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Thermochimica Acta 338 (1999) 45–55

thermochimica acta

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Studies on (non) energetic compounds. Part-14: Thermal decomposition of dimethylanilinium chlorides

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Received 9 November 1998; accepted 17 June 1999

Abstract

Six dimethylanilinium chlorides (DMACl) have been prepared and characterised. Thermal decomposition of these salts have been studied by TG and DSC techniques. Kinetic parameters have been evaluated from the isothermal and non-isothermal TG data, Contracting area, Contracting cube and Coats–Redfern equations have been found to give the best fits. The decomposition pathways have also been suggested. It has been observed that simultaneous sublimation/decomposition processes are involved during the thermal decomposition of DMACl.

Keywords: Thermal decomposition; Dimethylanilinium chloride; (Non) energetic compounds

1. Introduction

It has been reported in our earlier papers [1,2] that ring substituted arylammonium chlorides (RSACl) are formed when arylamines are treated with 20% hydrochloric acid in 1 : 1 molar ratio at room temperature. The thermal decomposition of RSACl involves simultaneous sublimation/decomposition processes. It is a general accepted fact that ammonium salts undergo thermolysis via proton transfer process [3].

In the present communication, the preparation, characterisation and thermal decomposition of dimethylanilinium chlorides (DMACl) are described. Thermoanalytical techniques provide the important measure of the overall kinetic of thermally-induced reactions, which reveal the mechanism of solid state decomposition reactions. Thus the decomposition of DMACl has been investigated using TG and DSC techniques. The kinetic parameters have been evaluated using mechanism and non-invoking mechanism models. Contracting area, Contracting cube and Coats–Redfern equations have been found to provide the best fits.The decomposition pathways have also been proposed.

2. Experimental

Materials: The following LR grade arylamines obtained from sources, given in parenthesis were purified by usual methods.

2,3-Dimethylaniline (Lancester), 2,4-dimethylaniline (Merck), 2,5-dimethylaniline (Merck), 2,6-dimethylaniline (Lancester), 3,4-dimethylaniline (Merck), 3,5-dimethylaniline (Lancester), hydrochloric acid (Qualigens), silica gel G (Qualigens).

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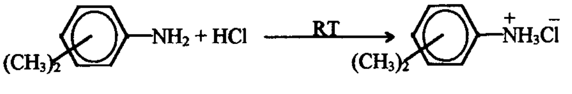
PII: S0040-6031(99)00191-4

2.1. Preparation and characterisation of dimethylanilinium chlorides (DMACl)

The chlorides of dimethylanilines were prepared by reacting 20% aqueous hydrochloric acid with corresponding dimethylaniline in 1 : 1 molar ratio at room temperature and the reaction can be represented as follows:



where $(CH_3)_2$ = 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-

Instant precipitation was obtained in all the cases except 3,4-dimethylanilinium chloride which precipitated out under cold condition.These salts were washed with petroleum spirit twice and recrystallised from aqueous solution and crystals were vaccum dried. Purity was checked by TLC, and these were characterised by elemental and gravimetric analyses. Their structures and physical parameters are presented in Table 1.

2.2. Gravimetric analysis

200 mg of each salt was dissolved in 150 ml of water and 0.5 ml of conc. HNO_3 was added. Thereafter $AgNO_3$ was added till precipitation was complete as given below:

The precipitates were filtered off in sinterred crucible, washed with ice cold water and dried in hot air oven. Percentage of chlorine is presented in Table 1.

2.3. Thermal decomposition of DMACl

Thermal decomposition of DMACl was investigated using following techniques:

1. *Non-isothermal TG*: TG studies on DMACl (wt 30 mg, 200–400 mesh) were undertaken in static air at heating rate of 5°C min^{-1} using indigeneously fabricated TG apparatus [4] fitted with temperature indicator cum controller (Model CT-808T century) and bucket type platinum crucible (H = 10 mm, dia = 10 mm) was used as sample holder. The fraction decomposed (α) versus temperature plots are given in Fig. 1. The temperature (T_f) for complete decomposition of these salts have been noted from Fig. 1 and data is reported in Table 2.
2. *Isothermal TG*: TG on DMACl samples (30 mg, 200–400 mesh) was carried out in static air with the same apparatus [4] at 140°C, 150°C, 160°C and 170 °C and (α) versus time (t) plots are reported in Fig. 2.
3. *DSC*: DSC studies (wt.∼2 mg, 200–400 mesh) were undertaken in nitrogen atmosphere (flow rate = 45 ml min^{-1}) using Mettler TA 4000. Weighed samples (Sartorivs – Weske Type 2405, Electrobalance, Germany) were sealed with sample sealer. A pin hole was made at the top of the lid so that gaseous products can escape during decomposition. The sample and the reference pans were positioned at the centre of the cell holder and were covered with aluminium domes. The thermograms (Fig. 3) were recorded at heating rate of 10°C min^{-1} using Hewlett-Packard 7475A plotter. The initial temperature (T_i) at start of decomposition, endothermic peak temperatures and corresponding (ΔH) are given in Table 2.

2.4. Kinetic analysis

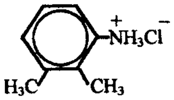
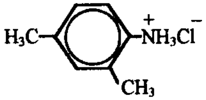
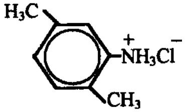
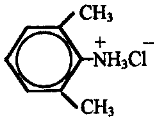
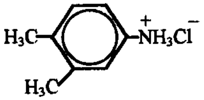
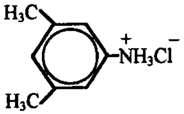
The kinetics of decomposition of DMACl have been evaluated by both isothermal and non-isothermal TG data. The former data has been fitted in the nine mechanism based models. Only Contracting area and Contracting cube equations [1,2] have been found to give the best fits (Figs. 4 and 5) and Arrhenius parameter (α = 0.1–1.0) are reported in Table 3.

$$1-(1-\alpha)^{1/2} = k_1 t, \tag{1}$$

$$1-(1-\alpha)^{1/3} = k_2 t. \tag{2}$$

The overall activation energy E_a was also estimated from non-isothermal TG data fitted in Coats–Redfern

Table 1
Structure, physical parameters, TLC, elemental and gravimetric analyses of DMACl

Sl. No.	Compound	Structure	Yield (%)	MP/decomposition (Temperature (°C))	Crystal colour	R_{f}[a]	Elemental and gravimetric analyses[b](%)				$\mathrm{p}K_{\mathrm{a}}$
							C (60.95)[b]	H (7.61)[b]	N (8.88)[b]	Cl (22.53)[b]	
(a)	2,3-dimethylanilinium chloride		72	180	White crystals	0.52	60.34	7.73	8.46	21.50	4.70
(b)	2,4-dimethylanilinium chloride		81	166 (d)	Brick needle like crystals	0.63	60.08	8.80	8.25	21.05	4.89
(c)	2,5-dimethylanilinium chloride		80	140	White amorphous	0.62	60.04	7.91	8.07	22.48	4.53
(d)	2,6-dimethylanilinium chloride		76	160 (d)	Grey crystals	0.72	60.00	7.10	8.41	22.00	3.95
(e)	3,4-dimethylanilinium chloride		72	172	White crystals	0.53	60.76	8.13	7.85	22.20	5.17
(f)	3,5-dimethylanilinium chloride		84	480	White crystal	0.58	61.33	7.03	8.02	22.20	4.77

[a] Locating reagent – iodine, eluents – hexane:ethyl acetate:DMSO (3 : 6 : 3).

[b] Calculated values are given in parenthesis.

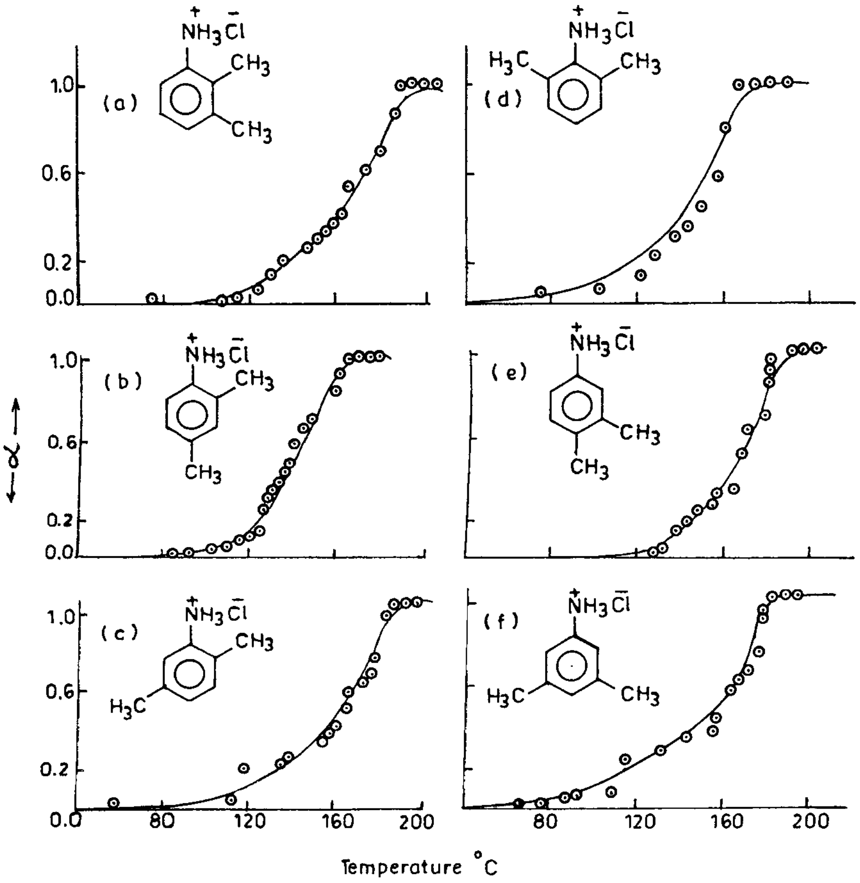


Fig. 1. Non-isothermal TG thermograms of DMACl.

Table 2
TG and DSC profile data on DMACl

Compound	TG (T_f[a], °C)	DSC		
		T_i[b] (°C)	Endothermic peak temperature (°C)	ΔH J/g
(a)	190	130	203	1347
(b)	165	55	198	1361
(c)	186	140	208	1308
(d)	165	100	67	311
			198	1391
(e)	180	130	66	84
			201	1264
(f)	180	120	217	1407

[a] T_f – final temperature at complete decomposition.

[b] T_i – initial temperature at start of decomposition.

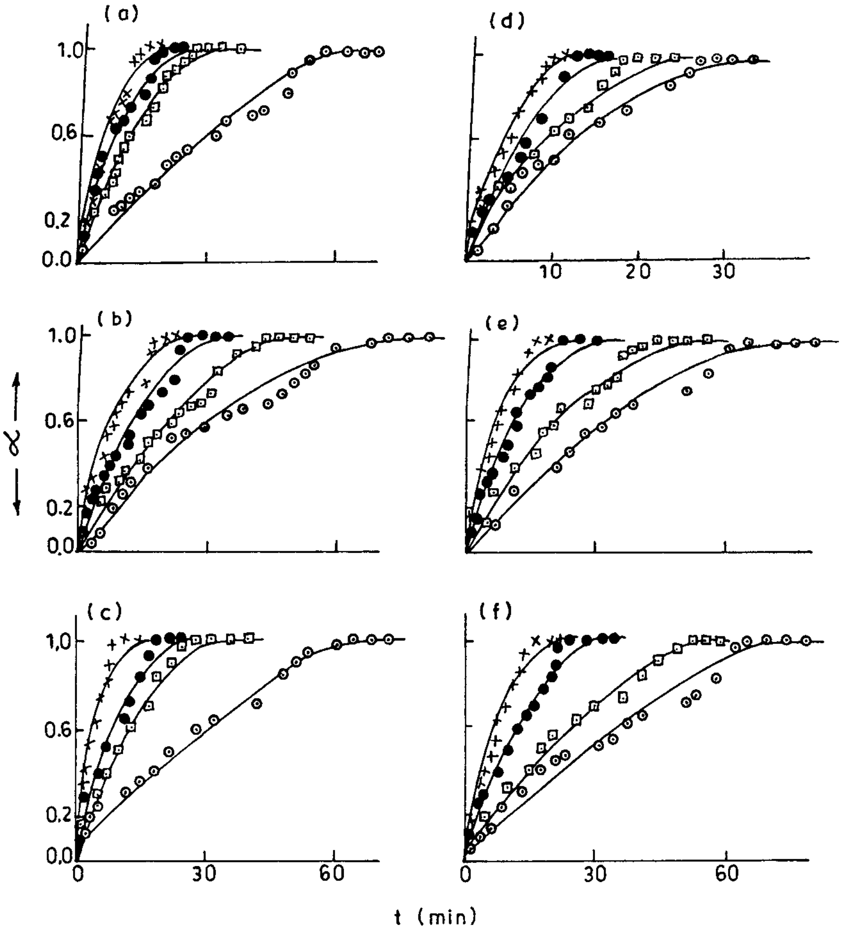


Fig. 2. Isothermal TG thermograms of DMACl.

[5] (CR), MacCallum–Tanner [6] (MCT) and Madhusudanan–Krishnan–Ninan [7] (MKN) Eqs. (3)–(5):

$$\ln\left[\frac{g\alpha}{T^2}\right] = \ln\left[\frac{AR}{\phi E_a}\left(1-\frac{2RT}{E_a}\right)\right]-\frac{E_a}{RT}, \qquad (3)$$

$$\log g(\alpha) = \log\left(\frac{AE_a}{\phi R}\right)-0.485E_a^{0.435} - \frac{(0.449+0.217E_a)\times 10^3}{T}, \qquad (4)$$

$$\ln\left[\frac{g(\alpha)}{T^{1.9219}}\right] = \ln\left(\frac{AE_a}{\phi R}\right)+3.7721-1.9215\ln E_a - \frac{0.12039}{T}E_a, \qquad (5)$$

where α is the fraction decomposition, n the order parameter, T the temperature in K, A the pre-exponential factor, E_a the activation energy (global/overall), R the gas constant and ϕ is the heating rate. E_a for thermolysis ($\alpha = 0.2$–1.0) of DMACl has been estimated from linear plots of LHS of Eqs. (3)–(5) against $1/T$ taking $n = 0$, 1/2, 2/3 and 1 and the results are reported in Table 4. CR equation was found to give the best fits. The fitting of Eqs. (1)–(5) has also been checked using following relation:

$$\text{Correlation coefficient} = \frac{\sum xy}{\sqrt{\sum x^2y^2}},$$

where x and y are values at abcissa and ordinate, respectively. The r values for each equation have

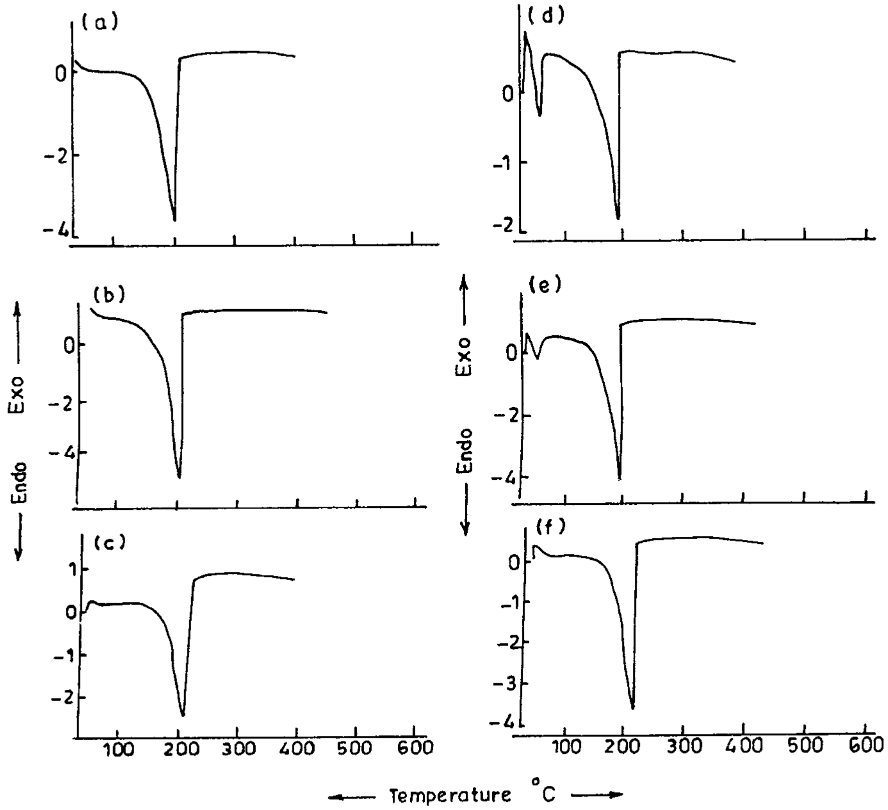


Fig. 3. DSC thermograms of DMACl.

been evaluated and results are reported in Tables 3 and 4.

3. Discussion

Elemental, gravimetric and other physical parameters reported in Table 1 clearly indicate the formation of DMACl. TG and DSC plots given in Figs. 1–3 and profile analysis data summerised in Table 2, show the decomposition behaviour of all these salts. Decomposition up to 100% was observed in all the salts. 2,4- and 2,6-DMACl have lowest decomposition temperature (165°C) and 2,3-DMACl has the highest decomposition temperature (190°C). DSC data show endotherms at various temperatures which may be due to melting, phase transitions, sublimation and decomposition processes. Sublimation (vapourisation) has also been confirmed at about 100°C for all of these salts. This shows that sublimation dominates at lower temperatures and simultaneous sublimation/decomposition take place at higher temperatures to form gaseous products.

Examination of Table 3 show that Arrhenius parameters determined for isothermal data using various equations are almost independent of the reaction models. Contracting area and Contracting cube equations provide the best fits. These two models describe quite similar mechanism and practically identical pair of Arrhenius parameters are obtained (Table 3). Therefore model fitting method works quite well in this case. In contrast, the E_a values obtained using CR, MCT, MKN equations (non-isothermal decomposition of DMACl) are highly variable. This may be due to the fact that most of the solid decomposition reactions involve multiple and parallel steps with different activation energies. The temperature ranges for isothermal (140–170°C) and non-isother-

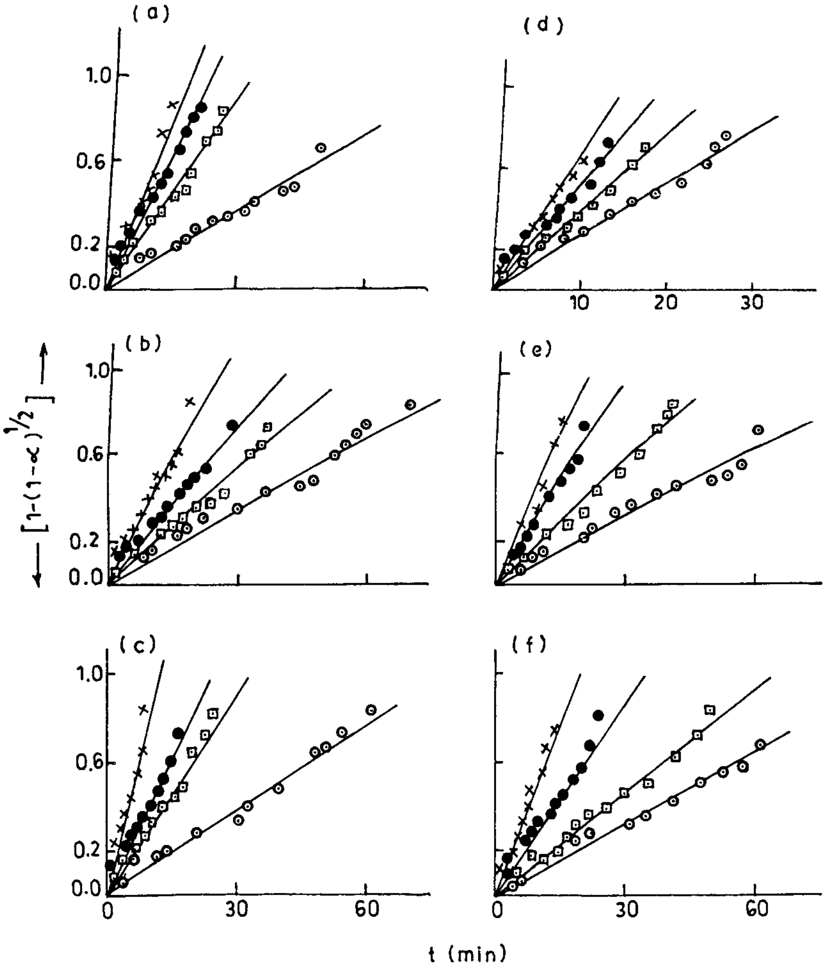


Fig. 4. Kinetic analysis of DMACl by Contracting area (n=2) equation.

mal (65–190°C) are also different. Inspite of these, E_a values (Table 4) obtained from CR equation are quite comparable with the E_a value obtained from isothermal TG data reported in Table 3. Linear plots are obtained when log k, E_a and T_i were plotted against pK_a (Fig. 6) which clearly shows that the increase in the acidity of arylamines causes a decrease in rate constants. Consequently, E_a would show opposite trend. However, T_i does not seem to depend upon pK_a values. Thus proton transfer process seems to be the rate controlling step for thermolysis of DMACl. Such behaviour for various ammonium and substituted ammonium salts have also been discussed in our earlier review [3].Thus it appears, as a general trend, that the thermal stability of chloride salts is enhanced by electron donating substituents. However, ortho and hyperconjugative effects are also involved which controls the thermal decomposition reactions to same extent. Since DMACl are structurally analogous to dimethylanilinium nitrates (DMAN), dimethylanilinium perchlorates and dimethylanilinium hydrogen sulphates (DMAHS) and hence their decomposition may also be controlled by proton transfer as reported earlier [8–10]. Since these salts undergo sublimation at lower temperatures and hence their thermal decomposition pathways can be suggested (Scheme 1), where $(CH_3)_2$=2,3-; 2,4-; 2,5-; 2,6-; 3,4-; 3,5-.

Table 3
Arrhenius parameters and correlation coefficient for isothermal decomposition of DMACl

Compound	Contracting area ($n = 2$) equation, rate constant ($k_1 \times 10^{-3}$ min^{-1})(temperature (K))				r	E_a (kJ mol^{-1})	ln(A) $\times 10^{-1}$	Contracting cube (n=3) equation, rate constant ($k_2 \times 10^{-3}$ min^{-1}) (temperature (K))				r	E_a (kJ mol^{-1})	ln(A) $\times 10^{-1}$
	(413)	(423)	(433)	(443)				(413)	(423)	(433)	(443)			
(a)	13.33	33.33	48.00	60.00	0.9583	76.20	4.0	10.85	26.66	38.46	60.00	0.9856	76.20	2.0
(b)	11.42	36.36	48.00	50.00	0.9468	79.97	4.0	10.00	13.33	20.00	33.30	0.9868	62.80	1.0
(c)	11.76	30.30	80.00	85.70	1.0000	100.90	8.0	12.00	21.10	32.00	80.00	0.9785	72.43	5.0
(d)	26.66	44.44	55.55	66.66	0.9752	46.47	2.8	20.86	34.00	42.00	60.60	0.9898	56.94	2.0
(e)	10.81	21.05	35.71	50.00	0.9941	72.43	2.0	8.00	20.00	25.71	48.00	0.9771	66.57	1.6
(f)	11.66	16.00	33.00	50.00	0.9884	76.20	3.0	7.00	12.00	21.00	36.36	0.9983	62.80	1.0

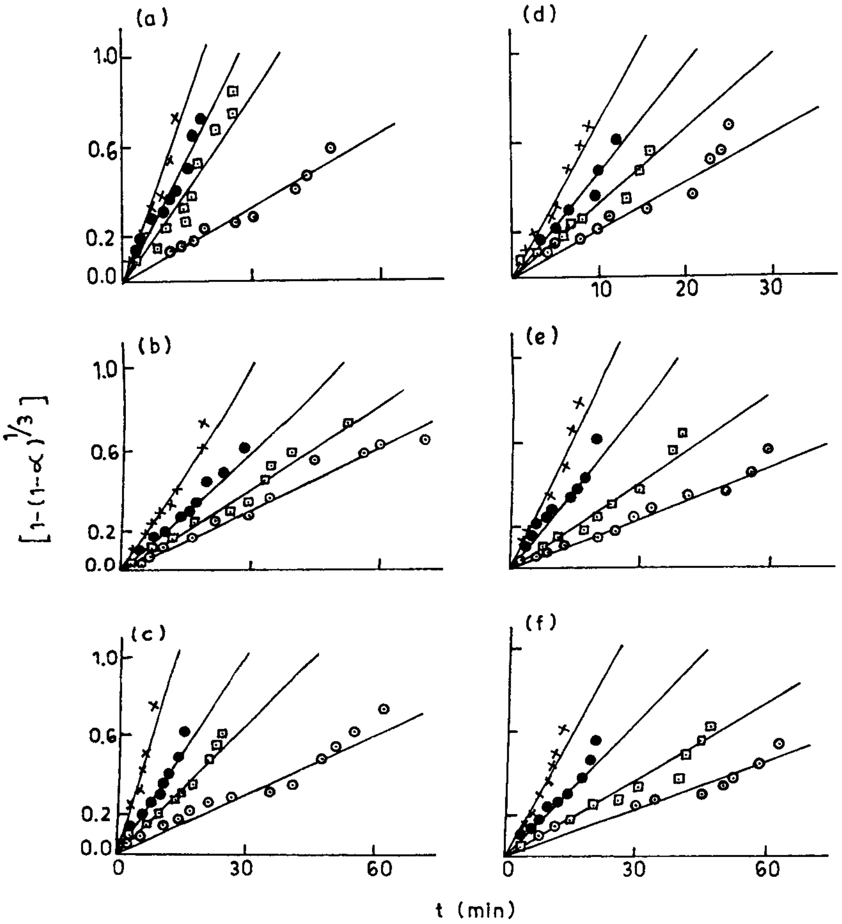
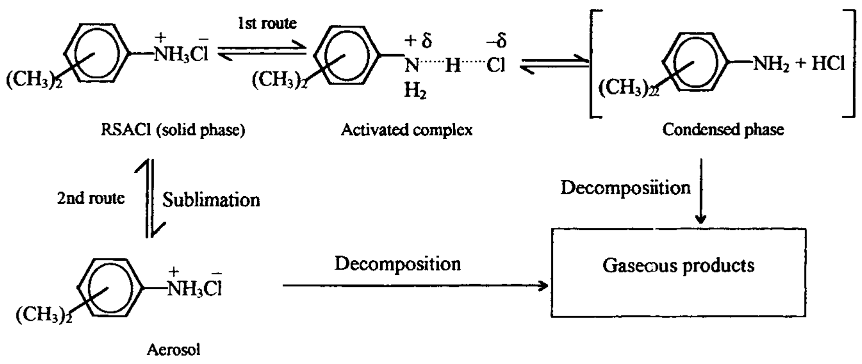


Fig. 5. Kinetic analysis of DMACl by Contracting cube (n=3) equation.



$(CH_3)_2$ = 2,3–; 2,4–; 2,5–; 2,6–; 3,4–; 3,5 –

Scheme 1.

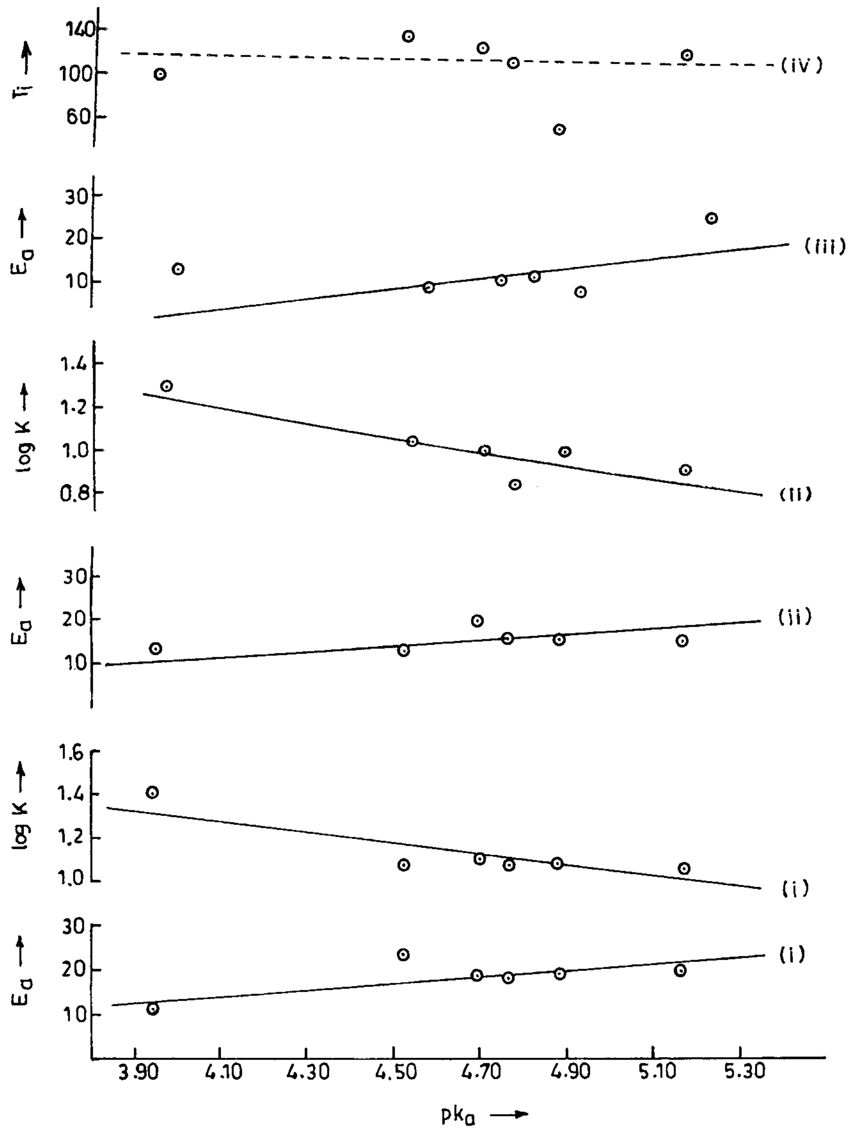


Fig. 6. Plots of log k, E_a and T_i versus pK_a; (i) log k_1(T = 413 K), E_a from Eq. (1); (ii) log k_2(T = 413 K), E_a from Eq. (2); (iii) E_a from Eq. (3); (CR); (iv) T_i from DSC thermograms.

Thus the overall decomposition process seems to commence by proton transfer through an activated complex from dimethyl arylammonium ion to chloride ion forming amine and HCl molecules in the condensed phase followed by the formation of gaseous products. In route 2, DMACl sublime (vapourise) prior to decomposition into the gaseous products. Summarising the results, it may be concluded that simultaneous decomposition/sublimation processes are involved during thermolysis of DMACl.

Acknowledgements

Thanks are due to DST, New Delhi for financial assistance, RSIC, Nagpur for DSC studies; RSIC,

Table 4
Kinetic parameters for non-isothermal decomposition of DMACl using CR, MKN and MCT equations

Compound	n=0		n=1		n=1/2		n=2/3	
	E_a (kJ mol^{-1})	r	E_a (kJ mol^{-1})	r	E_a (kJ mol^{-1})	r	E_a (kJ mol^{-1})	r
Coats–Redfern equation								
(a)	57.36	0.9987[a]	87.09	0.9393	71.18	0.9717	59.45	0.9373
(b)	51.50	0.9932[a]	96.30	0.9382	141.10	0.9788	119.32	0.9753
(c)	47.73	0.9904[a]	95.46	0.9226	76.20	0.9649	52.75	0.9493
(d)	52.75	0.9414	67.41	0.9224	58.62	0.9901[a]	61.96	0.9413
(e)	126.44	0.9181	143.19	0.9352	88.76	0.9557	119.32	0.9481
(f)	55.68	0.9900[a]	95.46	0.9726	58.62	0.9945[a]	71.59	0.9797
Madhusudanan–Krishnan–Ninan equation								
(a)	164.96	0.9962[a]	300.19	0.9900[a]	267.12	0.9932[a]	259.16	0.9900[a]
(b)	280.52	0.9947[a]	800.52	0.8251	640.58	0.9900[a]	512.46	0.9773
(c)	121.84	0.9577	330.34	0.9143	200.13	0.9479	231.95	0.9370
(d)	164.12	0.9761	239.48	0.9079	191.34	0.9367	200.13	0.9314
(e)	184.64	0.9630	280.10	0.9370	293.08	0.9900[a]	457.20	0.9713
(f)	200.13	0.9955[a]	380.16	0.9070	500.32	0.8991	571.50	0.8080
MacCallum–Tanner equation								
(a)	28.89	0.9968[a]	36.43	0.9559	25.96	0.9904[a]	28.89	0.9927[a]
(b)	29.73	0.8601	72.01	0.8217	37.68	0.9374	51.50	0.8560
(c)	25.54	0.9941[a]	25.54	0.9830	30.56	0.9975[a]	29.31	0.9977[a]
(d)	20.52	0.9618	10.05	0.8019	28.05	0.9495	28.89	0.9078
(e)	33.91	0.9588	42.29	0.9066	39.77	0.9535	38.52	0.9569
(f)	24.28	0.9807	27.21	0.9808	31.40	0.9780	33.91	0.9598

[a] One of the best statistically equivalent model.

Chandigarh for microanalysis, Head of Chemistry Department, DDU Gorakhpur University for laboratory and library facilities.

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