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THERMODYNAMICS AND KINETICS OF THE THERMAL DECOMPOSITION OF N,N,N-TRIMETHYLMETHANAMINIUM AND 1-METHYLPYRIDINIUM HALIDES[*]

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Abstract

The decomposition of the quaternary salts mentioned in the title was examined at the quantum mechanical Hartree–Fock level of theory employing pseudopotentials combined with a SBKJ** basis set. This enabled identification of intermediate and transition state species on the reaction pathway and prediction of the thermodynamic and kinetic barriers to the dissociation of the compounds in the gaseous phase. Application of classical methods permitted the lattice energies of salts, whose crystal structures had been established earlier, to be predicted. Combination of these latter characteristics with the heats of formation of gaseous halide ions (available from the literature) and the relevant cations (obtained at the density functional (B 3LYP)/6-31G** level of theory) provided heats of formation of the salts. On the basis of these values, the thermodynamic and kinetic barriers to the dissociation of the compounds were predicted. The characteristics thus obtained compare quite well with those available in the literature or determined in this work on the basis of TG or DSC measurements. These investigations have shed more light on the mechanism of the thermal dissociation of quaternary salts, and more generally on thermal processes involving solids.

Keywords: N,N,N-trimethylmethanaminium and 1-methylpyridinium halides, mechanism of decomposition, theoretical and thermoanalytical investigations

Introduction

The thermodynamics and kinetics of the thermal decomposition of solids has always been one of the main areas of Šesták's scientific interest [1–7]. However, a complete analysis from this point of view is possible only in the case of relatively simple solid phase systems. This was why we chose the quaternary (methyl) halides of nitrogen organic bases for these investigations. According to thermoanalytical measurements,

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[*] This paper is dedicated to Professor Jaroslav Šesták on his 60th birthday. For decades his work has traced out the development of important branches of chemistry and technology from the cognitive and utilitarian points of view. Wishing him good health, personal and professional successes and further interesting achievements, the authors would like to emphasise the great influence that his work has had on scientists working in the field of solid-state chemistry, themselves included.

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these model compounds decompose completely in one step to gaseous products [8–11]. This was confirmed by theoretical analysis that predicted the simple decomposition of these compounds to halomethanes and the corresponding nitrogen organic bases [11, 12]. In such investigations it is important to find correlations between experimental and theoretical results, e.g. values of the thermodynamic and kinetic barriers to decomposition. Unfortunately, these correlations did not appear to be so good when the theoretical data obtained from semi-empirical quantum mechanical calculations were compared with those extracted from the results of thermoanalytical investigations [11–13]. We thus extended the calculations to the ab initio (Hartree–Fock) and density functional theory levels. We focused our interest on the relatively well known N,N,N-trimethylmethanaminium halides, and on 1-methylpyridinium halides, which have not yet been examined from this angle. The main aim of the investigations was to discover the extent to which the results of theoretical predictions compare with predictions emerging from thermoanalytical measurements and how accurate a reflection they are of the pathways of the thermal decomposition of the compounds. If there were reasonable agreement between experimental and theoretical data, such an approach could be a convenient way of tackling problems concerning the mechanism of decomposition and reactivity of solids.

Methods

Syntheses

1-Methylpyridinium bromide and iodide were synthesised by heating pyridine with methyl bromide or iodide, all freshly distilled, in a heavy-wall ace pressure tube at 403 K [11, 13]. After completion of the reaction, the excess halomethanes were removed by distillation under reduced pressure. The salts were then suspended in acetone and filtered. The crude products were dissolved in ethyl alcohol and precipitated by the addition of diethyl ether. The compounds were purified by crystallisation from a 1/1 mixture of ethyl alcohol and water (the respective melting points of 1-methylpyridinium bromide and iodide are 427 and 394 K). The purity of the compounds was confirmed by elemental analysis on a Carlo Erba EAGER 200 instrument (% found/theoretical for 1-methylpyridinium bromide and iodide=C, 42.06/41.41 and 32.93/32.60; H, 4.65/4.63 and 3.51/3.65; N, 7.84/8.05 and 6.12/6.34 respectively). 1-Methylpyridinium chloride was synthesised by stirring overnight an aqueous solution of 1-methylpyridinium iodide with a slight excess of freshly precipitated silver chloride [11, 13] and purified as described above. As 1-methylpyridinium chloride is very hygroscopic, a reliable determination of its elemental composition was not possible.

Thermoanalytical investigations

Dynamic thermogravimetric measurements were conducted on a Netzsch TG 209 thermobalance coupled to a Bruker IFS 66 FTIR spectrometer. Samples weighing

9–12 mg were placed in a platinum crucible and heated at (β) 1.0 K min^{-1} in a dynamic Ar atmosphere.

Differential scanning calorimetry measurements were carried out on a Netzsch DSC 204 instrument. Samples weighing 8–17 mg were placed in an aluminium crucible covered with a lid (having a pinhole) and heated at 2.0–5.0 K min^{-1} in a dynamic Ar atmosphere.

From thermogravimetric traces (Fig. 1), α (extent of reaction)=$f(T)$ (temperature) relationships, enthalpies of activation ($\Delta_a H^o$) were derived according to the general equation [9, 10, 14]

$$g(1-\alpha)=(Z/\beta)T\exp[-\Delta_a H^o/(2RT)] \qquad (1)$$

(Z is the Arrhenius pre-exponential constant) employing the linear least squares method. Three reaction models were considered [3, 15–17]: zero kinetic order ($R1$), $g(1-\alpha)=\alpha$; surface decomposition ($R2$), $g(1-\alpha)=1-\ln(1-\alpha)^{1/2}$, and unimolecular decomposition ($F1$), $g(1-\alpha)= -\ln(1-\alpha)$.

Theoretical calculations

The unconstrained stationary geometries of all the entities appearing on the decomposition pathway were determined at the Hartree–Fock level of theory (HF) [18]. Baker's optimisation procedure [19] was employed in conjunction with the relativistic compact effective core potentials of Stevens *et al.* [20, 21], as well as their valence, energy optimised, shared exponents, contracted-Gaussian basis sets supplemented with standard polarisation functions (*d* functions for C, N, Cl, Br, I with the exponents 0.80, 0.80, 0.75, 0.389, 0.266, respectively, and *p* function for H with the exponent 1.1) [18], subsequently labelled as SBKJ**. For the C and N atoms 2 electrons and for Cl, Br and I – 10, 28 and 46 electrons, respectively, were incorporated into the pseudopotential. To model chemically an active 1*s* orbital in the case of H, 2*s* and 2*p* orbitals in the case of C and N, or *ns* and *np* orbitals for Cl, Br and I, double – zeta quality *s* and *p* basis sets were used. After geometry optimisations, the Hessian energy (second derivatives of the energy as a function of nuclear co-ordinates) was calculated to confirm that the structures corresponded to true minima or transition states [18, 22]. On the basis of the numerical values of second derivatives, the harmonic vibrational frequencies were derived and subsequently used to evaluate the thermal energy and entropy contributions by means of statistical thermodynamics routines.

Energies of N,N,N-trimethylmethanaminium (TetraMA^+) or 1-methylpyridinium (MPy^+) cations and the corresponding elements were predicted by geometry optimisation at the DFT level [23] using Becke 3LYP (B 3LYP) functional [24, 25] and the 6-31 G** basis set [26, 27] supplemented with the thermal energy contributions (obtained using statistical thermodynamics routines). Both of these are implemented in the GAUSSIAN 94 program [28]. The enthalpies of formation of the above entities were obtained from basic physico-chemical relationships [29]. This level of theory

Table 1 Thermodynamic and kinetic characteristics in kJ mol^{-1} for solid-phase quaternary halides

Compound	Crystal lattice energy		Enthalpy of formation $\Delta_{f,298}H°$		Enthalpy of dissociation $\Delta_{d,298}H°(s)^c$		Activation enthalpy of dissociation $\Delta_{a,298}H°(s)^c$		
							this work		
	this work[a]	others	this work[b]	others	this work[c]	others	theoretical[d]	experimental[e]	others[e]
$[N(CH_3)_4]Cl$	534.2 662.4	502 [52, 53] 523 [54] 534 [41] 537 [12] 538 [55] 548 [52] 535, 553 [56] 566 [57] 576 [8]	–226.7 –354.9	–272 [8] –274 [58] –276 [57]	121.1 (th) 249.3 (th)	167 [8, 59] 168 [8]	258.2 386.4		354(*R*1) [8] 408(*R*2) [8] 470(*F*1) [8]
$[N(CH_3)_4]Br$	526.0 646.6	494 [52] 516 [54] 524 [42] 526 [12,55] 531 [52] 533, 544 [56] 553 [57] 558, 587 [9]	–204.5 –325.1	–252 [57] –268 [9]	145.3 (th) 265.9 (th)	209 [9]	263.4 384.0		430(*R*1) [9] 518(*R*2) [9]
$[N(CH_3)_4]I$	507.3 616.2	477 [52] 498 [54] 506 [43, 55] 509 [12] 518 [56] 531 [10] 544 [57]	–162.8 –271.7	–190 [10] –203 [57] –204 [55]	153.8 (th) 262.7 (th)	170 [10, 59] 181 [10]	259.8 368.7		265(*R*1) [10] 311(*R*2) [10]

Table 1 Continued

$[PyCH_3]Cl$					244 (*R*1) 282 (*R*2) 328 (*F*1)
$[PyCH_3]Br$			143.8 (ex)		205 (*R*1) 241 (*R*2) 287 (*F*1)
$[PyCH_3]I$	498.0 595.6	15.2 –82.4	142.3 (ex) 139.9 (th) 237.5 (th)	260.4 358.0	203 (*R*1) 234 (*R*2) 272 (*F*1)

[a] $-E_{el}$ upper value and $-E_c$ lower value (mean values from those listed in Table 4)

[b] Calculated using $\Delta_{f,298}H^o$ of gaseous Cl^-, Br^- and I^- equal to –233, –219 and –196 kJ mol^{-1} [49, 50], respectively; $\Delta_{f,298}H^o$ of gaseous $[N(CH_3)_4]^+$ and $[PyCH_3]^+$ equal to 540.5 and 709.2 kJ mol^{-1} (were obtained at the DFT (B3LYP)/6-31G** level of theory); and mean crystal lattice energies obtained in this work ($-E_{el}$ (upper value) and $-E_c$ (lower value) listed in the second column of this Table)

[c] Theoretical (th) values were predicted using $\Delta_{f,298}H^o$ of gaseous CH_3Cl, CH_3Br, CH_3I, $N(CH_3)_3$ and pyridine equal to –81.9, –35.5, 14.7, –23.7 and 140.4 kJ mol^{-1} [51], respectively, and enthalpies of formation (upper values derived from $-E_{el}$, the lower ones from $-E_c$) obtained in this work (listed in the fourth column of this Table); experimental (ex) values were determined by DSC

[d] The sum of the theoretical values of $\Delta_{d,298}H^o$(s) predicted in this work (upper values from $-E_{el}$ and the lower ones from $-E_c$) – listed in the 6th column of this Table – and $\Delta_{a,298}H^o$(g) – listed in the 8th column of Table 2

[e] Evaluated fitting α *vs*. T dependencies (Fig. 1) with the equation: $\ln[g(1-\alpha)/T]=\ln(Z/\beta)-\Delta_{a,T}H^o(s)/(2RT)$ (Eq. (1)); $g(1-\alpha)$ is equal to $\alpha(R1)$, $1-(1-\alpha)^{1/2}$ $(R2)$ or $-\ln(1-\alpha)$ $(F1)$

has been found to enable reliable prediction of thermodynamic characteristics of chemical systems [29, 30].

The crystal lattice energy (E_c) was calculated by summing the electrostatic (E_{el}), dispersive (E_d) and repulsive (E_r) contributions [31–33]

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

E_{el} in Eq. (2) represents Coulombic interactions [32],

$$E_{el} = \frac{1}{2}\sum_i \sum_{j\neq i} \frac{Ne^2}{4\pi\varepsilon_0}\frac{Q_i Q_j}{R_{ij}} \tag{3}$$

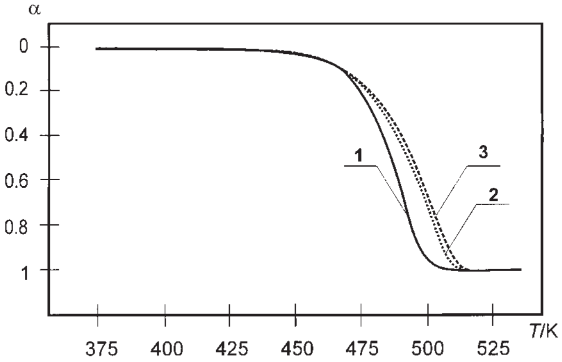

Fig. 1 Dynamic thermogravimetric traces reflecting the decomposition of 1-methylpyridinium chloride (1), bromide (2) and iodide (3)

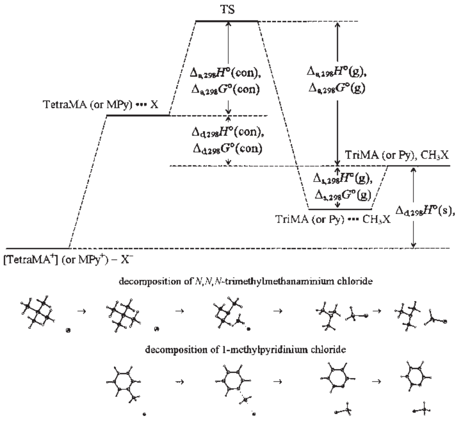

Fig. 2 Enthalpy and free enthalpy changes (upper part) along the reaction pathway (lower part) upon decomposition of crystalline N,N,N-trimethylmethanaminium (TetraMA$^+$) and 1-methylpyridinium (MPy$^+$) halides (X$^-$): [TetraMA$^+$] (or [MPy$^+$]) – X$^-$ represents the crystalline phase, TetraMA (or MPy) ••• X – conglomerate of ions, TS – transition state, TriMA (or Py) ••• CH_3X – complex of decomposition products and TriMA (or Py), CH_3X – isolated products

Table 2 Thermodynamic and kinetic barriers in kJ mol^{-1} to the decomposition and formation of quaternary halides obtained from quantum mechanical calculations at the HF/SBKJ** level (gaseous phase)

Compound	Thermodynamic[a]				Kinetic[a]			
	decomposition		formation		decomposition		formation	
	$\Delta_{d,298}H^o_{(con)}$	$\Delta_{d,298}G^o_{(con)}$	$\Delta_{s,298}H^o_{(g)}$	$\Delta_{s,298}G^o_{(g)}$	$\Delta_{a,298}H^o_{(con)}$	$\Delta_{a,298}G^o_{(con)}$	$\Delta_{a,298}H^o_{(g)}$	$\Delta_{a,298}G^o_{(g)}$
$[N(CH_3)_4]Cl$	–88.8	–133.2	–0.3	15.8	48.3	51.4	137.1	184.6
$[N(CH_3)_4]Br$			–2.3	21.9			118.1	165.1
$[N(CH_3)_4]I$			–1.6	17.5			106.0	152.6
$[PyCH_3]Cl$	3.5	–22.3	–3.5	22.3	35.4	36.9	153.3	192.5
$[PyCH_3]Br$			–3.6	22.1			133.4	172.4
$[PyCH_3]I$			–3.9	24.2			120.5	159.2

[a] See Fig. 2

Table 3 Theoretically predicted (DFT(B3LYP)/6-31G** level) relative charges on atoms in the 1-methyl pyridinium cation (crystalline phase structure)

Atom	Method			
	HF		DFT	
	Mul	MEP fit	Mul	MEP fit
N(1)	–0.668	0.068	–0.451	0.156
C(2)	0.266	0.075	0.222	0.010
C(3)	–0.201	–0.281	–0.096	–0.150
C(4)	0.004	0.163	0.028	0.061
C(5)	–0.202	–0.310	–0.089	–0.164
C(6)	0.275	0.131	0.218	0.036
C(7)	–0.128	–0.338	–0.186	–0.343
H(2)	0.226	0.184	0.173	0.171
H(3)	0.210	0.220	0.148	0.186
H(4)	0.217	0.158	0.154	0.153
H(5)	0.210	0.225	0.149	0.189
H(6)	0.230	0.172	0.177	0.163
H(7A)	0.175	0.180	0.170	0.178
H(7B)	0.194	0.178	0.192	0.177
H(7C)	0.193	0.177	0.191	0.177

while the sum of E_d and E_r can be expressed by the formulae of Lennard–Jones [34]

$$E_d + E_r = \frac{1}{2}\sum_i \sum_{j\neq i}\left[-\frac{D_i D_j}{R_{ij}^6} + \frac{A_i A_j}{R_{ij}^{12}}\right] \tag{4}$$

or Buckingham [35]

$$E_d + E_r = \frac{1}{2}\sum_i \sum_{j\neq i}\left[-\frac{D_i D_j}{R_{ij}^6} + B_i B_j \exp(-C_i C_j R_{ij})\right] \tag{5}$$

In Eqs (3)–(5) N is the Avogadro number, e the elementary charge, ε_0 the permittivity of free space, while $Q_i(Q_j)$ denotes the relative partial charges at atoms, $D_i(D_j)$, $B_i(B_j)$ and $C_i(C_j)$ atomic parameters, and R_{ij} the distance between interacting centres (the summation extends over all pairwise interactions between each atom of a molecule chosen as a basic stoichiometric unit (denoted by '*i*') and all atoms from its surroundings (denoted by '*j*')).

Crystal lattice energies were calculated using the structural data of N,N,N-trimethylmethanaminium chloride [36–38], bromide [36–38] and iodide [39], as well as of 1-methylpyridinium iodide [40], available in the literature. The electrostatic part of the crystal lattice energy was calculated assuming a 1+ charge on TetraMA$^+$ or

Table 4 Electrostatic lattice energies ($-E_{el}$) and crystal lattice energies ($-E_c$) – both in kJ mol^{-1}

Method of calculating $E_d + E_r^a$	Method of charge calculation							
	HF				DFT			
	Mul		MEP fit		Mul		MEP fit	
	$-E_{el}^b$	$-E_c^c$	$-E_{el}^b$	$-E_c^c$	$-E_{el}^b$	$-E_c^c$	$-E_{el}^b$	$-E_c^c$
N,N,N-trimethylmethanaminium chloride								
I	530.4	679.2	537.3	686.1	531.9	680.8	537.3	686.1
II	530.4	637.9	537.3	644.8	531.9	639.4	537.3	644.8
N,N,N-trimethylmethanaminium bromide								
I	522.6	660.2	528.6	666.1	524.1	661.6	528.6	666.2
II	522.6	626.2	528.6	632.2	524.1	627.7	528.6	632.2
N,N,N-trimethylmethanaminium iodide								
I	504.6	627.2	509.2	631.8	505.9	628.4	509.4	631.9
II	504.6	599.9	509.2	604.5	505.9	601.1	509.4	604.6
1-methylpyridinium iodide								
I	494.1	600.7	503.5	610.0	492.0	598.6	502.3	608.8
II	494.1	582.9	503.5	592.2	492.0	580.8	502.3	591.1

[a] For atomic parameters, see Table III in [48]; I – atomic parameters from the London equation, $E_d + E_r$ calculated using Eq. (4); II – atomic parameters from the London equation, $E_d + E_r$ calculated using Eq. (5)

[b] Calculated using the relevant relative atomic partial charges (see e.g. Table 3) and Eq. (3)

[c] Calculated on the basis of Eq. (2)

MPy^+ cations and a 1–charge on halogen anions (X^-) [41–43]. The charges on the atoms in the cations were derived from Mulliken population analysis (Mul) [44] or by fitting the electrostatic potential around molecules (MEP fit) [45], predicted at the HF [18] or density functional (DFT) [23] level of theory, to the Coulomb equation (e.g. Eq. (3)). The B 3LYP functional [24, 25] was applied in the DFT calculations and 6-31G** basis set [26, 27] in all the calculations, which were carried out using the GAUSSIAN 94 program package [28]. The crystal lattice energy was calculated using the PCK83 program [46]. The atomic parameters necessary for calculating E_d+E_r contributions were taken from our earlier publications [47, 48].

Results and discussion

Both N,N,N-trimethylmethanaminium [8–10] and 1-methylpyridinium (Fig. 1) halides decompose in one step with the release of the corresponding nitrogen organic bases (N,N-dimethylmethanamine or pyridine) and halomethanes. This was confirmed by analysis of infrared absorption spectra of the gaseous products released during the decomposition of 1-methylpyridinium halides. Fitting thermogravimetric traces for the latter compounds (Fig. 1) to the phenomenological equation (Eq. (1)) provided activation enthalpies for the $R1$, $R2$ and $F1$ reaction models given in Table 1. These barriers to the dissociation of N,N,N-trimethylmethanaminium halides were determined by us earlier and are also listed in Table 1. Complementary DSC measurements enabled the determination of the enthalpies of the thermal dissociation and melting of 1-methylpyridinium bromide and iodide (because the chloride salt is extremely hygroscopic, reliable DSC measurements could not be performed). Values of the first characteristic are given in Table 1, while the melting enthalpies of 1-methylpyridinium bromide and iodide are equal to 19.7 and 16.3 kJ mol^{-1} respectively (the melting points were given earlier in the text).

Theoretical analysis confirms that quaternary salts decompose to gaseous nitrogen bases and halomethanes (Fig. 2). As it had been postulated earlier that the dissociation of crystalline salts is preceded by the formation of a loosely bonded complex of ions [60, 61], we checked to see whether any such entity could appear. Theory predicts that ions can indeed form conglomerates prior to the dissociation of the salts (Fig. 2). However, such conglomerates would be thermodynamically unstable with respect to the decomposition products ($\Delta_{d,298}G^o$ (con) in Table 2) and would readily decompose to them, owing to the very low kinetic barriers to the process ($\Delta_{a,298}H^o$ (con) and $\Delta_{d,298}G^o$ (con) in Table 2). It is thus probable that even if conglomerates are present, they do not affect the dissociation kinetics of the salts. Dissociation of the compounds will therefore require energy and free energy barriers relevant to the transition state to be overcome (Fig. 2). At this stationary point the nitrogen atom in molecules of nitrogen organic bases, the carbon atom of the CH_3 group and halogen atoms lie on a line perpendicular to the plane created by all the atoms of the CH_3 group (this structure is similar to one predicted for SN2 processes). As the energy of solid substances cannot be determined by the quantum chemistry or density functional methods used, we determined the thermodynamic and kinetic characteristics of molecules in the transition state with respect to the gaseous products. Thus, the activation barriers to the formation of quaternary salts ($\Delta_{a,298}H^o$(g) and $\Delta_{d,298}G^o$(g) in Table 2) are also barriers to their decomposition. We noted that after passing the saddle point (TS), molecules of products can interact and form complexes (Fig. 2). Such complexes are energetically poorly stabilised, however are thermodynamically unstable at room temperature ($\Delta_{a,298}H^o$(g) and $\Delta_{d,298}G^o$(g) in Table 2) owing to the relatively high contribution of the entropy term. It is thus probable that when these salts are heated to temperatures at which decomposition occurs (Fig. 1), the released gaseous products exist as kinetically independent entities.

The quantum-mechanical calculations did not relate to the solid phase, so the results obtained thereby are not directly comparable with the experimental ones. To make such a comparison possible we calculated crystal lattice energies, which reflect the magnitude of interactions of molecules (ions) in the solid phase. The main contribution to this quantity is derived from electrostatic interactions (E_{el}). To calculate these, atomic partial charges were determined (an example is given in Table 3). On the other hand, dispersive and repulsive contributions to the crystal lattice energy were determined using atomic parameters evaluated by us earlier [48]. Crystal lattice energies and the electrostatic contributions to these are given in Table 4. The values of both quantities depend somewhat on the atomic partial charges or parameters used.

Table 5 Theoretically predicted (HF/SBKJ** level) changes in partial charges on the nitrogen and chlorine atoms along the decomposition pathway

Species[a]	Atom	MEP fit	Mul
	N,N,N-trimethylmethanaminium chloride		
[Tetra MA$^+$] – Cl^{-b}	N	0.239	–0.615
	Cl	–1	–1
Tetra MA ••• Cl$^-$	N	0.443	–0.286
	Cl	–0.926	–0.893
TS	N	0.343	–0.393
	Cl	–0.705	–0.635
TriMA ••• CH$_3$Cl	N	–0.168	–0.256
	Cl	–0.216	–0.201
TriMA, CH$_3$Cl	N	–0.242	–0.239
	Cl	–0.201	–0.184
	1-methylpyridinium chloride		
[MPy$^+$] – Cl^{-b}	N	0.068	–0.668
	Cl	–1	–1
MPy ••• Cl	N	0.344	0.295
	Cl	–0.916	–0.892
TS	N	–0.142	0.112
	Cl	–0.746	–0.680
Py ••• CH$_3$Cl	N	–0.467	0.202
	Cl	–0.231	–0.210
Py, CH$_3$Cl	N	–0.706	0.210
	Cl	–0.201	–0.184

[a] See Fig. 2
[b] Calculated for isolated ions

To facilitate further considerations we assumed that the mean value represents the best value of a given quantity. These mean values are given in Table 1. The crystal lattice energy cannot be measured directly in the case of ionic substances. These quantities are usually obtained from theoretical calculations or estimations based on theoretical and experimental data; the literature values listed in Table 1 are of this origin. The comparison leaves the impression that the electrostatic lattice energy compares better with literature values than the crystal lattice energy does. It may be that the approach we used overestimates the contribution of dispersive interactions.

To predict the heats of formation of crystalline salts it is necessary to know the enthalpies of formation of gaseous TetraMA$^+$ and MPy$^+$ [8–10]. These characteristics were predicted theoretically to be 540.5 and 709.2 kJ mol^{-1} respectively. The former value for TetraMA$^+$ correlates excellently with the one we estimated (542 kJ mol^{-1})

by extrapolating the experimental results [8]. The enthalpies of formation of crystalline salts were predicted (Table 1) using values of $\Delta_{f,298}H^{o}$ for TetraMA^{+} and MPy^{+}, as well as experimental enthalpies of formation of gaseous halide ions. Again, the values derived from the electrostatic lattice energies compare somewhat better with the literature values of this quantity. In the next step we calculated the enthalpies of dissociation of crystalline salts by subtracting the theoretically predicted values of the enthalpy of formation of these from literature (experimental) values of the enthalpy of formation of gaseous nitrogen organic bases and halomethanes. For 1-methylpyridinium iodide, the experimental value of $\Delta_{d,298}H^{o}$(s), determined by DSC, fits excellently to that obtained theoretically. In the case of N,N,N-trimethylmethanaminium halides, the dissociation enthalpies of these salts were not measured directly, so both theoretical and experimental values may be equally uncertain. Nevertheless, even in this case there is quantitative agreement between various sets of data. Finally, by supplementing $\Delta_{d,298}H^{o}$(s) (Table 1) with $\Delta_{a,298}H^{o}$(con) (Table 2), one obtains activation enthalpy barriers which can be compared with those derived by fitting thermogravimetric curves to classical kinetic equations (Eq. (1)). Quantitative agreement exists between both sets of characteristics.

Molecules (ion pairs) occupying certain positions at well-known sites in the crystal undergo numerous transformations before decomposing to gaseous products. These changes can be traced by analysing the structure of entities occurring along the reaction pathway (Fig. 2) or changes in the atomic partial charges on selected atoms (Table 5). Together with the transformation of ion pairs, the atomic partial charges at halogen (chlorine) atoms diminish. Thus ions lose their ionic nature upon decomposition [8, 60, 61].

One problem that should be tackled is the question of the pathways (mechanism) of decomposition of quaternary salts on the basis of the results of theoretical and experimental investigations. A relatively coherent picture can be inferred from the analysis of the data for 1-methylpyridinium iodide. Combined with the relevant heats of formation of gaseous ions, the electrostatic lattice energy yields the enthalpy of formation and subsequently dissociation of the salt, which compares very well with the experimental value of this latter quantity determined by DSC. Moreover, the activation enthalpy of dissociation, determined on the basis of this latter value, compares quite well with the value of this quantity obtained by fitting thermogravimetric curves to the phenomenological equation for unimolecular reactions. The unimolecular decomposition of solid substances, and of 1-methylpyridinium iodide in particular, seems very probable from the point of view of chemical intuition. The agreement between the theoretical and experimental data thus leaves the impression that the mechanism of dissociation of this compound is now understood. Unfortunately, a similar comparison of the data for N,N,N-trimethylmethanaminium halides, resulting from experimental and theoretical investigations, does not lead to unequivocal conclusions. Data from various literature sources and obtained by various routes are scattered and compare only qualitatively with those which we ourselves have determined. Hence, both the thermoanalytical and the theoretical investigations for these compounds need to be repeated. We think that the use of more advanced techniques will provide a deeper insight into the nature of chemical processes involving solids.

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