

Kinetics and mechanism of the oxidation of some α -hydroxy carboxylic acids by [bis(trifluoroacetoxy)iodo]benzene

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The oxidation of α -hydroxy carboxylic acids by [bis(trifluoroacetoxy)iodo]benzene (TFAIB), to the corresponding oxoacids is first order with respect to each, the hydroxy acid, TFAIB and hydrogen ions. The oxidation of α -deuteriomandelic acid (PhCDOHCO₂H) exhibits the presence of a substantial primary isotope effect confirming the cleavage of the α - C - H bond in the rate-determining step. The rate of oxidation of substituted mandelic acids correlates well with Brown's σ^+ values with large negative reaction constants. A mechanism involving transfer of a hydride ion from the hydroxy acid to the oxidant has been postulated.

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Oxidation of α -hydroxy carboxylic acids can take place by a number of different mechanisms. They can behave like simple alcohols to yield oxoacids or may undergo oxidative decarboxylation¹ to form carbonyl products. Oxidation of α -hydroxy carboxylic acids by benzyltrimethylammonium bromochromate², quinolinium fluorochromate³, tetrabutylammonium tribromide⁴, butyltriphenylphosphonium dichromate⁵, and benzyltrimethylammonium chlorochromate⁶, etc. leads to the formation of corresponding oxoacids. However, oxidants like nickel(IV)⁷ and cerium(IV)⁸ cause an oxidative decarboxylation to yield the corresponding carbonyl compounds. There seems to be no report on the mechanistic aspects of the oxidation of α -hydroxy carboxylic acids by any hypervalent iodine compound. We have recently studied some aspects of oxidation by hypervalent iodine compounds⁹⁻¹¹. We report here the kinetics of the oxidation of glycollic acid (GA), lactic acid (LA), mandelic acid [MA] and several substituted mandelic acids by [bis(trifluoroacetoxy)iodo]benzene (TFAIB). At-

tempts have been made to correlate rate and structure in the reaction.

Experimental

The α -hydroxy acids were commercial products or were prepared by known methods. TFAIB (commercial grade from Aldrich) was used as supplied. α -Deuteriomandelic acid (PhCDOHCO₂H or DMA) was prepared by the method of Kemp and Waters¹². ¹H NMR spectrum showed that nearly quantitative deuteration has been achieved. Perchloric acid was used as a source of hydrogen ions. Acetic acid was refluxed with chromic oxide and acetic anhydride for 3 h and then fractionated.

The product analysis was performed under kinetic conditions, i.e. with an excess of the hydroxy acid over of TFAIB. In a typical example, mandelic acid (1.52 g, 0.01 mol) and TFAIB (0.43 g, 0.001 mol) were made up to 50 mL in 1:1 acetic acid-water (v/v), in the presence of 0.20 mol perchloric acid. The reaction mixture was allowed to stand for *ca.* 18 h to ensure completion of the reaction. Most of the solvent was removed under reduced pressure. The residue was then treated with an excess (200 mL) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm⁻³ HCl and kept in refrigerator overnight. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The product was identical with the DNP of phenylglyoxylic acid. The yield of the DNP, before and after recrystallization, was 0.70 g (94%) and 0.60 g (81%), respectively. Similar experiments with other hydroxy acids led to the formation of DNP of the corresponding oxoacids in 73–88% yields, after recrystallization.

The reactions were studied under pseudo-first-order conditions by keeping an excess ($\times 10$ or greater) of the hydroxy acid over TFAIB. The solvent was 1:1 acetic acid-water (v/v), unless mentioned otherwise. The reactions were studied at constant temperature (± 0.1 K) and were followed by monitoring the decrease in [TFAIB] iodometrically for up to 80% of the reaction extent. Pseudo-first-order rate constants, k_{obs} , were evaluated from linear plots ($r^2 > 0.995$) of \log [TFAIB] against time. Duplicate kinetic runs showed that the rate constants are reproducible to

Table 1 — Rate constants for the oxidation of mandelic acid by TFAIB at 318 K

$10^3[\text{TFAIB}]$ mol dm ⁻³	[MA] mol dm ⁻³	[H ⁺] mol dm ⁻³	$10^4 k_{\text{obs}}$ s ⁻¹
1.0	0.10	1.0	1.12
1.0	0.20	1.0	2.25
1.0	0.30	1.0	3.28
1.0	0.50	1.0	5.63
1.0	0.70	1.0	7.84
1.0	1.00	1.0	11.3
1.0	1.50	1.0	16.8
2.0	0.50	1.0	5.73
3.0	0.50	1.0	5.59
5.0	0.50	1.0	5.68
7.5	0.50	1.0	5.55
1.0	0.50	0.2	1.13
1.0	0.50	0.4	2.28
1.0	0.50	0.8	4.50
1.0	0.50	1.2	6.80
1.0	0.50	1.0	5.60*

* Contained 0.001 mol dm⁻³ acrylonitrile

within $\pm 3\%$. Preliminary experiments showed that the reaction is not sensitive to changes in ionic strength. Therefore, no attempt was made to keep the ionic strength constant. The third order rate constant, k_3 , was calculated from the relation: $k_3 = k_{\text{obs}}/[\text{hydroxy acid}][\text{H}^+]$. Simple linear regression analyses were carried out by the least-squares method. We have used standard deviation (s.d.), coefficient of determination (r^2), and Exner's¹³ parameter, ψ , as measures of the goodness-of-fit in correlation analysis.

Results and discussion

Kinetic data were obtained for all the hydroxy acids studied. Since the results are similar, only representative data are reproduced here.

The oxidation of hydroxy acids by TFAIB resulted in the formation of the corresponding oxoacids. The overall reaction may therefore, be represented as:



The reaction is first order with respect to TFAIB. In individual kinetic runs, plots of $\log [\text{TFAIB}]$ versus time were linear ($r^2 > 0.995$). Further, it was found that the observed rate constant, k_{obs} , does not depend on the initial $[\text{TFAIB}]$. The reaction is of first order with respect to each, the hydroxy acid and hydrogen ions (Table 1).

The oxidation of mandelic acid in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile. In blank experiments (upon the hydroxy acid

being absent), no noticeable consumption of TFAIB was observed. The addition of acrylonitrile had no effect on the rate of oxidation (Table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm⁻³ of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

The rate of oxidation of the hydroxy acids was determined at four different temperatures and the activation parameters were calculated (Table 2).

To ascertain the importance of the cleavage of the $\alpha\text{-C-H}$ bond in the rate-determining step, oxidation of deuteriated mandelic acid was studied. The results (Table 2) showed that the presence of a substantial primary kinetic isotope effect.

The oxidation of mandelic acid was studied in solvents containing different amounts of acetic acid and water. The rate of oxidation increases with an increase in the amount of acetic acid in the solvent. For instance, with $[\text{TFAIB}] = 0.001 \text{ mol dm}^{-3}$, $[\text{MA}] = 0.5 \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$ and temperature = 318 K, the rate of oxidation ($10^4 k_{\text{obs}}$) is 1.74, 3.48, 5.63, 10.4, 22.4 s⁻¹, when the % AcOH (v/v) in the solvent is 30, 40, 50, 60 and 70, respectively.

There is a satisfactory correlation between the activation enthalpies and entropies of the oxidation of fourteen hydroxy acids ($r^2 = 0.9807$, s.d. = 1.8, $\psi = 0.14$), indicating the operation of a significant compensation effect¹⁴. The reaction exhibited an excellent isokinetic relationship also as determined by Exner's method¹⁵. An Exner's plot between $\log k_2$ at 288 K and at 318 K was linear ($r^2 = 0.9978$, sd = 0.04, $\psi = 0.05$, slope = 0.7913 ± 0.0108). The value of isokinetic temperature evaluated from the Exner's plot is $527 \pm 18 \text{ K}$. The linear isokinetic correlation implies that all the hydroxy acids are oxidized by the same mechanism and the change in the rate of oxidation is governed by changes in both the enthalpy and entropy of the activation.

The rate constants, k_2 , of the oxidation of substituted mandelic acids did not show a significant correlation in terms of Hammett's¹⁶ equation (Eq. 2).

$$\log k_3 = -2.93 \pm 0.22 \sigma - 3.21 \quad \dots (2)$$

($r^2 = 0.9500$, s.d. = 0.24, $\psi = 0.23$, $n = 11$, Temp. = 298 K)

The rates were, therefore, correlated in terms of Brown's σ^+ values¹⁷. The substituent constants were

Table 2—Rate constants and activation parameters for the oxidation of α -hydroxy acids by TFAIB

Substituent	$10^4 k_3$ (dm ⁶ mol ⁻² s ⁻¹)				ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔG^* (kJ mol ⁻¹)
	288 K	298 K	308 K	318 K			
H	1.25	2.70	5.75	11.2	53.4±0.3	-135±1	93.4±0.2
<i>p</i> -F	1.92	3.97	8.12	15.7	50.9±0.2	-140±1	92.4±0.2
<i>p</i> -Cl	0.71	1.58	3.44	7.11	56.0±0.1	-130±1	94.7±0.1
<i>p</i> -Br	0.49	1.19	2.75	5.52	59.2±0.7	-122±2	95.4±0.6
<i>p</i> -Me	6.97	13.3	25.0	43.7	44.2±0.2	-152±1	89.4±0.2
<i>p</i> -NO ₂	0.013	0.043	0.12	0.31	77.8±0.9	-88±3	103 ± 1.0
<i>p</i> -OMe	99.2	150	235	346	29.4±0.4	-182±2	83.4±0.3
<i>p</i> -Pr ⁱ	6.20	12.0	22.5	39.1	44.4±0.3	-153±1	89.7±0.2
<i>m</i> -Cl	0.17	0.44	1.02	2.24	62.8±0.5	-118±2	97.9±0.4
<i>m</i> -NO ₂	0.026	0.71	0.20	0.51	73.3±0.7	-98±2	102±0.5
<i>m</i> -Br	0.12	0.33	0.84	1.95	68.3±0.3	-102±1	98.6±0.3
GA	0.64	1.41	2.97	6.05	54.5±0.2	-136±1	95.0±0.2
LA	0.83	1.75	3.76	8.02	55.1±0.9	-132±3	94.4±0.7
DMA	0.23	0.51	1.11	2.21	55.1±0.3	-143±1	97.5±0.2
k_H/k_D	5.43	5.29	5.20	5.07			

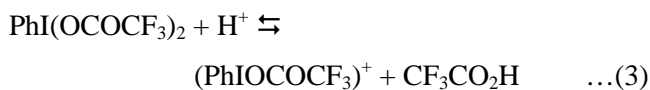
Table 3—Temperature dependence of the reaction constant

T (K)	ρ^+	r^2	sd	ψ
288	-2.46±0.03	0.9987	0.04	0.04
298	-2.26±0.02	0.9994	0.03	0.04
308	-2.07±0.02	0.9988	0.03	0.04
318	-1.93±0.01	0.9995	0.02	0.02

obtained from the compilation of Wiberg¹⁸. The correlation with Brown's σ^+ values is excellent; the reaction constant being negative (Table 3).

Mechanism

The observed hydrogen-ion dependence suggests that: (i) a fast protonation pre-equilibrium is involved, (ii) the equilibrium constant of protonation reaction is small, and (iii) only the protonated species is reactive. Therefore, it is proposed that TFAIB is protonated in a fast pre-equilibrium to give a stronger oxidant and electrophile (Eq. 3).

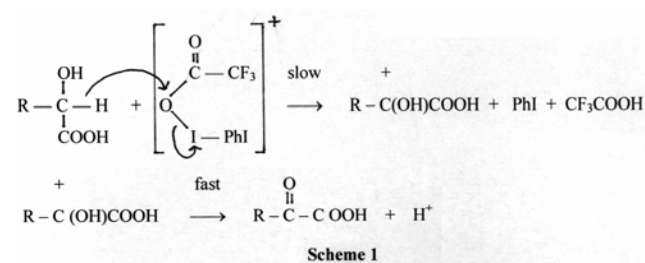


The observed solvent composition effect supports a protonation equilibrium. The lowering of relative permittivity, caused by an increase in the amount of acetic acid in the solvent mixture, favours a reaction

in which charge is distributed over a large area. Such an observation has been recorded in many redox reactions¹⁹.

The presence of a substantial primary kinetic isotope effect confirms the cleavage of the α -C – H bond in the rate-determining step. A hydrogen-abstraction mechanism leading to the formation of free radicals is unlikely in view of the failure to induce polymerization of acrylonitrile and no effect of acrylonitrile on the reaction rate. This is supported by the absence of any effect of BHT also.

The excellent correlation with Brown's σ^+ values, large negative reaction constants and a large kinetic isotope effect indicate that the transition state approaches a carbocation in character. This indicates a hydride-ion transfer from the hydroxy acid to the oxidant in the rate-determining step. The following mechanism (Scheme 1) accounts for all the experimental results.



The above mechanism leads to the following rate law, which is in accordance with the experimental results.

$$\text{Rate} = k_3 [\text{TFAIB}] [\text{hydroxy acid}] [\text{H}^+] \quad \dots(4)$$

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