the overall free energy change is due to favourable enthalpy term. Tables 3 and 4 also reveal that for all other mixed ligand systems, the entropy term is positive and overweighs the unfavourable enthalpy term. Therefore, the overall free energy change is due to favourable entropy term.

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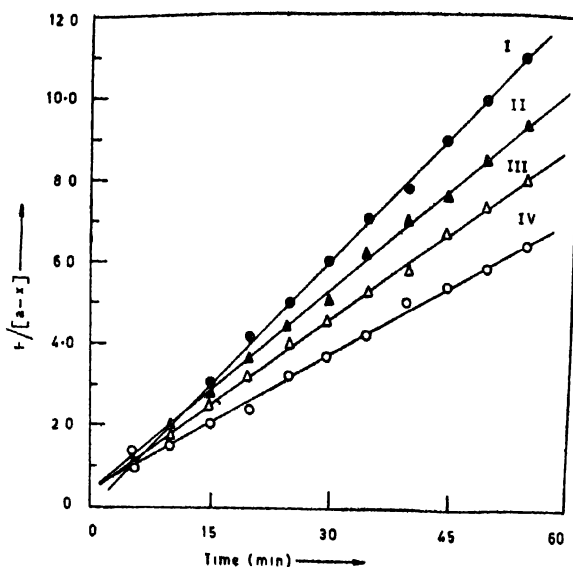7. H. M. IRVING and H. S. ROSSOTTI J. Chem. Soc., 1954, 2904.

Fig. 1. Second order rate constant for the oxidation of o-cresol by Ce^{IV}; initial concentrations of both o-cresol and Ce^{IV} are (I) 5.0×10^{-4}, (II) 7.5×10^{-4}, (III) 10.0×10^{-4}, and (IV) 12.5×10^{-4} M, at 30°.

Kinetics of Oxidation of o-Cresol by Cerium(IV) in Acidic Medium

J. P. SINGH*, S. J. S. SIROHI and (MISS) AISHWATI

Department of Chemistry, M. M. (P.G.). College, Modinagar-201 204

ALTHOUGH hexacyanoferrate(III)[1], vanadium(v)[2] peroxidisulphate(II) ion[3], lead(IV) acetate[4], $IO_4(I)$[5] have been employed as oxidants for the oxidation of organic compounds, yet similar studies on the oxidation of o-cresol by cerium(IV) are lacking. This communication describes the kinetics of the oxidation of o-cresol by ceric ion.

Experimental

For purification, o-cresol (AnalaR) was refluxed with zinc dust and ceric sulphate was recrystallised. o-Cresol was dissolved in aqueous acetone (50%, v/v), while ceric sulphate was dissolved in 2 M H_2SO_4. The kinetics of the process was measured by measuring the optical density at 380 nm on a Bausch and Lomb Spectronic-20 spectrophotometer. The overall order of reaction was evaluated from Fig. 1, while order with respect to each reactant was evaluated from Figs. 2 and 3.

Results and Discussion

Ionic strength dependence : The plot of K vs $\mu^{1/2}$ (Fig. 4) comes out to be linear, which shows a negative and primary exponential type of salt effect.
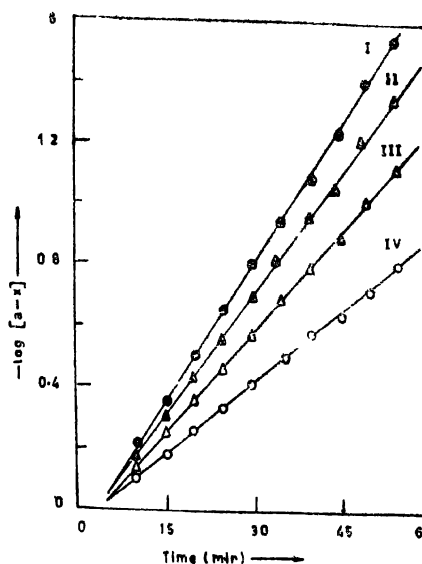

Fig. 2. Effect of concentration of Ce^{IV} on the oxidation of o-cresol by Ce^{IV}, concentration of o-cresol is 1.0×10^{-4} M, and concentrations of Ce^{IV} being (I) 2.0×10^{-3}, (II) 4.0×10^{-3}, (III) 6.0×10^{-3} and (IV) 8.0×10^{-3} M, at 30°.

This indicates that the rate determining step involves the interaction of two ions of the opposite charges.

The reaction rate increases with increasing acid concentration. Allyl alcohol, allyl acetate and EDTA act as radical traps.

Thermometric parameters : The energy of activation (ΔE^*), frequency factor (A), free energy

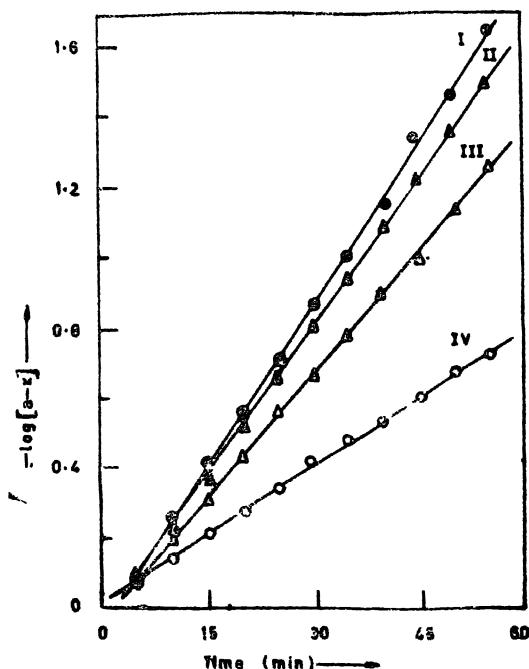* 3/3 Professor's Lodge, Modinagar-201 204.

Fig. 3. Effect of concentration of o-cresol on the oxidation of o-cresol by Ce^{IV}, concentration of Ce^{IV} is $1.0 \times 10^{-4} M$, and concentrations of o-cresol being (I) $2 0 \times 10^{-3}$, (II) 4.0×10^{-3}, (III) 6.0×10^{-3} and (IV) $8.0 \times 10^{-3} M$, at 30°.
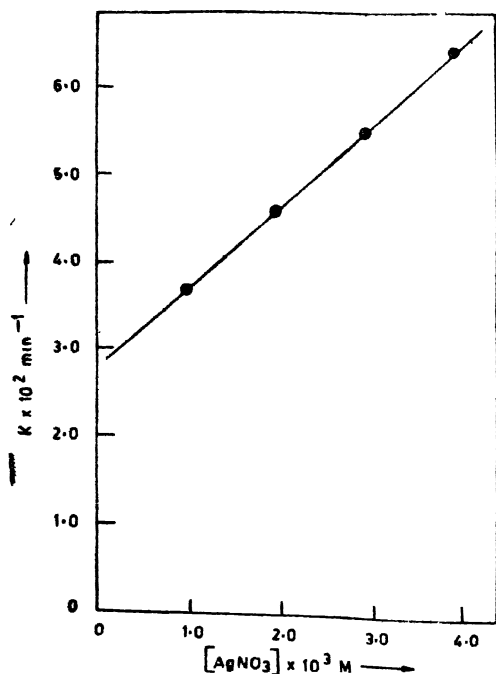

Fig. 4. Plot of rate constant (k) vs concentration of $AgNO_3$ on the oxidation of o-cresol by Ce^{IV} at 30°.

$(\Delta F^{\neq})$ and entropy of activation $(\Delta S^{\neq})$ were found to be 17.1 kcal mol^{-1}, 8.8×10^8 s^{-1}, 20.4 kcal mol^{-1},
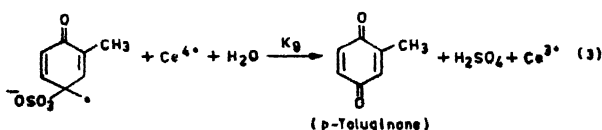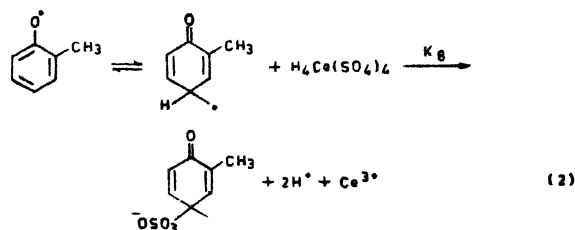
−25.7 e.u., respectively. The large negative value of entropy of activation may be attributed to the formation of the activated complex, which is more ordered than the reactants.

The product of the reaction mixture was identified by tlc and ir.

The existence of ceric sulphate in acidic medium in the various states[6-11] have been reported. The proposed mechanism is, therefore, based upon the same equilibria, where K_1, K_2, K_3, K_4, K_5 and K_6 are the rate constants for various ceric species. The rate determining process is given by

$$H_4Ce(SO_4)_4 + C_6H_4(OH)CH_3 \overset{K_7}{\rightleftharpoons}$$
$$C_6H_4(CH_3)O^{\cdot} + Ce^{3+} + H^+ \text{ (Slow)} \quad (1)$$
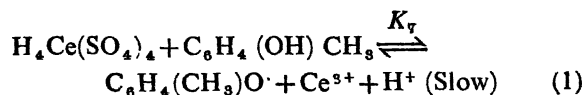
Followed by fast reactions,

(2)

(3)

(p-Toluquinone)

The above series of reactions lead to the relationship, $K'[Ce^{IV}][o\text{-cresol}] = K_7[H_4Ce(SO_4)_4][C_6H_4(OH)CH_3]$ where, K' is the experimental rate constant. By substituting the value of $[H_4Ce(SO_4)_4]$ and [o-cresol], we get the relationship,

$$K'[Ce^{IV}]\{1 + K_2[H^+]\} = K_7 K_6 K_5 K_4 K_3 [H^+]^4 [Ce^{IV}] \quad (4)$$

If $1 > K_3 K_4 K_5 K_6$, then

$$K' = K_7 \frac{K_3 K_4 K_5 K_6 [H^+]^4}{1 + K_2[H^+]}$$

If $K_2[H^+] > 1$, the above equation reduces to $K' = K[H^+]^3$ where $K_3 K_4 K_5 K_6 K_7/K_2 = K$. When K' is plotted against the cube of the sulphuric acid concentration $\{K' \propto [H_2SO_4]^3\}$, a straight line is obtained, which almost passes through the origin. The actual data have been plotted and the resulting line has been found to compare well with that predicted. p-Toluquinone has been identified as the final product of oxidation by tlc and ir.

Acknowledgement

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## Synthesis of some New 1-Alkoxycarbonyl-1-aryl/benzylsulphonyl-2-arylethylenes

G. BAGAVANT* and S. P. CHOUDHARI**

Department of Pharmaceutical Sciences, University Campus, Amravati Road, Nagpur-440 010

THE Knoevenagel condensations of the arylsulphonyl acetates unlike those of arylsulphonyl acetic acids, have not been extensively studied. Balasubramanian and Baliah[1] have carried out the condensation by warming ethylphenylsulphonyl acetate (1 ; R=Ph, R'=Et) with m-nitrobenzaldehyde and cinnamaldehyde in ethanol in presence of ammonium acetate. Following this procedure, Dressler and Grahm[2] condensed the same ester with piperonal and anisaldehyde, and have characterised[1,2] the products as 2.

$$RSO_2CH_2COOR' + ArCHO \longrightarrow$$
$$\mathbf{1}$$
$$RSO_2C(COOR') = CHAr + H_2O$$
$$\mathbf{2}$$
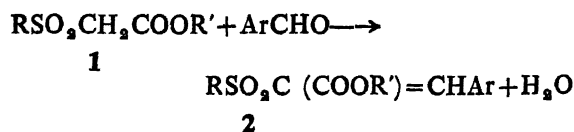
In this communication, different sulphonyl acetates (1a, R=Ph, R'=Et ; 1b, R=PhCH$_2$, R'=Et ; 1c, R=PhCH$_2$, R'=Me ; 1d, R=p-MeC$_6$H$_4$, R'=Et) were used for condensation in presence of ammonium acetate, ammonium carbonate, and ammonia solution[8]. However, under similar conditions, the condensation of 1a fails with m-nitrobenzaldehyde in presence of Triton-B, and anisaldehyde in presence of triethylamine[8]. Hence, these condensations may be described as Knoevenagel reaction[4] proceeding via imine intermediate. The products were assigned as 2 on the basis of the elemental analyses and ir spectral data[2,5,6] (Table 1).

It was observed that the treatment of the condensation product 2d with alcoholic ROH causes retro-Claisen change[8] as reported by Chodroff and Whitemore[7] for 2 (R=n-Bu, R'=Et).

Experimental

Condensation of sulphonyl acetates (1a – d) with aldehydes : To a solution of sulphonyl acetate (0.002 mol) and the aldehyde (0.002 mol) in dry ethanol (2 – 2.5 ml) was added the catalyst (0.002 mol dry ammonium acetate or ammonium carbonate or two drops of ammonia solution or 0.8 ml Triton-B). The reaction mixture was warmed, if necessary, to get a clear solution and finally kept overnight. The precipitate separated out on cooling in ice, was

TABLE 1—1-ALKOXYCARBONYL-1-ARYL/BENZYLSULPHONYL-2-ARYLETHYLENES*

Sl. no.	Sulphonyl ester	Aldehyde	Yield %	M.p. °C	ν_{max} cm^{-1}
		Catalyst : Ammonium acetate			
1.	a	p-Tolualdehyde	62.5 – 70.1	120 – 1	1 745, 1 645, 1 360, 1 150, 1 080
2.	a	o-Chlorobenzaldehyde	61.7	125 – 6	1 740, 1 630, 1 365, 1 150, 1 080
3.	a	p-Nitrobenzaldehyde	23.0	124	1 730, 1 640, 1 535, 1 360, 1 160, 1 090
4.	a	p-Dimethylaminobenzaldehyde	43.0	186 – 8	—
5.	b	m-Nitrobenzaldehyde	73.1	140 – 2	1 740, 1 645, 1 525, 1 350, 1 140
6.	b	Piperonal	—	Oily	1 735, 1 650, 1 350, 1 120
7.	c	Piperonal	66.8	129 – 30	—
8.	d	m-Nitrobenzaldehyde	57.7 – 64.3	148 – 9	1 745, 1 645, 1 530, 1 350, 1 155, 1 090
9.	d	p-Tolualdehyde	51.0	100 – 1	1 740, 1 645, 1 350, 1 145, 1 090
		Catalyst : Ammonium carbonate			
10.	a	m-Nitrobenzaldehyde	58.5 – 71.7	171 – 2	1 740, 1 640, 1 520, 1 365, 1 150, 1 080
11.	a	p-Tolualdehyde	62.0	120 – 1	—
		Catalyst : Ammonium hydroxide			
12.	a	p-Tolualdehyde	80.5	120 – 1	—

*All the compounds furnished satisfactory C (±0.32%) and H (±0.30%) analyses.

** Nabira Mahavidyalaya, Katol-441 302.