

This is in conformity with some earlier observations⁴. Hence the complexes are six-coordinated, presumably having a tetragonally distorted octahedral configuration. Though distorted octahedral Cu (II) complexes have three transitions ($2B_{1g} \rightarrow 2B_{2g}$, $2B_{1g} \rightarrow 2E_g$, $2B_{1g} \rightarrow 2A_{1g}$), often the three bands appear⁵ in a single broad asymmetric band envelope. The base adducts appear to be far more stable than their beta-diketonato analogues since in absence of the added base, there is no change in the position of absorption band in solution spectrum indicating "no appreciable dissociation" of the ligands.

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BROMINATION OF ACETANILIDE CATALYSED BY ANHYDROUS FERRIC CHLORIDE, ANHYDROUS ZINC CHLORIDE AND IODINE BROMIDE

It is a common practice in synthetic organic chemistry to speed up the halogenation of aromatic compounds by the addition of halogen carriers such as iodine, iron powder, anhydrous halides of iron, zinc and aluminium, silver salts and pyridine^{1,2}. Iodine bromide has been shown to be the effective catalyst in the presence of added amounts of iodine in the bromination of aromatic compounds³⁻⁵.

In the presence of IBr, ZnCl₂ and NaCl as catalysts, the bromination of anisole in 85% aqueous acetic acid has been shown⁶ to proceed by simultaneous catalysed and uncatalysed processes. In the present investigation⁷, the bromination of acetanilide in the presence of added salts was followed kinetically³ at 30°C by mixing 5 ml each of 0.02 M solutions of acetanilide and bromine in anhydrous acetic acid, allowing them to react for definite intervals of time and arresting the reaction by the addition of 10 ml of an aqueous solution of 1.0 g of KI. In the FeCl₃-catalysed reaction, the KI solution also contained 0.33 g of NaF, which complexes with Fe³⁺ preventing the oxidation of KI by Fe³⁺.

In the absence of catalysts, the acetanilide-bromine reaction was found to be of the third order in the range 0.02–0.01 M. The individual orders determined by the isolation method³ were 1.0 for acetanilide and 1.9 for bromine, in agreement with recent work⁸. When anhydrous ferric chloride was added to the reaction mixture, there was an increase in the rate of the reaction. When the concentration of FeCl₃ in the reaction mixture was increased (3.6×10^{-4} to 54×10^{-4} M), there was a steady increase in the observed average third order rate constant for 20–50% bromine consumption. A similar catalysis was observed in the presence of added anhydrous ZnCl₂ and iodine (which forms iodine bromide *in situ*), as seen from Table I.

The rate of bromination of acetanilide in the presence of added salts (A) may be expressed as follows:

$$-\frac{d(\text{Br}_2)}{dt} = k(\text{ArH})(\text{Br}_2)^2 + k_e(\text{ArH})(\text{Br}_2)^2(\text{A})$$

or (1)

$$k_3 = k + k_e(\text{A}) \quad (2)$$

where k_3 is the observed third order rate constant, and k and k_e are the rate constants for the uncata-

TABLE I

Effect of added salts on the bromination of acetanilide

Acetanilide = 0.010 M		Solvent: Anhy. HOAc			
Bromine = 0.010 M		Temp. 30.0 ± 0.1°C			
FeCl ₃ × 10 ⁴ (M)	$k_3 \times 10^{-2}$ (lit ² /mole ² /min)	ZnCl ₂ × 10 ⁴ (M)	$k_3 \times 10^{-2}$ (lit ² /mole ² /min)	IBr × 10 ⁴ (M)	$k_3 \times 10^{-2}$ (lit ² /mole ² /min)
3.6	3.73 ± 0.03	2.6	3.80 ± 0.04	0.8	3.78 ± 0.06
15.0	4.07 ± 0.04	5.3	4.07 ± 0.02	1.6	4.05 ± 0.10
32.7	4.53 ± 0.06	8.4	4.45 ± 0.03	2.9	4.55 ± 0.20
54.0	5.00 ± 0.05	16.6	5.34 ± 0.02	4.8	5.14 ± 0.38

All the concentrations quoted are those after mixing.

lysed and catalysed reactions, respectively. A plot of k_3 versus the molar concentration of A was found to be linear in each case. From the slopes and intercepts of these lines k and k_c , respectively, were calculated. The values thus obtained are given in Table II.

TABLE II
Relative reactivity of the added salts in the bromination of acetanilide

Added salt	Added salt conc. range $\times 10^4$ (M)	$k \times 10^{-2}$ (lit ² /mole ² /min)	$k_c \times 10^{-4}$ (lit ³ /mole ³ /min)	Relative reactivity
Nil	..	3.5
FeCl ₃	3.6-54.0	3.7	2.5	1.0
ZnCl ₂	2.6-16.6	3.5	11.2	4.5
IBr	0.8-4.8	3.5	35.2	14.1

From the last column of Table II it is seen that the order of reactivity of the three halogen carriers is IBr > ZnCl₂ > FeCl₃. The role⁹ of these catalysts is to polarise the bromine molecule and to remove Br⁻ as ABr⁻ in the rate-determining step. Their relative reactivity may be attributed to the following order of stability of ABr⁻:



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CHROMATOGRAPHIC IDENTIFICATION OF CERTAIN SULFOXIDES OF CYSTEINE PRESENT IN ONION (*ALLIUM CEPA* LINN.) EXTRACT

Introduction

VIRTANEN AND MATIKKALA^{1,2} isolated three sulfoxide amino acids, viz., cycloalliin, S-methyl cysteine sulfoxide and S-propyl cysteine sulfoxide from methanolic extracts of onions (*Allium cepa* Linn.). Bandyopadhyay *et al.*³ reported that some of the sulphur compounds of the etherial extracts of onion possess carbonyl and hydroxyl groups, but they did not identify them. The therapeutic effects of these extracts⁴ created some interest in their chemistry. In a preliminary study the diethyl ether extract of onion showed the presence of amino acids. This posed the question whether the suspected carbonyl compounds reported to be present in the etherial extract of onion³ really belonged to some of the sulfoxide amino acids of onion. In order to study this question the sulfoxide amino acids were separated from etherial and ethanolic extracts of onion, identified and compared by paper chromatography.

Experimental

Diethyl ether extract of fresh onion was prepared³ and petroleum ether (B.P. 40-60) soluble fraction⁴ was removed from it as reported previously. The insoluble fraction was further extracted with 20 ml of 1 N HCl and centrifuged. This process was repeated thrice. The combined solution was neutralised to litmus with 1 N NaOH and acetone was added to make it 50% acetone. The crystals separated on cooling were recrystallised from 50% acetone-water¹. The crystals were analysed for amino acids by paper chromatography using butanol: acetic acid: water system. A concentrated ethanolic extract of onion was prepared and the sulfoxide amino acids were separated by column chromatography according to the method of Carson and Wong⁵ with certain modifications that IR-120 (H⁺ form)¹ and IRA-93 (OH) were used in place of Dowex 50-X₄ (H⁺ form) and Duolite A-4 (amino form) respectively. To study the total amino acid pattern a sample of crystals obtained from the effluent from IR-120 were analysed by both one and two dimensional chromatography. The amino acids absorbed finally on IRA-93 (OH) were eluted with 0.1 N formic acid and one litre fractions were evaporated, acidified and further concentrated *in vacuo*⁶. Crystals separated were analysed by two-dimensional paper chromatography using butanol: acetic acid: water system first (12:3:5) and phenol ammonia: water system second⁶. Ninhydrin was used as the colour developing reagent. Each fraction was further recrystallised