*Journal of Thermal Analysis, Vol. 7 (1975) 33–40*

# KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA

## IX. THERMAL DECOMPOSITION OF SOME [$CoX_2$(amine)$_2$] TYPE COMPLEXES UNDER ISOTHERMAL CONDITIONS

J. ZSAKÓ and CS. VÁRHELYI

*Faculty of Chemistry of the "Babeş-Bolyai" University, Cluj, Romania*

(Received November 30, 1972)

The thermal decomposition rates of seven [$CoX_2(amine)_2$] type complexes (amine = aromatic amines) have been studied by thermogravimetry at 3 different temperatures for each compound. Apparent reaction orders, rate constants, activation energies, and preexponential factor values of the Arrhenius equation have been derived. The parameters obtained are compared with those derived from TG curves recorded under dynamic temperature conditions. The same reaction order, but higher activation parameters have been obtained as in the case of dynamic thermogravimetry. Nevertheless, the activation parameters derived seem to obey the same linear kinetic compensation law as the activation parameters reported earlier.

The cobalt(II) halides give [$CoX_2(amine)_2$] type complexes with aliphatic, aromatic and heterocyclic amines in non-aqueous solvents such as alcohols, acetone, etc. [1–4], Biltz and Fetkenhauer [5] observed some of them to exist in two modifications, $\alpha$ (blue) and $\beta$ (pink). Biltz et al. [6] and Hantsch [7] presume this isomerism to be the cis-trans type, but Mellor [8] assigns a chain structure to the violet isomer of [$CoCl_2Py_2$], with a co-ordination number of 6 for the $Co$, and a tetrahedral structure for the isomer. X-ray studies are consistent with these assumptions [9–10].

At higher temperatures these complexes decompose. Liberation of amine is observed, and the substance is transformed first to a black resinous mass, and then to the anhydrous cobalt halide or even the oxide. The thermal decompositions of a large number of analogous complexes, derivatives of $Ni$(II), $Co$(II), $Mn$(II), $Cu$(II) and $Cd$(II), have been studied by Fătu et al. [11–16] and the formation of a relatively stable [$MX_2(amine)_{2/3}$] type intermediate has frequently been observed [11].

In our previous papers [17, 18] the kinetics of the thermal decomposition of cobalt(II) complexes of this type have been studied under dynamic temperature conditions. Our results are consistent with the formation of a [$CoX_2(amine)_{2/3}$] type intermediate, which seems to be formed directly if $X = Cl$, and in two successive stages if $X = Br$ or $I$ [18]. The first stage of thermal decomposition frequently has two distinct kinetic stages, not separated by a plateau on the TG curve, the first kinetic stage needing a smaller activation energy, and the second a higher one [17, 18].

Derivation of the kinetic parameters has been performed by means of Coats and Redfern's method [19], by assuming a rate law of the type

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \tag{1}$$

and an Arrhenius equation of the type

$$k = Z \cdot e^{E_a/RT} \tag{2}$$

to be valid, where $\alpha$ stands for the conversion (fraction transformed), $n$ for the apparent reaction order, $k$ for the apparent rate constant, and $E_a$ for the apparent activation energy. Coats–Redfern linearizations have been tried with the following values for $n$: 0, 1/3, 1/2, 2/3, 1 and 2.

In order to derive the pre-exponential factor values, the following equation has been used [20]:

$$\log Z = \log g(\alpha) - \log p(x) + \log R \cdot q - \log E_a \tag{3}$$

where $g(\alpha)$ stands for the conversion integral

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} \tag{4}$$

$p(x)$ for the exponential integral tabulated in [20], $x$ for $E_a/RT$ and $q$ for the heating rate in $K \cdot s^{-1}$.

Since the shapes of the TG curves, and consequently also the kinetic parameters derived from these curves, depend on procedural variables [17], further measurements have been performed under identical working conditions for the different complex compounds studied.

The TG curves obtained can be characterized fairly well by means of the kinetic parameters $n$, $E_a$ and $Z$, the last two not being independent of each other, since they are correlated by a linear kinetic compensation law of the following type:

$$\log Z = a \cdot E_a + b \tag{5}$$

In the present paper a trial has been made to compare the kinetic parameters derived from TG data obtained under dynamic temperature conditions with those obtained under isothermal conditions. In order to modify as few procedural variables as possible, measurements have been performed by using the same thermobalance, the same sample holder, the same sample weight (100 mg) and the same atmosphere (air) as in our previous paper [18]. The only difference consisted in the temperature programme used. While a constant heating rate of 10°/min was used in our previous study, in the present paper this heating rate has been maintained only until the working temperature $T_i$ has been reached. After that the sample weight has been recorded at constant temperature.

If a type (1) rate law is valid, the graphical plot of $g(\alpha)$, given by (4), vs. time must be linear for a given $n$ value, if $t$ exceeds the time $t_i$ necessary to reach the working temperature $T_i$. In order to verify the validity of eq. (1), experimental weight loss values have been transformed to conversions $\alpha$, and by using the formulae given in reference [20], where $g(\alpha)$ values have been calculated for all the six hypothetical reaction orders. The graphical plot of $g(\alpha)$ vs. $t$ showed a good linearity for one of the $n$ values tried, generally beginning from $t_i$, as seen from the example given in Fig. 1.

It is worth mentioning that this linearity sometimes appeared only later, which is consistent with our earlier observations concerning the existence of two distinct kinetic stages. In the majority of kinetic runs, however, the first kinetic stage was accomplished in the heat-up period $t < t_i$, as in the case of the example given in Fig. 1.

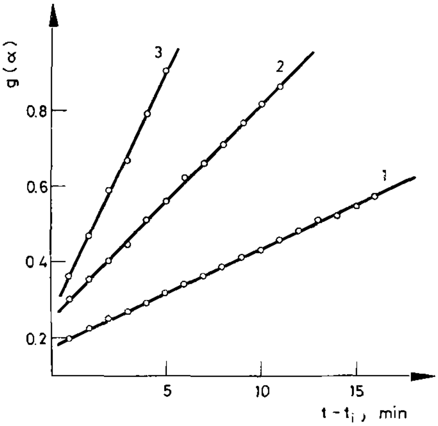

Fig. 1. Determination of rate constants for the thermal decomposition of [CoCl$_2$(p-toluidine)$_2$].
$n = 0$
1 – 160°C; 2 – 170°C; 3 – 180°C

The slope of the straight line obtained gives the apparent rate constant $k$ for the temperature $T_i$ directly. Table 1 presents the $n$ values which ensured the linearity of the above-mentioned graphical plots, as well as the rate constants derived for 7 complexes of the type studied.

It is significant that the $n$ values obtained are in all cases identical with those reported earlier on the basis of TG measurements performed under dynamic temperature conditions, i.e. the same $n$ value which ensured the linearity of the Coats–Redfern plot is also derived from our isothermal measurements. This means that although the apparent reaction order $n$ does not have the same physical significance as the reaction order in homogeneous kinetics, nevertheless it does have a definite meaning, i.e. it is more than a simple variation parameter. This is not in disagreement with our earlier statement that the physical meaning of kinetic parameters derived from TG curves is rather obscure, and that it cannot be cleared up on the basis of thermogravimetric data [21]. These parameters exist,

Table 1

Rate constants of the thermal decomposition of [$CoX_2(amine)_2$] type complexes. $k \times 10^4$, $s^{-1}$

| Amine | X | *n* | 130° | 140° | 145° | 150° | 155° | 160° | 170° | 175° | 180° |
|---|---|---|---|---|---|---|---|---|---|---|---|
| p-toluidine | Cl | 0 | — | — | — | — | — | 3.87 | 8.61 | — | 17.7 |
| | Br | 2/3 | — | — | — | 19.3 | — | 60.0 | 114 | — | — |
| | I | 1 | — | 17.1 | 44.7 | 89.2 | — | — | — | — | — |
| m-toluidine | Cl | 0 | 0.795 | — | — | 3.38 | — | — | 10.3 | — | — |
| | Br | 1/3 | — | — | — | — | — | — | 17.5 | 26.0 | 35.6 |
| o-ethyl-aniline | Cl | 0 | 4.62 | 8.89 | 12.5 | — | — | — | — | — | — |
| | Br | 2/3 | — | — | — | — | 14.7 | 21.0 | 40.0 | — | — |

can be reproducibly derived and do characterize the thermal decomposition process. However the formal analogy with homogeneous kinetics does not allow us to assign the same physical significance to these parameters as in homogeneous kinetics. In order to clear up the meaning of these parameters, other physical investigations are also necessary besides the thermogravimetric ones.

Table 2

Activation parameters for the thermal decomposition of [$CoX_2(amine)_2$] type complexes, derived from isothermal rate constant values (isoth.), as compared to the same parameters derived from TG measurements under dynamic temperature conditions (dynam.)

| Amine | X | $E_a$, kcal/mole | | log *Z* | |
|---|---|---|---|---|---|
| | | isoth. | dynam.* | isoth. | dynam.* |
| p-toluidine | Cl | 29.9 | 25.3 | 11.7 | 9.3 |
| | Br | 33.0 | 30.7 | 14.4 | 12.4 |
| | I | 57.6 | 32.3 | 27.7 | 13.5 |
| m-toluidine | Cl | 22.8 | 20.3 | 8.3 | 7.1 |
| | Br | 28.8 | 26.8 | 11.4 | 10.2 |
| o-ethylaniline | Cl | 22.1 | 18.2 | 8.7 | 6.4 |
| | Br | 25.1 | 23.6 | 10.0 | 9.3 |

* Taken from [18].

If the validity of eq. (2) is assumed, the graphical plot of log $k$ vs. $1/T$ must give straight lines. By using the rate constants given in Table 1, this graphical plot exhibits fairly good linearity, as seen in Fig. 2.

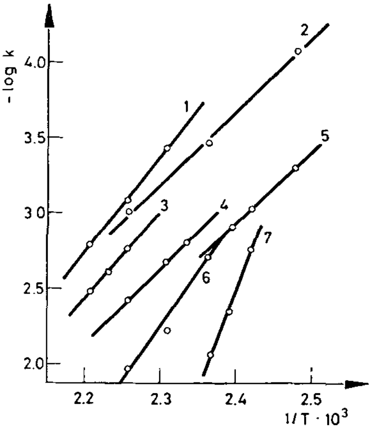

Fig. 2. Determination of activation parameters for the thermal decomposition of [$CoX_2$-(amine)$_2$] type complexes
1 — [$CoCl_2$(p-toluidine)$_2$]; 2 — [$CoCl_2$(m-toluidine)$_2$]; 3 — [$CoBr_2$(m-toluidine)$_2$; 4 — [$CoBr_2$(o-ethylaniline)$_2$]; 5 — [$CoCl_2$(o-ethylaniline)$_2$]; 6 — [$CoBr_2$(p-toluidine)$_2$]; 7 — [$CoI_2$(p-toluidine)$_2$]

Thus, our experimental results are consistent with the validity of both eq. (1) and eq. (2). This allows us to derive $E_a$ values from the slopes of the straight lines obtained, and $Z$ values from the ordinate intercepts. These kinetic parameters are presented in Table 2; the same Table also gives the kinetic parameters derived from the TG curves recorded under dynamic temperature conditions, by using a constant heating rate of $q = 10°C/min$, i.e. the $E_a$ and log $Z$ values of the second kinetic stage of the first de-amination reaction.

The comparison of these "isothermal" and "dynamic" activation parameters shows that under isothermal conditions one always obtains higher $E_a$ and $Z$ values than under dynamic temperature conditions. This is in very good agreement with our earlier observations concerning the influence of the heating rate upon the apparent activation parameters [17, 22, 23].

Both activation energy and pre-exponential factor diminish with increasing heating rate. Our isothermal measurements can be considered a boundary case, corresponding to zero heating rate. Thus, it is obvious that higher activation parameters can be expected than under dynamic temperature conditions.

As far as the kinetic compensation law (5) is concerned, the graphical plot of log $Z$ vs. $E_a$, given in Fig. 3, exhibits good linearity. The compensation parameters $a$ and $b$, derived by means of the least square method from our "isothermal" activation parameters given in Table 2, are presented in Table 3, together with

Table 3

Kinetic compensation parameters for the thermal decomposition of $[CoX_2(amine)_2]$ type complexes

| | *a* | *b* |
|---|---|---|
| Isothermal measurements | 0.549 ± 0.040 | −4.02 ± 1.34 |
| Dynamic temperature conditions* | 0.534 ± 0.020 | −3.75 ± 0.52 |

* Taken from [18].

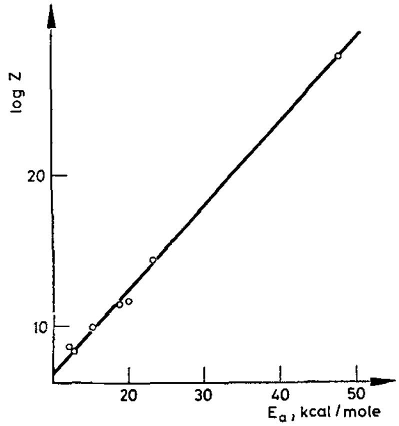

Fig. 3. Kinetic compensation effect in the thermal decomposition of $[CoX_2(amine)_2]$ type complexes

those reported earlier [18], derived from the TG curves recorded under dynamic temperature conditions.

It is clear that these parameters are consistent with each other within the limits of experimental error. The *a* values obtained are very close to those reported for the de-amination of $[Co(dioxime)_2(amine)_2]\,X$ type complexes [24], but much higher than the *a* values observed in the case of the thermal decompositions of carbonates [23, 25].

## Experimental

The complexes studied have been synthesized as described in our previous paper [18].

Thermogravimetric measurements have been carried out under the same conditions as reported earlier [18], with the exception of the temperature programme. A constant heating rate of $q = 10°C/min$ has been used from room temperature up to the isothermal working temperature $T_i$, and after this the temperature has been maintained at the constant value $T_i$.

## References

1. E. LIPPMANN and G. VORTMANN, Ber. dtsch. chem. Ges., 11 (1878) 1068; 12 (1879) 79.
2. W. HIEBER and F. MÜHLBAUER, Z. anorg. Chem., *186* (1930) 97.
3. W. HIEBER and E. LORY, Z. Elektrochem., 39 (1933) 26.
4. A. V. ABLOV, Z. P. BURNASHEVA and E. G. LEVITSKAIA, Zhur. neorg. Khim., 1 (1956) 2645.
5. W. BILTZ and B. FETKENHAUER, Z. anorg. Chem., 89 (1914) 126.
6. W. BILTZ and H. GRIMM, Z. anorg. Chem., 145 (1925) 63.
7. A. HANTSCH, Z. anorg. Chem., 159 (1926) 273.
8. D. D. MELLOR and C. D. CORNWELL, J. Amer. Chem. Soc., 60 (1938)
9. G. B. BOKII, T. J. MALINOVSKY and A. V. ABLOV, Kristallografiya, 1 (1956) 49.
10. A. V. ABLOV, C. B. KONUNOVA-FRID and V. A. PALKIN, Zhur. neorg. Khim., 5 (1960) 1544.
11. I. G. MURGULESCU, E. SEGAL and D. FĂTU, J. Inorg. Nucl. Chem., 27 (1965) 2677; Rev. Roumaine Chim., 11 (1966) 291.
12. E. SCHÖNBERGER, D. FĂTU and E. SEGAL, Rev. Roumaine Chim., 12 (1967) 1205.
13. D. FĂTU and E. SEGAL, Anal. Univ. Bucureşti, Chimie, 2 (1968) 49.
14. D. FĂTU and E. SEGAL, Rev. Roumaine Chim., 14 (1969) 709.
15. D. FĂTU, S. FĂTU and E. SEGAL, Rev. Roumaine Chim., 14 (1969) 1107.
16. D. FĂTU, S. FĂTU, A. TEODORESCU and E. SEGAL, Rev. Roumaine Chim., 15 (1970) 855.
17. J. ZSAKÓ, E. KÉKEDY and CS. VÁRHELYI, Proc. 3rd Inter. Conf. Therm. Anal., Davos, Switzerland, 1971, p. 487.
18. CS. VÁRHELYI, J. ZSAKÓ and M. BOÁRIU-FARKAS, Rev. Roumaine Chim., in press.
19. H. W. COATS and J. P. REDFERN, Nature, 201 (1964) 68.
20. J. ZSAKÓ, J. Phys. Chem., 72 (1968) 2406.
21. J. ZSAKÓ, J. Thermal Anal., 5 (1973) 239.
22. J. ZSAKÓ, E. KÉKEDY and CS. VÁRHELYI, J. Thermal Anal., 1 (1969) 339; Rev. Roumaine Chim., 15 (1970) 865.
23. J. ZSAKÓ and H. E. ARZ, J. Thermal Anal., 6 (1974) 651.
24. J. ZSAKÓ and M. LUNGU, J. Thermal Anal., 5 (1973) 77.
25. M. M. PAVLYUCHENKO, G. A. PRODAN and S. A. SLYSHKINA, Doklady Akad. Nauk S.S.S.R., 181 (1968) 1174.

RÉSUMÉ — On a étudié les vitesses de décomposition de sept complexes du type $CoX_2(amine)_2$ en se servant de la thermogravimétrie et en utilisant 3 températures différentes pour chaque composé (amine = amine aromatique). On en a déduit l'ordre apparent de la réaction, la constante de vitesse, l'énergie d'activation ainsi que le facteur préexponentiel de l'équation d'Arrhenius. On a comparé les paramètres ainsi obtenus à ceux qui ont été calculés à partir des courbes TG enregistrées dans des conditions d'échauffement dynamique. On a obtenu le même ordre de réaction mais pour l'activation, des paramètres plus élevés qu'avec la thermogravimétrie dynamique. Il semble cependant que les paramètres caractérisant l'activation suivant la même loi de compensation cinétique linéaire que ceux qui ont été publiés précédemment.

ZUSAMMENFASSUNG — Die thermische Zersetzungsgeschwindigkeit von sieben Komplexen des Typs $CoX_2(Amin)_2$ (Amin = aromatisches Amin) wurde thermogravimetrisch untersucht undzwar jede Verbindung bei 3 verschiedenen Temperaturen. Die scheinbare Reaktionsordnung, Geschwindigkeitskonstante, Aktivierungsenergie, sowie die Werte des präexponentiellen Faktors der Arrhenius-Gleichung wurden abgeleitet. Die erhaltenen Parameter wurden mit denjenigen verglichen, welche von den unter dynamischen Temperaturbedingungen registrierten TG-Kurven abgeleitet wurden. Dieselbe Reaktionsordnung, aber höhere Aktivierungsparameter als bei der dynamischen Thermogravimetrie wurden erhalten. Die abgeleiteten Aktivierungsparameter scheinen dem gleichen linearen kinetischen Kompensationsgesetz zu gehorchen wie diejenigen, über welche früher berichtet wurde.

Резюме — С помощью термогравиметрии исследована скорость термораспада 7 комплексов типа $[CoX_2(\text{амин})_2]$ (амин = ароматические амины), при трех различных температурах. Рассчитаны значения видимого порядка реакции, константы скорости, энергии активации и предэкспоненциального фактора уравнения Аррениуса. Полученные значения сравнены со значениями параметров, рассчитанными по кривым ТГ, снятым в неизотермических условиях. Установлено, что в случае изотермической термогравиметрии порядок реакции тот же, но параметры активации имеют более высокое значение. Тем не менее, рассчитанные параметры активации, повидимому, удовлетворяют тому же правилу линейной кинетической компенсации, что и ранее опубликованные параметры активации.