Kinetics of the Uncatalysed and Silver(I)-catalysed Oxidation of Hydrogen Peroxide by [Ethylenebis(biguanide)]silver(III) Ion in Acid Perchlorate Media†

Rupendranath Banerjee,* Amitava Das, and Subrata Dasgupta
Department of Chemistry, Jadavpur University, Calcutta 700 032, India

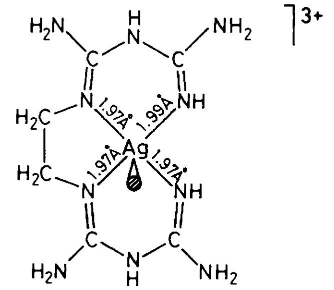
In aqueous acid media [ethylenebis(biguanide)]silver(III) oxidises H_2O_2 to O_2, itself being reduced to Ag^I and ethylenebis(biguanide): a 1 : 1 stoicheiometry has been established. The reaction is catalysed by Ag^+ and the empirical rate law is $-d[\text{complex}]/dt = (k_{uncat} + k_{cat}[Ag^+])[H_2O_2][\text{complex}]/[H^+]$. At 30 °C and $I = 1.0$ mol dm^{-3}, $k_{uncat} = (6.5 \pm 0.5) \times 10^{-5}$ s^{-1} and $k_{cat} = (9 \pm 1) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. For k_{uncat}, $\Delta H^\ddagger = 31 \pm 12$ kJ mol^{-1} and $\Delta S^\ddagger = -222 \pm 37$ J K^{-1} mol^{-1}, while for k_{cat} the values are 41 ± 16 kJ mol^{-1} and -167 ± 53 J K^{-1} mol^{-1} respectively. The inverse proton dependence of the rate arises from deprotonation of H_2O_2 facilitated by its axial co-ordination to the complex, forming an adduct; catalysis by Ag^I arises through complexation of Ag^I with this adduct. The probable mechanism and plausible role of any intermediate silver(II) species are discussed.

The kinetics of hydrogen peroxide oxidation by a number of strongly oxidising aquametal ions as well as complex metal ions has been investigated.[1-3] However, the involvement of Ag^{III} is uncommon and the only kinetic investigation reported[2] so far concerns a reaction with peroxide where $[Ag(OH)_4]^-$ was the oxidant in a strongly alkaline medium. We report herein a study of the reaction, in acid media, between the complex [ethylenebis(biguanide)]silver(III) and H_2O_2. The complex is well characterised[4-8] as square planar, definitely known to contain low-spin ($4d^8$) Ag^{3+} and extensively stabilised by the strong field acyclic ligand ethylenebis(biguanide) (H_2L). At and around ambient temperature, it is reasonably stable in acid media. Its base-catalysed intramolecular redox decomposition[9] becomes appreciable only when the media acidity is less than 0.02 mol dm^{-3}. Preliminary investigations showed that in aqueous acid media the complex oxidises H_2O_2 to O_2 at a measurable rate and that the process is significantly catalysed by Ag^I. To probe the mechanism of this catalysed oxidation the present kinetic investigation was initiated.

Experimental

Materials.—[Ethylenebis(biguanide)]silver(III) nitrate, $[Ag(H_2L)][NO_3]_3$, was prepared in the pure state following the method of Ray and Chakravarty,[10] with some modifications in the crystallisation procedure. We recrystallised the nitrate salt from its aqueous solution at ambient temperature by the addition of an excess of cold aerated 5% (v/v) HNO_3 solution. The orange-red crystals, thus prepared, are diamagnetic and give satisfactory elemental (C, H, and N) analysis. The crystallisation procedure reported earlier[10] produces a complex with irreproducible spectral characteristics. Bis(2,2′-bipyridyl)-silver(II) nitrate, $[Ag(bipy)_2][NO_3]_2$, was prepared by a known method.[11]

Solutions of H_2O_2 were prepared by dilution of G.R., E. Merck 30% (w/v) stabiliser-free H_2O_2 and were standardised by titrating against Ce^{IV} using a ferroin indicator. We verified the observations of previous workers[2,12] that decomposition of H_2O_2 in acid media under the kinetic conditions was minimal. Sodium perchlorate used for ionic strength adjustments was prepared by neutralisation of perchloric acid (70%, G.R., E. Merck) with a solution of sodium hydroxide (Excelar, A.R., chloride free). This was standardised by ion exchange on a Dowex-50W-X8 cation exchanger in the H^+ form. Solutions of silver(I) and mercury(II) perchlorates were prepared from the respective oxides which were freshly precipitated and treated with the minimum excess of dilute $HClO_4$. They were standardised gravimetrically as AgCl and $[Hg_5(IO_6)_2]$[13] respectively. Sodium chloride (A.R., B.D.H.) solutions were prepared by direct weighing.



$[Ag(H_2L)]^{3+}$

All other chemicals were of reagent grade and used as received. Twice distilled water was employed throughout.

Instruments.—Optical densities were obtained in a Shimadzu UV-240 spectrophotometer. Magnetic susceptibilities were measured with an EG & G PAR magnetometer-135 fitted with a vibrating sample magnetometer. E.s.r. spectra were recorded with a Varian EPR 4 *X*-band spectrometer at the following settings: field 3 000 G; scan range, 8 000 G; gain, 2.0 × 10^4. Reactant solutions containing 0.1—1.0 mmol dm^{-3} complex were monitored at various stages of their reaction. Prepared solutions of $[Ag(bipy)_2]^{2+}$ were used to assess the lower limit for the detection of silver(II) species under these experimental conditions.

Microanalytical data (C, H, and N) were obtained with a Perkin-Elmer 240C elemental analyser.

Product Analysis.—After removal of Ag^+ as AgCl from the product solution, ethylenebis(biguanide) was quantitatively

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† *Non-S.I. unit employed:* G = 10^{-4} T.

Table 1. Pseudo-first-order rate constants k_o for the uncatalysed oxidation of hydrogen peroxide by [ethylenebis(biguanide)]silver(III): effect of varying $[H_2O_2]$ and $[H^+]$; [complex] = 0.2 mmol dm^{-3}, I = 1.0 mol dm^{-3}

	$[H^+]$	$[H_2O_2]$	
θ_c/°C	mol dm^{-3}		10^5k_o/s^{-1}
30	0.20	0.05	1.7
	0.30	0.09	2.0
	0.40	0.16	2.6
	0.50	0.07	0.9
		0.09	1.2
		0.10	1.3
40	0.20	0.05	3.1
	0.30	0.09	3.6
	0.40	0.16	4.7
	0.50	0.07	1.6
		0.08	2.1
		0.09	2.4
		0.10	2.5
50	0.10	0.02	3.8
		0.03	3.6
		0.035	7.6
		0.04	6.8
		0.07	11.5
		0.08	14
		0.10	15
	0.15	0.075	7.6
	0.20	0.05	3.6

precipitated as its copper(II) complex. The amount of Cu^{II} thus complexed was estimated iodometrically after decomposition.

Stoicheiometry.—The reaction was too slow to determine $\Delta[H_2O_2]/\Delta$[complex] by using an excess of complex over H_2O_2. Instead, Δ[complex]$/\Delta[O_2]$ was measured under the kinetic conditions both in the presence and in the absence of added Ag^+. The average of two independent measurements was taken. The concentration of oxygen originating in the reaction solution was estimated using an Orion 901 microprocessor ion analyser equipped with an oxygen electrode (Orion Research model 97-08-00) which was sealed from the atmosphere. The electrode was calibrated using water saturated with air ($[O_2] = 2.5 \times 10^{-4}$ mol dm^{-3} at 25 °C).[14] The corresponding change in [complex] was determined spectrophotometrically at 380 nm and was corrected for the parallel autodecomposition of the complex. Such blank corrections were less than 2% of the total change. The blank correction for $[O_2]$ was insignificant.

Kinetics.—In acid media the complex exhibits a broad maximum at 380 nm (ε = 1 175 dm^3 mol^{-1} cm^{-1}), and its decay was generally followed at this wavelength under different experimental conditions. A pathlength of 1 cm was used throughout. Occasionally, the monitoring wavelength was 480 nm. At both of these wavelengths the reaction products are non-absorbing. The [complex] was varied from 0.1 to 1.0 mmol dm^{-3} with the concentration of H_2O_2 being in a minimum of a 200-fold excess. The acidity of the media was maintained sufficiently high ($\geqslant$0.04 mol dm^{-3}) to ensure that the base-catalysed autodecompostion[9] of the complex is always $< 5\%$ of the total change. The ionic strength I was generally 1.0 mol dm^{-3} unless specified otherwise.

Catalysis by Ag^I was studied in the pesence of at least a 50-fold excess of $AgClO_4$ over the complex. With the aim of excluding Ag^I from the medium, a few runs were performed in the presence of added NaCl. In such cases, optical densities were measured after dry filtration of quenched aliquots of the reactant solution. The effect of Hg^{2+} on the rate was studied by the addition of $Hg(ClO_4)_2$.

The temperature was controlled to within ±0.1 °C in a closed type of thermostat wherein the level of ambient light was very low.

The reactions were generally studied at least up to 70% completion. All data, except plots of $\log_{10}$(optical density) *versus* time, were analysed by a least-squares procedure where appropriate.

Results and Discussion

Stoicheiometry.—Ethylenebis(biguanide) (H_2L) and Ag^I were recovered from the product solution in near-quantitative yield, 96 and 99.5% respectively. The values of Δ[complex]$/\Delta[O_2]$ in the presence and in the absence of Ag^+ are respectively 0.95 ± 0.07 and 1 ± 0.05. This result, along with the results of stoicheiometric measurements with an excess of H_2O_2 in the absence as well as in the presence of 0.03 mol dm^{-3} Ag^+, are consistent with a redox reaction denoted by equation (1) within an experimental uncertainty of 5%.

$$[Ag(H_2L)]^{3+} + H_2O_2 \longrightarrow Ag^+ + LH_2 + 2H^+ + O_2 \quad (1)$$

Kinetics of Oxidation.—In all the cases H_2O_2 was in sufficient excess over the complex to ensure pseudo-first-order conditions and plots of $\log_{10}$(optical density) against time were linear for at least 70% reaction. Replicate runs reproduced the individual pseudo-first-order rate constants k_o within 5% for most of the kinetic measurements.

(*a*) Uncatalysed reation. In the absence of added Ag^+, a few kinetic runs showed a small initial increase in optical density. However, this was too erratic and of too small a duration for any significance to be ascribed to it.

(*i*) *Dependence on* [complex]. Without added Ag^+, but with constant $[H_2O_2]$ = 0.1 mol dm^{-3} in 0.1 mol dm^{-3} $HClO_4$ for I = 1.0 mol dm^{-3} at 50 °C, $k_o = (1.53 \pm 0.07) \times 10^{-4}$ s^{-1} for [complex] in the range 0.1—1.0 mmol dm^{-3}. It is therefore concluded that the uncatalysed reaction is first order in [complex].

(*ii*) *Acid and hydrogen perioxide dependences.* In the absence of added Ag^+, values of k_o for varying $[H_2O_2]$, $[H^+]$, and temperature at constant ionic strength of 1.0 mol dm^{-3} are collected in Table 1. Plots of k_o against $[H_2O_2]/[H^+]$ are linear (regression coefficient r better than 0.98) with insignificant intercepts. Thus a first-order dependence on $[H_2O_2]$ and an inverse first-order dependence on $[H^+]$ are indicated.

(*iii*) *Effect of other parameters.* Addition of ethylenebis-(biguanide) (0.01 mol dm^{-3}), removal of dissolved oxygen by purified nitrogen, the presence of ambient light, or a change in the monitoring wavelength have no appreciable effect on the reaction rate.

(*iv*) *E.s.r. studies.* Under the experimental conditions where Ag^{II} is detectable in concentrations less than about 10^{-6} mol dm^{-3}, the whole reaction course is e.s.r. silent.

(*v*) *Mechanism.* The complex is a weak acid. Its first and second pK_a values[15] are 3.8 and 6.8 respectively. Also, the pK_a values for H_2O_2 are much too high for any deprotonation to occur. The undissociated form of H_2O_2 and the complex are therefore the predominant ($\geqslant$99.8% for the complex, $\geqslant$99.99% for H_2O_2 in 0.1 mol dm^{-3} H^+) species in the experimental acidic solutions. The observed $[H^+]^{-1}$ dependence is therefore unlikely to arise from the deprotonation equilibrium (2) of the

$$[Ag(H_2L)]^{3+} \rightleftharpoons [Ag(HL)]^{2+} + H^+ \quad (2)$$

complex unless the deprotonated form is very much more

Table 2. Values of k_{uncat} obtained from the slopes of plots of k_o *versus* $[H_2O_2]/[H^+]$; [complex] = 0.2 mmol dm^{-3}, I = 1.0 mol dm^{-3}

θ_c/°C	10^5k_{uncat}/s^{-1}
30	6.5 ± 0.5
40	11.0 ± 1.0
50	15.7 ± 1.5

Table 3. Kinetic data for the silver(I)-catalysed oxidation of hydrogen peroxide by [ethylenebis(biguanide)]silver(III): effect of variation of [Ag^I]; [complex] = 0.2 mmol dm^{-3}, $[HClO_4]$ = $[H_2O_2]$ = 0.1 mmol dm^{-3}, I = 1.0 mol dm^{-3}

θ_c/°C	$[Ag^+]$/mol dm^{-3}	10^5k_o/s^{-1}
30	0.01	7.9
	0.02	8.5
	0.03	9.7
	0.035	10
	0.04	10.5
	0.045	11
40	0.01	12
	0.015	12.5
	0.04	17
	0.05	18
	0.065	20.5
	0.085	24
50	0.02	20.5
	0.05	28
	0.06	33
	0.065	32
	0.08	37
	0.085	38
	0.10	42

reactive than the undissociated form. Though such a situation is not impossible, we tentatively suggest the reaction Scheme 1 where the $[H^+]^{-1}$ dependence arises from deprotonation of H_2O_2 assisted by its axial co-ordination to the complex. Under the reasonable assumption that $K_1[H_2O_2] \ll 1$, reactions (3)

$$[Ag(H_2L)]^{3+} + H_2O_2 \overset{K_1}{\rightleftharpoons} \underset{(\mathbf{I})}{[Ag(H_2L)(HO_2)]^{2+}} + H^+ \quad (3)$$

$$(\mathbf{I}) \xrightarrow{k_1} Ag^+ + H_2L + O_2 + H^+ \quad (4)$$

Scheme 1.

and (4) lead to the rate law (5) so that k_o and k_{uncat} are defined as in equations (6) and (7). The observed dependences of k_o on

$$-d[\text{complex}]/dt = K_1k_1[H_2O_2][\text{complex}]/[H^+] \quad (5)$$

$$k_o = k_{uncat}[H_2O_2]/[H^+] \quad (6)$$

$$k_{uncat} = K_1k_1 \quad (7)$$

$[H_2O_2]$, $[H^+]$, and [complex] fit equations (5) and (6) within 6%. Values of k_{uncat} (= slope of plots of k_o *versus* $[H_2O_2]/[H^+]$) are presented in Table 2.

Inner-sphere adduct formation by hydrogen peroxide with metal complexes[2] and aquametal ions[16] like $[Ag(OH)_4]^-$, Ag^{2+}, *etc.*, is a well established phenomenon. Moreover, *X*-ray structure analysis revealed axial co-ordination of two counter anions for both $[Ag(H_2L)][NO_3]_3$[4] and $[Ag(H_2L)]SO_4(HSO_4)$,[6] while $[Ag(H_2L)][ClO_4]_3$[5] showed axial co-ordination of one perchlorate ion. Since HO_2^- is a far better nucleophile than ClO_4^-, NO_3^-, or SO_4^{2-}, co-ordination by HO_2^- at the axial site of $[Ag(H_2L)]^{3+}$ seems feasible even in solution. These observations, however, suggest but do not prove that reaction (4) occurs in reality. The alternative mechanism in which the adduct (**I**) is a 'dead end' and the electron transfer is bimolecular cannot be distinguished kinetically. Anyway, the tentative assumption of an inner-sphere mechanism for H_2O_2 oxidation is reasonable in view of the moderately weak oxidising character of $[Ag(H_2L)]^{3+}$. The $E_{\frac{1}{2}}$ value (Ag^{III}–Ag^{II}) for this complex is 0.05 V *vs.* a saturated calomel electrode (s.c.e.) according to a polarographic study,[17] corroborated by cyclic voltammetric measurements.[18] Again, it has been proposed[19] that Cu^{III} oxdises slowly, if at all, reductants which are not ligands in the inner sphere of copper ions. If similar mechanistic courses may be assumed for Cu^{III} and isoelectronic Ag^{III}, then an inner-sphere path seems reasonable for the present reaction. Now, both the above electrochemical studies[17,18] proposed $[Ag(H_2L)]^{2+}$ as an unstable silver(II) species. This has been postulated[20] also as a kinetic intermediate in the $S_2O_8^{2-}$ oxidation of $[Ag(H_2L)]^+$ to $[Ag(H_2L)]^{3+}$. Hence, a reaction Scheme 2 where equilibrium (3) is followed by two successive one electron steps, *viz.* (8) and (9), needs consideration, despite the fact that no silver(II)–biguanide complex has been isolated so far. Scheme 2 is kinetically indistinguishable from Scheme 1 proposed before and gives the same rate law with $k_{uncat} = K_1k_2$ in place K_1k_1 [*cf.* equation (7)]. However, in the course of the reaction, no e.s.r. signal attributable to either Ag^{II} or $HO_2^{\bullet}$ appeared. No direct evidence can, therefore, be offered for Scheme 2. However, this may not be sufficient grounds, for its rejection. It can be shown that for Scheme 2 the steady-state concentration of $[Ag(H_2L)]^{2+}$ is given by equation (10).

$$(\mathbf{I}) \xrightarrow{k_2} [Ag(H_2L)]^{2+} + HO_2^{\bullet} \quad (8)$$

$$[Ag(H_2L)]^{2+} + HO_2^{\bullet} \xrightarrow{k_3} Ag^+ + H_2L + H^+ + O_2 \quad (9)$$

Scheme 2.

$$[Ag(H_2L)^{2+}] = [HO_2^{\bullet}] = (k_{uncat}[H_2O_2][\text{complex}]/k_3[H^+])^{\frac{1}{2}} \quad (10)$$

Hence, unless k_3 is less than about 2×10^4 dm^3 mol^{-1} s^{-1}, $[Ag(H_2L)^{2+}]$ cannot exceed about 10^{-6} mol dm^{-3}, the lower limit for detection of silver(II) species under our experimental conditions. Both Ag^{II} and $HO_2^{\bullet}$ are likely to be highly reactive and there is every chance that k_3 will exceed this limit. Therefore, neither the kinetic data nor the e.s.r. results can distinguish here a rate-determining two-electron transfer process [equation (4)] from a succession of two one-electron transfer steps [equations (8) and (9)] of which one is much faster than the other ($k_3 \gg k_2$). However, emphasis on a mechanism for one-electron reduction of the silver(III) complex raises a problem in the thermodynamics (as suggested by one of the referees). The reduction potential for the process $HO_2^{\bullet} + H^+ + e^- \rightleftharpoons H_2O_2$ is +1.7 V,[21] which means that one-electron oxidation of H_2O_2 to $HO_2^{\bullet}$ can take place only with a high activation energy and is very difficult, far more difficult than oxidation to O_2. However, the subsequent one-electron step, $Ag^{II} + HO_2^{\bullet}$, can proceed without obstacle [$E^\circ(O_2$–$HO_2^{\bullet})$ −0.3 V][21,22] and $HO_2^{\bullet}$ should be quickly oxidised to O_2 before $HO_2^{\bullet}$ is detached from Ag^{II} and diffuses away in the bulk solvent.

The presence of radical species in the bulk of the solution can therefore be excluded.[23] Such a mechanism, however is very akin to an inner-sphere two-electron transfer process, from which it is rarely distinguishable with certainty.

(*b*) *Catalysed reaction*. (*i*) *Silver*(I) *dependence*. Table 3 shows

Table 4. Kinetic data[a] for the Ag^I-catalysed oxidation of hydrogen peroxide by [ethylenebis(biguanide)]silver(III): effect of variation of acid and hydrogen peroxide

θ_c/°C	$[H^+]$ mol dm^{-3}	$[H_2O_2]$ mol dm^{-3}	10^5k_o/s^{-1}
30	0.055	0.055	10
	0.10	0.07	6.4
		0.13	13
		0.15	14
		0.20	19
	0.20	0.10	4.6
	0.50	0.10	2.5
40	0.04	0.20	77
		0.26	98
	0.045	0.14	48
	0.05	0.22	65
	0.10	0.06	10
		0.08	13.5
		0.09	15
		0.19	30
		0.27	41
	0.20	0.22	17.5
50	0.05	0.13	62
		0.14	70
		0.16	77
		0.20	96
		0.23	109
	0.10	0.13	32
		0.17	42
		0.30	72
	0.20	0.05	6.6 (14)[b]
		0.10	12.5 (21)[b]
		0.12	16 (27)[b]
		0.14	17
		0.16	23 (37)[b]
		0.28	35
	0.30	0.12	11
	0.40	0.12	10
	1.0	0.20	5.8

[a] [complex] = 0.2 mol dm^{-3}, $[Ag^+]$ = 0.03 mol dm^{-3}, I = 1.0 mol dm^{-3}. [b] I = 0.5 mol dm^{-3}.

Table 5. Kinetic parameters for the Ag^I-catalysed oxidation at I = 1.0 mol dm^{-3}: values of the slopes (m_1) and intercepts (I_1) of plots of k_o *versus* $[Ag^+]$ and of the slopes (m_2) of plots of k_o *versus* $[H_2O_2]/H^+]$

θ_c/°C	10^5m_2/dm^3 mol^{-1} s^{-1}	10^5I_1/s^{-1}	10^4m_1/s^{-1}
30	9.4 ± 1.9	6.7 ± 0.3	9 ± 1
40	15 ± 2	10.1 ± 0.6	16 ± 2
50	23.5 ± 5.5	15.3 ± 1.6	27 ± 2.5

Table 6. Values for k_{cat} (= $K_1K_2k_4$) at I = 1.0 mol dm^{-3}

θ_c/°C	10^4k_{cat}/dm^3 mol^{-1} s^{-1}
30	9 ± 1
40	16 ± 2
50	27 ± 2.5

that for constant $[H_2O_2]$ and $[H^+]$ progressive replacement of Na^+ by Ag^+ appreciably increases k_o. Thus, with $[H_2O_2] = [H^+]$ = 0.1 mol dm^{-3} 10^5k_o (s^{-1}) increases from 15 to 42 when 0.1 mol dm^{-3} Ag^+ is added at 50 °C. Plots of k_o against $[Ag^+]$ at 30, 40, and 50 °C are good straight lines (r better than 0.97) with finite slope (m_1 say) and intercept (I_1 say); I_1 agrees within 1% of $k_{uncat}[H_2O_2]/[H^+]$ *i.e.* with k_o for the uncatalysed path. A Ag^I-catalysed path, first order in $[Ag^I]$ and parallel to the uncatalysed path, is thus indicated.

(*ii*) *Hydrogen peroxide and* $[H^+]$ *dependences.* In the presence of fixed $[Ag^+]$ = 0.03 mol dm^{-3}, k_o values for different $[H^+]$ and $[H_2O_2]$ are collected in Table 4. Plots of k_o *versus* $[H_2O_2]/[H^+]$ are linear (r better than 0.98) having slope m_2 (say) with negligible intercepts. Values for m_1, I_1, and m_2 are collected in Table 5, whereby the relations (11)—(14) may be

$$k_o = (k_{uncat} + k_{cat}[Ag^+])[H_2O_2]/[H^+] \qquad (11)$$

$$m_1 = k_{cat}[H_2O_2]/[H^+] \qquad (12)$$

$$I_1 = k_{uncat}[H_2O_2]/H^+] \qquad (13)$$

$$m_2 = k_{uncat} + k_{cat}[Ag^+] \qquad (14)$$

verified. From Table 5, k_{cat} was evaluated using equation (12) and its values are given in Table 6. They agree within 2% with k_{cat} calculated from equation (14). Experimental k_o values closely agree (within 10%) with those calculated from equation (11).

(*iii*) *Effect of other parameters.* It has been found that k_o is independent of [complex] (0.1—1.0 mmol dm^{-3}), added $Hg(ClO_4)_2$ (0.03 mol dm^{-3}), and added ethylenebis(biguanide) (0.01 mol dm^{-3}). As observed in the case of the uncatalysed oxidation, here also ambient light or a change in the monitoring wavelength do not appreciably affect k_o.

(*iv*) *Effect of ionic strength.* In presence of 0.03 mol dm^{-3} Ag^+ and various $[H^+]$ and $[H_2O_2]$, a decrease in the ionic strength increases k_o. At 50 °C, some representative k_o values at I = 0.5 mol dm^{-3} are shown in Table 4 along with corresponding k_o at I = 1.0 mol dm^{-3} for comparison.

(*v*) *E.s.r. experiments.* These were made in the presence of 0.03 mol dm^{-3} Ag^+ but under conditions otherwise essentially similar to those used for uncatalysed reactions. No resonance was observed.

(*vi*) *Mechanism.* The soft Lewis acids, Hg^{II} and Ag^I form sparingly soluble adducts with free as well as ligated biguanide.[24] Similar adduct formation, it is known, may result in non-redox metal-ion catalysis,[25] a process for which Hg^{II} is always a superior catalyst to Ag^I. Hence, the failure of Hg^{II} to catalyse the present reaction suggests that the catalysis observed with Ag^I is not a case of non-redox metal-ion catalysis, rather some redox catalytic cycle operates. The point of interest then is whether the redox couple Ag^I–Ag^0 or Ag^I–Ag^{II} is involved. Added ethylenebis(biguanide) does not affect the reaction rate. Also, Ag^+ has a negligible effect on k_o unless H_2O_2 is present. Neither is there any immediate spectral change on addition of ligand or Ag^+ to the reaction media. It may therefore be safely concluded that an equilibrium of the type (15) has no kinetic significance in the present reaction and should lie very far to the

$$[Ag(H_2L)]^{3+} + Ag^+ + H_2L \rightleftharpoons 2\,[Ag(H_2L)]^{2+} \qquad (15)$$

left, if it exists at all. Furthermore, the couple Ag^I–Ag^0 appears

$$Ag^{III}(H_2L) + H_2O_2 \overset{K_1}{\rightleftharpoons} \underset{\textbf{(I)}}{Ag^{III}(H_2L)(HO_2)} \qquad (3)$$

$$\textbf{(I)} + Ag^+ \overset{K_2}{\rightleftharpoons} \underset{\textbf{(II)}}{Ag^{III}(H_2L)(HO_2)Ag^I} \qquad (16)$$

$$\textbf{(II)} \underset{k_5}{\overset{k_4}{\rightleftharpoons}} \underset{\textbf{(III)}}{Ag^{II}(H_2L)(HO_2)Ag^{II}} \qquad (17)$$

$$\textbf{(III)} \xrightarrow{k_6} 2\,Ag^+ + H_2L + H^+ + O_2 \qquad (18)$$

Scheme 3.

unlikely since in that case catalysis by Hg^{II} would also be observable through Hg^{II}–Hg^0 or Hg^{II}–Hg^I. Secondly, under the experimental conditions there was no indication of the reduction of Ag^I by hydrogen peroxide, and thirdly, the observed first-order dependences of k_o on [complex] and on $[Ag^+]$ are unlikely for Ag^I–Ag^0. Scheme 3 may then be a plausible reaction sequence for the catalysed path which runs parallel to the uncatalysed path. Steady-state treatment of Scheme 3 for $d[(\mathbf{III})/dt = 0$, under the reasonable assumptions (19) and (20), leads to the experimental rate law (11) with k_{uncat}

$$\{K_1[H_2O_2] + K_1K_2[H_2O_2][Ag^+]\} \ll (k_5 + k_6)[H^+] \quad (19)$$

$$k_6 \gg k_5 \quad (20)$$

as defined earlier [see equation (7)] and k_{cat} as in equation (21).

$$k_{cat} = K_1K_2k_4 \quad (21)$$

Water-soluble binuclear Ag^{III}–Ag^I and Ag^{II}–Ag^{II} complexes are known.[26] These are analogous to species (**II**) and (**III**) (see Scheme 3) respectively and suggest that such species are feasible. We could not obtain any e.s.r. evidence for (**III**), but according to Scheme 3 its steady-state concentration will be as in equation (22). Under typical experimental conditions of $[Ag(H_2L)^{3+}] =$

$$[(\mathbf{III})] = K_1K_2k_4[Ag(H_2L)^{3+}][Ag^+][H_2O_2]/(k_5 + k_6)[H^+] \quad (22)$$

2×10^{-4}, $[Ag^+] = 0.03$, $[H_2O_2] = [H^+] = 0.1$ mol dm^{-3} and with the reasonable assumption that K_1 and K_2 are both less than 0.01 dm^3 mol^{-1} and that $k_4 \ll (k_5 + k_6)$, [(**III**)] may be well below 10^{-6} mol dm^{-3} at which its e.s.r. detection is not possible under our conditions. Electron transfer from HO_2^- to Ag^{II} (equation (18)] may occur either while they are bound within (**III**) or else after dissociation of H_2L and/or HO_2^- ligand(s) from the kinetically labile ($4d^9$) silver(II) system. There is absolutely no kinetic data that might resolve this ambiguity, but we prefer an inner-sphere electron-transfer step for reasons discussed for the uncatalysed reactions.

Our earlier kinetic studies[15] on Ag^I-catalysed oxidation of HCO_2H by $[Ag(H_2L)]^{3+}$ established a couple Ag^I–Ag^0 and we observed that direct oxidation of HCO_2H by this strongly ligated, thermodynamically stable silver(III) complexes is very much slower than the oxidation of HCO_2H by uncomplexed Ag^I. A direct oxidation path was thus undetectable kinetically. The contrasting absence of the Ag^I–Ag^0 catalytic cycle in the present reaction may then indicate an almost exclusive kinetic dominance of the direct oxidation of H_2O_2 by the complex, probably because H_2O_2 is a better nucleophile than HCO_2H and therefore can form adducts like (**I**) or (**II**) [equations (3) and 16)] better than can HCO_2H.

For k_{uncat} ($= K_1k_1$), $\Delta H^\ddagger = 31 \pm 12$ kJ mol^{-1} and $\Delta S^\ddagger = -222 \pm 37$ J K^{-1} mol^{-1} while for k_{cat} ($= K_1K_2k_4$) the values re 41 ± 16 kJ mol^{-1} and -167 ± 53 J K^{-1} mol^{-1} respectively. The large negative value of $\Delta S^\ddagger$ and the rather moderate $\Delta H^\ddagger$ or both the catalysed and the uncatalysed paths are similar to hose for reactions of hydrogen peroxide with $[Ag(OH)_4]^-$, $Ag(bipy)]^{2+}$, and bis(2,9-dimethyl-1,10-phenanthroline)coper(II) (refs. 2, 27, and 28 respectively) and, according to Heyward and Wells,[1] is a general feature in inner-sphere electron-transfer reactions of hydrogen peroxide with metal centres co-ordinated to multidentate ligands.

Since the reaction is catalysed by Ag^I which is a reaction product, autocatalysis might have been expected. However, the rate constants for the catalysed path is only about 15—20 times larger than that for the uncatalysed path (*cf.* Tables 2 and 6). The amount of Ag^+ generated *in situ* from the silver(III) complex ($\leqslant 0.001$ mol dm^{-3}) is therefore too small to affect the kinetics. Simple first-order behaviour is thus observed whether this Ag^+ is allowed to accumulate in the media or scavenged as AgCl.

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