

The constants a_0 , a_1 and a_2 are obtained by the method of least squares and are given in Table 3 along with the standard deviations $\sigma(\Delta \ln \eta_{\text{exp}})$.

The variation of d with composition (Table 1) shows that the molecular interactions are unsymmetrical in the four mixtures. Hence, Grunberg and Nissan relation, which is applicable to quadratic mixtures defined by Rowlinson¹² is not applicable to the four mixtures studied presently. Further, a comparison of the values of $\Delta \ln \eta$ and $\Delta \ln \eta_{\text{the}}$ (Table 1) indicates that the theory due to Bloomfield and Dewan is capable of predicting the sign of excess viscosity correctly in mixtures of carbon tetrachloride with toluene, *o*-xylene and *p*-xylene. However, the quantitative agreement between predicted and experimental excess viscosity is poor in the three systems. The theory fails to predict even the sign of excess viscosity over certain range of mole fractions in the system carbon tetrachloride + *m*-xylene.

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Kinetics & Mechanism of Oxidation of Diaryl Sulphoxides by Cr(VI)

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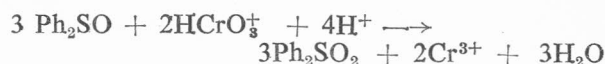
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The kinetics of oxidation of a few diaryl sulphoxides by Cr(VI) in 75% aqueous acetic acid has been studied. The reaction follows second-order kinetics, first-order each in sulphoxide and Cr(VI). A mechanism analogous to the one proposed for the oxidation of aryl methyl sulphoxides [*Indian J. Chem.*, **16A** (1978), 966] has been suggested.

DURING our investigations on the kinetics of oxidation of organic sulphur compounds we observed certain interesting features: (i) the oxidation of aryl methyl sulphides by peroxydisulphate^{1,2} and peroxydiphosphate³ ions is second order (first order in each reactant), but in contrast the oxidation of diphenyl sulphide by these peroxyanions^{4,5} is

first order in the peroxy anion and zero order in diphenyl sulphide; and (ii) while the oxidation of methyl phenyl sulphoxide by peroxydiphosphate⁶ is first order in each reactant, the oxidation of diphenyl sulphoxide (DPSO) by peroxydiphosphate⁷ is definitely different, i.e. zero order in DPSO and first order in the oxidant. The recent publication of Baliah and Satyanarayana⁸ on the oxidation of aryl methyl sulphoxides by Cr(VI) and the intrinsically exceptional behaviour of diphenyl sulphide and diphenyl sulphoxide with the isoelectronic and isostructural peroxyanions, prompted us to study in particular the kinetics of oxidation of a few diaryl sulphoxides by Cr(VI). The results are reported in this note.

All the diaryl sulphoxides were prepared and purified by standard methods. Acetic acid was purified by the method of Orton and Bradfield⁹. All the other chemicals employed were AR/GR grade. The kinetic studies were carried out in 75% (v/v) aqueous acetic acid under pseudo-first order conditions. The titrimetric procedure of Wiberg and Mill¹⁰ was followed for the estimation of the unreacted Cr(VI). The pseudo-first order rate constant, (k_1) for each run was evaluated from the slope of the linear plot of $\log(a-x)$ versus time by the method of least squares³ using a Micro 2200 diskette recorder (Hindustan Computers Limited). For each run the correlation coefficient, $r > 0.995$. The second order rate constants were obtained from the relation, $k_2 = k_1/[\text{sulphoxide}]$. The activation parameters were computed from the Arrhenius and Eyring plots. TLC of the reaction mixture of an actual kinetic run showed that DPSO was oxidised to diphenyl sulphone. Stoichiometric studies indicated that the reaction could be written as :



Effect of [Cr(VI)] and [DPSO] — There is a clean first order dependence on [Cr(VI)] (Table 1). The constancy of second order rate constants at different [DPSO] shows that the reaction is first order in DPSO (Table 1). Further a plot of k_1 versus [DPSO] is linear passing through the origin indicating that the reaction follows second order kinetics.

The oxidation is practically negligible in the absence of perchloric acid and the data in Table 2 reveal that the rate increases with increase in [perchloric acid] at constant ionic strength. The rate also increases slightly with increase in ionic strength (Table 2). The oxidation rate increases with increase in the acetic acid content in the solvent mixture (cf. Table 2). The decrease in rate with increase in water content of the solvent may be due to a greater solvation of the sulphoxide group and its consequent decreased nucleophilicity.

The rate constants and the activation parameters for a few 4,4'-disubstituted diphenyl sulphoxides are given in Table 3. The rate of the oxidation is accelerated by electron-releasing and retarded by electron-withdrawing substituents indicating a rate-determining electrophilic attack by the oxidant at the reaction site, sulphur. A good correlation is found to exist when $\Sigma\sigma^+$ values are plotted against

TABLE 1 — DEPENDENCE OF RATE ON Cr(VI) AND DPSO CONCENTRATION

[Solvent : 75% HOAc—25% H₂O (v/v); μ = 0.600 M; [HClO₄] = 0.500 M; temp. = 313K]

10 ³ [Cr(VI)] (M)	10 ³ [DPSO] (M)	$k_1 \times 10^5$ (sec ⁻¹)	$k_2 \times 10^3$ (litre mol ⁻¹ sec ⁻¹)
1.18	3.00	6.71	2.24
1.76	3.00	7.36	2.45
2.16	3.00	6.90	2.30
2.45	3.00	7.08	2.36
3.03	3.00	7.18	2.39
2.16	2.16	4.80	2.22
2.16	3.96	9.13	2.31
2.16	5.04	12.0	2.38
2.16	6.00	13.9	2.32

TABLE 2 — EFFECT OF [HClO₄], IONIC STRENGTH (μ) AND PERCENTAGE OF ACETIC ACID ON Cr(VI) OXIDATION OF DPSO

{[DPSO] = 3.00 × 10⁻²M; [Cr(VI)] = 2.16 × 10⁻³M; temp. = 313 K}

[HClO ₄]* (M)	0.440	0.500	0.600	0.700	0.750
k_2 (litre mol ⁻¹ sec ⁻¹)	2.15	3.57	4.77	6.23	8.43
μ † (M)	0.600	0.700	0.800	0.850	0.900
k_2 (litre mol ⁻¹ sec ⁻¹)	2.30	2.85	3.57	3.77	3.87
HOAc-H ₂ O(v/v)‡%	65	70	75	80	85
k_2 (litre mol ⁻¹ sec ⁻¹)	0.550	1.06	2.30	4.93	8.88

*Solvent : 75% HOAc—25% H₂O (v/v); μ = 0.800M;

†Solvent : 75% HOAc—25% H₂O (v/v); [HClO₄] = 0.500M

‡ μ = 0.600M; [HClO₄] = 0.500M.

TABLE 3 — SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE OXIDATION OF DIARYL SULPHOXIDES BY Cr(VI)

{Solvent : 75% HOAc—25% H₂O (v/v); μ = 0.600M; [Sulphoxide] = 3.00 × 10⁻² M; [Cr(VI)] = 2.16 × 10⁻³ M; [HClO₄] = 0.500 M}

Sulphoxide	$k_2 \times 10^3$ (litre mol ⁻¹ sec ⁻¹)			ΔH^\ddagger kJmol ⁻¹	$-\Delta S^\ddagger$ JK ⁻¹ mol ⁻¹
	308 K	313 K	318 K		
Diphenyl	1.58	2.30	3.18	54.8	121
4,4'-Dimethyldiphenyl	2.89	4.53	5.77	54.4	118
4,4'-Dichlorodiphenyl	1.05	1.62	2.05	52.3	132
4,4'-Dibromodiphenyl	1.13	1.72	2.35	57.8	114

log k_2 at 40° ($\rho^+ = -0.480$, $r = 0.989$, s.d. = 0.037). Baliah and Satyanarayana⁸ also observed a negative ρ^+ value (-0.690 at 30°) with substituted aryl methyl sulphoxides. The low reactivity of diaryl sulphoxides as compared to aryl methyl sulphoxides is reflected in its low value of reaction constant, inspite of the higher [HClO₄] employed in the former.

The foregoing experimental observations with DPSO are exactly analogous to those reported for the oxidation of aryl methyl sulphoxides⁸ by Cr(VI) and hence the mechanism proposed by Baliah and Satyanarayana⁸ is applicable in the present study also.

In the mechanism proposed by Baliah and Satyanarayana⁸, an electron transfer from the sulphoxide to Cr(VI) (HCrO₃⁺ being the active oxidant) occurs

in the rate determining step forming a cation radical. This view is consistent with small negative ρ^+ value.

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Five-coordinate Copper(II) Complexes with 1,5-Dimethylpyrazole-3-carboxylic Acid

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Mixed-ligand complexes of copper(II) with 1,5-dimethylpyrazole-3-carboxylic acid (dmpeH) as the primary ligand are described. The non-electrolytic species, Cu(dmpe)₂.B (where B = H₂O/pyridine/ α -, β - or γ -picoline) have been characterised on the basis of elemental analyses, derivatographic analyses, magnetic and diffuse reflectance spectral data. The dmpe anion acts as a bidentate ligand through the pyrazolyl (tertiary) nitrogen and carboxyl group. A five-coordinated structure has been proposed for these complexes.

AS part of a systematic study^{1,2} of the coordination behaviour of pyrazole derivatives with biologically important transition metal ions we wish to report here the isolation and physicochemical characterisation of a few five-coordinate copper(II) complexes with 1,5-dimethylpyrazole-3-carboxylic acid (dmpeH).

The ligand, dmpeH, was prepared by the interaction of the sodium salt of ethyl acetopyruvate and methyl hydrazine sulphate³ and the product recrystallised from hot water, m.p. 175-77°.

Preparation of the complexes: (A) Cu(dmpe)₂.H₂O — Addition of an aqueous solution of CuCl₂.2H₂O (0.01 mol) to an aq. solution of the sodium salt of the