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THERMAL DECOMPOSITION OF ALKYLAMMONIUM CHLORIDES

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ABSTRACT

Alkylammonium chlorides of the general formula $(R_nNH_{4-n})Cl$, with n=1-4 and R=alkyl, undergo thermal decomposition on heating to 700 K. Irrespective of the structure of R the thermal decomposition leads to the total volatilization of the salts. For n=4 thermolysis occurs in one step, whereas if n=1-3, two distinct steps of different kinetics are seen on the thermogravimetric curves. The enthalpies of the thermal decomposition were derived and based on them the enthalpies of formation and the energies of the crystal lattice of the salts were also estimated. The kinetics of the process was examined adopting the Jacobs and Russell-Jones approach. The effect of the structure of an alkylammonium cation on the values of some thermochemical quantities has also been analyzed.

INTRODUCTION

Although the nature of the thermal decomposition of alkylammonium chlorides seems to be well understood, the thermodynamics and kinetics of the process, in the case of individual compounds, have been less studied. Thermal analysis methods, i.e. TG, DTG and DTA appeared to be a very helpful tool in the examination of these problems [1]. Thus extending investigations, we applied the above mentioned methods to study thermal dissociation of alkylammonium chlorides other than mono-n-alkylammonium chlorides.

MEASURING METHODS

The amine hydrochlorides were synthesized by passing a stream of dried hydrogen chloride through a solution of an appropriate amine in anhydrous ethyl ether [1]. The resulting white precipitates were filtered, dried and stored in a vacuum desiccator over P_2O_5. The quaternary chlorides, obtained from Fluka AG, Buchs SG, were recrystallized from mixtures $EtOH+Et_2O$ and then filtered, dried, and stored as was described above [2].

The thermal analyses were performed on an OD-103 derivatograph (Monicon).

RESULTS AND DISCUSSION

Alkylammonium chlorides undergo various thermal transforma-

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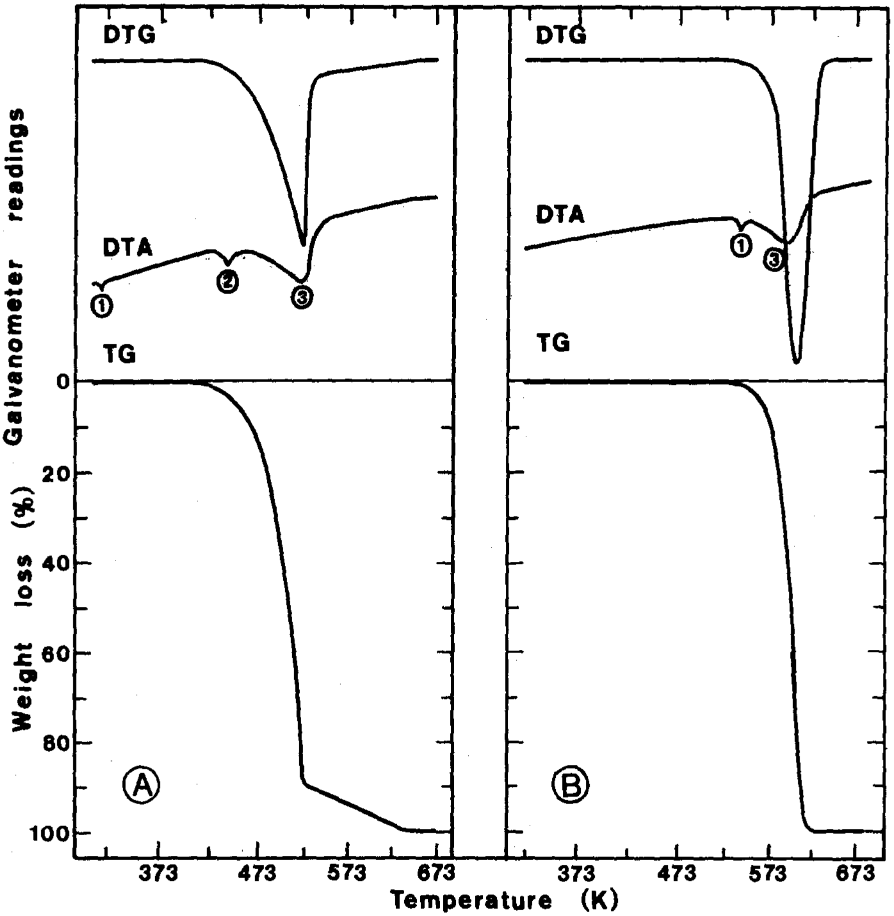

Figure 1. Thermal analyses of dimethylammonium chloride (A) and tetramethylammonium chloride (B). Mass of samples = 50 mg; sample holder, one platinum plate [3] (Appendix 1, No. 4); reference material, α-Al_2O_3; heating rate = 5 K/min; galvanometer sensitivities: DTG = 1/10, DTA = 1/5 and TG = 50 mg; dynamic atmosphere of N_2. ① -phase transition, ② -melting and ③ -decomposition.

tions upon heating to 700 K leading to the total volatilization of the compounds. The thermal analysis run recorded by a derivatograph for dimethylammonium chloride (Fig. 1A) is typical for all primary, secondary and tertiary alkylammonium chlorides, whereas, thermal analysis run for tetramethylammonium chloride (Fig. 1B) is characteristic for all quaternary salts investigated. The compounds belonging to both groups may undergo various solid phase transitions upon heating. Some of them melt before the onset of volatilization. The main difference between these two classes of compounds is revealed during the course of the thermal decomposition process. Dissociation of quaternary salts proceeds in one stage (Fig. 1B), and results in the formation of appropriate tertiary amines and alkyl chlorides, both in the gaseous phase [4].

$$(R_4N)Cl_{(c)} \longrightarrow R_3N_{(g)} + RCl_{(g)} \qquad (1)$$

Volatilization of the remaining compounds investigated proceeds according to the equation [1],

$$(R_nNH_{4-n})Cl_{(c)} \longrightarrow R_nNH_{3-n\,(g)} + HCl_{(g)} \qquad (2)$$

although two distinct steps are clearly seen in TG curves (Fig. 1A).

To investigate the latter effect we considered the kinetics of reaction (2). For this purpose we adapted the equation derived by Jacobs and Russell-Jones [5] to the dynamic conditions [1].

$$\frac{d\alpha}{dT} = \frac{\frac{1}{2}(X_1/\Phi)\left[3T^{1/2}e^{-E/2RT} + \left(E/RT^{1/2}\right)e^{-E/2RT}\right] - 3X_2\left[1-(1-\alpha)^{1/3}\right]}{\left[X_2T/(1-\alpha)^{2/3}\right] + 1/\left[(1-\alpha)^{1/3} + \Delta/a_o\right]} \qquad (3)$$

where α denotes the degree of conversion at temperature T, Φ is the heating rate, R represents the gas constant, X_1, X_2 and E are the constants and E can be identified with the activation energy for the process, a_o denotes the initial radius of particles corresponding to $\alpha=0$, and Δ is the distance between collisions (i.e. a molecule after leaving the condensed phase travels a distance Δ before a collision occurs). Initially $\Delta \ll a_o$ and the influence of this parameter on the rate of volatilization is negligibly small. However, as the geometric surface area of the condensed phase decreases, Δ approaches a_o in magnitude (that have place at the end of the process). Then, the term Δ/a_o becomes important and it causes a decrease of the rate of the process.

The values of constants X_1, X_2 and E were evaluated based on the integral form of (3) and values of α_i and T_i taken from TG traces. It was found that values of E thus derived are very close to the values of the enthalpy of volatilization.

The experimental data points, α_i and T_i, were also used for the evaluation of the enthalpy of the thermal decomposition (ΔH_d) of the salts based on the Van't Hoff equation. The values of ΔH_d enable the estimation of several thermochemical quantities; among others the enthalpies of formation ($\Delta H_{f,c}$) and the energies of the crystal lattice (U) of the compounds. We used for this purpose an adequate thermochemical cycle presented elsewhere [1]. The necessary ancillary data have been taken from the literature.

The values of $\Delta H_{f,c}$ increase together with the increase of both the number of alkyl substituents in the molecule (M) and the size of an individual alkyl substituent (p). The dependencies of the enthalpy of dissociation (Fig. 2A) and the crystal lattice energy of the salts (Fig. 2B) on both p and M are more complex. The effect of succesive substitution of hydrogen by alkyl groups upon the values of ΔH_d is surprisingy varied. Whereas, the values of U generally decrease with the increase of both P and M. The latter regularity can be qualitatively explained by the semi-empirical Kapustinskii-Yatsimirskii equation [6]. It is worth mentioning that similar dependencies have been found by other authors [7,8].

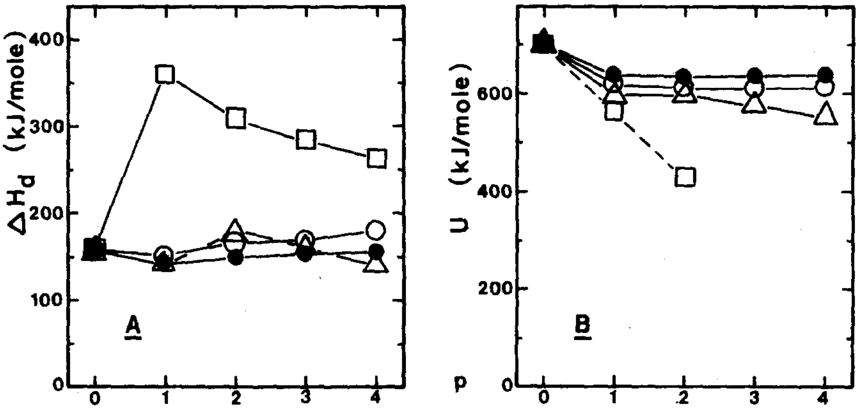

Figure 2. The enthalpy of the thermal decomposition(ΔH_d) and crystal lattice energy (U) versus p and M for $[(n\text{-}C_pH_{2p+1})_MNH_{4-M}]Cl$. ●, M=1; ○, M=2; △, M=3; □, M=4.

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