

Kinetics of Oxidation of Organic Compounds by Silver(II) in Aqueous Perchloric Acid Solution. Part 3.¹ Aliphatic Aldehydes

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The stoichiometries and kinetics of the silver(II) oxidation of formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, and pivaldehyde have been investigated at 8.0, 14.0, and 22.0 °C in aqueous perchloric acid media ($1.00 \leq [\text{HClO}_4] \leq 4.00\text{M}$; μ 4.0M). The kinetics were monitored by a stopped flow technique. The reactions occur with the stoichiometry $\text{H}_2\text{O} + 2\text{Ag}^{\text{II}} + \text{RCHO} \longrightarrow 2\text{Ag}^{\text{I}} + 2\text{H}^+ + \text{RCOOH}$. The rate-determining step is first order in each reactant, and involves both Ag^{2+} and AgOH^+ species. No direct evidence for complex formation between the reactants was obtained. The results are discussed with reference to enolization and hydration equilibria of the substrates. *gem*-Diol forms of the aldehydes are suggested as the active species.

PREVIOUS papers from this laboratory have reported the oxidation of formic acid² and of acetic, propionic, butyric, isobutyric, and pivalic acids by Ag^{II} .¹ In the oxidation of formic acid the reaction rates showed both first- and second-order dependence on $[\text{Ag}^{\text{II}}]$, indicating the involvement of Ag^{III} , generated from disproportionation of Ag^{II} , as a reacting species. The possibility of oxidation involving a two-equivalent step differentiated the reaction mechanism for formic acid from that operating for the other aliphatic acids, where the dependence on $[\text{Ag}^{\text{II}}]$ was solely first order. A general mechanism for the latter reductants was supported by a

Taft plot in which the points corresponding to formic acid were far from the common linear plot for the other acids.

In this paper we report results for the oxidation of the corresponding members in the aliphatic aldehyde series by Ag^{II} in order to investigate analogies or discrepancies with the results for acids and as a part of our study of the steps in the oxidative chain alcohols–aldehydes–acids– CO_2 . The kinetic features of the oxidation of aldehydes by oxidizing metal species often depend on such factors as keto–enol tautomerism,³ hydration,⁴ protonation, or deprotonation of the resulting *gem*-diol forms,⁵ and formation of intermediate complexes.⁶ Moreover, the occurrence of non-complementary cross-

¹ Part 2, E. Mentasti, E. Pelizzetti, and C. Baiocchi, *J.C.S. Perkin II*, 1976, 1841.

² E. Pelizzetti and E. Mentasti, *J.C.S. Dalton*, 1975, 2086.

³ T. J. Kemp, in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, New York, 1972, vol. 7, ch. 4; D. Benson, 'Reaction Mechanisms in Organic Chemistry. Monograph 10. Mechanisms of Oxidation by Metal Ions,' Elsevier, New York, 1976.

⁴ R. P. Bell, *Adv. Phys. Org. Chem.*, 1966, 4, 1.

⁵ G. Hargreaves and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1955, 51, 786; U. Shanker and M. P. Singh, *Indian J. Chem.*, 1968, 6, 702.

⁶ J. R. Jones and W. A. Waters, *J. Chem. Soc.*, 1963, 352.

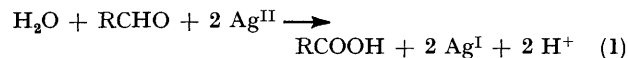
reactions sometimes enables rearrangement of radical intermediates, resulting in different reaction products.

EXPERIMENTAL

Reagents.—Acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde (Merck), and pivaldehyde (Fluka) were purified by distillation under nitrogen. Formaldehyde solutions were prepared by heating paraformaldehyde (Erba) on an oil-bath at 200 °C; the formaldehyde gas was introduced into water in an Erlenmeyer flask and titrated by standard iodometric methods. Solutions of the other aldehydes were titrated with hydrogen sulphite or hydroxylamine hydrochloride,⁷ and used immediately after preparation. Silver(II) perchlorate solutions were obtained as previously described,¹ and standardized spectrophotometrically ($\epsilon_{\text{Ag}^{\text{II}}}$ 138 \pm 2.1 mol⁻¹ cm⁻¹ at 470 nm).⁸

Kinetics.—All kinetic runs were performed on a Durrum-Gibson stopped-flow spectrophotometer (2.00 cm cell). Measurements were performed at 8.0, 14.0, and 22.0 °C. The acid dissociation constant for Ag²⁺ was assumed to be 0.15, 0.21, and 0.35 mol⁻¹ at 8.0, 14.0, and 22.0 °C, respectively.^{1,9} With exception of pivaldehyde, kinetic runs were performed under pseudo-first-order conditions, and the aldehyde was the reagent in excess (10⁻³–10⁻²M). Reaction rates were monitored at 470 nm by following the disappearance of Ag^{II}, the only absorbing species at this wavelength.

Stoichiometry.—A solution of Ag^{II} (1 \times 10⁻⁴–3 \times 10⁻³M) was mixed in the stopped-flow apparatus with solutions containing different formaldehyde concentrations ([Ag^{II}] was always more than twice the molar concentration of the aldehyde). A rapid consumption of Ag^{II} could be detected from the traces on the storage screen of the oscilloscope. The remaining [Ag^{II}] then decreased further in slower steps by reaction with the solvent and with the primary reaction product. The ratio between formaldehyde concentration and Ag^{II} reacted in the primary step (obtained from the decrease of transmittance between time 0 and the end of the first reaction) was 1 : 2, irrespective of acidity, temperature, and [Ag^I]. The same stoichiometric ratio was obtained with the other aldehydes so that the general overall reaction can be written as (1). In the case of pivaldehyde, the



oxidation of the primary product, pivalic acid, was fast enough to prevent a reliable evaluation of the stoichiometric factor as anticipated from its reactivity towards Ag^{II}.¹

The overall reaction (1) involves two one-electron steps; thus radical intermediate rearrangement and enolization of the aldehyde reductant could be responsible of the formation of minor side-products (acetone and formic acid from isobutyraldehyde, as formed in V^V oxidation;⁶ small amounts of BuⁱOH and isobutene in the oxidation of pivaldehyde by Cr^{IV}¹⁰). However the rapidity of the Ag^{II} oxidation of the aldehydes probably prevents side reactions due to radical rearrangements or to enolization (see below).

RESULTS AND DISCUSSION

Kinetic runs with [Ag^{II}]₀ in the range 5 \times 10⁻⁵–2 \times 10⁻³M and in the presence of either a large excess of

⁷ S. Siggia, 'Quantitative Organic Analysis via Functional Groups,' Wiley, New York, 1949, pp. 10–19.

[Ag^I]_T (1 \times 10⁻¹M) or of a small Ag^I concentration (5 \times 10⁻³M) always exhibited a first-order rate of disappearance

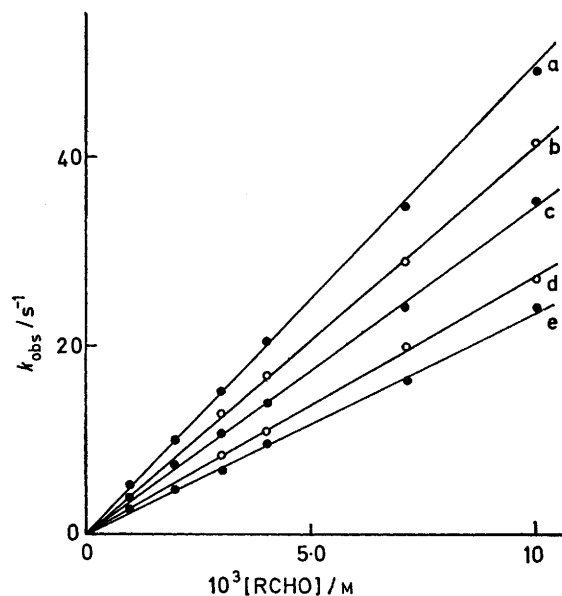


FIGURE 1 Plots of k_{obs} against [Aldehyde] for the oxidation of butyraldehyde by Ag^{II} at 14.0 °C and at different acidities: a, [HClO₄] = 1.00; b, 1.50; c, 2.00; d, 3.00; e, 4.00M

TABLE 1

Second-order rate constants, 10⁻³ k_0 /l mol⁻¹ s⁻¹, for the oxidation of aliphatic aldehydes at different temperatures and acidities^a

Aldehyde	<i>t</i> /°C	[HClO ₄]/M				
		1.00	1.50	2.00	3.00	4.00
HCHO	8.0	17	12.2	9.9	7.7	7.4
	14.0	24	19.0	16.6	13.6	10.9
	22.0	54	43	37	31	24
CH ₃ CHO	8.0	2.7	1.94	1.60	1.00	0.74
	14.0	4.3	2.7	2.2	1.75	1.20
	22.0	7.9	5.6	4.3	3.4	2.8
CH ₃ CH ₂ CHO	8.0	3.3	2.6	2.2	1.80	1.50
	14.0	4.9	4.2	3.4	2.9	2.4
	22.0	8.8	7.1	6.0	4.7	4.2
CH ₃ (CH ₂) ₂ CHO	8.0	3.3	2.6	2.4	1.75	1.40
	14.0	5.0	4.1	3.5	2.8	2.4
	22.0	8.9	6.8	5.6	4.8	4.4
(CH ₃) ₂ CHCHO	8.0	5.7	4.6	3.9	3.2	2.6
	14.0	7.2	5.7	4.5	3.9	3.3
	22.0	9.2	7.3	6.6	4.7	4.2
(CH ₃) ₃ CCHO	8.0	2.6	2.1	1.67	1.50	1.15
	14.0	3.8	2.8	2.7	2.1	1.70
	22.0	4.8	3.9	3.3	2.5	2.6

^a Each value is the average obtained from 3–6 runs performed with aldehyde in at least five-fold molar excess over Ag^{II} {[Ag^I] 0.10, [Ag^{II}] 0.5–5.0 \times 10⁻⁴, μ 4.0M(NaClO₄)}. The data for pivaldehyde, obtained under second-order conditions and treated accordingly, do not contain the factor 2 [see equations (7) and (8)] and were corrected for the contribution due to the oxidation of pivalic acid (see text).

of Ag^{II}. Thus, plots of ln A_t against time (where A_t is the absorbance at time t) showed good linearity for at

⁸ D. S. Honig and K. Kustin, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1599.

⁹ D. S. Honig, K. Kustin, and J. F. Martin, *Inorg. Chem.*, 1972, **11**, 1895.

¹⁰ J. Rocek and C. S. Ng, *J. Amer. Chem. Soc.*, 1974, **96**, 1522.

least two half-lives. This behaviour was independent of initial $[Ag^{II}]_0$ and $[Ag^I]_0$. Pseudo-first-order rate constants k_{obs} were obtained from the gradients of the above plots by means of a weighted least squares method; the standard deviation for each k_{obs} value (obtained from triplicate runs) was generally within 2–4%.

The pseudo-first-order rate constants (at constant $[H^+]$, $[Ag^I]$, and temperature) showed a linear dependence on $[Aldehyde]$ for all investigated compounds (see, for example, Figure 1) in the concentration ranges examined, and no spectroscopic or kinetic evidence for

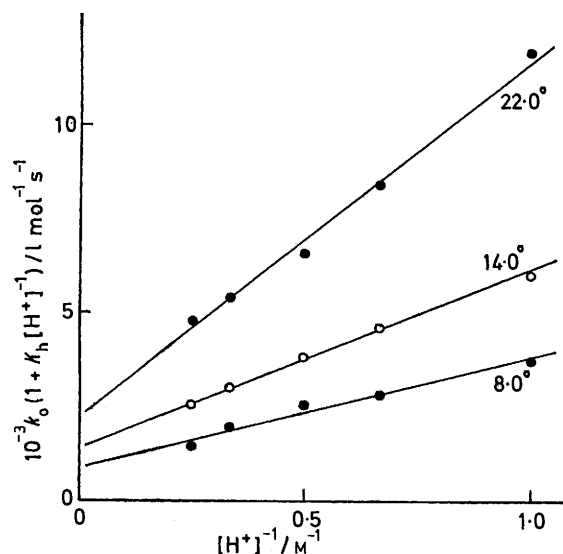


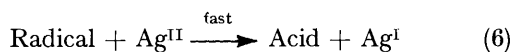
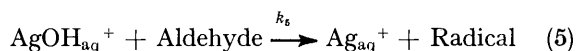
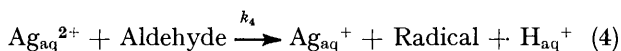
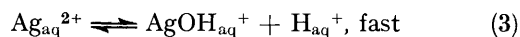
FIGURE 2 Plots of $k_0(1 + K_h[H^+]^{-1})$ as a function of $[H^+]^{-1}$ for the oxidation of butyraldehyde at different temperatures

intermediate complexes was obtained; thus the observed rate law is as in (2). Second order rate constants, k_0 ,

$$-d[Ag^{II}]/dt = k_0[Ag^{II}][Aldehyde] \quad (2)$$

calculated by using a weighted least-squares method, are in Table I; the weights were based on the standard deviations of the pseudo-first-order rate constants.

Large inverse dependences on acidity were observed for all the substrates. No deprotonation of the aldehydes is expected under the experimental conditions; thus the inverse dependence on acidity may be ascribed to acid dissociation of the oxidant, according to the following mechanism (3)–(6). If equilibrium (3) is



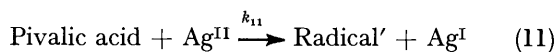
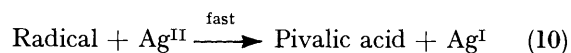
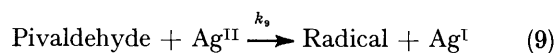
$$\frac{d[Ag^{II}]}{dt} = \frac{2(k_4 + k_5K_h[H^+]^{-1})[Ag^{II}]_{Tot}[Ald]_{Tot}}{1 + K_h[H^+]^{-1}} \quad (7)$$

very fast, the rate law (7) is derived which agrees with the empirical rate law (2), when equation (8) obtains.

$$k_0 = \frac{2(k_4 + k_5K_h[H^+]^{-1})}{1 + K_h[H^+]^{-1}} \quad (8)$$

Figure 2 shows examples of plots of $k_0(1 + K_h[H^+]^{-1})$ against $[H^+]^{-1}$ supporting the above assignment. In all cases such plots are linear with significant slopes ($2k_5K_h$) and intercepts ($2k_4$); however, in the case of acetaldehyde the path independent of $[H^+]^{-1}$ is very small.

The low solubility of pivaldehyde in aqueous solution did not enable us to perform the runs under pseudo-first-order conditions. This raised some complication in the evaluation of the second-order rate constant. In fact, under the experimental conditions, the rate of aldehyde oxidation was comparable with the rate of oxidation of the primary product of reaction, pivalic acid.¹



If $k_{11} \gg k_9$, the observed second-order rate constant would be twice the rate derived from the first oxidation step (9)–(10) (this arises from the stoichiometric ratio $1 : 2\Delta[Aldehyde] : \Delta[Ag^{II}] = \Delta[Pivalic\ acid] : \Delta[Ag^{II}]$). Thus if one does not take into account the possibility of further oxidation of pivalic acid the rate constant for reaction (9) can be overestimated by a factor 2. If we assume equations (13) and (14) for the early part of the reaction, where $x = [Ag^{II}]_t$, we obtain equation (15)

$$[Pivaldehyde] = C_{ald} - ([Ag^{II}]_0 - x)/2 \quad (13)$$

$$[Pivalic\ acid] = ([Ag^{II}]_0 - x)/2 \quad (14)$$

$$-dx/k_9dt = \{a - (b - x) + R(b - x)\}x \quad (15)$$

where $a = 2C_{ald}$, $b = [Ag^{II}]_0$, and $R = k_{11}/k_9$, from which, after integration, equation (16) is obtained. By

$$(a - b + Rb)^{-1} \ln \left| \frac{2(1 - R)x}{2(1 - R)x + 2(a - b + Rb)} \right| = -k_9t \quad (16)$$

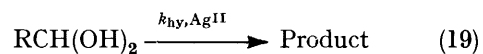
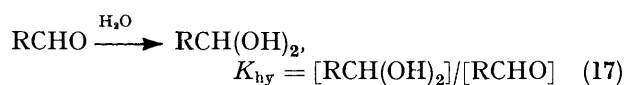
using this expression to analyse the early points of each run, we obtained after iteration the k_0 values which are in Table 2. R Values were computed from the second-order rate constants (k_{11}), previously determined, at the proper acidity, for pivalic acid,¹ and from a rough estimate of k_9 obtained with a second-order treatment without taking into account the further oxidation of pivalic acid.

Comparison with rates for Ag^{II} oxidation of the corresponding carboxylic acids¹ points out, first, that the

large effects played by the aliphatic chain bound to the carboxylic acid group (ρ ca. 8 for both independent and inverse acid dependent paths) are limited for the aldehydes; this can be accounted for by considering that, in the acids, a carbon-carbon bond, adjacent to the chain, must be broken.

Moreover, Table 2 shows a trend which is not a simple function of the structure of the chain bound to the formyl group, and this can be understood in terms of the tendency to hydration and enolization of these aldehydes, as follows. Formaldehyde (a non-enolizable aldehyde) is, in aqueous solution, completely hydrated in a *gem*-diol form;¹¹ pivaldehyde (also non-enolizable) is hydrated only to a slight extent,¹² while acet-, propion-, butyr-, and isobutyr-aldehydes are enolizable and, in the same order, increasingly less hydrated in aqueous

HCHO > Bu^tCHO, and this is unlikely to happen (an inverse order should result from the electron-withdrawing



$$k_{\text{dehy}} = k_{\text{tot}}(1 + K_{\text{hy}}), \quad k_{\text{hy}} = k_{\text{tot}}(1 + K_{\text{hy}}^{-1}) \quad (20)$$

ability of the carbon chain). On the contrary, if the hydrated form is the reactive species, similar reactivity is found for formaldehyde and pivaldehyde (see Table 2 where k_{tot} values, the specific rate constants referred

TABLE 2

Kinetic and activation parameters for the oxidation of aliphatic aldehydes by Ag^{II} at 22.0 °C and μ 4.0M (NaClO₄)

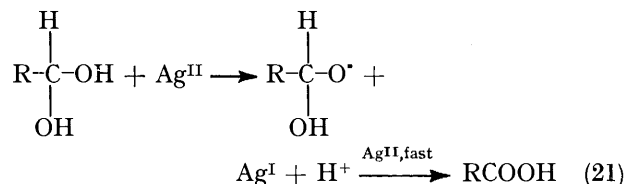
Aldehyde	$10^{-3} k_4/$ 1 mol ⁻¹ s ⁻¹	$\Delta H_4^\ddagger/$ kcal mol ⁻¹	$\Delta S_4^\ddagger/$ cal mol ⁻¹ K ⁻¹	$10^{-3} k_5 K_h/$ s ⁻¹	$\Delta H_5^\ddagger/$ kcal mol ⁻¹	$\Delta S_5^\ddagger/$ cal mol ⁻¹ K ⁻¹	$10^{-4} k_5/$ 1 mol ⁻¹ s ⁻¹	K_{hy}^a	$10^{-3} k_4 k_{\text{hy}}/$ 1 mol ⁻¹ s ⁻¹	$10^{-4} k_5 k_{\text{hy}}/$ 1 mol ⁻¹ s ⁻¹
HCHO	6.2 ± 1.0	14 ± 2	6 ± 5	30 ± 3	15 ± 1	12 ± 3	8.6 ± 0.9	1.800	6.2	8.6
CH ₃ CHO	~0.3			5.2 ± 0.5	14 ± 1	5 ± 3	1.5 ± 0.2	1.49	0.5	2.5
CH ₃ CH ₂ CHO	1.0 ± 0.2	10 ± 2	-11 ± 5	5.2 ± 0.5	14 ± 1	6 ± 3	1.5 ± 0.2	0.71	2.4	3.6
CH ₃ (CH ₂) ₂ CHO	1.1 ± 0.2	11 ± 2	-6 ± 5	4.6 ± 0.5	12 ± 1	-1 ± 3	1.3 ± 0.2	0.48	3.4	4.0
(CH ₃) ₂ CHCHO	1.0 ± 0.2	5 ± 2	-26 ± 5	5.2 ± 0.7	7 ± 1	-18 ± 3	1.5 ± 0.2		4 ^b	6 ^b
(CH ₃) ₃ CCHO	1.4 ± 0.6	7 ± 4	-20 ± 10	5.0 ± 2.0	9 ± 3	-13 ± 8	1.4 ± 0.5	0.24	7.1	7.1

^a See ref. 10. ^b Computed by assuming tentatively a K_{hy} value for isobutyraldehyde intermediate between those for butyr-aldehyde and pivaldehyde.

solution. Thus the rate constants for Ag^{II} oxidation of formaldehyde and pivaldehyde, which are not in an enol form, suggest that hydrated form is much more reactive than the keto-form (electron abstraction by Ag^{II} from the hydroxy-groups of benzene-1,2-diol, which can be compared to the *gem*-diol form of HCHO, is very fast).^{9,13} The other aldehydes react as enol or keto-forms. Since the reactions are always first order in [Ag^{II}] and the rates are always much faster than measured rates of enolization of the aldehydes,⁶ the latter process^{6,14-16} is never rate determining. Also the absence of terms on [Ag^{II}]² and effects from changes of [Ag^I] rule out the participation of Ag^{III} produced *via* disproportionation ($2\text{Ag}^{\text{II}} \rightleftharpoons \text{Ag}^{\text{I}} + \text{Ag}^{\text{III}}$). Turning now to the participation of the aldehydes in the keto or in the hydrated form, the relative rate constants can be computed, by considering in turn one of two forms as the only active species [equations (17)–(20)]. If RCHO is the active form, the reactivity would be depressed by a factor of ca. 10⁴ between the extremes in the order

to the stoichiometric concentration of the aldehydes, are reported together with K_{hy} and k_{hy} .

The small effect displayed by the carbon chain (ρ ca. 1.6 for the acid dependent path) could then be accounted for by considering that Ag^{II} attacks the hydroxy-group rather than the C–H bond (if this is the reaction centre, the non-hydrated form would be reactive) and consequently the effect of the alkyl chain is screened and depressed by the C–O system [equation (21)]. Another



possible explanation for the absence of a substrate effect on the rates could arise from a metal centred activation process.

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¹² P. Greenzaid, Z. Luz, and D. Samuel, *J. Amer. Chem. Soc.*, 1967, **89**, 749.

¹³ E. Pelizzetti, E. Mentasti, and C. Baiocchi, *J. Inorg. Nuclear Chem.*, 1976, **38**, 557.

¹⁴ A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 1953, 440.

¹⁵ P. T. Speakman and W. A. Waters, *J. Chem. Soc.*, 1955, 40.

¹⁶ B. T. Allen and W. A. Waters, *J. Chem. Soc.*, 1956, 1132.