 mM S(IV) at pH 1.5 by use of the oxygen electrode. The experiment was repeated with 3.0×10^{-5} M *trans*-[Au(CN)$_2$Cl$_2$]$^-$ added. The concentration decreased by ca. 7% during 120 min in both cases. The decrease can most likely be attributed to

catalysis by trace metal impurities, as described previously.[13-15] Similar results were also obtained for *trans*-[Au(CN)$_2$Br$_2$]$^-$ and [AuCl$_4$]$^-$. These experiments clearly demonstrate that the gold(III) complexes do not have any effect on the autoxidation of sulfur(IV). Since the concentration of sulfur(IV) in these experiments was ca. 5 times larger than the concentration of dissolved oxygen, ca. 2.5 × 10^{-4} M, effective catalysis of the autoxidation should deplete molecular oxygen completely. Thus, repeating the experiment with the efficient catalyst iron(III) (3 × 10^{-5} M), instead of gold(III), consumed the oxygen in 190 min.

Stopped-Flow Experiments. Reduction of *trans*-[Au(CN)$_2$X$_2$]$^-$ (X = Cl, Br) was monitored as a decrease of absorbance at 218 and 241 nm, repectively, due to the formation of [Au(CN)$_2$]$^-$. Similarly, reduction of [AuCl$_4$]$^-$ was followed at 230 or 315 nm; cf. Figure 1. The concentration of sulfur(IV) was always kept in at least 10-fold excess compared with the concentration of the gold(III) complexes, and the kinetics was evaluated as pseudo-first-order reactions according to eq 4. Reduction of the gold(III) complexes was studied as a function

$$-d[Au(III)]/dt = k_{obsd}[Au(III)] \qquad (4)$$

of excess sulfur(IV) and [H$^+$] using 5.3 × 10^{-6} M < [*trans*-[Au(CN)$_2$-Br$_2$]] < 8.5 × 10^{-5} M, 8.4 × 10^{-6} M < [*trans*-[Au(CN)$_2$Cl$_2$]] < 8.4 × 10^{-5} M, 1.0 × 10^{-5} M < [AuCl$_4$$^-$] < 7.5 × 10^{-5} M, 1.0 × 10^{-4} M < [S(IV)] < 8.0 mM, and 5 mM < [H$^+$] < 1.0 M. The experiments are summarized in Figure 2, and the slopes and intercepts of these plots are given in Table 2. The halide dependencies of the reduction of the complexes were studied under the experimental conditions given in Table 3. The observed rate constant did not vary significantly when [Au(CN)$_2$$^-$] < 6.6 × 10^{-6} M was present in the reduction of *trans*-[Au(CN)$_2$Br$_2$]$^-$ ([Au(III)] = 1.98 × 10^{-5} M, pH 1.5, and [S(IV)] = 1.1 mM).

Extended Hückel Calculations. The charge distributions within the Au(III) complexes summarized in Table 4 were calculated by use of the extended Hückel method[24,25] employing an idealized square-planar geometry. Energy and radial parameters were taken from the tested empirical parameters collected by Alvarez.[26] The bond lengths used were Au—Br = 2.43, Au—Cl = 2.26, Au—C = 2.02, and C—N = 1.06 Å.[27-29]

Results

***trans*-[Au(CN)$_2$Br$_2$]$^-$.** In the region 5.1 mM < [H$^+$] < 0.99 M, the plots of the observed rate constant vs the concentration of excess sulfur(IV) in Figure 2a indicate a simple rate law according to eq 5, where k denotes the pH-dependent, second-

$$-d[Au(CN)_2Br_2{}^-]/dt = k[S(IV)][Au(CN)_2Br_2{}^-] \qquad (5)$$

order rate constant and the total concentration of sulfur(IV) is given by [S(IV)] = [SO$_2$·nH$_2$O] + [HSO$_3$$^-$] + [SO$_3$$^{2-}$]. Figure 2a and Table 3 indicate that the concentration of added bromide does not influence the kinetics significantly. In the presence of added bromide and in strongly acidic solutions with [H$^+$] > 0.5 M, complicated kinetic traces were obtained. Those were not further studied.

***trans*-[Au(CN)$_2$Cl$_2$]$^-$ and [AuCl$_4$]$^-$.** Plots of k_{obsd} vs excess [S(IV)] are linear with an intercept for both *trans*-[Au(CN)$_2$Cl$_2$]$^-$ and [AuCl$_4$]$^-$, when the chloride concentration is low in the acidic medium used; cf. Figure 2b,c. Thus, the experimental rate law can be expressed as eq 6, where k_f is a first-order rate

$$-d[complex]/dt = [complex](k[S(IV)] + k_f) \qquad (6)$$

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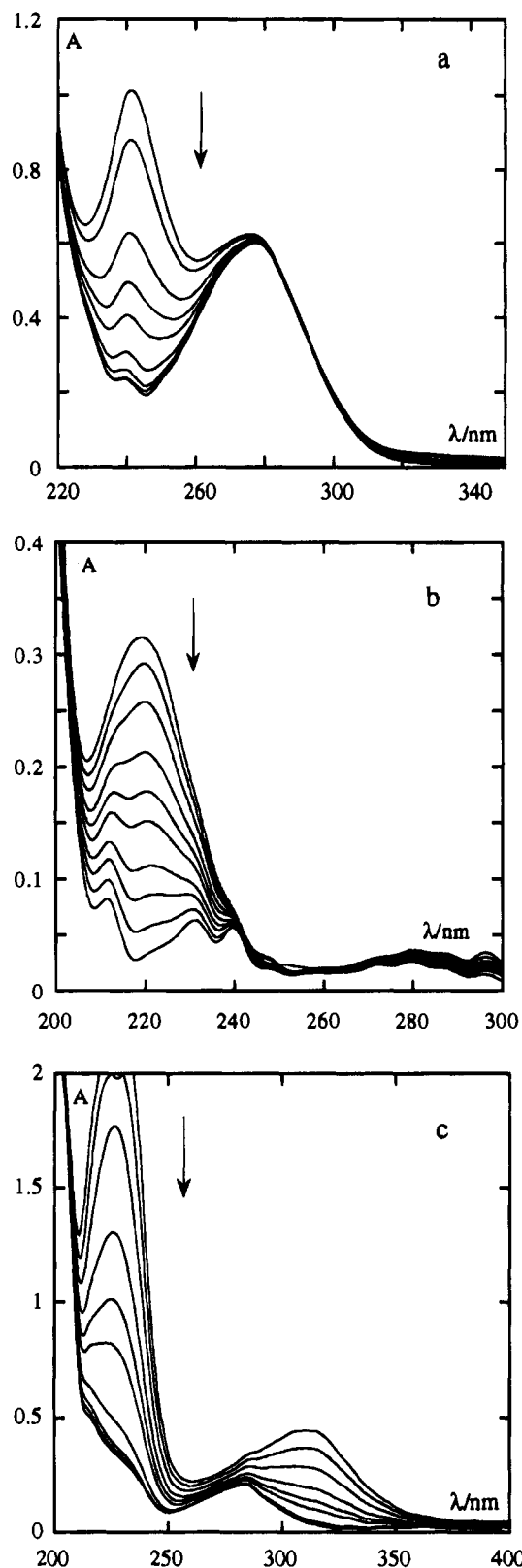(29) Jarring, K.; Holmberg, B; Bengtsson, L. *Inorg. Chem.* **1988**, *27*, 2445.

Figure 1. Time-resolved spectra at 25 °C and 1.0 M ionic strength for the redox reactions between sulfur(IV) and *trans*-[Au(CN)$_2$X$_2$]$^-$ (X = Cl, Br) and [AuCl$_4$]$^-$. Key: (a) [*trans*-[Au(CN)$_2$Br$_2$]$^-$]$_0$ = 4.2 × 10^{-5} M, [S(IV)]$_0$ = 1.9 mM, [H$^+$] = 30 mM (spectra recorded 5, 50, 100, 250, 375, 500, 750, 1000, 1500, and 5000 ms after mixing); (b) [*trans*-[Au(CN)$_2$Cl$_2$$^-$]]$_0$ = 2.0 × 10^{-5} M, [S(IV)]$_0$ = 0.20 mM, [Cl$^-$] = 10 mM, [H$^+$] = 10.1 mM (spectra recorded 0.060, 0.60, 1.5, 3.0, 4.5, 6.0, 9.0, 12, 18, and 48 s after mixing); (c) [AuCl$_4$$^-$] = 8.0 × 10^{-5} M, [S(IV)] = 1.0 mM, [H$^+$] = 10 mM, [Cl$^-$] = 1.0 M (spectra recorded 0.060, 0.60, 1.5, 3.0, 4.5, 6.0, 12, 24, 36, and 48 s after mixing). Water was used as a reference. Arrows indicate absorptivity changes.
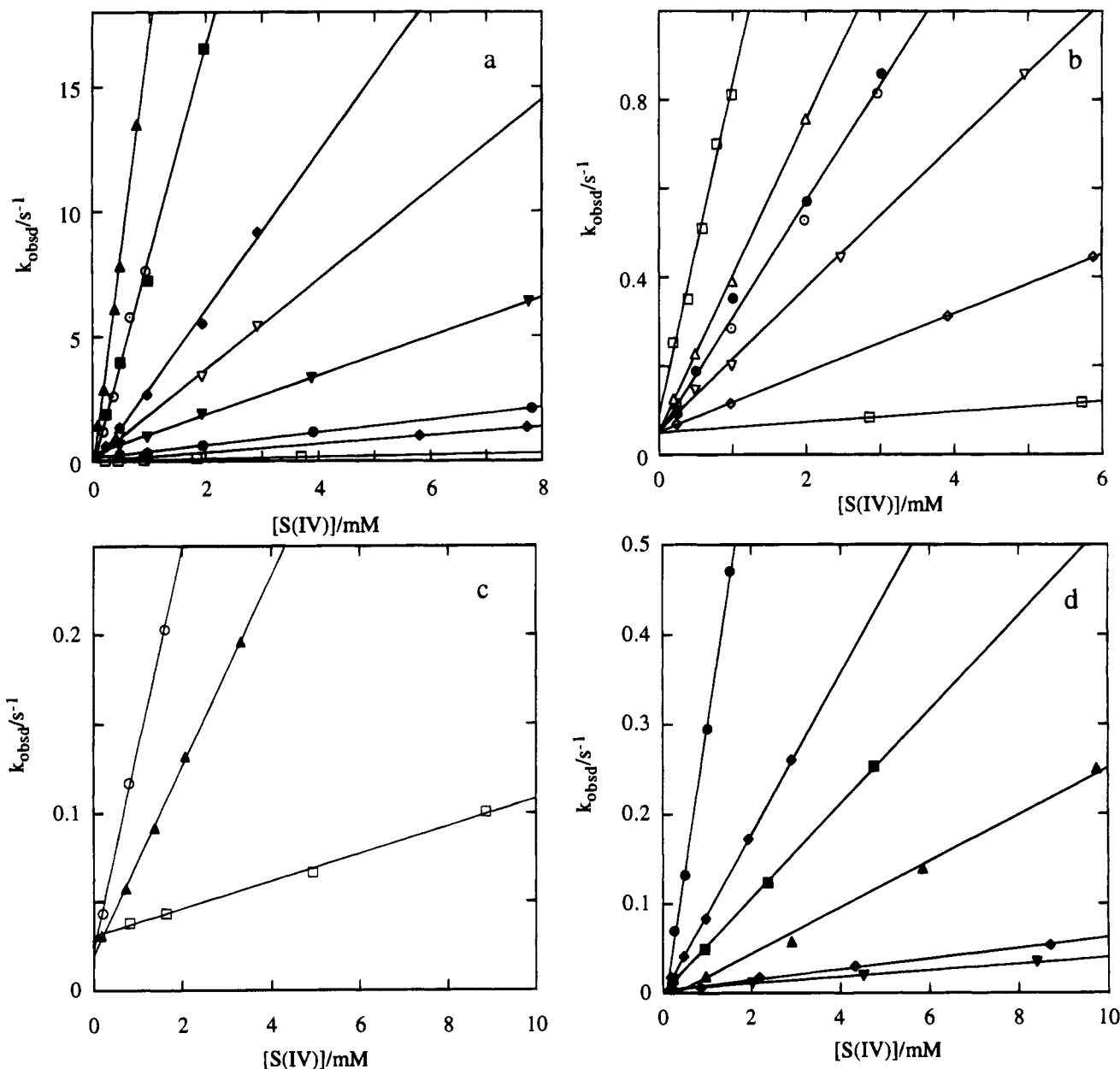
Figure 2. k_{obsd} at 25 °C as a function of excess S(IV) at different [H$^+$]. Key: (a) [*trans*-[Au(CN)$_2$Br$_2^-$]]$_0$ = (1.0−2.1) × 10^{-5} M, [Br$^-$] = 10 mM (filled symbols), [Br$^-$] = 0 (open symbols), [H$^+$] = 5.12, 10.2, 30.0, 50.0, 99.6, 299, 589, 990 mM; (b) [*trans*-[Au(CN)$_2$Cl$_2^-$]]$_0$ = 2.0 × 10^{-5} M, [Cl$^-$] = 0 (open symbols) [Cl$^-$] = 10 mM (filled symbols), [H$^+$] = 10.2, 20.1, 30.0, 49.8, 99.3, 495 mM; (c) [AuCl$_4^-$] = (1.6−2.3) × 10^{-5} M, [H$^+$] = 20.0 mM (circles), [H$^+$] = 207 mM (squares), [H$^+$] = 42 mM, [Cl$^-$] = 2 mM (triangles); (d) [AuCl$_4^-$] = 2.0 × 10^{-5} M, [Cl$^-$] = 1.0 M, [H$^+$] = 10.0, 30.0, 50.0, 99.9, 300, 500 mM. For all figures, the slopes decrease with increasing [H$^+$]. Ionic strength = 1.0 M.

constant given by the intercept. Under these conditions, fast processes due to reactions between sulfur(IV) and hydrolyzed gold(III) complexes were observed during the initial stages of the main reaction.

The hydrolysis constant for [AuCl$_4$]$^-$ is 1.6 × 10^{-5} M and the protolysis constant for [AuCl$_3$(OH$_2$)] is 0.23 M at 1.0 M ionic strength and 25 °C.[10,30] Thus, under the conditions given in Figure 2c, [H$^+$] = 0.21 M and 20.0 mM and no added chloride, the initial distributions of Au(III) species are 32% [AuCl$_4$]$^-$, 32% [AuCl$_3$(OH$_2$)], and 36% [AuCl$_3$(OH)]$^-$ for [H$^+$] = 0.21 M and 7% [AuCl$_4$]$^-$, 7% [AuCl$_3$(OH$_2$)], and 86% [AuCl$_3$(OH)]$^-$ for [H$^+$] = 20 mM, respectively. When 2 mM chloride is added, [AuCl$_4$]$^-$ is the predominant gold(III) complex. The hydrolysis constant for *trans*-[Au(CN)$_2$Cl$_2$]$^-$ is not known. However, without added chloride, the influence of the fast reactions was considerably larger at pH > 1.5 than at

lower pH. In the presence of 10 mM added chloride, the fast processes were suppressed.

These fast processes do not disturb the evaluation of the rate constants for reduction of *trans*-[Au(CN)$_2$Cl$_2$]$^-$ and [AuCl$_4$]$^-$. Perfect first-order fits were obtained when the first parts of the kinetic traces were excluded. The data in Table 3 also indicate that the concentration of added chloride does not influence the rate of reduction of either [AuCl$_4$]$^-$ or *trans*-[Au(CN)$_2$Cl$_2$]$^-$. In the [AuCl$_4$]$^-$-system, no fast processes were observed and no intercepts were obtained in the presence of 1.0 M added chloride; cf. Figure 2d.

Discussion

Mechanism. In the present systems, there is no evidence for any rapid substitution processes occurring prior to the redox reactions, as has been observed previously for reactions between various gold(III) complexes and thiosulfate, iodide, thiocyanate, and substituted thioureas.[1−9] The kinetics can be rationalized

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Table 2. Slopes and Intercepts Derived from Figure 2[a]

complex	$[X^-]_{added}/mM^b$	$[H^+]/M$	slope/$M^{-1}s^{-1}$	10^2(intercept)/s^{-1}
trans-[Au(CN)₂Br₂]⁻	10	5.12	$(17.4 \pm 0.5) \times 10^3$	
	0 or 10	10.2	$(8.4 \pm 0.3) \times 10^3$	
	10	30.0	$(3.2 \pm 0.1) \times 10^3$	
		50.0	$(1.8 \pm 0.1) \times 10^3$	
	10	99.6	$(0.79 \pm 0.01) \times 10^3$	
	10	299	$(0.25 \pm 0.01) \times 10^3$	
	10	589	0.17×10^3	
		990	$(0.042 \pm 0.002) \times 10^3$	
trans-[Au(CN)₂Cl₂]⁻		10.2	$(74 \pm 5) \times 10$	8 ± 3
		20.1	$(35 \pm 1) \times 10$	5.0 ± 0.8
	0 or 10	30.0	$(26.1 \pm 0.8) \times 10$	4.6 ± 1.4
		49.8	$(16.1 \pm 0.3) \times 10$	5.3 ± 0.8
		99.3	$(6.69 \pm 0.03) \times 10$	5.0 ± 0.1
		495	$(1.17) \times 10$	5.0
[AuCl₄]⁻	1000	10.0	$(32 \pm 1) \times 10$	
	1000	30.0	$(8.9 \pm 0.1) \times 10$	
	1000	50.0	$(5.3 \pm 0.1) \times 10$	
	1000	99.9	$(2.6 \pm 0.1) \times 10$	
	1000	300	$(0.60 \pm 0.03) \times 10$	
	1000	500	$(0.37 \pm 0.01) \times 10$	
	20	42.0	$(5.34 \pm 0.07) \times 10$	1.9 ± 0.1
		20.0	$(11.3 \pm 0.4) \times 10$	2.3 ± 0.4
		207	$(0.78 \pm 0.03) \times 10$	3.1 ± 0.2

[a] Errors are given as one standard deviation. [b] $X = Cl, Br$.

Table 3. Halide Dependence of the Rate of Reduction of the Au(III) Complexes.[a]

complex	$10^5[Au(III)]_0/M$	$[S(IV)]/mM$	$[H^+]/mM$	$[X^-]/mM^b$	k_{obsd}/s^{-1}
trans-[Au(CN)₂Br₂]⁻	1.0	0.99	10	1.0	8.6 ± 0.2
				10.5	9.0 ± 0.2
				50.5	9.4 ± 0.2
				100	9.4 ± 0.2
				400	10.0 ± 0.2
trans-[Au(CN)₂Cl₂]⁻	2.0	0.99	30	0	0.285 ± 0.004
				0.005	0.292 ± 0.004
				0.05	0.286 ± 0.003
				0.5	0.275 ± 0.004
				5.0	0.295 ± 0.003
				50	0.302 ± 0.003
[AuCl₄]⁻	2.0	0.97	20	0	0.143 ± 0.002
				1.0	0.147 ± 0.009
				10.0	0.15 ± 0.01
				100	0.130 ± 0.001
				500	0.130 ± 0.003

[a] Conditions: $I = 1.0$ M, 25 °C. Errors are given as one standard deviation. [b] $X = Cl, Br$.

Table 4. Charge Distribution in the Gold(III) Complexes Obtained from Extented Hückel Calculations

|	charge				
complex	Au	Br	Cl	C	N
trans-[Au(CN)₂Br₂]⁻	+0.30	−0.32		+0.42	−0.76
trans-[Au(CN)₂Cl₂]⁻	+0.67		−0.55	+0.45	−0.74
[AuCl₄]⁻	+1.11		−0.53		

by the mechanism in Scheme 1. Reduction is assumed to take place *via* two parallel reactions between the gold(III) complexes and HSO₃⁻ and SO₃²⁻ with rate constants k_1 and k_2, respectively. In addition, for the *trans*-[Au(CN)₂Cl₂]⁻ and [AuCl₄]⁻ systems, hydrolysis of the complexes with forward and reverse rate constants k_f and k_r has to be taken into account.

This mechanism gives the rate laws of eqs 4 and 7, where the total concentration of sulfur(IV) is given by $[S(IV)]$ =

$$k_{obsd} = k_f + \frac{[S(IV)]K_{a1}}{K_{a1} + [H^+]}(k_1 + k_2K_{a2}/[H^+]) \quad (7)$$

$[SO_2 \cdot nH_2O] + [HSO_3^{2-}] + [SO_3^{2-}]$ and Au(III) denotes *trans*-[Au(CN)₂X₂]⁻ (X = Cl, Br) and [AuCl₄]⁻, respectively.

Solvolytic Pathway. Reaction between sulfur(IV) and the hydrolyzed gold(III) chloro complexes is rapid and is observed

Scheme 1[a]
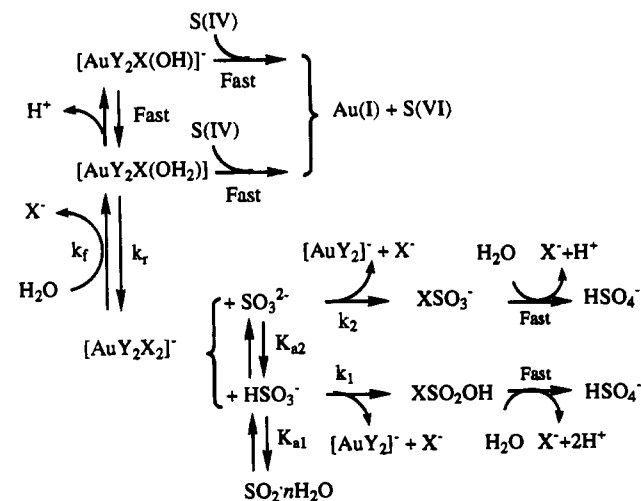
[a] $Y = CN, Cl; X = Cl, Br$.

as transient kinetics before steady-state concentrations of the aqua and hydroxo complexes are established. Then, acid hydrolysis of [AuCl₄]⁻ and *trans*-[Au(CN)₂Cl₂]⁻ with rate constant k_f becomes rate-limiting for the rapid reduction of the

Table 5. Second-Order Rate Constants at 25 °C Calculated from the [H$^+$] Dependence in Figure 3 by Use of the Mechanism of Scheme 1[a]

complex	nucleophile	k/M^{-1} s^{-1}
trans-[Au(CN)$_2$Br$_2$]$^-$	HSO$_3^-$	$(1.7 \pm 0.2) \times 10^3$
trans-[Au(CN)$_2$Br$_2$]$^-$	SO$_3^{2-}$	$(1.8 \pm 0.1) \times 10^8$
trans-[Au(CN)$_2$Cl$_2$]$^-$	HSO$_3^-$	$(1.5 \pm 0.2) \times 10^2$
trans-[Au(CN)$_2$Cl$_2$]$^-$	SO$_3^{2-}$	$(1.6 \pm 0.1) \times 10^7$
[AuCl$_4$]$^-$	HSO$_3^-$	35 ± 9
[AuCl$_4$]$^-$	SO$_3^{2-}$	$(6.8 \pm 0.4) \times 10^6$

[a] Errors are given as one standard deviation.

aqua and hydroxo species, as previously described for reduction of [AuCl$_4$]$^-$ by [Pt(CN)$_4$]$^{2-}$.[10] The intercepts of Figure 2b,c give k_f = $(5.6 \pm 1.4) \times 10^{-2}$ and $(2.4 \pm 0.6) \times 10^{-2}$ s^{-1} for *trans*-[Au(CN)$_2$Cl$_2$]$^-$ and [AuCl$_4$]$^-$, respectively. The latter value is in reasonably good agreement with the one determined previously for hydrolysis of [AuCl$_4$]$^-$, $(1.6 \pm 0.2) \times 10^{-2}$ s^{-1}.[10]

For high concentrations of chloride, the rate of the reverse process, determined by the rate constant k_r[Cl$^-$], becomes larger than the rate of reduction of the aqua and hydroxo complexes, and the solvolytic pathway is suppressed. This is the case for the experiments displayed in Figure 2d.

Direct Reduction. According to eq 7, the slopes, S, of the plots in Figure 2 can be expressed as eq 8. Plots of $S(K_{a1}$ +

$$S = \frac{K_{a1}}{K_{a1} + [H^+]}(k_1 + k_2 K_{a2}/[H^+]) \qquad (8)$$

[H$^+$])/K_{a1} vs 1/[H$^+$] using the literature value[20] of K_{a1} are shown in Figure 3. Values of k_1 and k_2 calculated from the intercepts and the slopes, respectively, of those lines using the literature value[20] pK_{a2} = 6.3 are summarized in Table 5.

The rate constants for reduction of the three gold(III) complexes in the present study are ca. $(1-2) \times 10^5$ times larger with sulfite than with hydrogen sulfite. Similarly, *trans*-[Pt-(CN)$_4$Cl$_2$]$^{2-}$ is reduced ca. 3×10^5 times,[14] ozone ca. 4×10^3 times,[31] and copper(III) complexes 30 times[32] faster by SO$_3^{2-}$ than by HSO$_3^-$. This corresponds to a larger driving force for reduction with SO$_3^{2-}$ than with HSO$_3^-$, the reduction potentials being -0.93 and $+ 0.17$ V, respectively.[33] Present experiments in this laboratory also indicate that cysteine and other S-containing ligands reduce metal complexes several orders of magnitude faster in their deprotonated than in their protonated forms.[34]

Molecular Mechanism. Reduction of gold(III) complexes has often been assumed to take place via an attack by an outer-sphere nucleophile Y on a coordinated ligand X, followed by bridged two-electron transfer to the metal and elimination of XY.[1-9] In the present systems, a similar mechanism would lead to elimination of halosulfuric acid and halosulfate which rapidly hydrolyze to HSO$_4^-$ and X$^-$ as final products;[35,36] cf. Scheme 1. According to Table 5, reduction of *trans*-[Au(CN)$_2$Br$_2$]$^-$ is ca. 10 times faster than reduction of *trans*-[Au(CN)$_2$Cl$_2$]$^-$, with both SO$_3^{2-}$ and HSO$_3^-$ as reductants. This supports a halide-bridged electron transfer, since bromide usually is a more efficient bridging ligand than chloride for reductive eliminations at gold(III) centers.[6]
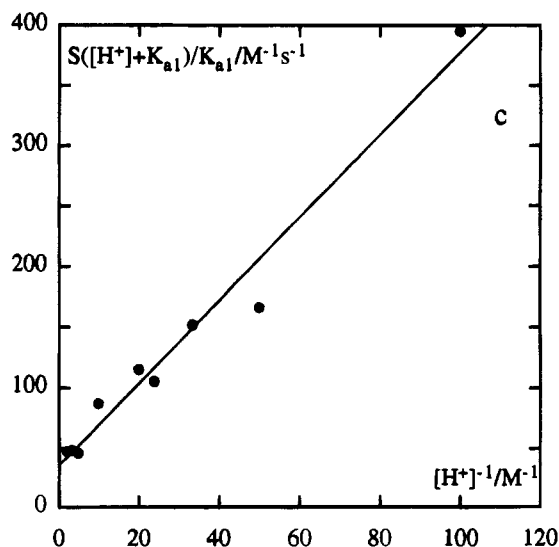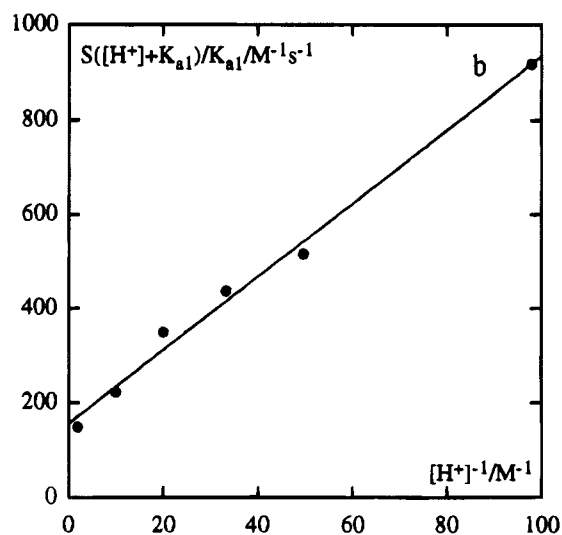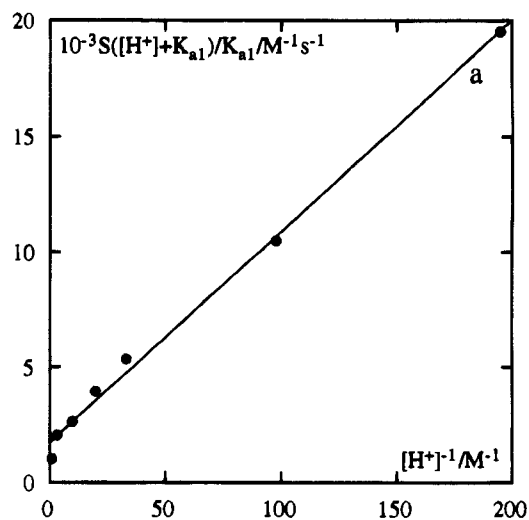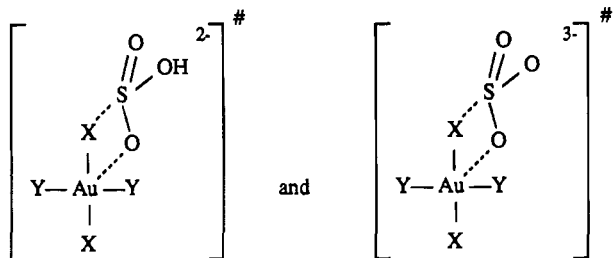
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Figure 3. [H$^+$] dependence for the redox reactions between sulfur-(IV) and *trans*-[Au(CN)$_2$X$_2$]$^-$ (X = Cl, Br) and [AuCl$_4$]$^-$. Conditions: see Figure 2. Key: (a) *trans*-[Au(CN)$_2$Br$_2$]$^-$; (b) *trans*-[Au(CN)$_2$Cl$_2$]$^-$; (c) [AuCl$_4$]$^-$. pK_{a1} = 1.37 has been used.[20]

The charge distribution on the gold(III) complexes summarized in Table 4 indicates that the transition states in the case of SO$_3^{2-}$ and HSO$_3^-$ as reducing agents might be stabilized by electrostatic interactions between the positively charged metal center and the negatively charged oxygen atoms of the reductants, in addition to the attraction between the positively charged

sulfur atom and the negatively charged halide ligand X according to

$$
\left[\begin{array}{c} O \\ \parallel \diagup OH \\ S \diagup \\ X \diagdown \quad O \\ \mid \diagup \\ Y-Au-Y \\ \mid \\ X \end{array}\right]^{2-\#} \quad \text{and} \quad \left[\begin{array}{c} O \\ \parallel \diagup O \\ S \diagup \\ X \diagdown \quad O \\ \mid \diagup \\ Y-Au-Y \\ \mid \\ X \end{array}\right]^{3-\#}
$$

This might be the reason for the high rates observed for reduction of the gold(III) complexes by these reductants. Similar interactions have been proposed previously by Kirschenbaum and co-workers for reduction of the isoelectronic square-planar complex [Ag(OH)₄]⁻ by sulfite, arsenite, and phosphite.[37-39] A similar stabilization of the transition states

might occur in the octahedral platinum(IV) systems studied previously,[14] through facial interaction with the negatively charged oxygens of the sulfite and hydrogen sulfite nucleophiles.

On the basis of measurements giving a stoichiometry of about 1.5 and a positive polymerization test, Sen Gupta and co-workers claimed formation of sulfite radicals and a gold(II) intermediate in the redox reaction between [AuCl₄]⁻ and sulfur(IV).[12] They also found a nonlinear dependence of the observed rate constant on the concentration of sulfur(IV) and therefore introduced complex formation between Au(III) and S(IV) in their reaction model. The present results do not give any support for that mechanism.

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