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## Kinetics and mechanism of the oxidation of some substituted aldonitrones by quinolinium chlorochromate in aqueous DMF medium in the absence and presence of oxalic acid

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**Abstract:** The kinetics of the oxidation of aldonitrones (nitrone) by quinolinium chlorochromate (QCC) was determined in 50 % DMF–water in the absence and presence of oxalic acid in order to study the effect of oxalic acid. It was considered worthwhile to investigate whether it undergoes co-oxidation or just functions as a catalyst in the reaction. The reaction was followed iodometrically. Under the employed experimental conditions, the reaction is first order each with respect to concentration of nitrone, QCC, and oxalic acid and fractional order with respect to H<sup>+</sup> concentration. There was no discernible effect with increasing in ionic strength but the rate of oxidation decreased with decreasing dielectric constant of the medium. Addition of MnSO<sub>4</sub> had a significant and acrylonitrile no effect on the reaction rate. A mechanism involving protonated nitrone and QCC as the reactive oxidant is proposed. The activation parameters were calculated and are presented.

**Keywords:** aldonitrones; quinolinium chlorochromate; isokinetic plot; entropy; enthalpy; free energy; oxalic acid.

### INTRODUCTION

The use of quinolinium chlorochromate (QCC) as an oxidant is well documented for the oxidation of primary and secondary alcohols,<sup>1–3</sup> organic sulphides,<sup>4,5</sup> substituted benzaldehydes,<sup>6,7</sup> benzyl alcohols,<sup>8</sup> aromatic anils,<sup>9</sup> lactic and glycolic acids,<sup>10</sup> methionine,<sup>11</sup> D-fructose,<sup>12</sup> D-mannose,<sup>13</sup> an unsaturated organic substrate,<sup>14</sup> acrylic acid,<sup>15</sup> 2-furaldehyde,<sup>16</sup> D-galactose,<sup>17</sup> etc. Quinolinium chlorochromate exists as a stable yellowish brown crystalline solid. It is freely soluble in water and aqueous solutions of QCC are stable for quite a long period.

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Oxalic acid was found to catalyse the oxidation of organic substrates by Cr(VI).<sup>18–20</sup> A survey of the literature showed that there are only a few reports on the kinetic studies with nitrones (nitrone).<sup>21–26</sup> There is no report on a mechanistic study of the oxidation of nitrones by QCC. Thus, in order to explore the mechanism of oxidation by QCC, the title reaction was studied in aqueous DMF medium.

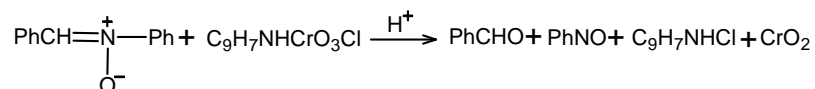
## EXPERIMENTAL

### *Materials and methods*

All the chemicals used were of high purity of mostly either AR or GR grade. Double distilled water was used throughout the work. Aldonitrones<sup>27</sup> and quinoline chlorochromate (QCC)<sup>28</sup> were prepared by known methods and recrystallized from water. The purity of the prepared QCC was checked by the iodometric method (assay 99 %). Nitrone solutions were prepared by dissolving appropriate amount of a recrystallized sample in DMF. The aqueous solution of QCC was obtained by dissolving the compound in double distilled water. Experiments were conducted in a thermostated bath which could maintain the temperature with an accuracy of  $\pm 0.1$  °C.

### *Kinetic studies*

The kinetic studies were carried out in 50 % (v/v) DMF–water medium under pseudo-first order conditions, keeping  $c(\text{nitrone}) \gg c(\text{QCC})$ . The course of the reaction was followed by estimating the unreacted QCC iodometrically. The reaction was followed at four different temperatures. Pseudo-first order rate constants were evaluated from the slopes of the linear plots of  $\log c(\text{QCC})$  versus time. The rate constant,  $k_2$  was calculated using the relation  $k_2 = k_{\text{obs}}/c(\text{nitrone})$ . The reaction mixtures containing excess of QCC over nitrone in absence and presence of oxalic acid were kept for one day. The estimation of the unreacted QCC indicated that one mole of QCC was consumed for one mole of nitrone:



The reaction mixture was extracted with chloroform from an actual kinetic run after completion of the reaction. The reaction mixture was monitored by Co-TLC along with authentic samples of *N*, $\alpha$ -diphenylnitron, benzaldehyde and nitrosobenzene. Then, the products were separated into individual components by column chromatography (silica gel 60–120 mesh) with benzene–chloroform as the eluent. The melting point of the solid product obtained was found to be 67 °C, which is almost identical with the melting point of the nitrosobenzene dimer, m.p. 67.5–68 °C.<sup>29</sup> The IR spectrum was recorded in a KBr pellet, using a model Jasco 700 instrument, in the range 400–4000  $\text{cm}^{-1}$ . Nitrosobenzene exhibits three bands at 1625, 1500 and 1019  $\text{cm}^{-1}$ , attributed to the stretching of C–N; one sharp band at 1452  $\text{cm}^{-1}$ , due to the stretching vibration of N–O, and one band at 530  $\text{cm}^{-1}$ , due to ring deformation and C–N–O bending vibrations.<sup>29</sup> The liquid product was confirmed to be benzaldehyde by its semicarbazone (m.p. 221 °C; literature data: 222 °C<sup>30</sup>) and 2,4-dinitrophenylhydrazone (m.p. 238 °C; literature data: 239 °C<sup>30</sup>) derivatives.

## RESULTS AND DISCUSSION

The kinetics of oxidation of nitrones by QCC was performed in 50 % aqueous DMF in the absence and presence of oxalic acid in order to study the be-

haviour of oxalic acid. It was considered worthwhile to investigate whether it undergoes co-oxidation or just functions as a catalyst in the reaction.<sup>18–20</sup> The reaction was followed iodometrically. In both the cases, *i.e.*, in the absence and presence of oxalic acid, the reaction is first order with respect to QCC. Furthermore, the pseudo-first order rate constant  $k_{\text{obs}}$  was found to be independent of the initial concentration of QCC.

The substrate, aldonitrone, was varied in the concentration range of  $5 \times 10^{-3}$  to  $15 \times 10^{-3}$  mol dm<sup>-3</sup> at 308 K in the absence of oxalic acid and  $5 \times 10^{-3}$  to  $20 \times 10^{-3}$  mol dm<sup>-3</sup> at 308 K in the presence of oxalic acid, keeping all other constituents and conditions constant (Tables I and II). The  $k_{\text{obs}}$  values increased with increasing concentration of nitrones. The plot of  $\log k_{\text{obs}}$  versus  $\log c(\text{nitrone})$  was a straight line with a slope of unity and a plot of  $k_{\text{obs}}^{-1}$  versus  $c(\text{nitrone})^{-1}$  was also linear ( $r = 0.999$ ), passing through the origin, which indicates a first order dependence on  $c(\text{substrate})$ . No complex formation occurred before the rate-determining step in absence of oxalic acid, whereas complex formation occurred before rate-determining step in its presence.

TABLE I. Effect of the variation of  $c(\text{QCC})$ ,  $c(\text{nitrone})$  and  $c(\text{H}^+)$  on the oxidation of nitrones by QCC in the absence oxalic acid at 308 K

$c(\text{QCC}) \times 10^3$ mol dm <sup>-3</sup>	$c(\text{nitrone}) \times 10^2$ mol dm <sup>-3</sup>	$c(\text{HClO}_4) \times 10^3$ mol dm <sup>-3</sup>	% DMF (v/v)	$k_{\text{obs}} \times 10^3$ s <sup>-1</sup>
0.50	1.00	6.00	50	1.530
0.75	1.00	6.00	50	1.480
1.00	1.00	6.00	50	1.527
1.25	1.00	6.00	50	1.519
1.50	1.00	6.00	50	1.536
1.00	0.50	6.00	50	0.756
1.00	0.75	6.00	50	1.141
1.00	1.00	6.00	50	1.529
1.00	1.25	6.00	50	1.918
1.00	1.50	6.00	50	2.308
1.00	1.00	1.50	50	1.184
1.00	1.00	3.00	50	1.364
1.00	1.00	6.00	50	1.529
1.00	1.00	7.50	50	1.705
1.00	1.00	9.00	50	1.852
1.00	1.00	6.00	30	1.650
1.00	1.00	6.00	40	1.592
1.00	1.00	6.00	50	1.529
1.00	1.00	6.00	60	0.844
1.00	1.00	6.00	70	0.642
1.00	1.00	6.00	80	0.546

The influence of  $\text{H}^+$  on the reaction rate was studied by varying the acidity from  $1.5 \times 10^{-3}$  to  $9 \times 10^{-3}$  mol dm<sup>-3</sup> while maintaining the ionic strength constant

at  $\mu = 0.10 \text{ mol dm}^{-3}$  with sodium perchlorate. The concentration of hydrogen ions was found to increase the reaction rate (Tables I and II). It was previously observed that the reaction showed a fractional order dependence on the hydrogen ion concentration in the presence and absence of oxalic acid.<sup>31,32</sup>

TABLE II. Effect of the variation of  $c(\text{QCC})$ ,  $c(\text{nitron})$ ,  $c(\text{H}^+)$  and  $c(\text{H}_2\text{C}_2\text{O}_4)$  on the oxidation of nitrones by QCC in the presence of oxalic acid at 308 K

$c(\text{QCC}) \times 10^3$ mol dm <sup>-3</sup>	$c(\text{nitron}) \times 10^2$ mol dm <sup>-3</sup>	$c(\text{HClO}_4) \times 10^3$ mol dm <sup>-3</sup>	$c(\text{H}_2\text{C}_2\text{O}_4) \times 10^2$ mol dm <sup>-3</sup>	% DMF (v/v)	$k_{\text{obs}} \times 10^3$ s <sup>-1</sup>
0.50	1.00	6.00	1.00	50	2.325
0.75	1.00	6.00	1.00	50	2.285
1.00	1.00	6.00	1.00	50	2.323
1.25	1.00	6.00	1.00	50	2.310
1.50	1.00	6.00	1.00	50	2.245
1.00	0.50	6.00	1.00	50	1.080
1.00	0.75	6.00	1.00	50	1.751
1.00	1.00	6.00	1.00	50	2.323
1.00	1.25	6.00	1.00	50	2.657
1.00	1.50	6.00	1.00	50	3.645
1.00	2.00	6.00	1.00	50	4.621
1.00	1.00	3.00	1.00	50	2.140
1.00	1.00	6.00	1.00	50	2.323
1.00	1.00	7.50	1.00	50	2.450
1.00	1.00	8.50	1.00	50	2.608
1.00	1.00	9.01	1.00	50	2.725
1.00	1.00	6.00	0.50	50	1.108
1.00	1.00	6.00	0.75	50	1.821
1.00	1.00	6.00	1.00	50	2.323
1.00	1.00	6.00	1.50	50	3.550
1.00	1.00	6.00	2.00	50	4.712
1.00	1.00	6.00	1.00	40	2.640
1.00	1.00	6.00	1.00	50	2.323
1.00	1.00	6.00	1.00	60	2.102
1.00	1.00	6.00	1.00	70	1.848
1.00	1.00	6.00	1.00	80	1.624

The effect of oxalic acid on the reaction at 308 K was studied by varying its concentration from  $5 \times 10^{-3}$  to  $20 \times 10^{-3} \text{ mol dm}^{-3}$  at constant concentrations of QCC, nitron and  $\text{HClO}_4$ . The reaction rate increased with increasing concentration of oxalic acid. The results are collected in Table II. The plot of  $\log k_{\text{obs}}$  versus  $\log c(\text{H}_2\text{C}_2\text{O}_4)$  was linear with a slope of unity (*ca.* 1.03;  $r = 0.998$ ) and the order with respect to oxalic acid was one. When the experiment was repeated with oxalic acid in the absence of nitron, there was no oxidation of oxalic acid under these experimental conditions. However, the addition of oxalic acid enhanced the rate of oxidation of nitron. This observation clearly establishes that oxa-

lic acid does not undergo co-oxidation under the experimental conditions employed in this investigation and that it acts only as a catalyst.

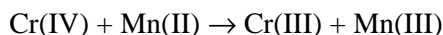
Effect of ionic strength was studied by varying the sodium perchlorate concentration from 0 to 0.15 mol dm<sup>-3</sup>. There was no discernible effect with increasing  $c(\text{NaClO}_4)$  (Table III).

TABLE III. Effect of ionic strength on the oxidation of nitron by QCC in the presence/absence of oxalic acid ( $c(\text{QCC}) = 1.0 \times 10^{-3}$  mol dm<sup>-3</sup>;  $c(\text{nitron}) = 1.0 \times 10^{-2}$  mol dm<sup>-3</sup>;  $c(\text{H}^+) = 6.0 \times 10^{-3}$  mol dm<sup>-3</sup>;  $c(\text{H}_2\text{C}_2\text{O}_4) = 1.0 \times 10^{-2}$  mol dm<sup>-3</sup>; 50 % v/v DMF)

$c(\text{NaClO}_4) / \text{mol dm}^{-3}$	$^a k_{\text{obs}} \times 10^3 / \text{s}^{-1}$	$^b k_{\text{obs}} \times 10^3 / \text{s}^{-1}$
0.00	1.529	2.323
0.050	1.439	2.001
0.075	1.387	1.800
0.100	1.256	1.743
0.125	1.100	1.525
0.150	0.918	1.304

<sup>a</sup>Absence of oxalic acid; <sup>b</sup>presence of oxalic acid

A variation in  $c(\text{Mn(II)})$  in both systems decreased the rate of reduction of Cr(VI) in the HClO<sub>4</sub> medium. The values of  $k_{\text{obs}}$  are listed in Table IV. Manganese(II) has an inhibitory,<sup>33</sup> catalytic<sup>34</sup> or no effect<sup>35,36</sup> in the redox chemistry of Cr(VI) in the presence of organic reductants. The decrease in the rate of Cr(VI) reduction on addition of Mn(II) was attributed to the removal of Cr(IV) by reaction with Mn(II):<sup>37</sup>



Thus, the observed inhibitory effect was due to the one-step, two-electron reduction of Cr(VI).

TABLE IV. Effect of  $c(\text{MnSO}_4)$  on the oxidation of nitron by QCC in the presence/absence of oxalic acid ( $c(\text{QCC}) = 1.0 \times 10^{-3}$  mol dm<sup>-3</sup>;  $c(\text{nitron}) = 1.0 \times 10^{-2}$  mol dm<sup>-3</sup>;  $c(\text{H}^+) = 6.0 \times 10^{-3}$  mol dm<sup>-3</sup>;  $c(\text{H}_2\text{C}_2\text{O}_4) = 1.0 \times 10^{-2}$  mol dm<sup>-3</sup>; 50 % v/v DMF)

$c(\text{MnSO}_4) \times 10^3 / \text{mol dm}^{-3}$	$^a k_{\text{obs}} \times 10^3 / \text{s}^{-1}$	$^b k_{\text{obs}} \times 10^3 / \text{s}^{-1}$
0.00	1.529	2.323
1.00	1.248	2.014
2.00	1.093	1.921
3.00	0.973	1.850
4.00	0.856	1.542

<sup>a</sup>Absence of oxalic acid; <sup>b</sup>presence of oxalic acid

Acrylonitrile added to both the reaction mixtures did not show any polymerization, thereby ruling out the possibility of a free radical mechanism.<sup>38</sup> The effect of dielectric constant on the rate of oxidation was also studied and the rate decreased moderately with decreasing dielectric constant of the medium. This result also supports the involvement of an ion-dipole species in the slow step.<sup>39</sup>

The reactions were also performed at four different temperatures (303, 308, 313 and 318 K) in the absence and presence of oxalic acid (298, 303, 308 and 313 K). The thermodynamic parameters, namely the entropy and enthalpy of activation,<sup>40</sup> were calculated from the linear plot of  $\ln(k_2/T)$  versus  $1/T$ . The calculated values are summarized in Tables V and VI.

TABLE V. Rate constants and activation parameters for the oxidation of nitrones with QCC in the absence of oxalic acid ( $c(\text{QCC}) = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $c(\text{nitron}) = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $c(\text{H}^+) = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $c(\text{NaClO}_4) = 0.100 \text{ mol dm}^{-3}$ ; 50 % v/v DMF)

R	$k_2 \times 10^2 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$				$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$-\Delta S^\ddagger$ J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>	$r$
	T / K							
	303	308	313	318				
H	10.90	15.30	19.84	24.63	40.82	129.38	80.67	0.996
<i>p</i> -Me	11.18	18.39	23.66	30.29	49.49	99.40	80.10	0.984
<i>p</i> -OMe	12.45	18.94	24.95	33.30	49.18	90.71	79.92	0.995
<i>p</i> -F	8.31	14.20	18.23	24.63	53.76	87.77	80.79	0.985
<i>p</i> -Cl	8.09	13.79	16.47	23.25	51.09	96.79	80.91	0.980
<i>p</i> -Br	7.92	12.94	15.26	22.43	50.15	100.26	80.03	0.983
<i>p</i> -NO <sub>2</sub>	4.67	8.43	11.21	13.96	54.80	88.88	82.17	0.973
<i>m</i> -F	5.33	10.12	14.23	18.63	63.21	60.03	81.70	0.960
<i>m</i> -Cl	5.91	10.77	14.47	18.99	58.42	75.04	81.53	0.980
<i>m</i> -Br	5.44	10.91	14.23	18.43	60.54	68.47	81.63	0.966
<i>m</i> -NO <sub>2</sub>	4.93	8.53	12.23	14.80	56.61	83.92	82.45	0.978

TABLE VI. Second-order rate constants and activation parameters for the oxidation of nitrones by QCC in the presence of oxalic acid ( $c(\text{QCC}) = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $c(\text{nitron}) = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $c(\text{H}^+) = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $c(\text{H}_2\text{C}_2\text{O}_4) = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $c(\text{NaClO}_4) = 0.100 \text{ mol dm}^{-3}$ ; 50 % v/v DMF)

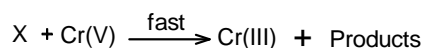
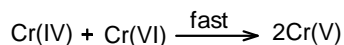
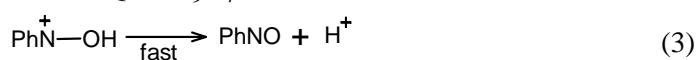
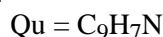
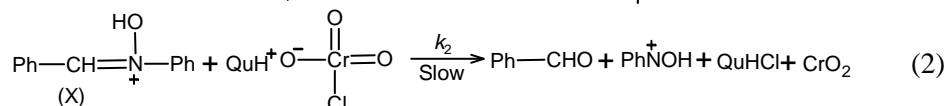
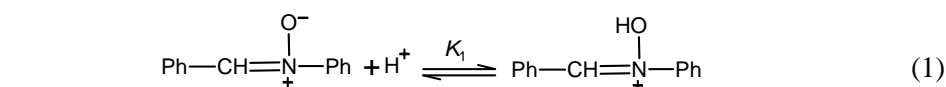
R	$k_2 \times 10^2 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$				$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$-\Delta S^\ddagger$ J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>	$r$
	T / K							
	298	303	308	313				
H	16.17	18.77	23.23	26.66	24.30	179.50	79.57	0.996
<i>p</i> -Me	16.24	18.94	23.65	27.06	26.17	172.32	79.23	0.997
<i>p</i> -OMe	16.37	19.23	24.32	28.88	27.50	167.78	79.17	0.997
<i>p</i> -F	16.08	18.70	22.16	25.87	22.21	185.64	79.39	0.999
<i>p</i> -Cl	15.70	18.12	21.40	24.83	21.36	188.69	79.48	0.999
<i>p</i> -Br	15.44	18.44	20.42	24.37	20.27	192.39	79.53	0.993
<i>p</i> -NO <sub>2</sub>	14.84	15.81	16.59	19.07	9.83	227.92	79.74	0.950

TABLE VI. Continued

R	$k_2 \times 10^2 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$				$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$-\Delta S^\ddagger$ J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>	$r$
	$T / \text{K}$							
	298	303	308	313				
<i>m</i> -F	15.80	16.50	18.54	20.71	16.83	200.37	73.53	0.973
<i>m</i> -Cl	15.58	16.20	18.44	20.35	11.86	220.77	79.86	0.970
<i>m</i> -Br	15.63	16.00	18.26	20.27	11.56	221.81	79.88	0.953
<i>m</i> -NO <sub>2</sub>	14.98	15.92	18.13	19.32	11.31	222.84	79.94	0.983

*Mechanism and rate law*

The kinetics of oxidation of nitrones by QCC was investigated in 50 % DMF–water in the absence of oxalic acid. The reaction was found to be first order with respect to both  $c(\text{QCC})$  and  $c(\text{nitron})$ . The reaction was catalysed by  $\text{H}^+$ . The addition of the radical scavenger acrylonitrile had no effect on the rate. The observed salt and solvent effects shows that the rate determining step of did not involve ionic species. Due to the above reasons, the nitron can be protonated before the rate determining step and it can then react with QCC in the slow step. A plausible mechanism is given below:



The rate law for the suggested mechanism is:

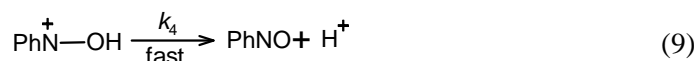
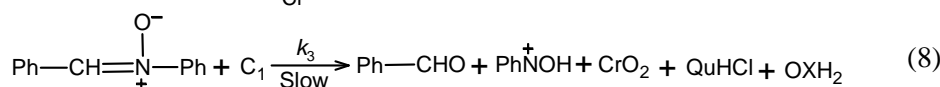
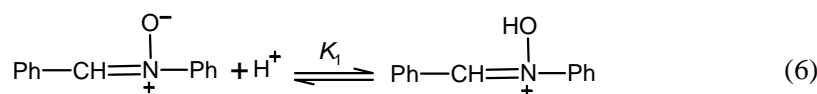
$$-\frac{dc(\text{QCC})}{dt} = \frac{K_1 k_2 c(\text{QCC})c(\text{S})c(\text{H}^+)}{1 + K_1 c(\text{H}^+)} \quad (4)$$

$$k_{\text{obs}} = \frac{K_1 k_2 c(\text{S})c(\text{H}^+)}{1 + K_1 c(\text{H}^+)} \quad (5)$$

where  $c(\text{S}) = c(\text{nitron})$ .

*Presence of oxalic acid*

The increase in the oxidation rate with acidity suggests the participation of protonated nitrene prior to the rate-limiting step. No polymerisation of acrylonitrile was observed, indicating that free radicals were not involved in the reaction. The order with respect to  $c(\text{substrate})$  and  $c(\text{H}_2\text{C}_2\text{O}_4)$  was found to be unity. The following mechanism is proposed to explain the observations:



The rate law for the mechanism is:

$$-\frac{dc(\text{QCC})}{dt} = \frac{K_1 K_2 k_3 c(\text{QCC}) c(\text{S}) c(\text{H}^+) c(\text{H}_2\text{C}_2\text{O}_4)}{1 + K_1 c(\text{H}^+)} \quad (10)$$

$$k_{\text{obs}} = \frac{K_1 K_2 k_3 c(\text{S}) c(\text{H}^+) c(\text{H}_2\text{C}_2\text{O}_4)}{1 + K_1 c(\text{H}^+)} \quad (11)$$

where  $c(\text{S}) = c(\text{nitrene})$ .

*Effect of substituents*

The rate of oxidation of a number of *m*- and *p*-( $\alpha$ -phenyl)-substituted *N*, $\alpha$ -diphenylnitrenes was studied at different temperatures in the presence and absence of oxalic acid and the activation parameters were calculated (Tables V and VI). The electron releasing groups enhanced and the electron with-drawing groups retarded the oxidation rate. The log  $k_2$  values were plotted against the  $\sigma$  values in a Hammett plot (Fig. 1). The small negative  $\rho$  values obtained indicate only a small structural influence on the rate. The negative  $\rho$  value (Table VII) was attributed to the development of a positively charged transition state. The entropies of activation were largely negative, as expected for bimolecular reactions.<sup>41</sup> The variation in  $\Delta H^\ddagger$  should be linearly related to the change in  $\Delta S^\ddagger$  ( $\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger$ ).<sup>42</sup> A plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  gave a straight line with a good correlation coefficient ( $r = 0.994$ ,  $\beta = 332$  K) in the absence of oxalic acid. The isokinetic temperature lies above the experimental temperature, showing thereby that these oxidations are enthalpy controlled and  $\beta = 296$  K,  $r = 0.990$ ,  $SD = 0.07$  in the



presence of oxalic acid. The isokinetic temperature lies within the experimental temperature showing thereby that these oxidations are entropy controlled. If this linearity between enthalpies and entropies is true, it should predict a meaningful correlation between  $\log k_2$  and  $\sigma$ .<sup>43</sup>

$$\log k_2(T_2) = a + b \log k_2(T_1) \quad (12)$$

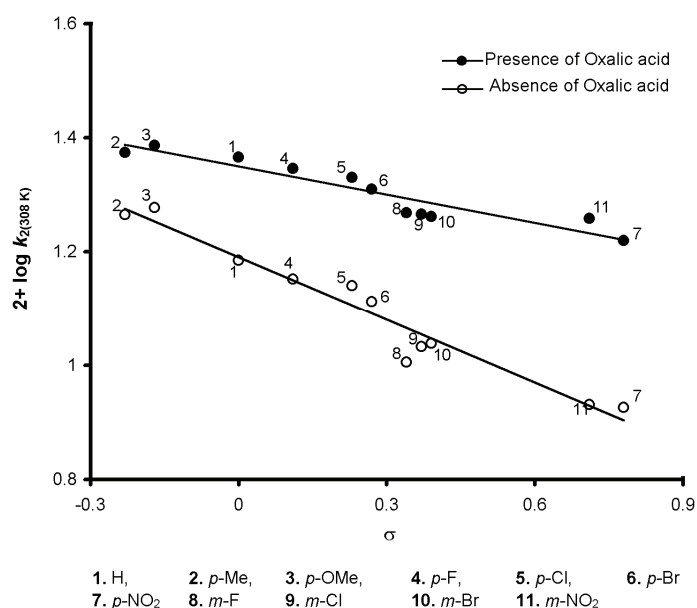


Fig. 1. Hammett plot of  $(2 + \log k_2(308 \text{ K}))$  versus  $\sigma$ .

TABLE VII. Reaction constants for the oxidation of *N*, $\alpha$ -diphenylnitrones by QCC in the absence and presence of oxalic acid

<i>T</i> / K	Absence of oxalic acid			Presence of oxalic acid		
	Reaction constant ( $\rho^-$ )	<i>r</i>	<i>SD</i>	Reaction constant ( $\rho^-$ )	<i>r</i>	<i>SD</i>
298	—	—	—	0.041	0.966	0.03
303	0.441	0.940	0.05	0.096	0.900	0.01
308	0.361	0.974	0.03	0.161	0.950	0.02
313	0.333	0.980	0.02	0.195	0.944	0.02
318	0.356	0.984	0.02	—	—	—

Using Equation (12), a good correlation coefficient for QCC ( $r = 0.980$ ) was obtained when  $\log k_2(T_2)$  was plotted against  $\log k_2(T_1)$  (Fig. 2).<sup>44</sup> This shows that the reaction under investigation follows a common mechanism. The  $\Delta G^\ddagger$  values were almost constant for all the investigated substituted nitrones, which confirmed the operation of a common mechanism. Irregularity in the values of either  $\Delta H^\ddagger$  or  $\Delta S^\ddagger$  may be due to solute – solvent interactions, which could affect both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  in a compensating manner. A negative value of entropy of ac-

tivation ( $\Delta S^\ddagger$ ) suggests the formation of an activated complex with a reduction in the degree of freedom of the reacting molecules.<sup>45</sup>

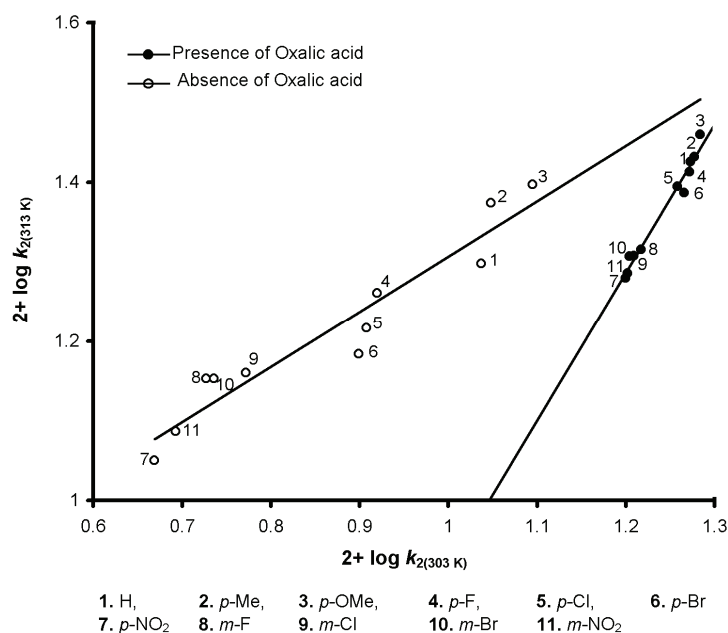


Fig. 2. Exner plot of  $(2 + \log k_2(313 \text{ K}))$  versus  $(2 + \log k_2(303 \text{ K}))$ .

### CONCLUSIONS

Based on the above facts, it is concluded that all the studied substituted nitrones follow the same mechanism when subjected to QCC oxidation in the presence and absence of oxalic acid under the conditions employed in the present study. The overall rate of reaction was greater in the presence than in the absence of oxalic acid.

### ИЗВОД

#### КИНЕТИКА И МЕХАНИЗАМ ОКСИДАЦИЈЕ НЕКИХ СУБСТИТУИСАНИХ АЛДОНИТРОНА СА ХИНОЛИНИЈУМ-ХЛОРХРОМАТОМ У ПРИСУСТВУ И ОДСУСТВУ ОКСАЛНЕ КИСЕЛИНЕ У ВОДЕНИМ DMF СРЕДИНАМА

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Кинетика оксидације алдонитрона (нитрона) хинолинијум-хлорхроматом (QCC) је праћена у 50 % DMF у води у присуству и одсуству оксалне киселине. Испитивано је да ли оксална киселина има каталитички ефекат или је кооксиданс. Реакција је праћена јодометријски. Реакција је првог реда у односу на нитрон и оксалну киселину, а разломљеног реда у односу на H<sup>+</sup>. Није уочен пораст брзине реакције са порастом јонске јачине раствора, а

брзина опада са смањењем диелектричне константе раствора. Додатак  $MnSO_4$  значајно утиче на брзину реакције, док додатак акрилонитрила нема утицаја. Предпостављен је механизам који укључује протонизацију нитрона и QCC као оксидационог средства. Израчунати су активациони параметри реакције.

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