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A mechanistic investigation of the oxidation of *N*,α-diphenylnitrones by dichloramine-T in aqueous acetonitrile medium – a non-linear Hammett plot

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Abstract: The kinetics of oxidation of a number of *meta*- and *para*-substituted *N*,α-diphenylnitrones (nitrone) by dichloramine-T (DCT) was investigated in the presence of alkali in aqueous acetonitrile medium. The order with respect to DCT was one and to OH^- an inverse fractional order. The reaction was first order with respect to nitrone. Both electron releasing and withdrawing substituents suppress the reaction rate. The observed rate constant for the substituents were plotted against the Hammett constant, σ, and a non-linear concave downward curve was obtained. The electron withdrawing substituents fall on one side of the curve, having a negative ρ value and the electron releasing substituents fall on the other side, with a positive ρ value. A mechanism is proposed and the derived rate law is in conformity with the observed results.

Keywords: nitrones; kinetics; dichloramine-T; non-linear concave downward curve.

INTRODUCTION

Many oxidation reactions[1–11] have been performed using dichloramine-T (DCT). DCT is an effective oxidizing and also chlorinating agent. The kinetics and oxidation of nitrone and substituted nitrones[12–16] have already been reported. However, there is no systematic kinetic report on the oxidation of some substituted *N*,α-diphenylnitrones by *N*-halo compounds. In this paper, results on the kinetics of oxidation of some *meta*-and *para*-substituted *N*,α-diphenylnitrons with dichloramine-T (DCT) in aqueous acetonitrile in the presence of sodium hydroxide are reported.

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EXPERIMENTAL

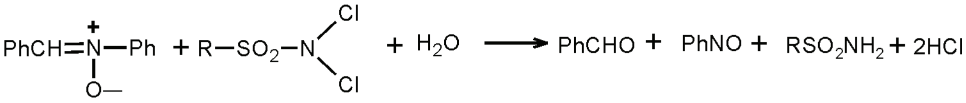
Dichloramine-T was prepared by the chlorination of *p*-toluenesulphonamide.[17] *N*,α-diphenylnitrone and substituted *N*,α-diphenylnitrones were prepared by literature methods.[18] The purity of the nitrones were checked by their melting point, mixed melting point and the TLC method. AnalaR grade sodium hydroxide and sodium perchlorate, and purified acetonitrile were used. Doubly distilled water was employed throughout this study.

Kinetic measurements

For the kinetic runs, a measured amount of DCT pre-equilibrated at 35 °C was rapidly added to a thermally equilibrated mixture containing the appropriate amounts of the nitrone, alkali, acetonitrile and water. The progress of the reaction was monitored for two half lives by the iodometric determination of unreacted DCT in a measured aliquot withdrawn at regular intervals of time. The first-order rate constants were reproducible within ±3 %.

Stoichiometry and product analysis

Stoichiometric runs, performed with an excess of DCT in the presence of sodium hydroxide, revealed that one mole of the oxidant was consumed by one mole of nitrone:



R = CH_3–C_6H_4–

For identification of the product, an excess of oxidant was mixed with a substrate under kinetic conditions. After completion of the reaction, the reaction mixture was extracted with chloroform. The solvent was removed under reduced pressure. Two spots were obtained; products were identical with benzaldehyde and nitrosobenzene. The crude products were separated by column chromatography, benzene–chloroform as the eluent (80 % benzene–chloroform, silica gel 60–120 mesh). The melting point of the obtained solid product was found to be 67 °C which is almost identical to the melting point of the nitrosobenzene (m.p. 68 °C). The other liquid product, benzaldehyde, was confirmed by its semicarbazone (m.p. 221 °C; lit. 222 °C) and 2,4-diphenylhydrazone (m.p. 237 °C; lit. 239 °C) and 2,4-diphenylhydrazone (m.p. 237 °C; lit. 239 °C) derivatives. The recorded IR spectrum of nitrosobenzene, exhibiting three bands at 1626, 1500 and 1019 cm^{-1}, attributed to the stretching frequency of C–N, one sharp band at 1452 cm^{-1}, due to the stretching vibration of N–O, and band at 530 cm^{-1}, due to ring deformation and the CNO bending vibration, was similar to that of the authentic sample.[19]

RESULTS AND DISCUSSION

The reaction was found to be first order with respect to the disappearance of dichloramine-T (DCT), as evidenced by the good linearity in the plot of log titre *versus* time. The pseudo-first order rate constant increased with increasing DCT concnetration (Table I).

The rate constant increased with increasing nitrone concentration (Table I). The plot of log k_{obs} *versus* log c(nitrone) for all the studied compounds was found to be linear with a slope of unity, indicating a first order kinetics with respect to nitrone. The double reciprocal plot of $1/k_{obs}$ *versus* $1/c$(nitrone) was linear with a finite intercept on the rate axis, indicating that the complex was formed before the rate-determining step in the reaction.

The effect of alkali has been studied by varying the concentration of $OH^–$ at a given substrate concentration. The plot of log k_{obs} *versus* log $c(OH^–)$ showed a fractional order with respect to $OH^–$ (Table II). The insignificant effects of sodium perchlorate on the reaction rate indicates that the reaction may be between dipoles (Table II) and neutral molecules.[20]

TABLE I. Effect of *c*(DCT) and *c*(nitrone) on the reaction rate at 35 °C. $c(OH^-) = 5.0\times10^{-3}$ mol dm^{-3}; AN–H_2O = 50 % (v/v); $c(NaClO_4)$ = 0.10 mol dm^{-3}

c(DCT) / 10^{-3} mol dm^{-3}	*c*(nitrone) / 10^{-2} mol dm^{-3}	k_{obs} / 10^{-4} s^{-1}
0.50	1.00	2.4
0.75	1.00	3.5
1.00	1.00	4.8
1.25	1.00	5.3
1.50	1.00	6.4
2.00	1.00	7.4
1.00	0.50	2.7
1.00	1.00	4.8
1.00	1.50	6.5
1.00	2.00	7.6
1.00	2.50	9.9
1.00	3.00	11

TABLE II. Effect of the variation of $c(OH^-)$ and $c(NaClO_4)$ on the reaction rate at 35 °C. *c*(DCT) = 1.00×10^{-3} mol dm^{-3}; *c*(nitrone) = 1.00×10^{-2} mol dm^{-3}; AN–H_2O = 50 % (v/v)

$c(OH^-)$ / 10^{-3} mol dm^{-3}	$c(NaClO_4)$ / 10^{-2} mol dm^{-3}	k_{obs} / 10^{-4} s^{-1}
2.50	10	3.6
3.75	10	4.0
5.00	10	4.8
6.25	10	5.8
7.50	10	6.4
5.00	2.5	4.5
5.00	8.7	4.6
5.00	10	4.8
5.00	12.5	4.9
5.00	15	5.0
5.00	18	5.4
5.00	20	5.7

The rate increased with increasing concentration of *p*-toluenesulphonamide (PTS), indicating a shift of the free hydration equilibrium towards the left during the production of HOCl (Table III). The rate increased with increasing $[Cl^–]$ (Table III). The rates of oxidation of nitrones were determined in solvents containing differrent amounts of acetonitrile. The k_{obs} value increased with increasing amount of acetonitrile in the medium (Table IV), which shows neutral and dipole interaction in the activated complex. The oxidation of nitrones by DCT in an atmosphere of nitrogen failed to induce polymerization of acrylonitrile. Furthermore, the addition of acrylonitrile did not affect the rate. This indicates that a one electron oxidation giving rise to free radicals is unlikely in the present reaction.[20e]

TABLE III. Effect of *p*-toluenesulphonamide (PTS) and Cl^- concentration on the reaction rate at 35 °C. c(DCT) = 1.00×10^{-3} mol dm^{-3}; c(nitrone) = 1.00×10^{-2} mol dm^{-3}; $c(OH^-) = 5.0\times10^{-3}$ mol dm^{-3}; AN–H_2O = 50 % (v/v)

c(PTS) / 10^{-3} mol dm^{-3}	$c(Cl^-)$ / 10^{-2} mol dm^{-3}	k_{obs} / 10^{-4} s^{-1}
0.00	–	4.8
2.5	–	6.0
5.0	–	7.1
7.5	–	10
10	–	15
–	2.5	7.6
–	5.0	7.8
–	7.5	9.1
–	10	20

TABLE IV. Effect of the dielectric constant on the reaction rate at 35 °C. c(DCT) = 1.00×10^{-3} mol dm^{-3}; c(nitrone) = 1.00×10^{-2} mol dm^{-3}; $c(OH^-) = 5.0\times10^{-3}$ mol dm^{-3}; $c(NaClO_4) = 0.10$ mol dm^{-3}

AN–H_2O, % (v/v)	k_{obs} / 10^{-4} s^{-1}
35	2.8
40	3.6
45	4.2
50	4.8
55	5.8
60	6.7

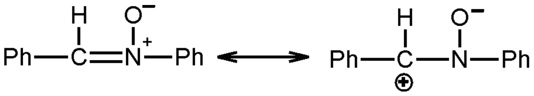
In order to investigate the effect of temperature on the reaction rate, the reaction was performed at 25, 30, 35 and 40 °C. The plot of ln (k_2/T) *versus* $1/T$ was found to be linear.[21] The rate constant and thermodynamic parameters are tabulated in Table V.

Mechanism and rate law

The order with respect to both DCT and nitrone was unity and with respect to $OH^–$ was fractional. The addition of sodium perchlorate or acrylonitrile had an insignificant effect on the rate of the reaction. The addition of toluene, PTS or $Cl^–$ increased the reaction rate.

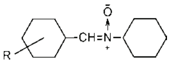
The observed stoichiometry for the reaction was 1:1 and the major oxidation products are found to be benzaldehyde and nitrosobenzene. Based on the above observations, a probable mechanism and rate law for the oxidation of *N*,α-diphenylnitrones by dichloramine-T is given below.

The substrate (nitrone), which behaves as an iminimum salt[22], exists in two resonance forms given in Eq. (1):

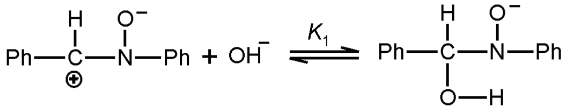


(1)

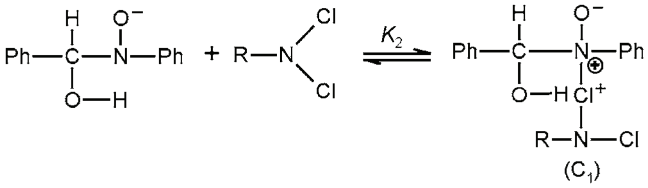
TABLE V. The rate constant and thermodynamic parameters for the oxidation of substituted nitrones by DCT. c(DCT) = 1.00×10^{-3} mol dm^{-3}; c(nitrone) = 1.00×10^{-2} mol dm^{-3}; c(OH$^-$) = 5.0×10^{-3} mol dm^{-3}; c(NaClO$_4$) = 0.10 mol dm^{-3}

	k_2 / 10^{-2} dm^{-3} mol^{-1} s^{-1}				$\Delta H^\#$ kJ mol^{-1}	$-\Delta S^\#$ J K^{-1} mol^{-1}	$\Delta G^\#$ kJ mol^{-1}	E_a kJ mol^{-1}	*R*	*SD*
	T / K									
	303	308	313	318						
H	4.17	4.75	5.43	6.27	19.15	208.31	83.33	29.74	0.999	0.007
p-Me	1.33	1.60	2.37	3.11	44.49	134.51	85.92	47.07	0.990	0.064
p-OMe	1.18	1.38	2.92	2.91	52.88	107.73	86.00	55.46	0.922	0.218
p-F	2.50	2.98	4.07	5.34	38.83	147.88	84.37	41.41	0.992	0.048
p-Cl	2.22	2.86	3.94	5.08	42.33	137.11	84.56	45.92	0.998	0.022
p-Br	2.02	2.62	3.83	4.86	45.70	126.78	84.50	49.11	0.995	0.041
p-NO$_2$	0.76	1.59	2.75	3.12	74.38	39.07	86.41	76.96	0.961	0.208
m-Me	2.50	3.45	4.36	5.65	40.38	142.31	84.21	42.96	0.998	0.024
m-F	2.03	2.61	3.79	4.66	43.55	134.47	84.96	45.93	0.994	0.046
m-Cl	2.08	2.50	3.28	4.41	37.52	152.72	84.56	40.40	0.992	0.046
m-Br	1.29	2.46	3.15	4.42	60.72	80.06	85.38	63.30	0.978	0.126
m-NO$_2$	1.00	1.45	2.80	3.22	62.27	71.15	84.18	66.85	0.974	0.146

The attack of an electrophile occurs at the nitrogen atom rather than the carbon atom.



(2)



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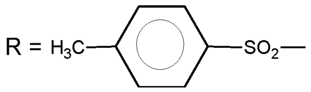
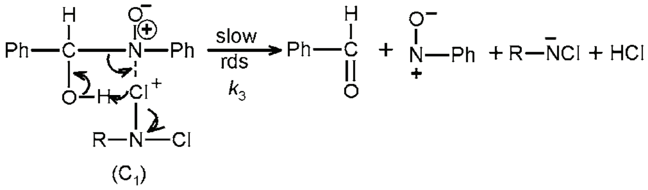
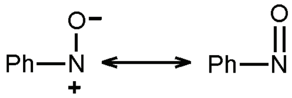




(4)

$$\mathrm{R{-}\bar{N}Cl + H_2O \xrightarrow{fast} R{-}NHCl + OH^-} \qquad (5)$$



$$\mathrm{Ph{-}\overset{O^-}{\underset{+}{N}} \longleftrightarrow Ph{-}\overset{O}{\overset{\|}{N}}} \qquad (6)$$

$$\text{Rate} = k_3c(\mathrm{C}_1) \qquad (7)$$

$$c(\mathrm{C}_1) = \frac{K_1\,K_2\,c(\mathrm{S_T})\,c(\mathrm{OH}^-)\,c(\mathrm{DCT})}{1+K_1\,c(\mathrm{OH}^-)} \qquad (8)$$

$$\frac{-\mathrm{d}\,c(\mathrm{DCT})}{\mathrm{d}t} = \frac{K_1K_2k_3c(\mathrm{S_T})\,c(\mathrm{OH}^-)\,c(\mathrm{DCT})}{1+K_1c(\mathrm{OH}^-)} \qquad (9)$$

$$k_{\mathrm{obs}} = \frac{K_1K_2k_3\,c(\mathrm{S_T})\,c(\mathrm{OH}^-)}{1+K_1\,c(\mathrm{OH}^-)} \qquad (10)$$

or

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{K_1K_2k_3c(\mathrm{S_T})\,c(\mathrm{OH}^-)} + \frac{1}{K_1k_3\,c(\mathrm{S_T})}$$

where $c(\mathrm{S_T})$ = c(nitrone$_\mathrm{T}$)

A double reciprocal plot of k_{obs} *versus* $c(\mathrm{OH}^-)$ is linear and the values of K_1, K_2 and k_3 are obtained from the slope and intercept, respectively. The obtained values of $K_1 = 235$ and $K_2k_3 = 9.33\times10^{-2}$ are consistent with the rate law.

Effect of substituents on the reaction rate

As an extension of the present investigation, the kinetics of the oxidation of some *meta*- and *para*-substituted *N*,*α*-diphenylnitrones with DCT was followed at four different temperatures (25–40 °C). The second-order rate constant and the thermodynamic parameters were calculated using the Eyring[21] plot of log (k_2/T) against $1/T$, which were linear and the obtained data are given in Table V.

As can be seen from Table V, the entropy of oxidation was not constant for all the substituents. One of the conditions necessary for the applicability of the linear free energy relationship is the constancy of the entropy of activation.[23,24] However, in most reaction series, this is not the case. If the Hammett equation is valid at one temperature, the condition for its validity at any other temperature is a linear relationship between the enthalpies and entropies and this is called the isokinetic relationship:[23,24]

$$\Delta H^{\#} = \Delta H_0^{\#} + \beta\Delta S^{\#}$$

A plot of $\Delta H^{\#}$ *vs.* $\Delta S^{\#}$ (Fig. 1) gave a straight line and the isokinetic temperature (β), obtained from the slope, was 326 K, which is greater than the experimental temperature, indicating that the reaction is enthalpy controlled. The linear isokinetic correlation implies that all the nitrones are oxidized by the same mechanism and the changes in the reaction rate are governed by changes in both the enthalpy and entropy of activation. This is further supported by fact that E_a values are the lowest for the fastest reaction and higher for the slowest reaction.

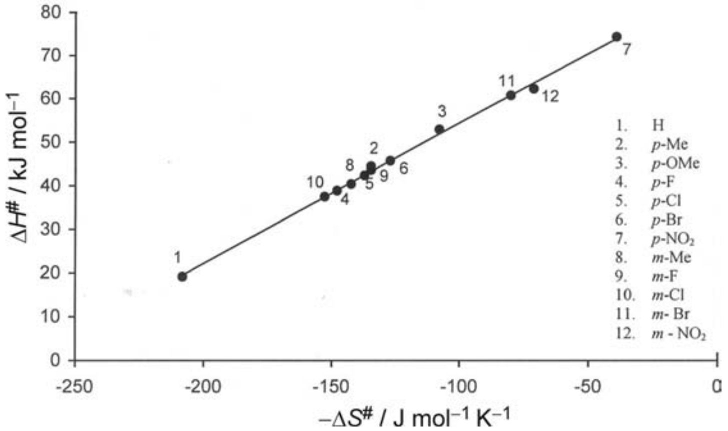


Fig. 1. The relationship between $\Delta H^{\#}$ and $\Delta S^{\#}$ for oxidation of nitrones by dichloramine-T.

Exner[25] criticized the validity of such a linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ as these quantities depend on each other. When measurements at two temperatures are made, the experimental data can be treated by the following equation:[26,27]

$$\log k_2(T_2) = a + b\log k_2(T_1)$$

where $T_2 > T_1$.

The good correlation obtained when log k_2(318 K) was plotted against log k_2(308 K) (Fig. 2) (R = 0.982; slope = 0.680) shows that the reactions under investigation followed the same mechanism. The constancy of the $\Delta G^{\#}$ values also confirms that the reactions of all the substituted compounds followed a common mechanism. The negative $\Delta S^{\#}$ values implies the formation of an ionic transition state with an extensive charge separation, which may have a high degree of solvation and hence loss of entropy.

Deviation from the Hammett relationship

Application of the Hammett equation with the usual substituent constant σ to the log k_{obs} data of the *meta*- and *para*-substituted N,α-diphenylnitrones resulted in a concave downward curve (Fig. 3). Similar types of non-linear Hammett plots were observed previously in some reaction kinetics.[28–30]

The obtained non-linear concave downwards type of Hammett plot (Fig. 3) is a composite of two straight lines, one with a positive ρ value and the other with a negative ρ value. A negative ρ value indicates the nucleophilic carbon is more positively charged in the transition state than in the reactant, while a positive ρ value indicates dispersal of the positive charge.[3] The values of the negative and positive ρ values, ρ^+ and ρ^-, respectively, at different temperature are given in Table VI.

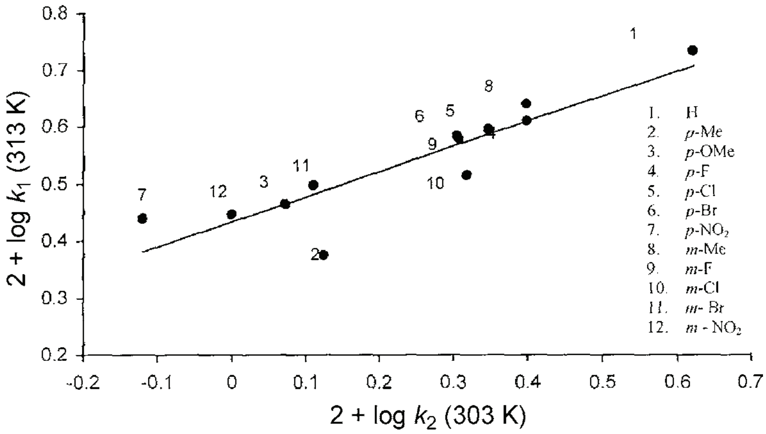


Fig. 2. Exner's plot.

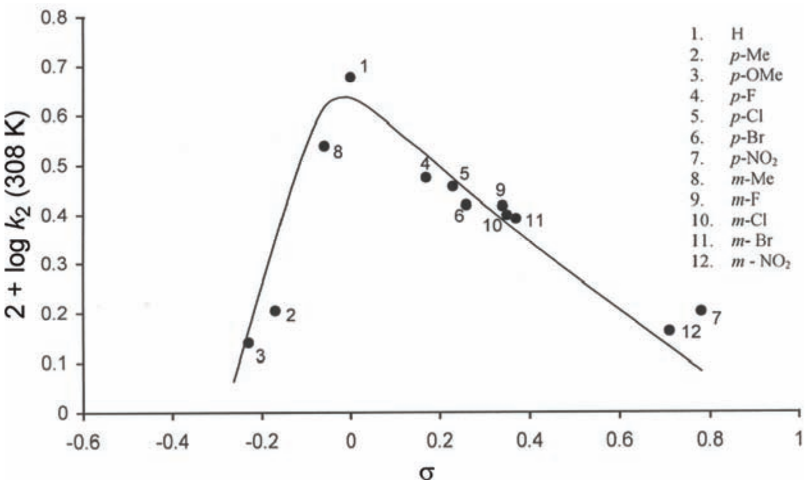


Fig. 3. Hammett plot.

TABLE VI. Values of ρ at different temperatures

t / °C	ρ^+	ρ^-
25	1.076	0.747
30	0.456	0.428
35	0.613	0.777
40	0.460	0.495

The reason for a break in the Hammett plot is either a change in the reaction mechanism or a change in the rate-determining step with change in the nature of the substituents.

In this reaction, a non-linear Hammett plot was obtained due to a change in the transition state in the reaction mechanism with respect to substituents because the isokinetic plot and the Exner plot gave a good correlation.

CONCLUSIONS

The oxidation of nitrones by DTC is of fractional order with respect to OH^- and first order with respect to DTC and nitrone. Under the employed experimental conditions, nitrones are oxidized to benzaldehyde and nitrosobenzene. The high negative entropy of activation suggests the formation of a complex in the slow step. The isokinetic and Exner plots show that the oxidations of all the studied nitrones follow a common mechanism. The obtained concave Hammett plot indicates a change of the transition state with respect to the substituent on the benzene nucleus under the employed experimental conditions.

ИЗВОД

МЕХАНИСТИЧКО ПРОУЧАВАЊЕ ОКСИДАЦИЈЕ *N*,*α*-ДИФЕНИЛНИТРОНА ПОМОЋУ ДИХЛОРАМИНА-Т У ВОДЕНОМ РАСТВОРУ АЦЕТОНИТРИЛА: НЕЛИНЕАРНИ HAMMETT-ОВ ГРАФИК

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Кинетика оксидације серије *мета*- и *пара*-суптитуисаних *N*,*α*-дифенилнитрона (нитрон) помоћу дихлорамина-Т (DCT) проучавана је воденом растору ацетонитрила у присуству базе. Реакција је првог реда у односу на DCT, и инверзног фракционог реда у односу на OH^-. Реакција је првог реда у односу на нитрон. Како електрон-донорски, тако и електрон-привлачни супституенти, смањују брзину реакције. Када су константе брзине за супституенте дате у односу на Hammett-ову константу σ, добијена је нелинеарна силазна конкавна крива. Електрон-привлачни супституенти налазе се са једне стране криве са негативном ρ вредношћу, док су електрон-донорски супституенти са друге стране криве са позитивном ρ вредношћу. Предложени механизам и изведена брзина реакције су у сагласности са добијеним резултатима.

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REFERENCES

1. E. Bishop, V. J. Jennings, *Talanta* **1** (1958) 197
2. T. Higuchi, K. Ikeda, A. Hussain, *J. Chem. Soc. B* (1967) 546
3. T. Higuchi, A. Hussain, *J. Chem. Soc. B* (1967) 549
4. H. M. K. Naidu, D. S. Mahadevappa, *Indian J. Chem.* **13** (1975) 976
5. N. M. Made Gowda, A. A. Anamlamurthy, D. S. Mahadevappa, *Indian Acad. Sci*. **44** (1975) 5

6. H. M. K. Naidu, D. S. Mahadevappa, *Curr. Sci.* **45** (1976) 216
7. Rangaswamy, D. S. Mahadevappa, *J. Indian Chem. Soc*. **55** (1978) 60
8. H. S. Yathirajan, Rangaswamy, D.S. Mahadevappa, *J. Indian Chem. Soc*. **56** (1979) 421
9. H. S. Yathirajan, D. S. Mahadevappa, Rangaswamy, *Talanta* **27** (1980) 52
10. B. Thimme Gowda, J. Ishwara Bhatt, *J. Indian Chem. Soc.* **65** (1987) 159
11. B. Thimme Gowda, N. S. Sherigara, *Indian J. Chem.* **26A** (1987) 930
12. M. Uma, M. Gopalakrishnan, J. Jayabharathi, V. Thanikachalam, *Indian J. Chem.* **34B** (1995) 612
13. M. Uma, M. Gopalakrishnan, J. Jayabharathi, V. Thanikachalam, *J. Indian Chem. Soc.* **73** (1996) 92
14. M. Gopalakrishnan, J. Jayabharathi, V. Thanikachalam, *Asian J. Chem*. **11** (1999) 1459
15. M. Gopalakrishnan, M. Uma, J. Jayabharathi, V. Thanikachalam, *Afinidad* **59** (2002) 688
16. M. Uma, M. Gopalakrishnan, J. Jayabharathi, V. Thanikachalam, *Oxid. Commun.* **30** (2007) 625
17. a) O. Tomicek, J. Valcha, *Collect. Czech, Chem. Commun.* **16** (1951) 113; b) J. E. Leffler, *J. Org. Chem.* **20** (1955) 1202
18. a) H. Studinger, K. Niescher, *Helv. Chim. Acta* **2** (1919) 554; b) P. Grammaticakis, *Bull. Soc. Chim. Fr.* (1951) 889; c) Chem. Abstr. **46** (1952) 11133; d) V. Bellavita, *Gazz. Chim. Ital.* **65** (1935) 889; e) Chem. Abstr. **30** (1936) 3419; f) E. Bamberger, *Ber. Dtsch. Chem. Ges*. **57** (1924) 2082; g) J. E. Leffler, *J. Chem. Phys*. **23** (1955) 2199
19. a) G. M. Bradley, H. L. Strauss, *J. Phys. Chem*. **79** (1975) 1953; b) R. C. Peterson, *J. Org. Chem*. **29** (1964) 3133
20. a) J. E. Quinlan, E. Amis, *J. Am. Chem. Soc.* **77** (1955) 4187; b) P. D. Sharma, Y. K. Gupta, *J. Chem. Soc., Dalton Trans.* (1972) 52; c) K. S. Gupta, S. Mittal, S. P. Ghosh, *Indian J. Chem*. **19A** (1980) 869; d) C. D. Ritchie, W. F. Sager, *Prog. Phys. Org. Chem.* **2** (1964) 323; e) J. S. Litiler, W. A. Waters, *J. Chem. Soc.* (1959) 1299
21. W. F. K. Wynne-Jones, H. Eyring, *J. Chem. Phys.* **3** (1935) 492
22. H. Bohme, M. Haake, *Adv. Org. Chem*. **9** (1976) 107
23. J. E. Leffler, *J. Org. Chem*. **20** (1955) 1202
24. N. R. Gilkerson, C. A. Gallup, M. M. Jones, *Trans. Kansas Acad. Sci*. **57** (1954) 391
25. a) J. E. Leffler, *J. Chem. Phys*. **23** (1955) 2199; b) O. Exner, *Collect. Czech. Chem. Commun*. **29** (1964) 488; c) O. Exner, *Nature* **201** (1964) 488; d) D. Noyce, A. Bottini, S. Smith, *J. Org. Chem*. **23** (1958) 752
26. B. H. Anderson, W. P. Jancks, *J. Chem. Soc*. **82** (1960) 1773
27. E. Pratt, M. J. Kamlet, *J. Org. Chem.* **28** (1963) 1366
28. J. Hoffmann, J. Klicnar, V. Sterba, M. Vecera, *Collect. Czech. Chem. Commun*. **35** (1970) 1387
29. J. F. Burneu, R. E. Zahler, *Chem. Rev*. **49** (1951) 294
30. S. Meenakshisundaram, M. Amutha, *J. Chem. Res. S* **2** (1999), *J. Chem. Res. M* (1999) 0219.