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THERMAL DECOMPOSITION OF 3-(4,5-DIMETHYL-2-THIAZOLYLAZO)-2,6-DIAMINOPYRIDINE

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ABSTRACT

3-(4,5-Dimethyl-2-thiazolylazo)-2,6-diaminopyridine and its complex with cobalt(III) have been synthesized and characterized for the first time in our laboratory. In the present work, the thermal decomposition of this ligand of analytical interest has been investigated. It undergoes a denitrogenation reaction as a first decomposition step whose kinetic parameters have been evaluated. The enthalpy for this reaction was found to be 33.41 kJ mol^{-1} from DSC curves.

INTRODUCTION

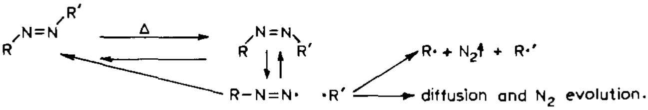
This work is part of an investigation to study the properties of synthetic ligands such as thiazolyl-azo derivatives of analytical interest as colorimetric reagents for many metal ions [1–7].

In the last few years the thermal properties of these ligands have been considered an important part of their investigation [8,9]. And, in general, thermoanalytical techniques are developing an increasing interest in the study of organic compounds, concerning their stability and structure i.e., physical and chemical transitions [10–12].

The thermolysis of organic heterocyclic compounds in the solid state may be studied with the aid of TG, DTG and DSC techniques. This can be a useful synthetic route to numerous ring systems, particularly those which are accessible by thermally allowed bond reorganization [9].

The decomposition chemistry of the azo compounds is potentially complicated because of the existence of *cis* and *trans* isomers. The *trans* form is the most stable one; the *cis* isomers are implicated as intermediates in photochemical decompositions starting from *trans*, but it is not clear whether they are also involved in the thermal decomposition [13–17].

The probable mechanism for the thermal decomposition of unsymmetric azo compounds is outlined in Scheme 1 [18].



Scheme 1.

The aim of the present work is to study the thermal decomposition pattern of 3-(4,5-dimethyl-2-thiazolylazo)-2,6-diaminopyridine (DMTADAP). TG, DTG and DSC measurements in a non-isothermal regime have been carried out. The gases produced by thermal decomposition have been analyzed by gas chromatography.

EXPERIMENTAL

The synthesis and characterization of the compound were described in a previous work [7].

TG, DTG and DSC curves were obtained from a Perkin–Elmer 7 Series thermal analysis system in a helium atmosphere. Five different heating rates of 3,4,5,6 and 7 K min^{-1} were used for TG and DTG scannings and a rate of 5 K min^{-1} was chosen for DSC measurements. Sample weights ranging from 9.0 to 10.0 mg were employed.

The gases proceeding from the thermogravimetric decomposition of the samples were analyzed by means of gas chromatography. The TGS-7 was connected to a Perkin–Elmer Sigma 3B gas-chromatograph provided with a Sigma 10-B data station and conductivity detector. Samples were injected through a gas valve, and helium gas was used as the carrier with a flow rate of 28 cm^3 min^{-1}.

RESULTS AND DISCUSSION

The non-isothermal TG and DTG curves show that the compound undergoes decomposition in three stages in the temperature ranges 348–398 K, 533–573 K and 713–943 K respectively (data from the experiment at a heating rate of 5 K min^{-1}). The weight loss observed at the end of the first stage was always found to be 5.5%. This amount of weight loss corresponds to that calculated if half of the nitrogen content as azo group 11.0% were lost per molecule of DMTADAP.

The residue at 400 K undergoes a thermal degradation into a dark-red material at 573 K with a weight loss of 25.8% along this step. No residue remained at 943 K indicating complete oxidation to gaseous products.

Figure 1 shows the chromatogram obtained for the gases lost along the

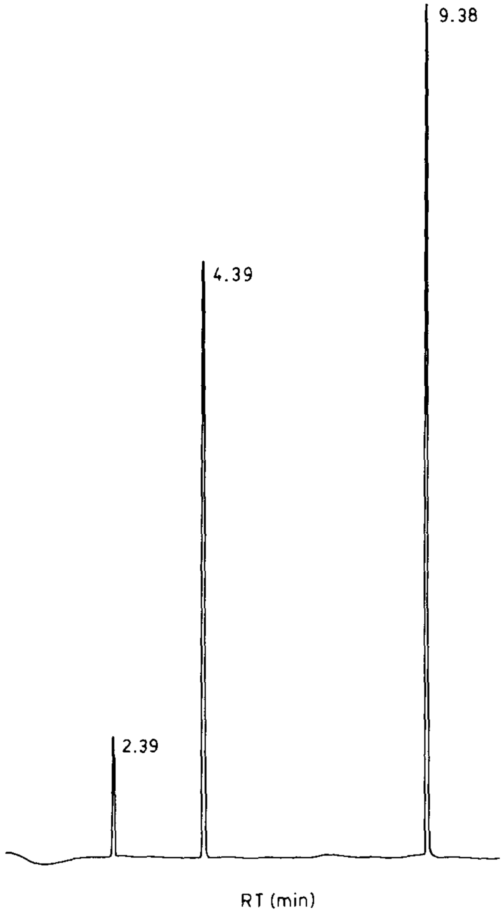


Fig. 1. Chromatogram of the gases from thermogravimetric decomposition of the compound between 350 and 400 K. Injection time 2, 4 and 9 min.

first decomposition step. As can be seen, only one peak appears corresponding to nitrogen in the working conditions.

This first decomposition step was studied in order to obtain the kinetic parameters for the denitrogenation reaction.

The DSC curve, in Fig. 2, shows one endothermic effect at 387 K, which corresponds to the weight loss observed in TG curves. From the area of this peak a value of 33.41 kJ mol^{-1} for the denitrogenation reaction enthalpy was calculated.

Figure 3 shows plots of α–T data obtained from TG curves at different heating rates. These are sigmoidal as corresponds with a nucleation–growth physical model.

Three methods of kinetic analysis have been employed: the one proposed by Jerez as a modification of the Freeman and Carroll method [19,20], on each TG–DTG curve, and two methods for the non-isothermal thermogravi-

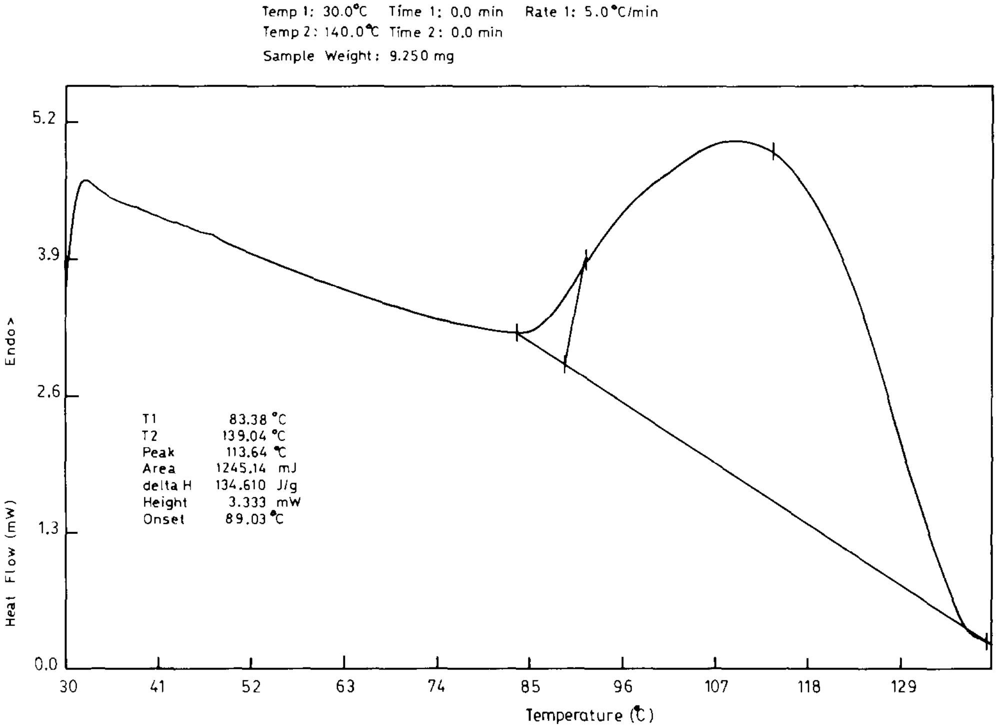


Fig. 2. DSC curve of the denitrogenation reaction.

metric analysis considering the heating rate as a variable [21–23]. Seventeen different kinetic models have been utilized in all the cases [24].

The plots ln $\alpha' - \ln f(\alpha)$ vs. $1/T$ (MFC method) showed poor linearity.

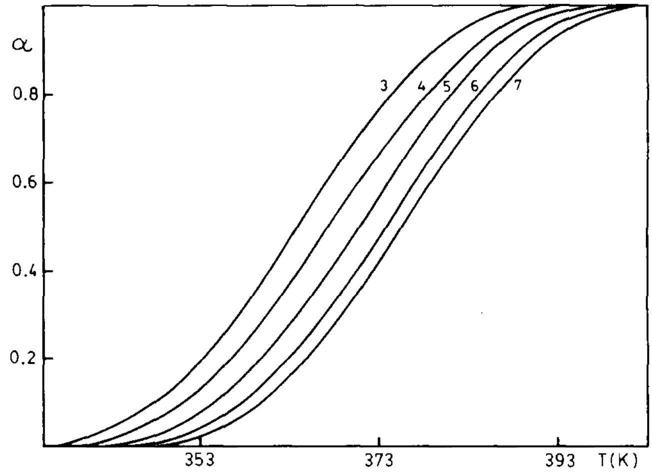


Fig. 3. α–T plots for the different heating rates.

TABLE 1

Activation energy E (kJ mol^{-1}), frequency factor A (s^{-1}) and correlation coefficient r, for the equations $f(\alpha) = \{d[(-\ln(1-\alpha))^n]/d\alpha\}^{-1}$. MFC method

n		β (°C min^{-1})				
		3	4	5	6	7
	E	−11	0.07	−0.8	−5	3
1/4	A	3.10^{-5}	2.10^{-3}	2.10^{-3}	5.10^{-4}	1.10^{-2}
	r	0.211	1.10^{-5}	1.10^{-3}	7.10^{-2}	2.10^{-2}
	E	0.14	10	9	5	14
1/3	A	2.10^{-3}	6.10^{-2}	6.10^{-2}	2.10^{-2}	0.37
	r	5.10^{-5}	0.185	0.152	8.10^{-2}	0.21
	E	22	30	30	26	35
1/2	A	3	6.10^{1}	6.10^{1}	2.10^{1}	4.10^{2}
	r	0.684	0.732	0.702	0.801	0.663
	E	44	50	50	47	56
2/3	A	6.10^{3}	5.10^{4}	6.10^{4}	2.10^{4}	4.10^{5}
	r	0.931	0.907	0.892	0.951	0.852
	E	89	91	92	90	98
1	A	2.10^{10}	3.10^{10}	4.10^{10}	2.10^{10}	3.10^{11}
	r	0.976	0.971	0.967	0.979	0.951
	E	155	151	153	153	160
3/2	A	6.10^{19}	1.10^{19}	2.10^{19}	2.10^{19}	2.10^{20}
	r	0.969	0.977	0.977	0.972	0.974

Thus, Table 1 gives only the results obtained for the six functions $F(\alpha) = [-\ln(1-\alpha)]^n$ for the curves scanned at the five heating rates. As can be seen the r coefficients are lower than 0.980, but the best values are close to 0.97. This method allows us to distinguish between the different equations on the basis of correlation coefficients on the assumption that the kinetic behaviour is the same throughout the transformation.

Table 2 shows the activation energies determined for different values from Ozawa's method [21,22]. It should be noted that this parameter increases as α increases. One of the reasons for this behaviour could be the variation of the relative influence of the controlling steps along the reaction. By using 84.28 kJ mol^{-1} as E value, the $1-\alpha$ vs. $\log[(E/\beta R)p(x)]$ curves were

TABLE 2

The activation energy E (kJ mol^{-1}) and correlation coefficient r, from the plots of log β vs. $1/T$. (Ozawa method [21,22])

α	0.2	0.3	0.4	0.5	0.6	0.7	0.8
E	79	80	82	83	86	87	90
r	0.989	0.989	0.987	0.994	0.999	0.996	0.995

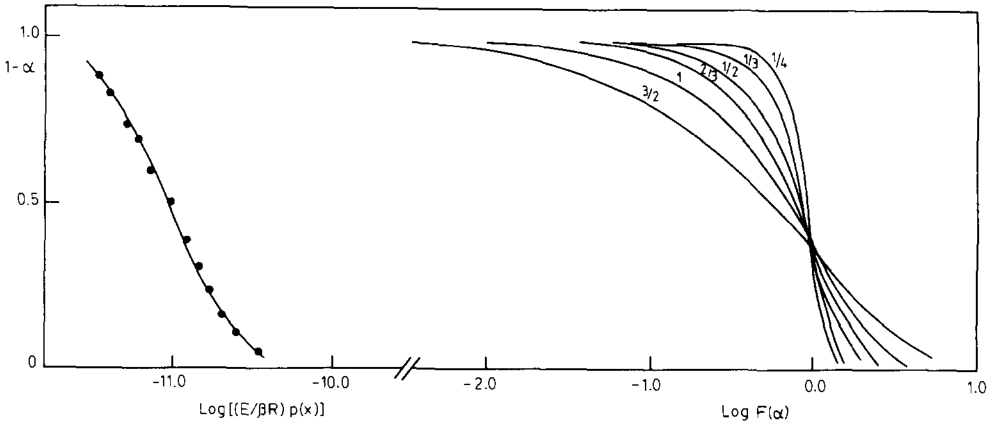


Fig. 4. The theoretical thermogravimetric curves for the kinetic equation $F(\alpha) = [-\ln(1-\alpha)]^n$, (right); and experimental curve (left).

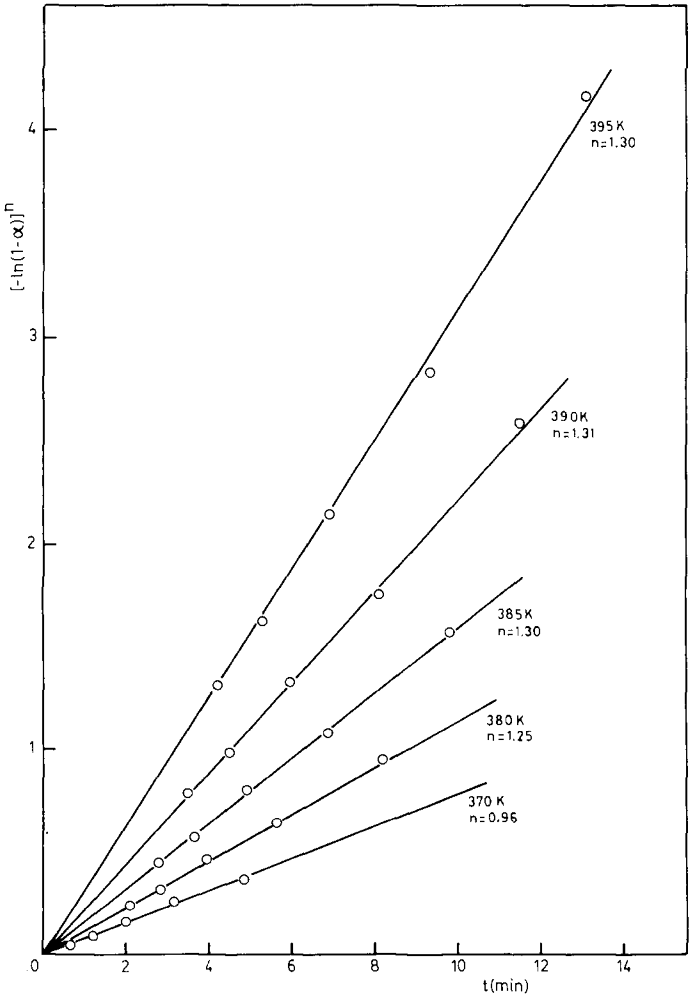


Fig. 5. $[-\ln(1-\alpha)]^n$ vs. t plots for several temperatures.

TABLE 3

Values of n and r (correlation coefficient) from Romero's method [23]

T (K)	369	370	375	380	385	390	395
n	0.92	0.96	1.14	1.25	1.30	1.31	1.30
r	0.998	0.998	0.998	0.998	0.998	0.998	0.998

plotted and superimposed to fit upon one of the theoretical curves $1-\alpha$ vs. log $F(\alpha)$, Fig. 4, but the experimental plot was not coincident with any of them. So, it is not possible to explain the relation of $F(\alpha)$ with α by using a simple kinetic model.

The method proposed by Romero et al. [23] allows us to choose between the kinetic models based on the separation of the temperature and conversion influence on the reaction rate. The conversion–time data at the same temperature can be obtained from the non isothermal curves at different heating rates. These values should be adjusted to the equation $F(\alpha)=K_T t$ assuming a kinetic model of separate variables. For the nucleation–growth, $\ln[-\ln(1-\alpha)]$ can be plotted vs. ln t and the n values can be obtained from the slopes of the straight lines for every temperature. The results obtained appear in Table 3. As can be seen, the n value increases with temperature and remains constant at about 1.3 above 112° C. Figure 5 shows the plots $F(\alpha)$ vs. t for each temperature with the n value obtained.

CONCLUSIONS

The three methods employed in the present work have shown that the most probable mathematical expressions for the α-functions are those for nucleation–growth with the n value increasing with temperature until it reaches 1.3 at 112° C.

This kinetic behaviour can be explained on the basis of the reaction mechanism proposed for the thermal decomposition of diazenes, yielding dinitrogen and radicals. The observed enthalpy change, which is considerably lower than the carbon–nitrogen bond energy, can be explained by the partial formation of dinitrogen and the *trans* isomer.

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