Kinetics and mechanism of the oxidation of substituted benzyl alcohols by [bis(trifluoroacetoxy)iodo]benzene

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The oxidation of substituted benzyl alcohols by bis(trifluoroacetoxy)iodo]benzene in aqueous acetic acid solution results in the formation of the corresponding benzaldehydes. The reaction is first order with respect to each of the alcohol, TFAIB and hydrogen ions. The oxidation of [1,1-^{2}H$_2$]benzyl alcohol exhibited the presence of a substantial primary kinetic isotope effect, indicating the cleavage of the α-C–H bond in the rate-determining step. Increase in the amount of water, in the solvent mixture of acetic acid and water, results in a decrease of the reaction rate. The analysis of the substituent effect in terms of Charton's LDR equation yielded an excellent correlation with negative reaction constants. A mechanism involving a hydride-ion transfer in the rate-determining step has been proposed.

Keywords: substituted benzyl alcohols, [bis(trifluoroacetoxy)iodo]benzene, kinetics

The oxidation of alcohols to carbonyl compounds is an important transformation in synthetic organic chemistry. A large number of oxidants are known to effect this transformation.[1] Most are salts of toxic heavy metals like chromium and manganese. This has lead to a search for eco-friendly oxidants. Hypervalent iodine compounds are mild and selective oxidising agents and their use in organic synthesis has been reported in recent years.[2] There seem to be no previous reports of the kinetics of oxidation of alcohols by hypervalent iodine compounds. We report here the kinetics of oxidation of several monosubstituted benzyl alcohols by [bis(trifluoroacetoxy)iodo]benzene (TFIAB) in aqueous acetic acid solution in the presence of perchloric acid.

Experimental

Materials: TFAIB was a commercial product (Aldrich) and was used as received. The preparation, purification and specification of the substituted benzyl alcohols have been described earlier.[3] [1,1-^{2}H$_2$]Benzyl alcohol was prepared by the reduction of ethyl benzoate by lithium aluminium deuteride.[4] Its isotopic purity, as ascertained by its ^{1}H NMR (100 MHz) spectrum, was 95±2%. To confirm the isotopic purity a proton-decoupled deuterium NMR[5] spectrum was recorded at 41.44 MHz (270 MHz for proton). The value of isotopic purity by this method was 96%. Acetic acid was refluxed for 3 h with acetic anhydride and chromic oxide and then distilled.[6] Perchloric acid (Merck) was used as a source of hydrogen ions.

Product analysis: The oxidation of substituted benzyl alcohols by TFAIB resulted in the formation of the corresponding benzaldehydes. The quantitative product analysis was performed under kinetic conditions *i.e.* with an excess of the alcohol over TFAIB. In a typical experiment, benzyl alcohol (1.08 g, 0.01 mol) and TFAIB (0.43 g, 0.001 mol) was made up to 100 ml in 1:1 acetic acid–water (v/v), in the presence of perchloric acid (0.05 mol), and was allowed to stand for *ca* 12 h for the completion of the oxidation. It was then treated with a saturated solution (200 ml) of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered, dried, weighed, recrystallised from ethanol and weighed again. The yield of the DNP was 2.69 g (94%) and 2.54 g (89%) before and after recrystallisation respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of benzaldehyde. The identity of the DNP was confirmed by the elemental analysis also. The observed values were C 54.25%, H 3.71% and N 19.39%, the calculated values for C$_{13}$H$_{10}$N$_4$O$_4$ are C 54.55%, H 3.50% and N 19.58%. In similar experiments, with the other substituted benzyl alcohols the yields of DNP, after recrystallisation, were in the range of 75-88%.

Kinetic measurements: Pseudo-first order conditions were attained by keeping a large excess (× 10 or greater) of the alcohols over the oxidant. The reactions were carried out at constant temperature (±0.1 K). The solvent was 1:1 acetic acid–water (v/v), unless stated otherwise. The reactions were followed by monitoring the decrease in the TFAIB concentration by an iodometric method for up to 80% of the reaction, taking usual precautions to avoid air oxidation of iodide ions.[7]

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Each kinetic run typically consists of 12–15 data points. The pseudo-first order rate constant, k_{obs}, was evaluated from the linear ($r^2 > 0.995$) plots of log [TFAIB] *versus* time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. In correlation analysis, we have used coefficient of determination (R^2 or r^2), standard deviation (sd) and Exner's parameter,[8] ψ, as the measures of the goodness of fit. The third order rate constants, k_3, were determined from the relation: $k_3 = k_{obs}/$ [benzyl alcohol] [H$^+$].

Results

The rate and other experimental data were obtained for all the alcohols. Since the results are similar, only representative data are reproduced here.

The oxidation of benzyl alcohols resulted in the formation of the corresponding benzaldehydes. The overall reaction may be represented as follows:

$$\text{ArCH}_2\text{OH} + \text{PhI(OCOCF}_3)_2 \rightarrow \text{ArCHO} + \text{PhI} + 2\text{CF}_3\text{CO}_2\text{H} \quad (1)$$
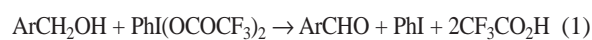
Test for free radicals: The oxidation of benzyl alcohol by TFAIB, in an atmosphere of nitrogen, failed to induce polymerisation of acrylonitrile. In blank experiments, with the alcohol absent, no noticeable consumption of TFAIB was observed. The addition of acrylonitrile had no effect on the rate of 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 reaction is first order with respect to TFAIB. Further, the pseudo-first-order rate constants are independent of TFAIB concentration. The rate increases linearly with an increase in the concentration of alcohol. The reaction is first order with respect to hydrogen ions also (Table 1).

Kinetic Isotope effect: To ascertain the role of C – H bond cleavage in the rate-determining step, the oxidation of [1,1 – ^{2}H$_2$]benzyl alcohol was studied. The results (Table 2) showed the presence of a substantial primary kinetic isotope effect.

Effect of solvent composition: The oxidation of benzyl alcohol was studied in solvents containing different amounts of acetic acid and water (Table 3). The rate of oxidation decreases with an increase in the amount of water in the solvent mixture.

Effect of substituents: The rates of oxidation of monosubstituted benzyl alcohols were obtained at different temperatures and the activation parameters were calculated (Table 4).

Discussion

The linear correlation ($r^2 = 0.9861$, sd = 1.01, slope = 0.524±0.010) between the values of the activation enthalpies and entropies of the reaction indicated the operation of a significant compensation effect in this reaction.[9] The reaction exhibited an excellent isokinetic effect also, as determined by Exner's method.[10] An Exner's plot between log k_2 at 288 K and at 318 K is linear ($r^2 = 0.9987$, sd = 0.02, slope = 0.7913±0.0049). The value of isokinetic temperature is 536±9 K.

Correlation analysis of reactivity: The effect of structure on reactivity has long been correlated in terms of the Hammett equation[11] or with dual substituent-parameter equations.[12,13] In the late 1980s,

Table 1 Rate constants for the oxidation of benzyl alcohol by TFAIB at 308 K

10^3[TFAIB] /mol dm^{-3}	[Alcohol] /mol dm^{-3}	[H$^+$] /mol dm^{-3}	$10^4 k_{obs}$ /s^{-1}
1.0	0.10	0.5	1.62
1.0	0.20	0.5	3.30
1.0	0.40	0.5	6.41
1.0	0.40*	0.5	6.53*
1.0	0.60	0.5	9.78
1.0	0.80	0.5	12.8
1.0	1.00	0.5	16.1
1.0	2.00	0.5	32.7
2.0	0.20	0.5	3.18
4.0	0.20	0.5	3.32
6.0	0.20	0.5	3.35
8.0	0.20	0.5	3.20
1.0	0.40	0.1	1.28
1.0	0.40	0.3	3.90
1.0	0.40	0.6	7.64
1.0	0.40	0.8	10.3
1.0	0.40	1.2	15.8

*Contained 0.001 mol dm^{-3} acrylonitrile.

Table 2 Kinetic isotope effect in the oxidation of benzyl alcohol by TFAIB

Temp/K	$10^4 k_3$/dm^6 mol^{-2} s^{-1}		k_H/k_D
	Benzyl alcohol (BA)	Deuterated BA	
288	4.84	0.84	5.76
298	12.6	2.25	5.60
308	32.3	5.87	5.50
318	78.9	14.6	5.40

Table 3 Effect of solvent composition on the rate of the oxidation of benzyl alcohol by TFAIB

[TFAIB] = 0.001 mol dm^{-3} [benzyl alcohol] = 0.40 mol dm^{-3}
[H$^+$] = 0.5 mol dm^{-3} Temp. = 308 K

% AcOH	25	40	50	60	72
$10^4 k_{obs}$/s^{-1}	1.13	3.75	6.41	10.6	20.7

Table 4 Rate constants and activation parameters of the oxidation of substituted benzyl alcohols by TFAIB

Subst	$10^4 k_3$/dm^6 mol^{-2} s^{-1}				ΔH^*	ΔS^*	ΔG^*
	288	298	308	318 K	/kJ mol^{-1}	/J mol^{-1} K^{-1}	/kJ mol^{-1}
H	4.84	12.6	32.3	78.9	68.4 ± 0.5	-71 ± 2	89.5 ± 0.6
p-Me	10.3	25.9	64.0	146	64.9 ± 0.8	-77 ± 2	87.7 ± 0.9
p-OMe	32.5	75.2	176	389	60.3 ± 0.6	-83 ± 2	85.1 ± 0.6
p-F	7.53	19.7	50.9	126	69.0 ± 0.5	-65 ± 1	88.4 ± 0.6
p-Cl	4.45	12.1	32.1	79.6	70.8 ± 1.0	-64 ± 3	89.6 ± 0.8
p-NO$_2$	0.29	1.01	3.22	9.67	86.4 ± 0.6	-32 ± 2	95.8 ± 0.5
p-CF$_3$	0.75	2.38	7.09	19.0	79.6 ± 0.7	-48 ± 2	93.7 ± 1.0
p-COOMe	1.12	3.21	9.36	25.1	76.6 ± 0.6	-55 ± 2	92.9 ± 0.5
p-Br	4.08	11.1	29.7	76.1	71.8 ± 0.9	-61 ± 3	89.8 ± 0.7
p-NHAc	15.0	35.8	86.3	201	63.4 ± 0.8	-79 ± 3	96.9 ± 0.8
p-COMe	0.84	2.46	7.26	19.7	77.7 ± 0.8	-54 ± 2	93.5 ± 0.8
p-SMe	18.0	43.5	104	236	62.9 ± 0.5	-80 ± 2	86.4 ± 0.7
p-NMe$_2$	144	298	628	1231	52.2 ± 0.5	-100 ± 2	81.7 ± 0.6
m-Me	8.34	21.2	52.7	123	65.9 ± 0.8	-76 ± 2	88.2 ± 0.6
m-OMe	10.1	25.1	61.1	152	66.1 ± 0.8	-75 ± 2	87.8 ± 0.7
m-Cl	1.75	5.21	13.9	35.1	74.1 ± 0.6	-60 ± 1	91.8 ± 0.6
m-Br	1.59	4.68	12.8	33.4	74.7 ± 0.5	-59 ± 1	92.0 ± 0.5
m-F	2.12	6.07	16.2	40.3	72.2 ± 0.7	-65 ± 2	91.4 ± 0.7
m-NO$_2$	0.21	0.70	2.15	6.45	84.2 ± 0.5	-42 ± 1	96.7 ± 0.4
m-CO$_2$Me	0.88	2.87	8.01	21.4	78.2 ± 0.6	-51 ± 2	93.3 ± 0.7
m-CF$_3$	0.55	1.82	5.48	15.1	81.6 ± 0.9	-44 ± 3	94.4 ± 0.8
m-I	2.13	6.02	15.8	40.2	71.9 ± 0.7	-66 ± 2	91.4 ± 0.6
m-SMe	6.83	17.6	44.8	108	67.1 ± 0.8	-78 ± 3	90.2 ± 0.6
m-NHAc	5.34	15.0	38.3	92.3	69.7 ± 0.6	-66 ± 1	89.2 ± 0.6
o-Me	33.4	76.8	170	358	57.7 ± 0.6	-92 ± 1	85.1 ± 0.7
o-OMe	41.1	93.2	221	472	59.8 ± 0.5	-83 ± 1	84.5 ± 0.4
o-NO$_2$	0.62	1.81	5.87	15.8	80.4 ± 1.0	-47 ± 3	94.2 ± 0.9
o-COOMe	3.01	8.11	22.5	56.1	72.0 ± 0.7	-63 ± 2	90.6 ± 0.5
o-NHAc	51.1	118	257	520	56.4 ± 0.4	-93 ± 1	84.0 ± 0.4
o-Cl	9.87	25.3	65.1	150	66.8 ± 0.5	-71 ± 1	87.8 ± 0.4
o-Br	12.9	32.4	80.4	185	65.2 ± 0.7	-74 ± 2	87.2 ± 0.6
o-I	19.9	45.3	107	235	60.4 ± 0.5	-87 ± 1	86.3 ± 0.6
o-CN	1.04	3.48	9.71	26.6	79.4 ± 0.7	-46 ± 2	92.8 ± 0.6
o-SMe	44.9	102	240	509	59.4 ± 0.6	-84 ± 2	84.3 ± 0.6
o-F	7.86	20.1	52.7	129	68.7 ± 0.7	-66 ± 2	88.3 ± 0.7
o-CF$_3$	6.38	16.1	41.0	95.4	66.4 ± 0.5	-76 ± 2	88.9 ± 0.5

Charton[14] introduced a triparametric LDR equation for the quantitative description of structural effects on chemical reactivities. In this work we have applied the LDR Eqn (2) to the rate constants, k_3.

$$\log k_3 = L \sigma_l + D \sigma_d + R \sigma_e + h \tag{2}$$

Here, σ_l is a localised (field and/or inductive) effect parameter, σ_d is the intrinsic delocalised electrical effect parameter when active site electronic demand is minimal and σ_e represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by Eqn (3).

$$\sigma_D = \eta \sigma_e + \sigma_d \tag{3}$$

Here η represents the electronic demand of the reaction site and is given by $\eta = R/D$, and σ_D represents the delocalised electrical parameter of the diparametric LD equation.

For *ortho*-substituted compounds, it is necessary to account for the possibility of steric effects and Charton,[14] therefore, modified the LDR equation to generate the LDRS Eqn (4),

$$\log k_3 = L \sigma_l + D \sigma_d + R \sigma_e + S \upsilon + h \tag{4}$$

where υ is the well known Charton's steric parameter based on Van der Waals radii.[15]

The rates of oxidation of *ortho*-, *meta*- and *para*-substituted benzyl alcohols show an excellent correlation in terms of the LDR/LDRS equations (Table 5). All three series of substituted benzyl alcohols meet the requirement of a minimum number of substituents for analysis by LDR and LDRS equations.[14]

The comparison of the *L* and *D* values for the substituted benzyl alcohols showed that the oxidation of *ortho*- and *para*-substituted benzyl alcohols is more susceptible to the delocalisation effect than to the localised effect. However, the oxidation of *meta*-substituted compounds exhibited a greater dependence on the field effect. In all cases, the magnitude of the reaction constants decreases with an increase in the temperature, pointing to a decrease in selectivity with an increase in temperature.

All three-regression coefficients, *L*, *D* and *R*, are negative indicating an electron-deficient carbon centre in the activated complex for the rate-determining step. The positive value of h adds a negative increment to σ_d, reflecting the electron-donating power of the substituent and its capacity to stabilise a cationic species. The positive value of *S* indicates that the reaction is subject to steric acceleration by an *ortho*-substituent.

To test the significance of localised, delocalised and steric effects in the *ortho*-substituted benzyl alcohols, multiple regression analyses were carried out with (i) σ_l, σ_d and σ_e (Eqn. (5)), (ii) σ_d, σ_e and υ (Eqn. (6)), and (iii) σ_l, σ_e and υ (Eqn. (7)). The absence of significant correlations showed that all the four substituent constants are significant.

$$\log k_3 = -1.26\ (\pm0.39)\ \sigma_l - 1.68\ (\pm0.28)\ \sigma_d - 2.89\ (\pm1.62)\ \sigma_e - 2.57 \quad (5)$$

$$R^2 = 0.8580;\ SD = 0.25;\ n = 12;\ \psi = 0.32;\ T = 298\ K$$

$$\log k_3 = -1.75\ (\pm0.38)\ \sigma_d - 1.48\ (\pm2.32)\ \sigma_e + 0.74\ (\pm0.43)\ \upsilon - 3.35 \quad (6)$$

$$R^2 = 0.7472;\ SD = 0.33;\ n = 12;\ \psi = 0.49;\ T = 298\ K$$

$$\log k_3 = -1.70\ (\pm0.69)\ \sigma_l - 0.17\ (\pm3.30)\ \sigma_e + 1.11\ (\pm0.62)\ \upsilon - 2.59 \quad (7)$$

$$R^2 = 0.4877;\ SD = 0.47;\ n = 12;\ \psi = 0.56,\ T = 298\ K$$

Similarly in the cases of the oxidation of *para*- and *meta*-substituted benzyl alcohols, multiple regression analyses with (i) σ_l and σ_d, (ii) σ_d and σ_e, and (iii) σ_l and σ_e, indicated that all three substituent constants are needed to explain the effect of structure on the rate constants. There is no significant collinearity between the various substituent constants for the three series.

The percent contribution[15] of the delocalised effect, P_D, is given by the following equation.

$$P_D = (\,|D|\ \times 100)\,/\,(\,|L|\ +\ |D|\,) \quad (8)$$

Similarly, the percent contribution of the steric parameter[15] to the total effect of the substituent, P_S, was determined by using Eqn (9).

$$P_S = (\,|S|\ \times 100\,)\,/\,(\,|L| + |D| + |S|\,) \quad (9)$$

The values of P_D and P_S are also recorded in Table 5. The value of P_D for the oxidation of *para*-substituted benzyl alcohols is *ca* 61% whereas the corresponding values for the *meta*- and *ortho*-substituted alcohols are *ca* 53 and 44% respectively. This shows that the balance of localisation and delocalisation effects is different for differently substituted benzyl alcohols. The less pronounced resonance effect from the *ortho*- position than from the *para*-position may be due to the twisting away of the hydroxymethyl group from the plane of the benzene ring. The magnitude of the P_S value shows that the steric effect is significant in this reaction.

Mechanism: The dependence on acidity indicated the presence of a protonation pre-equilibrium. It is proposed that TFAIB is protonated to yield a stronger electrophile and oxidant.

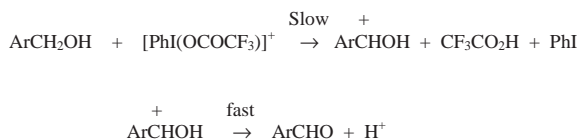$$PhI(OCOCF_3)_2 + H^+ \rightleftharpoons PhI(OCOCF_3)^+ + CF_3CO_2H \quad (10)$$
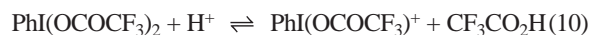
The observed solvent composition effect supports a protonation equilibrium. The lowering of relative permittivity, caused by an increase in the amount of acetic acid in the solvent mixture, favours a reaction in which charge is distributed over a larger area. Such an observation has been recorded in many redox reactions.[16]

A hydrogen abstraction mechanism leading to the formation of the free radicals is unlikely in view of the failure to induce polymerisation of acrylonitrile and no effect of acrylonitrile on the reaction rate. This is supported by the absence of any effect of BHT also. The presence of a substantial kinetic isotope effect confirms the cleavage of a α–C–H bond in the rate-determining step. The negative values of the localisation and delocalisation electrical effects *i.e.* of *L*, *D* and *R* points to an electron-deficient reaction centre in the rate-determining step. This is further supported by the positive value of η, which indicates that the substituent is better able to stabilise a cationic or electron-deficient reactive site. Therefore, a hydride-ion transfer in the rate-determining step is suggested.

The positive value of *S* showed a steric acceleration of the reaction. This may be explained on the basis of high ground state energy of the

Table 5 Temperature dependence for the reaction constants for the oxidation of substituted benzyl alcohols by TFAIB

T/K	L	D	R	S	η	R²	SD	ψ	P_D	P_S
Para-substituted										
288	−1.39	−2.06	−1.46	–	0.71	0.9993	0.03	0.01	59.7	–
	±0.04	±0.02	±0.11							
298	−1.25	−1.92	−1.35	–	0.71	0.9997	0.01	0.01	60.6	–
	±0.02	±0.01	±0.06							
308	−1.14	−1.79	−1.26	–	0.70	0.9996	0.01	0.01	61.1	–
	±0.02	±0.01	±0.05							
318	−1.03	−1.67	−1.14	–	0.68	0.9997	0.01	0.01	61.9	–
	±0.02	±0.01	±0.05							
Meta-substituted										
288	−1.80	−1.40	−1.26	–	0.88	0.9995	0.03	0.02	44.3	–
	±0.04	±0.04	±0.20							
298	−1.65	−1.31	−1.18	–	0.90	0.9987	0.02	0.02	44.3	–
	±0.03	±0.02	±0.13							
308	−1.55	−1.22	−1.12	–	0.92	0.9994	0.01	0.02	44.0	–
	±0.02	±0.01	±0.08							
318	−1.45	−1.14	−1.06	–	0.93	0.9991	0.01	0.03	44.0	–
	±0.02	±0.02	±0.09							
Ortho-substituted										
288	−1.59	−1.71	−1.05	1.06	0.61	0.9990	0.02	0.01	52.1	24.2
	±0.04	±0.03	±0.17	±0.03						
298	−1.46	−1.62	−1.01	0.98	0.62	0.9992	0.02	0.01	52.6	24.1
	±0.03	±0.02	±0.14	0.03						
308	−1.31	−1.51	−0.97	0.88	0.64	0.9996	0.01	0.01	53.5	23.8
	±0.02	±0.01	±0.09	±0.02						
318	−1.19	−1.42	−0.94	0.79	0.66	0.9998	0.01	0.01	54.2	23.2
	±0.01	±0.01	±0.05	0.01						

$$\text{ArCH}_2\text{OH} + [\text{PhI(OCOCF}_3)]^+ \xrightarrow{\text{Slow}} \overset{+}{\text{ArCHOH}} + \text{CF}_3\text{CO}_2\text{H} + \text{PhI}$$

$$\overset{+}{\text{ArCHOH}} \xrightarrow{\text{fast}} \text{ArCHO} + \text{H}^+$$

Scheme 1

sterically crowded alcohols. Since the crowding is relieved in the product carbocation as well as the transition state leading to it, the transition state energies of the crowded and uncrowded alcohols do not differ much and steric acceleration, therefore, results.

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