

Effect of Substituents on Rates of Reactions: Kinetics of Oxidation of Substituted Benzaldehydes by Vanadium(V)

G. S. S. MURTY, B. SETHURAM & T. NAVANEETH RAO

Department of Chemistry, Osmania University, Hyderabad 500007

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The reaction between benzaldehyde and V^{5+} in H_2SO_4 -HOAc mixtures in nitrogen atmosphere is found to obey a second order rate law. There is no evidence for complex formation between V^{5+} and benzaldehyde. The effect of substituents on the rate has been studied by using benzaldehyde and ten substituted benzaldehydes. The Hammett's plot is linear with a ρ value -0.68 . The order of reactivity of substituents is: $p\text{-Cl} > o\text{-Cl} > p\text{-CH}_3 > m\text{-CH}_3 > H > m\text{-Cl} > m\text{-NO}_2 > m\text{-Br} > o\text{-NO}_2 > p\text{-NO}_2$.

A TYPICAL mode of oxidation of aliphatic aldehydes and ketones by one electron metal ion oxidants¹ involves coordination with the carbonyl group followed by the loss of an α -hydrogen. The organic intermediate reacts with a second equivalent of the oxidant to give an acetal, a ketol or related compound. As a result, non-enolizable aldehydes such as benzaldehydes and pivaldehyde are not easily oxidized by many of these reagents. Wiberg and Ford² observed that Ce^{4+} in perchloric acid was readily reduced by benzaldehyde in 85% aqueous acetic acid and found that the substituents attached to the phenyl ring retarded the rate of oxidation regardless of the sign of the Hammett's σ value. In the oxidation of substituted benzaldehydes by chromic acid³, the electron withdrawing substituents increased the rate and the order of reactivity reported was $p\text{-NO}_2 > m\text{-NO}_2 > m\text{-Cl} > H > p\text{-CH}_3 > p\text{-OCH}_3$. A similar trend was observed when Mn^{3+} and Co^{3+} were employed as oxidants^{4,5}. In the present paper, the data on the kinetics of oxidation of some substituted benzaldehydes by V^{5+} in sulphuric acid medium are presented and discussed.

Materials and Methods

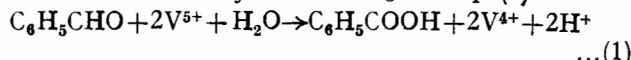
Analytical grade benzaldehyde was distilled in nitrogen and the middle fraction collected. Other liquid benzaldehydes were purified similarly, immediately before kinetic runs. Solid aldehydes were washed with aqueous sodium bicarbonate and recrystallized two or three times from ethanol-water to constant melting points. Acetic acid used was of BDH (AR) grade.

The rate of reaction was followed by the rate of disappearance of V^{5+} , as reported by earlier workers⁶. The rate constants were computed to an accuracy of $\pm 2\%$ error in duplicate runs.

Results and Discussion

Stoichiometry was determined in the usual way using excess of V^{5+} , which was estimated before and

after the completion of the reaction. The stoichiometry was calculated to be two moles of V^{5+} for one mole of benzaldehyde according to Eq. (1)



The final product of oxidation, benzoic acid (m.p. 122°), was isolated and the yield was quantitative. The evidence for the existence of free radicals was obtained from the polymerization tests with acrylamide which were positive.

Under the conditions of $[aldehyde] \gg [V^{5+}]$ the reaction followed first order kinetics. The pseudo-first order rate constants increased with increase in $[benzaldehyde]$ and the order with respect to $[benzaldehyde]$ was found to be one from the slope of the linear plot of $\log k'$ vs $\log [benzaldehyde]$.

The reaction rate increased with increase in $[H^+]$ thus exhibiting acid catalysis. For example, under the conditions in H_2SO_4 medium, viz. $[V^{5+}] = 0.0053N$; $[benzaldehyde] = 0.25M$; $[HOAc] = 50\%$ (v/v); and temp. = 50° , the rate constant ($k' \times 10^3$, min^{-1}) values at $[H^+] = 2.15, 2.81, 3.46, 4.11$ and $4.76M$ are 10.8, 16.6, 20.1, 24.1 and 31.1 respectively.

The rate of oxidation of benzaldehyde increased with increase in percentage of acetic acid. Under the reaction conditions in H_2SO_4 medium, viz. $[benzaldehyde] = 0.2M$; $[V^{5+}] = 0.0051M$; $[H^+] = 1.143M$ and temp. = 50° , the rate constants ($k' \times 10^3$, min^{-1}) in 50, 60, 70, 80 and 90% (v/v) acetic acid are 6.9, 10.8, 18.1, 55.2 and 172.6 respectively. A plot of $\log k$ vs $1/D$ was linear with a positive slope indicating the nature of the reaction to be ion-dipole type⁸.

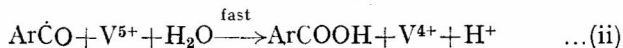
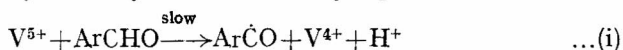
The acid catalysis of the oxidation by V^{5+} was explained by several workers as due to the presence of the equilibrium (2)



and may be assumed to be operative in this reaction as well. Mechanism involving formation of a complex between V^{5+} and benzaldehyde dissociating latter in a rate determining step is ruled out in the

present work as the order with respect to [aldehyde] was strictly one. The absence of complex formation was also proved by an independent optical method. The observed absorbance values of solutions of V^{5+} + aldehyde were same as those of V^{5+} + water at constant $[H^+]$ and [acetic acid].

The oxidation of benzaldehyde to benzoic acid by V^{5+} may be schematically represented as follows:



Step (i) involving C-H bond fission is the rate determining reaction, for, the second step involves free radicals and therefore, considered faster. The above mechanism explains both the stoichiometry and observed rate law

$$\frac{-d[V^{5+}]}{dt} = k[V^{5+}][ArCHO]$$

The increase in rate with decrease in dielectric constant which indicates the reaction to be ion-dipole type, also supports the mechanism suggested. Such a mechanism was also proposed by Wiberg and Richardson⁹ in the oxidation of benzaldehyde by Ce^{4+} . The possibility of the solvent itself undergoing induced oxidation was ruled out by conducting blank experiments in the absence of the aldehyde, when the concentration of V^{5+} remained unchanged.

Generally the rates of oxidation of various aldehydes are in accord with the theory of electronic effects of substituents. The effect of substituents on the rate was determined using benzaldehyde and ten mono substituted derivatives and the observed rates followed the order (Table 1): $p\text{-Cl} > o\text{-Cl} > p\text{-CH}_3 > m\text{-CH}_3 > H > m\text{-Cl} > m\text{-NO}_2 > m\text{-Br} > o\text{-NO}_2 > p\text{-NO}_2$. A Hammett's plot of the reaction under study showed a fair degree of linearity between $\log k'$ and σ (Fig. 1) and the slope of the least square plot gave a value of -0.68 for the reaction constant (ρ). The correlation coefficient for the plot was found to be 0.976. Walling and McElhill¹⁰

TABLE 1 — THERMODYNAMIC PARAMETERS FOR VARIOUS SUBSTITUENTS IN V^{5+} -BENZALDEHYDE REACTION IN SULPHURIC ACID MEDIUM

Substituent	$(\Delta E^\ddagger, \Delta H^\ddagger \text{ and } \Delta G^\ddagger \text{ in kcal mol}^{-1})$				
	$k' \times 10^{-1}$ litre mol ⁻¹ sec ⁻¹ at 50°	ΔE^\ddagger	ΔH^\ddagger	ΔG^\ddagger	ΔS^\ddagger e.u.
H	3.5	22.8	22.2	19.6	8.1
<i>m</i> -NO ₂	2.1	11.0	10.3	19.9	-29.7
<i>m</i> -Br	1.8	26.5	25.9	20.0	18.1
<i>m</i> -Cl	3.0	22.9	22.2	19.7	7.8
<i>m</i> -CH ₃	4.4	16.0	15.3	19.5	-12.7
<i>p</i> -Cl	7.2	25.6	25.0	19.1	17.9
<i>p</i> -CH ₃	6.9	17.8	17.2	19.2	-4.1
<i>p</i> -NO ₂	0.6	24.7	24.0	20.7	10.3
<i>o</i> -NO ₂	0.9	12.8	12.1	20.5	-25.7
<i>o</i> -Cl	5.0	24.7	24.0	19.3	14.7

The error limits: $k' \pm 2\%$; $\Delta E^\ddagger \pm 0.8$ kcal; and $\Delta S^\ddagger \pm 2.4$ e.u.

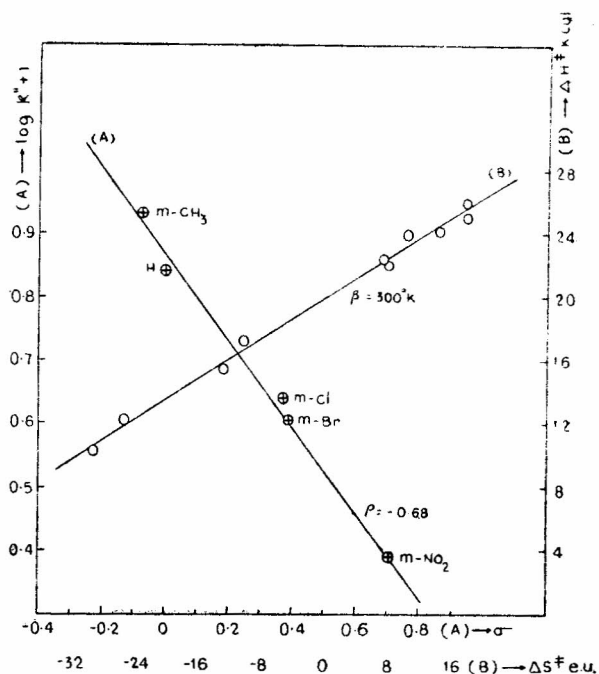


Fig. 1 — (A) Plot of $\log k'$ versus σ and (B) plot of ΔH^\ddagger versus ΔS^\ddagger

observed that a ρ value of about -0.8 would be expected for the reaction involving a hydrogen atom abstraction. The ρ value of -0.68 obtained in the present study agrees well with the above conclusion.

The oxidation of the substrate leading to the intermediate radicals involves production of an electron deficient transition state, *albeit* a weak one, since V^{5+} system is electrophilic and is expected to induce electron deficiency in the transition state.

Hence, a substituent which can increase the magnitude of negative charge on the carbonyl carbon atom of the aldehyde would stabilize the transition state, thereby allowing reaction to move in forward direction. The lowest value obtained for *p*-NO₂ benzaldehyde reaction, could be due to the combined effects of $-I$ and $-R$, inducing a positive charge on the carbonyl carbon atom. In *meta*-nitrobenzaldehyde the only effect operative is $-I$, and this explains the order of reactivity observed ($p\text{-NO}_2 < m\text{-NO}_2 < H$). In the case of chloro substituents *p*-chlorobenzaldehyde undergoes oxidation at a greater rate than unsubstituted compound. A chloro group in the *para*-position is capable of exerting $-I$ and $+R$ effect. Whereas $+R$ effect enhances the rate, $-I$ effect reduces it. However, $+R$ effect seems to be predominating in this reaction, as seen from the higher rate observed. In the case of the *meta*-chlorobenzaldehyde only $-I$ effect is important. This explains the retardation in the rate compared to the unsubstituted compound. Amongst the methyl groups studied the *para*-methyl group shows very high rate of oxidation which probably is due to the $+I$ effect coupled with positive hyper-conjugative effect, favouring the electrophilic attack. The retardation in the rate observed in the case of *ortho*-nitrobenzaldehyde could be due to the steric hindrance of substituent group as well as due to

intermolecular hydrogen bonding between the aldehyde and nitro groups.

For a series of compounds of slightly different structure but undergoing reaction essentially by the same mechanism, the ΔG^\ddagger values may be more or less constant with relative changes in enthalpy of activation (ΔH^\ddagger) and entropy of activation ΔS^\ddagger and the linear relationship between ΔH^\ddagger and ΔS^\ddagger (Fig. 1) is in accordance with equation $\Delta H^\ddagger = \Delta H^\ddagger_0 + \beta \Delta S^\ddagger$ where β is the isokinetic temperature. The β value for the reaction was found to be 300°K. As the temperature at which experiments were carried out is above the isokinetic temperature, the reaction may be assumed to be an entropy-controlled one. The nearness of the experimental temperature, (318-333°K) to the isokinetic temperature (300°K) is probably the reason for the small effects of the substituents observed.

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