Kinetics of Oxidation of Organic Compounds by Silver(II) in Aqueous Perchloric Acid Solution. Part 2.[1] Aliphatic Carboxylic Acids

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The reactions between Ag^{II} and acetic, propionic, n-butyric, isobutyric, and pivalic acids have been investigated kinetically, at 14.0, 22.0, and 30.0 °C, in aqueous perchloric acid media ($1.00 \leqslant [HClO_4] \leqslant 4.00$M; $\mu = 4.0$M) by a stopped-flow technique. The overall reaction is: $2Ag^{II} + RCO_2H \longrightarrow 2Ag^{I} + 2H^+ + CO_2$ + products. The reactions are second order and the rate constants increase with decreasing acidity. Alternative mechanisms for acid-dependent pathways are considered. The rate-determining step involves electron exchange with $R-CO_2H$ bond rupture. Two pathways were found to operate and their reactivities correlate with the σ^* values of the Taft equation. The results are discussed with reference to previous findings concerning Ag^{II} oxidation of formic acid.

DESPITE the high oxidation potential of aqueous Ag^{II} (E^0 Ag^{II}/Ag^{I} 2.0 V in 1M-$HClO_4$), its kinetic behaviour has received little attention, particularly for reactions with organic compounds. In Part 1[1] the kinetics of oxidation of formic acid were described and the results discussed with reference to previous findings on other oxidizing species. We have extended this study to homologous aliphatic acids, in order to obtain additional information on such redox reactions.

One-electron oxidants were found to be less reactive toward formic acid than two-electron oxidants of comparable redox potential.[2] This has been explained

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[1] Part 1, E. Pelizzetti and E. Mentasti, *J.C.S. Dalton*, 1975, 2086.

[2] J. Halpern and S. M. Taylor, *Discuss. Faraday Soc.*, 1960, **29**, 174.

in terms of an unfavourable free energy of reaction for one-electron mechanisms.[2,3] The high redox potential of Ag^{II}/Ag^{I} makes both pathways thermodynamically possible (a two-electron mechanism can occur *via* Ag^{III} formed by disproportionation of Ag^{II}). Silver(II) has been described as playing an important role as a metastable intermediate in the silver(I)-catalysed decarboxylation of aliphatic acids by peroxydisulphate;[4] the rate of such reactions was found to be first order in Ag^{I} and peroxydisulphate and zero order in carboxylic acid; reaction times were lowered by the catalyst to several minutes. Stabilised Ag^{II} (in the form of picolinate or bis-2,2′-dipyridyl complexes) and AgO have been found to be effective in the oxidation of such acids[5] (with reaction times of *ca.* 1 h) and a detailed study of the products of reaction has been reported. In the present paper a kinetic study of the reaction between silver(II) and acetic, propionic, n-butyric, isobutyric, and pivalic acid in aqueous acidic perchlorate solution is described.

EXPERIMENTAL

Reagents.—Acetic acid (Erba), propionic acid (Erba), n-butyric acid (Erba), isobutyric acid (Aldrich), and pivalic acid (Aldrich) were reagent grade chemicals. Stock solutions were analysed by conventional alkalimetric titrations. Perchloric acid and sodium perchlorate (obtained by neutralization of NaOH with $HClO_4$) were used for bringing the acidity ($1.00 \leqslant [HClO_4] \leqslant 4.00$M) and ionic strength ($\mu$ 4.0M) to the desired values. Lithium perchlorate was obtained by neutralization of Li_2CO_3 with perchloric acid, and recrystallized from water in order to remove Cl^-. A stock solution of $AgClO_4$ was prepared by dissolution of Ag_2O (Merck) in perchloric acid and titrated by standard methods. Silver(II) perchlorate solutions were obtained by anodic oxidation at a platinum electrode of silver(I) perchlorate solutions brought to $[HClO_4] \geqslant 1.0$M, as described in the literature.[6] The total Ag^{II} concentration was determined spectrophotometrically at 470 nm (ε 138 ± 2 l mol^{-1} cm^{-1}).[7] Silver(II) solutions were kept at *ca.* 0 °C in the dark and were used within 30 min of preparation. The silver(II) content was estimated before and after each kinetic run and no decomposition was found to occur during this period (< 1 min). Twice distilled water was used throughout.

Kinetics.—All kinetic runs were performed on a Durrum–Gibson stopped-flow spectrophotometer (2.00 cm cell) by following the disappearance of Ag^{II}, under pseudo-first order conditions at 470 nm; no contribution to the measured light absorption from the other reagents and products occur at this wavelength. Output data were registered on the memorized screen of a 564 Tektronix oscilloscope, and then treated by a weighted least-squares method.[8] Each pseudo-first-order rate constant was obtained with an error of *ca.* 2—3%.

Stoicheiometry.—In order to assess the stoicheiometry, an excess of Ag^{II} was mixed in the stopped-flow apparatus with different concentrations of pivalic acid (which has the fastest reaction among the investigated compounds) and reacted Ag^{II} was determined spectrophotometrically. A 1 : 2 ratio between added carboxylic acid and the reacted Ag^{II} was found. Similar measurements with the other acids gave the same ratio, though with great uncertainty due to the slowness of reaction (Ag^{II} of a suitable concentration for absorption readings) which was accompanied by Ag^{II} decomposition. Thus, as in the case of formic acid oxidation, the overall stoicheiometry[1] is obtained where

$$2\,Ag^{II} + RCO_2H \longrightarrow 2\,Ag^{I} + R(-H)_{ox} + 2\,H^+ + CO_2 \quad (1)$$

$R(-H)_{ox}$ are the possible oxidation products; the radical R· is the primary product of electron abstraction, and in turn, in a variety of ways, reacts directly with Ag^{II} or with H_2O or else with another RCO_2H molecule, so that final formation of alkanes, alkenes, alcohols, esters, and ketones takes place; interaction with H_2O or another acid molecule has been found to give rise to a hydrogen radical which is responsible for the second Ag^{II} ion reduction according to the 1 : 2 stoicheiometric ratio.[4,5,9]

RESULTS AND DISCUSSION

All kinetic measurements were made spectrophotometrically in aqueous perchloric acid–sodium perchlorate mixtures, using Ag^{II} in deficit relative to the substrate to be oxidized. Preliminary runs were performed by varying the total Ag^{I} and Ag^{II} concentration in the ranges: $0.100 \geqslant [Ag^{I}] \geqslant 0.005$M and $2.5 \times 10^{-3} \geqslant [Ag^{II}] \geqslant 1.5 \times 10^{-4}$M. In all cases, even by working with the lowest Ag^{I} and highest Ag^{II} concentration in these ranges, as well as with the highest Ag^{I} and lowest Ag^{II} concentrations, the observed rates were always strictly first order in oxidant (the carboxylic acid was in at least 100-fold excess) as shown by the linearity of plots of log A_t *versus* time for at least three half-lives (A_t is the absorbance due to Ag^{II} at time t); from the slopes of these plots, the pseudo-first-order rate constants, k_{obs}, were evaluated. Thus a complete absence of second-order terms in Ag^{II} was established in contrast to the behaviour previously found for the oxidation of formic acid.[1] A small increase of the rate (*ca.* 20%) by increasing $[Ag^{I}]_T$ from 0.005 to 0.100M was observed, while $[Ag^{II}]_0$ was kept constant; thus all kinetic runs were performed with constant $[Ag^{I}] \simeq [Ag]_T = 0.100$M.

Plots of the pseudo-first-order rate constants were linear with RCO_2H concentration at every acidity and temperature investigated; as an example, Table 1 collects the data for acetic acid and Figure 1 shows the trend observed for isobutyric acid. Furthermore no spectroscopic evidence for an Ag^{II}–RCO_2H intermediate species was found, upon performing kinetic runs between 320 and 600 nm. Additional measurements were performed at different ionic strengths by varying the

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[3] M. Thompson and J. C. Sullivan, *Inorg. Chem.*, 1972, **11**, 1707.

[4] J. M. Anderson and J. K. Kochi, *J. Amer. Chem. Soc.*, 1970, **92**, 1651.

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TABLE 1

Pseudo-first-order rate constants k_{obs} s^{-1} for the oxidation of acetic acid by Ag^{II} at different acidities and temperatures: $[Ag^{I}] = 0.10$, $[Ag^{II}] = 0.5 \div 1.0 \times 10^{-3}$, $\mu = 4.0$M ($NaClO_4$)

		$[HClO_4]$/M				
T_c/°C	$[RCO_2H]$/M	1.00	1.50	2.00	3.00	4.00
14.0	0.020	0.25	0.19	0.17	0.10	0.10
	0.040	0.35	0.32	0.32	0.16	0.19
	0.070	0.71	0.50	0.39	0.32	0.31
	0.100	1.00	0.79	0.54	0.42	0.41
	0.200	2.1	1.36	0.98	0.85	0.85
	0.400	3.5	2.7	1.95	1.78	1.76
22.0	0.040	0.96	0.76	0.64	0.49	0.55
	0.070	1.36	1.04	0.92	0.84	0.78
	0.100	1.75	1.63	1.33	1.10	1.13
	0.200	4.0	3.0	2.5	2.2	1.87
	0.400	8.0	5.8	4.9	4.2	3.8
30.0	0.040	2.5	1.55	1.42	1.13	0.96
	0.070	3.8	2.8	2.3	1.91	1.56
	0.100	5.4	4.0	3.2	2.8	1.93
	0.200	10.9	8.0	6.7	5.2	4.1
	0.400	21	16.4	12.9	10.0	8.2

TABLE 2

Second-order rate constants $10^{-2}k_0$/l mol^{-1} s^{-1}, for the oxidation of aliphatic carboxylic acids at different temperatures and acidities (each value is the average obtained from 3—6 runs performed with $[RCO_2H]$ in at least 20-fold stoicheiometric excess over $[Ag^{II}]$): μ 4.0M ($NaClO_4$), $[Ag^{I}]$ 0.10, $[Ag^{II}]$ 0.15—1.0 × 10^{-3}M

		$[HClO_4]$/M				
Acid	t_c/°C	1.00	1.50	2.00	3.00	4.00
Acetic	14.0	0.098	0.069	0.052	0.044	0.043
	22.0	0.20	0.149	0.124	0.106	0.096
	30.0	0.53	0.41	0.33	0.26	0.21
Propionic	14.0	0.37	0.28	0.20	0.171	0.169
	22.0	1.13	0.80	0.63	0.47	0.44
	30.0	2.7	2.1	1.69	1.30	1.11
Butyric	14.0	0.50	0.44	0.36	0.30	0.25
	22.0	1.20	0.99	0.86	0.68	0.63
	30.0	3.1	2.5	2.2	1.77	1.49
Isobutyric	14.0	7.6	5.4	4.3	3.1	2.7
	22.0	16.8	11.8	10.0	7.0	5.6
	30.0	34	26	20	15.7	12.0
Pivalic	14.0	68	52	43	31	27
	22.0	135	119	98	70	61
	30.0	320	260	210	154	116

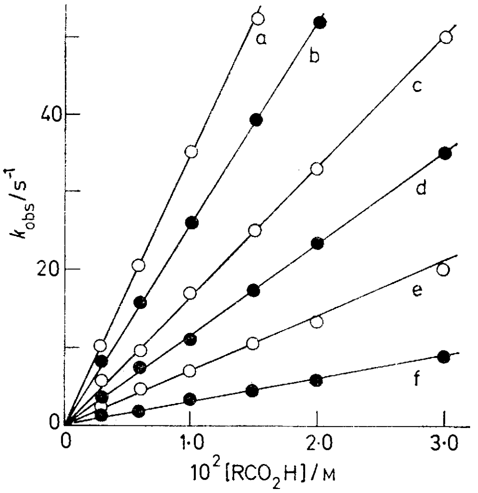

FIGURE 1 Plots of pseudo-first-order rate constants k_{obs} *versus* $[RCO_2H]$ for isobutyric acid, at different acidities and temperatures: a, 30.0 °C, $[HClO_4]$ 1.00; b, 30.0 °C, $[HClO_4]$ 1.50; c, 22.0 °C, $[HClO_4]$ 1.00; d, 22.0 °C, $[HClO_4]$ 1.50; e, 22.0 °C, $[HClO_4]$ 3.00; f, 14.0 °C, $[HClO_4]$ 3.00M

added $NaClO_4$ at $[HClO_4] = 1.00$M. A small decrease of the second-order rate constant has been found with increasing ionic strength (*ca.* 15% decrease when $[NaClO_4]$ varies from 0 to 3.0M). In addition, the effect of substituting Na^+ with Li^+ resulted in a small increase of the rate with increasing $[Li^+]$ (*ca.* 20% increase from $[Na^+] = 3.0$ to $[Li^+] = 3.0$ at $[HClO_4] = 1.00$M). An additional set of experiments (at 22.0 °C and with acetic acid) was performed in order to test the acidity dependence in $LiClO_4$ medium. The acid-independent path was not affected by replacing Na^+ with Li^+, while the rate constant for the acid-dependent path [see equation (9)] was 14.4 ± 1.2 compared with 11.4 ± 0.9 s^{-1} (see Table 3), showing a slight increase of reactivity in the medium with Li^+ as counterion. The second-order rate constants k_0, obtained from the slopes of plots similar to those reported in Figure 1, and collected in Table 2, decrease with increasing acidity according to the empirical rate law (2) where the subscript T refers to stoicheiometric concentrations and K_h is the equilibrium constant of the first Ag^{2+} hydrolysis [reaction (3)]. Figure 2, where k_0 $(1 + K_h[H^+]^{-1})$ is plotted as a function of $[H^+]^{-1}$ for n-butyric acid, shows agreement with equation (1). Values of 0.21, 0.35, and 0.48 mol l^{-1} were assumed for K_h at 14.0, 22.0, and 30.0 °C respectively.[1,10]

$$\frac{-d[Ag^{II}]_T}{dt} = k_{obs}[Ag^{II}]_T = \frac{(A + B[H^+]^{-1})[RCO_2H]_T[Ag^{II}]_T}{1 + K_h[H^+]^{-1}} \quad (2)$$

TABLE 3

Kinetic and activation parameters for the oxidation of aliphatic carboxylic acids by Ag^{II} at 22.0 °C and μ 4.0M

Acid	k_1/ l mol^{-1} s^{-1}	$\Delta H^‡$/ kcal mol^{-1}	$\Delta S^‡$/ cal mol^{-1} K^{-1}	$(k_2K_h + k_3K_a)$/ s^{-1}	$\Delta H^‡$/ kcal mol^{-1}	$\Delta S^‡$/ cal mol^{-1} K^{-1}
Acetic	1.9 ± 0.2	11 ± 1	−22 ± 3	11.4 ± 0.9	22 ± 1	+21 ± 3
Propionic	7.5 ± 0.6	14 ± 1	−9 ± 3	62 ± 5	25 ± 1	+32 ± 3
Butyric	17 ± 1	16 ± 1	−1 ± 3	65 ± 5	22 ± 1	+25 ± 3
Isobutyric	40 ± 3	15 ± 1	0 ± 3	1.1 ± 0.1 × 10^3	18 ± 1	+16 ± 3
Pivalic	1.0 ± 0.1 × 10^3	17 ± 1	+11 ± 3	8.9 ± 0.7 × 10^3	19 ± 1	+23 ± 3

The observed dependence on hydrogen ion and the reactants suggests the reaction sequence (3)—(8). If the first C–C bond cleavage, *i.e.* first electron abstraction

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[10] D. S. Honig, K. Kustin, and J. F. Martin, *Inorg. Chem.*, 1972, **11**, 1895.

from RCO_2H is slower than the second electron release, *i.e.* $R^{\bullet}$ radical disappearance through step (8), the rate law (9) is derived. Reactions involving both $AgOH^+$ and RCO_2^- are not taken into account because their contribution would give an inverse square dependence on acidity which is not present. Equation (9) agrees with the observed empirical equation (2), as for all investigated acids $K_a[H^+]^{-1} \ll 1$ in the acidity range investigated;[11] thus $A = 2k_1$ and $B = 2(k_2K_h + k_3K_a)$. Table 3 collects the values of k_1 and $(k_2K_h + k_3K_a)$ together with the activation parameters. Previous investigations on the oxidation of primary, secondary, and tertiary alkanecarboxylic acids by Pb^{IV}, Co^{III}, and Mn^{III} [12] showed that the rates varied significantly with the nature of the alkyl group in the order tertiary > secondary > primary, whereas for oxidation by Ce^{IV} or anodic oxidation no difference of reactivity was found.[13,14] In the latter case, formation of an intermediate acyloxyl radical $RCO_2^{\bullet}$ was advanced as the rate-determining step, whereas, in the former, a ' multibond mechanism ' with $R^{\bullet}$ radical formation during the rate-determining step could explain the different reactivities as being derived by the direct effect of the alkyl group on the $R{-}CO_2H$ bond. For the present reactions, the large increase of rates from butyric acid (primary) to pivalic acid (tertiary) seems to suggest a cleavage of the acids directly to carbon dioxide and alkyl radical.[4]

$$Ag_{aq}^{2+} \underset{}{\overset{K_h}{\rightleftharpoons}} AgOH_{aq}^{+} + H_{aq}^{+} \qquad (3)$$

$$RCO_2H_{aq} \overset{K_a}{\rightleftharpoons} RCO_{2\,aq}^{-} + H_{aq}^{+} \qquad (4)$$

$$Ag_{aq}^{2+} + RCO_2H_{aq} \longrightarrow Ag_{aq}^{+} + H_{aq}^{+} + CO_2 + R_{aq}^{\bullet} \qquad (5)$$

$$AgOH_{aq}^{+} + RCO_2H_{aq} \longrightarrow Ag_{aq}^{+} + CO_2 + R_{aq}^{\bullet} + H_2O \qquad (6)$$

$$Ag_{aq}^{2+} + RCO_{2\,aq}^{-} \xrightarrow{k_3} Ag_{aq}^{+} + CO_2 + R_{aq}^{\bullet} \qquad (7)$$

$$R^{\bullet} + Ag^{II} \longrightarrow Ag^{I} + H_{aq}^{+} + \text{products} \qquad (8)$$

$$\frac{-d[Ag^{II}]_T}{dt} = \frac{2\{k_1 + (k_2K_h + k_3K_a)[H^+]^{-1}\}[Ag^{II}]_T\,[RCO_2H]_T}{(1 + K_h[H^+]^{-1})(1 + K_a[H^+]^{-1})} \qquad (9)$$

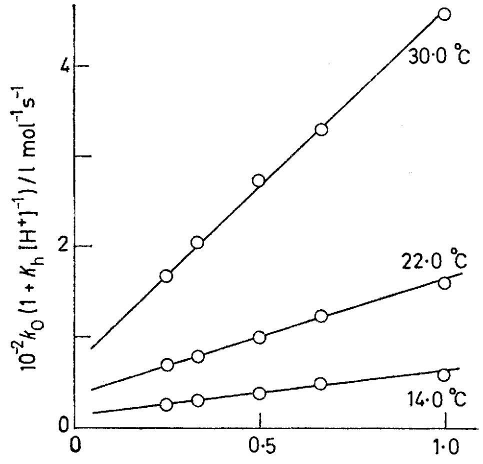

FIGURE 2 Plot of $k_0\,(1 + K_h[H^+]^{-1})$ *versus* $[H^+]^{-1}$ for oxidation of butyric acid by Ag^{II} at different temperatures

The contributions of paths (6) and (7) to the overall reaction progress are kinetically undistinguishable. If the assumption is made that step (7) does not contribute to the term *B*, the estimated reactivity of $AgOH^+$ with respect to Ag^{2+} is *ca.* 10^1—10^2; by making the opposite assumption, the estimated k_3 constants are well below the diffusion-controlled limit for the most unfavourable case, *i.e.* pivalic acid (the pK_a values range from 5.01 for acetic to 5.33 for pivalic acid at 25° and μ 3M, $NaClO_4$),[11] and the reactivity ratio between anion and undissociated acid (k_3/k_1) is *ca.* 10^6 which seems to be somewhat higher than previous results on the oxidation of similar systems. For example formate ion reacts with Co^{III} with a rate 1.2×10^4 higher than does formic acid,[15] and a ratio of 2×10^3 has been reported for the reactions of the same substrates with MnO_4^-,[2,16] in agreement with electrophilic attack of the oxidant on the negatively charged anion.[3]

Comparison of the reactivities of the acids shows that electron transfer is easier in the presence of groups which increase the electron density at the reaction centre for both pathways [reactions (5) and (6) + (7)], as shown by plots of log $(k_{RCO_2H}/_{CH_3CO_2H})$ against Taft σ^* values,[17] which give ρ 8.8 and 8.1 for the independent and acid-dependent paths (an example is shown in Figure 3 for the acid-dependent path). It is worth mentioning that the overall second-order rate constant $(k_2K_h + k_3K_a)$ for the oxidation of formic acid by Ag^{II} does not correlate with the observed linear trend suggesting that a different mechanism, with higher reactivity, is operating in this case. This is supported by the occurrence of a pathway second order in oxidizing agent which is not found to operate for the other acids. In this respect the different behaviour of the present substrates compared with formic acid supports the idea that in the latter case the oxidant acts on the H–C bond as previously advanced for Mn^{III} oxidation.[18]

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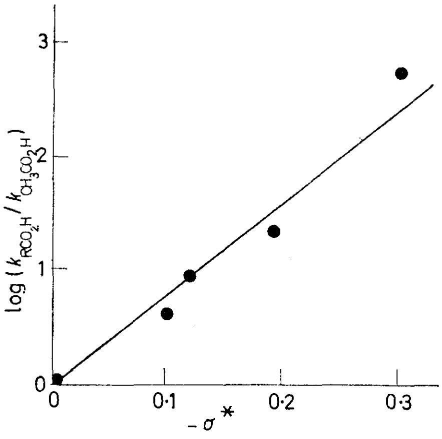


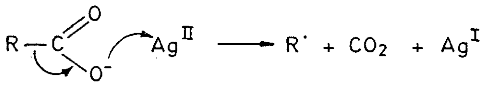
FIGURE 3 Plot of log ($k_{RCO_2H}/k_{CH_3CO_2H}$) (where k is the overall second-order rate constant for the inverse acid-dependent pathways) *versus* Taft σ^* values for the investigated reactions: t = 22.0 °C

Two-electron oxidants such as MnO_4^-, Hg^{2+}, Hg_2^{2+}, and Tl^{3+} have been described as reacting with formic acid [2,16,19] with a two-equivalent reduction of the metal ion by electron transfer from a co-ordinated formate ion coupled with proton transfer to a water molecule. Hydride transfer is also possible and this could explain the second-order dependence on Ag^{II} concentration.[1] A one-equivalent rate-determining step is hardly disfavoured on thermodynamic grounds due to the high redox potential of reaction (10) [2] by comparison with (11) and this seems to account for the lower reactivity

$$HCO_2^- \rightleftarrows H^\bullet + CO_2 + e \quad E^0\ ca.\ -1.8\ V \quad (10)$$

$$HCO_2^- \rightleftarrows H^+ + CO_2 + 2\,e \quad E^0 + 0.2\ V \quad (11)$$

of one-electron acceptors with respect to two-electron acceptors of similar oxidation ability.[18,20] The high redox potential of Ag^{II} makes possible the former mechanism; thus one-electron attack of Ag^{II} on the carboxylic group is thought to occur by reaction (12) or (13).



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