TABLE 1

X-ray PES parameters for p-bromobenzoylacetonates
$(p\text{-}Br\text{-}C_6H_4\text{-}CO\text{-}CHCOCH_3)_x M$

M	O 1s(eV)	Br 3p 1/2 (eV)	Br 3p 3/2 (eV)
$(p\text{-}BrC_6H_4CO\text{-}CHCOCH_3)_x M.2H_2O$			
Fe($x = 3$)	531.8	183.3	190.0
Co($x = 2$)	531.7	183.2	190.0
Ni($x = 2$)	531.7	183.5	190.2
Cu($x = 2$)	531.8	184.1	190.7
Zn($x = 2$)	532.0	184.1	190.7
Cd($x = 2$)	532.0	183.6	190.3
Hg($x = 2$)	531.9	184.0	190.6
$(p\text{-}BrC_6H_4COCH_2COCH_3)$	529.7	182.0	188.0

14 December 1981

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POTENTIOMETRIC STUDY OF THE KINETICS OF OXIDATION OF FORMALDEHYDE, ACETALDEHYDE, PROPIONALDEHYDE AND *n*-BUTYRALDEHYDE BY AMMONICAL SILVER NITRATE

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KINETICS of oxidation of some organic compounds like reducing sugars[1,2] and tartaric acid[3] by ammonical silver nitrate have been reported in the literature. Ammonical silver nitrate has also been used in analytical chemistry for the quantitative determination of aldehydes[4]. A systematic kinetic study has not been carried out with aliphatic aldehydes using ammonical silver nitrate as the oxidant. In this communication we report a potentiometric study of the kinetic features of oxidation of formaldehyde, acetaldehyde, propionaldehyde and n-butyraldehyde by ammonical silver nitrate.

All the chemicals used were of extra pure quality. The standard solution of silver nitrate was always freshly prepared and kept in a flask coated black outside. The experiments were carried out in a double-walled cell coated black outside to avoid any photochemical reaction. The cell was fitted with an air tight rubber cork having provision for dipping the electrodes into the reaction mixture. Any loss of ammonia due to evaporation during the progress of the reaction was prevented by maintaining the vapour pressure of ammonia constant as done by Modi and Gosh[1]. Water from a thermostat at the desired temperature was circulated through the outer jacket of the cell. The progress of the reaction was followed by measuring the potential of the silver electrode at various time intervals with the help of a Leeds and Northrup 7554, K-4 type potentiometer using a saturated calomel as the reference electrode. The products of oxidation were identified as the corresponding carboxylic acids by their characteristic spot tests[5]. Stoichiometric analysis revealed that two moles of silver nitrate are required for each mole of aldehyde.

Under the conditions [silver nitrate] $\ll$ [aldehyde] the plot of E *vs* time (where E is the potential at the silver electrode) was linear (figure 1A) indicating the order in $[Ag^+]$ to be unity. From the slopes of such plots the pseudo first order rate constants (k') were calculated. Plot of log k' *vs* log [aldehyde] was linear (figure 1B) with unit slope in each case indicating the

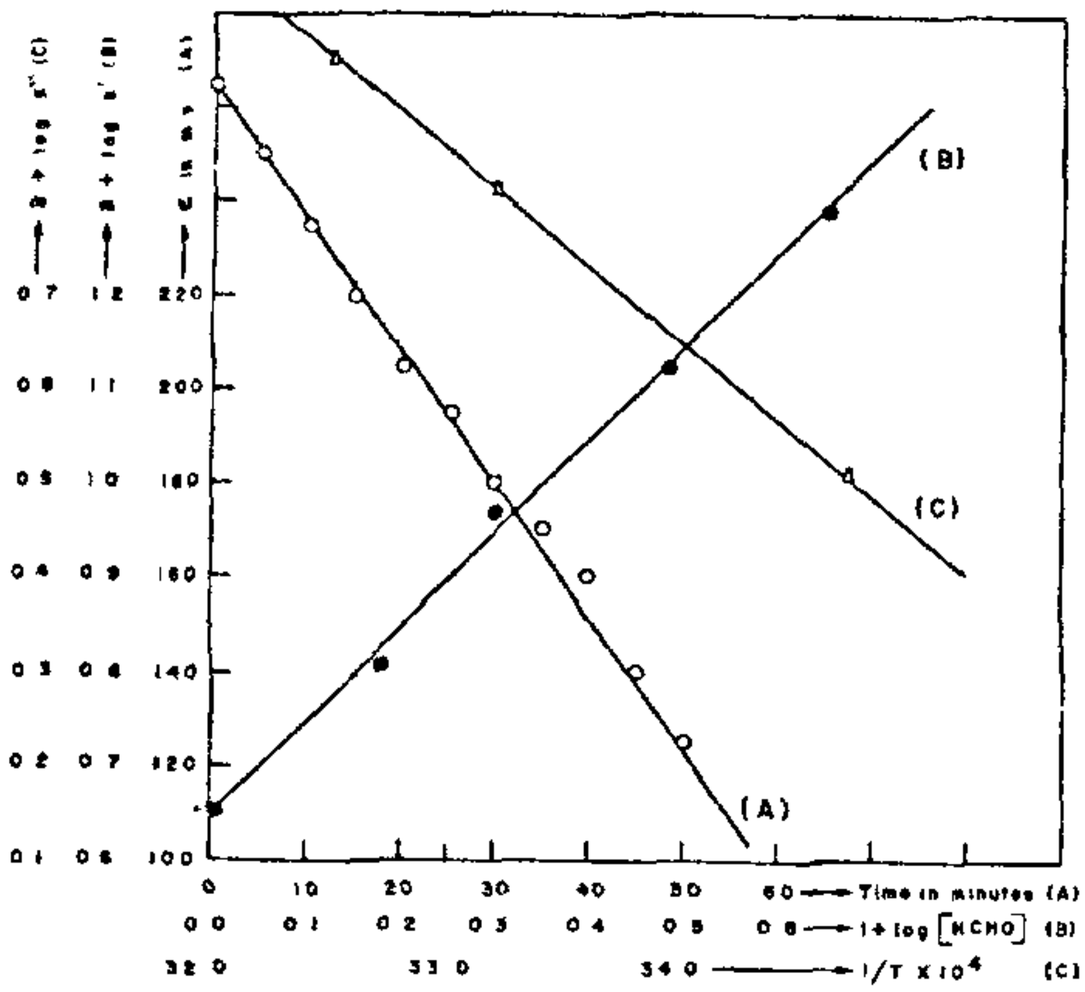

Figure 1A. Plot of time *vs.* Emf in M.V. $[Ag^+] = 1.00 \times 10^{-2}$ M $[HCHO] = 1.40 \times 10^{-1}$ M $[NH_4OH] \times 1.0 \times 10^{-2}$ M Temp. 298 K•**1B.** Plot $1 + \log [HCHO]$ *vs.* $3 + \log k'$ $[Ag^+] = 1.00 \times 10^{-2}$ M $[NH_4OH] = 1.00 \times 10^{-2}$ M Temp. 298 K•**1C.** Plot of $1/T \times 10^4$ *vs.* $2 + \log k'$ $[Ag^+] = 1.00 \times 10^{-2}$ M $[NH_4OH] = 1.00 \times 10^{-2}$ M $[HCHO] = 1.00 \times 10^{-1}$ M

order in [aldehyde] to be also unity. The rate of oxidation was found to decrease with the increase in $[NH_4OH]$. For instance, in the reaction with formaldehyde at constant [silver nitrate], [formaldehyde] and temperature (298 K) the rate constant decreased from 21.8×10^{-3} min^{-1} to 4.56×10^{-3} min^{-1} as $[NH_4OH]$ was increased from 1.00×10^{-2} M to 4.00×10^{-2} M.

In an ammonical solution of silver nitrate, silver ion exists in the free state as well as in the form of complexes *viz.*, $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$, depending upon the concentration of ammonia used. The fact that increasing ammonia concentration decreases the rate of reaction shows that free silver ion is the active species. The formation of an imine from the aliphatic aldehyde and ammonium hydroxide reaction is discounted in view of low aldehyde concentration used in these reactions. Under the experimental conditions employed the aldehydes exist mostly in their hydrated form[6]. Since there was no effect of $[OH^-]$ on the reaction rate, the involvement of the anion of the hydrated aldehyde in the reaction is ruled out. The rate of oxidation decreased with the addition of acrylonitrile indicating the presence of free radicals.

In the light of the above discussion, the probable mechanism of the reaction could be written as follows:

$$R\text{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}H + Ag(I) \xrightarrow[\text{slow}]{k'} R\text{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}\cdot + H^+ + Ag \quad (1)$$

$$R\text{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}\cdot + Ag(I) \xrightarrow[\text{fast}]{} R\text{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}^+ + Ag \quad (2)$$

$$R\text{-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}^+ \xrightarrow[\text{fast}]{H_2O} R\text{-}COOH \quad (3)$$

$$\frac{-d[Ag^+]}{dt} = k_1[Ag(I)][RCHO]$$

Taking step (1) as the rate determining one, the rate law could be written as

$$\frac{-d[Ag^+]}{dt} \quad k_1[Ag(I)][RCHO]$$

which is consistent with the observed results. The proposed radical mechanism gets further support from the absence of any induction period in which case there would have been complex formation involving silver[1,2].

TABLE 1

Activation parameters for Ag^+-aldehyde reactions

Aldehyde	k″ at 298 K $dm^3\ mol^{-1}\ min^{-1}$	ΔE‡	ΔG‡	ΔH‡	ΔS‡
		K J mol^{-1}			J deg^{-1} mol^{-1}
Formaldehyde	0.045	39.4	90.7	36.9	−181
Acetaldehyde	0.052	46.1	90.2	43.6	−156
Propionaldehyde	0.208	59.1	86.9	56.6	−102
n-butyraldehyde	1.54	63.3	81.9	60.8	−70.8

In table 1 the biomolecular rate constants and activation parameters are presented.

11 December 1981

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MYCOTOXINS FROM FUNGI ON MAIZE

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MYCOTOXINS from contaminated cereals and their products have been receiving increasing attention[1] and consumption of maize contaminated with mycotoxins had caused acute hepatitis and associated high mortality in Rajastan and Gujarat[2]. It is also reported that maize samples contaminated with toxigenic molds have yielded aflatoxin B^1 (8 to 1850 ppb)[3] and ochratoxin (30 to 50 ppb)[4]. In this context a screeening of maize samples used as a constituent in poultry feed, for natural mold contaminants and their toxins was carried out.

Maize samples from different poultry feed factories, located in the vicinity of Hyderabad were stored at 0° for 72 hr to kill the mites. The surface contamination of the grains was dertermined by washing a known weight of the sample in a known volume of sterile distilled water and then plating an appropriate dilution of the washing on Czapek's and "maltsalt agar" media. The density of contamination was expressed, as the number of fungal colonies grown per gram of sample. For internal contamination, the sterilized seeds were plated on the above media after disinfecting the surface of the seeds with 0.1% mercuric chloride and subsequent washings with sterile distilled water. Fungi from these isolations were purified and identified in our laboratory[5] and subsequently were confirmed by a local mycology laboratory. The toxin extraction from the infected maize samples was carried out by multi mycotoxin method[6], and qualitative and quantitative estimations were done[7]. The following results were obtained.

The surface washings of fifty grain samples gave high count of fungi (14-540 $\times 10^3$/g of sample), indicating high level of external contamination. The disinfected seeds also showed infection with the same type of fungi, indicating the invasion of the fungi inside the grains. The contaminated mycoflora mainly consisted of *Aspergillus flavus*, *A. candidus* and *A. sydowi* and *Pencillium* species.

The analysis of the infected maize samples showed the presence of three toxins; namely aflatoxin (B_1, B_2 and G), Ochratoxin and Sterigmatocystin. Out of fifty samples analyzed, five samples were contaminated with aflatoxin (four with B_1 and one with B_1, B_2 and G). Six samples were contaminated with ochratoxin, whereas three samples were contaminated with sterigamatocystin. The aflatoxin in three samples was above the tolerence level *i. e.* 34, 40 and 105 ppb[8]. The level of ochratoxin contamination ranged from traces to 187 ppb, whereas sterigamtocystin was detected from traces to 150 ppb.

Thus, the present study showed as much as 28% of the maize samples of poultry feed contaminated with three mycotoxins. This warrants screening of the maize to be used for poultry feed, for mycotoxins.

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