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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA, V

COMPENSATION EFFECT IN THE THERMAL DECOMPOSITION OF BISDIOXIMATOCOBALT(III) COMPLEXES

J. ZSAKÓ and M. LUNGU

Faculty of Chemistry, Babeş-Bolyai University, Cluj, Roumania

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The statistical analysis of activation energy and of log Z values derived from thermogravimetric data for 134 decomposition reactions of bisdioximatocobalt(III) complexes shows the validity of a linear compensation law, i.e. both the effects of heating rate and of the nature of the ligand manifest themselves in the kinetic compensation effect. The parameter a of the compensation law is sensitive to ligand effects and its value is influenced both by the nature of the coordinated dione-dioxime and by the nature of the outer sphere anion X, which replaces an ammonia molecule in the thermal decomposition reaction.

Procedural variables have a considerable influence on the kinetic parameters of thermal decomposition reactions. Variations of these parameters are not independent of each other and certain general correlations exist between them [1]. Of these correlations only the so-called kinetic compensation effect is well known. It was first observed in the case of copper catalysts [2] of different activities used for the dehydrogenation of ethanol. It has been found that an increase in the activation energy E of the reaction does not lead to the expected decrease of the rate constant, because there occurs a simultaneous increase in the pre-exponential factor Z in the Arrhenius equation, which compensates for the change in the exponential factor. This compensation effect has been observed to operate in various systems, not only in heterogeneous catalysis, but also in thermal decomposition [1]. Very frequently the relation between Z and E takes the form:

$$\log Z = aE + b \tag{1}$$

Pavlyuchenko et al. [1] observed the validity of this linear relationship in the case of the thermal decomposition of $CdCO_3$ and of $MnCO_3$, synthesized under different conditions and submitted to various thermal pretreatments. On the basis of literature data, these authors have found the thermal decomposition of $CaCO_3$ and $MgCO_3$ to obey the same law. In all the cases b is nearly zero and a is a constant of about 0.2—0.3 kcal/mol, larger for $CdCO_3$ and $MnCO_3$ and smaller for $CaCO_3$ and $MgCO_3$.

Although in the thermogravimetric literature pre-exponential factor data derived from TG curves are very scarce, the compensation effect seems to be very general. A systematic and parallel decrease of both log Z and E values with increasing heating rate has been reported [3, 4]. On the other hand, the decomposition temperature interval is known to be increased and shifted towards higher temperatures when increasing the heating rate [5 – 10]. In terms of kinetic parameters this effect also means the simultaneous reduction in both log Z and E values with increasing heating rate, as one can easily show taking into account the theoretical shape of TG curves, and its dependence on the parameteres Z and E [11]. The systematic decrease of the activation energy, derived from TG curves, with increasing heating rate has been observed also in the case of thermal degradation of polymers [12 – 15]. All these phenomena involve the kinetic compensation effects.

A theoretical explanation of the compensation effect has been made in the case of catalysts in terms of active sites of different activities [2]. On the other hand, a relationship of the type (1) is consistent with the Polányi – Wigner equation [16], too, since the expression of the pre-exponential factor contains the activation energy as a factor raised to a positive power. Similarly, the pre-exponential factor Z derived by Murgulescu and Segal for diffusion-controlled thermal decompositions [17] contains the vibration frequency of the product in the crystal lattice, which should be proportional to the activation energy.

In the present paper the relationship between log Z and E values has been studied in the case of the thermal decomposition of bisdioximatodiaminocobalt(III) complexes.

Results and discussion

The thermal decomposition of $[Co(DioxH)_2(Am)_2]X$ type complexes has been studied under dynamic conditions, using a constant heating rate. In the above formula $DioxH_2$ stands for dimethylglyoxime DH_2, cyclohexanedionedioxime $NioxH_2$ or diphenylglyoxime $DiphH_2$. Am stands for ammonia, various aromatic and heterocyclic amines as aniline, *o*-, *m*-, *p*-toluidine, *o*-, *p*-ethylaniline, *p*-propylaniline, *o*-, *p*-anisidine, *o*-, *p*-phenetidine, *o*-, *m*-, *p*-chloroaniline, *o*-, *m*-, *p*-bromoaniline, *m*-aminophenol, 1,2,4-toluylenediamine, 2,4-dimethylaniline, benzylamine, *p*, *p*′-diaminodiphenylmethane, α-naphthylamine, pyridine, β-, γ-picoline. X stands for various univalent anions. Results of thermogravimetric measurements have been reported in our previous papers [18 – 22].

If the anion X is Cl, Br, I or NCS, the first stage of the thermal decomposition is the following substitution reaction:

$$[Co(DioxH)_2(Am)_2]X = [Co(DioxH)_2\,Am\,X] + Am \qquad (2)$$

i.e. an amine molecule is replaced by the outer sphere anion, the liberated amine is volatilized and a relatively stable intermediate of nonelectrolytic character is formed [18]. From the TG curves activation energy E and log Z values have been derived for substitution reaction (2), using our integral method [24]. These data have been reported in our previous papers [20 – 22] for 134 complexes of the above type. In the case of about 50 complexes various heating rates were used [21], for the others the heating rate was 10°/min.

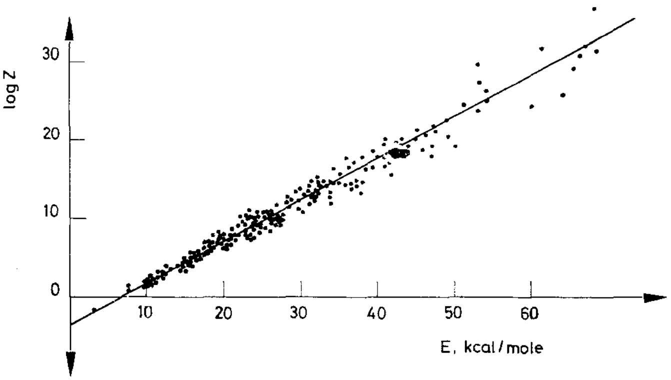

Fig. 1. Compensation effect in the case of thermal decomposition reactions (2)

The interval covered by both the log Z and E values is considerable. Although a great number of complexes have been studied, no clear relationship was found between the above kinetic parameters and the nature of the ligands. Meanwhile a parallel variation of log Z with E has been observed. This and the systematic decrease of both log Z and E with increasing heating rate [21] indicate manifestation of the kinetic compensation effect.

The graphical plot of log Z vs. E for all the above complexes, viz. for a total of 206 pairs of log $Z-E$ values, is shown in Fig. 1. It is apparent from this figure that the same linear compensation law (1) operates in the whole class of the complex compounds studied, i.e. the effect of the nature of ligands takes the form of a compensation effect. The slope of the straight line is a little larger than reported for the decomposition of carbonates [1], viz. about $a = 0.5$ kcal/mol, and the zero E ordinate has a relatively small negative value of about $b = -3$.

We have carried out a statistical analysis of these data and by means of the least squares method determined the constants a and b for all the data, and separately for the derivatives of a given ligand (dioxime), or for the salts of a given anion. Thus the parameters of the straight line have been determined for all the DH_2, $NioxH_2$ and $DiphH_2$ derivatives, irrespective of the nature of Am and X. In a second set of calculations the same parameters have been determined separately for the chlorides, bromides, iodides and thiocyanates, irrespective of the nature of Am and of $DioxH_2$. These results, together with the same parameters derived from all the 206 points (referred to as "total"), are given in Table 1. The same table contains also Jaffé's correlation coefficient r [25], in order to characterize quantitatively the linearity of the relationship. Errors have been calculated in the usual statistical way, on the basis of standard deviations.

The data in this table show that a good overall linearity can be observed. The correlation coefficient r is rather large even for the "total", which shows all our data to give in the first approach a single straight line, i.e. it is consistent with our above statement that the same compensation law operates in the whole class of the complexes studied.

Nevertheless, this statistical study enables us to discern the influence of ligands in terms of parameter *a* of the compensation law (1). It is very interesting that the value of *a* increases in the series Cl < Br < I < NCS, i.e. in the same order as the Co-X bond strength does in $[Co(DH)_2X_2]^-$ type complexes [26]. This effect suggests the idea that Co-X bond formation may play an important part in reaction (2).

On the other hand, from the *a* values presented in Table 1 the influence of the coordinated $DioxH_2$ molecules is apparent. In this respect the $DiphH_2$ complexes clearly differ from the derivatives of the other two dioximes. This is the single ligand effect observed in our previous studies, too, but only in the case of the thiocyanates [23]. This effect has been explained through the formation of a delocalized π-bond system in the coordinated DiphH-group, for which also a clear IR evidence has been obtained [22].

Table 1

Parameters *a* and *b* of the compensation law (1) and correlation coefficient *r* for different derivatives

Ligand or outer sphere anion	*a* kcal/mol	*b*	*r*
DH_2	0.517±0.020	−2.75±0.73	0.979
$NioxH_2$	0.501±0.033	−3.09±0.73	0.985
$DiphH_2$	0.446±0.010	−2.55±0.28	0.997
Cl	0.443±0.075	−2.36±0.58	0.995
Br	0.461±0.038	−2.75±0.78	0.984
I	0.506±0.019	−2.90±0.66	0.985
NCS	0.554±0.020	−3.70±0.59	0.988
"Total"	0.520±0.014	−3.30±0.43	0.983

Conclusions

1. The kinetics of the thermal decomposition reaction (2) are governed by a linear compensation law of the type (1). Not only the effect of experimental variables, but also the effect of the ligands are manifested, as a first approximation in the compensation effect.

2. The parameter *a* of the compensation law (1) is sensitive to ligand effects and the comparison of *a* values gives more information with respect to the influence of ligands than the comparison of activation energy values only.

References

1. M. M. PAVLYUCHENKO, E. A. PRODAN and S. A. SLYSHKINA, Dokl. Akad. Nauk SSSR, 181 (1968) 1174.
2. J. M. THOMAS and W. J. THOMAS, "Introduction to the Principles of Heterogeneous Catalysis", Academic Press, New York—London 1967, p. 263.
3. R. C. TURNER, I. HOFFMANN and D. CHEN, Canad. J. Chem., 41 (1963) 243.
4. I. C. HISATSUNE, E. C. BEAHM and R. I. KEMPF, J. Phys. Chem., 74 (1970) 3444.
5. T. TOUISSANT, J. J. FRIPIAT and M. C. GASTOUCHE, J. Phys. Chem., 26 (1963) 26.
6. L. G. BERG, "Vvedenie v termografiu", 2nd Ed., Nauka, Moscow 1969, p. 99.
7. P. MAURET and P. VICAIR, Bull. Soc. Chim. France 1958, 1083.
8. H. MAURAS, Bull. Soc. Chim. France 1960, 260.
9. J. ŠESTAK, Talanta, 13 (1966) 567.
10. D. A. VASSALLO, Anal. Chem., 33 (1961) 1823.
11. J. ZSAKÓ, J. Chim. Phys., 66 (1969) 1041.
12. D. FURNICĂ and I. A. SCHNEIDER, Makromol. Chem., 108 (1967) 182.
13. I. A. SCHNEIDER, C. VASILE, D. FURNICĂ and A. ONU, Makromol. Chem., 117 (1968) 41
14. I. A. SCHNEIDER, Makromol. Chem., 125 (1969) 201.
15. C. N. CAŞCAVAL, C. VASILE and I. A. SCHNEIDER, Makromol. Chem. 131 (1970) 55.
16. M. POLÁNYI and E. WIGNER, Z. phys. Chem., 139 (1928) 439.
17. I. G. MURGULESCU and E. I. SEGAL, Rev. Roum. Chim., 10 (1965) 307.
18. J. ZSAKÓ, CS. VÁRHELYI and E. KÉKEDY, Studia Univ. Babeş-Bolyai, Ser. Chem. 10 (2) (1965) 7.
19. J. ZSAKÓ, CS. VÁRHELYI and E. KÉKEDY, Anal. Univ. Bucureşti, Ser. St. Nat., Chim., 14 (1965) 15; J. Inorg. Nucl. Chem., 28 (1966) 2637; Acta Chim. Acad. Sci. Hung., 51 (1967) 53; Zh. Neorg. Khim., 13 (1968) 3279.
20. J. ZSAKÓ, E. KÉKEDY and CS. VÁRHELYI, Studia Univ. Babeş-Bolyai, Ser. Chem., 14 (1969) 117.
21. J. ZSAKÓ, E. KÉKEDY and CS. VÁRHELYI, J. Thermal Anal., 1 (1969) 339; Rev. Roum. Chim., 15 (1970) 865.
22. J. ZSAKÓ, CS. VÁRHELYI and E. KÉKEDY, J. Inorg. Nucl. Chem., 32 (1970) 2999.
23. J. ZSAKÓ, Studia Univ. Babeş-Bolyai, Ser. Chem. 15 (1970) 113.
24. J. ZSAKÓ, J. Phys. Chem., 72 (1968) 2406.
25. H. H. JAFFÉ, Chem. Rev., 53 (1953) 191.
26. Z. FINTA, CS. VÁRHELYI and J. ZSAKÓ, J. Inorg. Nucl. Chem., 32 (1970) 3013.

RÉSUMÉ — L'analyse statistique des valeurs des énergies d'activation et de celles de log Z obtenues à partir des résultats thermogravimétriques de 134 réactions de décomposition des complexes différent de bisdioximato-cobalt(III) montre la validité d'une loi de compensation linéaire du type (1); ceci signifie que l'effet de la vitesse de chauffage et celui de la nature du ligand sont responsables en première approximation de l'effet de compensation cinétique. Le paramètre a de la loi de compensation est sensible aux effets du ligand et la nature de la bis-dioxime coordonnée ainsi que la nature de l'anion X dans la sphère externe remplaçant une molécule d'amine durant la réaction de décomposition thermique influencent sa valeur.

ZUSAMMENFASSUNG — Die statistische Analyse der aus den thermogravimetrischen Resultaten erhaltenen Aktivierungsenergiewerte und log Z-Werte von 134 Zersetzungsreaktionen der verschiedenen bisdioxamato Kobalt(III) Komplexen zeigte die Gültigkeit eines Gesetzes der linearen Kompensation, d.h. der Effekt der Heizungsgeschwindigkeit und der Natur des

Liganden verursachten in erster Näherung den kinetischen Kompensationseffekt. Parameter *a* des Kompensationsgesetzes (1) repräsentiert den Ligandeffekt. Sein Wert wird durch die Natur des koordinierten Dion-dioxims und des Anions X in der äußeren Sphäre beeinflußt, das ein Aminmolekül während der thermischen Zersetzungsreaktion ersetzt.

Резюме — Статистический анализ величин энергии активации и log *Z*, выведенных из рермогравиметрических данных для 134 реакций распада комплексов бис-Диоксиматокобальта(III), показывает справедливость закона линейной компенсацми. Параметр *a* закона компенсации чувствителен к лиганду и на его значение влияет природа координированного дион-диоксима и внешнесферного аниона X, который замещает молекулу аммиака в ходе реакции термического распада.