Kinetics of Bromination of Some Aromatic Oxocarboxylic Acids

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Rates of enolization, monitored by bromine scavenging, are determined for some aromatic carboxylic acids, $ArCO[CH_2]_nCO_2H$.

It was first suggested by Lapworth[1] that ketones undergo α-halogenation only through their enol form. This was followed by extensive investigation into the halogenation of dialkyl and alkyl aryl ketones by Dawson and co-workers,[2–4] Nathan and Watson,[5] and Zucker and Hammett.[6] Bell and co-workers studied the α-halogenation of alicyclic mono- and di-ketones,[7] and oxo esters,[8] *etc.* So far a systematic kinetic study on the bromination of aromatic oxocarboxylic acids has not been carried out. This prompted us to undertake the title investigation to understand the steric and electronic effects of substituents on the rate of bromination of aryloxocarboxylic acids.

A kinetic study on the acid-catalysed bromination of $ArCO[CH_2]_nCO_2H$ (**1**) reveals that the order with respect to $[Br_2]$ is zero and that with respect to [**1**] and $[H^+]$ is one. Thus the rate of disappearance of bromine is determined solely by the rate at which the oxocarboxylic acid is transformed into the enolic form.

The rates of the tautomeric change of $ArCO[CH_2]_nCO_2H$ are presented in Table 4. Kinetic data reveal that electron-releasing substituents in the benzene ring accelerate the rate while electron-withdrawing groups retard it. Hammett correlation of this substituent effect is obtained with σ values and the reaction constant is found to be -0.78 at 303 K. 3′-Nitro-4′-methoxy- and 3′-bromo-4′-methoxy-substituted oxoacids deviate considerably from the linear Hammett plot obtained with other substituents. The reduced reactivity of these two compounds may not be due to steric effects[17] but may be ascribed to hydrogen bonding interactions between OMe and H_3O^+ or other acidic solvent species.[18]

The rate of enolization is found to be enhanced to a greater extent by the introduction of a methyl group *ortho* to the carbonyl moiety. The enhanced reactivity is explained by considering their preferred conformations. ^1H and ^{13}C NMR spectral data of these compounds reveal that the carbonyl moiety is twisted out of the benzene ring plane. These compounds which are in a higher energy level in the ground state due to reduced conjugative interaction pass through the energy barrier in a facile manner.

The reactivity of 1′-naphthyloxobutanoic acid is very high compared to the 2′-naphthyl analogue. This may be ascribed to the conformation-dependent conjugation effect as in *ortho*-substituted compounds.

Lengthening of the alkyl chain leads to an increase in the reaction rate. This suggests that the opposing effect caused by coordination of H_3O^+ with carbonyl oxygen by CO_2H decreases as it is far removed from the reaction centre.

Enolization rate constants of 4′-OMe and 2′,4′,6′-Me_3 substituted oxoacids could not be measured owing to ring bromination.

Table 4 Enolization rate constants of 4-oxo 4-substituted phenylbutanoic acids at 303 K[a]

Entry	Substituent	$10^6\ k_2$/dm^3 mol^{-1} s^{-1}
1	H	6.89 ± 0.15
2	4′-Me	9.49 ± 0.26
3	4′-Et	8.44 ± 0.22
4	4′-Ph	7.48 ± 0.14
5	4′-Cl	4.56 ± 0.11
6	4′-Br	4.60 ± 0.12
7	4′-I	5.73 ± 0.23
8	3′-NO_2	1.94 ± 0.06
9	3′,4′-Me_2	10.2 ± 0.24
10	3′-Me-4′-Cl	5.32 ± 0.12
11	3′-NO_2-4′-Me	2.38 ± 0.06
12	3′-NO_2-4′-OMe	2.17 ± 0.04
13	3′-Br-4′-OMe	4.56 ± 0.11
14	2′,4′-Me_2	21.9 ± 0.58
15	2′-Me-4′-Cl	13.3 ± 0.23
16	3′-Br-2′,4′,6′-Me_3	22.1 ± 0.39
17	3-Oxo-4-(1′-naphthyl)butanoic acid	18.0 ± 0.31
18	4-Oxo-4-(2′-naphthyl)butanoic acid	5.51 ± 0.07
19	5-Oxo-5-phenylpentanoic acid	21.4 ± 1.4
20	6-Oxo-6-phenylhexanoic acid	29.7 ± 0.67

[a][Substrate] = 1.2×10^{-2} mol dm^{-3}, $[Br_2] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[HClO_4]$ = 1.0 mol dm^{-3}, [NaBr] = 0.2 mol dm^{-3}, μ = 1.2 mol dm^{-3}, solvent = 75% HOAc (v/v).

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Techniques used: ^1H and ^{13}C NMR, IR

References: 28

Tables 1–3: Kinetic data

Table 5: ^1H and ^{13}C NMR data

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References cited in this synopsis

1 A. Lapworth, *J. Chem. Soc*., 1904, 30.
2 H. M. Dawson and H. Ark, *J. Chem. Soc*., 1911, 1740.
3 H. M. Dawson and F. Powis, *J. Chem. Soc*., 1913, 2135.
4 H. M. Dawson, C. R. Hoskins and J. E. Smith, *J. Chem. Soc*., 1929, 1884.
5 W. S. Nathan and H. B. Watson, *J. Chem. Soc*., 1933, 217.
6 L. Zucker and L. P. Hammett, *J. Am. Chem. Soc*., 1939, **61**, 2779.
7 R. P. Bell and O. M. Lidwell, *Proc. R. Soc. London, A*, *Math. Phys. Sci*., 1940, **176**, 88.
8 R. P. Bell and H. F. F. Ridgewell, *Proc. R. Soc. London, A*, *Math. Phys. Sci*., 1967, **298**, 178.
17 M. Krishna Pillay and S. Palanivelu, *J. Indian Chem. Soc*., 1986, **63**, 1055.
18 R. G. Coombes, J. G. Golding and P. Hadjigeorgiou, *J. Chem. Soc*., *Perkin Trans. 2*, 1979, 1451.