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Kinetics of Silver(I)-Catalyzed Oxidation of Formic Acid by the (Ethylenebis(biguanidine))silver(III) Cation in Acid Perchlorate Media¹

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In the presence of added Ag⁺, the title reaction follows the rate law $-d[\text{complex}]/dt = k^0 = Kk_1[\text{Ag}^+]^2[\text{HCO}_2\text{H}]/([\text{H}^+] + K[\text{HCO}_2\text{H}])$, where k^0 is the observed zero-order rate constant for a large excess of Ag⁺, H⁺, and HCO₂H over the complex. 10^3k_1 was found to be $1.0 \pm 0.1 \text{ M}^{-1} \text{ min}^{-1}$ at 30 °C and $I = 1.0 \text{ M}$. Corresponding ΔH^\ddagger and ΔS^\ddagger values are $13 \pm 1 \text{ kcal/mol}$ and $-37 \pm 3 \text{ eu}$, respectively. Under these conditions, K , the formation constant of Ag(HCO₂) from HCO₂H and Ag⁺, was found from kinetic results to be 0.1 ± 0.01 . The acid dissociation constants (pK_1 and pK_2) of the complex cation under similar conditions in a 50% (v/v) aqueous-DMF medium are 3.8 ± 0.2 and 6.8 ± 0.3 . There is evidence for the Ag⁺ ion acting here as the actual oxidant for HCO₂H with use of the complex as an oxidant regenerating Ag⁺ from Ag⁰ formed as an intermediate. Under the experimental conditions where Ag(II) is detectable in concentrations less than about 10^{-6} M , the whole reaction course is EPR silent. This has been discussed in terms of possible reaction schemes.

The chemistry of silver(III) has aroused much recent interest.^{2,3} Even then, it is considerably more restricted than that of silver(II),⁴ and true involvement of silver(III) in kinetics continues to be an uncommon phenomenon. This is true⁵ even for the Ag(I)-catalyzed oxidation reactions where instead of the operation of the earlier believed⁶ Ag(I)/Ag(III) catalytic cycles, Ag(I)/Ag(II) or Ag(I)/Ag(0) cycles are involved.⁷ Examples of Ag(III) entering through disproportionation of Ag(II) also are not many,^{8,9} and the disproportionation equilibrium (eq 1) lies far to the left.^{6,10}



Similarly, direct use of authentic Ag(III) complexes in kinetics is also limited and largely restricted to some interesting reports involving a few silver (III) porphyrins^{11,12} and reactions of Ag(OH)₄⁻—the simplest solution species containing Ag(III). This latter species is moderately stable in strongly alkaline media where kinetics of its reactions with different substrates have been reported.¹³

The title complex (Figure 1) is a rare example of an authentic¹⁴⁻¹⁸ cationic complex of Ag(III), extensively stabilized¹⁹ by an acyclic ligand environment and stable in acid solutions.²⁰ Investigations on kinetics of its reactions in acid media with extraneous reductants thus appeared interesting. To our knowledge, no such investigation has so far been reported, though

kinetics have been measured for its base-catalyzed decomposition²⁰ and for its formation by S₂O₈²⁻ oxidation of Ag(I) in the presence of the ligand.²¹

Experimental Section

Materials. (Ethylenebis(biguanidine))silver(III) nitrate, [Ag(C₆N₁₀H₁₆)](NO₃)₃, was prepared by a known method²² and recrystallized from water, adding, in the cold, an excess of aerated 5% (v/v) nitric acid solution and all the time avoiding boiling.²³ The orange-red crystals thus prepared are diamagnetic and give a satisfactory elemental (C, H, N, Ag) analysis. Bis(2,2'-bipyridyl)silver(II) nitrate, [Ag(C₁₀N₂H₈)₂](NO₃)₂, was prepared by a known procedure.²⁴

Formic acid (G.R., E. Merck) solutions were prepared by dilution before use. Silver perchlorate solutions were obtained by dissolving freshly precipitated Ag₂O in dilute perchloric acid (G.R., E. Merck) and were estimated gravimetrically as AgCl. Triply crystallized NaClO₄ (L.R., Loba) was used to prepare solutions and was standardized by ion exchange through Dowex 50W-X8 cation exchanger in H⁺-form. Dimethylformamide (G.R., Loba) was further purified by distillation.²⁵ All other chemicals were of reagent grade and used as received. Twice-distilled water was employed throughout.

Instrumentation. Solution spectra and absorbances were obtained on a Shimadzu Graphicord (UV-240) spectrophotometer. Magnetic susceptibilities were measured with a EG&G PAR magnetometer (Model 155) fitted with a vibrating sample magnetometer. X-Band EPR spectra were recorded with a Varian EPR 4 spectrometer having the following instrumental setups: field set, 3000 G; scan range, 8000 G; gain 2.0×10^4 ; modulation (p-p), $0.8 \times 10 \text{ G}$; time constant, 0.250 s; scan time, 4 min; microwave power, 24 dB; microwave frequency, 9.45 GHz. Reactant solutions containing 0.1–1.0 mM concentrations of complex were run at varying stages in their decomposition. Prepared solutions of Ag-(bpy)₂²⁺ were used to assess the lower limit for the detection of Ag(II) species under these experimental conditions.

Microanalytical data (C, H, N) were obtained with use of a Perkin-Elmer (Model 240 C) elemental analyzer. A Systronics (Model 335) digital pH meter having a glass-calomel electrode assembly was utilized for pH measurements.

Product Analysis. After removal of Ag⁺ as AgCl, free ligand was precipitated from the completely reacted solutions as the corresponding copper(II) complex, and the amount of Cu(II) thus held was estimated iodometrically after the Cu(II) complex was decomposed. Carbon dioxide was qualitatively detected by purging purified dinitrogen through the reaction mixture and passing the outgoing gas through a narrow, long absorber tube containing limewater.

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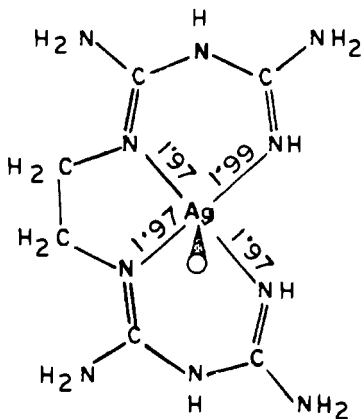


Figure 1. Structure for the perchlorate salt of the title complex.

Equilibrium Measurements. Protonation constants of the complex were determined by pH metric titration of 1.0 mM perchloric acid in the absence and in the presence of 1.0 mM complex at 30 °C in a 50% (v/v) aqueous-dmf medium having a constant ionic strength of 1.0 M. pH values were measured with reference to the 50% (v/v) aqueous-dmf standard state by applying appropriate correction factors.²⁶ pH values thus obtained were used throughout while evaluating pK_1 and pK_2 by the procedure of Irving and Rossotti.²⁷

Kinetic Measurements. Reactions were monitored by following the disappearance of the complex spectrophotometrically at 380 nm and (occasionally) at other wavelengths. Kinetic runs were taken at an ionic strength of 1.0 M and in the presence of large excesses of $AgClO_4$, formic acid, and perchloric acid over the complex. Under such experimental conditions the zero-order rate constants ($k^\circ = -\text{slope of the } [complex]_t \text{ vs time } (t) \text{ plot}$) at different temperature were evaluated from the linear least-squares slope (B) of absorbance (A_t) vs time (t) data and the known ϵ value (1175 units) of the complex in acid media ($k^\circ = -B/\epsilon$). For this purpose the built-in least-squares program of a Casio (Model fx-3600P) scientific calculator was utilized. Errors associated with kinetic parameters were estimated by using standard formulas and procedures. Average values of at least two independent determinations of k° were taken. Some kinetics were run in the absence of added $Ag(I)$ or formic acid or both. A few runs were also done (a) after bubbling purified dinitrogen or carbon dioxide through the experimental solution, (b) after adding excess ethylenebis(biguanide) and (c) at different wavelengths of measurements. Ambient light was very low in the closed thermostatic system used for kinetics. The effect of ambient light on the reaction, if any, was assessed by carrying some reactions in volumetric flasks blackened outside with Black Japan, and some in transparent flasks exposed to ambient light.

Stoichiometry. A 50-mL aliquot of 0.01 M complex solution in 0.03 M $HClO_4$ was allowed to react completely in the presence of 0.05 M HCO_2H and 0.10 M Ag^+ at 50 °C. Unreacted formic acid was estimated by ceric oxidimetry as catalyzed by bromide ions²⁸ at room temperature.

Results and Discussion

The high positive charge of the central metal brings about a rather facile loss of proton, probably from the terminal amino groups. This deprotonation causes a marked change in the electronic spectrum, which is seen as a yellow-to-red conversion when the medium is made alkaline. The measured pK values are $pK_1 = 3.8 \pm 0.2$ and $pK_2 = 6.8 \pm 0.3$ at 30 °C, $I = 1.0$ M. These suggest that above 0.05 M $[H^+]$ the complex exists almost exclusively (>99%) in the undissociated H_2C^{3+} , i.e., $[Ag-(C_6N_{10}H_{16})]^{3+}$ form. Its spectrum in aqueous acid media is represented in Figure 2A and is characterized by a broad band²⁹ with a maximum at 380 nm ($\epsilon = 1175$ units). This remains unchanged in the acidity range $0.01 \text{ M} > [H^+] < 1.0 \text{ M}$. When the solution was made alkaline, practically complete loss of both of the protons occurs above pH, 7 and C^+ is produced when a new

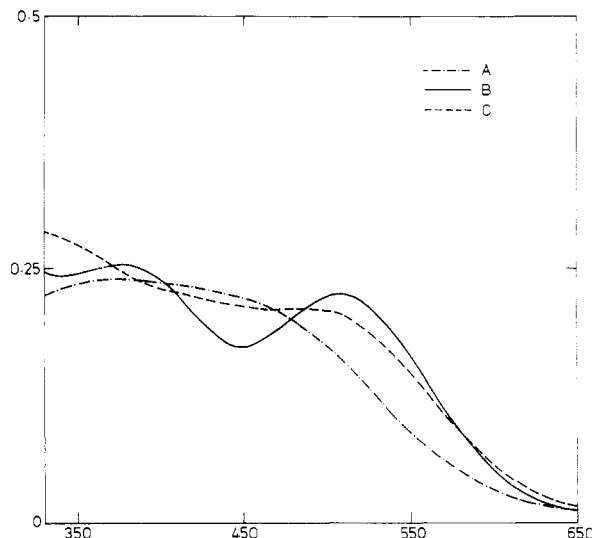
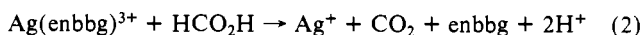


Figure 2. Spectra of 0.2 mM complex: (A) the H_2C^{3+} form (Figure 1 (>99%) in aqueous 0.1 M $HClO_4$; (B) the C^+ form (>99%) in 50% (v/v) aqueous dmf media, pH = 8; (C) the HC^{2+} form (~93%) in 50% (v/v) aqueous dmf media, pH = 5 (with reference to the nonaqueous standard state, see text).

maximum appears at 507 nm with $\epsilon = 1120$ units (Figure 2B). The spectrum in Figure 2B remains unchanged up to pH 9.5 and then precipitation sets in.

At pH 5.0 (with reference to a 50% aqueous-dmf standard state), concentration of the HC^{2+} form reaches a maximum (~93%). The spectrum of the complex at this pH is shown in Figure 2C. The spectra shown in Figure 2B,C were taken in 50% (v/v) aqueous-dmf media to avoid precipitation and are not probably comparable to Figure 2A in the strictest sense. The complex spectra are independent of an added excess of ligand (1.0 mM), and the solution absorbances at 380 and 507 nm obey Beer's law throughout the investigated concentration range (0.1–1.0 mM). In freshly prepared solutions, therefore, dissociation or molecular association of the complex into species having appreciably different UV-vis spectral characteristics appears unlikely.

This complex possesses fascinating thermodynamic stability¹⁹ and in aqueous acid media ($[H^+] > 0.1 \text{ M}$) suffers little decomposition (<5%) over a period of 36 h at room temperature.²⁰ However, when both $Ag(I)$ and formic acid are added, the complex in acid media is quantitatively reduced to Ag^+ and the free ligand. In this process, each mole of the complex consumes 0.93 mol of formic acid and produces carbon dioxide, detected as one of the reaction products. This is in accordance with the generally accepted view⁸ that formic acid is oxidized by metal ions and metal complexes into carbon dioxide. In the present case the stoichiometric equation can thus be represented by eq 2.



The absorbance vs time data fit well ($r \geq 0.99$) to a straight-line relationship for extent of reaction exceeding 70%. Least-squares intercepts are reproducible within 1% of the initial absorbance value. Individual k° values (see Table I) are reproducible within 5%. $[Ag^+]^2/k^\circ$ vs $[H^+]/[HCO_2H]$ data also nicely follow ($r \geq 0.98$) linear relation. The observed rate law is thus representable by eq 3. Changes in complex concentration from 0.1 to 0.8 mmol,

$$-\frac{d[complex]}{dt} = k^\circ = \frac{Kk_1[Ag^+]^2[HCO_2H]}{[H^+] + K[HCO_2H]} \quad (3)$$

changes in wavelength for kinetic measurements from 380 to 510 nm, addition of excess (1.0 mM) ligand, and ambient light have no appreciable effect on the reaction rate.

When either formic acid or Ag^+ is absent, the complex disappears only very slowly, the rate being <5% of that observed in the presence of Ag^+ and HCO_2H . It is further noted that faint blackish suspension of $Ag(0)$ forms when the solutions prepared for kinetic runs are kept overnight without added complex. This

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Table I. Representative Values^a of k°_{calcd} and k°_{expt} at different $[\text{H}^+]$, $[\text{HCO}_2\text{H}]$, $[\text{Ag}^+]$, and Temperatures in the Ag(I)-Catalyzed (Ethylenebis(biguanidine))silver(III)- HCO_2H Reaction

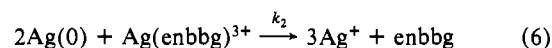
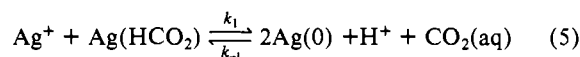
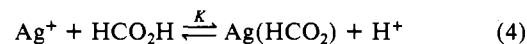
temp, °C	$[\text{H}^+]$, M	$[\text{HCO}_2\text{H}]$, M	$10^2[\text{Ag}^+]$, M	10^7k° , M min ⁻¹	$10^7k^{\circ}_{\text{calcd}}^b$, M min ⁻¹	
30	0.1	0.1	3.0	0.8	0.8	
				1.5	1.5	
				1.9	2.0	
				2.5	2.5	
				3.6	3.7	
				3.9	4.0	
				4.5	4.5	
				4.5	4.3	
	0.05	0.5	1.0	3.7	3.5	
				3.1	3.0	
				1.9	1.8	
				1.1	1.1	
				0.3	0.3	
				1.3	1.3	
				3.1	3.0	
				5.4	5.3	
				8.3	8.3	
40	0.1	0.3	3.0	7.4	6.8	
				9.8	9.0	
				10.8	9.8	
				11.8	11.1	
				12.7	12.0	
				8.6	8.0	
				6.8	6.0	
				5.9	5.1	
	0.05	0.2	1.0	4.4	3.8	
				3.5	3.5	
				0.7	0.6	
				2.4	2.3	
				5.6	5.1	
				9.1	9.1	
				14.1	14.3	
				10.1	10.3	
				14.0	13.5	
50	0.1	0.1 ^c	3.0	15.0	16.0	
				18.7	18.0	
				20.4	19.6	
				20.4	21.0	
				29.5	29.5	
				21.3	22.1	
				20.5	20.6	
				18.7	18.0	
	0.05	0.2 ^d	0.5	0.5	15.0	16.0
					18.7	18.0
					20.4	19.6
					20.4	21.0
					29.5	29.5
					21.3	22.1
					20.5	20.6
					18.7	18.0
					11.2	12.0
50	0.1	0.2	0.5	10.7	10.3	
				7.8	7.5	
				5.8	5.9	
				5.0	5.0	
				0.4	0.4	
				1.7	1.7	
				7.0	7.1	
				15.0	16.0	
	0.05	0.2 ^d	0.5	0.5	29.0	28.4
					44.4	44.4
					2.0 ^e	2.0
					3.0	3.0
					4.0	4.0
					5.0 ^f	5.0
					15.0	16.0
					29.0	28.4
					44.4	44.4

^aUnless otherwise stated $[\text{complex}] = 0.2$ mM, wavelength of kinetic measurements = 380 nm, $I = 1.0$ M. Reported k° values are generally the average of two independent measurements; individual k° values are reproducible within 5%. ^bCalculated by using k_1 and K values from Table III via eq 3. ^c $[\text{Complex}]$ varied from 0.1 to 0.8 mM. ^dThese kinetics were repeated (i) in the presence of excess (1 mM) ligand, (ii) at 510 nm, (iii) after purging with purified dinitrogen. ^eExperiment repeated after passing purified CO_2 through the mixture. ^fExperiment repeated in the presence and in the absence of ambient light.

is more significant when $[\text{H}^+]$ is relatively low and $[\text{HCO}_2\text{H}]$ is relatively high. In the presence of the complex, however, no detectable amount of $\text{Ag}(0)$ develops, but if a suspension of freshly precipitated $\text{Ag}(0)$ (obtained by heating AgNO_3 with HCO_2H solution) is added to an acidified solution of the complex alone, then the complex absorbance, measured from time to time after filtering off $\text{Ag}(0)$ from the aliquot, drops at a distinctly faster rate than that measured in the absence of added $\text{Ag}(0)$. Shaking

the spectrophotometer cell does not affect the absorbances measured in this experiment.

In the experimental acidity range both formic acid and the complex exist almost exclusively in their respective undissociated forms. Also, under the experimental conditions where $\text{Ag}(\text{bpy})_2^{2+}$ is detectable in concentrations less than about 10^{-6} M, the whole reaction course ($[\text{complex}] = 0.1\text{--}1.0$ mmol) is EPR silent. The following kinetic scheme thus may be proposed:



Formation of $\text{Ag}(\text{HCO}_2)$ and its subsequent decomposition into metallic silver and carbon dioxide is a well-known reaction.³⁰ However no data for the stability constant, K are available.

Steady-state analysis of the above scheme for $d[\text{Ag}(0)]/dt = 0$ readily gives

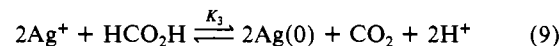
$$\frac{d[\text{complex}]}{dt} = \frac{Kk_1k_2[\text{Ag}^+]^2[\text{HCO}_2\text{H}][\text{complex}]}{([\text{H}^+] + K[\text{HCO}_2\text{H}])(k_{-1}[\text{H}^+][\text{CO}_2(\text{aq})] + k_2[\text{complex}])} \quad (7)$$

Like $\text{Hg}(0)$,³¹ $\text{Ag}(0)$ is also known to be slightly but definitely soluble in water.³² Trace solubility of $\text{Ag}(0)$ in aqueous media is probably indicated also from the high degree of the oligodynamic effect,³³ the lethal effect of metals toward bacteria and lower life forms exhibited by metallic silver kept in contact with water. If, now

$$k_{-1}[\text{H}^+][\text{CO}_2(\text{aq})] \ll k_2[\text{complex}] \quad (8)$$

then eq 7 reduces to the observed rate law (eq 3).

Saturation of the reaction media with CO_2 does not retard the reaction nor does this affect the zero-order kinetic pattern. The inequality thus holds even at the highest attainable $[\text{CO}_2(\text{aq})]$ in experimental solutions. Assuming that the right-hand side of eq 8 is at least 100 times larger than the left-hand side, a lower limit for k_2 may be estimated as $5000 k_{-1}$ when $[\text{H}^+] = 0.2$ M and $[\text{complex}] = 0.2$ mmol; solubility of CO_2 under the experimental conditions is 0.02 M (ref 32, p 465), and it is assumed to be present solely as $\text{CO}_2(\text{aq})$. Reduction potentials³⁴ for $\text{Ag}(\text{I})/\text{Ag}(0)$ (0.799 V) and $\text{HCO}_2\text{H}/\text{CO}_2$ (-0.196 V) couples suggest that the equilibrium constant, K_3 , for the overall reaction (eq 9) is likely to be very large. Since K of eq 4 is on the order



of 10^{-1} (this study), the equilibrium constant for step 5 ($K_4 = k_1/k_{-1}$) should also be very large. Hence k_{-1} should be very small since k_1 is on the order of 10^{-3} M⁻¹ min⁻¹ (this study).

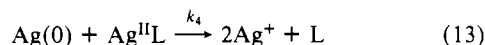
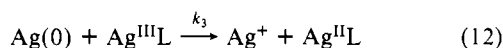
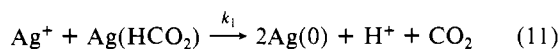
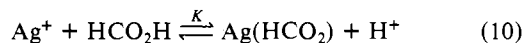
The comproportionation reaction 6 in the proposed scheme may also be replaced by a combination of steps 12 and 13 as shown

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Table II. Analysis of $[Ag^+]^2/k^\circ$ vs $[H^+]/[HCO_2H]$ Data

temp, °C	$10^{-3}(\text{slope}),$ M min	$10^{-3}(\text{intercept}),$ M min	K	$10^3 k_1,$ $M^{-1} \text{min}^{-1}$
30	10 ± 0.2	1.0 ± 0.1	0.10 ± 0.01	1.0 ± 0.1
40	2.1 ± 0.02	0.50 ± 0.02	0.23 ± 0.05	2.0 ± 0.1
50	0.63 ± 0.01	0.25 ± 0.01	0.40 ± 0.05	4.0 ± 0.2

in the following reaction scheme, which is kinetically indistinguishable from the earlier one:



As discussed previously, step 11 should be associated with a very large equilibrium constant, and its presentation as a unidirectional process is logical. It can then be shown that in this scheme the $Ag^{II}L$ concentration under the steady-state conditions is given by eq 14. Under the experimental conditions, $Ag(II)$ is detectable

$$[Ag^{III}L]/[Ag^{II}L] = k_4/k_3 \quad (L = \text{enbbg}) \quad (14)$$

by EPR measurements in concentration less than about 10^{-6} M. We have used initial $[Ag^{III}L]$ up to 1.0 mM in our EPR studies. Hence, $Ag^{II}L$ would be detectable if k_4 is not far larger than $10^3 k_3$. Otherwise, the intermediate $Ag^{II}L$ may evade its detection. In the absence of definite data for k_3 and k_4 , it is difficult to assess if $Ag^{II}L$ has any role in this reaction. No Ag^{II} complex with any of the several biguanidines has ever been isolated. But here presence of any $Ag^{II}L$ as a reaction intermediate is likely to be reflected, under favorable conditions, in the overall reaction stoichiometry. The hypothetical $Ag^{II}L$, which is a d^9 system, is expected to be a much more labile complex and a stronger oxidant than $Ag^{III}L$. In compliance with these speculations, $Cu^{II}L$ ($3d^9$) undergoes acid-catalyzed aquation $\sim 10^4$ times faster than $Ni^{II}L$ ($3d^8$), and Ag^{II} -complexes, such as $Ag(\text{bpy})_2^{2+}$, are extremely rapid oxidants, oxidizing e.g., HCO_2H to CO_2 in acid media. In the presence of any appreciable quantity of accumulated $Ag^{II}L$, the present reaction had a chance to consume a larger proportion

of HCO_2H than expected for eq 2. But this has not been observed.

K and k_1 were evaluated from the least-squares slopes and intercepts of $[Ag^+]^2/k^\circ$ vs $[H^+]/[HCO_2H]$ data (Table II). By use of these K and k_1 values, k° can be reproduced in most of the cases within 10% of experimental values. (see Table I). ΔH^\ddagger and ΔS^\ddagger values corresponding to k_1 were evaluated by using the Eyring equation to be 13 ± 1 kcal/mol and -37 ± 3 eu, respectively.

The proposed reaction scheme, in effect, depicts the reaction studied to be the reduction of Ag^+ to $Ag(0)$ by formic acid, with use of the complex as an oxidant regenerating Ag^+ from $Ag(0)$. The reaction thus appears to be Ag^+ -catalyzed oxidation of HCO_2H by the complex; but the rate measured is that for HCO_2H oxidation by Ag^+ not by the complex. Thus toward HCO_2H the $Ag(III)$ complex used here appears to be a weaker oxidant, at least in the kinetic sense, than Ag^+ . It is known⁸ that uncomplexed $Ag(III)$ rapidly oxidizes HCO_2H in acid perchlorate media into CO_2 . Also in the Ag^+ -catalyzed oxidation of HCO_2H by $S_2O_8^{2-}$, $Ag(III)$ is the active oxidant.³⁶ The superiority of $Ag(I)$ over $Ag(III)$ here as an oxidant may, therefore, reflect the circumstances that $Ag(III)$, but not $Ag(I)$, is strongly ligated in a substitutionally inert ($4d^8$ system) complex.³⁷ The present investigation is thus probably the first instance of a $Ag(I)/Ag(0)$ cycle operating in the presence of a $Ag(III)$ species.

Little work has so far been carried out on the mechanism of oxidation by the mild oxidant $Ag(I)$; one of the few investigated systems is the oxidative coupling of the electron-rich olefins $>C=C(NH_2)_2$ by Ag^+ in acetonitrile.³⁸ Also, in the presence of suitable macrocyclic ligands, $Ag(I)$ is known^{39,40} to disproportionate into $Ag(0)$ and $Ag(II)$, $Ag(I)$ acting as an oxidant for $Ag(I)$. The title complex may be useful, in favorable situations, in investigating the kinetics of oxidation by $Ag(I)$ bypassing the problems arising from the precipitation of $Ag(0)$.

Registry No. HCO_2H , 64-18-6; $Ag(HCO_2)$, 13126-70-0; Ag^+ , 14701-21-4; $Ag(\text{enbbg})^{3+}$, 50578-37-5.

Supplementary Material Available: A table of representative absorbance versus time data (1 page). Ordering information is given on any current masthead page.

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