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KINETICS OF DECOMPOSITION OF ALKYLAMMONIUM SALTS

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Abstract

The thermogravimetric curves of di-*n*-propylammonium, di-*iso*-propylammonium, di-*n*-butylammonium and di-*iso*-butylammonium chlorides showed similar profiles, characterized by mass loss in only one stage, corresponding to decomposition of compounds. The following thermal stability order was obtained: $[\mathrm{Bu}_2^n\mathrm{NH}_2]\mathrm{Cl}>[\mathrm{Pr}_2^n\mathrm{NH}_2]\mathrm{Cl}>[\mathrm{Pr}_2^i\mathrm{NH}_2]\mathrm{Cl}>[\mathrm{Bu}_2^i\mathrm{NH}_2]\mathrm{Cl}$. The values of activation energy for non-isothermal data obtained by Ozawa and Coats–Redfern integral methods were in agreement and stability order obtained by thermogravimetry were reproduced in both methods. The decomposition reactions of $[\mathrm{Pr}_2^n\mathrm{NH}_2]\mathrm{Cl}$, $[\mathrm{Pr}_2^i\mathrm{NH}_2]\mathrm{Cl}$ and $[\mathrm{Bu}_2^i\mathrm{NH}_2]\mathrm{Cl}$ were better described by A3 model and $[\mathrm{Bu}_2^n\mathrm{NH}_2]\mathrm{Cl}$ by A2 model.

Keywords: dialkylammonium chlorides, kinetic, thermal decomposition

Introduction

Dialkylammonium chlorides of general formula $[(\mathrm{C}_n\mathrm{H}_{2n+1})_2\mathrm{NH}_{4-x}]\mathrm{Cl}$, with n=1–5 and x=2, are of considerable synthetic interest. They present voluminous cations and for this reason, they are frequently used for stabilization in other unstable complex anions. Their ionic nature besides their solubility in aqueous and non-aqueous solvents permits their use in many solvent systems. On the other hand, nitrogenated bases are constituent parts of many biological systems both in the natural form or as fragments of macromolecules. The behavior of derivatives is predominantly determined by the presence of a lonely pair of electrons in the nitrogen atom, which confer basic properties to these molecules. Many characteristics of nitrogenated organic bases result from possibility of their interaction with organic or inorganic acids. Such interactions become possible due to formation of a strong hydrogen bridge type bond, between nitrogen and proton. Molecules of nitrogenated organic bases

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can take part in electron-donor-acceptor interactions [1]. A kinetic study involves measurements of α (reaction fraction) as a function of time (t) at a constant temperature, or as a function of temperature (T). For isothermal method, α *vs.* t corresponds to conventional curve of concentration *vs.* t of homogeneous kinetics, while for non-isothermal (or dynamic) method the measurements of α *vs.* T, are the basis of thermal analysis [2–4].

In this work the thermal decomposition process and the kinetic parameters of di-*n*-propylammonium, di-*iso*-propylammonium, di-*n*-butylammonium and di-*iso*-butylammonium chlorides have been studied using isothermal and non-isothermal TG.

Experimental

Di-*n*-propylammonium chloride $[\mathrm{Pr}_2^{\mathrm{n}}\mathrm{NH}_2]\mathrm{Cl}$, di-*iso*-propylammonium chloride $[\mathrm{Pr}_2^{\mathrm{i}}\mathrm{NH}_2]\mathrm{Cl}$, di-*n*-butylammonium chloride $[\mathrm{Bu}_2^{\mathrm{n}}\mathrm{NH}_2]\mathrm{Cl}$ and di-*iso*-butylammonium chloride $[\mathrm{Bu}_2^{\mathrm{i}}\mathrm{NH}_2]\mathrm{Cl}$ were prepared according to literature [5–7]. The corresponding amine solution was slowly added to 18.5% (*m*/*m*) hydrochloric acid solution maintained under constant agitation in ice bath. Then, water and excess of amine were evaporated and the salts were recrystallized in ethanol. The crystals thus obtained were separated by filtration and under nitrogen atmosphere.

Physicochemical measurements

The mass spectra were obtained in Varian MAT-31A Spectrometer. The infrared spectra were obtained in Bomem MB-102 Spectrophotometer, KBr pellets and 400–4000 cm^{-1} region. The thermogravimetric curves (TG) were obtained in Shimadzu TGA-50 Thermobalance and the calorimetric curves (DSC) were obtained in Shimadzu DSC-50 Calorimeter, under nitrogen atmosphere, flux 50 mL min^{-1}, interval of temperature of 28–500°C and mass 3 mg.

Results and discussion

The results of mass spectrometry showed fragments of ions, which confirm the structures of dialkylammonium chlorides. The most intense peak in the spectra appears from cleavage of carbon-carbon, bond invariably originating a resonance structure. The following order of relative intensity of the $[\mathrm{R}_2\mathrm{NH}]^+$ cations was observed: $[\mathrm{Pr}_2^{\mathrm{n}}\mathrm{NH}]>[\mathrm{Bu}_2^{\mathrm{n}}\mathrm{NH}]>[\mathrm{Pr}_2^{\mathrm{i}}\mathrm{NH}]>[\mathrm{Bu}_2^{\mathrm{i}}\mathrm{NH}]$. These data can indicate a higher stability of linear chain cations than that of branched chain in gaseous phase.

The infrared spectra show characteristic absorption bands of dialkylammonium chlorides. The bands observed in the region 3000 to 2700 cm^{-1} are attributed to N–H stretching vibrational frequencies for amine salts and C–H stretching for organic radicals [8, 9]. It was observed that in the compounds of type $[\mathrm{Et}_2\mathrm{NH}]\mathrm{X}$ (X=Cl, Br and I), N–H and C–H stretching vibrations are not simple absorptions, but a multicomponent complex extended at least to 400 cm^{-1} [9]. Therefore, the bands, which appear in this region, are superimposed bands resulting from N–H and C–H stretchings. It is difficult to localize N–H deformation band which occurs in the region 1610–1550 cm^{-1}

due to its weak intensity, and because water also presents deformity in the same region. It is possible to observe CH_2 band due to scissors deformation usually at 1465 cm^{-1} and CH_3 band usually at about 1375 cm^{-1}.

Thermogravimetric curves of dialkylammonium chlorides present similar profiles, characterized by mass loss in only one stage, corresponding to decomposition reaction of compounds (Table 1).

Table 1 Thermal decomposition data of compounds and melting temperature

Compound	T_i(DTG)/ °C	T_f(DTG)/ °C	T_{max}(DTG)/ °C	Mass loss/ mg, (%)	T_{max}(DSC)/ °C	$T_{melting}$[10]/ °C
$[\mathrm{Pr}_2^{n}\mathrm{NH}_2]\mathrm{Cl}$	150.03	245.97	253.71	2.82 (95.74)	266.85	268
$[\mathrm{Pr}_2^{i}\mathrm{NH}_2]\mathrm{Cl}$	145.58	234.88	224.67	2.72 (98.27)	217.05	216
$[\mathrm{Bu}_2^{n}\mathrm{NH}_2]\mathrm{Cl}$	159.94	254.92	245.47	3.30 (97.14)	281.55	281
$[\mathrm{Bu}_2^{i}\mathrm{NH}_2]\mathrm{Cl}$	140.69	254.11	238.17	3.35 (98.02)	259.15	262

T_i – initial temperature; T_f – final temperature; T_{max} – maximum decomposition temperature

A gradual increase in thermal stability, with an increase in molecular mass of linear chain dialkylammonium chlorides, was observed. On the other hand, the thermal stability of branched chain compounds increased with decrease in molecular mass. Such behavior can be attributed to structure of substituent alkyl group. According to data of Table 1 the following thermal stability order was obtained:

$$[\mathrm{Bu}_2^{n}\mathrm{NH}_2]\mathrm{Cl}>[\mathrm{Pr}_2^{n}\mathrm{NH}_2]\mathrm{Cl}>[\mathrm{Pr}_2^{i}\mathrm{NH}_2]\mathrm{Cl}>[\mathrm{Bu}_2^{i}\mathrm{NH}_2]\mathrm{Cl}$$

The DSC curves of compounds present superposition of events. The thermal effect associated to melting is masked by effect of volatilization process. The results of Table 1 evidenced a good correlation among the literature data associated to melting [10] and maximum temperatures of events observed in DSC curves.

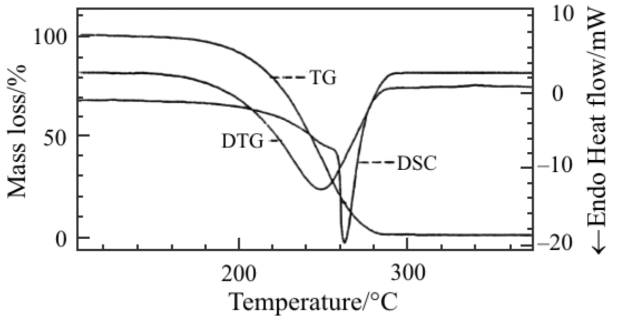

Fig. 1 TG/DTG/DSC superimposed curves of $[\mathrm{Bu}_2^{i}\mathrm{NH}_2]\mathrm{Cl}$ at 15°C min^{-1}

The TG/DTG/DSC superimposed curves for $[Pr_2^n NH_2]Cl$, $[Bu_2^i NH_2]Cl$ (Fig. 1) and $[Bu_2^n NH_2]Cl$ indicated that the decomposition process began in solid phase. The melting of salts occur at 259.2, 266.9 and 281.6°C for $[Bu_2^i NH_2]Cl$, $[Pr_2^n NH_2]Cl$ and $[Bu_2^n NH_2]Cl$, respectively. Therefore, it can be possible that transition partially occurs for liquid phase.

For $[Pr_2^i NH_2]Cl$, the melting (217°C) occurs just in the beginning of decomposition. It is possible that transition occurs completely for the liquid phase.

Investigations evidence that alkylammonium chlorides in condensed phases behave as typical ionic substances [11, 12]. From this, one should expects that thermal decomposition process is followed by transfer of condensed phase molecules to gaseous phase. Blażejowski [10] proposed that the same mechanism could be considered for the case of dialkylammonium chlorides. Therefore, complete process can be reduced to following reaction:

$$[R_2NH_2]Cl_{(l)} \rightarrow R_2NH_{(g)} + HCl_{(g)} \tag{1}$$

Other possibility for thermal decomposition mechanism of dialkylammonium chlorides was done by Rodd [13]. This mechanism is summarized in reaction:

$$[R_2NH_2]Cl_{(l)} \rightarrow [RNH_2]_{(g)} + RCl_{(g)} \tag{2}$$

A rough approximation made on basis of Clausius–Clayperon equation, using appropriate values of ebullition points [14] and vaporization heats [15] for amines, indicate that all products formed in the reactions (1) and (2) are in gaseous phase. However, it does not inform if the products behave kinetically as free fragments or if they interact with others forming aggregates. The formation of unstable complexes between amines and HCl can be expected on basis theoretical considerations [16].

Non-isothermal kinetic

The kinetic analysis of non-isothermal data of thermal decomposition reactions of salts was realized using integral methods of Ozawa [17] and Coats–Redfern [18] and derivative method of Freeman–Carrol [19]. Table 2 presents kinetic parameters obtained for heating rates of 5, 10, 15 and 20°C min^{-1} and $0.21<\alpha<0.86$. The kinetic parameters obtained by Ozawa and Coats–Redfern methods indicated that the dispersion in activation energy values was small and standard deviation for all salts was lower than 3.3%. These methods showed to be a convenient means of comparison of stability of substituent alkyl group in salts studied. Thus, based on average values of activation energy, the following order was obtained:

$$[Bu_2^n NH_2]Cl > [Pr_2^n NH_2]Cl > [Pr_2^i NH_2]Cl > [Bu_2^i NH_2]Cl$$

This order corroborates with earlier data of thermal decomposition these salts.

The kinetic parameters obtained by Coats–Redfern method [18] were realized by Calibra algorithm [20]. The values of activation energy (E) and lg$A$, calculated by Coats–Redfern method, reflect known kinetic compensation effect, in which lg$A$ increases linearly with activation energy when an experimental factor (heating rate) is

Table 2 Estimated kinetic parameters for dialkylammonium chlorides

Compound	β/°C min^{-1}	Coats–Redfern			Freeman–Carrol		Ozawa		
		E/kJ mol^{-1}	lg$A$/s^{-1}	n	E/kJ mol^{-1}	n	E/kJ mol^{-1}	lg$A$/s^{-1}	n
[$Pr_2^nNH_2$]Cl	5	97.20	7.58	0.4	84.48	0.04	102.24	8.49	0.1
	10	92.24	6.95	0.1	82.89	0.09	103.24	8.49	0.1
	15	92.50	7.10	0.9	89.93	0.70	101.32	8.49	0.1
	20	91.23	5.95	0.7	78.64	0.04	97.96	8.49	0.1
	sd	2.30			4.04		2.86		
[$Pr_2^iNH_2$]Cl	5	91.99	7.15	0.2	86.04	0.23	94.84	7.15	0.1
	10	91.10	7.02	0.3	72.74	0.10	93.56	7.15	0.1
	15	89.22	6.85	0.7	78.26	0.50	91.60	7.15	0.1
	20	87.99	5.75	0.1	68.16	0.10	88.35	7.15	0.1
	sd	1.57			6.66		2.94		
[$Bu_2^nNH_2$]Cl	5	99.34	7.65	0.5	89.44	0.10	112.35	8.70	0.3
	10	91.26	6.79	0.2	88.26	0.20	109.14	8.70	0.3
	15	94.41	7.10	0.4	87.18	0.30	107.55	8.70	0.3
	20	92.96	7.14	0.6	87.17	0.40	105.63	8.70	0.3
	sd	3.01			0.93		2.95		
[$Bu_2^iNH_2$]Cl	5	94.50	7.54	0.5	91.88	0.30	90.93	6.88	0.1
	10	86.39	6.61	0.2	73.11	0.04	88.96	6.88	0.1
	15	86.90	6.70	0.4	81.74	0.40	86.82	6.88	0.1
	20	90.66	7.08	0.6	84.64	0.40	87.63	6.88	0.1
	sd	3.26			6.72		3.25		

E – activation energy; lg$A$ – lg10 pre-exponential factor; n – reaction order; *sd* – standard deviation modified. The constant variation in the value of reaction order (n) confirms the limitation this method in defining a precise value for n.

The most unsatisfactory aspect of determination of kinetic parameters was result obtained by Freeman–Caroll method [19]. Dispersion appears to be applied to a limited portion of decomposition curves and considerable difficulties exist for obtaining a real value of reaction order (n).

Isothermal kinetics

The determinations were done with reference to different models of heterogeneous reactions in solid state. Under isothermal conditions, curves of reaction fraction *vs.* time (α–t) are expressed in the form $f(\alpha)=kt$, where k is velocity constant and function $f(\alpha)$ depends of mechanism which controls the reaction [20–22]. The experimental data were analyzed according to these models in range of $0.1<\alpha<0.9$. Thus, data (α, t) obtained were analyzed examining linearity of $f(\alpha)$ *vs.* t. According to results of variance analysis and explained variance [20] the models which showed better agreement with experimental data were presented in Table 3.

The decomposition reactions of $[\mathrm{Pr}_2^n\mathrm{NH}_2]\mathrm{Cl}$, $[\mathrm{Pr}_2^i\mathrm{NH}_2]\mathrm{Cl}$ and $[\mathrm{Bu}_2^i\mathrm{NH}_2]\mathrm{Cl}$ were better described by model of tridimensional growth of A3 nucleus. Different behavior was shown by $[\mathrm{Bu}_2^n\mathrm{NH}_2]\mathrm{Cl}$ whose reaction was better described by model of bidimentional growth of A2 nucleus.

Though the A4 model presented good agreement with experimental data of decomposition reaction of $[\mathrm{Pr}_2^n\mathrm{NH}_2]\mathrm{Cl}$, according to results of Variance Analysis there was no doubt that the A3 model, would be more adequate to describe reaction at all temperatures studied. In spite of liquid phase being introduced in thermal decomposition of $[\mathrm{Pr}_2^i\mathrm{NH}_2]\mathrm{Cl}$, no attempt was made to adjust a model of liquid phase formation. Out of adjusted solid state models, the A3 model presented better results for all temperatures. An evidence of agreement between the considerations made for the nature of thermal process of $[\mathrm{Bu}_2^n\mathrm{NH}_2]\mathrm{Cl}$ and experimental data was found by adjustment of solid state models. Different of other salts, the $[\mathrm{Bu}_2^n\mathrm{NH}_2]\mathrm{Cl}$ presented better adjustment for A2 and R2 models. However, in a general way, adjustment A2 was slightly better than R2. In the case of $[\mathrm{Bu}_2^i\mathrm{NH}_2]\mathrm{Cl}$, for temperature 209°C, it becomes difficult to determine if A3 or A4 models agrees better to the experimental data, by comparing explained variance alone. However, by comparing the Variance Analysis results, the A4 model was selected. For the temperatures 199 and 215°C, the A3 model presented better agreement.

Then, in decomposition process of dialkylammonium chlorides in the beginning of reaction the solid phase predominates and migration of molecules occur to gaseous phase directly:

$$[\mathrm{R_2NH_2}]\mathrm{Cl}(s)\rightarrow[\mathrm{R_2NH}](g)+\mathrm{HCl}(g) \tag{3}$$

When the liquid phase is introduced, the migration of molecules on the surface of condensed phase followed by its diffusion through the gaseous phase occurs:

$$[\mathrm{R_2NH_2}]\mathrm{Cl}\ (\text{liquid, condensed})\rightarrow\mathrm{R_2NH}(g)+\mathrm{HCl}(g) \tag{4}$$

Table 3 Comparison of kinetic models of isothermal decomposition of compounds

Compounds	Temperature/° C	$k\cdot10^4/\mathrm{s}^{-1}$	Model	Explained variance/%
$[\mathrm{Pr}_2^{\mathrm{n}}\mathrm{NH}_2]\mathrm{Cl}$	200	72.0	A3	99.24
	200	72.0	A4	99.10
	205	77.0	A3	99.26
	205	77.0	A4	99.03
	210	82.0	A3	99.59
	210	82.0	A4	99.45
$[\mathrm{Pr}_2^{\mathrm{i}}\mathrm{NH}_2]\mathrm{Cl}$	210	6.8	A3	98.89
	210	6.8	A4	98.69
	215	7.2	A3	98.45
	215	7.2	A4	98.44
	220	7.7	A3	99.18
	220	7.7	A4	98.94
$[\mathrm{Bu}_2^{\mathrm{n}}\mathrm{NH}_2]\mathrm{Cl}$	223	102.0	A2	99.81
	223	102.0	R2	99.74
	228	108.0	A2	99.13
	228	108.0	R2	99.07
	233	115.0	A2	99.54
	233	115.0	R2	99.54
$[\mathrm{Bu}_2^{\mathrm{i}}\mathrm{NH}_2]\mathrm{Cl}$	199	4.0	A3	99.24
	199	4.0	A4	98.97
	209	4.5	A3	98.71
	209	4.5	A4	98.71
	215	4.7	A3	99.36
	215	4.7	A4	99.10

Conclusions

The determination of activation energy by Ozawa and Coats–Redfern methods is a convenient means of comparing stability of substituent alkyl group of studied salts, corroborating with the order of thermal stability obtained by analysis of thermogravimetric curves. The decomposition reactions of $[\mathrm{Pr}_2^{\mathrm{n}}\mathrm{NH}_2]\mathrm{Cl}$, $[\mathrm{Pr}_2^{\mathrm{i}}\mathrm{NH}_2]\mathrm{Cl}$ and $[\mathrm{Bu}_2^{\mathrm{i}}\mathrm{NH}_2]\mathrm{Cl}$ were better described by A3 model and $[\mathrm{Bu}_2^{\mathrm{n}}\mathrm{NH}_2]\mathrm{Cl}$ by A2 model. The existence of condensed phase can be the determining factor of kinetic process in the case of $[\mathrm{Pr}_2^{\mathrm{n}}\mathrm{NH}_2]\mathrm{Cl}$, $[\mathrm{Pr}_2^{\mathrm{i}}\mathrm{NH}_2]\mathrm{Cl}$ and $[\mathrm{Bu}_2^{\mathrm{i}}\mathrm{NH}_2]\mathrm{Cl}$. It was expected, therefore, that the mechanism which explains decomposition of $[\mathrm{Bu}_2^{\mathrm{n}}\mathrm{NH}_2]\mathrm{Cl}$ should be different than the mechanism which explain the decomposition of other salts, since liquid phase is not introduced.

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