JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 6, 1-6 (1993)

KINETICS AND MECHANISM OF THE OXIDATION OF SUBSTITUTED BENZALDEHYDES BY ETHYL *N*-CHLOROCARBAMATE

SEEMA VARSHNEY, SEEMA KOTHARI AND KALYAN K. BANERJI*

Department of Chemistry, J.N.V. University, Jodhpur 342 005, India

The kinetics of the oxidation of a number of *para*- and *meta*-monosubstituted benzaldehydes by ethyl *N*-chlorocarbamate (ECC) were studied in aqueous acetic acid solution in the presence of perchloric acid. The main product of the oxidation is the corresponding benzoic acid. The reaction is first order with respect to the aldehyde, ECC and hydrogen ions. The oxidation of benzaldehyde exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 5 \cdot 20 \pm 0 \cdot 10$). Addition of ethyl carbamate has no effect on the rate. $[EtOC(OH)NHCl]^+$ is postulated as the reactive oxidizing species. The rates of oxidation of *para*-substituted benzaldehydes exhibit an excellent correlation with Taft's σ_I and σ_R^+ values whereas those of the *meta*-substituted compounds correlate best with σ_I and σ_R^0 values. The reaction constants are large and negative. A mechanism involving transfer of a hydride ion from the aldehyde to the oxidant, in the rate-determining step, is proposed.

INTRODUCTION

The use of *N*-halocarbamates in synthetic organic chemistry is well documented.[1] We have been interested in the elucidation of the mechanism of the oxidation by *N*-halogenated reagents for some time and oxidation of alcohols by ethyl *N*-chlorocarbamate (ECC) has been reported previously.[2,3] In this paper we report the kinetics of the oxidation of substituted benzaldehydes by ECC in aqueous acetic acid solution, in the presence of perchloric acid. Attempts have been made to correlate structure and reactivity in this reaction. Mechanistic aspects are discussed.

EXPERIMENTAL

Materials. The details of the preparation and the specifications of the benzaldehydes have been described earlier.[4] ECC was prepared by a reported method.[5] [^{2}H]Benzaldehyde (PhCDO) was prepared[6] by the reduction of benzil by lithium aluminium deuteride (Fluka) to give the diol, followed by oxidation of the diol with lead tetraacetate. Acetic acid was refluxed with CrO_3 and acetic anhydride for 6 h and distilled before use.

Product analysis. Freshly distilled benzaldehyde (0·03 mol) and ECC (0·01 mol) were made up to 100 ml in acetic acid–water [1 : 1 (v/v)] in the presence of $0 \cdot 5 \text{ mol dm}^{-3}$ $HClO_4$. The reaction mixture was allowed to stand for *ca* 10 h to ensure completion of the reaction. The solution was extracted with diethyl ether (3 × 100 ml). The ether solution was extracted with a saturated solution of $NaHCO_3$. The $NaHCO_3$ extract was concentrated by evaporating the solvent at 80 °C. The concentrated solution was acidified with concentrated HCl and cooled in ice to furnish the crude acid (88%), which was recrystallized from hot water to produce pure benzoic acid (m.p. 124 °C).

Stoichiometry. To determine the stoichiometry, benzaldehyde was treated with an excess of ECC. When the reaction was complete, unreacted ECC was determined iodometrically. Several determinations, using substituted benzaldehydes, indicated a 1 : 1 stoichiometry. The overall reaction may be written as follows:

$$PhCHO + EtOOCNHCl + H_2O \rightarrow PhCOOH + HCl + EtOOCNH_2 \quad (1)$$

Kinetic measurements. Pseudo-first-order conditions were maintained by keeping a large excess (tenfold or greater) of the aldehyde over ECC. The reactions were carried out at constant temperatures (±0·1 K) and in

---

[*] Author for correspondence.

0894-3230/93/010001-06$08.00

Received 7 April 1992
Revised 12 June 1992

flasks blackened on the outside to prevent any photochemical reaction. The reactions were followed iodimetrically for up to 70% of the reaction. The solvent was acetic acid–water [1 : 1 (v/v)], unless specified otherwise. The pseudo-first-order rate constant, k_{obs}, was calculated from the linear (r > 0·98) plots of log [ECC] vs time. Duplicate kinetic runs showed that the rates were reproducible to within ±3%. The specific rate constant, k, was obtained by the equation $k = k_{obs}/[H^+][\text{aldehyde}]$. Preliminary experiments showed that the reaction is not sensitive to ionic strength and hence no attempt was made to keep the latter constant during the experiments.

RESULTS

The rate laws and other experimental data were obtained for all the benzaldehydes investigated. As the results were similar, only representative data are given here.

Rate laws

The reaction was found to be first order with respect to ECC. Further, the first-order rate constants do not vary with the initial concentration of ECC. The effect of variation of the concentration of aldehyde on the reaction showed that the reaction is first order with respect to the aldehyde also. The reaction rate increases linearly with increase in the concentration of hydrogen ions (Table 1). Addition of ethyl carbamate had no effect on the rate.

Table 1. Rate constants for the oxidation of benzaldehyde by ECC at 308 K

[PhCHO] (mol dm^{-3})	10^3[ECC] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	$10^5 k_{obs}$ (s^{-1})
0·1	5·0	1·0	4·14
0·2	5·0	1·0	8·00
0·3	5·0	1·0	12·4
0·4	5·0	1·0	16·5
0·5	5·0	1·0	20·9
0·5	5·0	1·0	21·0[a]
0·5	2·0	1·0	21·0
0·5	3·5	1·0	20·8
0·5	7·0	1·0	20·8
0·5	10·0	1·0	20·9
0·5	15·0	1·0	20·9
0·2	5·0	0·3	2·40
0·2	5·0	0·6	5·00
0·2	5·0	0·9	7·25
0·2	5·0	1·5	12·0
0·2	5·0	1·8	15·0
0·2	5·0	3·0	24·1
0·2	5·0	1·0	7·90[b]

[a] Contained 0·5 mol dm^{-3} acrylonitrile.
[b] Contained 0·01 mol dm^{-3} ethyl carbamate.

Kinetic isotope effect

To ascertain the importance of the cleavage of the aldehydic C—H bond in the rate-determining step, the oxidation of [^{2}H]benzaldehyde was studied. The specific rate constants for the oxidation of ordinary and deuteriated benzaldehydes, at 303 K, are 10^5k = 41·3 ± 0·1 and 7·80 ± 0·2 dm^6 mol^2 s^{-1}, respectively. The value of primary kinetic isotope effect, k_H/k_D, is 5·20 ± 0·10.

Effect of substituents

The oxidation of a number of *para*- and *meta*-monosubstituted benzaldehydes was studied at different temperatures and the activation parameters, at 303 K, were evaluated (Table 2).

Effect of solvent composition

The rate of oxidation of benzaldehyde was determined in solvents containing different proportions of acetic acid and water. The rate increased with increase in the proportion of acetic acid in the solvent (Table 3).

Induced polymerization of acrylonitrile

The oxidation of the benzaldehyde by ECC in an atmosphere of nitrogen failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the reaction rate (Table 1).

DISCUSSION

The activation enthalpies and entropies of the oxidation of 22 aldehydes are linearly related (r = 0·9676). The value of the isokinetic temperature is 490 ± 54 K. The correlation was tested and found to be genuine by applying Exner's criterion.[7] Exner's plot between log k at 303 K and 318 K was linear (r = 0·9984, slope = 0·8904 ± 0·0112). The value of the isokinetic temperature evaluated from Exner's plot is 536 ± 31 K. The linear isokinetic correlation implies that all the aldehydes are oxidized by the same mechanism and the changes in the rate are governed by changes in both the enthalpy and entropy of activation.

There seems to be no report about the various equilibria and species present in an acidified aqueous solution of ECC. However based on the reactions of structurally related *N*-haloarylsulphonamides,[8] one can suggest the following equilibria:

$$\text{EtOOCNHCl} + \text{H}_2\text{O} \rightleftharpoons \text{EtOOCNH}_2 + \text{HOCl} \quad (2)$$

$$2\text{EtOOCNHCl} \rightleftharpoons \text{EtOOCNH}_2 + \text{EtOOCNCl}_2 \quad (3)$$

Hence the possible oxidizing species are ECC, EtOOCNCl_2 and HOCl. Ethyl dichlorocarbamate can be ruled out as the oxidizing species in view of the strict

Table 2. Temperature dependence and activation parameters for the oxidation of monosubstituted benzaldehydes by ECC

	10^6k ($dm^6\,mol^{-2}\,s^{-1}$)						
Substituent	303 K	308 K	313 K	318 K	ΔH^* ($kJ\,mol^{-1}$)	ΔS^* ($J\,mol^{-1}\,K^{-1}$)	ΔF^* ($kJ\,mol^{-1}$)
H	187	243	365	570	57·4 ± 1·6	− 128 ± 3	95·4 ± 2·0
p-Me	810	935	1360	2160	50·4 ± 1·8	− 139 ± 4	91·8 ± 2·2
p-NHCOMe	9550	11,800	16,600	24,000	47·1 ± 1·0	− 129 ± 2	85·5 ± 0·8
p-OMe	22,400	28,200	38,900	57,600	47·9 ± 1·2	− 119 ± 2	83·4 ± 1·0
p-F	1000	1250	1650	2230	40·4 ± 1·6	− 170 ± 5	90·9 ± 1·3
p-Cl	352	470	703	1130	59·9 ± 1·1	− 115 ± 2	93·9 ± 1·5
p-Br	268	371	528	800	55·6 ± 1·9	− 131 ± 6	94·4 ± 1·4
p-NO_2	12·5	18·0	33·2	56·8	79·9 ± 1·3	− 76 ± 2	103 ± 2·0
p-CN	18·3	27·5	42·2	79·0	74·5 ± 1·4	− 91 ± 3	101 ± 2·2
p-COOMe	36·5	55·6	82·2	144	69·6 ± 1·2	− 101 ± 3	99·6 ± 1·8
p-CF_3	33·0	45·1	79·0	140	75·3 ± 1·5	− 84 ± 3	100 ± 2·5
p-SMe	3570	4500	5650	7480	36·6 ± 1·1	− 172 ± 4	87·7 ± 1·0
m-Me	300	382	535	809	50·5 ± 1·3	− 147 ± 3	94·1 ± 1·1
m-OMe	182	248	350	552	56·2 ± 0·9	− 132 ± 2	95·4 ± 0·9
m-F	48·3	71·5	107	185	68·4 ± 1·2	− 103 ± 2	98·9 ± 1·2
m-Cl	43·0	57·6	87·7	163	68·1 ± 1·5	− 105 ± 4	99·3 ± 1·4
m-Br	41·3	62·4	92·4	164	70·7 ± 1·2	− 99 ± 2	99·3 ± 1·0
m-NO_2	6·52	9·28	17·3	36·7	90·3 ± 1·7	− 48 ± 1	104 ± 1·7
m-CN	10·2	16·0	28·4	47·3	80·3 ± 1·1	− 76 ± 2	103 ± 1·0
m-NHCOMe	108	150	232	380	64·8 ± 1·3	− 108 ± 3	96·9 ± 1·3
m-CF_3	19·3	27·4	47·1	90·4	80·2 ± 1·2	− 72 ± 1	101 ± 1·0
m-SMe	112	166	225	367	59·3 ± 1·2	− 126 ± 3	96·6 ± 1·3

Table 3. Effect of solvent on the oxidation of benzaldehyde by ECC at 308 K[a]

	AcOH (%, v/v)				
Parameter	30	40	50	60	70
Dielectric constant	55·6	48·4	41·5	34·4	27·4
10^5k_{obs} (s^{-1})	7·00	10·1	16·0	27·6	44·5

[a] [PhCHO] = 0.40 mol dm^{-3}; [*ECC*] = 0.005 mol dm^{-3}; $[H^+]$ = 1.0 mol dm^{-3}.

first-order dependence of the reaction rate on ECC. Moreover, the absence of any effect of ethyl carbamate on the reaction precludes both HOCl and $EtOOCNCl_2$ as the reactive species. Therefore, the most likely oxidizing species is EtOOCNHCl.

The linear increase in the oxidation rate with acidity suggests that ethyl chlorocarbamate is protonated to give a stronger oxidant and electrophile:

$$EtOOCNHCl + H_3O^+ \rightleftharpoons [EtOC(OH)NHCl]^+ + H_2O \tag{4}$$

The observed solvent effect indicates that the transition state is less polar than the reactant state. The dielectric constants of acetic acid–water mixtures have been calculated earlier.[9] A plot of log k_{obs} against the reciprocal of the dielectric constant of the solvent is linear with a positive slope ($r = 0{\cdot}9866$), indicating an interaction between a positive ion and a dipolar molecule in the rate-determining step.[10] The variation in the reaction rate may, however, be simply explained by assuming that if a cationic chlorine species reacts with a neutral aldehyde molecule in a rate-determining step, the charge will be dispersed over a larger area in the transition state. Since the charge density has thus been diminished, the transition state requires less solvation. Therefore, the reaction should be more rapid in a solution of lower dielectric constant. The effect of varying solvent composition is thus in accord with the suggestion that the active oxidizing species is $[EtOC(OH)NHCl]^+$.

Correlation analysis of reactivity

Table 2 shows that the rate of oxidation of a *para*-substituted compound is greater than that of the corresponding *meta*-substituted compound. Similar observations have been recorded earlier in the oxidation of substituted benzaldehydes by pyridinium fluorochromate (PFC)[11] and by *N*-bromoacetamide (NBA).[12]

The rates of oxidation of the substituted benzaldehydes failed to show satisfactory correlation with any single substituent-parameter equation. The rates of oxidation of *para*- and *meta*-substituted benzaldehydes were, therefore, analysed separately using Taft's and Swain's dual substituent-parameter (DSP) equations.[13,14] Both the *meta* and *para* series meet the basic require-

Table 4. Correlation analysis of the rate constant with DSP equations at 303 K

Substitution	Substituent constant	ρ_I	ρ_R	R^2	SD	f	n
para	σ_I, σ_R^0	-1·12 (±0·30)	-5·04 (±0·54)	0·8947	0·39	0·373	12
	σ_I, σ_R^{BA}	-1·26 (±0·23)	-4·07 (±0·32)	0·9400	0·29	0·274	12
	σ_I, σ_R^-	-0·20 (±0·53)	-3·07 (±0·73)	0·6277	0·73	0·696	11[a]
	σ_I, σ_R^+	-1·25 (±0·002)	-2·37 (±0·002)	0·9999	0·003	0·003	12
	Swain's	-0·05 (±0·05)	-1·15 (±0·04)	0·9882	0·12	0·115	12
meta	σ_I, σ_R^0	-1·98 (±0·005)	-1·16 (±0·008)	0·9999	0·006	0·008	11
	σ_I, σ_R^{BA}	-2·00 (±0·03)	-0·90 (±0·05)	0·9946	0·042	0·057	11
	σ_I, σ_R^-	-1·73 (±0·07)	-0·80 (±0·10)	0·9727	0·093	0·127	10[a]
	σ_I, σ_R^+	-2·01 (±0·08)	-0·50 (±0·06)	0·9735	0·091	0·126	11
	Swain's	-1·08 (±0·02)	-0·37 (±0·01)	0·9951	0·040	0·054	11

[a] NHCOMe substituent not considered, no σ_R^- value available.

ment of the minimum number of substituents.[15] We did not use the NH_2 group, as it was protonated in acidic solution and ceased to be an electron-donor group. We used the acetylamino group instead.

The rates of oxidation of *para*-substituted benzaldehydes showed an excellent correlation with Taft's σ_I and σ_R^+ values (Table 4). We used the standard deviation (SD), coefficient of multiple correlation (R^2) and the parameter f as measures of goodness of fit; f has been defined[13] as SD/root mean square of data (here $\log k/k_0$). Comparison showed that f is smaller for the σ_R^+ scale than for the other scales by factors of *ca* 38–230.

The rates of oxidation of *meta*-substituted compounds showed an excellent correlation with Taft's σ_I and σ_R^0, although the discriminating factor for the precision of fit with other σ_R scales or with Swain's scale is not as sharp as in the case of *para*-substituted com-

Table 5. Temperature dependence of the reaction constants

Substitution	Temperature (K)	ρ_I	ρ_R	λ[a]	R^2	SD	f
para	303	-1·25 (±0·002)	-2·37 (±0·002)	1·89	0·9999	0·003	0·003
	308	-1·19 (±0·02)	-2·31 (±0·01)	1·91	0·9995	0·021	0·018
	313	-1·13 (±0·02)	-2·24 (±0·02)	1·89	0·9991	0·026	0·020
	318	-1·06 (±0·04)	-2·16 (±0·03)	2·03	0·9972	0·047	0·036
meta	303	-1·98 (±0·005)	-1·16 (±0·01)	0·59	0·9999	0·006	0·008
	308	-1·89 (±0·02)	-1·14 (±0·04)	0·60	0·9979	0·025	0·020
	313	-1·79 (±0·015)	-1·01 (±0·026)	0·56	0·9987	0·018	0·013
	318	-1·65 (±0·04)	-1·00 (±0·031)	0·60	0·9968	0·027	0·023

[a] $\lambda = \rho_R/\rho_I$.

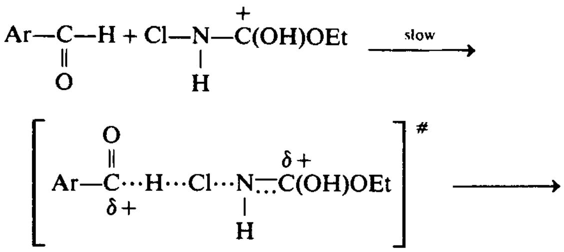
pounds. The correlations with σ_R^{BA} and in Swain's scale meet the requirements for a satisfactory fit ($f < 0.1$). This agrees with the observation of Ehrensen *et al.*[16] that the correlation of rates of *meta*-substituted compounds is generally best with σ_R^0 and *meta*-substituted compounds are generally less discriminating.

The reaction constants and statistical data at different temperatures are given in Table 5. The value of λ_p (*ca* 1·9) showed that the oxidation of *para*-substituted benzaldehydes is more susceptible to resonance effects than to inductive effects. In the oxidation of *meta*-substituted compounds, however, the contribution of inductive effects is greater than that of resonance effects ($\lambda_m = 0{\cdot}60$). The magnitude of the reaction constants decreases at higher temperatures, indicating a decrease in selectivity. In both the *meta* and *para* series, the decreases in the inductive and resonance effects are of similar order, reflected in almost constant values of λ_p and λ_m.

Mechanism

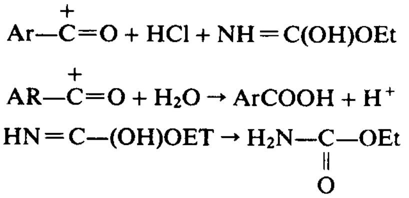
The presence of a substantial primary kinetic isotope effect confirmed the cleavage of the aldehydic C—H bond in the rate-determining step. In view of the absence of any effect on the reaction rate of radical scavengers such as acrylonitrile, it is unlikely that a one-electron reaction, giving rise to free radicals, is operative in this oxidation.

The large negative reaction constants point to a highly electron-deficient carbon centre in the transition state. Further, the excellent correlation obtained with σ_R^+ values in the oxidation of *para*-substituted benzaldehydes and the large value of λ_p showed that there is an extensive through-conjugation, in the transition state, between a developing positive charge and the *para*-substituent. In the oxidation of *meta*-substituted compounds the through-conjugation is not possible and the resonance effect of the substituent operates indirectly. Therefore, the contribution of the inductive effect is relatively greater. These facts, coupled with the large deuterium isotope effect, showed that the transition state approaches a carbocation in character. Hence the transfer of a hydride ion in the rate-determining step is indicated. A concerted mechanism, involving simultaneous attack by a water molecule, is unlikely for three reasons. First, a termolecular reaction is highly improbable. Second, the concerted mechanism is inconsistent with the extensive through-conjugation observed in this case. Finally, the large value of kinetic isotope effect militates against a non-linear transition state implied in a concerted reactions. Therefore, the mechanism shown in equations (5)–(7) is proposed for the oxidation of aldehyde by ECC.



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{C}{-}H + Cl{-}\underset{\underset{H}{|}}{\overset{+}{N}}{-}C(OH)OEt} \xrightarrow{\text{slow}}$$

$$\left[\mathrm{Ar{-}\underset{\delta+}{\overset{\overset{O}{\|}}{C}}\cdots H\cdots Cl\cdots \underset{\underset{H}{|}}{\overset{\delta+}{N}}\overset{\dots}{-}C(OH)OEt}\right]^{\#} \longrightarrow$$



$$\mathrm{Ar{-}\overset{+}{C}{=}O + HCl + NH{=}C(OH)OEt} \qquad (5)$$

$$\mathrm{AR{-}\overset{+}{C}{=}O + H_2O \rightarrow ArCOOH + H^+} \qquad (6)$$

$$\mathrm{HN{=}C{-}(OH)OET \rightarrow H_2N{-}\underset{\underset{O}{\|}}{C}{-}OEt} \qquad (7)$$

The observed negative entropy of activation also supports the above mechanism. When two reacting molecules combine to form a single activated complex, the restrictions on their movements obviously increase as they cannot move independently.[17] This results in a decrease in the entropy.

It is of interest to compare the results of oxidation of substituted benzaldehydes by ECC with those by *N*-bromobenzamide (NBB),[4] PFC[11] and NBA.[12] The oxidations by NBB and NBA are more susceptible than the oxidation by ECC to substituent effects and the reaction constants are larger. This difference is more pronounced in the case of the inductive effects and the values of λ_p and λ_m are relatively higher in the oxidation by ECC. The resonance effects are therefore more important in the oxidation by ECC than in the oxidations by NBB and NBA. The rate laws of the three reactions are similar. All the three reactions exhibited large kinetic isotope effects. Similar mechanisms have been postulated for the three reactions. The oxidation by PFC,[11] in dimethyl sulphoxide as solvent, showed a different kinetic picture. The reaction exhibited Michaelis–Menten-type kinetics with respect to the aldehyde. The oxidation of *para*-substituted benzaldehydes showed excellent correlation with Taft's σ_I and σ_R^{BA} values. This indicated a weak through-conjugation in the transition state. A mechanism involving the rapid formation of an initial complex between PFC and the aldehyde, followed by its slow decomposition, had been postulated.

ACKNOWLEDGEMENTS

Thanks are due to the University Grants Commission, India, for financial assistance.

REFERENCES

1. M. M. Campbell and G. Johnson, *Chem. Rev.* **78**, 65 (1978).
2. S. Mittal, V. Sharma and K. K. Banerji, *Int. J. Chem. Kinet.* **18**, 689 (1986).
3. S. Jain and K. K. Banerji, *Bull. Chem. Soc. Jpn.* **61**, 1767 (1988).
4. K. K. Banerji, *J. Org. Chem.* **51**, 4769 (1986).
5. C. Bachand, D. Hughes, J. M. Paton, T. Daniel and J. Lessard, *J. Org. Chem.* **39**, 3137 (1974).
6. K. B. Wiberg, *J. Am. Chem. Soc.* **76**, 5371 (1954).
7. O. Exner, *Collect. Czech. Chem. Commun.* **29**, 1094 (1964).
8. K. K. Banerji, D. S. Mahadevappa and B. Jayaraman, *J. Sci. Ind. Res.* **46**, 65 (1987).
9. K. K. Banerji, *Indian J. Chem., Sect. A* **16**, 595 (1978).
10. E. S. Amis, *Solvent Effects on Reaction Rates and Mechanism*, pp. 42–50. Academic Press, New York (1967).
11. S. Agarwal, K. Chowdhury and K. K. Banerji, *J. Org. Chem.* **56**, 5111 (1991).
12. A. Gupta, S. Mathur and K. K. Banerji, *J. Chem. Res. (S)* 6 (1988); *(M)* 0201 (1988).
13. S. K. Dayal, S. Ehrensen and R. W. Taft, *J. Am. Chem. Soc.* **94**, 9113 (1974).
14. C. S. Swain, S. H. Unger, N. R. Rosenquest and M. S. Swain, *J. Am. Chem. Soc.* **105**, 492 (1983).
15. J. Shorter, *Correlation Analysis of Organic Reactivity*, p. 65. Research Studies Press, Chichester (1982).
16. S. Ehrensen, R. T. C. Brownlee and R. W. Taft, *Prog. Phys. Org. Chem.* **10**, 1 (1973).
17. S. Gould, *Mechanism and Structure in Organic Chemistry*, p. 181. Holt, Rinehart & Winston, New York (1964).