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A THEORETICAL APPROACH TO THE DESCRIPTION OF THE THERMAL DISSOCIATION OF N,N,N-TRIMETHYLMETHANAMINIUM HALIDES

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Abstract

MNDO/d and PM3 quantum chemistry methods were used to examine reaction pathways and predict thermodynamic and kinetic barriers for the thermal dissociation of isolated conglomerates of N,N,N-trimethylmethanaminium cations (TMA^+) and halide anions ($X = Cl^-$, Br^- and I^-). Theoretically obtained changes in enthalpy and entropy for the above-mentioned process were subsequently supplemented with theoretically determined crystal lattice energies, that enabled prediction of relevant characteristics for the dissociation of crystalline phases. Data thus obtained compare only qualitatively with those available in literature and resulting predominantly from thermoanalytical investigations, although values of theoretical characteristics generally follow the same trends as experimental ones.

Keywords: decomposition, kinetics, N,N,N-trimethylmethanaminium halides, theory, thermodynamics

Introduction

N,N,N-trimethylmethanaminium halides are the simplest representatives of quaternary salts. The latter group of compounds is the subject of special interest since it contains relatively stable cationic forms of amines. Completely substituted amines become better soluble in water than amines themselves. Protonation gives rise to a similar effect, however, proton is easily removed from aminium cations when pH increases, while it is commonly known that detachment of a substituent from quaternary cations proceeds with greater difficulty. It is thus interesting to reveal the reasons for increased stability of quaternary, as compared with that of protonated aminium cations. We touched on this problem earlier investigating the thermal behaviour of N,N,N-trimethylmethanaminium chloride [1], bromide [2] and iodide [3] by thermoanalytical methods. These investigations revealed that the above-mentioned quaternary salts behave differently than relevant protonated aminium salts, this fact being interpreted by the existence of the kinetic energy barrier for decomposition of the former com-

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pounds. In this work we performed relatively simple quantum mechanical calculations in order to check whether decomposition of the above-mentioned quaternary salts proceeds through the transition state and requires the overcoming of the kinetic energy barrier. Subsequently, we calculated values of crystal lattice energies for the salts which added to values of thermochemical quantities predicted by quantum chemistry methods provided thermodynamic characteristics for the dissociation process. These latter values were compared with data derived from thermogravimetric curves.

Methods

Quantum mechanical calculations were carried out on the level of the MNDO/d [4, 5] and PM3 [6] semiempirical methods using the SPARTAN 4.0 and 5.0 program packages [7]. These two methods were chosen since the most up to date parameters for Cl, Br and I are included in the first [5] and the second performs very well in terms of predicting the geometries and properties of molecules [6]. Primary structures for the geometry optimizations were extracted from X-ray data for N,N,N-trimethylmethanaminium chloride [8–10], bromide [8–10] and iodide [11]. Pairs of $TMA^+ - X^-$ were optimized first to obtain the structures of TMA...*X*. Transition states for the decomposition of the latter entities to N,N-dimethylmethanamine and halomethanes were then found by employing the 'saddle' procedure. The commonly used AM1 method [12] most probably failed in the case of systems investigated by us due to unsound parameterization (we were unable to find the stationary geometries of TMA...*X* conglomerates and entities corresponding to saddle points in the case of systems containing Br and I).

The electrostatic part of the crystal lattice energy was calculated using PCK 83 program [13] and assuming the 1+ charge on TMA^+ and the 1– charge on X^-. Charges on atoms in the cation were those fitted so as to reproduce the molecular electrostatic potential around molecules (MEP fitted charges) [14]. They were derived on the density functional level of theory (DFT) [15] using the Becke3LYP functional [16, 17] together with the 6-31G** basis set [18, 19] – all included in the SPARTAN 5.0 program package [7]. Crystal structures necessary for these calculations were taken from literature [8–11].

Final values were obtained following basic thermodynamic relationships [1–3].

Results and discussion

Figure 1 demonstrates the structures of the conglomerate (TMA...I) obtained after optimization (MNDO/d level) of the TMA^+-I^- unit extracted from X-ray data [11], the entity in the transition state for decomposition and dissociation products (N,N-dimethylmethanamine and CH_3I). This figure therefore presents the decomposition pathway for quaternary halide salts.

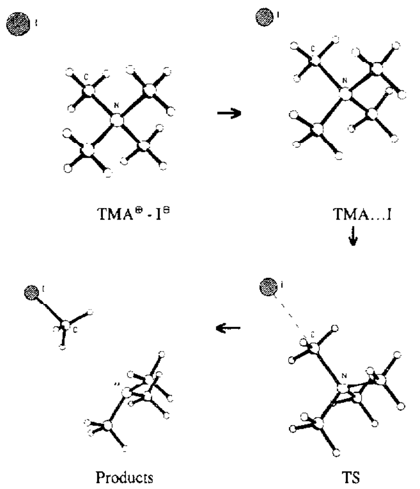

Fig. 1 $TMA^+–I^-$ unit in the crystalline phase together with the MNDO/d optimized structures of the TMA...I conglomerate, the entity in the transition state (TS) and products of decomposition

Basic thermodynamic characteristics for the TMA...*X*, transition state and dissociation products compiles Table 1, while Table 2 – thermodynamic and kinetic barriers for the decomposition. All these data arise from theoretical calculations. Table 3, on the other hand, contains theoretically predicted crystal lattice energies, enthalpies of formation and dissociation, as well as activation enthalpies for the decomposition of crystalline compounds, together with data available in literature, this in many cases originating from thermogravimetric investigations. Crystal lattice energies obtained using more sophisticated atomic partial charges than in our previous calculations [18–20] seem to match the literature values better. Theoretically determined enthalpies of formation of crystalline N,N,N-trimethylmethanaminium halides, particularly MNDO/d originating data, compare poorly with literature values (Table 3), nevertheless, they are, to our knowledge, the first predicted purely theoretically for this group of compounds. Dissociation of quaternary halides should be endothermic, if considered relative to crystalline substrates (Table 3), and exothermic, when treated relative to TMA...*X* (Table 2). Only the first case refers to the real situation. However, comparison of purely theoretically predicted dissociation enthalpies of crystalline compounds with those from the literature, does not come out well. It seems that the origin of discrepancies of dissociation and formation enthalpies of solid salts is to be found in the approximate character of the quantum chemistry methods applied. Activation enthalpies for decomposition of crystalline quaternary salts are highly positive (Table 3), which implies that the process can take place in elevated temperatures. The theoretically predicted value of this quantity for

N,N,N-trimethylmethanaminium iodide (PM3 method) matches the one derived on the basis of thermogravimetric investigations very well. Unfortunately, in the case of the two remaining compounds, discrepancies between theoretical and experimental values are high. As regards the activation enthalpies of dissociation, however, it is difficult to judge which characteristics, theoretical or experimental [1–3] are more reliable.

Table 1 Thermodynamic data arising from quantum mechanical calculations

Compound	Method	Conglomerate[a,b] (TMA...X)		Transition state[a,b] (TS)		Products[a,b,c] (CH_3X)	
		$\Delta_{f,298}H^{o}$	$_{298}S^{o}$	$\Delta_{f,298}H^{o}$	$_{298}S^{o}$	$\Delta_{f,298}H^{o}$	$_{298}S^{o}$
$[N(CH_3)_4]Cl$	MNDO/d	225.8	395.8	230.4	377.4	–80.5	233.4
	PM3	74.8	398.3	97.0	386.5	–61.4	234.3
$[N(CH_3)_4]Br$	MNDO/d	246.5	405.8	250.4	388.5	33.3	244.5
	PM3	51.1	397.5	82.8	399.2	– 8.3	245.4
$[N(CH_3)_4]I$	MNDO/d	278.0	410.2	281.4	395.9	19.2	252.5
	PM3	52.4	404.1	118.9	412.5	39.5	251.5

[a] See Fig. 1

[b] The enthalpy of formation ($\Delta_{f,298}H^{o}$) and entropy ($_{298}S^{o}$) in kJ mol^{-1} and J (mol K)$^{-1}$, respectively

[c] Values for N,N-dimethylmethanamine are as follows:

MNDO/d $\Delta_{f,298}H^{o}$=–11.6; $_{298}S^{o}$=303.5
PM3 $\Delta_{f,298}H^{o}$=–45.5; $_{298}S^{o}$=300.5

Table 2 Thermodynamic and kinetic barriers in kJ mol^{-1} for the dissociation of quaternary halides referring to the gaseous phase

Compound	Method	Thermodynamic data		Kinetic data			
		Relative to TMA...X[a]		Relative to TMA...X[a]		Relative to gaseous products[b]	
		$\Delta_{r,298}H^{o}$	$\Delta_{r,298}G^{o}$	$\Delta_{a,298}H^{o}$	$\Delta_{a,298}G^{o}$	$\Delta_{a,298}H^{o}$	$\Delta_{a,298}G^{o}$
$[N(CH_3)_4]Cl$	MNDO/d	-317.9	-360.0	4.6	10.1	322.5	370.1
	PM3	-181.7	-222.4	22.2	25.7	203.9	248.1
$[N(CH_3)_4]Br$	MNDO/d	-291.4	-333.8	3.9	9.1	295.3	342.9
	PM3	-104.9	-149.1	31.7	31.2	136.6	180.3
$[N(CH_3)_4]I$	MNDO/d	-270.4	-313.9	3.4	7.7	273.8	321.5
	PM3	-58.4	-102.5	66.5	64.0	124.9	166.5

[a] Enthalpy ($\Delta_{r,298}H^{o}$) and free enthalpy ($\Delta_{r,298}G^{o}$) of reaction (r), as well as enthalpy ($\Delta_{a,298}H^{o}$) and free enthalpy ($\Delta_{a,298}G^{o}$) of activation (a) upon dissociation of the TMA...X to N,N-dimethylmethanamine and halomethanes

[b] Enthalpy ($\Delta_{a,298}H^{o}$) and free enthalpy ($\Delta_{a,298}G^{o}$) of activation (a), upon formation of quaternary halides from N,N-dimethylmethanamine and halomethanes

Table 3 Thermodynamic and kinetic characteristics in kJ mol^{-1} for quaternary halides referring to the solid phase

Compound	Crystal lattice energy			Enthalpy of formation		Enthalpy of dissociation		Activation enthalpy of dissociation	
	Theoretical		others						
	this work	previous works		this work^a	others	this work^a	others	this work^a	others^b
[N(CH$_3$)$_4$]Cl	537	534 [20]	502 [23, 24] 523 [25] 538 [26] 548 [23] 535, 553 [27] 566 [28] 576 [1]	–27.3 –131.1	–272 [1] –274 [29] –276 [28]	–64.8 24.2	167 [1, 30] 168 [1]	258 228	364 [1]
[N(CH$_3$)$_4$]Br	526	524 [21]	494 [23] 516 [25] 526 [26] 531 [23] 533, 544 [27] 553 [28] 558, 587 [2]	–1.4 –141.1	–252 [28] –268 [2]	–43.5 87.3	209 [2]	252 224	444 [2]
[N(CH$_3$)$_4$]I	509	506 [22]	477 [23] 498 [25] 506 [26] 518 [27] 531 [3] 544 [28]	40.0 –159.2	–190 [3] –203 [28] –204 [26]	–32.4 153.2	170 [3, 30] 181 [3]	241 278	275 [3]

[a] Calculated using $\Delta_{f,298}H^0$ for gaseous Cl$^-$, Br$^-$ and I$^-$ equal to (MNDO/d / PM3): –227.7/–214.3, –212.8/–235.3 and –188.4/–270.4 (all in kJ mol^{-1}), respectively; $\Delta_{f,298}H^0$ for gaseous [N(CH$_3$)$_4$]$^+$ equal to 742.4 (MNDO/d) or 525.2 (PM3) (both in kJ mol^{-1}); crystal lattice energies determined in this work; and enthalpies of formation of other entities derived either on the MNDO/d (upper value) or PM3 (lower value) level of theory (Table 1)

[b] Values obtained by fitting the Clausius-Clapeyron equation to thermodynamic curves

Upon synthesis of quaternary halides from gaseous substrates the substantial enthalpy and free enthalpy activation barriers have to be overcome (last two columns in Table 2). If these barriers are passed, energetically (third column in Table 2) and thermodynamically (fourth column in Table 2) stable TMA...*X* conglomerates should occur. Further energetic stabilization of these entities should take place upon formation of crystalline phases (Table 3). Both $\Delta_{a,298}H^0$ and $\Delta_{a,298}G^0$ are the lowest in the case of formation of N,N,N-trimethylmethanaminium iodide, higher for bromide and the highest for chloride. This means that the iodide salt should be the easiest to obtain.

Table 4 MEP fitted relative charges on selected atoms of TMA...*X* and TS obtained on the MNDO/d or PM3 level

Compound	Method	TMA...*X*		TS	
		N	*X*	N	*X*
$[N(CH_3)_4]Cl$	MNDO/d	0.07	–0.96	0.00	–0.86
	PM3	0.68	–0.96	0.39	–0.79
$[N(CH_3)_4]Br$	MNDO/d	0.08	–0.94	0.01	–0.84
	PM3	0.65	–0.95	0.29	–0.71
$[N(CH_3)_4]I$	MNDO/d	0.10	–0.92	0.02	0.81
	PM3	0.66	–0.94	0.19	–0.68

Our earlier thermoanalytical investigations afforded us the opportunity to consider more details concerning decomposition of aminium halide salts [1–3]. Very important from the cognitive point of view is the mechanism of decomposition or formation of quaternary salts. Such a mechanism proposed by others for sublimation of NH_4Cl and adopted by us [31] assumes that the transformation of an ion pair present in the crystalline phase to a conglomerate of products which subsequently evolve to the gaseous phase, takes place through the transition state. Theoretical studies of this work reveal that $TMA^+–X^-$ first transforms to TMA...*X* which directly decompose into products (Fig. 1). Transformation from $TMA^+–X^-$, to TMA...*X*, transition state and products should be accompanied by a decrease in net charges on the cation (the N atom) and anions, which indeed theoretical calculations predict (Table 4). Despite somewhat different approaches to the mechanism of decomposition of aminium salts in this work and literature both explain experimental findings, although our enables real insight into chemical changes on the molecular level.

This publication is an example of the application of theoretical methods to explain chemical changes in the systems and interpret the results obtained by thermoanalytical methods. We shed more light on the mechanism of dissociation of N,N,N-trimethylmethanaminium halides and showed that theoretical results compare qualitatively with those originating from thermogravimetric curves.

Our studies revealed that the formation of the above-mentioned quaternary salts is accompanied by the enthalpy release and is thus energetically spontaneous, however, the process requires the overcoming of a substantial kinetic barrier and can take place at elevated temperatures.

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