Kinetics and Mechanisms of Redox Reactions in Aqueous Solution. Part 7.[1] Decarboxylation of Aliphatic Acids by Aquasilver(II) Ions

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The overall reaction $2Ag^{II} + RCO_2H \longrightarrow 2Ag^{I} + 2H^+ + CO_2$ + products has been studied at different acidities ($1.0 \leqslant [HClO_4] \leqslant 4.0$ and $I = 4.0$ mol dm^{-3}) and temperatures ($283 \leqslant T \leqslant 303$ K). The rate slightly increases (18%) with increasing [Ag^{I}] within the range investigated. The rate-limiting reactions are the electron transfers from the carboxylic acids to Ag^{2+}(aq) and $[Ag(OH)]^+$(aq). The decrease in rate with increasing [H$^+$] is considered to be due to the formation of the unreactive $RCO_2H_2^+$ species as a result of protonation of the carboxylic acids. This assumption is more plausible than an earlier one favouring carboxylate anion as the reactive entity in solutions of acid at between 1.0 and 4.0 mol dm^{-3} HClO$_4$ because $K_c \gg K_a$ where K_c and K_a are respectively the protonation and dissociation constants of the carboxylic acid. The rate constants with Ag^{2+}(aq) and $[Ag(OH)]^+$(aq) may be correlated with Taft σ^* values giving ρ values of -10.7 ± 0.7 and -9.8 ± 0.4 respectively. The thermodynamic parameters corresponding to the rate-limiting electron transfer to Ag^{2+}(aq) and $[Ag(OH)]^+$(aq) are reported.

STUDIES of the kinetics of the redox reaction between aquasilver(II) ions and aliphatic carboxylic acids have led to the postulation of the mechanism in equations (i)—(vi).[2] The corresponding rate law for the disappearance of silver(II) is given by equation (vii).

$$Ag^{2+}(aq) \xrightleftharpoons{K_h} [Ag(OH)]^+(aq) + H^+ \qquad (i)$$

$$RCO_2H \xrightleftharpoons{K_a} RCO_2^- + H^+ \qquad (ii)$$

$$Ag^{2+}(aq) + RCO_2H \xrightarrow{k_1} Ag^+(aq) + CO_2 + R^{\cdot} + H^+ \qquad (iii)$$

$$[Ag(OH)]^+(aq) + RCO_2H \xrightarrow{k_2} Ag^+(aq) + CO_2 + R^{\cdot} + H_2O \qquad (iv)$$

$$Ag^{2+}(aq) + RCO_2^- \xrightarrow{k_3} Ag^+(aq) + CO_2 + R^{\cdot} \qquad (v)$$

$$R^{\cdot} + Ag^{II} \xrightarrow{\text{fast}} Ag^{I} + H^+ + \text{products} \qquad (vi)$$

$$\frac{-d[Ag^{II}]_0}{dt} = \frac{2\{k_1 + (k_2K_h + k_3K_a)[H^+]^{-1}\}[Ag^{II}]_0[RCO_2H]_0}{(1 + K_h[H^+]^{-1})(1 + K_a[H^+]^{-1})} \qquad (vii)$$

The pK_a values of aliphatic carboxylic acids range from 5.0 for acetic acid to 5.33 for pivalic acid[3] at 25 °C and $I = 3$ mol dm^{-3} (Na[ClO$_4$]). Therefore $K_a[H^+]^{-1} \leqslant 1$ in the acidity range investigated ($1{\cdot}0 \leqslant [HClO_4] \leqslant 4{\cdot}0$ mol dm^{-3}) and it was assumed that reaction (v) does not contribute to the term within the braces.[2] The retardation in the rate of reaction with increasing acidity was explained in terms of the estimated reactivity ratio for carboxylate anion and the undissociated acid, *i.e.* k_3/k_1 is *ca.* 10^6. However, this ratio was stated[2] to be somewhat higher than the values obtained in the oxidation of formic acid with cobalt(III)[4] and MnO_4^-.[5,6]

The carboxylic acids are known to be protonated in aqueous solutions of strong acids. A comparison of the protonation constant K_c (0.14, 0.33, 0.52, 0.47, and 0.41 dm^3 mol^{-1} for acetic, propionic, butyric, isobutyric, and pivalic acid[7] respectively) with the corresponding K_a values[8] (1.76×10^{-5}, 1.35×10^{-5}, 1.54×10^{-5}, and 1.44×10^{-5} mol dm^{-3} for the first four acids respectively) indicated that $K_c \gg K_a$. Hence there is a possibility that the retardation in the rate with increasing acidity is due to the increased removal of the reactive RCO_2H as $RCO_2H_2^+$. This paper describes an attempt to examine the problem of decreasing rate with increasing acidity from this point of view.

EXPERIMENTAL

Reagents.—The solutions of acetic[9a] (Basynth), propionic[9b] (Koch-Light), and n-butyric acid[9c] (Narden) were purified by distillation as described. Isobutyric (Fluka, puriss) and pivalic acid (Koch-Light, puriss) were used as received. The stock solutions were standardised by conventional alkalimetric titrations to a phenolphthalein end-point. Perchloric acid (E. Merck), was similarly standardised. Sodium perchlorate (G. F. Smith, anhydrous) was used to maintain the ionic strength at the desired value (4.0 mol dm^{-3}). Similar results were obtained with sodium perchlorate prepared by the neutralisation of sodium carbonate with perchloric acid.

Solutions of silver(II) were freshly prepared by the anodic oxidation of silver(I) perchlorate (G. F. Smith) in $\geqslant 1.0$ mol dm^{-3} HClO$_4$ under nitrogen.[10,11] Solutions of silver(I) perchlorate were standardised by the standard titrimetric method. The [Ag^{II}] was estimated spectrophotometrically using $\varepsilon = 140$ dm^3 mol^{-1} cm^{-1} at 470 nm.[12] Care was taken in handling the silver(II) solutions.[2] Silver(I) was always present in excess (40 fold) in silver(II) solutions to prevent the disproportionation of Ag^{II} into Ag^{III} and Ag^{I} *via* the equilibrium[12,13] (1), which is known to lie far to the left.[12,14,15]

$$2Ag^{II} \rightleftharpoons Ag^{I} + Ag^{III} \qquad (1)$$

Kinetics.—A Durrum stopped-flow spectrophotometer (model D-130) connected to a Tektronics oscilloscope (model 5103N) was used. The disappearance of silver(II) was monitored at 470 nm under pseudo-first-order conditions, the carboxylic acid always being present in excess. The observed pseudo-first-order rate constant $k_{obs.}$ was calculated as 2.303 times the gradient of plots ($r > 0.994$) of log A_t against time, where A_t is the absorbance at time t. Such plots were linear for more than three half-lives for all the carboxylic acids. The [Ag^I] was kept constant (0.1 mol dm^{-3}) in all kinetic runs except when the effect of [Ag^I] was under investigation. However, the ionic strength (I = 4 mol dm^{-3}, Na[ClO_4]) was always kept constant.

The reproducibility of $k_{obs.}$ was nearly 98%. The $k_{obs.}$ values reported in Table 1 are the mean values from at least two runs. Neither the carboxylic acids nor the reaction products absorbed at 470 nm.

Stoicheiometry.—Mentasti and co-workers reported that 2 equivalents of Ag^{II} were used per mol of formic [16] and other carboxylic acids.[2] The stoicheiometry was given by equation (2) where R($-$H)$_{ox}$ represents the possible oxidation products.

$$2Ag^{II} + RCO_2H \longrightarrow 2Ag^I + R(-H)_{ox} + 2H^+ + CO_2 \quad (2)$$

The primary oxidation product, except in the case of formic acid, is the alkyl radical R$^{\cdot}$ which reacts in a variety of ways. It can react with Ag^{II} or with a water molecule or even with a second RCO_2H molecule which explains the formation of alkanes, alkenes, alcohols, esters, and ketones as products. The interaction of R$^{\cdot}$ with H_2O or a second RCO_2H molecule produces a hydrogen radical which reduces the second silver(II) ion in accordance with the 1 : 2 stoicheiometry observed for the oxidation of these acids by several other metal ions such as Co^{III},[17,18] Ce^{IV},[19] and silver(II) complexes.[20]

The applicability of equation (2) was tested by mixing an excess of Ag^{II} with different concentrations of propionic and pivalic acids in the stopped-flow apparatus. It was noted that the final absorbance at 470 nm decreased towards zero on approaching the limiting ratio [RCO_2H] : [Ag^{II}] = 2 : 1. The calculations of the unreacted Ag^{II} (when 2[RCO_2H] < [Ag^{II}]) after the completion of the reaction indicated that $\Delta[Ag^{II}]/\Delta[RCO_2H] = 0.5$.

RESULTS AND DISCUSSION

Dependence on [Ag^{II}].—The invariance of $k_{obs.}$ over a ten-fold variation in [Ag^{II}] (2×10^{-4}—2×10^{-3} mol dm^{-3}) confirmed the first-order dependence on [Ag^{II}].

TABLE 1

Observed pseudo-first-order rate constants $k_{obs.}$ (s^{-1}) for the oxidation of propionic acid by Ag^{II} at different [$HClO_4$] and temperatures with [Ag^{II}] = 1.3×10^{-3}, [Ag^I] = 0.1, and I = 4 mol dm^{-3}

		[$HClO_4$]/mol dm^{-3}				
θ_c/°C	[$C_2H_5CO_2H$]/ mol dm^{-3}	1.0	1.5	2.0	3.0	4.0
10	0.02	0.450	0.326	0.228	0.152	0.116
	0.05	1.12	0.813	0.572	0.390	0.293
	0.10	2.23	1.62	1.15	0.79	0.595
	0.21	4.69	3.41	2.40	1.65	1.24
	0.40	8.91	6.51	4.58	3.15	2.38
18	0.02	1.29	0.955	0.713	0.495	0.387
	0.05	3.22	2.40	1.79	1.27	0.968
	0.10	6.45	4.78	3.56	2.48	1.94
	0.21	13.5	10.1	7.50	5.30	4.08
	0.40	25.8	19.2	14.2	10.0	7.66
25	0.02	3.04	2.30	1.82	1.30	1.04
	0.05	7.65	5.77	4.56	3.34	2.64
	0.10	15.3	11.6	9.15	6.70	5.30
	0.21	32.1	24.3	19.1	14.1	10.8
	0.40	61.4	46.2	36.3	26.5	20.7
30	0.02	5.51	4.22	3.48	2.61	2.24
	0.05	13.8	10.5	8.80	6.45	5.62
	0.10	27.5	21.2	17.4	12.9	11.4
	0.21	57.6	44.0	36.5	27.4	23.4
	0.40	112.0	84.6	69.7	51.5	44.6

Dependence on [RCO_2H].—The rate measurements over a 20-fold variation in each of the carboxylic acids at different acidities ($1.0 \leqslant [HClO_4] \leqslant 4.0$ mol dm^{-3}) and temperatures (10, 18, 25, and 30 °C) indicated a first-order dependence on the concentration of each carboxylic acid. Plots of $k_{obs.}$ against [RCO_2H] were linear ($r > 0.99$) and passed through the origin at all temperatures and acidities. A representative plot for butyric acid is illustrated in Figure 1.

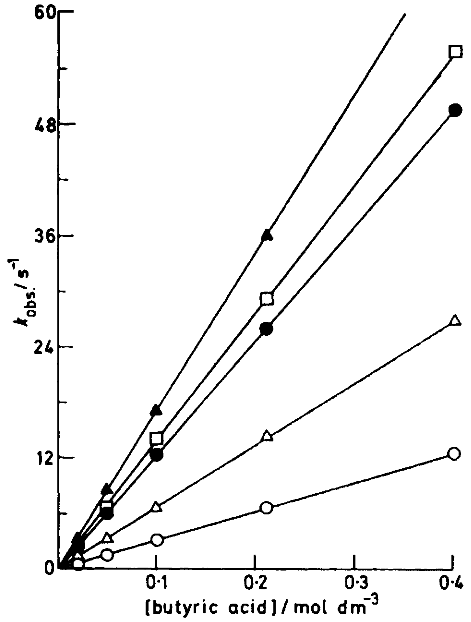

FIGURE 1 Plots of $k_{obs.}$ against [butyric acid] at different temperatures and acidities which indicate the first-order dependence on [RCO_2H]. Conditions: [Ag^{II}] = 0.13×10^{-3}, [Ag^I] = 0.1, and I = 4.0 mol dm^{-3} with [$HClO_4$] = 1.0 mol dm^{-3} and 10 °C (○), [$HClO_4$] = 1.5 mol dm^{-3} and 18 °C (△), [$HClO_4$] = 2 mol dm^{-3} and 25 °C (●), [$HClO_4$] = 3 mol dm^{-3} and 30 °C (▲), and [$HClO_4$] = 4 mol dm^{-3} and 30 °C (□)

The values of k_2, the second-order rate constant, reported in Table 2 were obtained as the gradients of the linear plots such as that shown in Figure 1. Least-squares values were determined with a TI 55 calculator. A 99% correspondence between the present k_2 values and those reported by Mentasti *et al.*[2] at 30 °C and [$HClO_4$] = 4 mol dm^{-3} was noted. However, a further comparison at other temperatures and acidities was not possible.

Dependence on [Ag^I].—The dependence of $k_{obs.}$ on [Ag^I] was investigated for the oxidation of propionic acid at three acidities, Table 3. Unlike the retardation observed in the oxidation of formic acid [16] and Pr^{i}OH,[10] a slight increase in the rate (*ca.* 18% at the highest [Ag^I]), consistent with the previous observation,[2] was noted. In the oxidation of formic acid $k_{obs.}$ was independent of [Ag^I] for the reaction path involving a first-order dependence on [Ag^{II}].[16]

The first-order dependence on [Ag^{II}] thus excludes the possibility of Ag^{III} being an active oxidant as had been observed for the path involving a second-order dependence on [Ag^{II}] in the oxidation of formic acid.[16] Had this been the case, the order with respect to [Ag^{II}] would

TABLE 2

Second-order rate constants k_2 (dm^3 mol^{-1} s^{-1}) for the oxidation of aliphatic acids at different temperatures and acidities: $[Ag^{II}] = 1.3 \times 10^{-3}$, $[Ag^{I}] = 0.1$, and $I = 4$ mol dm^{-3}

		$[HClO_4]$/mol dm^{-3}				
Acid	θ_c/°C	1.0	1.5	2.0	3.0	4.0
Acetic	10	5.92 ± 0.03	4.14 ± 0.02	3.12 ± 0.05	2.35 ± 0.03	1.98 ± 0.04
	18	14.5 ± 0.1	10.5 ± 0.1	8.22 ± 0.05	6.44 ± 0.15	4.87 ± 0.16
	25	30.2 ± 0.2	22.7 ± 0.1	18.4 ± 0.2	14.9 ± 0.1	11.7 ± 0.1
	30	50.5 ± 0.6	39.1 ± 0.2	32.2 ± 0.1	25.8 ± 0.1	21.6 ± 0.2
Propionic	10	22.4 ± 0.2	16.3 ± 0.1	11.4 ± 0.1	7.82 ± 0.11	5.90 ± 0.06
	18	64.4 ± 0.3	47.9 ± 0.2	35.6 ± 0.1	25.0 ± 0.3	19.3 ± 0.1
	25	153 ± 1	116 ± 1	91.1 ± 0.3	66.4 ± 0.8	52.1 ± 0.6
	30	277 ± 3	211 ± 2	174 ± 1	129 ± 1	112 ± 1
Butyric	10	31.2 ± 0.4	26.6 ± 0.3	23.1 ± 0.1	18.3 ± 0.1	15.2 ± 0.1
	18	79.6 ± 0.5	67.9 ± 0.3	57.2 ± 0.7	45.7 ± 0.6	37.4 ± 0.5
	25	174 ± 2	144 ± 1	124 ± 2	100 ± 1	81.7 ± 0.4
	30	303 ± 2	243 ± 2	215 ± 2	171 ± 1	140 ± 1
Isobutyric	10	513 ± 6	362 ± 2	292 ± 3	203 ± 2	159 ± 1
	18	1 125 ± 5	805 ± 5	659 ± 7	478 ± 3	390 ± 2
	25	2 186 ± 7	1 600 ± 6	1 280 ± 3	965 ± 5	752 ± 6
	30	3 423 ± 13	2 580 ± 8	2 035 ± 5	1 550 ± 2	1 188 ± 2
Pivalic	10	4 306 ± 8	3 368 ± 9	2 820 ± 5	2 120 ± 3	1 733 ± 4
	18	9 855 ± 5	7 856 ± 8	6 569 ± 11	4 875 ± 11	4 022 ± 21
	25	19 516 ± 13	15 500 ± 14	13 010 ± 20	9 510 ± 20	7 638 ± 12
	30	31 520 ± 40	25 420 ± 80	21 180 ± 45	15 280 ± 50	11 990 ± 80

have changed from one to two as can be seen from equilibrium (1).

The retardation by Ag^I need not always be ascribed to the involvement of Ag^{III} as the active oxidant. Thus, in the absence of a change in the order of the reaction with respect to $[Ag^{II}]$ from one to two in the oxidation of Pr^iOH [10] the retardation was ascribed to the formation of a Ag^I–Pr^iOH complex.

The slight increase in the rate with Ag^I is clearly not due to medium effects. Silver(I) is known to form adducts [21] and a very large number of silver(I) compounds of carboxylic acids is also known.[22] However, silver(I) formate does not appear to have been prepared,[23] although the preparation of diamminesilver formate has been described.[24] Further, the presence of silver(I) in moderate concentration was found to accelerate the rate of oxidation of carboxylic acids by cerium(IV) in a nitrate medium.[25]

In view of the above facts, two situations must be considered in order to attempt to explain the small increase in rate with increasing $[Ag^I]$. First, as a result of formation of $RCO_2H{\cdot}Ag^+$ [21] or RCO_2Ag,[22] equilibrium (1) is likely to be disturbed giving a slight increase in the formation of Ag^{III}. One might thus be tempted to ascribe the slight increase in rate to oxidation of carboxylic acids by silver(III). However, this possibility can be discounted in view of the strict first-order dependence on $[Ag^{II}]$.

TABLE 3

Dependence of $k_{obs.}$ (s^{-1}) on $[Ag^I]$ at different acidities keeping the $I = 4.0$ mol dm^{-3} at 25 °C: $[Ag^{II}] = 1.3 \times 10^{-3}$, $[C_2H_5CO_2H] = 0.02$ mol dm^{-3}

	$[HClO_4]$/mol dm^{-3}		
$[Ag^I]$/mol dm^{-3}	1.0	2.0	4.0
0.004	2.60	1.56	0.90
0.10	3.02	1.82	1.04
0.12	3.07	1.85	1.06

Thus, the only other plausible explanation is that the adduct or the silver(I) compound or both may be oxidised slightly more readily than the carboxylic acid itself. This argument is supported by the fact that an appreciably higher $[Ag^I]$ than that needed for a catalytic effect is required in the oxidation of these carboxylic acids by ammonium cerium(IV) nitrate in nitric acid.[25] Further support is given by the fact that no similar increase in rate by Ag^I was noted in the oxidation of formic acid by Ag^{II}, probably because HCO_2Ag is not formed.[23]

Dependence on $[H^+]$.—The effect of acidity on $k_{obs.}$ was investigated at five different $[HClO_4]$ and four different temperatures; $k_{obs.}$ decreased with increasing acidity at all the temperatures. The results in terms of the second-order rate constant k_2 are reported in Table 2.

This decrease in the rate is considered more likely to be due to the protonation of the carboxylic acids [reaction (4)] rather than to their restricted dissociation because $K_c \gg K_a$. Because of the protonation there is increased formation of the unreactive $RCO_2H_2^+$ species with increasing acidity, whereas in the former case [2] there is decreased formation of the highly reactive carboxylate anion.

Since the ρ value obtained from plots of log K_c against $\Sigma\sigma^*$, the sum of the Taft function,[26] is the same (−6.3) for primary alcohols, ketones, and carboxylic acids,[7] it can be assumed that for carboxylic acids the variation of K_c with temperature exhibits a similar broad maximum to that observed in the case of alcohols.[27] Thus there is justification in using the known K_c values [7] at 25 °C at other temperatures.

The formation of an Ag^{II}–RCO_2H intermediate is not considered in the postulated mechanism because no spectrophotometric evidence for such an intermediate was found by previous workers.[2] It is interesting that no intermediate formation between Ag^{II} and other substrates such as Pr^iOH,[10] phosphorous acid,[11] formic acid,[16] and dithionate ion[28] has been reported in the kinetics of oxidation of these substrates.

In view of the above facts and the observed kinetics, the sequence of reactions (3)—(8) is considered plausible.

$$Ag^{2+}(aq) \underset{}{\overset{K_h}{\rightleftharpoons}} [Ag(OH)]^+(aq) + H^+ \quad (3)$$

$$RCO_2H(aq) + H^+ \overset{K_c}{\rightleftharpoons} RCO_2H_2^+(aq) \quad (4)$$

$$RCO_2H(aq) + Ag^{2+}(aq) \xrightarrow{k} Ag^+(aq) + H^+(aq) + RCO_2^{\cdot} \quad (5)$$

$$RCO_2H(aq) + [Ag(OH)]^+(aq) \xrightarrow{k_1} Ag^+(aq) + H_2O + RCO_2^{\cdot} \quad (6)$$

$$RCO_2^{\cdot} \xrightarrow{\text{fast}} R^{\cdot} + CO_2 \text{ (refs 19, 29)} \quad (7)$$

$$Ag^{II} + R^{\cdot} \xrightarrow{\text{fast}} Ag^+(aq) + H^+(aq) + \text{products} \quad (8)$$

The rate of disappearance of Ag^{II} is then expressed by equation (9) and the second-order rate constant k_2 by equation (10).

$$\frac{-d[Ag^{II}]_0}{dt} = \frac{2(k + k_1K_h[H^+]^{-1})[Ag^{II}]_0[RCO_2H]_0}{(1 + K_h[H^+]^{-1})(1 + K_c[H^+])} \quad (9)$$

$$k_2 = \frac{k_{obs.}}{[RCO_2H]_0} = \frac{2(k + k_1K_h[H^+]^{-1})}{(1 + K_h[H^+]^{-1})(1 + K_c[H^+])} \quad (10)$$

Equation (10) indicates that a plot of $k_2(1 + K_h[H^+]^{-1})(1 + K_c[H^+])$ ($dm^3\ mol^{-1}\ s^{-1}$) against $[H^+]^{-1}$ should be linear with an intercept on the rate ordinate. Such plots were found to be linear for all the carboxylic acids at all temperatures ($r > 0.994$). A representative plot for each of the carboxylic acids investigated is illustrated in Figure 2. The values of K_h at the temperatures investigated were calculated from known K_h values at other temperatures[30] as 0.17, 0.27, 0.38, and 0.49 mol dm^{-3} at 10, 18, 25, and 30 °C respectively.

The values of the rate constants k(= intercept/2) and k_1(= slope/$2K_h$) were calculated from plots like those shown in Figure 2, for each of the carboxylic acids at different temperatures, and are collected in Table 4 wherein are also reported the corresponding thermodynamic parameters. A perusal of the respective values of the rate constants k and k_1, expressed in dm^3 mol^{-1} s^{-1}, indicates that k is definitely less than k_1, *i.e.* $[Ag(OH)]^+(aq)$ is more reactive than $Ag^{2+}(aq)$. This conclusion is supported by the corresponding $\Delta H^{\ddagger}$ values, the only exception being butyric acid where there is little difference between the two $\Delta H^{\ddagger}$ values.

It is interesting that in the oxidation of cyclohexanone,[1] diols,[31] and 4-ketopentanoic acid[32] by aquamanganese(III) ions, the ion $[Mn(OH)]^{2+}(aq)$ is more reactive than $Mn^{3+}(aq)$. One of the referees of the present paper has drawn attention to the fact that a similar situation exists in several oxidations by aqua-ions of Ce^{IV} and Co^{III}. The higher reactivity of the hydroxo-metal ions, in the opinion of the referee, is possible even in outer-sphere reactions if there is a specific configuration of the OH group such that a ' bridge ' could be formed. A critical study of the oxidations by aquamanganese(III) ions[33] indicated that $[Mn(OH)]^{2+}(aq)$ is selectively more reactive towards substrates from which a hydrogen atom can be abstracted as a proton, whereas $Mn^{3+}(aq)$ is the active oxidant where a simple electron transfer is involved. The oxidation of tetramethylhydrazine[34] is effected by $Mn^{3+}(aq)$.

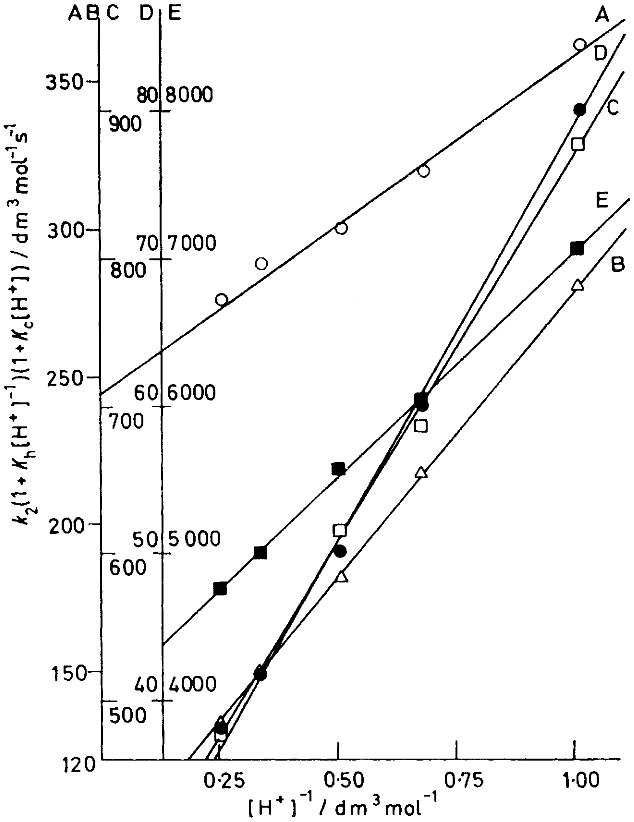

FIGURE 2 Plots according to equation (10) of $k_2(1 + K_c[H^+])$-$(1 + K_h[H^+]^{-1})$ against $[H^+]^{-1}$ for different carboxylic acids at different temperatures. Conditions: $[Ag^{II}] = 1.3 \times 10^{-3}$, $[Ag^I] = 0.1$, and $I = 4.0$ mol dm^{-3} with butyric acid, 25 °C (○), propionic acid, 25 °C (△), isobutyric acid, 10 °C (□), acetic acid, 30 °C (●), and pivalic acid, 10 °C (■)

The extension of the above generalisation on reactivity to the present silver(II) oxidations of carboxylic acids, because of the similar aqueous chemistry of manganese(III) and silver(II) $\{M^{n+}(aq) + H_2O \rightleftharpoons H^+ + [M(OH)]^{(n-1)+}(aq)\}$ and the fact that $[Ag(OH)]^+(aq)$ is more reactive than $Ag^{2+}(aq)$, strengthens the assumption that the reactive carboxylic acid species is the undissociated RCO_2H molecule and not the carboxylate ion, RCO_2^-. This reactivity pattern is due to the fact that the carboxylic hydrogen atom can be abstracted as a proton during the oxidation.

Plots of log (k_{RCO_2H}/k_{MeCO_2H}) or log ($k_{1,RCO_2H}/k_{1,MeCO_2H}$) against Taft's σ^* values[26] are reasonably linear as illustrated in Figure 3, with slopes of -10.7 ± 0.7 and

TABLE 4

Values of the rate constants k and k_1 ($dm^3\ mol^{-1}\ s^{-1}$) and associated thermodynamic parameters: $[Ag^{II}] = 1.3 \times 10^{-3}$, $[Ag^{I}] = 0.1$, and $I = 4.0\ mol\ dm^{-3}$

	Carboxylic acid	θ_c/°C 10	18	25	30	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
(*a*) k							
	Acetic	0.73 ± 0.025	1.97 ± 0.08	5.59 ± 0.06	10.5 ± 0.1	107 ± 13	84 ± 12
	Propionic	3.60 ± 0.09	13.6 ± 0.3	41.7 ± 0.9	96 ± 2	131 ± 16	172 ± 12
	Butyric	23.3 ± 0.1	56.9 ± 0.7	123 ± 1	208 ± 2	86 ± 10	46 ± 12
	Isobutyric	170 ± 2	433 ± 3	836 ± 6	1 324 ± 11	82 ± 9	50 ± 6
	Pivalic	1 995 ± 7	4 600 ± 30	8 550 ± 40	13 180 ± 250	75 ± 8	50 ± 6
(*b*) k_1							
	Acetic	18.5 ± 0.1	31.2 ± 0.2	46.8 ± 0.3	65.3 ± 1	44 ± 2	−71 ± 6
	Propionic	82.6 ± 0.7	153 ± 1	260 ± 3	357 ± 8	53 ± 2	−31 ± 6
	Butyric	26.7 ± 1.9	75.1 ± 2.0	152 ± 5	266 ± 5	82 ± 5	62 ± 16
	Isobutyric	1 580 ± 15	2 220 ± 30	3 565 ± 45	4 910 ± 80	41 ± 1	−49 ± 5
	Pivalic	9 160 ± 80	15 800 ± 160	27 900 ± 150	41 560 ± 630	54 ± 1	14 ± 4

-9.8 ± 0.4 respectively at 25 °C. The mechanistic significance of these plots and their slopes, the values of the latter being close to those reported previously,[2] has been discussed [2] and therefore is not repeated here.

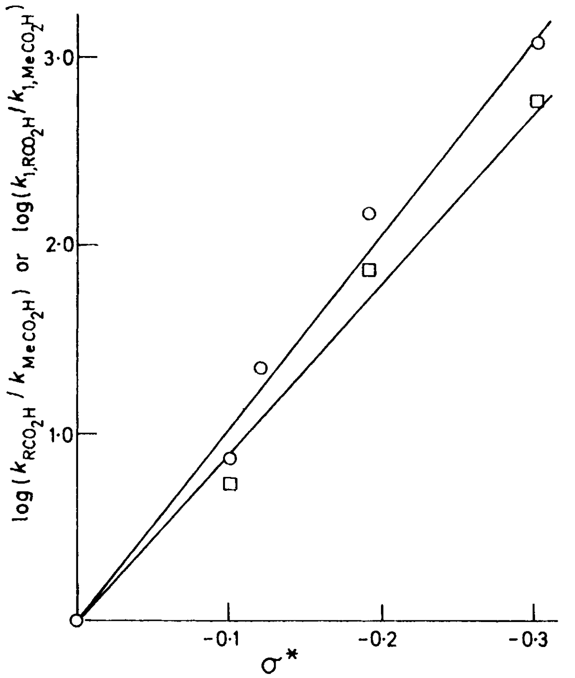

FIGURE 3 Plots of log (k_{RCO_2H}/k_{MeCO_2H}) (○) and log ($k_{1,RCO_2H}/k_{1,MeCO_2H}$) (□) against Tafts' σ* values

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