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Note

KINETIC STUDY OF THE THERMAL DECOMPOSITION OF TETRAETHYLTHIOURANUMDISULPHIDE (TETUDS)

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TETUDS is used as a drug against alcoholism, due to its ability to prevent the change of ethyl alcohol into the acetaldehyde stage. In this paper the results of a non-isothermal kinetic study, concerning the thermal decomposition of TETUDS are discussed. In order to carry out this study, three well-known methods: Freeman–Carroll, Coats–Redfern and Ozawa were used and a comparison of the results from each is also available.

EXPERIMENTAL

TETUDS, $C_{10}H_{20}S_4N_2$, as white crystals, previously purified by extraction, was used. The heating curves were recorded by a Paulik–Paulik–Erdey derivatograph type Q-1500 D. The resulting products were analyzed by a chromatograph with a TCD-80 °C sensor, a 120 mA bridge, a 1.5 m column Porapak R as stationary phase, and a flow rate of 40 ml min^{-1}. The X-ray diffractograms were recorded with the help of a Philips PW 1140 diffractometer using Cr$K\alpha$ radiation.

The TG, DTG and DTA curves of TETUDS in the 25–500 °C range, with three different heating rates (2.5, 5 and 10 K min^{-1}) were recorded with sensitivities of 250 μV for DTA and 1 mV for DTG. As reference material, alumina was used, with platinum crucibles.

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THEORETICAL

To evaluate the kinetic parameters the following Freeman and Carroll relationship was used [1]

$$\frac{\Delta \ln \dot{\alpha}}{\Delta \ln (1-\alpha)} = n - \frac{E}{R} \frac{\Delta 1/T}{\Delta \ln (1-\alpha)} \tag{1}$$

where Δ is the difference operator; α is the conversion degree; t is the time; n is the reaction order; E is the activation energy (kcal mol^{-1}); T is the temperature (K); and $R = 1.987$ cal mol^{-1} K^{-1}.

The numerical data were computed through the least-squares method in order to obtain the slope and the intercept of the straight lines

$$\left[\frac{\Delta \ln \dot{\alpha}}{\Delta \ln (1-\alpha)}, \frac{\Delta 1/T}{\Delta \ln (1-\alpha)}\right]$$

i.e., E and n, respectively. The pre-exponential factor, A, was computed from the following equation

$$\dot{\alpha} = A(1-\alpha)^n \exp(-E/RT) \tag{2}$$

where E and n are the previously known values. The method of Coats and Redfern is based on the following equation [2]

$$\begin{array}{l} -\ln\left[-\dfrac{\ln(1-\alpha)}{T^2}\right]_{n=1} \\ -\ln\left[\dfrac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right]_{n\neq 1} \end{array} = \frac{E}{RT} - \ln\left[\frac{AR}{aE}\left(1-\frac{2RT}{E}\right)\right] \tag{3}$$

where a is the heating rate. In order to minimise the errors which can occur during trials for the reaction order, a FORTRAN program was used (see Appendix).

The third method, given by Ozawa [3], requires thermograms with different heating rates. For the same conversion degree (isoconversion condition) the following relationship is used to evaluate the activation energy

$$-\ln a - 0.457\, E/RT = \text{const.} \tag{4}$$

Indeed, from the slope of the following set of straight lines

$$(\ln a, 1/T)$$

for a certain conversion degree, the activation energy can be obtained. The gaseous products of the thermal decomposition were identified by chromatography as CS_2, N_2, H_2O and CO_2.

RESULTS AND DISCUSSION

The derivatograms corresponding to the heating of the samples from room temperature to 500 °C with $a = 2.5$, 5 and 10 K min^{-1} are given in Fig. 1.

TABLE 1

Bragg angles, θ, and the distances between parallel planes for the samples: (a) unheated; (b) heated at 75 °C and subsequently cooled at room temperature

θ	d (Å)	θ	d (Å)
(a)		(b)	
20°12	3.32	10°24	6.45
24°26	2.80	10°45	6.30
25°06	2.70	12°51	5.28
28°06	2.43	13°00	5.08
32°45	2.13	14°36	4.60
		16°00	4.15
		21°15	3.17

They exhibit a first endothermic phase change on the DTA curve, which occurs between 65 and 75 °C. The X-ray diffractograms of the unheated samples and those heated to 75 °C and subsequently cooled at room temperature exhibit some differences as shown in Table 1. These experimental facts support the statement that the above mentioned phase change is an irreversible one. A second significant change which occurs with a maximum rate at 195 °C corresponds to the oxidative thermal degradation of the substance according to the following chemical reaction

$$(C_2H_5)_2N\text{-}S\text{-}CS\text{-}CS\text{-}S\text{-}N(C_2H_5)_2(s) + 13O_2(g) \rightarrow 2CS_2(g) + N_2(g) + 8CO_2(g) + 10H_2O(g) \qquad (I)$$

The kinetic parameters of this reaction have been evaluated by all three methods and the results are given in Table 2.

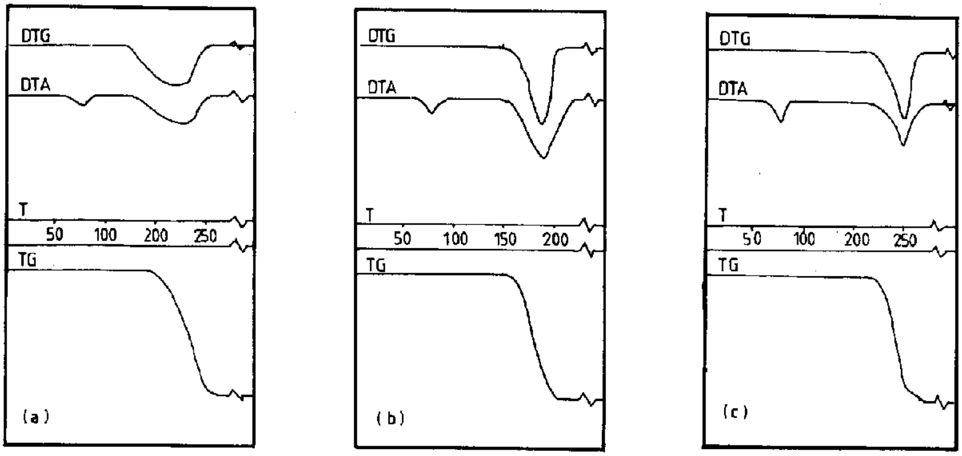

Fig. 1. The derivatograms of TETUDS heated with: (a) a = 2.5 K min^{-1}; (b) a = 5 K min^{-1}; (c) a = 10 K min^{-1}.

TABLE 2

The values of the kinetic parameters of reaction (I)

Method	A (s^{-1})	E (kcal mol^{-1})	n
Freeman–Carroll			
$a = 5$ K min^{-1}	7.2×10^3	33.6	0
Coats–Redfern			
$a = 2.5$ K min^{-1}	2×10^4	31	0
$a = 5$ K min^{-1}	7.2×10^3	33.4	0
Ozawa		30	0

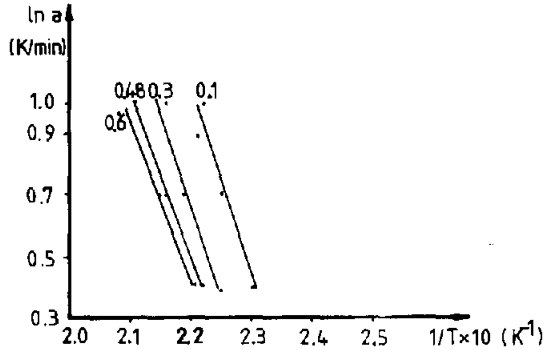

Fig. 2. The straight lines of (ln a, $1/T$).

The results are in very good agreement with each other. This allows us to propose $E = 32$ kcal mol^{-1}, $A = 10^4$ s^{-1}, and $n = 0$ as the kinetic parameters of reaction (I). As the graphs of

$$\ln a = f(1/T)$$

are parallel straight lines (see Fig. 2), a single reaction mechanism (I) can be supposed.

CONCLUSIONS

A kinetic study of the decomposition of TETUDS under non-isothermal conditions has been performed. In order to compute the kinetic parameters of the proposed reaction (I) three methods were used. The values of the kinetic parameters obtained by these three methods are in reasonable agreement with each other. The mean values of the kinetic parameters are: $E = 32$ kcal mol^{-1}, $A = 10^4$ s^{-1}, and $n = 0$.

APPENDIX

```
      DIMENSION Q(10),Y(10,21),W(10),B(21),A(21),ERO(21),X(21)
      READ(105,1)N,BETA,SM,(W(I),I = 1,N),(T(I),I = 1,N)
    1 FORMAT(I2,2F4.2/(1.F5.2))
      SX = 0.
      SX2 = 0.
      DO 2 I = 1,N
      T(I) = T(I) + 273.15
      W(I) = W(I)/SM
      X(I) = 1000./T(I)
      A1 = X(I)
      A2 = A1*A1
      SX = SX + A1
      SX2 = SX2 + A2
    2 CONTINUE
      EN = -0.05
      DO 3 J = 1,21
      EN = EN + 0.05
      SY = 0.
      SXY = 0.
      DO 4 I = 1,N
      IF(EN.EQ.1) GO TO 5
      E = 1.-EN
      A4 = 1./T(I)
      A3 = A4**2
      YIJ = -ALOG10((1.-(1.-W(I))**E)*A3/E)
      GO TO 6
    5 YIJ = -ALOG10((-ALOG(1.-W(I))*A3))
    6 SY = SY + YIJ
      SXY = SXY + XIJ**(I)
      Y(I,J) = YIJ
    4 CONTINUE
      DET = N*SX2-SX**2
      IF(DET)12,7,12
   12 DET1 = SY*SX2-SX*SXY
      DET2 = N*SXY-SX*SY
      A(J) = DET2/DET
      B(J) = DET1/DET
      ERO(J) = 0.
      DO 3 I = 1,N
      A5 = A(J)*X(I)*B(J)*Y(I,J)
    3 ERO(J) = ERO(J) + A5*A5
      EROMIN = ERO(J)
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```
      IA = 1
      DO 10 J = 2,21
      IF(EROMIN.LE.ERO(J)) GO TO 10
      EROMIN = ERO(J)
      IA = J
10    CONTINUE
      EN = 0.05*(IA-1)
      E = 4.576*B(IA)*1000
      WRITE(108,50)((Y(I,J),J = 1,21),I = 1,N)
50    FORMAT(21F6.5)
      WRITE(108,50)(A(I),I = 1,21),(B(I),I = 1,21)
      WRITE(108,51)N
51    FORMAT(' ','PE PRIMELE',I3,'NODURI APAR VALORILE
      YIJ,PE)
      *E 2 APAR A SI E CORESPUNZATOR LUI N')
      Z = 10* *(-B(IA))*BETA*E/(1.9871(1-2*1.987*(T(I) +
      T(N))/E))
      WRITE(108,I1)EN,A(IA),B(IA),E,Z
11    FORMAT(' ','ORDINUL DE REACTIE = ',F4.2,'COEFI-
      CIENTII A,B:
      *,'ENERGIA DE ACTIVARE',F6.3,'FACTORUL PREEX-
      PONENTIAL',F8
      WRITE(108,15)
15    FORMAT(60X,'SE TRECE LA ALT SET DE DATE',//)
      STOP
      END
```

REFERENCES

1 D. Fătu and E. Segal, J. Therm. Anal., 9 (1976) 65.

2 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.

3 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.