

THEORETICAL AND EXPERIMENTAL INVESTIGATIONS OF THE DECOMPOSITION OF 10-METHYLACRIDINIUM HALIDES

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Abstract

10-Methylacridinium chloride, bromide and iodide were prepared in crystalline forms (the first two salts as monohydrates) and subjected to thermogravimetric investigations. Decomposition of the compounds is initially accompanied by the liberation of water (in case of monohydrates), halo-methanes and acridine molecules. As decomposition proceeds, side reactions occur which are reflected in a complex pattern of thermogravimetric curves. TG traces corresponding to the initial decomposition stage were used to determine the kinetic characteristics of the thermal dissociation of the salts. MNDO/d, AM1 and PM3 methods were employed independently to examine reaction pathways and to predict thermodynamic and kinetic barriers for the thermal decomposition of the compounds. These data were subsequently supplemented with theoretically determined crystal lattice energies, which enabled the relevant characteristics for the decomposition of crystalline phases to be predicted. The theoretically predicted characteristics are qualitatively comparable with those originating from thermogravimetric investigations, which allows one to believe that both are valid.

Keywords: kinetics, 10-methylacridinium halides, thermodynamics, thermogravimetric investigations

Introduction

10-Methylacridinium halides [10-MeAcr]X are some of the simplest salts containing quaternary heteroaromatic nitrogen atom which have so far been obtained in crystalline form and whose solid phase structures have been determined by X-ray diffractometry [1]. These compounds are therefore convenient subjects for experimental and theoretical investigations into the behaviour of quaternary ammonium salts. In one of our recent publications we compiled results concerning the thermochemistry of N,N,N-trimethylmethan ammonium halides published so far, supplemented with our own theoretical studies [2]. The investigations showed that these compounds are quite stable, since their decomposition requires a relatively high activation barrier to be overcome. This feature influences the properties of quaternary salts, which are different from those of protonated ammonium salts. In order to obtain more information on the features and behaviour of quaternary ammonium salts it seemed necessary to extend investigations to other group of derivatives, namely those containing the heteroaromatic nitrogen base acridine. Thus we focused our attention to (i)

thermogravimetric investigations of [10-MeAcr]X in order to discover their thermal properties and dissociation pathway, (ii) theoretical studies leading to the prediction of lattice energies, thermodynamic characteristics of solid phases, and dissociation pathways of the salts and the kinetic parameters characterizing them, and (iii) a comparison of experimental and theoretical results in order to shed more light on the chemistry of quaternary salts and the usefulness of the two approaches.

Methods

Syntheses

10-Methylacridinium iodide and bromide were prepared by heating acridine (purified by sublimation) with freshly distilled methyl iodide or bromide in a thick sealed-glass tube at 393 K [3]. The crude products were dissolved in ethyl alcohol and precipitated by the addition of diethyl ether. The respective deep-red or yellow needles of 10-methylacridinium iodide (**3**) or bromide monohydrate (**2**) were obtained after repeated recrystallization from an 80/20 mixture of ethyl alcohol and water (*m.p.* of 10-methylacridinium bromide monohydrate=472 K (d) [4]. 10-Methylacridinium chloride monohydrate (**1**) was synthesized by stirring overnight an aqueous solution of 10-methylacridinium iodide with a slight excess of freshly precipitated silver chloride [4]. White crystals of the compound were obtained after repeated recrystallization from an 80/20 mixture of ethyl alcohol and water (*m.p.* of 10-methylacridinium chloride monohydrate=456 K (d) [4].

Thermogravimetric investigations

Dynamic thermogravimetric investigations were conducted on a Netzsch TG 209 thermobalance coupled to a Bruker IFS 66 FTIR spectrometer. Samples weighing ca 3 mg were placed in a platinum crucible, and heated at (Φ) 1.0 or 20.0 K min⁻¹ in a dynamic Ar atmosphere. IR spectra of gaseous products were recorded at a heating rate of 20.0 K min⁻¹.

From thermogravimetric traces, α (extent of reaction)= $f(T)$ (temperature) relationships, kinetic parameters, i.e. enthalpies of activation ($\Delta_a H^\circ$) and Z [5–8] were derived for (i) the F1 model (unimolecular decomposition) [5, 6, 9]

$$-\ln(1-\alpha)^{1/2} = \frac{Z}{\Phi} T \exp\left(\frac{-\Delta_a H^\circ}{RT}\right) \quad (1)$$

(ii) the R2 model (surface decomposition) [5, 6, 9]

$$1-\ln(1-\alpha)^{1/2} = \frac{Z}{\Phi} T \exp\left(\frac{-\Delta_a H^\circ}{RT}\right) \quad (2)$$

employing the Marquardt (non-linear least squares) method [10].

Theoretical calculations

Quantum mechanical calculations were carried out at the level of the MNDO/d [11], AM1 [12] and PM3 [13] semi-empirical methods using the Spartan 5.0 program package [14]. Primary structures for the geometry optimizations were extracted from X-ray data [1]. Transition state structures for the decomposition of [10-MeAc]X to acridine halomethanes were assumed similar to those for the dissociation of N,N,N-trimethylmethan ammonium halides [2]; they were found by employing the gradient minimization (EF) procedure [15].

The electrostatic part of the crystal lattice energy was calculated using the PCK83 program [16] and assuming a 1+ charge on 10-MeAc⁺ and 1- charge on X⁻. The charges on the atoms in the cation were fitted to reproduce the molecular electrostatic potential around the molecules (MEP fitted charges) [17]. They were derived from the Hartree-Fock (HF) [18] or density functional level of theory (DFT) [19] (the Becke 3LYP functional [20, 21]) using the 6-31G** basis set [22, 23]. The crystal structures used in these calculations were taken from [1].

The final values of the thermodynamic and kinetic characteristics were obtained from basic physicochemical relationships [2, 24].

Results and discussion

The decomposition of all the compounds studied begins with the release of water (in case of monohydrates), halomethanes and acridine molecules. This was demonstrated by the analysis of the IR spectra of gaseous products. As decomposition proceeds, side reactions become more pronounced; this is demonstrated in Fig. 1. Starting the earliest in case of **1** and **2** the latest in case of **3**, these processes reduce the rate of decomposition, and a complex pattern of thermogravimetric curves emerges.

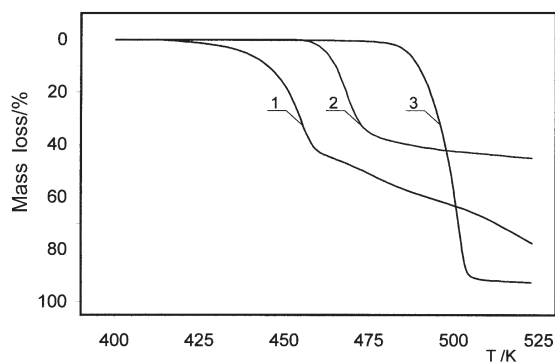


Fig. 1 Dynamic thermogravimetric traces reflecting the decomposition of (1) – [10-MeAc]Cl·H₂O; (2) – [10-MeAc]Br·H₂O; (3) – Conditions (mass of the sample in mg/heating rate in K min⁻¹): 1 – (3.330/1.0), 2 – (3.000/1.0), 3 – (3.000/1.0)

Fragments of TG curves reflecting the simple initial step of decomposition, corresponding to α : 0.08–0.35, 0.03–0.26 and 0.10–0.82 in cases 1, 2 and 3 respectively, were fitted by Eq. (1) or (2) describing the unimolecular process (F1) or that occurring on the surface of a solid phase (R1). The enthalpy activation barriers arising from this fit are shown in Table 3.

Table 1 Thermodynamic data from quantum mechanical calculations^a

Compound/entity ^b	Method					
	MNDO/d		AM1		PM3	
	$\Delta_{f,298}H^\circ$	${}_{298}S^\circ$	$\Delta_{f,298}H^\circ$	${}_{298}S^\circ$	$\Delta_{f,298}H^\circ$	${}_{298}S^\circ$
Cl ⁻	-227.7	153.1	-157.6	153.1	-214.3	153.1
Br ⁻	-212.8	163.2	-85.4	163.2	-235.3	163.2
I ⁻	-188.4	169.3	-9.3	169.3	-270.4	169.3
H ₂ O	-255.0	188.1	-247.9	188.6	-223.5	188.2
CH ₃ Cl	-80.5	233.4	-79.3	233.7	-61.4	234.3
CH ₃ Br	-33.2	244.5	-25.9	245.5	-8.3	245.4
CH ₃ I	19.2	252.5	23.7	252.7	39.5	251.5
Acridine (Acr)	269.3	399.0	322.9	396.0	290.3	401.5
[10-MeAcr] ⁺	929.7	433.1	934.3	430.7	888.6	431.0
[10-MeAcr]Cl (TS)	480.7	481.8	489.3	483.9	414.6	481.3
[10-MeAcr]Br (TS)	501.5	493.3	555.0	496.0	403.4	493.1
[10-MeAcr]I (TS)	533.5	500.8	621.0	501.4	441.4	502.9

^a The enthalpy of formation ($\Delta_{f,298}H^\circ$) and entropy ${}_{298}S^\circ$ of gaseous entities in kJ mol^{-1} and $\text{J mol}^{-1} \text{K}^{-1}$ respectively

^b See Fig. 2

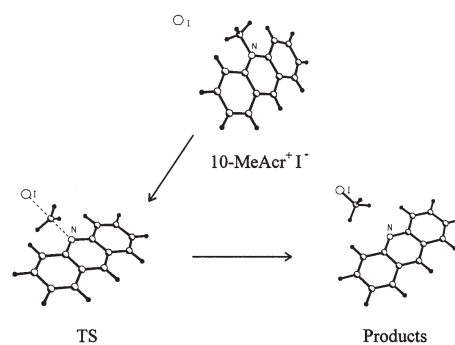


Fig. 2 [10-MeAcr]⁺-I⁻ unit in the crystalline phase together with the PM3 optimized structures of the entity in the transition state (TS) and decomposition products

Table 2 Thermodynamic characteristics in kJ mol^{-1} for 10-methylacridinium halides in the solid phase

Compound	Crystal lattice energy		Enthalpy of formation ^b			Enthalpy of decomposition ^b		
	Method of charge calculation	Value	MNDO/d	AM1	PM3	MND O/d	AM1	PM3
[10-MeAcr]Cl·H ₂ O	HF	552.1	-112.5	-30.7	-108.8	46.3	26.4	114.2
	DFT	539.9	-100.3	-18.5	-96.6	34.1	14.2	102.0
[10-MeAcr]Cl	HF	460.3 ^a	236.7	311.4	209.0	-47.9	-67.8	19.9
	DFT	453.5 ^a	243.5	318.2	215.8	-54.7	-74.6	13.1
[10-MeAcr]Br·H ₂ O	HF	532.6	-78.1	61.0	-110.3	59.2	-11.9	168.8
	DFT	520.6	-66.1	73.0	-98.3	47.2	-23.9	156.8
[10-MeAcr]Br	HF	450.4 ^a	261.5	393.5	197.9	-25.4	-96.5	84.1
	DFT	443.8 ^a	268.1	400.1	204.5	-32.0	-103.1	77.5
[10-MeAcr]I	HF	454.7	281.6	465.3	158.5	6.9	-118.7	171.3
	DFT	450.6	285.7	469.4	162.6	2.8	-122.8	167.2

^a Obtained disregarding the H₂O molecule in the crystalline phase^b Calculated on the basis of the thermodynamic cycle [2, 24], the relevant thermodynamic data in Table 2 and the crystal lattice energies listed in the preceding column

Table 3 Kinetic barriers in kJ mol^{-1} the formation and dissociation of 10-methylacridinium halides

Compound/entity	Method	Formation			Decomposition			
		From gaseous substrates		From solid acridine and gaseous halomethanes ^a	HF ^b	DFT ^b	$\Delta_{a,298}H^\circ$	
		$\Delta_{a,298}H^\circ$	$\Delta_{a,298}G^\circ$	$\Delta_{a,298}H^\circ$			experimental	
						R1 ^c	F1 ^d	
[10-MeAcr]Cl	MNDO/d	291.9	336.8	360.4	244.0	237.2	195	206
	AM1	245.7	289.2	367.8	177.9	171.1		
	PM3	185.7	231.7	275.2	205.6	198.8		
[10-MeAcr]Br	MNDO/d	265.4	310.2	333.9	240.0	233.4	429	443
	AM1	257.9	301.3	380.0	161.4	154.8		
	PM3	121.4	167.2	210.9	205.5	198.9		
[10-MeAcr]I	MNDO/d	244.9	289.9	313.4	251.8	247.7	363	415
	AM1	274.4	318.3	396.4	155.7	151.6		
	PM3	111.6	156.4	201.1	282.9	278.8		

^a The value of $\Delta_{a,298}H^\circ$ for solid acridine was taken to be $200.8 \text{ kJ mol}^{-1}$ [25]

^b The method of charge evaluation in the calculations of the crystal lattice energy (Table 4)

^c Evaluated by fitting Eq.(1) to the experimental TG curves

^d Evaluated by fitting Eq. (2) to the experimental TG curves

To gain an insight into the mechanism of decomposition of the compounds studied we carried out quantum mechanical calculations, which enabled us to predict the structure and properties of decomposition products and transition state entities for the process. Figure 1 demonstrates the structures of the (10-MeAcr)⁺I⁻ unit extracted from X-ray data [1], the entity in the transition state for decomposition (TS) and dissociation products (iodomethane and acridine), and thus the decomposition pathway for quaternary aromatic halide salts. Basic thermodynamic characteristics for solid phase and transition state entities, as well as primary decomposition products, are set out in Table 1. On the other hand, Table 2 shows the thermodynamic characteristics of the formation and decomposition of 10-methylacridinium halides, together with electrostatic crystal lattice energies. From these values the enthalpies of formation and decomposition could be determined. Table 3 presents the kinetic barriers to the formation of acridinium halides and their decomposition to gaseous products.

Crystal lattice energies are only slightly influenced by the method of charge evaluation (Table 2). Values of this quantity are always higher for hydrated than anhydrous compounds and decrease gradually on moving from chloride to iodide salts.

Thermodynamic and kinetic characteristics obtained theoretically are much influenced by the theoretical method used. This applies both to auxiliary data (Table 1) as well as thermodynamic (Table 2) and kinetic characteristics (Table 3) for 10-methylacridinium halides and their dissociation process. Positive enthalpies of decomposition are always predicted for 1, and in most cases for 2 and 3. On the other hand, anhydrous 10-methylacridinium chloride and bromide should decompose spontaneously to acridine and halomethanes, according to data originating from the MNDO/d and AM1 methods (Table 2). 10-Methylacridinium chloride and bromide monohydrates are predicted to be thermodynamically stable with respect to the standard states of elements (Table 2).

The barriers to the formation and decomposition of the compounds studied are relatively high, which implies that once formed, they are quite stable (Table 3). Their synthesis is not, however, easy: this was indicated in the experimental section. The interesting data are those concerning the decomposition of the compounds. Table 3 shows both the theoretical and the experimental barriers to the process. Since the theoretical values are relevant to a unimolecular process, they should be compared with those corresponding to the F1 model. It may be noted that only in case of the decomposition of 1 do the theoretical and experimental values compare quite well. On moving from chloride to iodide salts the experimentally derived activation barriers increase substantially, though the theoretical ones do so only slightly. This suggests that 10-methylacridinium iodide is the most resistant to decomposition and that the chloride is the most susceptible to this process.

While performing the calculations, we noted that the charge separation, which can be assumed to be complete in the crystalline phase, is reduced during decomposition (Table 4). A similar effect accompanies the decomposition of N,N,N-trimethylmethan ammonium halides [2] and is due to the fact that solid ionic substances decompose to uncharged molecules.

Table 4 MEP fitted relative charges on nitrogen and halogen atoms of [10-MeAcr]⁺ (crystalline phase) and TS at various levels of theory

Compound	Method	Crystalline phase		TS	
		N (10-MeAcr) ⁺	X ⁻	N	X
[10-MeAcr]Cl·H ₂ O	MNDO/d	-0.22	-1.00	-0.37	-0.82
	AM1	-0.14	-1.00	-0.31	-0.70
	PM3	0.26	-1.00	-0.18	-0.79
[10-MeAcr]Br·H ₂ O	MNDO/d	-0.21	-1.00	-0.36	-0.79
	AM1	-0.13	-1.00	-0.28	-0.72
	PM3	0.29	-1.00	-0.20	-0.71
[10-MeAcr]I	MNDO/d	-0.14	-1.00	-0.38	-0.76
	AM1	-0.02	-1.00	-0.40	-0.67
	PM3	0.44	-1.00	-0.31	-0.68

This paper affords an example of the application of theory to the explanation of chemical changes in solid systems, and an interpretation of the results obtained on the basis of thermoanalytical investigations. An insight was obtained into the mechanism of decomposition of simple quaternary heteroaromatic halides. It is similar to that in the case of N,N,N-trimethylmethan ammonium halides. What differentiates these two types of derivatives is that while the enthalpies of dissociation of alkan ammonium salts are always negative (and thus the relevant processes are spontaneous), those of quaternary heteroaromatic salts may be either positive or negative. However, decomposition always requires substantial activation barriers to overcome, which makes these substances quite stable even at elevated temperatures.

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