Structure and Thermal Stability Relationships in Ring-substituted Arylammonium Nitrates

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The thermal stability of ring-substituted arylammonium nitrates has been investigated using thermal methods of analysis. The decomposition temperature of *meta*- and *para*-substituted derivatives is found to be linearly related to the Hammett substituent constant σ. The activation energy for decomposition determined by isothermal gravimetry increases with the increasing basicity of the corresponding amine. The results suggest that the primary step in the decomposition process of these salts is proton abstraction by the anion from the arylammonium ion.

INTEREST in a systematic study of the characteristics of thermal decomposition of substituted ammonium nitrates thrives due to the fact that the nitrogen base salts of inorganic oxidising acids like HNO_3, $HClO_4$, *etc.* find application in explosive compositions with ammonium nitrate.[1,2] Anilinium nitrate is commonly found as an intermediate in the combustion of the aniline–nitric acid liquid rocket system.[3] The nitrates of toluidines and aniline have been suggested as hypergolic fuels with red fuming nitric acid.[4] A study of the decomposition mechanism may add to our understanding of the combustion and explosion characteristics of systems involving substituted ammonium nitrates.

The thermal decomposition of ammonium nitrate has been explained by postulating [5] dissociation involving proton transfer as a primary process before decomposition. A similar process has been envisaged in the case of methyl-substituted ammonium nitrates [6] and perchlorates.[7] All these compounds decompose exothermically in air and sublime under low pressure resulting in an endotherm in the differential thermal analysis (DTA). Assuming dissociation involving proton transfer to be the rate-determining step in the decomposition process, the thermal stability of substituted ammonium nitrates may depend upon the tendency of the amine to release a proton, *i.e.*, on the basicity of the central nitrogen atom. In monosubstituted arylammonium nitrates an aryl ring bonded to the basic nitrogen atom provides a very convenient way of altering the basicity. The thermal stability of monoarylammonium nitrates with different substituents on the aryl ring has therefore been determined using DTA and thermogravimetry (TG) to investigate this aspect.

EXPERIMENTAL

Materials.—Ring-substituted arylammonium nitrates were prepared by treating the appropriate ring-substituted anilines with cold dilute nitric acid. The nitrates of *m*-chloroaniline, aniline, *o*-toluidine, 2,5-dimethylaniline, and 2,6-dimethylaniline readily precipitated from the solution. The other nitrates were obtained by reducing the volume of the reaction mixture by evaporation under vacuum and cooling. The mononitrate of *p*-phenylenediamine was obtained by reaction of calculated amounts of the base and acid. Analytical, m.p., and i.r., spectral data are given in Table 1.

The i.r. spectra of these compounds show the characteristic absorptions of the amine salts.[8,9] The characteristic bands of the $\overset{+}{N}$–H and NO_3^- ions are listed in Table 1. The $\overset{+}{N}$–H and C–H stretching bands overlap resulting in a broad band between 3 200 and 2 800 cm^{-1}. The $\overset{+}{N}$–H deformation bands appear in the ranges 1 645—1 610 and 1 510—1 480 cm^{-1}. In the case of *p*-phenylenediamine mononitrate these bands appear at the high frequency side, while *p*-nitroaniline nitrate absorbs at the low frequency side of the range, the $\overset{+}{N}$–H deformations of other salts falling in between. The N–H_2 stretching (doublet) due to the free *p*-amino group in *p*-phenylenediamine mononitrate appears at 3 435 and 3 350 cm^{-1}. The nitrate absorptions are reported [10] to occur at 1 050, 830, 1 390, and 715 cm^{-1} corresponding to ν_1, the totally symmetric stretching mode, ν_2, the out-of-plane bending mode, ν_3, the doubly degenerate, predominant stretching mode, and ν_4, the doubly degenerate, predominant bending mode. The absorptions of other substituents appear at appropriate characteristic frequencies.

Instruments.—DTA was carried out using an apparatus similar to that described by Nambiar.[11] The differential thermograms were recorded using a two-pen potentiometric strip-chart recorder. All experiments were carried out using platinum cups held in position by placing them inside the two cavities of a stainless steel block which also served to reduce self-heating. The platinum cups rest on the beads of two thermocouples (chromel–alumel). Sample (25 mg) was used keeping an equal amount of γ-Al_2O_3 in the reference cup. A uniform heating rate of 12 °C min^{-1} was employed in all experiments. For vacuum DTA,[11] the thermocouple–sample assembly was enclosed in a Pyrex glass tube. The system, after keeping the sample in the holder was evacuated to constant pressure (0.1 mmHg) and the thermograms were recorded. The same system was used for carrying out DTA under nitrogen, with a flow rate of 1 l min^{-1}.

TG was carried out on a conventional McBain–Bakr quartz spring balance [11,12] using a small platinum bucket suspended by means of a quartz fibre. In isothermal TG experiments sample (25 mg) was taken and the weight loss was followed at intervals after suspending the bucket containing the sample in the TG tube held at constant temperature ($\pm$0.5 °C).

TABLE 1

Analytical data

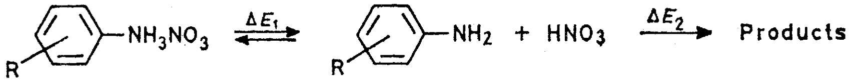
Compound	Carbon (%)		Hydrogen (%)		M.p.* (°C)	ν_{max}/cm^{-1}	
	Calc.	Found	Calc.	Found		NO_3	NH
$C_6H_5NH_3NO_3$	46.15	45.5	5.15	5.05	190	1 390br,s 1 035m 830m 730w	1 615m 1 505s
p-$CH_3C_6H_4NH_3NO_3$	49.4	48.85	5.9	6.2	205 (decomp.)	1 390br,s 1 030m 820s 730w	1 625m 1 510s
p-$NH_2C_6H_4NH_3NO_3$	42.1	41.7	5.3	5.65	215	1 395br,s 1 025w 830s	1 645s 1 520s
o-$CH_3C_6H_4NH_3NO_3$	49.4	48.7	5.9	6.15	185	1 390br,s 1 040s 830m 730m	1 615m 1 510m
p-$ClC_6H_4NH_3NO_3$	37.8	37.2	3.7	4.0	165	1 390br,s 1 040w 815s	1 620w 1 495s
m-$ClC_6H_4NH_3NO_3$	37.8	37.35	3.7	3.95	182 (decomp.)	1 390br,s 1 050m 830m 730m	1 620w 1 490s
p-$CO_2HC_6H_4NH_3NO_3$	42.0	41.65	4.05	4.05	183 (decomp.)	1 395br,s 1 040m 835w 720w	1 620m 1 520m
p-$NO_2C_6H_4NH_3NO_3$	35.8	35.3	3.5	3.95	152	1 370br,s 1 020s 800s	1 610s 1 480s
2,5-$(CH_3)_2C_6H_3NH_3NO_3$	52.15	52.65	6.6	6.9	192 (decomp.)	1 390br,s 1 040m 835w 720m	1 615m 1 520s
2,6-$(CH_3)_2C_6H_3NH_3NO_3$	52.15	52.8	6.6	7.0	188 (decomp.)	1 390br,s 1 035m 830m 730w	1 635s 1 485s

* The reported [3] m.p.s of anilinium and o- and p-toluidinium nitrates are 191, 185, and 175 °C, respectively. p-Toluidinium nitrate, however, does not appear to melt but decomposes at 205 °C.

RESULTS AND DISCUSSION

The DTA traces of one of the compounds, anilinium nitrate, in air, nitrogen, and under reduced pressure are presented in Figure 1. The DTA trace in air remains virtually unaltered when it is carried out under nitrogen. All the compounds show terminal exotherms due to decomposition immediately after liquification. The anilinium, p-aminoanilinium, and p-chloroanilinium nitrates, show extra endotherms at 108, 127, and 86 °C apart from those due to melting at 192, 212, and 162 °C, respectively. These transitions may be attributed to structural changes in the solid state as these endotherms appear as exotherms on cooling. A black residue remains in the DTA cup after the exothermic decomposition process. The terminal exotherms observed in air due to decomposition were replaced by endotherms when the DTA was carried out at a pressure of 0.1 mmHg. A sublimate also appeared on the cooler parts of the vacuum DTA apparatus and therefore the endotherms observed may be due to sublimation.

It appears therefore that the decomposition of these compounds may proceed through dissociation as postulated earlier in the case of monomethylammonium nitrate [6] [reaction (1) where ΔE_1 is the dissociation energy (endothermic) and ΔE_2 is the decomposition energy (exothermic) resulting from the oxidation reactions between the amine and nitric acid and/or their decomposition products]. The exotherm in air is a combined effect of the two processes. At low pressures dissociation (sublimation) being predominant, the overall effect is endothermic.



(1)

It may be noted that dissociation involving a proton transfer is analogous to ionisation of benzoic acids in water and consequently the effect of the substituent in the phenyl ring on proton release may be accounted for in terms of Hammet constant σ. This constant is defined [13] by the Hammett equation in the familiar form (2). The DTA data along with the δ values [13,14] for

$$\log K/K_0 = \rho\sigma \qquad (2)$$

various substituents and pK_b values [15] for the corresponding amines are reported in Table 2.

It is interesting to see from Figure 2 that for *meta*- and *para*-substituted derivatives, plots of the decomposition temperatures as well as dissociation temperatures (under low pressure) against the Hammett substituent constants show linear relationships. It therefore appears that the thermal stability of these salts depends upon the relative ease of proton transfer and the decomposition temperatures are governed by the dissociation process.

TABLE 2

Thermal decomposition data

Compound	DTA peak temperature (°C) * At atmospheric pressure	At 0.1 mmHg	pK_b of amine	Hammett substituent constant σ
$C_6H_5NH_3NO_3$	108 (−)	111 (−)	9.40	0.0
	192 (−)	173 (−)		
	202 (+)			
p-$CH_3C_6H_4NH_3NO_3$	209 (+)	184 (−)	8.91	−0.17
p-$NH_2C_6H_4NH_3NO_3$	127 (−)	128 (−)	7.92	−0.66
	212 (−)	214 (−)		
	245 (+)			
o-$CH_3C_6H_4NH_3NO_3$	182 (−)	167 (−)	9.61	−0.13
	195 (+)			
p-$ClC_6H_4NH_3NO_3$	86 (−)	87 (−)	10.01	+0.23
	162 (−)	160 (−)		
	190 (+)			
m-$ClC_6H_4NH_3NO_3$	183 (−)	159 (−)	10.66	+0.37
	187 (+)			
p-$CO_2HC_6H_4NH_3NO_3$	183 (−)		11.62	+0.40
	185 (+)			
p-$NO_2C_6H_4NH_3NO_3$	150 (−)	152 (−)	13.01	+0.78
	166 (+)			
2,5-$(CH_3)_2C_6H_3NH_3NO_3$	190 (−)	178 (−)	9.47	
	204 (+)			
2,6-$(CH_3)_2C_6H_3NH_3NO_3$	190 (+)	157 (−)	10.05	

* (+) and (−) denote exotherm and endotherm respectively.

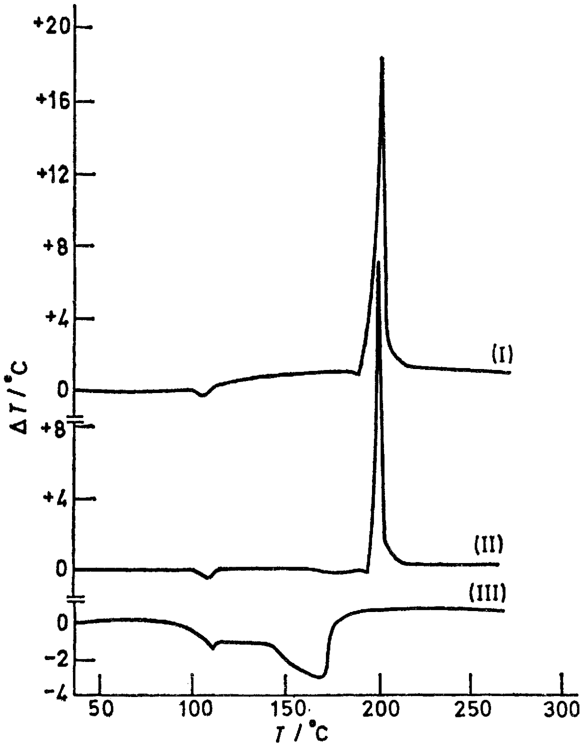


FIGURE 1 DTA traces of anilinium nitrate in air (I), in nitrogen (II), and at 0.1 mmHg pressure (III)

In a way, these results are markedly similar to the linear relationship observed[16] between the free energy of activation for benzoylation of substituted anilines and the free energy of dissociation. The failure of *ortho*-substituted derivatives to obey the linear relationship between σ and log K/K_0 is well known[13] and has been attributed to steric effects. In the present case also the *ortho*-substituted salts deviate from the linear relationship between σ and decomposition or dissociation temperature. In fact, a critical examination of the decomposition of 2,5- and 2,6-dimethylanilinium nitrates and *o*-toluidinium nitrate clearly demonstrates the importance of *ortho*-effects on the thermal characteristics of *ortho*-substituted arylammonium nitrates. The decomposition temperature decreases with *ortho*-substitution by methyl groups even though methyl groups are electron donating due to inductive effects. It is known[17] that in general

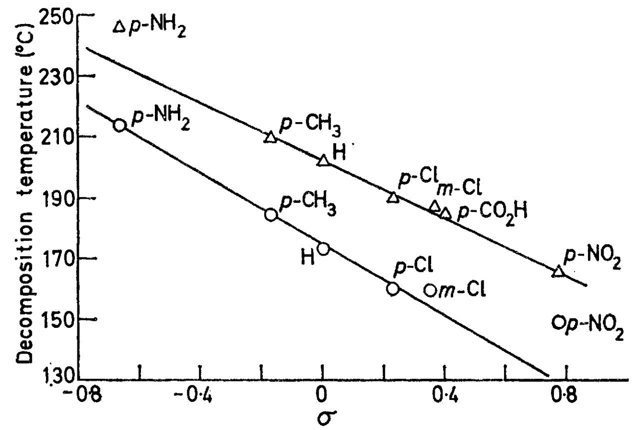


FIGURE 2 Plots of Hammett substituent constant σ against decomposition temperature (△) and dissociation temperature (○)

all *ortho*-substituents exert an effect of the same kind, base weakening, whether they are electron withdrawing or releasing.

It is evident from Table 2 that the decomposition temperatures of the arylammonium nitrates increase with decreasing pK_b values (increasing basicity). However the relationship between decomposition temperature and pK_b does not quite approximate to linearity and the deviation may be attributed to solvent effects since pK_b values are determined in aqueous solution. In the evaluation of σ, the ratio of the ionization constants of substituted and pure benzoic acids is involved and the solvent effects if any, get cancelled out. In this sense σ approximates to the true effect of substituent on the basicity.

In order to ascertain the rate-determining step in the decomposition of these salts, the isothermal decompositions of some typical nitrates were studied employing thermogravimetric analysis. Fractional decomposition α *versus* time plots for typical salts are shown in Figure 3.

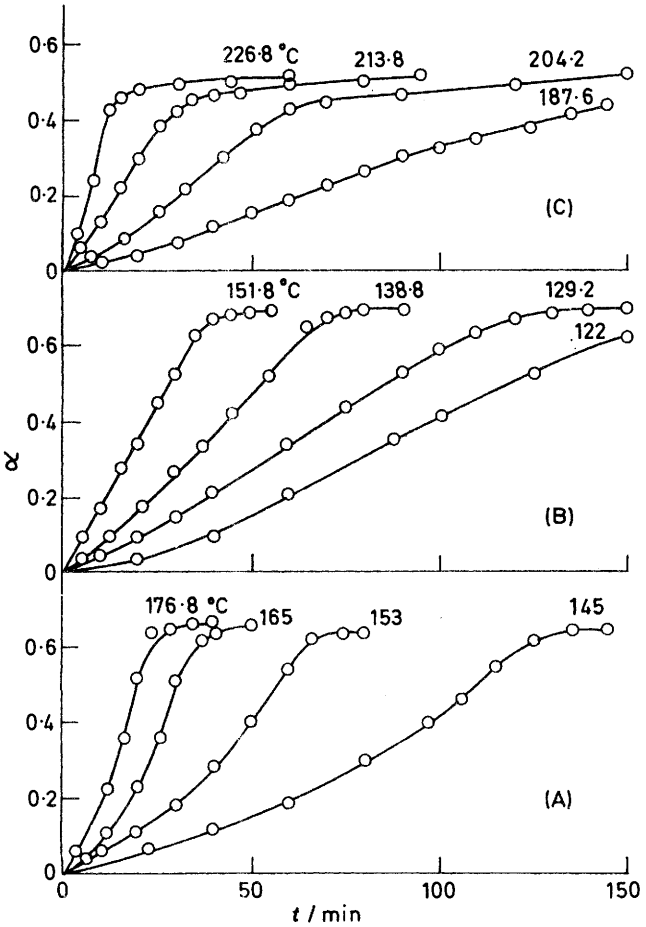


FIGURE 3 Isothermal decomposition curves of: (A) anilinium nitrate, (B) *p*-nitroanilinium nitrate, and (C) *p*-aminoanilinium nitrate

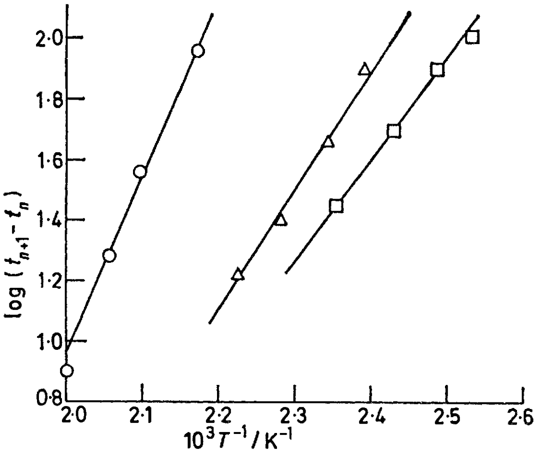


FIGURE 4 log $(t_{n+1} - t_n)$ *versus* $1/T$ plots for anilinium nitrate (△), *p*-nitroanilinium nitrate (□), and *p*-aminoanilinium nitrate (○)

TABLE 3

Kinetic data

Compound	E_a/kcal mol^{-1}	α
$C_6H_5NH_3NO_3$	17.5	0.1—0.5
p-$NO_2C_6H_4NH_3NO_3$	15.2	0.1—0.5
p-$NH_2C_6H_4NH_3NO_3$	26.8	0.1—0.4

The compounds show incomplete weight loss as they are highly fuel rich and a black residue remains. The activation energy for the decomposition has therefore been calculated by the Jacobs–Kureishy method,[18] where the logarithm of time taken for α to go from one value to another *versus* the reciprocal of the absolute temperature is plotted as shown in Figure 4. A very thin layer of sublimate collects on the TG tube during isothermal decomposition showing that even at atmospheric pressure these salts sublime. There may be some uncertainty involved therefore in the calculation of activation energy using weight loss data. Comparison of the activation energies (Table 3) however shows that they increase with the introduction of electron-donating groups into the ring. This suggests that the activation energy corresponds to the basicity of the nitrogen atom and consequently is related to the proton transfer (dissociation process) in these salts. It therefore appears both from decomposition temperatures and activation energy values that the thermal stability of substituted ammonium nitrates is decided by the basicity of the amine.

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