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Kinetics and Mechanism of Oxidation of Diphenacyl Sulphide by Imidazolium Dichromate and Quinolinium Chlorochromate

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Kinetics of oxidation of diphenacyl sulphide (DPS) by imidazolium dichromate (IDC) and quinolinium chlorochromate (QCC) has been studied in 60% acetic acid under varying conditions. In both the cases of study the order of the reaction is found to be one each with respect to oxidant and substrate. The rate in each case increases with the increase in acetic acid composition of the solvent and with increase of $[H^+]$. The reaction does not induce polymerisation of acrylonitrile and addition of Mn(II) decreases the rate considerably. On the basis of the results, a suitable mechanism has been proposed for each oxidation.

INTRODUCTION

The mechanism of oxidation of many organic sulphides are very well explained in many reports.[1–3] But kinetics of oxidation of diphenacyl sulphide (DPS) by Cr(VI) is so far not yet reported. In this paper oxidation of diphenacyl sulphide by two oxidants namely quinolinium chlorochromate (QCC) and imidazolium dichromate (IDC) are reported and the results are analysed.

EXPERIMENTAL

Diphenacyl sulphide was prepared and recrystallised by known procedure.[4] IDC and QCC were prepared by the methods described in literature.[5, 6] The purity of oxidants was determined by iodometric procedure. Acetic acid was refluxed over chromic oxide for 6 h and then fractionated. Both the kinetic studies were carried out under pseudo-first order conditions by maintaining a large excess of the substrate over oxidant. The progress of the reactions was followed by estimating the unreacted oxidant iodometrically. The rate constants were evaluated from the linear plots ($r > 0.99$) of log [oxidant] against time by least squares method and reproducible within ± 3%.

The stoichiometry of the reaction was determined by allowing excess of oxidant to react with DPS under kinetic conditions. The determination of the unreacted oxidant after 2 h showed that the stoichiometry was 1 : 1 between the substrate and oxidant. Product analysis under kinetic conditions gave diphenacyl sulphoxide for both the oxidations which was identified with IR spectrum.

RESULTS AND DISCUSSION

In both cases, a plot of log k_{obs} *vs.* log [DPS] is linear with unit slope exhibiting first-order dependence of rate on [DPS]. This was further demonstrated by constancy of k_2 ($k_2 = k_{obs}/[DPS]$). In both the cases the plots of logtitre *vs.* time were linear indicating a first-order dependence of rate in [oxidant]. It has been observed that increasing percentage of acetic acid in the medium increases the rate. This might probably be due to the interaction of the reactants in the slow step. In both cases the added salt ($NaClO_4$) has no appreciable effect.

It was found that increase in concentration of Mn(II) decreased the rate considerably. A two-electron transfer process will result in the formation of Cr(IV) and addition Mn(II) removes the Cr(IV) formed.[7] So it is possible that the reaction involves a two electron transfer process. Also the absence of polymerisation when acrylonitrile was added to the reaction mixture, rules out the possibility of a one electron step.

In both the cases rate constants were found to increase with increase in $[H^+]$ The order with respect to H^+ was found to be one in IDC oxidation whereas fractional in the case of oxidation by QCC. The linear increase in rate with acidity suggests the involvement of protonated oxidant species in the rate determining step. The results and thermodynamic parameters are given in Table-1 and Table-2.

TABLE-1
RATE DATA ON THE OXIDATION OF DPS WITH IDC AND QCC AT 308 K

S. No.	10^3 [DPS] M	10^4 [IDC] M	10^4 [QCC] M	% AcOH-H_2O (v/v)	10^2 $[HClO_4]$ M	10^2 $[HClO_4]$	10^5 [Mn(II)]	10^4 k_{obs} sec^{-1}	k_2 lit mol^{-1} sec^{-1}
1.	1.25–2.25	1.5	—	60	4.0	—	—	2.88–5.50	2.38
2.	1.5	1.25–2.25	—	60	4.0	—	—	3.44–2.68	—
3.	1.5	1.5	—	60	2–10	—	—	1.78–8.81	—
4.	1.5	1.5	—	55–75	4.0	—	—	2.82–7.13	—
5.	1.5	1.5	—	60	4.0	0–5	—	3.44–3.55	—
6.	1.5	1.5	—	60	4.0	—	0.5	3.44–1.97	—
7.	1.25–2.25	—	1.5	60	4.0	—	—	2.32–4.22	1.70
8.	1.5	—	1.25–2.25	60	4.0	—	—	2.82–1.62	—
9.	1.5	—	1.5	60	1.5–11.5	—	—	1.72–4.93	—
10.	1.5	—	1.5	55–75	4.0	—	—	2.02–3.56	—
11.	1.5	—	1.5	60	4.0	0–5	—	2.82–2.67	—
12.	1.5	—	1.5	60	4.0	—	0–5	2.82–1.92	—

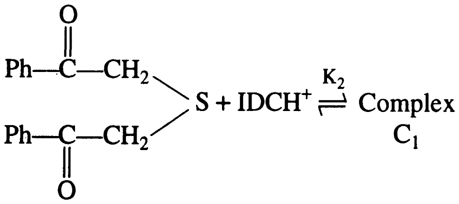
TABLE-2
THERMODYNAMIC PARMETERS

IDC Oxidation		QCC Oxidation	
ΔH kJ mol^{-1}	$-\Delta S$ J K^{-1} mol^{-1}	ΔH kJ mol^{-1}	$-\Delta S$ J K^{-1} mol^{-1}
74.71	14.68	38.92	133.97

The experimental results can be accounted in terms of a mechanism involving oxygen transfer from oxidant to substrate similar to the mechanism suggested for the oxidation of sulphides by pyridinium chlorochromate[8] and pyridinium dichromate.[9] Electron transfer from sulfur to Cr(IV) occurs, resulting in the formation of a polar transition state. The protonated forms of the oxidants are found to be the effective oxidising species in acid medium. Similar to pyridinium chlorochromate oxidations.[10, 11] The protonated oxidant attacks the substrate to form a complex. The complex decomposes to give the product in a slow step. The probable mechanism will be:

(a) IDC as oxidant

$$IDC + H^+ \overset{K_1}{\rightleftharpoons} IDCH^+$$



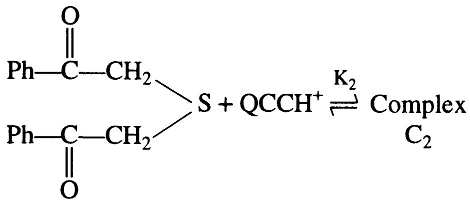
$$C_1 \xrightarrow[\text{slow}]{k_3} \text{Product}$$

The above mechanism gives the following rate equation:

$$\text{Rate} = \frac{-d[\text{Oxidant}]}{dt} \rightarrow = k_{obs}[DPS][IDC][H^+]$$

(b) QCC as oxidant

$$QCC + H^+ \overset{K_1}{\rightleftharpoons} QCCH^+$$



$$C_2 \xrightarrow[k_3]{\text{Slow}} \text{Product}$$

For the above mechanism the rate law is written as follows:

$$\text{Rate} = \frac{-\,d[\text{QCC}]}{dt}$$

$$= k_3C_2$$

$$= K_2k_3[\text{S}][\text{QCC}]$$

$$= \frac{K_1K_2k_3[\text{S}][\text{QCC}][\text{H}^+]}{1 + K_1[\text{H}^+]}$$

$$k_{obs} = \frac{K_1K_2k_3[\text{S}][\text{H}^{+]}}{1 + K_1[\text{H}^+]}$$

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