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THERMAL DECOMPOSITION OF HYDRAZINIUM HYDROGEN OXALATE AND DIHYDRAZINIUM OXALATE

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ABSTRACT

Thermal decompositions of hydrazinium hydrogen oxalate (HHOX) and dihydrazinium oxalate (DOX) have been studied. DOX on heating is converted into HHOX and thereafter both follow the same pattern of decomposition.

INTRODUCTION

Hydrazine forms two compounds with oxalic acid, $N_2H_4 \cdot H_2C_2O_4$ and $2\ N_2H_4 \cdot H_2C_2O_4$. Pratt and Richards [1], based on proton magnetic resonance studies, have formulated these as hydrazinium hydrogen oxalate (HHOX), $N_2H_5HC_2O_4$ and dihydrazinium oxalate (DOX), $(N_2H_5)_2C_2O_4$, respectively. Infrared spectra [2,3] of both the oxalates and X-ray [4,5] and neutron [6] diffraction studies of the former have been reported. Thermal analyses of these simple hydrazinium oxalates have not been reported, though there is a report [7] on the thermal decomposition of dihydrazinium oxalate which is at variance with the results obtained in this laboratory. We report the thermal analyses of the title compounds in this paper.

EXPERIMENTAL

HHOX and DOX were prepared according to Turrentine [8] by mixing suitable amounts of hydrazine hydrate and oxalic acid dihydrate. HHOX is obtained by mixing hot aqueous solutions, whereas DOX is prepared in the cold. Efforts to recrystallise DOX from hot solution always resulted in HHOX. It is interesting to note that even the slighest warming of the solution of DOX effects its conversion to HHOX. Hence, what has been reported as the thermal decomposition of DOX by Udupa [7] is, in fact, the thermal data for HHOX.

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The hydrazine content of the samples was estimated by titrating them against standard KIO_3 under Andrews' conditions [9]. The oxalate content was estimated by converting it into calcium oxalate which was then dissolved in dilute H_2SO_4 and titrated against standard $KMnO_4$.

DTA thermograms were recorded on an instrument described elsewhere [10] fitted with an Omniscribe strip chart recorder. Thermogravimetric analysis was done on a Stanton Redcroft TG 750 thermobalance. Both the thermal experiments were done in air, with platinum cups as sample holders. The heating rate employed was 10°C min^{-1} in both cases.

Infrared spectra of the oxalates and their intermediates were recorded as KBr discs on a Perkin-Elmer PE 599 spectrophotometer. Mass spectral analysis of the evolved gases on decomposition was done on an AEI MS 10 mass spectrometer.

X-Ray powder diffraction patterns of the samples were obtained on a Philips PW 1050/70 diffractometer. Single crystal Weissenberg photographs of DOX were taken using Nonius Y809 camera. CuK_α radiation was used both for powder diffractograms and Weissenberg photographs.

RESULTS AND DISCUSSION

The composition and purity of the samples were checked by chemical analysis, which was in very good agreement.

The infrared spectra (Fig. 1) of both HHOX and DOX agree very well with the reported literature [2,3].

Though the crystal structure of HHOX has been reported [4,5], that of DOX is yet to be reported. HHOX has been reported to be monoclinic, space group $P2_1/m$ with two formula units in a cell with dimensions $a = 3.583$, $b = 13.318$, $c = 5.103$ Å and $\beta = 102.72°$. Single crystal Weissen-

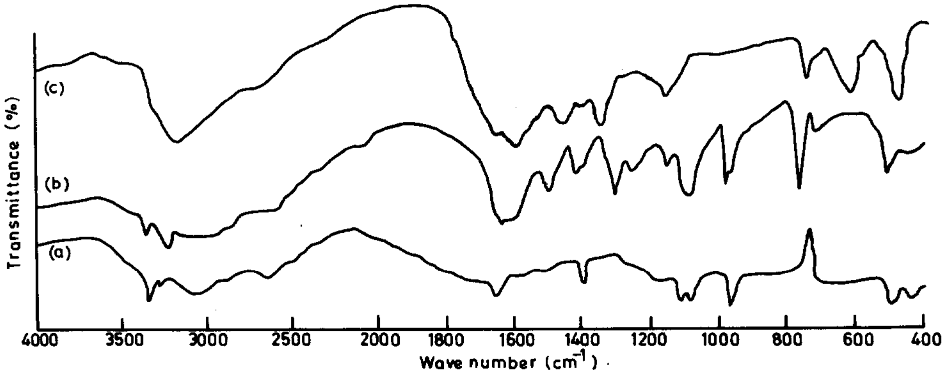


Fig. 1. Infrared spectra of (a) HHOX, (b) DOX; (c) intermediate.

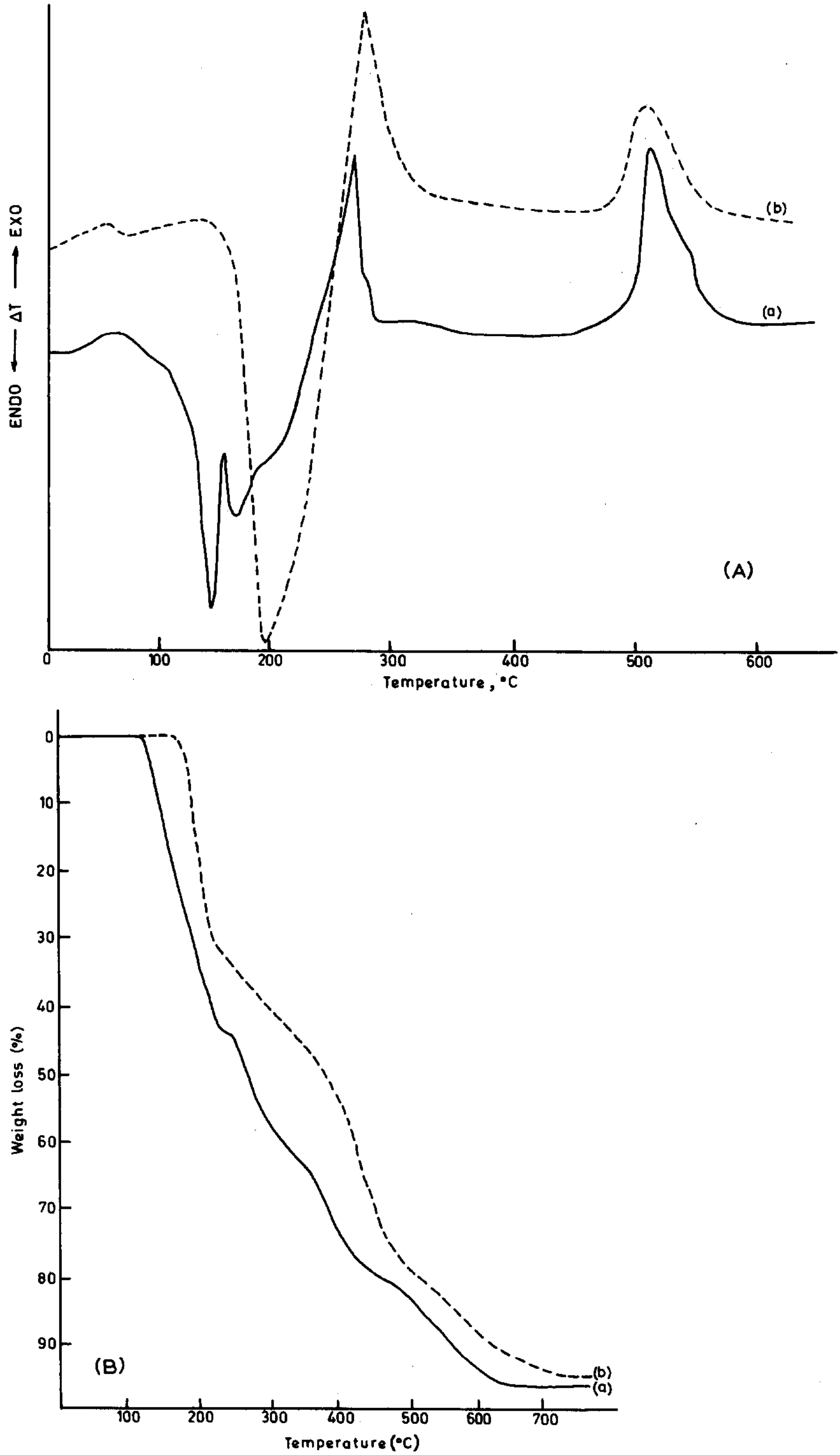


Fig. 2. (A) DTA curves of (a) DOX and (b) HHOX. (B) TG curves of (a) DOX and (b) HHOX.

berg photographs of DOX reveal that it is monoclinic, space group *Cc* (noncentric) or *C* 2/*c* (centric) according to systematic absences, the unit cell dimensions being $a = 13.07$, $b = 3.74$, $c = 12.40$ Å and $\beta = 96°$. The measured density of 1.72 g cm^{-3} suggests that there are four molecules in a unit cell. The details of the crystal structure of DOX will be published elsewhere.

All the above experiments were done to distinguish clearly between the samples of HHOX and DOX.

DTA and TG thermograms of both HHOX and DOX are given in Fig. 2.

Thermal decomposition of HHOX

HHOX melts at 200°C with simultaneous decomposition. This has also been observed visibly under a hot stage microscope. DTA shows an endotherm at 200°C followed immediately by an exothermic peak at 266°C. The intermediate formed after the exotherm at 266°C undergoes further exothermic decomposition at 494°C.

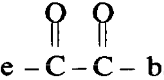
The thermal data reported as that of DOX [7] almost matches with the above except for the exotherm at 266°C. Udupa has identified the intermediate after the endotherm as oxamide. We could not collect the intermediate after the endotherm as the decomposition is continuous and the endotherm is immediately followed by an exotherm. But the intermediate collected after the exotherm at 266°C does not correspond to oxamide.

The infrared spectrum of the intermediate (Fig. 1) has very few peaks compared with the literature data for oxamide [11]. A further X-ray diffraction pattern shows three broad peaks corresponding to *d* values of 3.93, 3.25 and 2.26 Å, which do not correspond to that of oxamide.

Other supporting evidence that the intermediate cannot be oxamide is that oxamide is reported to melt around 417°C [11] followed by decomposition. This should be observed as an endotherm followed by an exotherm in the DTA, which is not so. Melting of the intermediate has not been observed when it is heated under a hot stage microscope up to 500°C.

The TG of HHOX shows a continuous weight loss with a break at 31% and not 43% as reported in ref. 7. The intermediate obtained is insoluble in almost all the common solvents, suggesting the polymeric nature of the compound.

The weight loss and the infrared data suggest an intermediate with a probable structure $-(NH-CO-CO-NH)_n-$. The infrared spectrum shows the characteristic–CONH– band around 1620 cm^{-1} and the $-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-$ band around 1700 cm^{-1}. Further, bands corresponding to C–N stretching and N–CO– bending are observed at 1350 and 1450 cm^{-1}, respectively. The spectra do not contain any $-NH_2$ scissoring and bending vibrations of oxamide which are supposed to absorb around 1600, 1103, 792 and 678 cm^{-1}. These assignments are made based upon the literature [11].



Thermal decomposition of DOX

The only available thermal data on DOX is that it melts at 148°C [12]. We have also observed the melting at 147°C, as reported, followed by another endotherm at 170°C and an exothermic peak at 263°C. The intermediate formed at 263°C further decomposes exothermically at 494°C.

The exothermic decomposition temperatures of DOX are almost the same as those of HHOX. This strongly suggests that DOX might have been converted into HHOX after melting by losing a hydrazine molecule. This transformation has been observed as an endothermic peak at 170°C. In solution, this transformation takes place even around 60°C.

Mass spectral analysis of the evolved gases obtained by decomposing both the oxalates at ~200°C shows that the decomposition pattern is the same in both cases except for an additional peak at $m/e = 32$ in the case of DOX, suggesting the loss of a N_2H_4 molecule, which fragments further giving the molecular ion of N_2H_4.

The fact that only one hydrazine molecule is easily lost from DOX suggests that the two hydrazine moieties are differently held in this compound. This is evidenced from the infrared spectrum which shows two different N–N stretching frequencies at 960 and 975 cm^{-1}, respectively, (Fig. 1).

The TG of DOX also shows a continuous weight loss. A small break at 43% suggests that the same intermediate as in the case of HHOX is formed. This is further confirmed by infrared and X-ray powder pattern which are identical with those obtained for the intermediate of HHOX.

CONCLUSION

DOX on heating loses a molecule of N_2H_4 and is converted into HHOX and hence the thermal analysis of the two compounds are similar.

What has been reported as the thermal analysis of DOX by Udupa [7] is actually the thermal data of HHOX only. While preparing the compound, Udupa heated the solution of DOX in order to recrystallise the sample, which resulted in the conversion of DOX into HHOX. Strong evidence for this argument is that the characteristic melting of DOX at 148°C, which is well known, has not been observed in the DTA reported by Udupa.

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