

DCOF have been observed by Stratton *et al.*³ and a set of rotational constants has been reported by them. Potential constants and generalized mean square amplitudes of vibration have been evaluated for these molecules recently.^{4,5} In this note we report their Coriolis coupling coefficients. The non-vanishing Coriolis constants for these molecules are of type ζ_{ij}^x and ζ_{ij}^z arising from the $a_1 \times a_2$ coupling. After obtaining the force constant matrix elements and the Coriolis C elements, the zeta values are determined from the relation $\zeta^{x,z} = L^{-1} C^{x,z} L'^{-1}$, L^{-1} being the inverse of the normal co-ordinate transformation matrix. The results are presented in Table I and they are found to satisfy the square sum rule to a high degree of accuracy. The high magnitude of ζ_{16}^x and ζ_{56}^z indicate that these couplings are significant.

TABLE I

Coriolis coupling coefficients for HCOF and DCOF molecules

ζ_{ij}^x	HCOF	DCOF	ζ_{ij}^z	HCOF	DCOF
ζ_{16}^x	0.8937	0.8982	ζ_{16}^z	0.0002	0.0189
ζ_{26}^x	-0.3063	-0.3090	ζ_{26}^z	0.0763	0.3038
ζ_{36}^x	-0.2420	-0.2093	ζ_{36}^z	0.0867	-0.0959
ζ_{46}^x	0.1559	0.3695	ζ_{46}^z	-0.0579	-0.1750
ζ_{56}^x	0.1704	0.0568	ζ_{56}^z	0.9899	0.9311

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KINETICS OF OXIDATION OF 1, 3-PROPANE DIOL BY PEROXY-DISULPHATE CATALYSED BY SILVER IONS

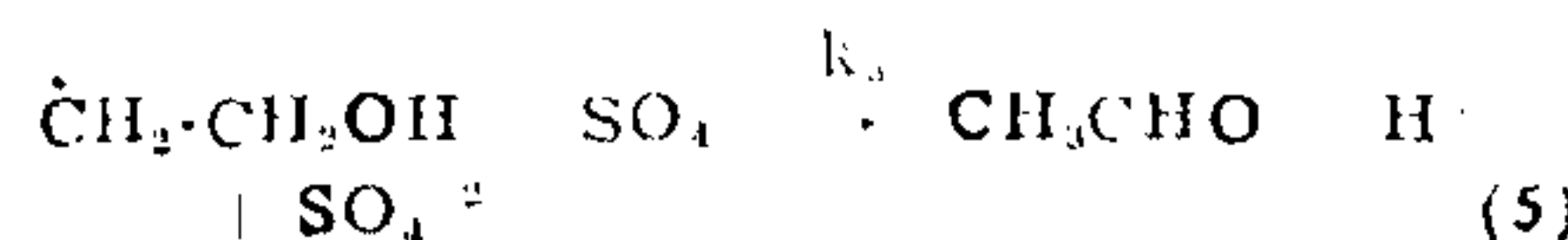
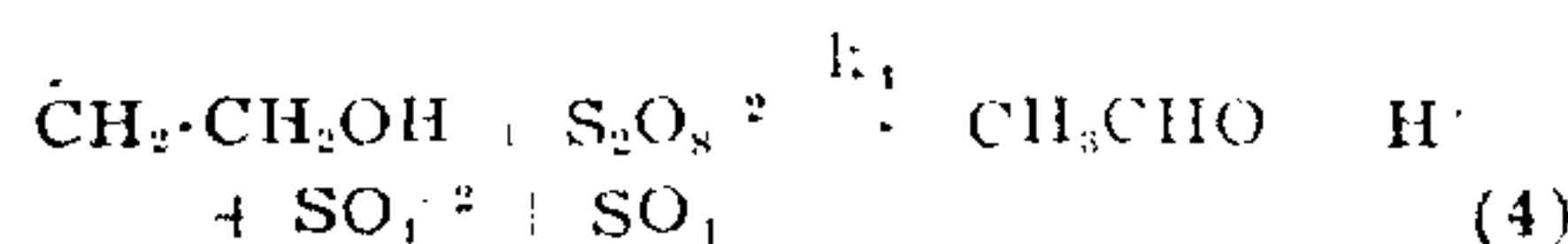
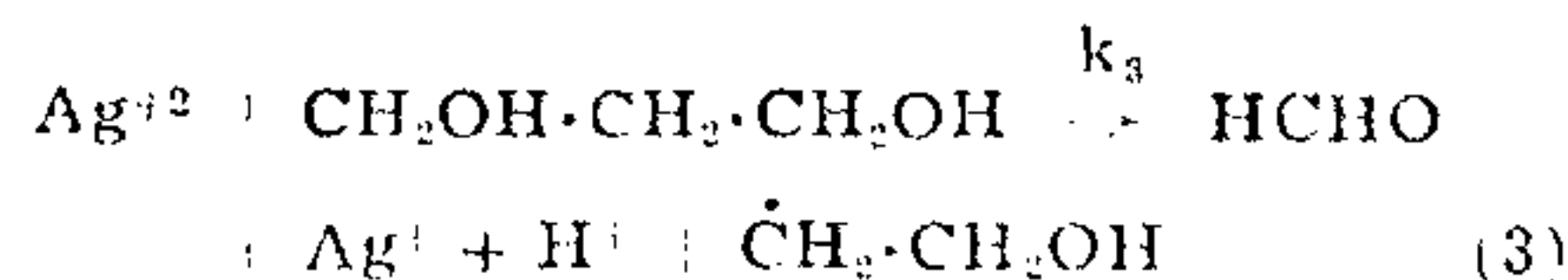
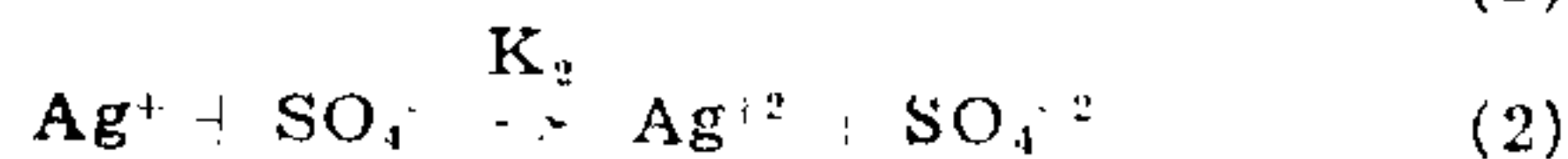
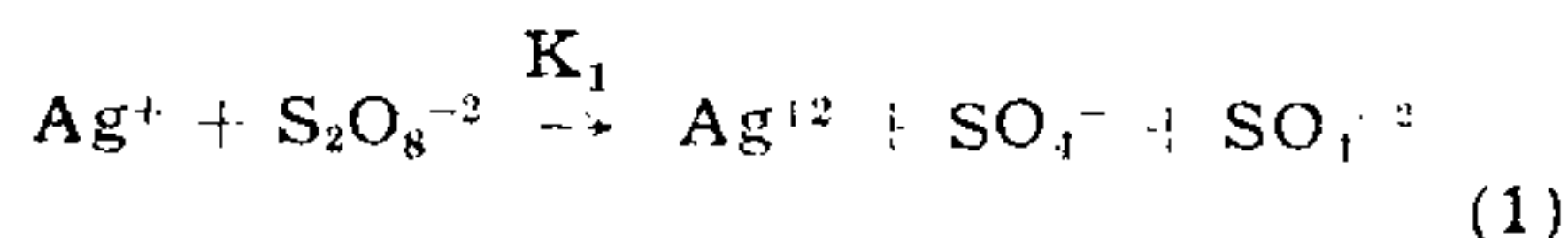
A SYSTEMATIC study of the oxidation of 1,2- and 1,3-diols was undertaken by the authors to investigate the role of silver ions as a catalyst. The present communication indicates the results of oxidation of 1,3-propane diol by peroxydisulphate catalysed by silver (I) ions.

The rate at which peroxydisulphate was consumed was estimated by the method of Bartlett and Cotman.¹ Typical runs indicated that the order with respect to $S_2O_8^{2-}$ is one and that the rate is independent of concentration of 1,3-propane diol at 48.5°C. The increasing concentration of Ag^+ ions (2.6×10^{-4} — 13.0×10^{-4} moles/litre) results in increased catalytic activity ($K_1 = 1.66 \times 10^{-4}$ — 7.80×10^{-4} sec.⁻¹) and bears a linear relationship to rate constants.

The effect of H^+ ion concentration was studied by the addition of sulphuric acid, at constant ionic strength maintained by potassium sulphate. Rate constant decreases appreciably up to H^+ ion concentration of 4.81×10^{-2} moles litre⁻¹, but remains constant at higher concentrations. The reaction was studied at different temperatures ranging from 32.4°C. to 50.2°C. for determination of various thermodynamical parameters.

In the oxidations by peroxydisulphate, both $Ag(II)^+$ and $Ag(III)^2$ are reported. However in the oxidation of 1,3-propane diol authors have postulated the mechanism based on the formation of reactive Ag^{+2} species, which also accords with the observation of Higgenison and Marshall.³

The following mechanistic steps are suggested:



On the basis of this mechanism

$$- \frac{d[S_2O_8^{2-}]}{dt} = K [Ag^+] [S_2O_8^{2-}]$$

where

$$K = k_1 + k_4 \left\{ \frac{k_1 k_2}{k_4 k_5} \right\}^{\frac{1}{2}}$$

The energy of activation as calculated from the results at three temperatures was 18.2 K cal. mole⁻¹. The frequency factor and the ΔS calculated are 5.36×10^{12} l mole⁻¹ sec.⁻¹ and +1.23 E.U. respectively. A standard value for comparison for bimolecular reactions is about -12. E.U. (Calculated for frequency factor 10^{11}), increase in entropy is expected if reactants are oppositely charged ions and hence slow step (2) is supported by a positive entropy change. A 1:1 Stoichiometry for $\Delta S_2O_8^{2-}/\Delta$ 1,3-propane diol was evaluated from 85% completed reactions by estimating $S_2O_8^{2-}$ and corresponding 2:4, dinitrophenyl hydrazones. Thus proposed mechanism leads to the observed rate law and explains pronounced catalysing effect of Ag^+ and dependence of the rate constant on the first power of the catalyst ion. Different from this Subbaraman and Santappa⁴ found the oxidation of secondary and tertiary alcohols running proportional to $[Ag^+]^{\frac{1}{2}}$. Acetaldehyde and formaldehyde were mainly identified as products of oxidation along with traces of formic and acetic acid.

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DISSOCIATION CONSTANTS OF 3,5-DINITROSALICYLIC ACID

THE dissociation constants of 3,5-dinitrosalicylic acid were determined potentiometrically at constant ionic strength. The pK_1 and pK_2 values obtained at $35 \pm 0.2^\circ$ C. are 2.96 ± 0.04 and 7.61 ± 0.08 respectively.

The dissociation constants of 3,5-dinitrosalicylic acid (3,5-DNS) have not been reported in the literature. In view of this and for the study of metal complexes with 3,5-DNS, it was of interest to determine the dissociation constants of this acid.

3,5-Dinitrosalicylic acid (Reidel-De Heen AG Seclze-Hannover, Made in Germany) and AnalaR (B.D.H.) reagents KNO_3 and $NaOH$ were used and their solutions were prepared in doubly distilled air-free conductivity water. Freshly prepared solutions of reagents were used to avoid the effects of age and hydrolysis.

A Cambridge bench pattern (null-deflection type) pH meter was used for pH measurements, which gives values accurate up to 0.02 pH unit. A glass electrode of 0-14 pH range, calibrated frequently by using buffer solutions of different pH values, was used in conjunction with a saturated calomel electrode connected to the cell by a low resistance salt bridge. All measurements were performed at a constant ionic strength of 0.1 M, which was maintained by adding a requisite quantity of KNO_3 . The temperature was maintained constant by placing the titration cell in an electrically regulated thermostat. The values of pK_1 and pK_2 were determined by using the Albert and Serjeant's¹ method. The pK_1 and pK_2 values obtained at $35 \pm 0.2^\circ$ C. are 2.96 ± 0.04 and 7.61 ± 0.08 respectively.

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CADMIUM (II) COMPLEXES WITH 2-METHYL QUINOLINE

As a part of our investigations on nitrogen-bonded metal complexes, we had earlier reported¹ some cadmium (II) complexes with substituted pyridines. This communication describes some more complexes using a substituted (2-methyl) quinoline as a ligand (L).

All the compounds were prepared in ethanolic medium by reacting cadmium halide CdX_2 , where $X = Cl^-, Br^-, I^-$ and CNS^- and the ligand in 1:2 ratio. There was an almost immediate formation of the compounds which were filtered, washed with ethanol followed by petroleum ether and dried *in vacuo*. The purity of the isolated compounds was established by estimating the metal as $Cd NH_4 PO_4 \cdot H_2O$ and the halogen as silver halide. The conductance measurements were carried out in acetone medium at 25° C. using a Toshniwal conductance bridge. The analytical and conductance data are recorded in Table I.