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Studies on (non) energetic compounds (Part 22) — Preparation and thermal decomposition of ring substituted arylammonium fluorides

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Ring substituted arylammonium fluorides (RSAF) have been prepared and characterised. The thermal decomposition of these salts has been investigated by thermoanalytical techniques and kinetic parameters are evaluated. The thermal decomposition pathways have also been proposed.

The proton transfer mechanism has been postulated to play an important role in the thermal decomposition of large number of ammonium salts. Erdey *et al.*[1,2] have investigated twenty six ammonium salts derivatographically and results have been explained by applying acid-base theory. The decomposition processes have also been reported which are on the basis of thermograms. The formation of intermediate has been suggested where plateaux occur on TG curves. The thermal decomposition of NH_4F involve the following reaction pathway.

$$2NH_4F \longrightarrow NH_4F.HF + NH_3$$

The intermediate ammonium hydrogen fluoride begins to decompose slowly at this temperature but decomposition rate is highest at 255°C and NH_3 and HF are reported to be evolved. Therefore, it was thought appropriate to investigate the role of ring–substituted phenyl groups, when substituted for hydrogen atom of ammonium cation.

A lot of work has already been reported on the preparation, characterisation and thermolysis of arylammonium nitrates[3–5], perchlorates[6–8], sulphates[9–12], chlorides[13,14] and bromides[15,16]. These salts have been found to dissociate to parent arylamine and acid molecules [H_2SO_4, HNO_3, $HClO_4$, HCl, HBr] and proton transfer [N–H bond heterolysis] seems to be the primary and rate controlling step. A large number of ring substituted arylammonium fluorides [RSAF]. have been prepared and characterised. Their thermal decomposition has also been investigated using TG and simultaneous TG–DTA in order to understand their mechanism of decomposition.

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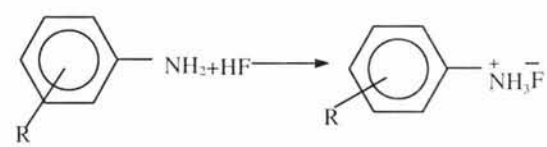
Experimental Procedure

Aniline (Qualigens), *m*–toluidine (Johnson Chemical Limited), *p*–toluidine (BDH), *m*–chloroaniline (CDH), *p*–chloroaniline (CDH), *m*–aminobenzoic acid (Merck), *p*–aminobenzoic acid (SISCO), *m*–nitroaniline (Robert Johnson), *p*–nitroaniline (Johnson Chemical Co.) were purified by usual methods. Hydrofluoric acid (CDH), silica gel G for TLC (Qualigens) were used as received.

Preparation and characterisation of mono ring substituted arylammonium fluorides (RSAF)

RSAF were prepared by reacting corresponding arylamines with hydrofluoric acid in molar ratio 1:1 at 0°C and reaction can be represented as follows :

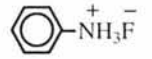
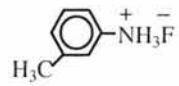
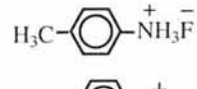
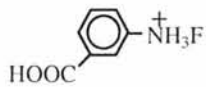
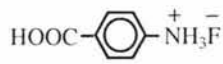
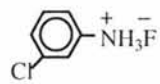
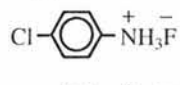
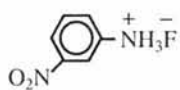
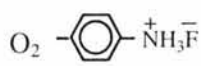


where R = H, *m*–CH_3, *p*–CH_3, *m*–COOH, *p*–COOH, *m*–Cl, *p*–Cl, *m*–NO_2, *p*–NO_2,

[Caution: All the fluorides are reactive toward glass apparatus and hence plastic apparatus should be used.]

Precipitation was obtained when their solutions were super–cooled. The precipitates were washed with petroleum spirit and then recrystallised from water/alcohol mixture. The salts of aniline and *p*–chloroaniline were precipitated out under slightly acidic condition. These salts were dried in an incubator at 40±1°C for 20-25 h. These salts are slightly hygroscopic in nature and hence were subjected to vaccum drying. Purity was checked by TLC and were characterised by elemental, gravimetric and spectroscopic methods.

Table 1 — Structure, physical parameters, TLC, elemental and gravimetric analysis of RSAF

Compd No.	Compound	Structure	Crystal colour	Yield (%)	R_f	pK_a	Elements C%	H%	N%	F%
a	Anilinium fluoride		white	40	0.62	4.60	62.0 (63.7	6.2 7.0	11.3 12.3	14.1 16.8)
b	3–Methylanilinium fluoride		white	64	0.58	4.17	66.3 (66.1	6.4 7.9	10.1 11.0	12.2 14.9)
c	4–Methylanilinium fluoride		white	72	0.65	5.08	66.6 (66.1	6.0 7.9	10.1 11.0	13.2 14.9)
d	3–Carboxylicanilinium fluoride		white	66	0.72	3.07	53.5 (53.5	5.3 5.1	8.6 8.9	11.0 12.1)
e	4–Carboxylicanilinium fluoride		yellow	54	0.75	2.41	53.5 (53.5	4.7 5.1	8.0 8.9	11.0 12.1)
f	3–Chloroanilinium fluoride		white	48	0.54	3.52	47.7 (48.8	3.7 4.7	9.9 9.5	12.0 12.8)
g	4–Chloroanilinium fluoride		white	40	0.51	3.99	47.9 (48.8	4.9 4.7	9.7 9.5	11.1 12.8)
h	3–Nitroanilinium fluoride		white	62	0.62	2.46	46.3 (45.6	4.9 4.4	17.9 17.7	11.1 12.0)
i	4–Nitroanilinium fluoride		yellow	64	0.58	1.01	45.5 (45.6	6.0 4.4	16.2 17.7	11.2 12.0)

Locating reagents – IodineEluents – Hexane: Ethyl acetate : alcohol (2:1:1), R_f – Retention factor, pKa - Acidity constant

Table 2 — IR spectral data of RSAF

Assignments	Absorption frequencies (cm^{-1}) of RSAF a	b	c	d	e	f	g	h	i
Primary amine salt (arom.)	3422	3588	3531	3488	3250	3559	3598	3397	3458
m–substituted	–	680	–	749	–	736	–	810	–
p–substituted	–	–	805	–	840	–	813	–	837
ν(N – H)	1628	1659	1565	1566	1602	1631	1600	1551	1587
δ(N – H)	739	901	870	801	893	782	813	865	837
ν (C – N)	1232	1251	–	1386	1309	1325	1308	1342	1296
ν (C=C)	1612	1492	1608	1632	1623	1513	1469	1615	1627
ν (C–H) in CH_3	–	3019	2913	2942	3151	–	–	3033	3066
δ (C–H) in CH_3	–	2927	3032	–	–	–	–	–	–
ν (C=O, OH) in -COOH	–	–	–	2942 (-OH), 1315(C=O) 2937 (-OH), 1309 (C=O)		–	–	–	–
ν(C–Cl)	–	–	–	–		1089	1097	–	–
ν(C–NO_2)	–	–	–	–	–	–	–	1452	1475

Gravimetric analysis

The fluoride content (%) in all the RSAF salts was estimated gravimetrically[17] as CaF_2 and results are reported in Table 1.

Elemental and spectroscopic analysis

The C, H, N analysis was done with Heraeus carlo Erba 1108 instrument and percentage of each element is given in Table 1. IR was taken on Perkin Elmer 983 DS System using KBr pellets and data is summarised in Table 2.

Thermal decomposition of RSAF

Non isothermal TG

TG studies on RSAF (wt. 30 mg, 200–400 mesh) were undertaken in static air at heating rate of 5°C min^{-1} using indigenously fabricated TG apparatus

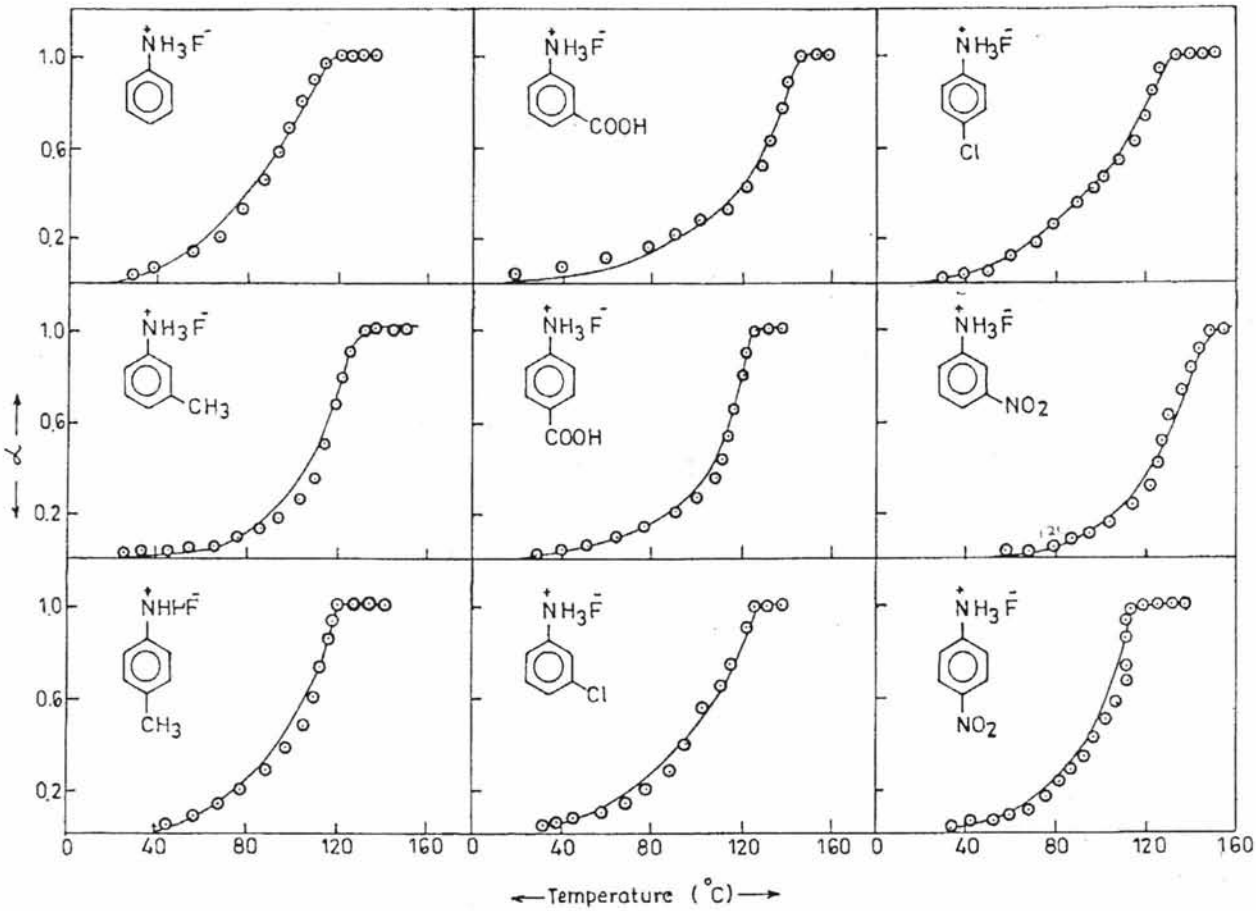


Fig. 1 — Non-isothermal TG thermograms of RSAF.

Table 3 — TG and DTA profile data of RSAF

Compound No.	DTA (N_2) Onset (°C)	DTA (N_2) Peak temperature (°C)	DTA (N_2) Endset (°C)	TG (N_2) Onset (°C)	TG (N_2) Inflection point (°C)	TG (N_2) Endset (°C)	Residue (%)	TG (air) T_f (°C)
a	89.0	126	182	100	154	164	0.31	120
b	149	191	208	162	188	196	10.34	130
c	117	145	164	130	147	150	0.35	120
d	168, 186	173, 232	184, 261	186, 417	228, 450	242, 500	20.50	150
e	186, 210	188, 235	195, 247	108, 195	130, 230	139, 240	18.27	130
f	94	117	140	116	145	147	1.58	130
g	44, 141	62, 182	111, 198	154	179	188	8.82	120
h	110, 182	113, 211	121, 219	183	210	213	3.96	160
i	186, 208	189, 238	196, 253	110, 208	126, 235	135, 244	16.73	110

T_f = Temperature at complete decomposition

fitted with temperature indicator cum controller (Model 8087 Century). A bucket type platinum crucible (h = 10 mm, dia = 10 mm) was used as sample holder. The fractional decomposition (α) versus temperature plots are given in Fig. 1. The endset temperatures T_f noted from Fig. 1 are given in Table 3.

Simultaneous TG–DTA

These studies on RSAF [~3.5 mg, 200-400 mesh] were undertaken in N_2 atmosphere using Mettler Toledo Stare System and plots are given in Fig. 2. The onset, endset, inflection point and peak temperatures from TG–DTA (N_2) thermograms are reported in Table 3.

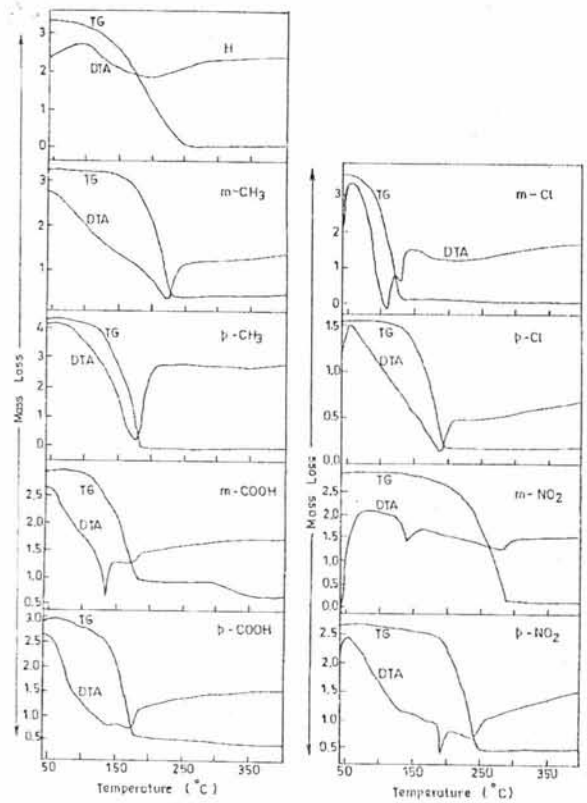


Fig. 2 — Simultaneous TG - DTA thermograms of RSAF.

Isothermal TG

TG on samples of RSAF (30 mg, 200-400 mesh) was carried out in static air with the same apparatus as described above at 80, 90, 100, 110 and 120°C. α versus time (t) plots are reported in Fig. 3.

The kinetic parameters were evaluated by nine mechanism based kinetic models[18-20]. Of these, only contracting area and contracting cube equations (Eqs (1) and (2)) gave the best fits which are reported in Fig. 4 and 5.

$$1-(1-\alpha)^{1/2}=kt \qquad \ldots(1)$$

$$1-(1-\alpha)^{1/3}=kt \qquad \ldots(2)$$

The correlation coefficient values (r) were also evaluated using the relation:

$$\text{Correlation coefficient } (r)=\Sigma xy/\sqrt{(\Sigma x^2)(\Sigma y^2)}$$

where x and y are values at absicissa and ordinates respectively. The calculated values for rate constant (k), activation energy E_a and correlation coefficient (r) are given in Table 4.

Results and Discussion

Elemental, gravimetric, and spectral data reported in Tables 1 and 2 clearly confirms the formation of RSAF. TG and DTA thermograms reported in Fig. 1

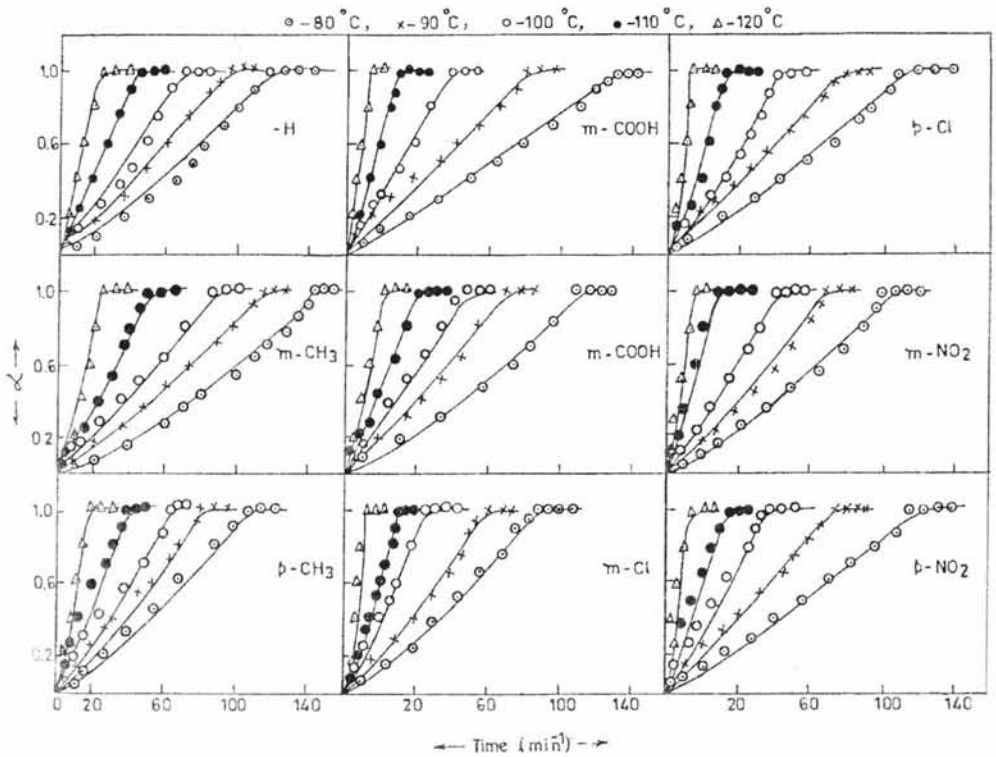


Fig. 3 — Isothermal TG thermograms of RSAF.

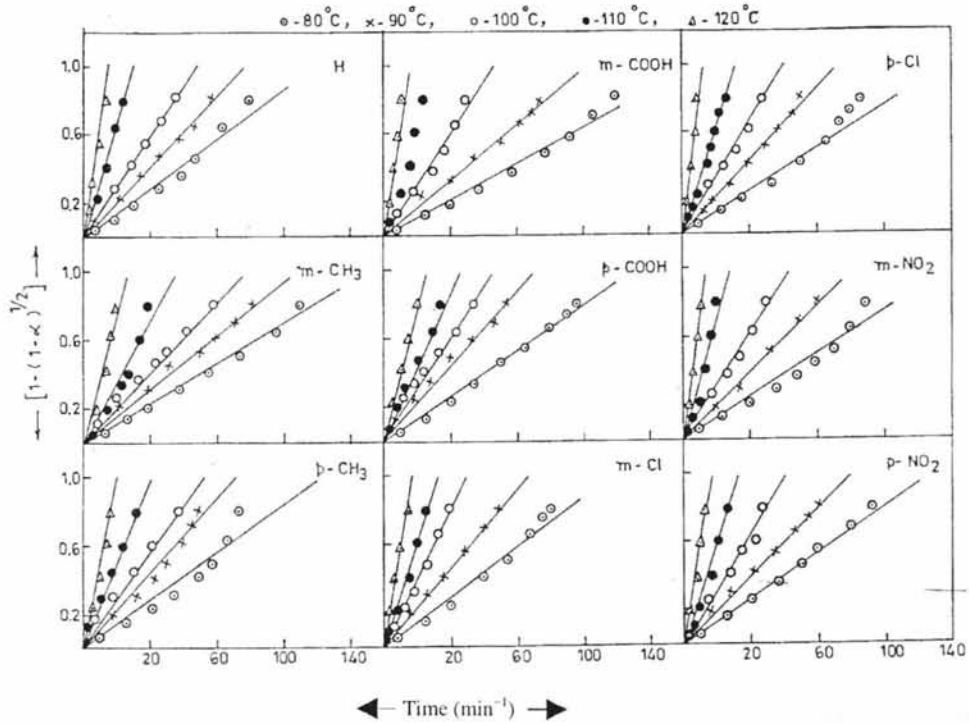


Fig. 4 — Kinetic analysis of RSAF by contracting area ($n = 2$) equation.

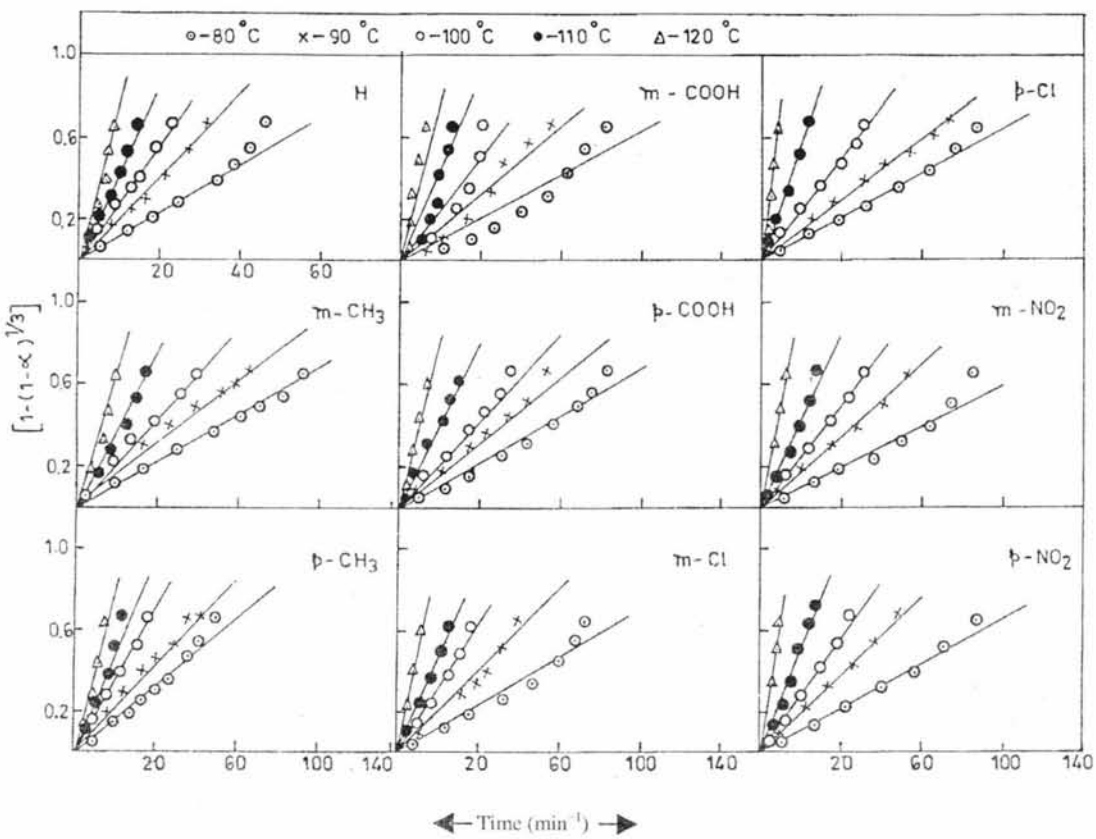


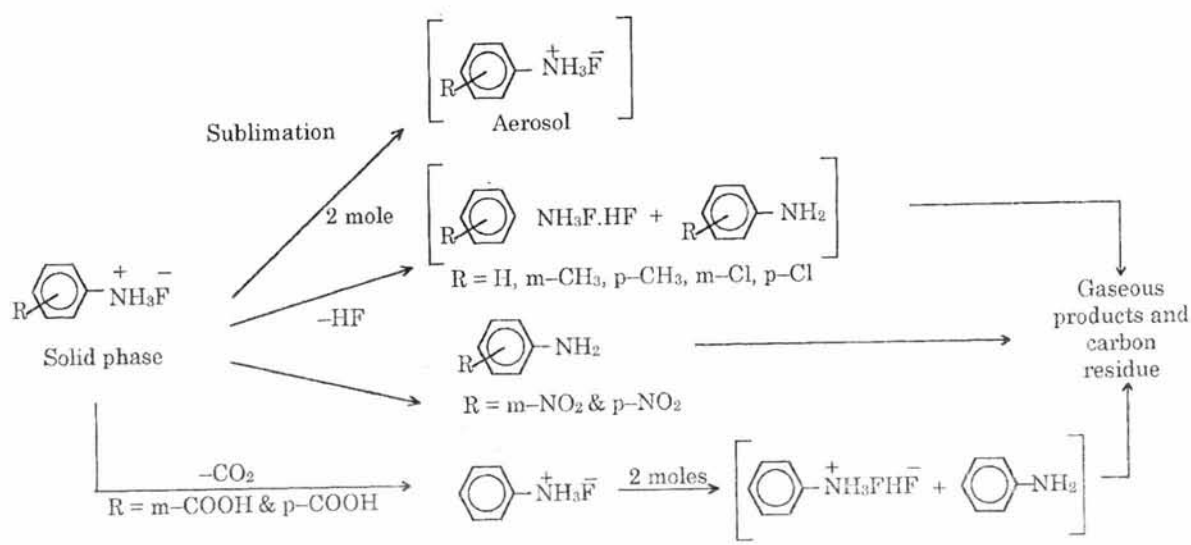
Fig. 5 — Kinetic analysis of RSAF by contracting cube ($n = 3$) equation.

and 2 show that all the salts undergo approximately 100% mass loss in static air and small amount of residue was obtained when TG was run in N_2 atmosphere (Table 3). Lower T_f were also observed when TG was taken in air as compared to N_2 which may be due to the oxidising behaviour of the surrounding (air). Two endotherms were obtained for compound Nos. d, e, g, h and i while only one endotherm was obtained for rest of the salts. The first endotherm may be due to phase transition and second endotherm may involve sublimation, dissociative vaporisation and decomposition processes. It seems that a part of the sample undergo sublimation followed by dissociative vaporisation and decomposition but it is very difficult to isolate these processes. However, sublimation was confirmed by heating the sample in platinum crucible and sublimated amount was collected on another inverted crucible which was confirmed by co-TLC technique. Thus, the thermal decomposition pathways have been reported in Scheme 1. Simultaneous plots reported in Fig. 2 show that compound Nos. a, b, c, f and g decompose via arylammonium hydrogen fluoride formation (similar to NH_4F decomposition) as reported by Erdey *et al.*[2]. HF was found to evolved in case of nitro substituted salts and compounds d and e decomposed via decarboxylation.

Examination of Table 4 shows that kinetic parameters are almost independent of the reaction models. Linear plots were observed when log k and E_a values were plotted against pK_a values of the ring substituted arylammines (RSA) in aqueous solution (Fig. 6). However, no relationship was observed between onset, endset, inflection point and T_f when

Table 4 — Kinetic parameters and correlation coefficients for isothermal decomposition of RSAF

	Contracting area(n=2)							Contracting cube(n=3)						
	Rate constant ($k \times 10^{-3}$)min^{-1} at Temp (K)					r	E_a	Rate constant ($k \times 10^{-3}$) min^{-1} at Temp (K)					r	E_a
Compd No.	(353)	(363)	(373)	(383)	(393)		(kJ mol^{-1})	(353)	(363)	(373)	(383)	(393)		(kJ mol^{-1})
a	5.0	8.0	10.0	16.0	75.0	0.9539	63	11.0	22.0	30.0	44.0	83.0	0.9919	49
b	6.0	10.0	13.0	20.0	40.0	0.9238	78	3.0	8.0	11.0	20.0	28.0	0.9863	72
c	10.0	16.0	30.0	60.0	150.0	0.9902	61	8.0	11.0	16.0	20.0	40.0	0.9858	39
d	13.0	22.0	40.0	50.0	170.0	0.9844	91	10.0	16.0	36.0	40.0	100.0	0.9868	79
e	17.0	23.0	40.0	80.0	100.0	0.9672	76	14.0	15.0	20.0	40.0	100.0	0.9630	70
f	12.5	22.0	30.0	70.0	200.0	0.9914	57	12.0	20.0	40.0	50.0	120.0	0.9747	103
g	10.0	26.0	30.0	80.0	200.0	0.9739	95	13.0	15.0	26.0	57.0	200.0	0.9736	83
h	10.0	28.0	30.0	70.0	150.0	0.9277	91	10.0	16.0	20.0	40.0	100.0	0.9751	71
i	13.0	24.0	36.0	72.0	140.0	1.0000	81	17.0	20.0	22.0	37.0	133.0	0.9379	68



Scheme 1 — Thermal decomposition path ways of RSAF

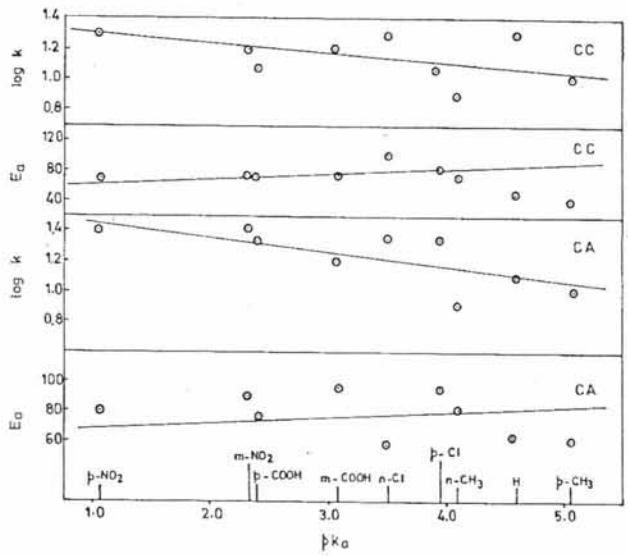


Fig. 6 — Plots of pK_a verses (i) activation energy (E_a) and log k for contracting area ($n=2$) equation and (ii) activation energy (E_a) and log k for contracting cube ($n=3$) equation.

plotted against pK_a which show that the proton transfer reaction does not seem to involve during the thermal decomposition of fluoride salts.

Acknowledgements

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