

Thermal decomposition of the diammonium salt of ethylenebisdithiocarbamic acid

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The thermal decomposition of the diammonium salt of ethylenebisdithiocarbamic acid which could be a possible source of ethylenethiourea present in some dithiocarbamic fungicides was investigated. The kinetic and activation parameters were determined. It has been confirmed that one of the products arising in the decomposition of the diammonium salt of ethylenebisdithiocarbamic acid is ethylenethiourea. At the same time, a method for the determination of ethylenethiourea based on gas-liquid chromatography was developed.

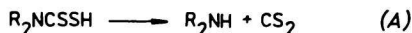
Изучалось термическое разложение диаммониевой соли этиленбисдитиокарбамидной кислоты, что может быть источником присутствия этилентииомочевины в некоторых дитиокарбамидных фунгицидах. Установились кинетические и активационные параметры, а также подтвердилось, что между продуктами разложения диаммониевой соли этиленбисдитиокарбамидной кислоты находится этилентииомочевина. Одновременно разработана методика определения этилентииомочевины с помощью газожидкостной хроматографии.

Different metal salts of ethylenebisdithiocarbamic acid represent the most important and frequently used group of organic fungicides in the practice [1]. During recent years, these chemicals are given increased attention from the view-point of the presence of ethylenethiourea (ETU) which is an undesirable accompanying impurity [2—4].

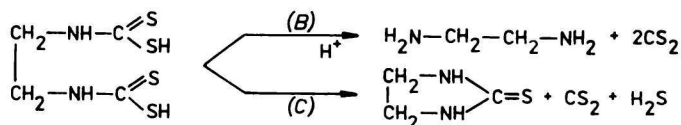
The diammonium (DA) salt of ethylenebisdithiocarbamic (EBDT) acid is the most frequently used starting material for a manufacturing of the above-mentioned fungicides [5, 6]. By studying systematically the data concerning the manufacturing of Mancozeb (Novozir MN-80), we have found that a potential source of ETU present in this type of fungicides could be the DA salt of EBDT acid itself.

It is well-known that free EBDT acid is instable and undergoes decomposition to give carbon disulfide and ETU [7]. In contrast to monodithiocarbamic acids which

decompose to yield unambiguously amine and carbon disulfide according to the following scheme



the decomposition of bisdithiocarbamic acids, for instance EBDT acid, may proceed in two ways



The decomposition according to scheme (B) is very well known in analytical chemistry, and because of its quantitative course, it is the basis of an analytical method for the determination of ethylenebisdithiocarbamides in various fungicide formulations [8]. It is known that the decomposition according to scheme (C) is much slower and proceeds at lower temperatures, however, it has not been investigated in more detail [8]. Therefore we considered to be necessary to investigate more thoroughly the thermal decomposition of the DA salt of EBDT acid taking place in aqueous solution according to scheme (C).

The results obtained will be useful for the elucidation of some problems concerning manufacturing impurities in the fungicide Mancozeb.

Experimental

Chemicals

The aqueous solution of the DA salt of EBDT acid was prepared according to a procedure developed in the Research Institute of Agrochemical Technology in Bratislava.

Apparatus

The apparatus used consisted of a two-necks round bottom boiling flask (100–150 ml) placed in a thermostated bath (temperature variation $\pm 1^\circ\text{C}$). A thermometer with ground glass joint and reflux condenser were attached to the flask.

Kinetic measurements

A weighed amount of the aqueous solution of the DA salt of EBDT acid of known concentration was given in the flask which was then placed into the thermostated bath heated to a given temperature. Since these temperatures were higher (over 60°C) and the

weighed amounts of the DA salt were rather small (~ 30 g), the time required for heating the substance to the chosen temperature could be neglected when compared with the time interval of measurements (5—25 h).

The sample was processed in regular time intervals as follows. The content of the flask was immediately and quantitatively poured into an Erlenmeyer flask and put into a thermostated refrigerator for 45—50 h. After freezing-out, the separated crystals of ETU were sucked and quickly washed with ice distilled water. The optimum time interval necessary for complete freezing-out of ETU was determined using standard samples. The filtrate was weighed and analyzed for the content of the nonconsumed DA salt of EBDT acid. The crystalline ETU was dried over phosphorus pentoxide, weighed, and subjected to analysis by gas-liquid chromatography (g.l.c.). Since the measurements required much time, rough errors could be avoided by processing three independent samples in each time interval.

Analytical determinations

The content of ETU was determined by the g.l.c. method using a column packed with 3 mass % of NPGS on Gas-Chrom Q (100/120 mesh). For evaluation the technique of calibration curve was used after preceding extraction of ETU with methanol. In these measurements nitrogen as carrier gas and flame ionization detector were applied. The lower limit of determination under these conditions was 0.025 mass %. The content of the DA salt of EBDT acid in aqueous solutions was determined by complete decomposition of the DA salt by boiling in acid medium. The carbon disulfide evolved was absorbed in methanolic potassium hydroxide to afford potassium methyl xanthate which was then determined iodometrically [8].

Results and discussion

The time behaviour of both the decrease in concentration of the DA salt of EBDT acid and the increase in concentration of ETU formed by the thermal decomposition of the DA salt of EBDT acid was measured at 60, 70, 80, 90, and 98°C (Figs. 1 and 2).

The dependence measured at 70, 80, 90, and 98°C was used for calculating the rate constants from the decrease in concentration of the DA salt of EBDT acid while for the calculation of the rate constant of ETU formation the determined increase in ETU concentration at 60, 70, and 80°C was used.

The reaction order was determined by the integral method [10]. Thus we obtained the value $n=1$ which corresponds to reaction scheme (C). The rate constants were calculated according to the rate equation of the first-order reactions [9]

$$(a - x) = a e^{-kt}$$

The concentrations were expressed in mole %. The correlation coefficients for the

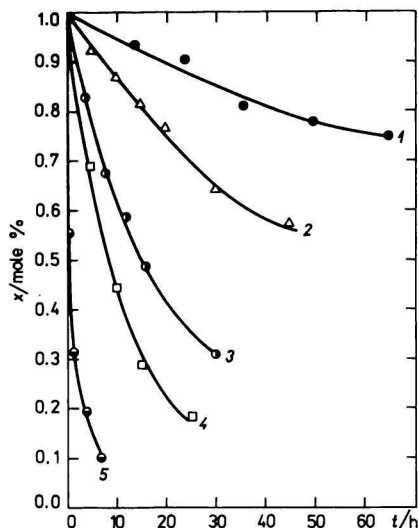


Fig. 1. Variation of concentration of the DA salt of EBDT acid with time for temperatures: 1. 60°C; 2. 70°C; 3. 80°C; 4. 90°C; 5. 98°C.

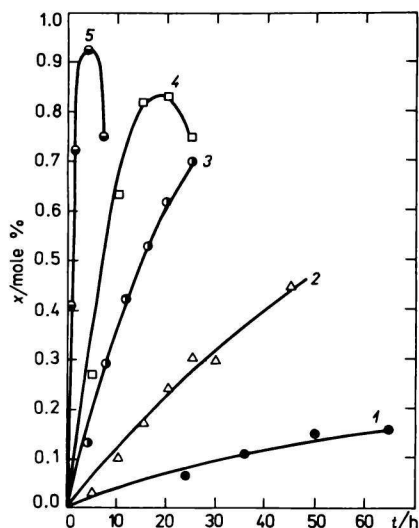


Fig. 2. Variation of ETU concentration with time for temperatures: 1. 60°C; 2. 70°C; 3. 80°C; 4. 90°C; 5. 98°C.

rate constants calculated by computer technique were never lower than 0.997. The relative error of the determination of rate constants did not exceed $\pm 7\%$. The values obtained are given in Table 1. Activation energy and frequency factor were calculated on the basis of the Arrhenius equation from the plot $\log k/s^{-1} = f(1/T)$. Thus we obtained the following values for the activation energy

$$E_A^a = 124.9 \text{ kJ mol}^{-1}; \quad E_A^b = 130.9 \text{ kJ mol}^{-1}$$

whereas the values of frequency factor were $A_a = 4.28 \times 10^{13} \text{ s}^{-1}$; $A_b = 2.97 \times 10^{14} \text{ s}^{-1}$.

Table 1

Values of the rate constants calculated for different temperatures

- a) from concentration decrease of the DA salt of EBDT acid
b) from concentration increase of ETU

$\theta/^\circ\text{C}$	k_a/s^{-1}	k_b/s^{-1}
98	1.61×10^{-4}	
90	2.23×10^{-5}	
80	1.28×10^{-5}	1.26×10^{-5}
70	3.70×10^{-6}	3.48×10^{-6}
60	1.36×10^{-6}	9.00×10^{-7}

The absolute error of the determination of activation energy was calculated according to the subsequent equation [10]

$$\delta E_A = \frac{RT_1 T_2}{T_2 - T_1} \left[\left| \frac{\Delta k_1}{k_1} \right|^2 + \left| \frac{\Delta k_2}{k_2} \right|^2 \right]^{1/2}$$

where T_1 and T_2 are temperatures expressed in K, R is a gas constant, and Δk_1 , Δk_2 are the mean errors of rate constant assuming the mean errors of temperatures to be negligible. Then the relative error of activation energy is not greater than $\pm 10\%$. Provided the error of activation energy is respected, a comparison of the values obtained for activation energy shows that both values $E_A^a = 124.9 \text{ kJ mol}^{-1}$ and $E_A^b = 130.9 \text{ kJ mol}^{-1}$ are equal in the range of the above-mentioned experimental error.

The mean values of activation energy and frequency factor make it possible to write the rate equation in the form

$$k/s^{-1} = 1.70 \times 10^{14} \exp\left(-\frac{127\,900 \text{ kJ mol}^{-1}}{RT}\right)$$

The rate equation was used for calculating the rate constants of the decomposition of aqueous solution of the DA salt of EBDT acid in the temperature range 20–50°C which is important from the view-point of further processing of the DA salt in the course of Mancozeb manufacturing. Moreover, the time required for the concentration to decrease by a factor of two ($t_{0.5}$) was also determined for the DA salt of EBDT acid at those temperatures. The relevant data are given in Table 2.

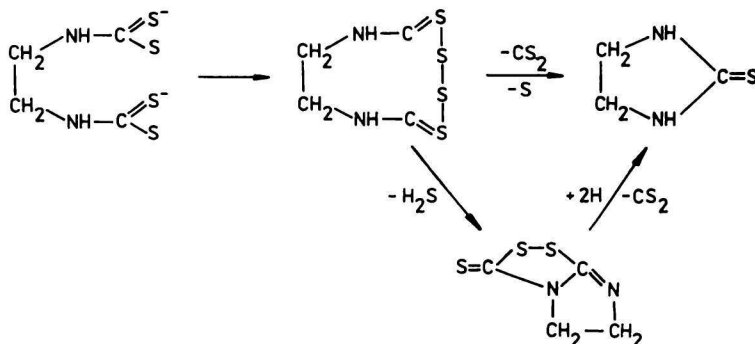
The results obtained allow to state that an unambiguous decomposition of the DA salt of EBDT acid giving rise to ETU is limited by temperatures of 80°C. At higher temperatures (up to 98°C), an aqueous solution of the DA salt of EBDT acid is also subjected to decomposition, however, the final products have not yet been more closely identified.

Table 2

Values of the rate constants and $t_{0.5}$ calculated from the rate equation for different temperatures

$\theta/^\circ\text{C}$	k/s^{-1}	$t_{0.5}/\text{h}$
20	1.75×10^{-9}	1.1×10^5
25	4.08×10^{-9}	4.6×10^4
30	9.90×10^{-9}	1.9×10^4
35	2.27×10^{-8}	8.5×10^3
40	5.01×10^{-8}	3.8×10^3
50	2.43×10^{-7}	8.5×10^2

The kinetic study of the decomposition of the disodium salt of EBDT acid carried out by some authors [11] suggests that this decomposition gives rise to ethylenethiuram disulfide, ethylenethiuram monosulfide, and ETU according to the reaction scheme



In our case, the dependence of the concentration increase of ETU on time at 90 and 98°C (Fig. 2) makes it possible to assume the origination of an intermediate which precedes the formation of ETU. That could, to a certain extent, correspond to the above reaction scheme proposed by *Marshall et al.* [11]. We were able to detect the presence of CS₂ and H₂S in some of our samples after the decomposition of the DA salt of EBDT acid.

The calculated values of rate constants at lower temperatures (or half-life of the decomposition of the DA salt of EBDT acid) (Table 2) suggest that the minimum infiltration of ETU into EBDT fungicides may be ensured already in the process of their preparation by choice of convenient technological conditions.

Symbols

- a* initial concentration of reactant (mole %)
- x* concentration of the substance at time *t*
- k* rate constant (s⁻¹)
- t* time (h)
- t*_{0.5} time required for the concentration to decrease by a factor of two
- E*_A activation energy (kJ mol⁻¹)
- A* frequency factor (s⁻¹)
- T* temperature (K)
- R* molar gas constant (kJ K⁻¹ mol⁻¹)
- Δk mean error of the rate constant (s⁻¹)
- δE_A absolute error of activation energy (kJ mol⁻¹)

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