Journal of Thermal Analysis, Vol. 43 (1995) 239-246

THERMODYNAMICS OF THE THERMAL DECOMPOSITION OF CALCIUM OXALATE MONOHYDRATE EXAMINED THEORETICALLY

J. Rak[1], *P. Skurski*[1], *M. Gutowski*[1,2] *and J. Błażejowski*[1]

[1]Department of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland
[2] Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA

Abstract

Geometries and energies of isolated $CaC_2O_4{\cdot}H_2O$, CaC_2O_4, $CaCO_3$, CaO, H_2O, CO and CO_2 were determined at the ab initio level using effective core potential valence basis sets of double-zeta quality, supplemented with polarization functions. The effects of electron correlation were taken into account at the second order Møller-Plesset level of theory. For $CaC_2O_4{\cdot}H_2O$, the correlation for the basis set superposition error was also included. Common routines were employed to evaluate entropies, heat capacities, as well as enthalpies and free enthalpies of formation of all entities. The enthalphies and free enthalpies of consecutive dehydration of $CaC_2O_4{\cdot}H_2O$, decarbonylation of CaC_2O_4 and decomposition of $CaCO_3$ towards CaO and CO_2 were determined on the basis of available data from the literature or those predicted theoretically. Assuming that upon all the above mentioned processes the system maintains equilibrium, the fractions reacted, enthalpy changes and differential dependencies of these *vs.* temperature were derived and compared with experimental thermoanalytical data.

Keywords: calcium oxalate, theory, thermodynamics of decomposition

Introduction

Calcium oxalate monohydrate is used as a standard substance in thermal analysis [1, 2]. Investigations revealed that upon both dynamic [1, 3–6] and quasi isothermal-isobaric [2] thermoanalytical experiments the compound loses water, carbon monoxide and finally carbon dioxide at around 470, 650 and 920 K, respectively [2]. The nonvolatile product is CaO. Numerous works have been devoted to elucidation of the thermodynamics [6–8] and kinetics [4–6,9] of the processes, but only on the purely phenomenological bases. The aim of this study is to get an insight into the nature of decomposition on the molecular level. This was achieved combining quantum chemistry with statistical thermodynamics and appropriate use of thermochemical data of experimental origin available in the literature.

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

Methods

Stationary geometries and force field calculations

Stationary geometries of all the entities at unconstrained symmetry were determined at the Hartree-Fock level of the theory (*HF*) employing Baker's optimization procedure [10] together with the relativistic compact effective core potentials of Stevens *et al.* [11, 12] and their valence, energy optimized, shared exponents, contracted-Gaussian basis sets supplemented with standard polarization functions [13] labeled subsequent as *SBKJ** (examples are given in Fig. 1). For the C and O atoms 2 electrons and for Ca 18 electrons were incorporated into the pseudopotential. To model chemically active 2*s* and 2*p* orbitals, in the case of C and O, or 4*s* and 4*p* orbitals for Ca, the double-zeta quality *s* and *p* basis sets were used.

Validity of geometry optimization was proved in the subsequent hessian (second derivative of the energy *vs.* nuclear coordinates) calculations followed by

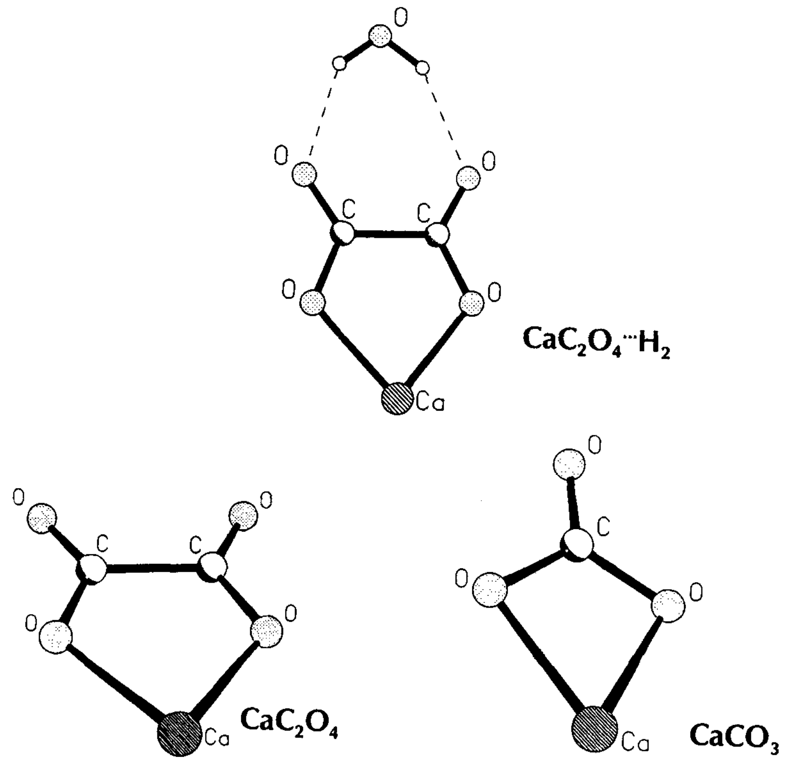

Fig. 1 Geometries of isolated $CaC_2O_4{\cdot}H_2O$, CaC_2O_4 and $CaCO_3$ determined at the ab initio level

the normal mode analysis. For all stationary points corresponding to the minima on the potential energy surfaces all curvatures were found to be positive. This enabled determination of vibrational frequencies in the harmonic approximation (used subsequently in evaluation of enthalpy (H-E_t) and free enthalpy (G-E_t) of an entity relative to its total energy (E_t) on the basis of the statistical thermodynamics).

All the quantum mechanical calculations were carried out on the Hewlett-Packard 730 Apollo workstation employing the GAMESS program package [14].

Thermochemical quantities

The energies of formation of gaseous species $\Delta_f E$ were determined following Hess's Law, i.e. subtracting from the energy of molecules the energies of gaseous atoms (C, Ca) and molecules (H_2, O_2) in the lowest electronic state. As values of thermodynamic quantities are usually affected by the electron correlation effects [13], the *HF* results were supplemented with the second order Møller-Plesset (*MP2*) electron correlation correction [15] calculated at the *SKBJ** geometry (relevant values are referred to as *MP2/SBKJ*||HF/SBKJ**). For $CaC_2O_4{\cdot}H_2O$ the correction for the basis set superposition error was included additionally [16].

The enthalpies ($\Delta_{f,298}H$) and free enthalpies ($\Delta_{f,298}G$) of formation of gaseous molecules were evaluated analogously as in the case of $\Delta_f E$ [17]. For this purpose routine incorporated in GAMESS [14], based on the statistical thermodynamics, were used to determine entropies (${}_{298}S$), heat capacities (${}_{298}C_p$), as well as enthalpies and free enthalpies of all entities relative to their ab initio energies. To bring $\Delta_{f,298}H$ and $\Delta_{f,298}G$ to standard conditions in the usual sense (relevant values are referred to as $\Delta_{f,298}H^0$ and $\Delta_{f,298}G^0$), the ab initio energies of C and Ca were lowered by (in kJ·mol^{-1}) 716.7 and 178, in the case of enthalpies, or 671.3 and 144, in the case of free enthalpies, respectively, i.e. enthalpies or free enthalpies of atomization [18, 19].

Thermochemical data for calcium oxalate monohydrate and its decomposition products are compiled in Table 1.

Thermodynamics of decomposition

Decomposition of calcium oxalate monohydrate is accomplished in three stages, which are represented by reactions (1)–(3) (Table 2). Enthalpy and free enthalpy changes for these processes, demonstrated in Table 2, were determined using data from Table 1. These former characteristics were subsequently used to evaluate the equilibrium extent of decomposition (α) for each step, which is

Table 1 Thermochemical characteristics of calcium oxalate monohydrate and its decomposition products

Compound	Method[a]	Thermochemical data[b]							
		$\Delta_f E$	$\Delta_{f,298}H^0$		$\Delta_{f,298}G^0$		$_{298}S^0$		$_{298}C_p^0$	
			This work	Lit.[c]	This work	Lit.[c]	This work	Lit.[c]	This work	Lit.[c]
$CaC_2O_4 \cdot H_2O$	A	–2170	–495.6	–1673*	–431.5	–1512*	420.3	156.0*	133.7	
	B	–2452	–777.6		–713.5					
	C	–2448	–773.6		–709.5					
CaC_2O_4	A	–1907	–262.8	–1392*	–243.0	(–1295*)[d]	340.3		90.1	
	B	–2203	–558.9		–539.0					
$CaCO_3$	A	–1186	–274.2	–1207*	–266.2	–1129*	295.0	92.9*	62.1	82.3*
	B	–1328	–416.2		–408.2					
H_2O	A	–221.4	–198.5	–241.8	–188.5	–228.6	194.4	188.8	33.4	33.6
	B	–201.2	–178.3		–168.3					
CO	A	–664.7	58.6	–110.5	25.1	–137.2	197.5	197.7	29.1	29.1
	B	–780.6	–57.3		–90.8					
CO_2	A	–904.0	–171.8	–393.5	–180.7	–394.4	212.8	213.7	35.7	37.1
	B	–1043.3	–311.1		–320.0					
CaO	A	156.7	330.8	–635.2*	309.1	–603.9*	221.2	39.3*	33.3	42.5*
	B	–70.2	103.9		82.2					

[a] Basis set||geometry: A, *HF/SBKJ**||*HF/SBKJ**; B, *MP2/SBKJ**||*HF/SBKJ**; and C, *MP2* +correction for basis set superposition error/*SBKJ**||*HF/SBKJ**.

[b] $\Delta_f E$, $\Delta_{f,298}H^0$ and $\Delta_{f,298}G^0$ in kJ·min^{-1}; $_{298}S^0$ and $_{298}C_p^0$ in J·mol^{-1}·K^{-1}.

[c] Refs. [18-23]; Values with an asterisk correspond to the solid phase, others – to the gaseous phase.

[d] Value estimated assuming that $\Delta_{f,298}G^0$ of gaseous and solid $CaC_2O_4 \cdot H_2O$, CaC_2O_4 and $CaCO_3$ are proportionally related.

Table 2 Thermodynamics of consecutive decomposition of $CaC_2O_4 \cdot H_2O$

No.	Reaction	Theoretical[a]		Experimental[a]	
		$\Delta_{d,298}H^0$	$\Delta_{d,298}G^0$	$\Delta_{d,298}H^0$	$\Delta_{d,298}G^0$
(1)	$CaC_2O_4 \cdot H_2O_{(g,s)} \rightarrow CaC_2O_{4(g,s)} + H_2O_{(g)}$	36.4	2.2	39.2	-11.6
(2)	$CaC_2O_{4(g,s)} \rightarrow CaCO_{3(g,s)} + CO_{(g)}$	85.4	40.0	74.5	28.8
(3)	$CaCO_{3(g,s)} \rightarrow CaO_{(g,s)} + CO_{2(g)}$	209.0	170.4	178.3	130.7

[a] Values (in $kJ \cdot mol^{-1}$) determined using data from Table 1 and following Hess's Law (theoretical values correspond to the gaseous state of all reactants, while those of experimental origin–to the heterogeneous systems).

equal to the equilibrium constant (K) in the case of heterogeneous processes [24]. When equilibrium is maintained between exclusively gaseous reactants, $K = \alpha^2/(1-\alpha)$. If reactions (1)–(3) are separated in the temperature scale (which indeed has been confirmed experimentally [1, 2] the fraction of weight loss (TG) is given by the equation

$$\mathrm{TG} = 1 - \frac{M\,[\mathrm{H_2O}]\,(1-\alpha_1) + M\,[\mathrm{CO}](1-\alpha_2) + M\,[\mathrm{CO_2}](1-\alpha_3) + M\,(\mathrm{CaO}]}{M\,[\mathrm{CaC_2O_4 \cdot H_2O}]} \qquad (4)$$

where M denote molar masses of species given in square brackets and $\alpha_1, \alpha_2, \alpha_3$- fractions decomposed corresponding to reactions (1), (2), (3), respectively.

TG *vs.* T dependencies arising from experimental thermochemical data were revealed combining van't Hoff equation with the Kirchhoff Law. Heat capacity changes necessary for determination of these dependencies were taken to be $4R$, in the case of reaction (1), and 3.5 R for reactions (2) and (3), i.e. were assumed to result from the increase in the possibilities of the storage of energy in translational and rotational degrees of freedom of molecules released to the gaseous phase. TA dependency was obtained analogously, taking into account relevant enthalpy changes.

$$\mathrm{TA} = \alpha_1 \Delta_{d,298} H^0\,(1) + \alpha_2 \Delta_{d,298} H^0\,(2) + \alpha_3 \Delta_{d,298} H^0\,(3) \qquad (5)$$

Finally, differential curves, i.e. DTG and DTA were derived analytically starting from expressions for TG and TA, respectively. The results are presented in Fig. 2B.

Expressions (4) and (5) were also employed if thermoanalytical dependencies referred to all gaseous reactants. In this latter case α values were obtained using enthalpy changes for decomposition processes predicted by ab initio method and employing statistical thermodynamics to reveal dependencies of H and G on temperature. Differential curves were derived by standard iterative procedure. Thus predicted dependencies are shown in Fig. 2A.

Comparison of both predicted sets of equilibrium thermoanalytical curves with experimental dependencies reveals that the general pattern of these is reasonably well reflected by theory. Differences in temperatures of thermal effects can be accounted for by deficiencies of theory. But they may also result from the fact that thermoanalytical experiments are markedly affected by conditions of their realization [1, 2]. Nevertheless, the approach presented emphasizes the importance of chemistry in consideration of the mechanism of heterogeneous processes involving solids on the molecular level.

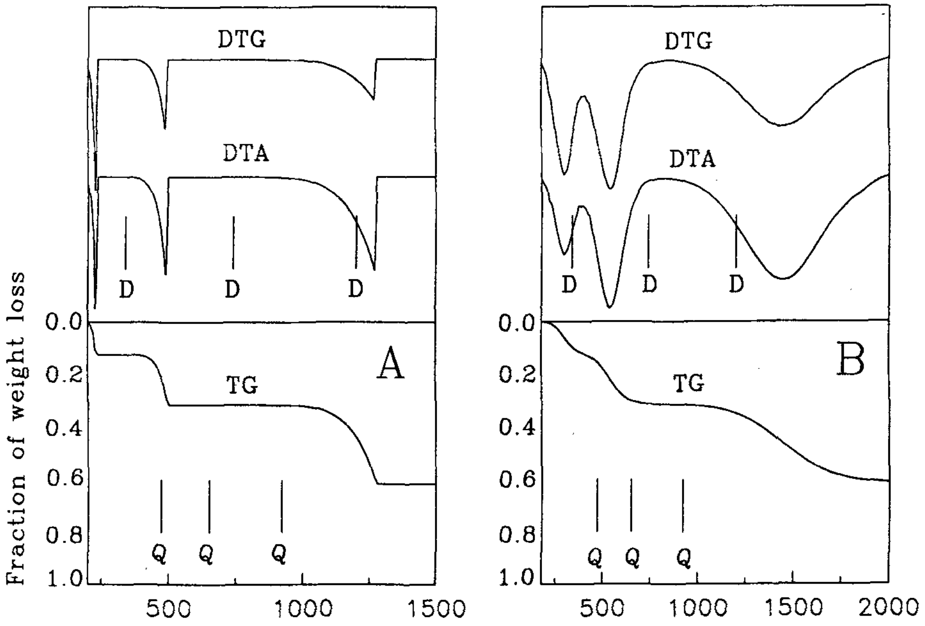

Fig. 2 Equilibrium thermoanalytical curves (DTG, DTA, TG) predicted on the basis of literature data of experimental origin (A) and the theoretical ones (B); bars indicate characteristic temperatures of dynamic (D) DTA and DTG curves (peaks) or quasi isothermal-isobaric (Q) TG curve (steps)

* * *

The authors gratefully acknowledge the financial support of this work form the Polish State Committee for Scientific Research (KBN)-DS.

References

1 Atlas of Thermoanalytical Curves, G. Liptay (Ed.), Akadémiai Kiadó, Budapest 1973.
2 J. Paulik and F. Paulik, Comprehensive Analytical Chemistry, Vol. 12, Part A, Elsevier, Amsterdam 1981, p. 83.
3 M. R. Alvarez, J. J. Icaza, E. H. Bocanegra and M. J. Tello, Thermochim. Acta, 12 (1975) 117.
4 C. G. R. Nair and K. N. Ninan, Thermochim. Acta, 23 (1978) 161.
5 K. N. Ninan and C. G. R. Nair, Thermochim. Acta, 37 (1980) 161.
6 J. Blazejowski, J. Szychlinski and K. Windorpska, Thermochim. Acta, 46 (1981) 147.
7 G. Beech, J. Chem. Soc. A, (1969) 1903.
8 M. S. Subramanian, R. N. Singh and H. D. Sharma, J. Inorg. Nucl. Chem., 31 (1969) 3789.
9 S. Gurrieri, G. Siracusa and R. Cali, J. Thermal Anal., 6 (1974) 293.
10 J. Baker, J. Comput. Chem., 7 (1986) 385.
11 W. J. Stevens, H. Basch and M. Krauss, J. Chem. Phys., 81 (1984) 6026.
12 M. Krauss, W. J. Stevens, H. Basch and P. G. Jasien, Can. J. Chem., 70 (1992) 612.

13 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, Ab initio Molecular Orbital Theory, Wiley, New York 1986.
14 M. Dupuis, D. Spangler and J.J. Wendoloski, National Resource for Computations in Chemistry Software Catalog; University of California: Berkeley, 1980 (Program QG 01); current version M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Koseki, M. S. Gordon, K. A. Nguyen, T. L. Windus and S. T. Elbert, QCPE Bull., 10 (1990) 52.
15 C. Møller and M. S. Plesset, Phys. Rev., 46 (1934) 618.
16 M. Gutowski, F. B. van Duijneveldt, G. Chalasinski and L. Piela, Mol. Phys., 61 (1987) 233.
17 J. A. Pople, B. T. Luke, M. J. Frish and J. S. Binkley, J. Phys. Chem., 89 (1985) 2198.
18 P. W. Atkins, Physical Chemistry, W. H. Freeman, New York, 3rd edn., 1986.
19 Handbook of Chemistry and Physics, D. R. Lide (Ed.), 73 rd edn., CRS Press, Boca Raton 1992-1993.
20 Gmelins Handbuch der Anorganischen Chemie, 8 Auflage, Teil B - Lieferung 3, Verlag Chemie, Weinheim/Bergstrasse, 1961.
21 K. P. Mishchenko and A. A. Ravdel, Kratki Spravochnik Fiziko, Khimicheskikh Velichin, 5th edn., Khimiya, Leningrad 1967.
22 J. C. Bailar, H. J. Emeleus, R. Nyholm and A. F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, Pergamon Press, Oxford 1975, chapters 10 and 13.
23 Handbook of Chemistry and Physics, 59th edn., CRS Press, Boca Raton, 1978/1979.
24 J. Lubkowski and J. Blazejowski, J. Chem., Soc. Faraday Trans. 1, 82 (1986) 3069.

Zusammenfassung — Geometrie und Energien von isoliertem $CaC_2O_4 \cdot H_2O$, CaC_2O_4, $CaCO_3$, CaO, H_2O, CO und CO_2 wurden auf dem ab initio Level unter Anwendung von Kernpotential-Valenz-Basissets, ergänzt durch Polarisationsfunktionen bestimmt. Die Effekte der Elektronenkorrelation wurden auf dem Moller-Plesset level zweiten Grades berücksichtigt. Für $CaC_2O_4 \cdot H_2O$ wurde auch die Korrelation für den Basissetüberlagerungsfehler inbegriffen. Zur Ableitung der Entropien, Wärmekapazitäten als auch Enthalpien und freien Bildungsenthalpien aller Gebilde wurden die üblichen Routinen verwendet. Die Enthalpien und freien Enthalpien der konsekutiven Dehydratation von $CaC_2O_4 \cdot H_2O$, der Dekarbonylierung von CaC_2O_4 und der Zersetzung von $CaCO_3$ zu CaO und CO_2 wurde auf der Grundlage der zugänglichen Literaturangaben bestimmt. Unter der Annahme, daß das System in allen oben erwähnten Prozessen im Gleichgewicht bleibt, wurden die Enthalpieänderungen und differentialen Abhängigkeiten derselben von der Temperatur abgeleitet und mit den experimentellen thermoanalytischen Angaben verglichen.