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Thermochemical properties of dialkylammonium halides

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Abstract

Thermochemical properties of dialkylammonium halides of the general formula $[(C_nH_{2n+1})_2NH_2]X$, where (X=Br, I and n=3 or 4) they were analyzed by the methods of thermoanalysis (TG, DTG, DTA, DSC). The kinetic parameters were studied using non-isothermal thermogravimetric curve. The lattice energy was obtained considering the contributions of the calorific capacity in solid phase and effects of polymorphic transitions that these compounds suffer in the 0–298 K. The volatilization kinetics were analyzed by the method of Ozawa. The results were according to the data of the literature using the standard method, being verified that the value of activation energy was twicely that of volatilization enthalpy. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermal decomposition; Thermogravimetry; Activation energy; Lattice energy

1. Introduction

Nitrogened organic bases are part of biological systems as molecules or macromolecules where the nitrogen possesses an electron pair that cannot integrate in phase condensed with acids or bases of Lewis or Bronsted forming complexes or typical salts. The organic bases meet in the form of protoned, influencing the increase in solubility in a little aqueous and in its volatility, the importance of the study of the characteristics of compositions that contains forms protoned of nitrogened bases, could be useful for understanding of the operation of biological systems [1–4].

The reasons to that took a study of the thermal behavior of bromide and iodide dialkylammonium, with ramified chains or lineal, basically they consist of the attempt to reveal some characteristics of the process of the thermal decomposition and to identify regularities between the structure of the amine and the thermal and thermochemical properties of the salts. The identification of the thermal properties will facilitate an adapted application of these salts in syntheses, especially for effect of stabilization of different unstable complexes anions [5] and as catalysts. Besides, its solubility characteristics in aqueous and nonaqueous solvents allow its use in several solvent systems.

The determination of thermodynamic parameters, the enthalpies, standard molar of formation in solid phase, lattice energy and thermochemical radii can be

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done from thermogravimetric data for solution-reaction calorimetry. Standard molar formation of di-*n*-propylammonium halides, values of enthalpies, molars and di-1-methylethylammonium for presented healthy solution-reaction calorimetry [6], these results were used for calculation of the lattice energy of the salts, and the values decrease of the chlorides to the iodides. Lattice energy of alkylammonium salts obtained starting from the enthalpy standard molar of formation and experimental data of capacity calorific molar in solid phase, they are also presented in the literature [7].

The literature data of enthalpy of standard molar formation in solid phase [8] derived from solution-reaction calorimetry, and the data of calorific capacity in solid phase to determine the lattice energy, thermochemical radii and the enthalpy of volatilization of the compounds were used in this work: $Pr_2{}^nNH_2I$, $Pr_2{}^iNH_2I$, $Pr_2{}^nNH_2Br$, $Pr_2{}^iNH_2Br$, $Bu_2{}^nNH_2I$, $Bu_2{}^iNH_2I$, $Bu_2{}^nNH_2Br$ and $Bu_2{}^iNH_2Br$. The thermolysis parameters were also analyzed starting from the TG and DTA curves.

2. Experimental

2.1. Chemical

Di-*n*-propylamine, di-iso-propylamine, di-*n*-butylamine, di-iso-butylamine, were treated for distillation, being collected at 383, 357, 432 and 412 K, respectively.

2.2. Preparations

Bromides and iodides of di-*n*-propyl, di-iso-propyl, di-*n*-butyl and di-iso-butylammonium, were prepared according to method described in the literature [7,8] using equimolar solution of the hydrobromic acid bromides or iodides in water, where it was added slowly and under constant agitation of the corresponding amine. The excess of water and amine were evaporated and the salts recrystallized in ethanol, filtrates are dried in vacuum.

2.3. Other measurements

The mass spectra were obtained in a spectrometer gas–mass, Hewlett-Packard, model 5988A, with energy of ionization of 70 eV, temperature in the region of 623 K, with adjustment of the experimental parameters for maximizer the signs of the registered ions. The spectra (H^1 RMN) were obtained in methanol deuteride, using as internal pattern the tetramethylsilane (TMS), and frequency of 60 Hz, in an apparel Varian model T-60. The spectra FT–IR was accomplished in an apparel BOMEM, model MB102, in windows of KBr, in the region from 200 to 4000 cm^{-1}.

2.4. Thermal measurements

The measures of differential thermal analysis (DTA) they were accomplished in an equipment Shimadzu model DTA-50, in four heating speeds 2, 5, 10 and 20 K/min, under atmosphere of nitrogen, with flow of 30 ml/min. The curves derived of thermogravimetry/thermogravimetry (TG/DTG) were obtained in a Thermobalance Shimadzu model TGA-50, in four heating rates 2, 5, 10 and 20 K/min, under flow of nitrogen, 20 ml/min, of the temperature sets up to 773 K. The calorific capacities in solid phase were obtained in a Calorimeter Exploratory Differential, Shimadzu model DSC-50, in two strips of temperature 288–328 K and 298–373 K.

3. Results and discussion

The mass spectra of salts revealed the presence of the parent ions for the following composed with the following relative intensities: $[Bu_2{}^nNH_2Br]^+$ (5.38%) $>[Bu_2{}^iNH_2Br]^+$ (0.47%)$>[Bu_2{}^nNH_2I]^+$ (0.13%) these data can indicate a larger stability of these species in gaseous phase when compared to the other compounds.

The results of nuclear magnetic resonance (^1H RMN) showed that the protons of the amine group in the salts are found in low field among 8.5–6.0 ppm and coupled the protons on the atom of adjacent carbon ($J\sim7$) [9]. In studies already accomplished with these composed [7], it presented a simple sign of proton of the amine group $[RNH^3]^+$ in the high field 4.99–4.80 ppm and it attributes the displacement to the influence of the halogen that decreases the electronic density in the neighborhood of the proton. In this work, the sign of the protons of the group

$[R_2NH_2]^+$ appear among 4.50–4.90 ppm, agreeing with the observations of the literature [7]. The spectra of the di-*n*-propylammonium iodide show an integration of 2:4:4:6, with singlet corresponding to the two protons of the amine group 4.50 ppm, triplet in 2.66 ppm of the protons of the ($-CH_2$), multiplet in 1.43 ppm ($-CH_2$) and a triplet in 0.70 ppm attributed to the protons of the ($-CH_3$); the di-*n*-propylammonium bromide presents similar characteristics, as well as the bromides and di-*n*-butylammonium iodides. The groups di-iso-propyl presents integration 2:2:12, with singlet 4.82 ppm for the di-iso-propylammonium iodide, multiplet in 3.46 and doublet in 1.20 ppm, configuring a radical di-iso-propyl, the same can be described for the spectrum of the di-iso-propylammonium bromide. The spectra of the di-iso-butylammonium iodide show an integration of 2:4:2:12 with singlet in 4.59 ppm attributed of ($-NH_2$), multiplet in 1.89 ppm (CH), doublet in 2.69 ppm ($-CH_2$) and doublet in 0.80 ppm ($-CH_3$), characterizing a radical di-iso-butyl.

The spectra infravermelho presented bands in the region of 2700–2250 cm^{-1} attributed to the symmetrical and asymmetric stretchings ($v_{as}NH_2^+$ and $v_sNH_2^+$), bands of medium intensity among 1600–1575 cm^{-1} attributed to angular deformations (αNH_2^+) besides characteristic vibrations of the organic radicals. In studies accomplished with composed of the type Et_3NHX (X=CI, Br, I) [10] were observed that the vibration of stretching v(N–H) is not a simple absorption, but a complex multicomponent with extension for at least 400 cm^{-1}, this behavior was verified in the region from 2360 to 2800 cm^{-1} for the compounds studied in this work. Studies of FT–IR [11], also correlated the stretching vibrations (N–H) that usually appear in the region from 3300 to 3500 cm^{-1}, with compound $(CH_3)_2NH_2CI$, NH_4Cl, CH_3NH_3Cl where this band is moved for region of 3100 cm^{-1} and attributes to the degree of connection of hydrogen between the cation and the anion. This same behavior was verified for some of the studied composition appearing as a band between 3100 and 3150 cm^{-1}.

The DTA and TG curves were obtained in four heating speeds, whose results are shown in the Tables 1–3. All the compositions suffered complete volatilization with thermal dissociation, accompanied by the liberation of the appropriate amines and HBr or HI. The thermolysis of some of the compounds was preceded by melting ($Pr_2{}^nNH_2I$, $Pr_2{}^iNH_2I$ and $Pr_2{}^iNH_2Br$), by the comparison of the melting point values of the literature obtained by the method of capillary pattern, they facilitated the identification of the melting points. The salts are $Bu_2{}^iNH_2Br$, $Bu_2{}^nNH_2Br$, $Bu_2{}^nNH_2I$ and $Bu_2{}^iNH_2I$, found when the volatilization process is in advanced, as shown in the Table 1.

The thermogravimetric curves show that the salts decomposes in a fast stage, and in a speed of heating of 5 K/min, it reaches the maximum around 73% of the mass loss, followed by a slower stage to and volatilization of all material Table 3. This behavior has been verified for several *n*-alkylammonium halides [1–3], alkylammonium hexachloroestanates [12] and it was attributed to kinetic effects caused by decrease in the volatilization speed due to discontinuous changes in the geometric superficial region of the condensed phase [2].

The thermolysis temperatues, T_p (TG and DTA), $T_{0.1}$, $T_{0.73}$, and ΔT are characteristics for a compound and some regularities can be verified, agreeing with data of the literature [2,3]. The results presented in Table 3, demonstrate a tendency of the decrease in values of T_p, $T_{0.1}$, $T_{0.73}$ when compared the compositions of the *n*-alkyl to iso-alkyl of a same halide, except for the compounds $Bu_2{}^iNH_2I$ and $Bu_2{}^iNH_2I$ that presented T_f and higher T_p than the corresponding *n*-alkyl. The values of ΔT do not seem to be influenced significantly by the radicals *n*-alkyl or iso-alkyl. Studies showed that the values of T_p, $T_{0.1}$, $T_{0.73}$ for the salts with substituents, *n*-alkyl decrease gradually with the increase in the region of the cation and ΔT does not present significant variation with the region of the cation [3]. The results of DTA show that the values of T_f, T_p for the *n*-alkyl iodides and iso-alkylammonium is lower than the one of the bromides, except for $Bu_2{}^iNH_2I$ and $BU_2{}^iNH_2Br$ whose values are plenty, similarly, this can be related qualitatively with the compound thermal stability of those referred.

It is important to understand that the results of mass spectra show ionic peaks $[Bu_2{}^nNH_2Br]^+$ (5.38%) $>[Bu_2{}^iNH_2Br]^+$ (0.47%)$>[Bu_2{}^nNH_2I]^+$ (0.13%), showing the existence of these species in gaseous phase and contributed to reveal a larger tendency of the stability of the bromides compared to the iodides.

Table 1
Thermal characteristics of the salts

Compound	ϕ (K/min)	T_{p1} (K)	T_{p2} (K)	T_f (K)	Mass (mg)
$Pr_2{}^nNH_2I$	2	539.29		516.15	3.873
	5	522.41	556.00	519.58	2.401
	10	520.20	565.36	515.15	2.444
	20	526.72	566.13	522.47	2.191
$Pr_2{}^iNH_2I$	2	508.44	531.11	506.96	5.436
	5	509.19	556.77	507.84	6.945
	10	509.53	578.01	507.51	4.734
	20	509.83	569.19	508.13	1.201
$Bu_2{}^nNH_2I$	2	540.45		537.81	8.158
	5	550.33		540.83	1.960
	10	562.77		540.54	2.293
	20	583.63		543.70	2.160
$Bu_2{}^iNH_2I$	2	574.05		569.39	1.604
	5	585.63		582.57	1.750
	10	593.29		588.34	1.560
	20	595.91		594.46	1.836
$Pr_2{}^nNH_2Br$	2	541.13		539.83	2.874
	5	546.32		539.01	2.985
	10	542.30		539.75	4.096
	20	542.75	564.83	540.21	3.164
$Pr_2{}^iNH_2Br$	2	516.21		513.76	2.720
	5	515.62	524.06	512.80	3.349
	10	515.82	545.85	512.28	3.468
	20	517.77	553.61	511.31	3.079
$Bu_2{}^nNH_2Br$	2	563.82		562.66	1.907
	5	568.83		566.11	2.566
	10	571.43		568.12	1.923
	20	578.82		567.76	1.944
$Bu_2{}^iNH_2Br$	2	562.10		519.60	3.724
	5	584.97		582.93	2.302
	10	580.13		583.88	3.679
	20	594.94		587.29	1.900

T_f – melting temperature (capillar or DTA), T_p – maximum peak temperature, ϕ – leating speed.

The lattice energies were determined [13] by using a thermochemical cycle, as shown in Fig. 1, which are derived the following Eqs. (1)–(4):

$$\begin{aligned}\Delta_f H_m^0\,[R_2NH_2X_{(g)}] &= \Delta_f H_m^0\,[R_2NHX_{(g)}]\\ &\quad + \Delta_f H_m^0\,[HX_{(g)}] - \Delta_r H_m^0 \qquad (1)\end{aligned}$$

$$\begin{aligned}U^0 &= \Delta_f H_m^0\,[R_2NH_{2(g)}]^+ + \Delta_f H_m^0\,[X_{(g)}]^-\\ &\quad -\Delta_f H_m^0\,[R_2NH_2X_{(g)}] - 2RT. \qquad (2)\end{aligned}$$

The enthalpy of volatilization of the dialkylammonium halides does not refer to 298.15 K. Thus, they were modified in agreement with the Eq. (3):

$$\Delta_v H_m^0 = \Delta_v H + \sum \Delta_\alpha H^0 + \Delta_{cr}{}^l H_m^0 - \int_{298.15}^{T} \Delta C_{p,m}^0\, dT, \qquad (3)$$

Table 2
TG/DTG curve results

Compound	Mass (mg)	ϕ (K/min)	$T_{0,1}$ (K)	T_p (K)	ΔT	DTG (α)	T (K)
$\mathrm{Pr_2}^n\mathrm{NH_2I}$	3.387	2	493.54	537.38	43.84	0.8045	
	2.435	5	496.13	546.13	50.00	0.7798	571
	2.115	10	507.69	559.27	51.58	0.6554	
	2.176	20	530.09	575.22	45.13	0.5211	
$\mathrm{Pr_2}^i\mathrm{NH_2I}$	3.744	2	487.89	539.99	52.10	0.8379	
	4.991	5	510.98	565.03	54.05	0.7223	
	2.337	10	514.85	570.59	55.74	0.6605	
	2.418	20	532.66	580.83	48.17	0.5095	
$\mathrm{Bu_2}^n\mathrm{NH_2I}$	2.103	2	494.83	536.01	41.18	0.8167	
	2.078	5	508.57	550.81	42.24	0.7345	571
	2.050	10	526.02	570.46	44.44	0.6841	
	2.050	20	538.88	580.03	40.15	0.5222	
$\mathrm{Bu_2}^i\mathrm{NH_2I}$	3.154	2	490.81	532.29	41.48	0.8053	
	1.547	5	497.05	534.58	37.53	0.6811	
	2.181	10	514.46	558.91	44.45	0.6725	
	2.190	20	521.41	562.36	40.95	0.5365	
$\mathrm{Pr_2}^n\mathrm{NH_2Br}$	2.720	2	484.72	525.71	40.99	0.7994	
	3.337	5	504.88	546.13	41.25	0.7173	552
	3.372	10	517.39	562.61	45.22	0.6661	
	3.645	20	531.82	572.58	40.76	0.5082	
$\mathrm{Pr_2}^i\mathrm{NH_2Br}$	2.644	2	482.32	521.83	39.51	0.8071	
	2.306	5	494.47	535.23	40.76	0.7242	
	3.723	10	514.89	558.91	44.02	0.6275	
	3.471	20	525.33	569.03	43.70	0.5184	
$\mathrm{Bu_2}^n\mathrm{NH_2Br}$	1.830	2	585.35	525.58	40.23	0.8300	
	1.989	5	502.93	543.97	41.04	0.7023	
	2.477	10	520.24	562.82	42.58	0.6858	562
	2.544	20	530.94	568.27	37.37	0.4805	
$\mathrm{Bu_2}^i\mathrm{NH_2Br}$	3.330	2	481.34	521.43	40.09	0.8374	
	2.480	5	491.68	532.85	41.17	0.7805	
	3.979	10	513.00	556.95	43.95	0.6705	
	2.846	20	516.03	553.53	37.50	0.4988	

DTG(α) – maximum of decomposition, ϕ – healting speed.

where the term $\sum\Delta H$ appears in polymorphic transitions that the compounds can suffer between 298.15 K and the beginning of the melting or volatilization, is the melting enthalpy and it quantifies the change in the calorific capacity of the reagents. In Eq. (2), U_0 is the lattice energy for 298.15 K and it is related the lattice energy at 0 K [24], for the derived equation (4):

$$\begin{aligned} U^0 = {} & \Delta_f H^0_m(\mathrm{R_2NH_2^+}, \mathrm{g}) + \Delta_f H^0_m(\mathrm{X^-}, \mathrm{g}) \\ & - \Delta_f H^0_m(\mathrm{R_2NH_2X}, \mathrm{cr}) + \sum \Delta T \\ & + \int_0^{298.15} [C^0_{p,m}(\mathrm{R_2NH_2X}, \mathrm{cr}) \\ & - C^0_{p,m}(\mathrm{R_2NH_2^+}, \mathrm{g}) - C^0_{p,m}(\mathrm{X^-}, \mathrm{g})]\,\mathrm{d}T. \end{aligned} \tag{4}$$

Table 3
TG/DTA curve results

Compounds	$T_{0,10}$ (K)	$T_{0,73}$ (K)	ΔT
$Pr_2{}^nNH_2I$	496.13	546.13	50.00
$Pr_2{}^iNH_2I$	510.98	565.03	54.05
$Bu_2{}^nNH_2I$	508.57	550.81	42.24
$Bu_2{}^iNH_2I$	497.05	534.58	37.53
$Pr_2{}^nNH_2Br$	504.88	546.13	41.25
$Pr_2{}^iNH_2Br$	494.47	535.23	40.76
$Bu_2^nNH_2Br$	502.93	543.97	41.04
$Bu_2{}^iNH_2Br$	491.68	532.85	41.17

$T_{0,10}$ – temperature at 10% of decomposition, $T_{0,73}$ – temperature of maximum decomposition, $\Delta T=T_{0,73}-T_{0,10}$.

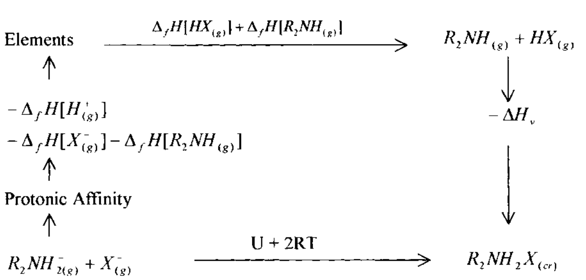

Fig. 1. Thermochemical cycle.

Therefore, the calculation of the lattice energy was made by means of the Eqs. (2) and (4), respectively. The results are presented in Table 4.

The values of molar standard enthalpies of formation for $Pr_2{}^nNH_2^+$, $Pr_2{}^iNH_2^+$, $Bu_2{}^nNH_2^+$ and $Bu_2{}^iNH_2^+$ cations in gaseous phase were estimated from the known molar standard enthalpy of formation of methylammonium cation in gaseous phase, which value is tabulated as 582 kJ/mol [14]. In both cases the appropriate groups [15–17] contribute to the above enthalpy data. Then, the contribution of the groups gave: [C–(C)(H)$_3$]=−42.13; [C–(C)$_2$(H)$_2$]=−20.69; [C–(C)(N)(H)$_2$]=−27.59; [C–(C)(H)$_3$]=−7.94; [C–(C)$_2$(N)(H)=−21.74 and [C–(N)(H)$_3$]=−42.13. By considering these contributions of the molar standard enthalpies of formation for the same sequence of these salts gave the values: 485, 454, 444 and 426 kJ/mol, respectively.

Table 4
Results of calorific capacity (kJ/mol K) and lattice energy (kJ/mol)

Compound	C_p^{0a}	C_p^{0b}	$U^0_{298\,K}{}^c$	$U_{0\,K}{}^d$
$Pr_2{}^nNH_2I$	0.2985	0.5797	554.96	600.82
$Pr_2{}^iNH_2I$	0.3438	0.4237	552.35	611.71
$Bu_2{}^nNH_2I$	0.4087	0.5926	574.52	661.01
$Bu_2{}^iNH_2I$	0.3071	0.5675	562.11	618.31
$Pr_2{}^nNH_2Br$	0.2384	0.5069	607.15	635.09
$Pr_2{}^iNH_2Br$	0.2695	0.3970	600.98	638.19
$Bu_2{}^nNH_2Br$	0.3335	0.4618	622.19	627.14
$Bu_2{}^iNH_2Br$	0.4177	0.5068	604.79	701.46

[a] region temperature (283.15–308.15 K).
[b] region temperature (313.15–328.15 K).
[c] obtained by Eq. (2).
[d] obtained by Eq. (4).

The solid phase heat capacities, $C^0_{p,m}$, of the salts were determined by means of differential scanning calorimetry, the results are listed in Table 4. The corresponding gas phase heat capacities for $Pr_2{}^nNH_2^+$, $Bu_2{}^iNH_2^+$ 1, $Bu_2^nNH_2^+$ and $Bu_2{}^iNH_2^+$ cations in gas phase gave 0.140±0.002, 0.140±0.008, 0.114±0.003 and 0.114±0.003 kJ/mol K, respectively, which results were estimated by using the method of generalized vibrational assignment [15,18,19]. The gas phase heat capacities was assumed to be 0.021 kJ/mol K for the halide anions and the term $\sum\Delta T$ was used as 1.0 kJ/mol in this work [14]. The other auxiliary amounts for the calculation of the lattice energy are listed in Table 5.

Studies of the variation of the values of lattice energy in *n*-alkylammonium salts showed an order of stability U(I)<U(Br)<U(Cl), the one which, they decrease parallely with the decrease in the region of the anion [5]. Another aspect shown is that the distances N–H–X for the iodides and bromides is on the average 0.346, 0.360 and 0.330 nm, respectively, seeming to be the interaction in the strongest bromides than in the iodides, attributed to the fact of the cohesive forces in an ionic crystal be mainly of electrostatics interaction and the differences among the centers of positive loads (nitrogen) and negative loads (halogen) in the bromides it is more intense than in the iodides, given the largest electronegativity of the bromine in relation to the iodine, strengthening for consequence of the connection N–H–X [2,3].

In this work the bromine salts presented the values of lattice energy superior to the values of the iodine salts, as the structural factor it was not object of this study, it is possible to refer only for analogy, even so analyzing the data of enthalpy of volatilization dissociative values for the dialkylammonium bromides is not very higher compared to the iodides, this can reinforce the supposition that the interaction energy

Table 5
Auxiliary quantities

Compounds	$\Delta_f H^0_m$ (kJ/mol)	$\Delta_g{}^l H^0_m$ (kJ/mol)[a]	$C^0_{p,m}$ (kJ/mol K)
$Pr_2{}^nNH_2I$	271.47 [8]	6.79	
$Pr_2{}^iNH_2I$	300.04 [8]	6.62	
$Bu_2{}^nNH_2I$	332.41 [8]	7.15	
$Bu_2{}^iNH_2I$	337.39 [8]	7.61	
$Pr_2{}^nNH_2Br$	345.73 [8]	9.83	
$Pr_2{}^iNH_2Br$	370.74 [8]	9.28	
$Bu_2{}^nNH_2Br$	402.15 [8]	10.24	
$Bu_2{}^iNH_2Br$	409.63 [8]	10.51	
$Pr_2{}^nNH(g)$	114.66 [8]		0.1592[b]
$Pr_2{}^iNH(g)$	143.98 [8]		0.1601[b]
$Bu_2{}^nNH(g)$	157.88 [8]		0.2052[b]
$Bu_2{}^iNH(g)$	179.07 [8]		0.2029[b]
HBr(g)	34.60 [3]		0.0293 [19]
HI(g)	26.50 [2]		0.0293 [15]
$I^-(g)$	197.00 [8]		0.0209 [15]
$Br^-(g)$	219.07 [8]		0.0209 [15]

[a] Estimated by Benson method.
[b] Estimated by $\Delta^l_{cr}S^0_m = \Delta^l_{cr}H^0_m/T_f$ = constant

in the bromides is larger than in the dialkylammonium iodides.

The study for DSC for the measure of the capacity of calorific exhibition of that the eight studied compounds the di-*n*-propylammonium bromide when analyzed it presented a maximum peak at 292.25 K, attributed the structural conformations of the cation possibly. The values of calorific capacity in the strip of 313.15–328.15 K are not very higher than enters 283.15–308.15 K. The results are gathered in Table 4, showing the tendency of the calorific capacity with the temperature in these conditions.

Taking into account the ionic nature of these salts, the thermochemical radii of $Pr_2{}^nNH_2^+$, $Pr_2{}^iNH_2^+$, $Bu_2{}^nNH_2^+$ and $Bu_2{}^iNH_2^+$ cations were calculated [19–21] by using a classical semi-empirical procedures based on the Kapustinskii–Yatsimirskii equation (5):

$$U^0 = 108.0\,v\frac{Z^+Z^-}{r_c + r_a}. \tag{5}$$

The interactive combination in the above simplest formula considers the number or ions v as two with unitary charge for mono cation and anion Z^+ and Z^- and the respective ionic radii r_c and r_a in nanometers were used. For this calculation U^0 was taken from Table 4 and Goldschmidt radii [22] of 0.195 and 0.216 nm for bromide and iodide, respectively, were used. The thermochemical cations radii, r_c, were obtained and these values are listed in Table 6.

Table 6
Thermochemical radii of the cations (nm)

Cation	Equation of Kapustinskii		Equation of Yatsiminskii	
	R_2NH_2Br	R_2NH_2I	R_2NH_2Br	R_2NH_2I
$[Pr_2{}^nNH_2]^+$	0.150	0.144	0.163	0.160
$[Pr_2{}^iNH_2]^+$	0.148	0.137	0.161	0.152
$[Bu_2{}^nNH_2]^+$	0.125	0.112	0.168	0.121
$[Bu_2{}^iNH_2]^+$	0.118	0.133	0.124	0.148

In spite of the equation of Kapustinskii to define a theoretical model, purely electrostatic, she especially supplies a good approach in the cases in that the structure of the salt is not known [24]. The values found by the equation of Kapustinskii were compared to that obtained by the equation optimized by Yatsimiskii [24] in agreement with Eq. (5) and they are listed in Table 6.

$$U = 120.2\frac{N.n_1.n_2}{r_c + r_a} \times \left[1 - \left(\frac{0.0345}{r_c + r_a}\right) + 0.087(r_c + r_a)\right]. \tag{6}$$

The method of Ozawa [23] is based on the equation of Arrhenius, so much for the bromides as for iodides,

Table 7
Kinetics parameters

Compound	ΔE (kJ/mol)	$2\times\Delta E$	A (min^{-1})	Standard deviation	Coefficient variance	n
$\mathrm{Pr_2}^{n}\mathrm{NH_2I}$	106.32	212.64	3.32×10^{9}	2.99	2.81	0.4
$\mathrm{Pr_2}^{i}\mathrm{NH_2I}$	98.16	196.32	3.34×10^{9}	3.37	3.43	0.5
$\mathrm{Bu_2}^{n}\mathrm{NH_2I}$	101.91	203.82	4.45×10^{7}	3.36	3.30	0.3
$\mathrm{Bu_2}^{i}\mathrm{NH_2I}$	116.71	233.42	4.87×10^{10}	7.74	6.63	0.7
$\mathrm{Pr_2}^{n}\mathrm{NH_2Br}$	96.82	193.64	3.94×10^{8}	4.12	4.26	0.3
$\mathrm{Pr_2}^{i}\mathrm{NH_2Br}$	86.50	173.00	3.22×10^{7}	3.53	4.08	0.0
$\mathrm{Bu_2}^{n}\mathrm{NH_2Br}$	96.66	193.32	3.89×10^{8}	3.88	4.01	0.3
$\mathrm{Bu_2}^{i}\mathrm{NH_2Br}$	103.14	206.28	2.46×10^{9}	7.02	6.81	0.5

n – reaction order, A – constant, ΔE – activation energy.

the values of the activation energy Table 7, they are around twice smaller than the volatilization enthalpy, Table 8, correcting these values for a factor of two is obtained compatible values with the volatilization enthalpy and activation energy, besides when compared the data of the literature [2,3]. The values of activation energy do not seem to present any regularity with the structure of the cation or the halogen type (Br or I). Kinetic studies [1,2] done on complex chlorides of lead (IV) where it applies the methods of Freeman and Carroll, Coats and Redfern, Horowitz and Metzger, to obtain kinetic parameters and suggests some model of reaction mechanism, considering that $E/\Delta H_v$ for a kinetic model is a constant value [1,4,5], as shown in Table 9.

Comparing the data of the Table 9 with the results of the Tables 7 and 8 can be verified that the models, R_1 and R_2 are shown more appropriate to describe the kinetics of volatilization of the studied compounds, except for the di-*n*-propylammonium iodide and di-iso-butylammonium iodide, it is possible that this is due to the experimental conditions or to the fact that the mechanism of volatilization of the iodides is more complex than of the bromides, considering the possible presence of iodine molecules, resultant of the decomposition of HI, that is taken in the conditions of temperature of the experiment are quite unstable. The iodine has a potential oxidative similar to the O_2 ($I_2/I=0.535$ eV and $O_2/OH=0.401$ eV), could act as oxidizer of the organic fragments and interfering in the decomposition process [2].

Table 8
Volatilization enthalpy (kJ/mol)

Compound	$\Delta_v H^{a}$	$\Delta_v H_m^{0\,b}$	$\Delta_v H_m^{0\,c}$	Kinetic models[d]		$E/\Delta_v H_m^{0\,b}$	ΔH_v^0
				R_1	R_2		
$\mathrm{Pr_2}^{n}\mathrm{NH_2I}$	182.21	190.00	183.31	193 [2]	219 [3]	0.56	202
$\mathrm{Pr_2}^{i}\mathrm{NH_2I}$	206.09	213.86	182.58			0.46	
$\mathrm{Bu_2}^{n}\mathrm{NH_2I}$	217.56	224.88	201.03	198 [2]	224 [3]	0.45	220
$\mathrm{Bu_2}^{i}\mathrm{NH_2I}$	222.17	229.85	184.82			0.51	
$\mathrm{Pr_2}^{n}\mathrm{NH_2Br}$	209.20	220.08	194.67	190 [3]	213 [2]	0.44	198
$\mathrm{Pr_2}^{i}\mathrm{NH_2Br}$	206.52	216.88	190.38			0.40	
$\mathrm{Bu_2}^{n}\mathrm{NH_2Br}$	218.46	229.79	207.87	171 [3]	193 [2]	0.42	180
$\mathrm{Bu_2}^{i}\mathrm{NH_2Br}$	222.64	234.34	194.16			0.44	

[a] $\Delta_v H$: Equation of Van't Hoff.

[b] $\Delta_v H_m^0$: Data corrected for 298.15 K of [a].

[c] $\Delta_v H_m^0$: Derived from thermochemical cycles with auxiliary quantities.

[d] R_1: $[g(1-\alpha)]=\alpha$; R_2: $[g(1-\alpha)]=[1-(1-\alpha)^{1/2}]$, where, $[g(1-\alpha)]=\frac{AT}{\phi}\left[\exp\frac{-E}{2RT}\right]$.

Table 9
Kinetic models

$g(1-\alpha)$	Simbol	Process of kinetic control	Description of the process
α	R_1	Phase	Move in a dimension
$[1-(1-\alpha)^{1/2}]$	R_2	Superficial reactions	Move in two dimensions, contraction of regions
$[1-(1-\alpha)^{1/3}]$	R_3	Superficial reactions	Move in three dimensions, contraction of the volume

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