

THERMAL BEHAVIOUR OF RIBOFLAVIN

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From the thermal decomposition curves of riboflavin at various heating rates in static air atmosphere, the stages of thermal decomposition of this compound were established. The following kinetic parameters were calculated for the first decomposition stage of this process: activation energy (E_a), reaction order (n), preexponential factor (A) and reaction rate constant (k). A mechanism of the changes is proposed.

In studies on the physical and chemical properties and the structures of solid complexes of transition metal ions with organic ligand, it is of value to investigate the thermal decompositions of these compounds so as to obtain useful data on the metal-ligand bonds [1-4]. The literature appears to contain no information on the thermal properties of riboflavin and its complexes with metal ions. Riboflavin, 7,8-dimethyl-10-(1'-D-ribityl)-isoalloxazine, also called vitamin B₂, is a water-soluble vitamin. In living organism, it occurs as riboflavin phosphate (flavinomononucleotide, FMN) or as a dinucleotide with adenine (FAD), which are combined by enzymatic protein to give compounds called flavoproteins. FAD and FMN are prosthetic groups functioning as oxyreductase in biological oxidation. The only information on the thermal stability of riboflavin is that it melts and decomposes simultaneously at a temperature of about 290° [6]. Therefore, we decided to carry out a detailed thermal investigation of this compound in order to be able to study the thermal decompositions of riboflavin complexes with metal ions.

Experimental

Thermal decomposition curves of riboflavin were taken with a Paulik-Paulik derivatograph (MOM, Hungary) provided with a four-channel recorder. Samples were heated in corundum crucibles, using α -Al₂O₃ as a reference compound, in

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static air atmosphere within the temperature range 15–1000°. The heating rates were 2.5, 5, 10 and 20 deg min⁻¹, and the recording paper rate was set at the maximum value so as to obtain thermal curves elongated as possible. The sample mass was not higher than 50 mg, due to the strong exothermic effect in the second stage of decomposition at higher heating rates, leading even to an explosion. Samples of riboflavin of Analar grade were obtained from Reanal (Budapest, Hungary) and Merck.

Results and discussion

Figure 1 shows the curves of thermal decomposition of riboflavin at various heating rates. When the curves are compared, it is observed, that as the heating rate is increased there is a rise (by about 20 deg) in the temperature at which the first transition associated with mass loss takes place. From the DTA curve, it is seen that the endothermic effect corresponding to the melting of the sample at low heating

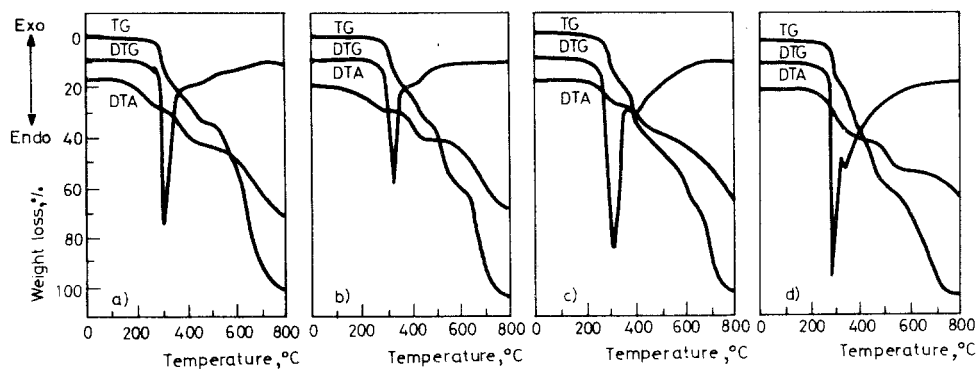


Fig. 1 Thermal decomposition curves for riboflavin in static air atmosphere: $t = 15\text{--}1000^\circ$, $m_0 = 50$ mg, DTG = 1/10, DTA = 1/5, a) $q = 2.5$ deg/min, b) $q = 5$ deg/min, c) $q = 10$ deg/min, d) $q = 20$ deg/min

rates disappears at higher rates, which indicates the decomposition of riboflavin without melting at higher heating rates. Independently of the heating rate, riboflavin decomposes in four nearly overlapping stages in static air atmosphere. Decomposition is completed by about 700°, with 100% weight loss. The DTA curve shape indicates that the first and third degradation stages are accompanied by endothermic effects, and the other stages by exothermic ones. The determined temperature ranges, mass losses and thermal effects accompanying the changes of riboflavin on heating are given in Table 1. Very delicate and slow heating made it

Table 1 The decomposition stages of riboflavine in static air atmosphere, sample mass $m_0 = 50$ mg, DTA = 1/5, DTG = 1/10

Temperature range, °C	Mass loss, %	Thermal effect	No of change
Heating rate $q = 2.5$ deg/min			
280–290	13	endo	I
290–340	21	exo	II
340–410	28	endo	III
410–610	38	exo	IV
$q = 5$ deg/min			
280–300	13	endo	I
300–350	21.5	exo	II
350–410	26	endo	III
410–640	39.5	exo	IV
$q = 10$ deg/min			
290–310	14	endo	I
310–350	22	exo	II
350–410	26	endo	III
410–660	38	exo	IV
$q = 20$ deg/min			
300–320	14	endo	I
320–370	24	exo	II
370–460	28	endo	III
460–700	36	exo	IV

possible to separate an intermediate compound, which we discovered on the basis of microanalysis (Table 2) and the IR data to be lumichrome. Separation of this compound was very difficult and we could not usually stop the reaction earlier than after the third stage of degradation, when we found carbon black in the crucible.

Table 2 Microanalysis data

	C, %		N, %		H, %	
	found	calc.	found	calc.	found	calc.
Riboflavin $C_{17}O_6N_4H_{20}$	54.20	54.25	14.92	14.89	5.35	5.36
Lumichrome $C_{12}O_4N_4H_{10}$	59.60	59.50	23.00	23.12	4.18	4.16

for given $\frac{dm}{dt}$, c and T read from the thermal curves, where $\frac{dm}{dt}$ = distance between

DTG curve and base line, mm,

m = mass loss, mg,

c = extent of change given by Eq. (2):

$$c = \frac{\Delta m_{\infty} - \Delta m}{\Delta m_{\infty}} \quad (2)$$

where Δm_{∞} = maximum loss during the given change, mg.

It was assumed for the calculation that the decomposition process satisfies the Arrhenius equation, i.e. there are definite values of A , E_a and x . In addition, it was assumed that the increase in the reaction rate depends mainly on physical processes (desorption, evaporation, etc.). Details concerning the calculation procedure are given in previous papers [7-9].

The activation energy was calculated from Eq. (3):

$$E_a = 2.303 R \tan \alpha_1 \quad (3)$$

where

R = universal gas constant

$\tan \alpha_1$ = directional coefficient

$$\log \frac{dm}{dt} = f\left(\frac{1}{T}\right) \quad (4)$$

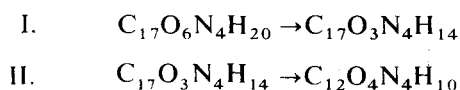
The reaction order n was determined as $\tan \alpha_2$ for the straight line of Eq. (5):

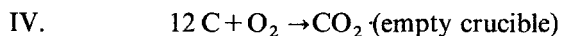
$$\log \frac{dm}{dt} + \frac{1}{T} \tan \alpha_1 = \tan \alpha_2 \cdot \log c + a_2 \quad (5)$$

The preexponential factor $\log A$ is the value cut off by straight line (5) on the y axis. The graphical relationship described by Eqs (4) and (5) are illustrated in Fig. 3. The parameters of these equations and the scatter of the results were calculated by the linear regression method [10].

The results are given in Table 3. Since the riboflavin samples of Reanal and Merck gave the same results, we have not detailed the producers.

To summarize, we have shown that riboflavin is a compound with relatively high thermal stability: its decomposition does not begin before 280-300° and it runs through four rapid stages (Eqs I-IV), while at a temperature of 700° (independently of the heating rate) the decomposition is complete, with 100% mass loss:





As could be expected, in stage I of the decomposition, the structure of the ribityl chain is disarranged. Two overlapping processes are observed. The first is assigned

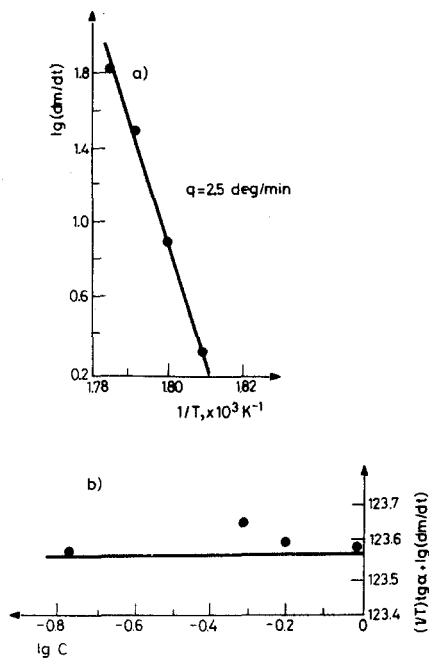


Fig. 3 Graphical determination of the kinetic parameters for the first stage of riboflavin decomposition:

$$\text{a) } \frac{dm}{dt} = \tan \alpha_1 \frac{1}{T} + a_2; \quad \tan \alpha_1 \cdot 2.303 \cdot R = E_a; \quad \text{b) } \log \frac{dm}{dt} + \frac{1}{T} (\tan \alpha_1) = \log c \cdot \tan \alpha_2 + a_2;$$

$\tan \alpha_2 = n$ in turn for various heating rates

Table 3 Kinetic parameters of the I stage of decomposition of riboflavin, calculated by the least square method from the thermal curves taken in static air atmosphere at various heating rates

Heating rate, deg min ⁻¹	Activation energy, E_a , kJ mol ⁻¹	Preexponential factor, A , s ⁻¹	Reaction order, n	Rate constant, $k_{293\text{K}}$
2.5	1305 ± 55	4 × 10 ¹²³	0.05 ± 0.1	9.6 × 10 ⁻¹¹⁰
5.0	796.5 ± 13	5.75 × 10 ⁷⁵	0.01 ± 0.04	5.3 × 10 ⁻⁶⁷
10	920 ± 17	3.86 × 10 ⁸⁶	0.03 ± 0.09	6.6 × 10 ⁻⁷⁸
20	985 ± 52	6.02 × 10 ⁹⁰	0.1 ± 0.5	1.6 × 10 ⁻⁸⁵

to the elimination of 3 molecules of water. The second leads to the elimination and combustion of the residue side-chain. Lumichrome is the solid residue, which was successfully separated when heating was provided very slowly. Further thermal degradation seems to be a one-stage process, after which only carbon black remains in the crucible. This is consistent with the data relating to the decomposition temperature of 7,8-dimethylisoalloxazine (Lumichrome) [6].

The combustion of the carbon black takes place in the last stage. Figure 2 shows the proposed stages of the thermal decomposition of riboflavin. It follows from the thermal analysis and the calculated kinetic parameters that the pyrolysis of riboflavin is a highly energetic process, which is confirmed by the high activation energy. On the other hand, the order of the reaction is exceptionally low, which indicates that the intermolecular interaction does not affect the process. The calculated decomposition rate k is extremely high for all the investigated heating rates. Our data concerning the riboflavin complexes with metal ions show that their thermal stabilities are generally lower than that of the free ligand. This question will form the subject of our next paper.

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Zusammenfassung — Die Stadien der thermischen Zersetzung von Riboflavin wurden aus den Kurven der thermischen Zersetzung in Luftatmosphäre bei verschiedenen Aufheizgeschwindigkeiten ermittelt. Für den ersten Zersetzungsschritt dieses Prozesses werden die Werte für die Aktivierungsenergie (E_a), die Reaktionsordnung (n), den präexponentiellen Faktor (A) und die Reaktionsgeschwindigkeitskonstante (k) berechnet. Für die Umwandlungen wird ein Mechanismus vorgeschlagen.

Резюме — На основе кривых термического разложения рибофлавина, полученных в статической атмосфере воздуха и при различных скоростях нагрева, установлены пути его термического разложения. Для первой стадии разложения рибофлавина были вычислены такие кинетические параметры, как энергия активации (E_a), порядок реакции (n), предэкспоненциальный множитель (A) и константа скорости реакции (k). Предложен также механизм разложения.