

Kinetics and Mechanism of the Reduction of Tetrachloroaurate(III) by Malonate in Acidic Aqueous Solution

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The reaction between tetrachloroaurate(III) and malonic acid/malonate ion was studied kinetically over a wide range of temperatures, malonate, hydrogen and chloride ion concentrations at ionic strength 1.0 M. The suggested reaction mechanism consists of a series of substitution reactions during which Au(III) malonato chloride species are produced. These species undergo a redox reaction for which the rate constant was determined radiochemically as $1.1 \times 10^{-5} \text{ sec}^{-1}$ at 40 °C. Kinetic evidence for some form of catalytic action by chloride ion is reported, and the results are discussed with reference to literature data.

Introduction

In a recent paper [1] we reported preliminary rate data for the reaction between tetrachloroaurate(III) and a series of carboxylic acids, from which it followed that the reactions with malonic and methylmalonic acid show a peculiar $[\text{Cl}^-]$ dependence. The reported rate constant increases with an increase in $[\text{Cl}^-]$ at a constant $[\text{H}^+]$, which is exactly the opposite of that found for the reactions with oxalic [2] and formic acid [3]. Louw and Robb [4–6] reported a similar feature in going from the reaction of tetrachloroaurate(III) with ethylenediamine to the reactions with methyl substituted ethylenediamines. In a parallel study, De Waal and Robb [7] could only find this deviation to occur in the reaction between PdCl_4^{2-} and tetramethylethylenediamine.

We have in the meantime completed a detailed kinetic investigation of the reaction between tetrachloroaurate(III) and malonic acid. The obtained rate data and suggested reaction mechanism, which are now reported, supplement and account for our earlier observations.

Experimental

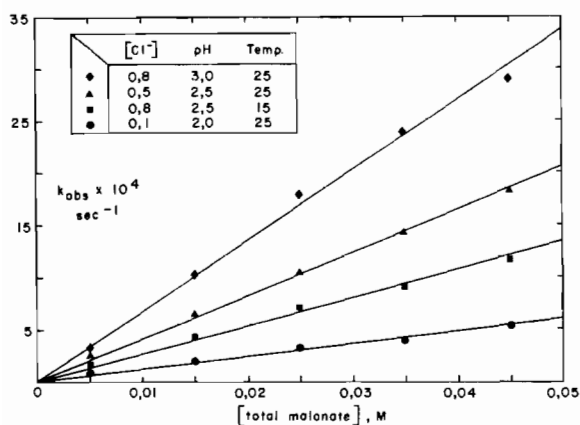
The kinetic and radiochemical experiments were performed in the manner described previously [2], under the following experimental conditions: $[\text{HAuCl}_4] = 1.5 \times 10^{-4} \text{ M}$, $[\text{total malonate}] \leq 0.045$

M (added as malonic acid), $0.01 \leq [\text{Cl}^-] \leq 0.8 \text{ M}$ (added as NaCl), $1.5 \leq \text{pH} \leq 3.5$ (by addition of HClO_4 and NaOH), ionic strength = 1.0 M (by addition of NaClO_4) and $15 \leq \text{temperature} \leq 35 \text{ }^\circ\text{C}$. No buffer was added since malonate solutions are self-buffering in the pH range concerned. Chemicals of analytical and reagent grade were used throughout the investigation. The gaseous reaction products were removed from the test solutions with argon as carrier gas, and analysed with a mass spectrometer and gas chromatograph [8].

The acid dissociation constants for malonic acid were experimentally determined by pH titration at 25 °C in 1 M NaClO_4 : $\text{pK}_1 = 2.43 \pm 0.05$, $\text{pK}_2 = 4.90 \pm 0.05$.

Results and Discussion

The reactions were followed kinetically by measuring the decrease in the concentration of the Au(III) chloride reagent species spectrophotometrically at 313 nm [2, 9]. The semilogarithmic pseudo-first-order plots of absorbance versus time are linear for the present experimental conditions, provided that $[\text{Cl}^-] \leq 0.1 \text{ M}$. At high $[\text{Cl}^-]$ the plots are only linear for the initial 40% of the reaction, after which they curve to indicate a second slower reaction. These plots were considered to be evidence for the participation of two consecutive reactions for which the rate constants were calculated by using a curve-stripping procedure [4, 10]. The values of k_{obs} for the faster reaction seem to be independent of $[\text{Cl}^-]$ whereas those for the slower reaction increase with an increase in $[\text{Cl}^-]$. The determination of k_{obs} for the slower (second) reaction at long reaction periods is subjected to considerable errors, which make the calculation of k_{obs} for the faster (first) reaction according to the above – procedure, even more inaccurate. The values of k_{obs} for the faster and slower reactions only differ by a factor of five at $[\text{Cl}^-] = 0.8 \text{ M}$, which adds to the inaccuracy of the curve-stripping method. It was, therefore, decided to treat the experimental data at $[\text{Cl}^-] > 0.1 \text{ M}$ according to an initial rate procedure in which k_{obs} was calculated over the initial 40% of the reaction.

Fig. 1. Plots of k_{obs} vs. [total malonate].

Plots of k_{obs} versus [total malonate] are linear and without intercept (see Figure 1), such that

$$k_{\text{obs}} = k[\text{total malonate}]$$

The values of k , the second-order rate constant, are summarized in Table I as a function of pH, temperature and $[\text{Cl}^-]$. At constant pH and temperature, k

TABLE I. Second-order Rate Constant k as a Function of pH, $[\text{Cl}^-]$ and Temperature.

$[\text{Cl}^-], M$	0.8 ^a	0.5 ^a	0.3 ^a	0.1	0.05	0.01
Temp. °C	pH	$k \times 10^2, M^{-1} \text{sec}^{-1}$				
25	1.5	1.9	1.4	0.9	0.6	0.4
25	2.0	4.1	2.8	2.2	1.2	1.0
15	2.5	2.7	1.9	1.4	0.9	0.7
25	2.5	5.5	4.1	3.1	1.9	1.7
35	2.5	11.2	8.6	6.6	4.7	3.8
25	3.0	6.7	5.4	3.9	2.5	1.8
25	3.5	8.4	6.4	4.5	2.6	1.9

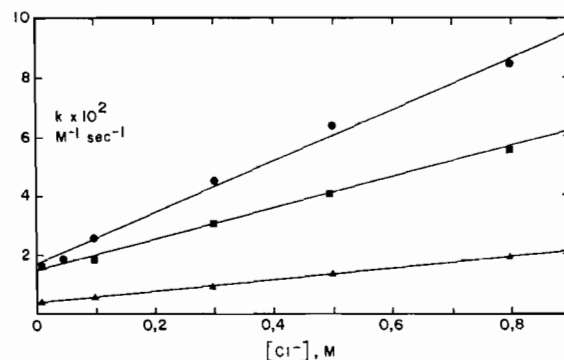
^a The pseudo-first-order rate constant k_{obs} was calculated over the initial 40% of the reaction.

increases with increasing $[\text{Cl}^-]$, as illustrated in Figure 2, which can be described by the equation

$$k = k_a + k_b[\text{Cl}^-]$$

The values of k_a and k_b were calculated using a linear regression programme and are summarized, together with the activation parameters for the data at pH 2.5, in Table II. According to this data, k_a and k_b are $[\text{H}^+]$ dependent constants.

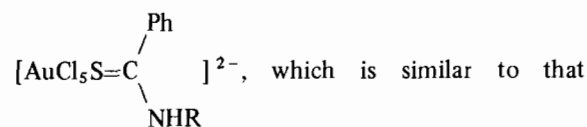
The $[\text{Cl}^-]$ dependence of k is in agreement with the preliminary data reported previously [1]. A number of authors have reported a similar catalytic effect of halide ion on the reactions of Au(III), which may be due to an interaction with the Au(III) species

Fig. 2. k versus $[\text{Cl}^-]$ for pH 1.5 (\blacktriangle), 2.5 (\blacksquare) and 3.5 (\bullet) at 25 °C.TABLE II. Values of k_a and k_b as a Function of pH and Temperature.

pH	Temp. °C	$k_a \times 10^2 M^{-1} \text{sec}^{-1}$	$k_b \times 10^2 M^{-2} \text{sec}^{-1}$
1.5	25	0.41	1.90
2.0	25	0.91	3.98
2.5	15	0.67	2.55
2.5	25	1.57	5.01
2.5	35	3.79	9.44
3.0	25	1.92	6.35
3.5	25	1.76	8.65
ΔH^\ddagger Kcal mol ⁻¹ ^a		14.7 ± 0.4	10.9 ± 0.0
ΔS^\ddagger cal deg ⁻¹ mol ⁻¹		-17.4 ± 1.7	-27.6 ± 0.1

^a Activation parameters are reported for the data at pH 2.5.

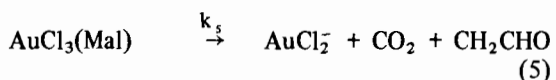
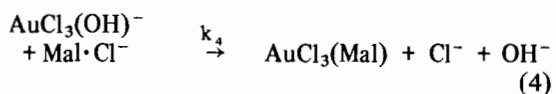
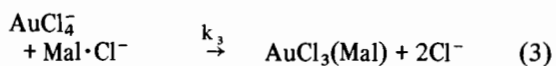
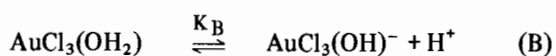
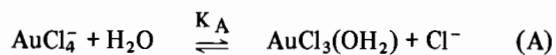
or the entering nucleophile. Annibale and co-workers report that the rate constants for the reaction of $[\text{Au}(\text{bipy})_2\text{X}_2]^+$ with X^- to produce AuX_4^- (bipy = 2,2'-bipyridyl, X = Cl or Br) depend on the first and third power of the halide ion concentration [11]. To explain the third-order dependence, the authors propose that the reactant is in equilibrium with a six-coordinate species with two halide ions occupying axial positions in a distorted octahedral configuration. Hall and Satchell report a similar $[\text{Cl}^-]$ dependence for the decomposition of various tetrachloroaurate(III)-N-cyclohexylthiobenzamide complexes during which S-amide-gold complexes decompose to the corresponding O-amide and Au_2S_3 [9]. The six-coordinate intermediate species is suggested to be



proposed by Annibale and co-workers [11]. Several other authors have also proposed hexa-coordinate Au(III) complexes [12-15]. Robb and co-workers [6, 7] report a $[\text{Cl}^-]$ dependence for the substitution reactions of AuCl_4^- and PdCl_4^{2-} with methyl-substi-

tuted ethylenediamines, which is similar to that reported in this investigation. They explain their results in terms of an interaction of chloride ion with the entering nucleophile.

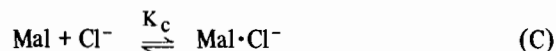
The two possible explanations for the catalytic action by chloride ion, as outlined above, will produce similar theoretical rate laws [6] and will both be in agreement with the experimental results of this investigation. From our earlier observations [1-3], and due to the lack of any spectral evidence for the association of chloride ion with the Au(III) complex species, we prefer to ascribe the observed $[\text{Cl}^-]$ dependence to an interaction between chloride ion and the various malonate species. A mechanism consistent with this concept and the reported kinetic data, is presented by equilibria (A) and (B) and reactions (1) to (5):



Equilibria (A) and (B) are established rapidly [16] and maintained throughout the course of reactions (1) to (5) such that $K_A = 0.95 \times 10^{-5} M$ and $K_B = 0.25 M$ [17]. From arguments presented previously [2, 3, 6], it follows that mainly AuCl_4^- and $\text{AuCl}_3(\text{OH})^-$ will participate in the reactions with malonate under the present experimental conditions. Reactions (1) to (4) are rate-determining substitution processes in which Mal represents the different acidic and basic forms of malonic acid. The rate constants k_1 to k_4 should, therefore, be $[\text{H}^+]$ dependent.

Reactions (1) and (2) are similar to those suggested for the reactions of AuCl_4^- and $\text{AuCl}_3(\text{OH})^-$ with oxalic acid/oxalate ion [2] and formic acid/formate ion [3]. Reactions (3) and (4) are included in the suggested mechanism to account for the positive influence of $[\text{Cl}^-]$ on the second-order rate constant k . The species $\text{Mal} \cdot \text{Cl}^-$ represents the various acidic and basic forms of malonic acid, which have in some or other way interacted with chloride ion to produce species that are more reactive than

malonate itself. This increase in reactivity is attributed to the influence of the chloride ion on the central CH_2 moiety of the malonate group [1], during which the carboxylic groups become more reactive, possibly due to an increase in acidity. The formation of $\text{Mal} \cdot \text{Cl}^-$ may in its simplest form be described by an equilibrium



which is similar to, but not necessarily, an ion pair formation equilibrium [6]. The value of K_C is expected to be small ($< 0.1 M$, ref. 7) and may well be pH dependent, since the interaction with chloride ion may differ for malonic acid, bimalonate and malonate ion.

The substitution products formed in reactions (1) to (4) are represented by $\text{AuCl}_3(\text{Mal})$ since the exact nature of these species is unknown. The radiochemical data, which are reported further on, indicate that the reaction between $\text{AuCl}_4^-/\text{AuCl}_3(\text{OH})^-$ and malonate proceeds via a substitution followed by a redox process. No spectral evidence for the formation of an Au(III) malonato chloride species could, however, be found. The suggested intermediate may undergo ring-closure as reported for the reaction with oxalate [2], or further substitution to produce species such as $\text{AuCl}_2(\text{Mal})^-$, $\text{AuCl}_2(\text{Mal H})_2^-$ or $\text{Au}(\text{Mal})_2^-$ prior to the redox reaction (5). Such reactions may partially account for the second slower reaction observed in the first-order plots at $[\text{Cl}^-] > 0.1 M$ (see earlier discussion). This intermediate Au(III) malonate species now decomposes according to reaction (5) to produce AuCl_2^- and Au(0), of which the latter is only formed at low $[\text{Cl}^-]$. The gaseous decomposition products of malonate were analysed as CO_2 and CH_3CHO , which enabled us to follow the redox reaction radiochemically using C^{14} -labelled malonic acid [8].

In an effort to find experimental evidence for the suggested interaction between malonate and chloride ion, the acid dissociation constants for malonic acid were determined in chloride solutions. The results indicated that the pK values are, within experimental error, not affected by the presence of chloride ion. Conductivity measurements [6] of chloride/malonate mixtures could neither support evidence for some form of interaction between these species. We conclude that the suggested interaction (equilibrium (C)) occurs to a slight extent (*i.e.* K_C is small) such that only a small portion of Mal exists as $\text{Mal} \cdot \text{Cl}^-$.

The theoretical rate law for the substitution process, *i.e.* equilibria (A) to (C) and reactions (1) to (4), can be derived [2, 18] as

$$k = \frac{k_1[\text{Cl}^-] + k_2K_AK_B/[\text{H}^+] + k_3K_C[\text{Cl}^-]^2 + k_4K_AK_BK_C[\text{Cl}^-]/[\text{H}^+]}{[\text{Cl}^-] + K_AK_B/[\text{H}^+]}$$

if the assumption is made that $K_C[\text{Cl}^-] \ll 1$ (see earlier discussion) such that $1 + K_C[\text{Cl}^-] \sim 1$. For the experimental conditions concerned, *i.e.* for all the values of k in Table I, $[\text{Cl}^-] \gg K_A K_B / [\text{H}^+]$ and the above rate law can be simplified to

$$k = k_1 + k_2 K_A K_B / [\text{H}^+] [\text{Cl}^-] + k_3 K_C [\text{Cl}^-] + k_4 K_A K_B K_C / [\text{H}^+]$$

The second term of this equation decreases while the third term increases with increasing $[\text{Cl}^-]$. The overall effect, however, is an increase in k with increasing $[\text{Cl}^-]$ (see Figure 2), from which it is concluded that the second term is of minor importance. This is understandable since $K_A K_B / [\text{H}^+] [\text{Cl}^-]$ is always small and so reduces the contribution of the second term. The first and last terms are independent of $[\text{Cl}^-]$ such that the slopes of the plots of k versus $[\text{Cl}^-]$ (*i.e.* k_b in Table II) are the values for $k_3 K_C$. The intercepts of the plots of k versus $[\text{Cl}^-]$ (*i.e.* k_a in Table II) are not equal to some of the terms in the above-simplified rate law since the condition that $[\text{Cl}^-] \gg K_A K_B / [\text{H}^+]$, is not satisfied by the intercept where $[\text{Cl}^-] \rightarrow 0$.

According to the overall rate law, however, $k \rightarrow k_2$ when $[\text{Cl}^-] \rightarrow 0$, which is a limiting condition beyond the concentration ranges of this investigation. When it is assumed that the experimental values of k in Table I can be extrapolated to $[\text{Cl}^-] \rightarrow 0$ as shown in Figure 2, then it follows that the values of k_a in Table II are those for k_2 . This is within reasonable expectations since at very low $[\text{Cl}^-]$, $\text{AuCl}_3(\text{OH})^-$ will be the main rate contributing species and the formation of $\text{Mal}\cdot\text{Cl}^-$ will be negligible, such that reaction (2) is the only one that can proceed effectively.

The increase in k_2 with increasing pH is attributed to an increase in the substitution reactivity in going from malonic acid to bimalonate ion. From a plot of k_2 versus pH it is concluded that the reaction between $\text{AuCl}_3(\text{OH})^-$ and malonic acid occurs at a low rate ($< 0.2 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$), whereas the reaction between $\text{AuCl}_3(\text{OH})^-$ and bimalonate ion occurs at a rate of $\sim 1.9 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ at 25 °C. These values are considerably smaller than those reported for the corresponding reactions with oxalic acid and bioxalate ion [2], which is attributed to the better complex forming properties of the latter. The values are, however, considerably larger than those reported for the reaction with formic acid and formate ion [3], which points to the effect of the bidentate character of malonic acid and malonate ion. k_2 increases with a factor of ~ 10 in going from low to higher pH, in agreement with the results reported for the other systems studied [2, 3].

The values for k_3 are considerably higher than those for k_2 (K_C was assumed to be small), which once again emphasizes the higher reactivity of the $\text{Mal}\cdot\text{Cl}^-$ species. This tendency is further confirmed

by the activation parameters for k_2 and $k_3 K_C$ reported in Table II. The pH dependence of $k_3 K_C$ is also attributed to the participation of the different malonate species as discussed for k_2 . No direct conclusions concerning the rate constants for the reactions between AuCl_4^- and the different $\text{Mal}\cdot\text{Cl}^-$ species (reaction (3)), could be made since the pK values of the $\text{Mal}\cdot\text{Cl}^-$ species and the K_C values are unknown.

TABLE III. Radiochemical Results.

pH = 2.5; [total malonate] = $1 \times 10^{-3} \text{ M}$; $[\text{HAuCl}_4] = 1.5 \times 10^{-4} \text{ M}$. Temp. = 40 °C; $\text{C}^{14} = 2.0 \mu \text{ Ci}/20 \text{ ml}$ test solution

$[\text{Cl}^-]$ (M)	Time (hours)	Absorbance at 313 nm	Count Rate (Count min^{-1})
0.8	0	0.75	0
	1.5	0.31	490
	3.75	0.07	7990
	5.5	0.02	13600
	7.75	—	18200
	12.25	—	22800
	23.0	—	29850
	35.5	—	37430
	47.5	—	43460
	∞	—	50000
0.01	0	0.71	0
	1.75	0.50	2450
	3.25	0.35	4530
	7.0	0.14	11210
	11.25	0.05	18140
	22.75	—	30700
	28.75	—	33710
	36.0	—	38800
	71.0	—	47390
	∞	—	50000

Table III summarizes the results obtained with malonic acid of which the carboxylic carbon atoms were labelled. At high $[\text{Cl}^-]$ the decrease in absorbance at 313 nm is, during the first half-life of the reaction, accompanied by a very low count rate ($\sim 1\%$ of the total count rate), indicating that the observed decrease must be due to a substitution process. At longer reaction periods the count rate increases substantially, which points towards a slow redox reaction. At low $[\text{Cl}^-]$ a larger count rate is obtained over the first half-life of the reaction, and amounts to 10% of the total count rate observed. Under this condition the substitution process is considerably slower (see data in Table I) and the redox reaction will occur to a larger extent during the initial reaction period. In both cases, however, the increase in count rate obeys first-order kinetics and the such-calculated rate constants are 1.17×10^{-5} and $1.13 \times 10^{-5} \text{ sec}^{-1}$ at 0.8 and 0.01 M Cl^- respectively. The reported rate constants are nearly

equal and independent of the $[Cl^-]$ as one would expect for such a redox process. We conclude that the redox process is considerably slower than the substitution process, in contradiction to that reported for the reactions with oxalate [2] and formate [3]. A possible reason for this tendency is the smaller reducing property of malonic acid/malonate ion compared to the other carboxylic acids studied. A considerably lower count rate ($\sim 10\%$) was obtained, under similar experimental conditions, using malonic acid of which the central CH_2 moiety was labelled. This is attributed to the presence of acetylaldehyde in trace quantities in the gaseous decomposition products, since this product is mainly present in solution. A similar result was reported for the thermal decomposition of trismalonatocobalt(III) [8, 19]. In this reaction CO_2 originates from an electron transfer process during which the central metal ion is reduced to the $2+$ state and the ligand is oxidized. A possible route for the formation of CH_3CHO was suggested [8], which may be applied to the system under investigation.

Acknowledgments

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