

MECHANISTIC STUDIES OF OXIDATION OF DIPHENYLMETHANOLS BY SODIUM *N*-CHLOROBENZENESULPHONAMIDE CATALYSED BY RUTHENIUM(III)

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The kinetics of oxidation of six *para*-substituted diphenylmethanols (Y-DPM, where Y = H, Cl, Br, NO₂, CH₃ and OCH₃) by sodium *N*-chlorobenzenesulphonamide [chloramine-B (CAB)] in the presence of HCl and catalysed by RuCl₃ in 30% (v/v) methanol medium was studied at 35 °C. The experimental rate law is $\text{rate} = k'[\text{CAB}]_0[\text{DPM}]_0^{1/2}[\text{RuCl}_3]^{1/2}[\text{H}^+]^2$, where *x*, *y* and *z* are fractions. Addition of reaction product, benzenesulphonamide (BSA), retards the reaction. An increase in the dielectric constant of the medium decreases the rate. Rate studies in D₂O medium showed that the solvent isotope effect $k'(\text{H}_2\text{O})/k'(\text{D}_2\text{O}) = 0.53$. Proton inventory studies were carried out using H₂O–D₂O mixtures. The rates correlate satisfactorily with the Hammett σ relationship and the plot is biphasic. The reaction constant ρ is -2.8 for electron-releasing groups and -0.31 for electron-withdrawing groups at 35 °C. The activation parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$, $\Delta G^\ddagger$ and $\log A$ were calculated. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are linearly related and an isokinetic relationship is observed with $\beta = 343$ K, indicating enthalpy as a controlling factor. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

N-Metallo *N*-arylhalosulphonamides (organic haloamines) contain halogen in the +1 state. They behave as mild oxidants and are suitable for the limited oxidation of specific groups. The important chlorine compound of this class, chloramine-T (CAT), is a byproduct of saccharin manufacture, and is a well known analytical reagent. The benzene analogue sodium *N*-chlorobenzenesulphonamide [chloramine-B (C₆H₅SO₂NCINa · 1.5H₂O) (CAB)] can be easily prepared and is effective in oxidizing aromatic and aliphatic primary alcohols^{1,2} to the aldehyde stage. A considerable amount of work has been performed on the mechanistic studies involving oxidations of alcohols by transition metal ions³ such as chromium(VI), vanadium(V), cobalt(III), manganese(VII) and cerium(IV) in an acidic medium and with copper(II)⁴ and ruthenium tetroxide in an alkaline medium and ferrate(VI)^{5,6} ion. However, information is lacking concerning the oxidation of secondary aromatic alcohols by organic haloamines. A detailed examination of CAB showed that it is an excellent reagent for performing oxidations of secondary alcohols to ketones in an acidic medium in the presence of RuCl₃ catalyst and this system is adaptable for large-scale operations. To shed

some light on the mechanism of CAB oxidation of secondary alcohols, we have studied the reactions of six substituted diphenylmethanols with this oxidant. Optimum conditions were established for the formation of benzophenone, which is an important constituent of perfumes and is also used in the manufacture of antihistamines, hypnotics and insecticides. The Hammett free energy relationship was tested and an isokinetic relationship was deduced together with the computed thermodynamic parameters.

EXPERIMENTAL

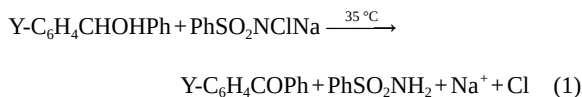
Chloramine-B (CAB) was prepared as reported previously.^{1,2} An aqueous solution of the compound was prepared, standardized iodometrically and stored in brown bottles to prevent its photochemical deterioration. Diphenylmethanols (Aldrich) were of accepted grades of purity and were used without further purification; solutions were prepared in 30% (v/v) methanol. A solution of RuCl₃ (Arora Matthey) in 0.5 mol dm⁻³ HCl was used as a catalyst in an acidic medium. Allowance was made for the amount of HCl present in the catalyst solution while preparing solutions for kinetic runs. All other chemicals were of analytical grades. Triply distilled water was used for preparing aqueous solutions. Solvent isotope studies were carried out with D₂O (99.2%) supplied by the Bhabha

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Atomic Research Centre (Bombay, India). The ionic strength of the reaction mixture was kept at high value with a concentrated solution of NaClO_4 . Regression analysis of the experimental data was carried out on an EC-72 statistical calculator supplied by the Electronic Corporation (India).

Kinetic measurements. The reaction was carried out in glass-stoppered Pyrex boiling tubes whose outer surface was coated black to eliminate photochemical effects. Solutions containing appropriate amounts of DPM, HCl , RuCl_3 and water (to keep the total volume constant for all runs) were placed in the tube, which was thermostated at 35°C . A measured amount of CAB solution, also thermostated at 35°C , was rapidly added to the mixture. The progress of the reaction was monitored by withdrawing aliquots from the reaction mixtures at different time intervals and determining the unreacted CAB iodometrically. The course of the reaction was studied up to two half-lives. The calculated pseudo-first-order rate constants, k' , were reproducible to within $\pm 3\%$.

Stoichiometry. Investigations under the conditions $[\text{CAB}] \gg [\text{DPM}]$ revealed that 1 mol of CAB was consumed by 1 mol of DPM according to the equation



where $\text{Y} = \text{H}, \text{Cl}, \text{Br}, \text{CH}_3, \text{OCH}_3$ and NO_2 .

Product analysis. The reaction products were subjected to column chromatography on silica gel (60–200 mesh) using gradient elution (dichloromethane). After initial separation, the products were further purified by recrystallization. Materials were identified by comparison with commercially available samples.

Benzophenone. This was recrystallized from ethanol, m.p. = $49\text{--}50^\circ\text{C}$; known m.p. = $49\text{--}51^\circ\text{C}$ (Merck Index 11, 1108). The compound was identified by TLC using

dichloromethane as the solvent and iodine as the spray reagent ($R_f = 0.82$). The benzophenone was further identified as its 2,4-dinitrophenylhydrazone (2,4-DNP) derivative, which was recrystallized from ethanol (recovery 72.2%) and was found to be identical with the DNP derivative of an authentic sample; m.p. = $237\text{--}238^\circ\text{C}$, known m.p. = 238°C .

Benzenesulphonamide (BSA). BSA was recrystallized from dichloromethane and light petroleum and detected by thin-layer chromatography using light petroleum–chloroform–butan-1-ol (2:2:1, v/v/v) as the solvent and iodine for detection ($R_f = 0.88$).

RESULTS

Effect of reactants

With the substrate in excess, at constant $[\text{HCl}]$, $[\text{DPM}]_0$ and $[\text{RuCl}_3]$, plots of $\log[\text{CAB}]$ vs time are linear ($r = 0.9989$), indicating a first-order dependence of rate on $[\text{CAB}]_0$. Values of pseudo-first-order rate constants (k') are given in Table 1. Further, the values of k' are unaltered with variation in $[\text{CAB}]_0$, confirming the first order dependence on $[\text{oxidant}]_0$.

The rate increases initially with increase in $[\text{DPM}]_0$. A plot of $\log k'$ vs $\log[\text{DPM}]_0$ is linear ($r = 0.998$, Table 1) with a fractional slope of 0.81. The rate levels off at higher $[\text{DPM}]_0$.

Effect of $[\text{HCl}]$

The rate increases with increase in $[\text{HCl}]$ and the plot of $\log k'$ vs $\log[\text{HCl}]$ is linear ($r = 0.9979$, Table 2) with a fractional slope of 0.80.

Effect of $[\text{H}^+]$

At constant $[\text{Cl}^-] = 0.4 \text{ mol dm}^{-3}$, maintained by adding NaCl , the rate increased with increase in $[\text{H}^+]$, which was varied by adding HCl . A plot of $\log k'$ vs $\log[\text{H}^+]$ is linear

Table 1. Effect of varying reactant concentration on the rate^a

$[\text{CAB}]_0 \times 10^4$ (mol dm^{-3})	$[\text{DPM}]_0 \times 10^3$ (mol dm^{-3})	$k' \times 10^4$ (s^{-1})	$[\text{CAB}] \times 10^4$ (mol dm^{-3})	$[\text{DPM}]_0 \times 10^3$ (mol dm^{-3})	$k' \times 10^4$ (s^{-1})
05.0	10.0	4.09	10.0	05.0	1.99
10.0	10.0	4.18	10.0	07.5	2.95
15.0	10.0	4.20	10.0	10.0	4.18
20.0	10.0	4.29	10.0	15.0	6.30
25.0	10.0	4.05	10.0	20.0	8.91
30.0	10.0	4.26	10.0	30.0	12.6
35.0	10.0	4.09	10.0	40.0	18.2
40.0	10.0	4.30	10.0	50.0	19.5
50.0	10.0	4.32	10.0	60.0	20.0

^a $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$, $[\text{RuCl}_3] = 4.82 \times 10^{-5} \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$, $\text{MeOH} = 30\%$ (v/v), $T = 308 \text{ K}$.

Table 2. Effect of varying HCl, H^+ and $RuCl_3$ concentrations on the rate^a

$[HCl] \times 10^2$ (mol dm ⁻³)	$k' \times 10^4$ (s ⁻¹)	$[H^+]^b \times 10^2$ (mol dm ⁻³)	$k' \times 10^4$ (s ⁻¹)	$[RuCl_3] \times 10^5$ (mol dm ⁻³)	$k' \times 10^4$ (s ⁻¹)
05.0	2.51	10.0	4.18	1.96	2.34
08.0	3.30	15.0	5.49	2.52	2.82
10.0	4.18	20.0	7.08	3.64	3.46
15.0	5.62	25.0	8.51	4.82	4.18
20.0	6.92	30.0	10.0	7.24	5.37
30.0	9.55	40.0	12.6	9.30	6.30
40.0	11.5	50.0	—	11.21	7.08

^a $[CAB]_0 = 10.0 \times 10^{-4}$ mol dm⁻³, $[DPM]_0 = 10.0 \times 10^{-3}$ mol dm⁻³, $\mu = 0.4$ mol dm⁻³, MeOH = 30% (v/v), $T = 308$ K.

^b Variation at constant $[Cl^-] = 0.4$ mol dm⁻³.

($r = 0.996$, Table 2) with a fractional slope of 0.79. The results were the same even when $[Cl^-]$ was not maintained constant.

Effect of halide ions

Addition of Cl^- or Br^- ions in the form of NaCl or NaBr (5×10^{-4} – 20×10^{-4} mol dm⁻³) at fixed $[H^+] = 0.1$ mol dm⁻³ had no effect on the reaction rate.

Effect of $RuCl_3$

The rate increases with increase in $[RuCl_3]$ ($r = 0.976$, Table 2) and the plot of $\log k'$ vs $\log[RuCl_3]$ is linear with a fractional slope of 0.62.

Effect of benzenesulphonamide (BSA)

The rate decreased with the addition of BSA. A plot of $\log k'$ vs $\log[BSA]$ is linear with a negative fractional slope of 0.47 ($r = 0.989$, Table 3), indicating that BSA is involved in a pre-equilibrium before the rate-limiting step.

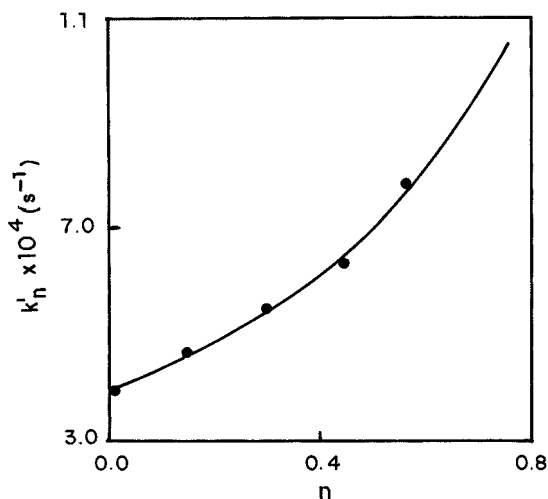
Effect of ionic strength

Variation of the ionic strength of the medium by adding $NaClO_4$ (0.2 – 1.0 mol dm⁻³) had a negligible effect on the rate.

Table 3. Effect of varying BSA concentration and dielectric constant on the rate^a

$[BSA] \times 10^4$ (mol dm ⁻³)	$k' \times 10^4$ (s ⁻¹)	MeOH (% v/v)	Dielectric constant (D)	$k' \times 10^4$ (s ⁻¹)
2.0	3.75	30.0	56.73	4.18
4.0	2.63	40.0	51.08	3.46
6.0	2.13	50.0	45.30	2.81
10.0	1.73	55.0	42.66	2.45
15.0	1.48	60.0	40.40	2.00

^a $[CAB]_0 = 10.0 \times 10^{-4}$ mol dm⁻³, $[DPM]_0 = 10.0 \times 10^{-3}$ mol dm⁻³, $[HCl] = 0.1$ mol dm⁻³, $[RuCl_3] = 4.82 \times 10^{-5}$ mol dm⁻³, $\mu = 0.4$ mol dm⁻³, $T = 308$ K.

Figure 1. Proton inventory plot of k'_n vs the deuterium atom fraction (n) in H_2O – D_2O mixtures

Effect of varying the dielectric constant of the medium

The dielectric constant (D) of the medium was varied by adding methanol (30–60%, v/v) to the reaction mixture. The rate decreased with increase in methanol content. A plot

Table 4. Proton inventory studies for DPM in H_2O – D_2O mixtures at 308 K^a

Atom fraction of deuterium (n)	$k'_{obs} \times 10^4$ (s ⁻¹)
0.00	4.18
0.15	4.72
0.30	5.50
0.45	6.42
0.56	7.80

^a $[CAB]_0 = 10 \times 10^{-4}$ mol dm⁻³, $[DPM]_0 = 10 \times 10^{-3}$ mol dm⁻³, $[HCl] = 0.1$ mol dm⁻³, $[RuCl_3] = 4.82 \times 10^{-5}$ mol dm⁻³, $\mu = 0.4$ mol dm⁻³, MeOH = 30% (v/v), $T = 308$ K.

Table 5. Temperature dependence of the oxidation of substituted diphenylmethanols by CAB^a

Substrate Y-DPM: Y =	$k' \times 10^4 \text{ (s}^{-1}\text{)}$			
	303 K	308 K	313 K	318 K
4-NO ₂	1.46	1.94	2.38	2.82
4-Cl	2.08	2.69	3.38	4.26
4-Br	2.24	2.95	4.36	5.52
4-H	3.16	4.18	5.96	8.32
4-CH ₃	7.58	12.0	18.3	28.3
4-OCH ₃	12.5	22.4	40.7	60.8

^a [CAB]₀ = $10 \times 10^{-4} \text{ mol dm}^{-3}$, [DPM]₀ = $10 \times 10^{-3} \text{ mol dm}^{-3}$, [HCl] = 0.1 mol dm^{-3} , [RuCl₃] = $4.82 \times 10^{-5} \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$, MeOH = 30% (v/v).

of $\log k'$ vs $1/D$ is linear ($r = 0.9978$, Table 3) with a negative slope, supporting a rate-limiting step with partial ionization. A blank experiment with methanol showed that there is a slight decomposition of solvent under the experimental conditions. This was allowed for in the calculation of the net reaction rate constant for the oxidation of diphenylmethanols.

Solvent isotope studies

Studies of the rate of oxidation of DMP by CAB in D₂O revealed that whereas $k'(\text{H}_2\text{O})$ is $4.18 \times 10^{-4} \text{ s}^{-1}$, $k'(\text{D}_2\text{O})$ is $7.80 \times 10^{-4} \text{ s}^{-1}$. The solvent isotope effect $k'(\text{H}_2\text{O})/k'(\text{D}_2\text{O})$ is thus found to be 0.53. Proton inventory studies were performed by carrying out the reaction in H₂O–D₂O mixtures with varying atom fractions n of deuterium (Figure 1, Table 4).

Effect of temperature on the rate

The reaction was studied at different temperatures (303–318 K) and, from the Arrhenius plots of $\log k'$ vs $1/T$, values of the activation parameters for the composite reaction were calculated (Tables 5 and 6).

Test for free radicals

Addition of the reaction mixtures to acrylamide did not initiate polymerization, showing the absence of free radical species.

DISCUSSION

Sodium *N*-chlorobenzenesulphonamide (chloramine-B) acts as an oxidizing agent in both acidic and alkaline media. In general, CAB undergoes a two-electron change in its reactions. The oxidation potential of CAB–PhSO₂NH₂ is pH dependent and decreases with increase in the pH of the medium. Depending on the pH of the medium, CAB furnishes different types of reactive species in solutions [equations (2)–(7)], such as PhSO₂NHCl, PhSO₂NCl₂, HOCl and possibly H₂O⁺Cl in acidic solutions.^{7,8}



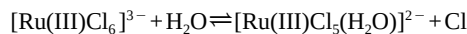
If the dichloramine, PhSO₂NCl₂, were to be the reactive species, then the rate law would predict a second-order dependence of rate on [CAB]₀ [equation (4)], which is contrary to the experimental observations. The rate increases with increase in [H⁺] but is retarded by the added reaction product benzenesulphonamide. Hence equations (6) and (7) play a dominant role in the oxidation of DPM by CAB.

Table 6. Thermodynamic parameters for the oxidation of substituted diphenylmethanols by CAB^a

Substrate Y-DPM: Y =	E_a	$\Delta H^\ddagger$	$-\Delta S^\ddagger$	$\Delta G^\ddagger$	Log <i>A</i>
	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J K ⁻¹ mol ⁻¹)	(kJ mol ⁻¹)	
4-NO ₂	33.2	31.0	213.4	98.4	8.1
4-Cl	40.2	37.6	192.0	97.4	9.2
4-Br	46.7	44.2	170.0	97.1	10.4
4-H	57.4	54.8	132.1	96.1	12.4
4-CH ₃	70.5	67.8	80.8	93.5	15.0
4-OCH ₃	77.0	73.9	55.7	91.6	16.3

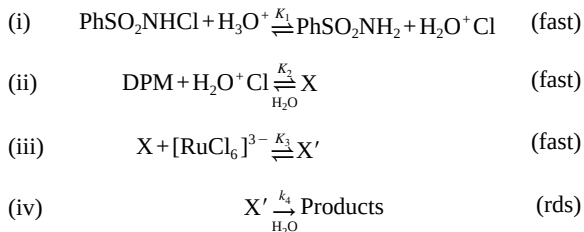
^a [CAB]₀ = $10 \times 10^{-4} \text{ mol dm}^{-3}$, [DPM]₀ = $10 \times 10^{-3} \text{ mol dm}^{-3}$, [HCl] = 0.1 mol dm^{-3} , [RuCl₃] = $4.82 \times 10^{-5} \text{ mol dm}^{-3}$, $\mu = 0.4 \text{ mol dm}^{-3}$, MeOH = 30% (v/v).

Electronic spectral studies by Cady and Connick⁹ and Connick and Fine¹⁰ reveal that species such as $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$, $[\text{RuCl}_4(\text{H}_2\text{O})_2]^-$, $[\text{RuCl}_3(\text{H}_2\text{O})_3]$, $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ and $[\text{RuCl}(\text{H}_2\text{O})_5]^{2+}$ do not exist in an aqueous solution of RuCl_3 . A study on the oxidation states of ruthenium has shown that Ru(III) exists in the following equilibrium¹¹⁻¹³ in acidic medium:



Singh and co-workers^{14,15} employed the above equilibrium in the Ru(III) -catalysed bromamine-T oxidation of some primary alcohols in acidic medium and in the Ru(III) chloride-catalysed oxidation of ethylene glycols by *N*-bromoacetamide (NBA) in HClO_4 medium. However in the present case, addition of Cl^- ion in the form of NaCl at fixed $[\text{H}^+]$ had no effect on the rate, indicating that $[\text{Ru(III)Cl}_6]^{3-}$ itself is the most likely catalysing species.

Ultraviolet spectral measurements showed that diphenylmethanol solution has two sharp absorption bands at 255.2 and 222.4 nm while bands around 204 and 226.4 nm were noticed for Ru(III) and CAB solutions, respectively, in the presence of 0.1 mol dm^{-3} HCl . With mixtures of (i) diphenylmethanol and Ru(III) and (ii) CAB and Ru(III) solutions, there were no changes in λ_{max} , but when CAB and DPM solutions are mixed in presence of 0.1 mol dm^{-3} HCl a single, sharp absorption band was noticed at 216.2 nm, indicating that complex formation takes place only between CAB and DPM. In view of these facts, Scheme 1 is proposed for the oxidation of diphenylmethanol by CAB.



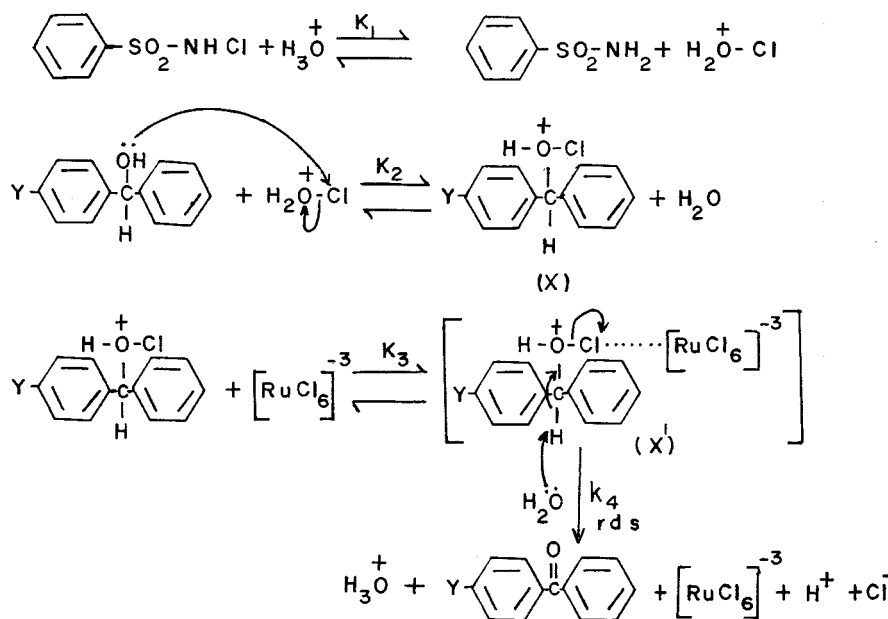
Scheme 1

Scheme 1 assumes the formation of $\text{H}_2\text{O}^+ \text{Cl}^-$ due to the protonation of PhSO_2NHCl by H^+ ion and subsequent hydrolysis, which complexes with DPM (X). The latter reacts with RuCl_3 through an equilibrium step to form a complex (X') which decomposes in a rate-limiting step to yield products. The fractional order on $[\text{RuCl}_3]$ indicates a pre-equilibrium step (iii) in Scheme 1. Assuming $[\text{CAB}] = [\text{PhSO}_2\text{NHCl}] + [\text{H}_2\text{O}^+ \text{Cl}^-] + [\text{X}] + [\text{X}']$, the following rate law can be derived for the oxidation of DPM by CAB:

$$-\frac{d[\text{CAB}]}{dt} = \frac{k_4 K_1 K_2 K_3 [\text{CAB}]_0 [\text{H}_3\text{O}^+] [\text{DPM}]_0 [\text{Ru}]}{[\text{PhSO}_2\text{NH}_2] + K_1 [\text{H}_3\text{O}^+] + K_1 K_2 [\text{H}_3\text{O}^+] [\text{DPM}]_0 (1 + K_3 [\text{Ru}])} \quad (8)$$

The detailed mode of oxidation of diphenylmethanols by CAB and the probable structures of the intermediates is shown in Scheme 2

It is interesting that the rate has increased in D_2O



Scheme 2

medium. Since D_3O^+ ion is a stronger acid than H_3O^+ ion by a factor of 2–3, a solvent isotope effect of this magnitude is to be expected. However, the observed inverse solvent isotope effect $k'(\text{D}_2\text{O})/k'(\text{H}_2\text{O})$ of 1.86 probably shows that since the protonation is followed by hydrolysis in the rate-limiting step which involves O–H bond scission, the normal kinetic isotope effect $k'_\text{H}/k'_\text{D} > 1$ could counterbalance the solvent isotope effect. Proton inventory studies in H_2O – D_2O mixtures could throw light on the nature of the transition state. The dependence of the rate constant (k_n) on n , the atom fraction of deuterium in a solvent mixture of D_2O and H_2O , is given^{16,17} by a form of Gross–Butler equation:

$$\frac{k_{\text{obs}}^0}{k_{\text{obs}}^n} = \frac{\prod_{\text{TS}} (1 - n + n\Phi_i)}{\prod_{\text{RS}} (1 - n + n\Phi_j)} \quad (9)$$

where Φ_i and Φ_j are the isotopic fractionation factors for isotopically exchangeable hydrogen sites in the transition states (TS) and reactant site (RS), respectively. Equation (9) allows the calculation of the fractionation factor of TS, if the reactant fractionation factors are known. However, the curvature of the proton inventory plot could reflect the number of exchangeable protons in the reaction.¹⁸ A plot of k_{obs}^n vs the deuterium atom fraction n (Figure 1, Table 4) in

the present case is a curve and comparison with the standard curves¹⁸ indicates the involvement of a single proton or H–D exchange during the reaction sequence. Hence the participation of H^+ ion in the formation of transition state is inferred.

The moderate values of the enthalpy of activation, a large negative entropy of activation and the fairly high $\Delta G^\ddagger$ values support the mechanism. The near constancy of the $\Delta G^\ddagger$ values indicates a solvated state and operation of a similar mechanism for the oxidation of all diphenylmethanols.

Structure–reactivity correlations

The Hammett plot shows two distinct (Figure 2) lines for each of which there is a good correlation between the substituent constants and the logarithm of the rate constants, particularly when the McDaniel–Brown constant (σ_p),¹⁹ is used. Of these, one has a much larger value of $\rho = -2.8$ for electron-releasing groups and the other relatively low value of $\rho = -0.31$ for electron-withdrawing groups at 35 °C. The break in the Hammett plot could suggest a concerted mechanism, the degree of concertedness depending on whether the hydride transfer from the C–H bond to the oxidant is synchronous with the removal of a proton from

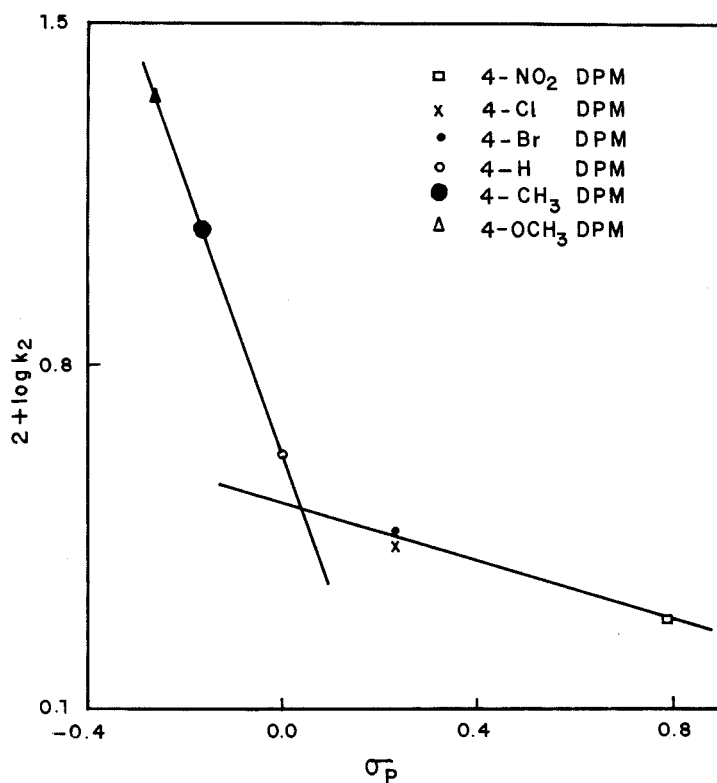


Figure 2. Plot of $\log k_2$ vs σ_p for diphenylmethanols at 308 K

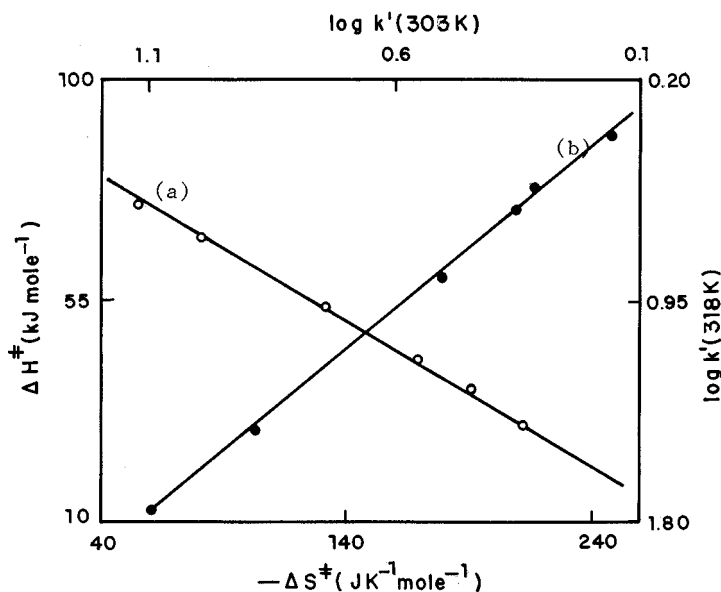


Figure 3. (a) Isokinetic plot of $\Delta H^\ddagger$ vs $\Delta S^\ddagger$ for the oxidation of diphenylmethanols by CAB. (b) Exner plot of $\log k'$ (318 K) vs $\log k'$ (303 K)

the OH group by a water molecule. In earlier work on the oxidation of primary alcohols by organic haloamines,¹ it was noted that electron-donating groups increase the rate. This indicates that the rupture of the C—H bond occurs ahead of O—H bond cleavage, creating a carbonium ion centre which is stabilized by the electron-donating groups. In the present case, the decrease in rate with electron-withdrawing groups is in agreement with this observation. Also, a reaction involving a carbonium ion in the transition state will be aided by electron-donating substituents and the value of ρ will be negative. On the other hand, a reaction involving a decrease in the carbonium ion charge will be facilitated by electron-withdrawing substituents. Therefore, the carbonium ion is more stable when the electron donors are attached to benzene ring system, which disperse the positive charge on the carbonium ion ($\rho = -2.8$), than the electron-withdrawing groups on the benzene ring system ($\rho = -0.31$). Because of the above facts, no linearity was found in the Hammett plot (Figure 2).

Isokinetic relationship

The enthalpy of activation is low for the oxidation of diphenylmethanols by chloramine-B. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the oxidation of diphenylmethanols are linearly related [Table 6, Figure 3(a), $r = 0.9997$] and the isokinetic temperature $\beta = 343$ K. The genuine nature of the isokinetic relationship was verified by the Exner²⁰ criterion by plotting $\log k'$ (318 K) vs $\log k'$ (303 K). The value of β was calculated from the equation

$$\beta = \frac{T_1(1-q)}{(T_1/T_2) - q}$$

where q is the slope of the Exner plot and $T_1 > T_2$. The value of β is 353 K [Figure 3(b)]. It is seen that the value of β is higher than the experimental temperature (308 K), indicating enthalpy control of the reactions.

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