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Organic substances

LATTICE ENERGY OF ORGANIC IONIC CRYSTALS AND ITS IMPORTANCE IN ANALYSIS OF FEATURES, BEHAVIOUR AND REACTIVITY OF SOLID-STATE SYSTEMS

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A general approach to the theoretical evaluation of the crystal lattice energy of ionic substances, particularly those composed of monoatomic ions, is outlined in detail. Subsequently, the possibilities of theoretical prediction of the lattice energy of complex organic and inorganic ionic substances are discussed. Lastly, the importance of the lattice energy in examinations of the properties and behaviour of solid-state systems, is treated, together with the prospects of developing a model describing the kinetics of solid-state processes.

Keywords: kinetics, lattice energy, solid-state systems

General problems

The crystal lattice energy (E_c) is the most important thermochemical characteristic accounting for the structure, properties and behaviour of solids. It is generally defined as the amount of energy which has to be supplied to transfer the species from the crystal lattice to the gaseous phase, where no interactions occur. This means that the crystal lattice energy reflects the magnitude of cohesive forces keeping the species in the solid phase, or in other words it determines the energy of interaction between the species in the solid phase.

In the case of molecular crystals, where the species in the solid and gaseous phases are the same molecules, the lattice energy is simply the sublimation ener-

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gy. For such substances, this quantity can be measured directly. When one deals with ionic substances, the situation is changed, since the species existing and interacting in the solid phase are actually the ions. In this latter case, our considerations concern the energy which must be provided to transfer ions from the lattice to the gaseous phase. If an ionic substance is given by the general formula K_mA_n, then the crystal lattice energy is defined as the energy change for the process [1]

$$K_mA_{n(c)} \rightarrow mK^{\beta n+}_{(g)} + nA^{\beta m-}_{(g)} \tag{1}$$

where β is the multiplier accounting for the actual valence of both ions. Unfortunately, the values of the lattice energy of ionic substances cannot be determined directly. They can, however, be obtained on the basis of the Hess law (appropriate thermochemical cycle), using values of other measurable quantities [1–3]. Equation (1) is significant therefore, if one uses data of experimental origin for determination of the E_c of ionic substances.

Theoretical predictions of lattice energy

As mentioned above, a solid phase exists as a result of attractive and repulsive interactions between the species forming the lattice. It is generally recognized that these interactions contribute to the crystal lattice energy in the form of four effects, which constitute Eq. (2) [4–6]

$$E_c = -E_{el} + E_r - E_d + E_0 \tag{2}$$

where E_{el} represents the electrostatic (Coulombic) interactions between charged centres, E_r the repulsive interactions, E_d the van der Waals interactions (dispersive interactions) and E_o the zero-point energy.

In the case of molecular crystals, it may be expected that all four terms in Eq. (2) are significant in the determination of the lattice energy. In ionic substances, which will be the subject of further considerations, the terms E_r and E_d do not usually exceed 10 per cent of the value of E_{el} and, since they have opposite signs, their sum becomes negligible [5, 7, 8]. Also, the term E_o is negligible in comparison with any other term in Eq. (2) [8, 9]. Therefore, for ionic substances, $-E_{el}$ describes the crystal lattice energy reasonably well.

The electrostatic energy of 1 mol of an ionic substance composed of structural units $(K^{\beta n+})_m(A^{\beta m-})_n$ is defined by the equation [1]

$$E_{el} = \frac{1}{2} N_A \left[mE_p^{(\beta n+)} + nE_p^{(\beta m-)}\right] \tag{3}$$

where N_A is the Avogadro number, while the factor 1/2 eliminates duplication of the electrostatic interactions. The terms $E_p^{(\beta n+)}$ and $E_p^{(\beta m-)}$ in Eq. (3) express the potential energies which result from the interactions of a single cation and anion, respectively, with all other ions in the lattice. The potential energy, on the other hand, is determined by the product of the actual charge of an ion and the potential(V_p) created at the site of its location by all other ions in the lattice [1]. With this in mind, Eq. (3) can be written in the form

$$E_{el} = \frac{1}{2} N_A \left[m\,(\beta n+)\,e_{el} V_p^{(\beta n+)} + n\,(\beta m-)\,e_{el} V_p^{(\beta m-)} \right] \tag{4}$$

where e_{el} denotes the elementary charge. The problem of evaluating the electrostatic energy is therefore reduced to the calculation of $V_p^{(\beta n+)}$ and $V_p^{(\beta-)}$

Methods of Coulombic energy (electrostatic potential) evaluation

It can be assumed, to a first approximation, that the charges are situated at the points of location of atoms in the crystal lattice. In such a case, we are dealing with an infinite lattice of charges. The electrostatic potential ($V^{(Z_i)}$) at site i (at which a net charge Z_i is located), taken as the origin of the coordinate system, can then be evaluated by using the basic equation

$$V^{(Z_i)} = \frac{1}{4\pi\varepsilon_o} \sum_{j\neq i}^{n} \frac{Z_j}{r_{ij}} \tag{5}$$

where Z_j is the net charge at site j, which is situated at a distance r_{ij} from site i. All lattices of interest to chemists are heteroionic. The summation therefore extends over all positive and negative ionic centres (n), excluding, of course, site i. Since the charged centres in the lattice are located periodically, the expression for the potential presents a series which always converges poorly. To calculate the electrostatic potential, several approaches have been proposed in the past [10–16]. Of these, the Ewald method is the one most often considered [11]. The

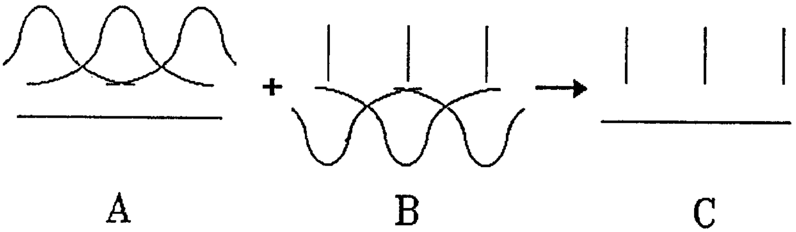

Fig. 1 The schematic representation of the imaginary Bravais lattices of a given type of charges (A and B) and their superposition (C)

method is based on the assumption that the part of an electrostatic potential caused by a certain type of ions (positive or negative) is a superposition of the components of two imaginary Bravais lattices of charges (Fig. 1) [11, 17]. The first of these lattices forms a three-dimensional system normalized to $|1|$ Gaussian functions (centred at the locations of point charges) and neutralized by a uniform charge distribution of opposite sign (Fig. 1A), whereas the second is a lattice of actual unit point charges neutralized by corresponding three-dimensional Gaussian functions of opposite sign (Fig. 1B). For complementary ions, similar Bravais lattices can be considered. In the final expression for the potential at site i (given below by Eq. (6)) due to the monopoles of both types at sites j, the Fourier representations of both two-component Bravais lattices corresponding to negative and positive ions are combined, which results, on appropriate choice of the half-width of the Gaussian function, in the rapid convergence of pairs of these series [11, 15].

$$V^{(Z_i)} = \frac{1}{4\pi\varepsilon_o}\left[\frac{1}{\pi V}\sum_{h=0}\frac{F(h)}{h^2}\exp\left(\frac{\pi h^2}{\chi^2}\right) - 2\chi z_i e_{el} + \sum_{j\neq i}\frac{z_j e_{el}}{r_{ij}}\, erfc(\sqrt{\pi}\chi r_{ij})\right] \qquad (6)$$

In Eq. (6), ε_o denotes the permittivity of free space; V is the volume of a unit cell; h is a vector in reciprocal space; $F(h)$ represents the Coulombic structure factor

$$F(h) = \sum_{s} z_s e_{el} \cos(2\pi h r_{is})$$

with s running over a unit cell with its origin at site i; κ is the convergence parameter to obtain optimal convergence of the series (it is often assumed that $\kappa = V^{1/3}$); r_{ij} (r_{is}) is, as mentioned above, the distance vector between the origin site $i (r_{ij} = 0;\ r_{is} = 0)$ and the site j (s) with charges $Z_j = z_j \cdot e_{el}$ ($Z_s = z_s \cdot e_{el}$), where z_j and z_s denote relative charges; and

$$erfc = \frac{2}{\sqrt{\pi}}\int_{x}\exp(-t^2)\,\mathrm{d}t$$

is the complementary error function. In Eq. (6), the symbol $\Sigma_h = 0$ indicates summation over reciprocal space, whereas $\Sigma_{j\neq i}(\Sigma_s)$ indicates summation over the real lattice, $r_{ij}(r_{is}) = 0$ being omitted, of course.

A certain physical meaning can be ascribed to the terms on the right-hand side of Eq. (6). The first term describes the potential created at site i by all other charged sites. The second denotes the 'self-energy', and results from the fact that the distributed charge itself creates a potential at the site of its location. The third accounts for the effect of the overlapping of Gaussian distributions of charges.

The Ewald method holds a certain mathematical 'trick', which brings about a better convergence of lattice sums which occur, among others, in expressions for the lattice potential. This 'trick' comes down to the assumption that the point charge can be represented by the three-dimensional Gaussian function. Bertaut later showed that many other functions mathematical functions can be used for this purpose [15]. The application of other functions leads to very similar values of lattice sums [9, 15]. However, as Jenkins and Pratt [18] have demonstrated, a Gaussian distribution function characterizes a high convergence of lattice sum series.

After the above presentation, the question can be raised as to the real charge distribution in the lattice. The assumption as to the location of point charges at the positions of atoms forms a convenient framework on which to consider many features of solid substances. This assumption is also often made to consider chemical features of the matter at a molecular level. On the other hand, the assumption made by Ewald that charge is diffused around the sites of location of ions does not seem to be only artificial. It might also have some physical significance. One should remember, however, that a mathematical procedure based on the superposition of two Bravais lattices of charges helps only in performing calculations.

Application of the Ewald method

The Ewald method was originally developed to calculate the electrostatic potential (lattice sums) for crystals composed of monoatomic ions. The application of this method to solids containing polyatomic ions requires additional assumptions. These are:

(i) in the species constituting the simplest formula unit of the molecule, one distinguishes positive and negative fragments;

(ii) to each fragment one ascribes, as a first approximation, charges which are whole multiples of e_{el};

(iii) it is assumed that within each such fragment a charge is distributed among all the atoms forming it, or is placed on certain chosen atoms;

(iv) it is further assumed that each partial charge contributes to the electrostatic potential (i.e. is considered independently in the calculations);

(v) lastly, the electrostatic potential is determined at the sites of the location of each partial charge (atom) of a given fragment, with the elimination on of partial charges ascribed to the remaining atoms forming the fragment.

To evaluate the crystal lattice energy of any substance, information on its solid-phase structure is necessary. Most structural data for organic ionic substances originate from X-ray diffraction studies. These are gathered in the Cambridge Structural Database System [19, 20]. In some cases, however, the information is incomplete. One can then evaluate unknown positions of atoms by the careful employment of quantum-chemistry methods [21, 24].

The distribution of charge between the atoms in complex ions can sometimes be guessed by using values of certain physicochemical quantities. This was done, among others, in the case of octahedral MX_6^{2-} ions (M = metal(IV) and X = halogen) [5]. For the purpose of crystal lattice energy calculations, this information can also be obtained by employing quantum-chemistry methods. In several recent papers, we have done this for numerous nitrogen organic bases by using the INDO [25] and MNDO [26] methods [21–24]. These calculations revealed that the excess of negative charge usually occurs on N and sometimes C atoms. This means that the charge is distributed following the electronegativity of the atoms forming the complex ions. The examination of theoretical charge distributions therefore gives the impression that N and C atoms form the core gathering the excess of charge, surrounded by a layer containing H atoms exhibiting a deficiency of charge. This finding does not correlate with our traditional belief that the (1+) charge which comes with H^+ or other ions upon formation of the cation remains on the neighbouring N atom.

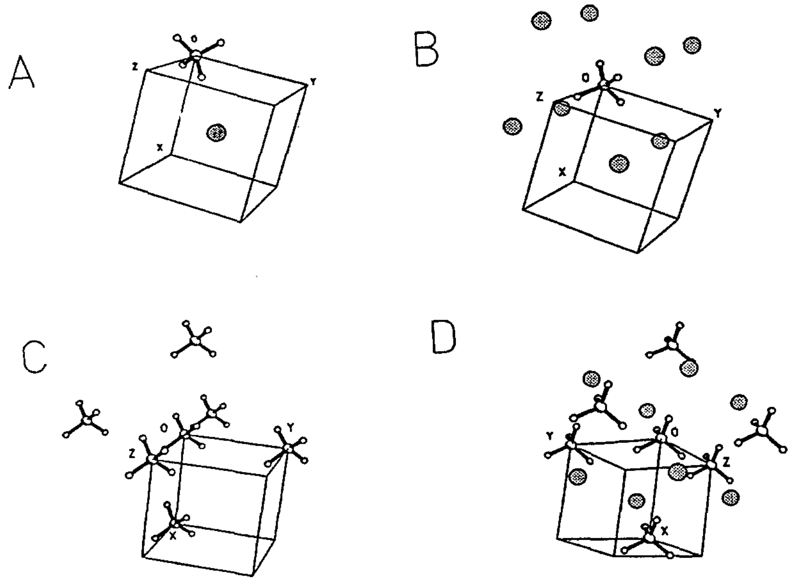

Fig. 2 Geometries of conglomerates of NH_4^+ ...Br^- (*A*), (NH_4^+ ...8Br^-)$^{7-}$ (*B*), (NH_4^+ ...6NH_4^+)$^{7+}$ (*C*), and (NH_4^+ ...8Br^-, 6NH_4^+)$^-$ (*D*)

The above approach provides the charge distributions for isolated cations. In the solid phase, a given ion is part of the whole lattice. It would therefore be interesting to know how far the inclusion of the surroundings of an ion affects the charge distributions predicted by quantum-chemistry methods [23]. The magnitude of this effect can be evaluated by considering supermolecules formed of a given complex ion and surrounding ionic fragments. Unfortunately, the capability of commonly available computers is such that this estimation is possible only for very simple complex salts. Figure 2 shows ionic conglomerates of NH_4^+ surrounded by neighbouring Br^- and NH_4^+ in the NH_4Br lattice [4]. For such conglomerates, the distribution of charge between the atoms was evaluated by using the AM1 quantum-chemistry method [27]. The results obtained (Table 1) reveal that the charge on the ionic fragments, i.e. NH_4^+ and Br^-, is predicted to be lower than primarily assumed (1+ or 1–). The surroundings also affect the relative values of the net atomic charges on the atoms in NH_4^+. The net charges on the atoms of the fragments of a crystalline substance are their characteristic feature, and form the necessary basis for lattice energy calculations. Quantum-chemistry methods seem to be most reliable for the prediction of these characteristics. However, various methods and approaches provide different values. Therefore, the distribution of charge is sometimes assumed arbitrarily [5, 28]. This has also been done here, assuming that a 1+ charge is located on the N atom of mononitrogen organic bases.

Table 1 Influence of surroundings on charge distribution in the NH_4Br lattice (calculated by AM1 method)

Species		Atom		
Formula	Figure	N	H	Br[a]
NH_4^+		–0.0888	0.2722	–1.0
$NH_4^+ \ldots Br^-$	3A	–0.0798	0.2532	–0.9330*
$(NH_4^+ \ldots 8Br^-)^{7-}$	3B	–0.0873	0.2539	–0.9283*
$(NH_4^+ \ldots 6NH_4^+)^{7+}$	3C	–0.1132	0.2781	–0.9992*
$(NH_4^+ \ldots 8Br^-, 6NH_4^+)^-$	3D	–0.1334	0.2526	–0.8770*

[a] Values marked with an asterisk (*) denote the complementary negative charge to the total positive charge evaluated for ammonium ion. They do not result from the calculations.

Examples of crystal lattice energy calculations

The data presented in Table 2, as well as those for many other salts of mononitrogen organic bases [21–24], reveal that the Coulombic energy values evaluated theoretically compare quite well with the crystal lattice energies obtained from the thermochemical cycle. The method of evaluation of the charge distribution in the cation has only a minor effect on the Coulombic energy. On the other hand, if the influence of the surroundings of the ion upon the charge distribution evaluation is taken into account, the calculated Coulombic energies decrease (Table 3), which is mostly due to the decrease in the overall charge on ionic fragments (Table 1) [23]. It is also very interesting that Coulombic energies obtained with an arbitrarily assumed unit charge on the N atom in the cation correlate surprisingly well with the experimentally found crystal lattice energies.

Table 2 Crystal lattice energies (kJ/mol) of salts of mononitrogen organic bases

	Lattice energy			
Compound	Coulombic energy			Lit[b]
	Method of charge distribution evaluation in the cation			
	INDO	MNDO	N-X[a]	
$[CH_3NH_3]Cl$[c]	688	688	704	656
$[C_6H_{11}NH_3]Cl$[c]	609	611	660	636
$[C_5H_{10}NH_2]Cl$[c]	588	588	636	626
$[(CH_3)_4N]Br$[d]	523	523	525	533
$[(n\text{-}C_3H_7)_4N]Br$[d]	425	428	460	423
$[C_6H_5NH_3]Br$[d]	568	589	656	
$[(CH_3)_4N]I$[e]	505	505	506	506
$[(CH_3)_3NH]I$[e]	538	535	551	565
$[C_2H_5NH_3]_2SnCl_6$[f]	1116	1169	1133	1191
$[(CH_3)_2NH_2]_2SnCl_6$[f]	1247	1229	1281	1275
$[(CH_3)_2NH_2]_2PtCl_6$[g]	1312	1313	1237	
$[C_5H_5NH]_2SnBr_6$[h]	1131	1127	1177	

[a] Location of +1 charge at N atom.

[b] See references cited in refs (21)–(24).

[c] Ref. (23).

[d] Ref. (22).

[e] Ref. (21).

[f] Ref. (24)

[g] This work; charge distribution in $PtCl_6^{2-}$: Pt(+0.64), Cl(−0.44) [5].

[h] This work; charge distribution in $SnBr_6^{2-}$: Sn(+1.60), Br(−0.66) [5].

The location of the 1+ charge on the N atom of the protonated base is rather artificial. We have therefore tried to find some kind of physical significance for the fact that such a simple assumption leads to correct values of the electrostatic energy. An explanation which seems reliable results from examination of the electrostatic potential around the charged species. Calculations have shown that this potential has a spherical symmetry around even very complex ions at distances where other ions occur in the lattice. Only at a close distance from the molecule is this symmetry disturbed. This means that a given complex ion is 'seen' by surrounding ions in the crystal lattice to be similar to a monoatomic ion (around which the electrostatic potential always exhibits spherical distribution). Such a spherical electrostatic potential around the complex ion could be considered to result from a unit positive charge located at some centre of the charge. It is rather accidental that for the cations of nitrogen organic bases this centre correlates with the location of N atoms.

Table 3 Crystal lattice energy (kJ/mol) of NH_4Br calculated for various charge distributions

Species	E_{el}	Lit(E_c)
NH_4^+	706.2	615 [30]
	712, 711, 707, 697 [22]	633 [31]
	691 [29]	644 [32]
$NH_4^+ ... Br^-$	614.7	654, 670 [33]
$(NH_4^+ ... 8Br^-)^{7-}$	608.6	661 [34]
$(NH_4^+ ... 6NH_4^+)^{7+}$	706.5	682 [35]
$(NH_4^+ ... 8Br^-, 6NH_4^+)^-$	543.7	

Importance of lattice energy in examinations of properties and behaviour of solids

Since the crystal lattice energy reflects the magnitude of the cohesive energy in the solid phase, it should determine most features of solids, such as structure, physicochemical properties, volatility, capability of undergoing phase transitions and, what is most important, their reactivity in the solid phase. First of all, this latter problem is of great interest to chemists. All quantum-chemistry methods currently used permit the examination of chemical reactions in which isolated molecules participate. For study of the reactivity of solids, the energy of the system must refer to the solid phase. This requires consideration of the interaction between molecules in this phase. In other words, on lowering the energy of isolated molecules by the crystal lattice energy, one finds the system in the ground state relative to which any considerations regarding chemical processes should be made. The problem of reactivity is inseparably associated with the problem of reaction mechanism and kinetics. As regards solid-state systems, much attention has been devoted in the past to developing a model for the description of the reaction kinetics [36–38]. So far, all approaches are based on the phenomenological Arrhenius equation [39], which was primarily proposed for gaseous reactions. For solid-state processes, the basic kinetic relationship for isothermal conditions is given by the differential equation [36–38]

$$\frac{d\alpha}{dt} = f(1-\alpha)\, B \exp[-\frac{E_a}{RT}] \qquad (7)$$

where R is the gas constant; α is the extent of reaction; t and T express time and temperature (constant), respectively; and B and E_a are the Arrhenius constants (in the case of gaseous reactions, E_a is identified with the activation barrier for the process and B with the frequency factor). $f(1-\alpha)$ in Eq. (7) is a function describing the kinetic model for the process, or, in other words, the reaction mechanism. At our present level of knowledge we are able to predict what is called the reaction pathway, employing quantum-chemistry methods, but only for reactions in the gaseous phase. This affords us an insight into the changes which occur in the system at the molecular level. Therefore, such calculations allow verification of the phenomenological description of reaction kinetics based on the Arrhenius model. Moreover, it is possible to predict the activation barrier for the process and calculate the rate of reaction and consequently the extent of reaction as a function of time and temperature. Such possibilities do not yet exist for reactions proceeding in the solid phase. We believe, however, that a combination of quantum-chemistry procedures, predicting the energy of molecules and the pathways of reactions in which they participate, with methods of evaluation of crystal lattice energy should provide information on the mechanism of processes occurring in the solid phase. Furthermore, the extension of theoretical methods of prediction

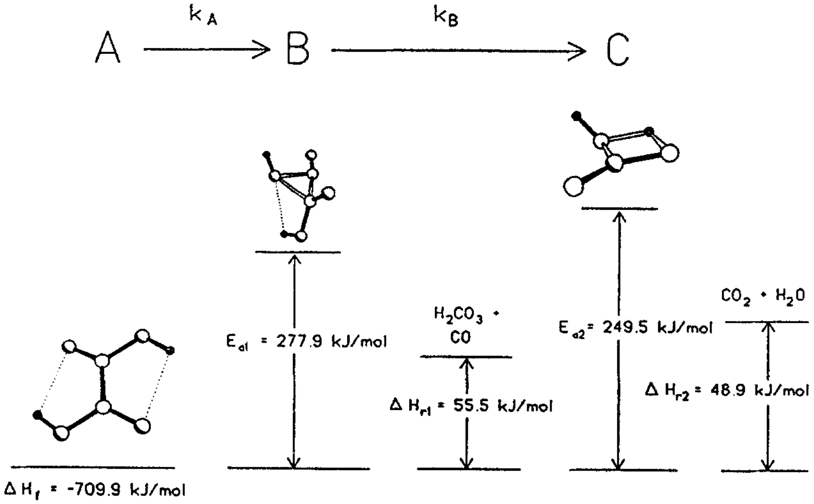

Fig. 3 The route of oxalic acid (*A*) decomposition through primary CO elimination and consecutive carbonic acid dissociation (*B* and *C* represent transition state structures

of rate constants in the gaseous phase, e.g. the RRKM method [40], should in future provide possibilities of theoretical analysis of the kinetics of solid-phase processes.

To give some idea as to how this could be done, we present below a complete theoretical treatment of the kinetics of thermal decomposition of oxalic acid in the gaseous phase. This example was chosen since the calcium salt of the acid is widely used as a standard in thermal analysis.

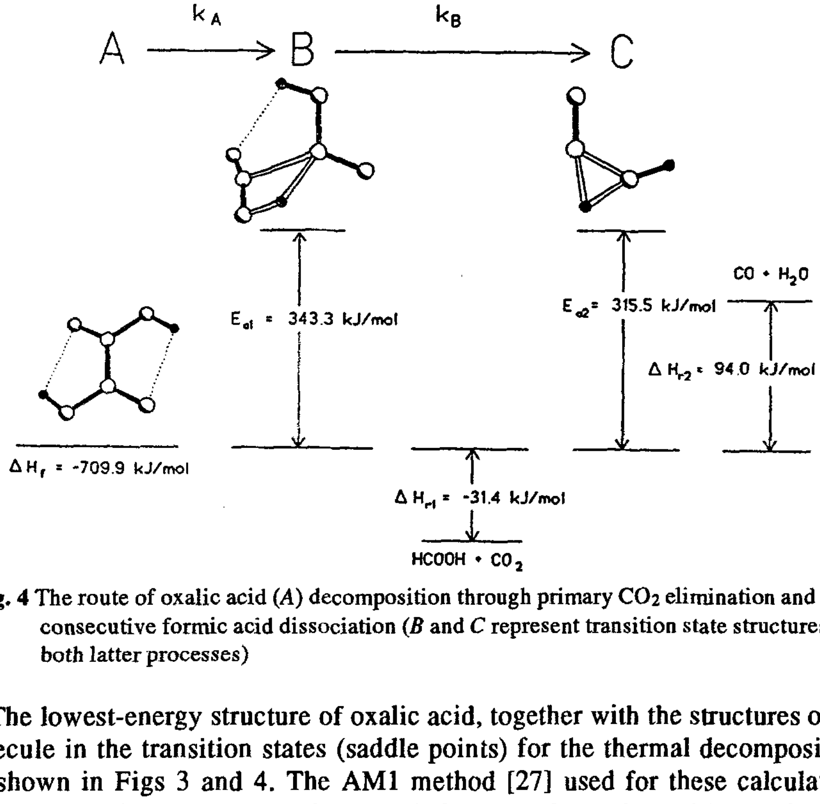

Fig. 4 The route of oxalic acid (*A*) decomposition through primary CO_2 elimination and consecutive formic acid dissociation (*B* and *C* represent transition state structures for both latter processes)

The lowest-energy structure of oxalic acid, together with the structures of the molecule in the transition states (saddle points) for the thermal decomposition, are shown in Figs 3 and 4. The AM1 method [27] used for these calculations predicts that the substrate molecule admits a conformation with two internal hydrogen-bonds (indicated by dashed lines). It can be expected that the primary step in the thermal decomposition of oxalic acid is the elimination of either CO or CO_2 as fragments. AM1 reveals that the primary elimination of CO is energetically favourable. As the secondary step, the consecutive decomposition of the resulting molecule $(HO)_2CO$ can be expected. The pathway demonstrated in Fig. 3 therefore determines the overall kinetics of decomposition. To evaluate the extent of oxalic acid decomposition as a function of temperature and time theoretically, one has to know the rate constants corresponding to each reaction step. These were derived by using Eq. (8), resulting from the RRKM method [40]:

$$k_{\mathrm{uni}}(T,P) = \frac{L^+}{N_A h Q_v}\exp\left(-\frac{E_0}{RT}\right)\int_0^{\infty}\frac{P(E_v^+)\exp\left(-\frac{E_v^+}{RT}\right)}{1+\frac{k_a(E)}{\sum_i \lambda_i B_i P_i}}\,dE_v^+ \qquad (8)$$

where

$$k_a(E) = \frac{L^+}{N_A h}\frac{P(E_v^+)}{N(E_v^*)}$$

In Eq. (8), N_A, h, R, and T are the Avogadro number, the Planck constant, the gas constant and temperature, respectively; Q_v is the partition function; L^+ is the reaction-path degeneracy (equal to 4 in the case of CO elimination, and 2 for $(HO)_2CO$ dissociation); E_0 is the critical energy (taken to be 277.9 kJ/mol for CO elimination and 249.5 kJ/mol for $(HO)_2CO$ decomposition); $P(E_v^+)$ and $N(E_v^*)$ express sums and densities of states (values of Q_v, $P(E_v^+)$ and $N(E_v^*)$ were evaluated on the basis of known procedures [40], using vibrational frequencies for the oxalic acid and $(HO)_2CO$ molecules in the ground and transition states, derived by AM1); the term $\Sigma_i \lambda_i B_i P_i$ denotes the collision rate constants and its value can be derived on the basis of the collision theory of gased (λ_i is the efficiency of collisions, assumed to be equal to 1; B_i is the frequency of two-centre

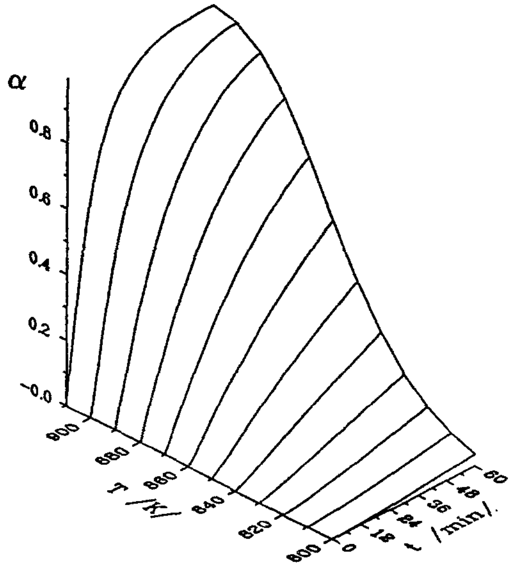

Fig. 5 Predicted extent of oxalic acid decomposition (in mass fraction) in a function of time at various constant temperatures

collisions – the diameters (in nm) of the oxalic acid and $(HO)_2CO$ molecules were taken to be 0.700 and 0.615, respectively [41]; P_i is the pressure of a given component of the reaction mixture).

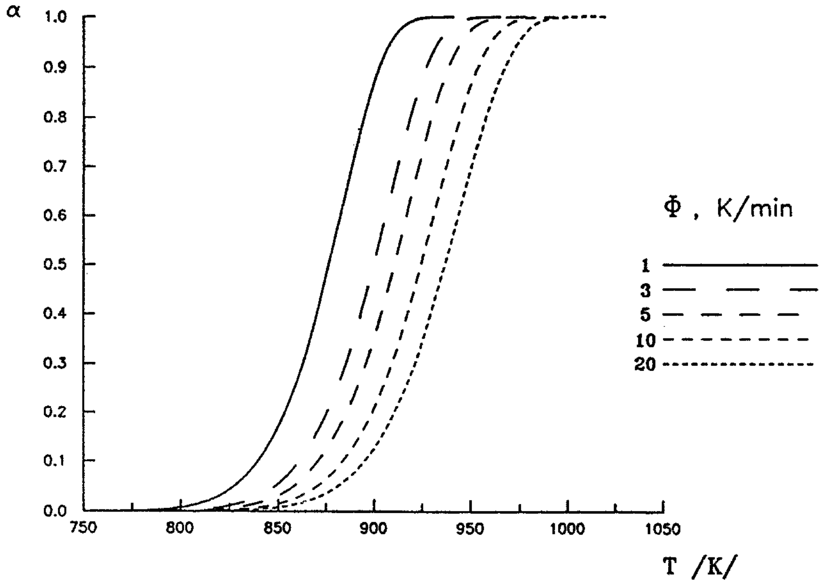

Fig. 6 Predicted extent of oxalic acid decomposition (in mass fraction) in non-isothermal conditions at different heating rates

To visualize the expected changes in the system due to the thermal processes, the extent of decomposition as a function of time and temperature is presented in Figs 5 and 6. These dependences were derived by assuming that 1 mol of oxalic acid is closed in a cell which is immersed in a bath of gas whose pressure is constant at $1.03 \cdot 10^5$ N/m^2. The walls of the cell are assumed to be such that at any moment the pressure inside the cell is the same as that outside. Moreover, it is assumed that the final reaction products, i.e. CO, H_2O and CO_2, can migrate freely through the walls to the outside. This means that, with increase of the extent of reactions, the volume of the cell decreases to 0. Under such conditions, the only important encounters are those between oxalic acid and carbonic acid molecules. It is further assumed in the model that the whole system reaches a given temperature instantaneously, which implies that the heat and mass transport are both realized instantaneously, with the except of restrictions regarding the mass transport mentioned above. It may therefore be considered that under such conditions, merely the kinetics of the chemical reactions determine the overall change in the system.

The above conditions of realization of the thermal processes can be identified with those prevailing for thermal analyses in open systems (e.g. in the derivatograph).

The curves of α *vs*. time (t) or temperature (T) shown in Figs 5 and 6 were found by using Eq (9), derived on the basis of the classical rate equations for consecutive unimolecular reactions [1] and material balances for the decomposition process

$$\alpha = \frac{\sum_{\mathrm{t,T}} (n_{\mathrm{A}}^{0})_{\mathrm{t,T}} (1 - e^{-k_{\mathrm{A}}t}) M_{\mathrm{co}}}{n_{\mathrm{A}}^{0} M_{(\mathrm{COOH})_2}} + \frac{\sum_{\mathrm{t,T}} (n_{\mathrm{A}}^{0})_{\mathrm{t,T}} \left[1 + \frac{(n_{\mathrm{B}}^{0})_{\mathrm{t,T}}}{(n_{\mathrm{A}}^{0})_{\mathrm{t,T}}} - \frac{k_{\mathrm{B}}}{k_{\mathrm{B}} - k_{\mathrm{A}}} e^{-k_{\mathrm{A}}t} - \left(\frac{(n_{\mathrm{B}}^{0})_{\mathrm{t,T}}}{(n_{\mathrm{A}}^{0})_{\mathrm{t,T}}} - \frac{k_{\mathrm{A}}}{k_{\mathrm{B}} - k_{\mathrm{A}}} \right) e^{-k_{\mathrm{B}}t} \right] M_{(\mathrm{HO})_2\mathrm{CO}}}{n_{\mathrm{A}}^{0} M_{(\mathrm{COOH})_2}} \tag{10}$$

where k_{A} and k_{B} are the unimolecular rate constants, dependent on the temperature and composition of a reactant mixture (calculated via Eq. (8) for decarbonylation and carbonic acid decomposition, respectively (Fig. 3)); n_{A}^{0} is the initial amount of substrate (in our case n_{A}^{0} is always equal to 1 mol); $(n_{\mathrm{A}}^{0})_{\mathrm{t,T}}$ and $(n_{\mathrm{B}}^{0})_{\mathrm{t,T}}$ are the initial amounts of substrate and intermediate species, respectively, before a given iteration; and M_{co}, $M_{(\mathrm{HO})_2\mathrm{CO}}$ and $M_{(\mathrm{COOH})_2}$ are the molar masses of the molecules indicated in the subscripts. The curves is Fig. 5 can be identified with isothermal thermogravimetric curves. On the other hand, the dependences demonstrated in Fig. 6 can be related to non-isothermal TG curves. Both above dependences were evaluated by the iterative procedure which assumed step-by-step realization of the process. This procedure permitted calculation of the amount of substrate depleted in the first unit of time (or temperature), the instantaneous change of time or temperature (according to the rate of its increase), and adjustment of the amount of reactants in the system.

The question could be asked: When shall we be able to derive such curves for reactions proceeding in the solid phase? The answer is not simple, since we are still at the initial stages. Nevertheless, the outlined route seems to be the only one that affords an insight into the chemical changes in solid systems at a molecular level. The phenomenological approach to the investigation of reaction pathways (reaction mechanism) and kinetics, though very useful in solving many applicative problems, is not able to provide information on the nature of solid-phase chemical processes.

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Zusammenfassung — Es wird eine allgemeine Methode zur theoretischen Ableitung der Kristallgitterenergie von ionischen Verbindungen, insbesondere von Verbindungen mit einatomigen Ionen beschrieben. Anschließend werden die Möglichkeiten einer theoretischen Voraussage der Gitterenergie komplexer organischer und anorganischer Ionenverbindungen diskutiert. Zuletzt wird die Bedeutung der Gitterenergie bei der Untersuchung der Eigenschaften und des Verhaltens von Feststoffsystemen im Zusammenhang mit der Aussicht auf die Entwicklung eines Modelles zur Beschreibung der Kinetik von Feststoffprozessen gezeigt.