Asian Journal of Chemistry Vol. 6, No. 3 (1994), 523–531

Kinetic Study of Homogeneous Acid Catalysed Oxidation of Certain Aliphatic Amines by Potassium Permanganate in Acidic Media

J.M.S. REDDY and G.S. MOSES*
Post-Graduate Department of Chemistry,
Government College, Rajahmundry-533 105, India.

The rate of oxidation of ethylamine, diethylamine and triethylamine by potassium permanganate in concentrated sulphuric acid and perchloric acid media is proportional to the concentration of ethyl, diethyl and triethylamines respectively. In each case, the total order of the reaction is two, *i.e.*, one with respect to the given substrate and also one with respect to permanganate ion, at the given concentration of sulphuric acid and perchloric acid. The mechanism pertinent with the experimental observations has been proposed.

INTRODUCTION

Although the oxidation of primary, secondary and tertiary amines by potassium permanganate has been the subject of considerable publications[1–5], no attempt seems to have been made to study systematically, the kinetics and mechanism of oxidation of ethyl, diethyl and triethyl amines by potassium permanganate, in moderately concentrated sulphuric acid and perchloric acid media. This investigation is, therefore, an attempt in this direction, besides correlating the rates with acid concentrations employed.

EXPERIMENTAL

All the amines used were of Riedel quality. Potassium permanganate, sulphuric acid and chemicals other than those below were of B.D.H AnalaR products. Perchloric acid GR was supplied by E. Merck (Germany). Caesium sulphate used was supplied by Hopkin & Williams Ltd., England. Potassium permanganate solution was prepared as given by Vogel[6] and all the amines used were prepared and standardised as given by Siggia[7]. Doubly distilled water was used to prepare all the solutions.

The reactants were left in a thermostat to attain the desired temperature before the final mixing. The kinetics were followed by removing 5 ml. of aliquot portions of reaction mixture at suitable intervals and the unreacted permanganate was estimated iodometrically. Throughout the investigation the reaction was followed under pseudo first order conditions, with the organic substrate in large excess.

The pseudo first order rate constants (K_1) reported are the average values from two to three similar runs, for first 70–75%, 65–70% and 60–65% of the reaction in the case of oxidation of ethyl, diethyl and triethyl amines respectively. The reproducibility of duplicate rate constants are always within 3–4%.

RESULTS AND DISCUSSION

It is observed that at constant concentrations of sulphuric (or perchloric) acid and substrate, the order of reaction with respect to permanganate is one. The values of pseudo first order rate constants, K_1 for various concentrations of potassium permanganate are given in Table 1.

TABLE 1
CONSTANCY OF REACTION RATE WITH PERMANGANATE CONCENTRATION AT 30°C

$[MnO_4^-] \times 10^4$ (M)	8.00	10.00	13.33	20.00
Ethylamine (0.5M)				
10^3K_1 (min^{-1}) (5M H_2SO_4)	6.41	6.50	6.62	6.58
10^3K_1 (min^{-1}) (5M $HClO_4$)	4.38	4.26	4.32	4.21
Diethylamine (0.1 M)				
10^3K_1 (min^{-1}) (4M H_2SO_4)	2.96	2.89	2.94	2.81
10^3K_1 (min^{-1}) (4M $HClO_4$)	2.39	2.24	2.34	2.27
Triethylamine (0.1M)				
10^3K_1 (min^{-1}) (4M H_2SO_4)	4.09	4.03	4.12	3.97
10^3K_1 (min^{-1}) (4M $HClO_4$)	3.76	3.71	3.62	3.69

The results obtained on varying substrate concentration are given in Table 2. The plots of rate constants against respective amine concentrations give straight lines passing through the origin, in the cases of both the sulphuric acid and perchloric acid media. This not only shows that the order of reaction with respect to substrate is one in both the acidic media but also that there is apparently no kinetic evidence for the intermediate complex formation between substrate and oxidant[8], and if, at all any complex is formed, its formation constant should be extremely small[9].

Effect of Acid Concentration and Acid Catalysis:

The effect of the mineral acid concentration on the rate has been investigated in 3M–7M sulphuric and perchloric acids. The rate of oxidation is higher in sulphuric acid than in perchloric acid medium, at their equal concentrations. Increase of acid concentration causes rapid increase in reaction velocity (Table 3). Further in an attempt to correlate the rate of oxidation with acid concentration, various hypotheses for the mechanism of acid catalysis were tested.

TABLE 2
FIRST ORDER DEPENDENCE ON SUBSTRATE CONCENTRATION IN 5M SULPHURIC ACID AT 30°C. $[MnO_4^-] = 13.33 \times 10^{-4}$

[Ethylamine] (M)	0.30	0.50	0.60	0.80	1.00	1.50	2.00
10^3K_1/ (min^{-1})	3.94	6.50	7.85	10.32	12.97	19.68	25.76
10^3K_1/[substrate]	13.33	13.00	13.08	12.90	12.97	13.12	12.88

Average 10^3K_1/[substrate] = 13.01 ± 0.08 l $moles^{-1}min^{-1}$

[Diethylamine] (M)	0.05	0.10	0.20	0.25	0.30	0.35	0.40
10^3K_1 (min^{-1})	3.01	6.05	12.21	15.14	18.31	21.26	24.19
10^3K_1/[substrate]	60.20	60.50	61.05	60.56	61.03	60.74	60.47

Average 10^3K_1/[substrate] = 60.65 ± 0.25 l $moles^{-1}min^{-1}$

[Triethylamine] (M)	0.05	0.10	0.20	0.25	0.30	0.35	0.40
10^3K_1 (min^{-1})	4.28	8.52	16.97	21.38	25.64	29.91	34.24
10^3K_1/[substrate]	85.60	85.20	84.85	85.52	85.47	85.45	85.60

Average 10^3K_1/[substrate] = 85.33 ± 0.24 l $moles^{-1}min^{-1}$

Similar results are obtained when the substrate concentration is varied in perchloric acid medium. The average value of 10^3K_1/substrate in 5M–perchloric acid is 8.52 ± 0.09, 54.71 ± 0.26, and 65.18 ± 0.22 l $mole^{-1}min^{-1}$ respectively for ethyl, diethyl and triethyl amines.

TABLE 3
VARIANCE OF RATE CONSTANT WITH ACID CONCENTRATION AT 30°C. $[MnO_4^-] = 13.33 \times 10^{-4}$ M

[Acid] (M)	3.50	4.00	4.50	5.00	5.50	6.00	6.50
Ethylamine (0.5M)							
10^3K_1 (min^{-1}) (H_2SO_4)	2.08	2.89	4.37	6.50	9.79	17.41	24.85
10^3K_1 (min^{-1}) ($HClO_4$)	1.12	1.47	2.29	4.26	7.12	12.64	21.03
Diethylamine (0.1M)							
10^3K_1 (min^{-1}) (H_2SO_4)	2.04	2.86	3.97	6.05	9.62	15.23	25.51
10^3K_1 (min^{-1}) ($HClO_4$)	1.79	2.34	3.82	5.44	8.86	14.21	20.07
Triethylamine (0.1M)							
10^3K_1 (min^{-1}) (H_2SO_4)	3.44	4.03	5.49	8.52	12.19	19.02	27.87
10^3K_1 (min^{-1}) ($HClO_4$)	3.07	3.62	4.87	6.50	8.90	14.69	21.08

The acid catalysed reaction is represented conveniently in generalized fashion:

$$S + H^+ \rightleftharpoons SH^+ \qquad (1)$$

$$SH^+ + \text{Oxidant} \ (+H_2O) \rightleftharpoons \text{Products} \qquad (2)$$

In the present case of strongly basic substrates, which are totally protonated throughout the range of mineral acid concentration used, only step (2) need be taken into account. The rates of acid catalysed reactions generally increase with the acid concentration, but the steepness of increase in moderately concentrated mineral acids is sharply dependent on the identity of the substrate. Also, as was first evident to Hammett[11,12], there are some relationships between steepness of increase and the mechanism of the reaction which occurs. The two Zücker-Hammett's relations[11,12] *i.e.*, (i) log K_1 vs H_0 and (ii) log K_1 vs log [Acid] are plotted and the slopes of the respective linear plots are quoted in Table-4. However, no straight line of Zücker-Hammett plots in the case of oxidation of the present 3^0, 2^0 and 1^0 amines produces the ideal slope value of unity.

The mineral acid medium dependence of reaction rates is alternatively expressed by Bunnett's parameters[13]. A summary of slope values (ω and ω^*) for the two Bunnett's plot *i.e.*, (i) log K_1 vs log a_{H_2O} and (ii) (log K_1–H_0–log [Acid]) vs log a_{H_2O} are given in Table-4, for the present case of strongly basic substrates[13].

TABLE 4
SUMMARY OF RATE CORRELATIONS WITH ACID CONCENTRATIONS EMPLOYED

Correlation	Slope					
	Ethylamine		Diethylamine		Triethylamine	
	H_2SO_4	$HClO_4$	H_2SO_4	$HClO_4$	H_2SO_4	$HClO_4$
log K_1 vs H_0	0.7	1.5	0.8	0.8	0.8	0.6
log K_1 vs log [Acid]	4.8	5.8	4.6	4.6	3.9	3.4
log K_1 vs log a_{H_2O}	4.1	6.7	4.0	5.2	3.7	3.9
(log K_1 – log $[H^+]$ – H_0) vs log a_{H_2O}	7.5	8.0	7.3	7.5	7.0	6.9
log K_1 vs (H_0 + log $[H^+]$)	1.0	1.0	1.0	0.9	0.9	0.7

According to Bunnett's emperical observations the ω and ω^* values in both sulphuric acid and perchloric acid media indicate that the water molecule should act as a proton abstracting agent in the rate determining step.[13]

The observed data (Table 3) is correlated quite well by the linear free energy relationship (LFER) of the equation

$$\log K_1 = -\phi\,(H_0 + \log [H^+]) + \text{constant} \qquad (3)$$

proposed by Bunnett and his coworkers[14] for strongly basic substrates. The slope of correlation plot of log K_1 with (H_0 + log $[H^+]$) constitutes a parameter, ϕ, whch characterises the kinetic response of the reaction to changing acid concentration. The ϕ parameters obtained (>0.58), (Table 4) further lead us to confirm that the role of water molecule in the rate controlling step is as a proton abstracting agent[14]. We have taken the molar concentration of hydrogen ion to be equal to the molar concentration of the mineral acid.[14] The values of H_0 and log a_{H_2O} are taken from Paul and Long[15], and Bunnett[13] respectively.

Effect of Temperature:

In case of the oxidation of all the three amines by permanganate, reactions were studied at 25°, 30°, 35°, 40° and 45°C. Energies of acitvation (ΔE), entropies of activation (ΔS) and frequency factors (PZ), for the reactions are summarised in Table 5.

TABLE 5
ACTIVATION PARAMETERS FOR ETHYL, DIETHYL AND TRIETHYL AMINES FOR 30°C

	ΔE (K. Cals)		PZ		ΔS(e.u)	
	H_2SO_4	$HClO_4$	H_2SO_4	$HClO_4$	H_2SO_4	$HClO_4$
Ethylamine	10.3	22.4	17.570×10^4	61.66×10^{12}	–35.5	–4.417
Diethylamine	9.2	19.4	2.617×10^4	5.14×10^{11}	–39.3	–5.89
Triethylamine	8.8	17.7	0.902×10^4	2.63×10^{10}	–41.4	–11.8

Neutral Salt Effect and Effect of Ionic strength:

No primary kinetic salt effect was observed in the case of oxidation of 3°, 2° and 1° amines. But at higher concentrations of added neutral salts, logarithm of rate constant is linearly related to ionic strength. This is in accordance with the equation proposed for the higher concentrations range of added neutral salts[16]

$$\log K_1 = \log K_0 + (b_0 + b_a - b_c)\mu \qquad (4)$$

where b_0, b_a and b_c are constants and largely emperical. This relationship was found true for a number of neutral salts studied in case of oxidation of all the three amines by permanganate. Percentage of increase of rate for a number of salts when the ionic strength was varied from 0.2 to 0.4 M has been given Tables 6 and 7. The applicability of equation (4) shows that the reaction should involve two neutral molecules or a neutral molecule and an ion, in the rate determining stage. The positive salt effect (Tables 6 and 7) further indicates that the reaction in between a positive ion and a molecule[17].

Specific Ionic Effects:

In order to investigate the specific effects of cations and anions on the reaction velocity, sodium salts of anions and sulphates of cations were taken at their identical molar concentrations. It is to be noted that various anions and cations are not equally effective in increasing the rate. The order of effectiveness of the anions can be given by the series, $PO_4^{3-} > HSO_4^- > SO_4^{2-} > NO_3^- > CH_3COO^- > ClO_4^-$, and in case of cations the order of effectiveness for univalent ions is, $Cs^+ > Li^+ > NH_4^+ > Na^+ > K^+$ and for bivalent ions is $Be^{2+} > Mg^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+}$.

TABLE 6
SPECIFIC EFFECTS OF CATIONS AT 30°C
[MnO_4^-] = 13.33 × 10^{-4}; [Ethylamine] = 0.5M; [Diethylamine] = 0.1M;
[Triethylamine] = 0.1M

Cations	Li^+	Na^+	K^+	Be^{2+}	Mg^{2+}	Zn^{2+}	Ni^{2+}	Al^{3+}
Ethylamine (5M H_2SO_4)								
10^3K_1(min^{-}1) (0.2M salt)	7.99	6.84	6.75	9.30	8.91	8.55	7.94	8.41
10^3K_1(min^{-1}) (0.4M salt)	9.35	7.22	6.98	12.87	12.45	11.55	9.55	10.97
Increase of K_1 per cent	16.75	5.56	3.41	49.12	39.72	35.08	20.27	30.43
Diethylamine(5M H_2SO_4)								
10^3K_1(min^{-1}) (0.2M salt)	10.28	6.45	6.31	9.16	8.70	8.56	7.37	9.58
10^3K_1(min^{-1}) (0.4M salt)	17.36	6.86	6.62	13.89	12.35	12.06	8.55	13.45
Increase of K_1 per cent	68.94	6.69	4.91	51.62	41.72	40.88	16.01	40.40
Triethylamine (4M H_2SO_4)								
10^3K_1(min^{-1}) (0.2M salt)	4.96	4.58	4.47	5.33	5.23	4.86	5.34	4.78
10^3K_1(min^{-1}) (0.4M salt)	6.28	5.01	4.82	7.16	6.98	6.18	6.35	5.69
Increase of K_1 per cent	26.67	9.39	7.83	34.32	33.19	26.89	18.69	18.75

The examination of the Tables 6 and 7 shows that the effect on the rate due to added neutral salts is due predominently to the cations, the nature of many of the anions having little effect. Thus the rate is better correlated with the concentration of a specific cation than with an anion. This specific effect of cations might be due to incorporation of a cation into the activated complex[18]. It is also possible that the specific cationic effect is due to the more generalised influence of the reactants and atmosphere on the activity coefficients of the reactants and activated complex. And it may also be reasonable that cations having different ionic radii might effect activity coefficients and therefore rates differently[19]. The greater specific ionic effect in the case of beryllium and magnesium is due to their smaller size and higher charge. The cations of these elements are significantly better complex formers than those of the preceding group[21]. Beringer and Gindler[20] in discussing kinetic effects of added inert electrolytes conclude that from kinetic data only the choice is difficult, if not impossible. From our data and above interpretations, we may suggest that the specific effects of anions and cations depend more or less on their nature *i.e.*, various physico-chemical properties and also on their complexing tendency.

Mechanism:

The following mechanism is in accordance with the experimental results and discussion.

$$H^+ + MnO_4^- \xrightleftharpoons{K_1} HMnO_4 \qquad \text{(i)}$$

TABLE 7

SPECIFIC EFFECTS OF ANIONS AT 30°C [MnO_4^-] = 13.33×10^{-4} M; [Ethylamine] = 0.5M; [Diethylamine] = 0.1M; [Triethylamine] = 0.1M

Anions	PO_4^{3-}	SO_4^{2-}	HSO_4^-	NO_3^-	CH_3COO^-	ClO_4^-
Ethylamine (5M H_2SO_4)						
$10^3K_1(min^{-1})$(0.2M salt)	9.55	6.84	7.45	6.76	6.69	6.64
$10^3K_1(min^{-1})$(0.4M salt)	13.12	7.22	8.71	7.07	6.87	6.79
Increase of K_1 per cent	37.38	5.56	16.91	4.58	2.69	2.26
Diethylamine (5M H_2SO_4)						
$10^3K_1(min^{-1})$ (0.2M salt)	9.56	6.45	7.62	6.36	6.29	6.21
$10^3K_1(min^{-1})$ (0.4M salt)	14.84	6.86	9.74	6.69	6.53	6.33
Increase of K_1 per cent	55.27	6.69	27.80	5.19	3.81	1.93
Triethylamine (4M H_2SO_4)						
$10^3K_1(min^{-1})$ (0.2M salt)	6.40	4.58	5.74	4.39	4.32	4.26
$10^3K_1(min^{-1})$ (0.4M salt)	10.26	5.01	8.29	4.72	4.57	4.41
Increase of K_1 per cent	60.32	9.39	44.42	6.36	5.79	3.52

$$CH_3CH_2NR'R'' + H^+ \overset{K_2}{\rightleftharpoons} CH_3CH_2\overset{+}{N}HR'R'' \qquad \text{(ii)}$$

$$CH_3CH_2\overset{+}{N}HR'R'' + HMnO_4 + H_2O \xrightarrow[\text{slow}]{K} CH_3\dot{C}H\overset{+}{N}HR'R'' + HMnO_4^- + H_3O^+ \qquad \text{(iii)}$$

$$CH_3\dot{C}HH\overset{+}{N}R'R'' + HMnO_4 \xrightarrow{\text{fast}} CH_3CH{=}\overset{+}{N}R'R'' + HMnO_4^- + H^+ \qquad \text{(iv)}$$

$$CH_3CH{=}\overset{+}{N}R'R'' + H_2O \xrightarrow{\text{fast}} CH_3CHO + NHR'R'' + H^+ \qquad \text{(v)}$$

where $R' = R'' = H$, $R' = H$ and $R'' = C_2H_5$, $R' = R'' = C_2H_5$ for ethylamine, diethylamine and triethylamine respectively.

The above mechanism leads us to give the following rate of expression.

$$\frac{-d[MnO_4^-]}{dx} = \frac{KK_1K_2[H^+]^2[H_2O][MnO_4^-][C_2H_5NR'R'']}{1 + K_1[H^+]}$$

The cleavage of C–H bond in the rate determining step (iii) supports the proposal of Stewart[22(a)] that oxidation of amines by permanganate involves an initial attack on the C–H bond adjacent to the nitrogen. Similar types of C–H bond breaking mechanisms in the case of amines have been proposed by many workers.[2,3,22(a),23–26] In the present case of moderately concentrated acid media (>20%), the formation of more powerful oxidant $HMnO_4$ is due to the protonation of the oxidant.[22(b)] The values of ω, ω^* and ϕ parameters (Table 4) confirms the role of water molecule as a proton abstracting agent in the rate controlling step.

The values of energies of activation, entropies of activation and frequency factors support the cleavage of C-H bond in step (iii) (Table 5). Similar orders of thermodynamic parameters have been reported by Wiberg and Stewart[27] for the oxidation of number of aldehydes in which C–H bond cleavage taken place. Further the negative entropy of activations and effects of ionic strength support the interaction between an uncharged molecule and an ion in the rate determining step[28].

Permanganate substrate system in moderately concentrated acid media, reduce mercuric chloride to mercurous state. It can, therefore, be inferred that the free radicals responsible for the reduction of Hg^{2+} ions are produced in the oxidation-reduction reactions[29].

The manganate formed in the reaction path reacts to give manganese dioxide as in equation (vi).

$$3MnO_4^{2-} + 2H_2O \rightarrow 2MnO_4^- + MnO_2 + 4OH^- \quad \text{(vi)}$$

This reaction is too fast to enter into the kinetics under concentrated acid media. The dissolution of MnO_2 is helped by hydrogen ion concentration[30].

A number of reaction mixtures containing amine and permanganate with appropriate concentrations of mineral acids have been studied at 30°C. Actual concentration of the substrates reacting with permanganate has been determined.[22(c)] The stoichiometry of the reaction between permanganate and substrate is given by the equation

$$2MnO_4^- + 3C_2H_5NR'R'' + 2H^+ \rightarrow 3CH_3CHO + 3NHR'R'' + 2MnO_2 + H_2O \quad \text{(vii)}$$

The proposed mechanism is further supported by the analysis of products. Ammonia has been detected as ammonium ions in the solution in case of oxidation of ethylamine. Acetaldehyde has been detected as the oxidation product for all the amines studied. As given by Feigl, acetaldehyde was detected with morpholine and sodium nitroprusside[31]. The production of acetaldehyde supports the statement of Rawalay and Schetcher that primary, secondary and tertiary amines containing carbon α to nitrogen are oxidised to the corresponding aldehyde(s) and/ ketone(s) by permanganate.

The rates of oxidation of ethyl, diethyl and triethyl amines by potassium permanganate in moderately concentrated sulphuric acid and perchloric acid media are in the order.

Triethylamine > Diethylamine > Ethylamine

The order of the relative reactivities of the amines, putforth above, is similar to that given by Roseblatt[3] and Perrine[26], for primary, secondary and tertiary amines. As we move from primary to secondary and then to tertiary, the number of C–H bonds α to nitrogen are increased. Probably this increment of C–H bonds adjacent to nitrogen may be the reason for increasing order of activity.

ACKNOWLEDGEMENT

Thanks to the authorities of Government College, Rajahmundari for providing facilities.

REFERENCES

1. S.S. Rawalay and H. Schechter, *J. Org. Chem.*, **32,** 3129 (1967).

2. M.M. Wei and R. Stewart, *J. Am. Chem. Soc.*, **88,** 1974 (1966).
3. D.M. Rosenblatt, G.T. Davis, L.A. Hull and G.D. Forberg, *J. Org. Chem.*, **33,** 1949 (1968).
4. (a) H. Schechter, S.S. Rawalay and M. Tubis, *J. Am. Chem. Soc.*, **86,** 1701. (1964)
   (b) H. Schechter and S.S. Rawalay, *J. Am. Chem. Soc.*, **86,** 1706 (1964).
5. K. Kindler, Ann., **43,** 187 (1923).
6. A.I. Vogel, "A Text Book of Quantitative Inorganic Analysis", Longman Green and Co. Ltd., p. 282 (1964).
7. S. Siggia, "Quantative Organic Analysis via Functional Groups" John Wiley & Sons, Inc., p. 423 (1963).
8. R.N. Mehrotra, *J. Chem. Soc.*, **B,** 1123 (1968).
9. P.S. Sankhla and R.N. Mehrotra, *Indian J. Chem.*, **10,** 1077 (1972).
10. J.F. Bunnett, R.L. McDonald and F.P. Olsen, *J. Am. Chem. Soc.*, **96,** 2855 (1974).
11. L. Zücker and L.P. Hammett, *J. Am. Chem. Soc.*, **61,** 2791 (1939).
12. L.P. Hammett, "Physical Organic Chemistry", McGraw Hill, New York, N.Y., p. 267–277 (1940).
13. J.F. Bunnett, *J. Am. Chem. Soc.*, **83,** 4956, 4968, (1961).
14. J.F. Bunnett and F.P. Olsen, *Can. J. Chem.* **44,** 1899, 1917 (1966).
15. M.A. Paul and F.A. Long, *Chem. Revs.*, **57,** (1957).
16. A.A. Frost and R.G. Pearson, "Kinetics and mechanism" John wiley & Sons, Inc., Now York, p. 1951–53 (1965).
17. A.K. Wadhawan, P.S. Sankhla and R.N. Mehrotra, *Indian J. Chem.*, **11,** 568 (1973).
18. J.C. Sheppard and A.C. Wahl, *J. Am. Chem. Soc.*, **79,** 1020 (1957).
19. G. Scatchard, *Natl. Bur. Standard Circular,* 524, 185 (1953).
20. F.M. Beringer and B.M. Gindler, ________ , **77,** 3200 (1955).
21. R.T. Sanderson, Inorganic Chemistry, East-West Press, pp. 394–401 (1971).
22. R. Stewart in "Oxidation in Organic Chemistry", Edited by K.B. Wiberg, Part A, Academic Press, New York (a) pp. 1–61; (b) p. 57; (c) p. 17.
23. D.H. Rosenblalt, A.J. Hayes, Jr., B.L. Harrison, R.A. Streaty and K.A. Moore, *J. Org. Chem.*, **28,** 2790 (1963).
24. E. Muller, Ed. 'Houben-Weyl's Methods of Organic Chemistry' Vol. XI/1, George Thieme Publishing Co., Stuttgart, p. 976–984 (1957).
25. N.J. Leonard and D.F. Morrow, *J. Am. Chem. Soc.*, **67,** 49 (1945).
26. T.D. Perrine, *J. Org. Chem.*, **16,** 1303 (1951).
27. K.B. Wiberg and R. Stewart, *J. Org. Chem.*, **77,** 1791 (1955).
28. M.C. Agarwal and S.P. Mushran, *J. Phys. Chem.*, **75,** 838 (1971).
29. A.Y. Durmmond and W.A. Waters, *J. Chem. Soc.*, 2837, 3119 (1953).
30. Y.K. Gupta and S. Ghosh, Akademische Verlags Gesellischeff Gust and Prtigh-G, Leipzig, Part-III (1958).
31. F. Feigl, 'Spot Tests in Organic Chemistry', Elsevier Publishing Company, Amsterdam, p. 331 (1956).

(*Received:* 30 January 1993; *Accepted:* 23 September 1993) AJC-687