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BRIEF COMMUNICATION

A Plausible Mechanism of Thermal Decomposition of Oxalohydroxamic Acid and Formation of Novel Products

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The mechanism of thermal decomposition of oxalohydroxamic acid is proposed from the characterization of the various decomposition products with the help of crystallographic and spectroscopic investigations.

Introduction

Study of the chemistry of the hydroxamic acids has received considerable attention due to their broad based potential as antitumor, pharmaceutical, and analytical agents, in addition to being used as coolants in cool propellants in space applications (*1*, *2*). Our endeavors to study the thermal behavior of oxalohydroxamic acid (OXHA) to evaluate the mechanism of its thermal decomposition, has led to the discovery of novel compounds with "short" hydrogen bonds and better coolant properties. The preliminary results are reported herein.

Experimental

The thermal behavior of OXHA was investigated by differential thermal analysis (DTA), thermogravimetry (TG), and differential scanning calorimetric (DSC) techniques. The products formed during thermal treatment and thermal decomposition were characterized by single-crystal X-ray diffraction, spectroscopic, and elemental microanalysis techniques.

Results and Discussion

The DTA, TG, and DSC curves obtained in flowing nitrogen atmosphere and static air were identical, indicating a similar behavior in nitrogen atmosphere as well as in static air.

The dynamic DTA curve of OXHA showed a sharp exotherm at 168°C attributed to decomposition. In dynamic TG, OXHA started losing weight from 152°C upward and it was 15% up to 168°C where a sudden weight loss of the remaining 85% occurred. The dynamic DTG showed two

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peaks, one for 15% weight loss and the other for 85% weight loss. The dynamic DSC obtained using sealed sample holder showed an exotherm at 168°C similar to the one seen in DTA which was immediately followed by a small endotherm and an exotherm at 217°C. The uniqueness of OXHA decomposition is that though it decomposes at 168°C on dynamic heating it can even decompose at much lower temperatures when heated isothermally for longer times. The isothermal decomposition was evidenced from isothermal DTA, TG, and DSC techniques.

When OXHA was heated isothermally at 95°C for about 27 hr it yielded a milky white powder (OWMP) and the decomposition had progressed to about 15%. We also obtained a similar product (OWMP) in an oven which was maintained at 95°C. The OWMP was cooled to room temperature and during cooling the DTA or DSC curves did not indicate any endo- or exotherm nor did the TG show any weight loss or gain. The OWMP was characterized at room temperature by mass, ^{1}H-NMR, IR, ^{13}C-NMR, Raman spectroscopy, and X-ray diffraction techniques. From these investigations, it was found to be a mixture of OXHA, a novel ammoniated form of oxalohydroxamic acid (OXHA.Am), a higher melting point isomer of hydroxy urea, urea, hydroxalamine, and a new form of ammoniated 1,2,4-oxadiazolidine-3,5-dione (ODD.Am).

We isolated from the mixture OXHA.Am and OXHA crystals by crystallizing OWMP from distilled water. The crystals were filtered off and the clear filtrate on evaporation provided a white solid substance (WS). The characterization of WS by various spectroscopic techniques showed that it contains a higher melting point isomer of hydroxy urea, urea hydroxylamine, and ODD.Am. The decomposition products of higher melting point isomer of hydroxy urea were investigated in the past (*3*) and found to be ammonia, urea, carbon dioxide, and nitrogen. Thus the ammonia formed due to the decomposition of hydroxy urea forms a source for the ammination of OXHA and 1,2,4-oxadiazolidine-3,5-dione. The structure of ODD.Am is being established by single-crystal X-ray diffraction studies.

To understand the thermal decomposition mechanism, OXHA was heated at *ambient* conditions in a petri dish covered with an inverted funnel. At 168°C it decomposed giving dense white fumes which condensed on the cooler sides of the funnel giving a white solid sublimate (WSS). The characterization of WSS by various spectroscopic techniques showed that it is same as WS. Thus it proves that the *same product* of decomposition results during isothermal and dynamic heating of OXHA. In the dynamic DSC curve a small endotherm which is observed after the decomposition exotherm at 168°C may be attributed to sublimation process and the exotherm at 217°C to the decomposition of ODD.Am. As the DTA and TG experiments are carried out in an open sample holder the gaseous products escape after decomposition. A mechanism of decomposition of OXHA involving Lossen rearrangement is reproduced in Fig. 1. The Lossen rearrangement is interesting in this case because it has taken place without preliminary *O*-acylation. The removal of a mole of water from the molecule during Lossen rearrangement accounts for 15% weight loss in dynamic TG curve prior to 168°C. The characterization of various products in Fig. 1 by spectroscopic and X-ray techniques along with thermal data strongly support the mechanism.

Furthermore, the OWMP is found to be a better coolant in "cool propellants" as it can be pelletized, unlike OXHA. Also, the OXHA.Am crystals were separated and the structure was established by single-crystal X-ray diffraction techniques. An interesting feature of such studies is that the crystals of

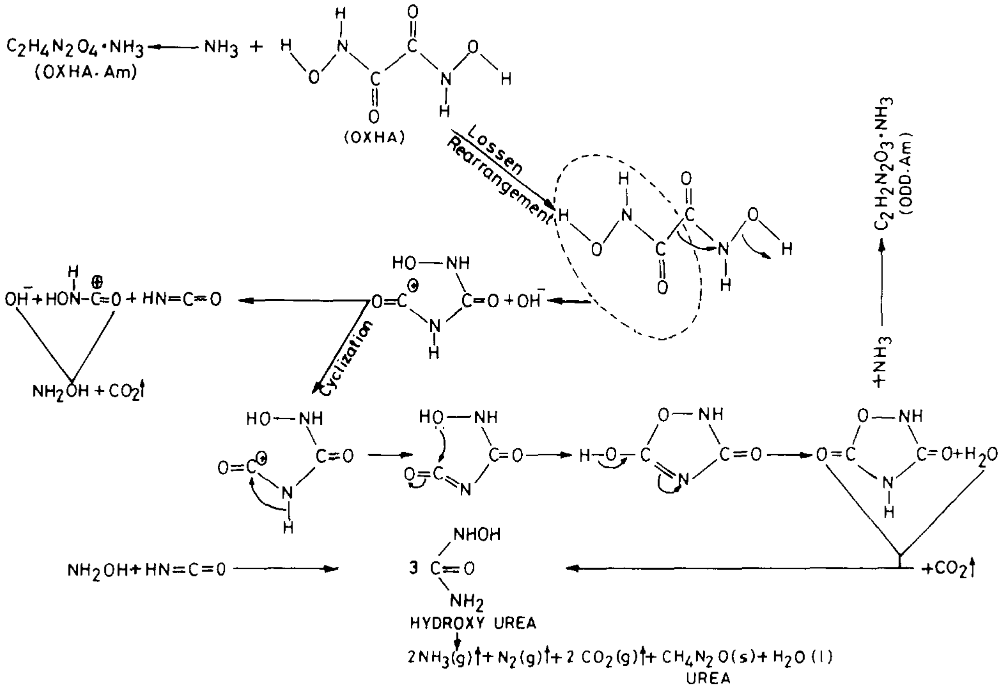

FIG. 1. Plausible mechanism of thermal decomposition of OXHA.

OXHA.Am contain "short" O . . . O hydrogen bonds (2.456, 2.450 Å). It might be mentioned that the crystals of OXHA are shown to be monoclinic (*4, 5*). It is worth mentioning that molecular systems with short O . . . O hydrogen bonds have been considered as candidates for electronic devices (*6*) and thus the possibility of OXHA.Am or similar systems for such purpose may be explored.

Conclusion

The preliminary results reported herein provide a mechanism of the decomposition of OXHA and the formation of novel products during the decomposition process.

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References

1. E. S. SUTTON, E. J. PACANOWSKY, AND S. F. SARNER, *J. Spacecr. Rockets* **4,** 1543 (1967).
2. R. A. BIDDLE, W. C. VRISON, AND E. S. SUTTON, US patent, US4,298,412 (Cl 149-19.5; Appl. 75 140 882, 03 Nov. 1981, Appl. 35, 956, 04 May 1979 5pp.).
3. H. KOFOD AND T. HUANG, *Acta Chem. Scand.* **8,** 485 (1954).
4. C. K. LOWE-MA AND D. L. DECKER, *Acta Crystallogr. Sect. C* **42,** 1648 (1986).
5. A. SAMEENA BEGUM, V. K. JAIN, C. L. KHETRAPAL, AND C. N. SHIVAPRAKASH, *J. Crystallogr. Spectrosc. Res.* **17,** 545 (1987).
6. C. SEVENSON, S. C. ABRAHAMS, J. L. BERNESTEIN, AND R. C. HADDON, *J. Amer. Chem. Soc.* **101,** 5759 (1979).