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STUDIES ON (NON) ENERGETIC COMPOUNDS
Part 38. Kinetics of thermolysis of dichloroanilinium bromide salts

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Five salts of dichloroanilinium bromide (DCABr) were prepared and characterized by elemental and spectral studies. The thermal decomposition of DCABr was studied by using TG-DTG-DTA techniques and the results are discussed here. Kinetic parameters with the help of model fitting and isoconversional methods have been evaluated critically. A mechanism of decomposition has also been suggested.

Keywords: *characterisation, dichloroanilinium bromide, isoconversional method, proton transfer, thermolysis*

Introduction

Alkyl and arylammonium halides have been reported as phase-transfer catalysts [1] and corrosion-inhibitors for mild steel [2] in H_2SO_4. Erdey and coworkers [3–5] have investigated the thermal decomposition of various ammonium salts and the results have been explained on the basis of acid – base theory. Sublimation/vaporization is also involved during the decomposition of ammonium halides [6].

Singh *et al*. [7–15] reported a lot of work on the thermolysis of various ring-substituted anilinium sulfates (RSAS) [7, 8], hydrogen sulfates (RSAHS) [9], nitrates (RSAN) [10] and perchlorates (RSAP) [11]. The thermolyses of ring-substituted anilinium chlorides (RSACl) [12], fluorides (RSAF) [13] and bromides (RSABr) [14,15] have been studied and proton transfer was generally found to be the primary step during thermolysis with some exception [13]. A study of various dimethylanilinium bromides (DMABr) showed that the acidity of the dimethyl anilines causes a decrease in the rate of decomposition [15]. It is evident that a correlation exists between the proton transfer equilibrium and the relative stabilities of the DMABr. In the light of these findings, thermal decomposition studies on dichloroanilinium bromides (DCABr) have been found to be more interesting because the chloro group is deactivating in nature.

The kinetics of a homogeneous reaction are generally characterised by a rate equation and a single set of Arrhenius parameters (kinetic triplet). Solid-state reactions are heterogeneous in nature but Arrhenius-type of behaviour is still assumed. Various rate equations, based on models of heterogeneous processes, have been developed over the years [16]. Attempts to obtain a complete kinetic triplet from experiments using a single heating rate, yielded non-reliable data that led to strong criticism of solid-state reaction kinetics [17, 18]. The Kinetic Committee formed by ICTAC recently suggested the use of isoconversional type of methods that yield the activation energy as a function of extent of conversion. We have attempted comparison of model-fitting methods and a model-free isoconversional method in describing the thermolysis of energetic materials [19], transition metal complexes [20] and aryl ammonium hydrogen sulfate [9]. These studies revealed that the use of isoconversional methods helps to reveal the complexity of thermolysis in the solid state.

The kinetic parameters have been evaluated using mechanism based kinetic fitting and isoconversional methods and the results are presented in the present communication.

Experimental

Materials

2,3; 2,4; 2,5; 2,6 and 3,4-dichloroaniline (DCA, E-Merck) were purified by distillation and/or recrystallisation, conc. H_2SO_4 (E-Merck), silica gel TLC grade (Qualigens) and silver nitrate were used as received.

Preparation of DCABr

2,3-DCA instantly gave a white precipitate with 20% HBr, but 2,4; 2,5 and 3,4-DCA gave white precipitates

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when saturated solutions of the corresponding amines in absolute alcohol reacted with HBr. 2,6-DCA reacted with HBr only in the molten state. All these salts were washed with ethyl acetate and recrystallised with methanol. The purity was checked by thin-layer chromatography (TLC) and their corresponding retention factors (R_f) are reported in Table 1, along with the physical parameters, microanalysis, Fourier transform infrared spectroscopy (FTIR) and fast-atom bombardment (FAB) mass spectral analysis.

Thermolysis of DCABr

The thermal decompositions of the salts were investigated as follows:

Simultaneous TG-DTG-DTA studies

Simultaneous TG-DTG-DTA studies on 100–200 mesh powder samples of the salts (heating rate ~5°C min^{-1}) were undertaken in N_2 atmosphere. The resulting curves are given in Fig. 1 and data are summarized in Table 2.

Non-isothermal TG and DTA in static air

Non-isothermal TG on these salts was undertaken at a heating rate of 5°C min^{-1} using home-made TG-apparatus [21] under static air. The curves are given in Fig. 2 and the data are summarized in Table 3. DTA analysis of the samples was carried out in flowing air (60 mL min^{-1}) atmosphere at a heating rate of 10°C min^{-1}, using a DTA apparatus (Universal Thermal Analysis Instrument, Mumbai). Sample mass was taken as 30 mg for each run. All corresponding curves are given in Fig. 3 and the data are given in Table 3.

Isothermal TG studies

Isothermal TG curves of all the salts (mass 30 mg, 100–200 mesh) were carried out in static air at appropriate temperatures using home-made TG apparatus and extent of conversion (α) *vs.* time plots are reported in Fig. 4.

Kinetic analysis of isothermal TG data

Kinetics of thermal decomposition of DCABr have evaluated with the help of mechanism-based kinetic models and isoconversional method.

Mechanism-based kinetic models

The most recent compendium of the reaction models are given by Galwey and Brown [16]. The basic equation of solid-state kinetics is:

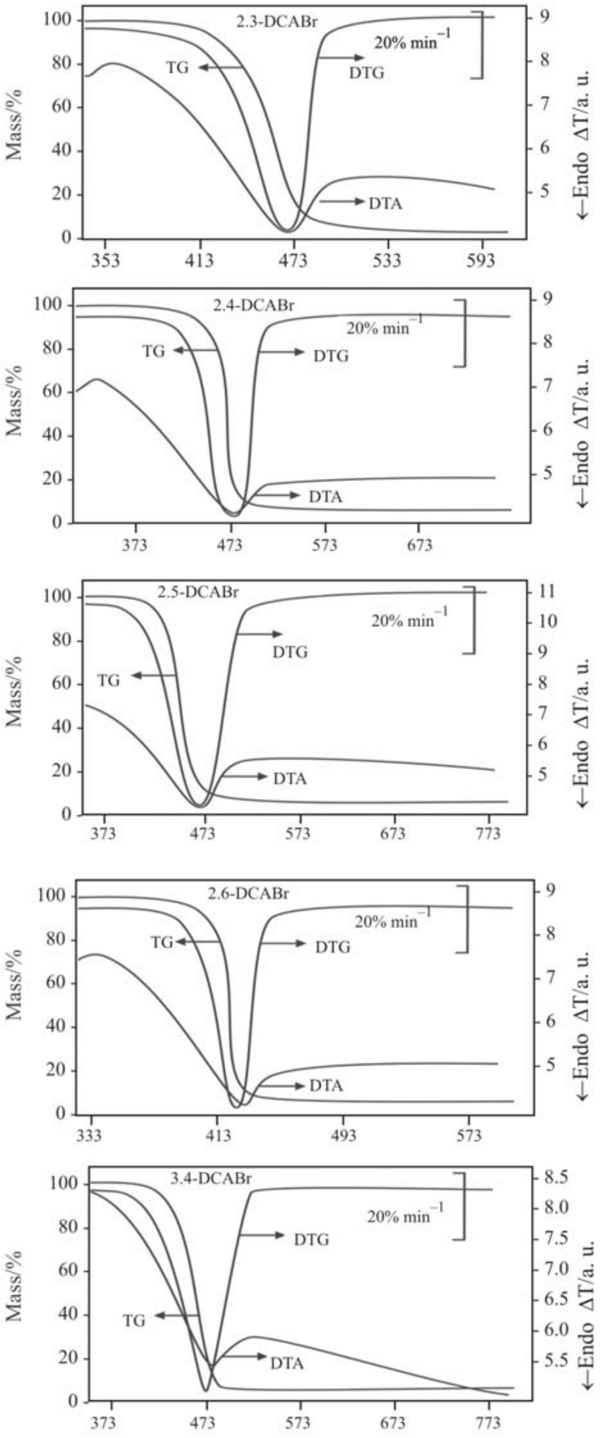


Fig. 1 Simultaneous TG-DTG-DTA curves of DCABr salts in N_2 atmosphere

$$g(\alpha)=\int_0^\alpha d\alpha/f(\alpha)=k(T)t \qquad (1)$$

where t represents time, T is absolute temperature, $k\,(T)$ is the temperature dependent rate constant and $f(\alpha)$ is the reaction model, $g(\alpha)$ is the integrated form of the reac-

Table 1 Physical parameters, TLC, elemental and spectral data of DCABr salts

Name of compound	Crystal structure	R_f*	m.p./d/ K	Elemental analysis/%				m/z Relative abundance	IR frequency/cm^{-1}
				C (29.63)	H (2.50)	N (7.05)	Br (32.92)		
2,3-DCABr	Cubic shaped single crystal	0.85 1.5:0.5:0.5 a:b:c	393 (d)	29.81	2.54	6.48	33.77	154(100%), 136(90%), 120(20%), 107(32%),	3436(prim.aminesalt),2818;υ(C–H,1926(Disubstituted), 1618;υ(N–H),1697; υ(C=C),1194; υ(C– N),870;δ(N–H)
2,4-DCABr	White amorphous	0.9 1.5:0.5:0.5 a:b:c	508 (d)	29.87	2.51	6.35	30.22	154(100%), 137(100%), 120(25%), 107(60%),	3448(prim.aminesalt),2824;υ(C–H,1928(Disubstituted), 1637;υ(N–H),1686; υ(C=C),1210; υ(C–N),868;δ(N–H)
2,5-DCABr	Single crystal of rectangle shape	0.65 1.5:0.5:0.5 a:b:c	483 (d)	29.59	2.45	6.27	31.11	154(100%), 136(100%), 120(15%) 107(32%),	3436(prim.aminesalt),2771;υ(C–H,1660(Disubstituted), 1753;υ(N–H),1697; υ(C=C),1208; υ(C–N),878;δ(N–H)
2,6-DCABr	Small needles	0.69 1.5:0.5:0.5 a:b:c	433 (d)	29.90	2.38	6.09	29.90	157(100%), 137(100%), 120(20%) 107(45%),	3431(prim.aminesalt),2768;υ(C–H,1947(Disubstituted), 1624;υ(N–H),1686; υ(C=C),1208; υ(C–N),868;δ(N–H)
3,4-DCABr	Pink amorphous	0.75 1.5:0.5:0.5 a:b:c	503 (d)	29.69	2.55	6.27	30.46	157(100%), 154(70%), 137(100%), 120(15%) 107(40%),	3448(prim.aminesalt),2824;υ(C–H,1928(Disubstituted), 1637;υ(N–H),1686; υ(C=C),1206; υ(C–N),868;δ(N–H)

R_f = Retention factor, m.p.=melting point, d = decomposition temperature, m/z = mass to charge ratio of the ion

* Eluent, a (ethylacetate), b (acetic acid), c (methanol), Locating reagent – iodine

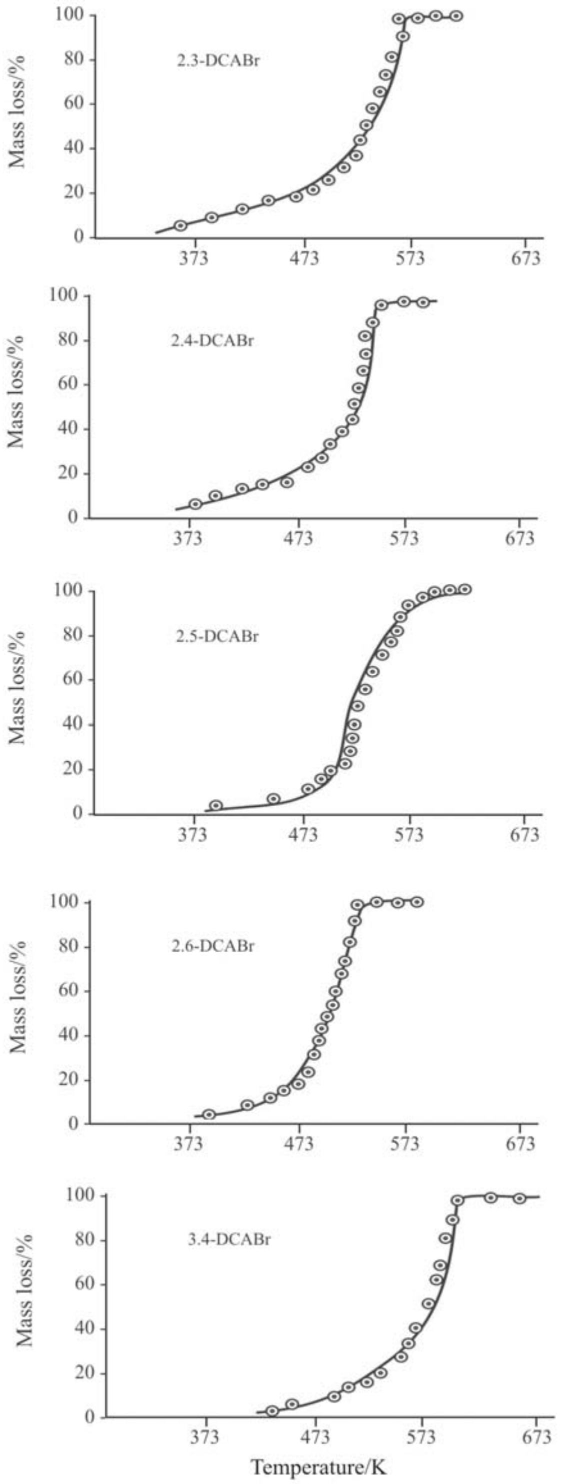


Fig. 2 TG curves of DCABr salts in static air

tion model. Substituting a particular reaction model into Eq. (1) results in evaluating the corresponding rate constant, which is found from the slope of the plot of $g(\alpha)$ *vs.* t. For each reaction model [16, 22–24] selected, the rate constants are evaluated at several temperatures and the Arrhenius parameters are obtained from logarithmic form of Arrhenius equation.

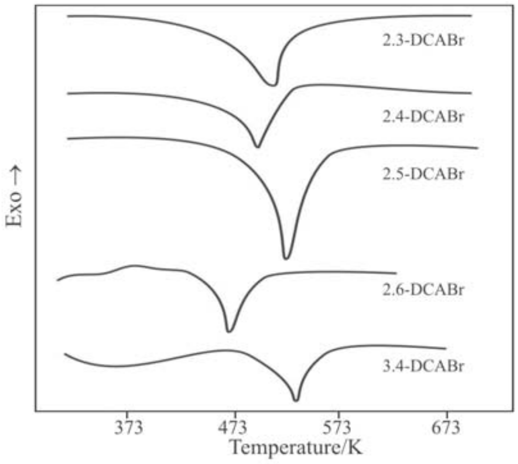


Fig. 3 DTA curves of DCABr in static air

$$\ln k(T) = \ln A - E/RT \qquad (2)$$

For all five DCABr salts, kinetic parameters are obtained from isothermal TG data and are given in Table 5–9.

Model free isoconversional method

Recently Vyazovkin [25, 26] has described an advanced isoconversional method. This method is based on the assumption that the reaction model, $g(\alpha)$ is independent of the heating program. Under isothermal conditions, we may combine Eqs (1) and (2) to get:

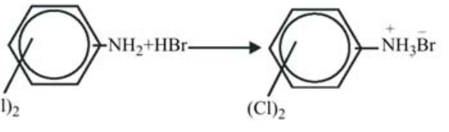
$$-\ln t_{\alpha,i} = \ln[A/g(\alpha)] - E_\alpha/RT \qquad (3)$$

where E_α is evaluated from the slope of the plot of $-\ln t_{\alpha,\mathrm{i}}$ *vs.* T_i^{-1}. Thus values of E_α for each salt were evaluated at various α_i. The dependencies of activation energy (E_α) on extent of conversion are given in Fig. 5.

Results and discussion

Results of micro and gravimetric analysis (Table 1) clearly confirmed the formation of DCABr salts. The reaction may be represented by Scheme 1.

As can be seen from the thermoanalytical data (Tables 2, 3 and Figs 1, 2) the decompositions of all these salts take place in single endothermic steps in nearly same range of temperature, except 2,6-DCABr, which decomposes at lower temperature. The mass loss approaches to completion (>95%) for all these



Scheme 1 Formation of DCABr salts

Table 2 Non-isothermal TG and DTA data profile of DCABr salts in N_2 atmosphere

Compound	TG-DTG				DTA	
	T_i/K	T_s/K	T_f/K	Mass loss/%	Peak temperature Endo/K	Peak area T/K^2
2,3-DCABr	444	473	492	1.66	475	691
2,4-DCABr	430	461	482	5.27	466	258
2,5-DCABr	425	463	486	4.48	468	933
2,6-DCABr	400	429	451	2.79	432	641
3,4-DCABr	443	481	499	5.57	483	107

T_i – onset temperature, T_s – inflection temperature and T_f – endset temperature

Table 3 Non-isothermal TG and DTA data profile of DCABr salts in air atmosphere

Compound	TG data			DTA peak temperature Endo/K
	SDT	FDT	Mass loss/%	
2,3-DCABr	350	568	99	506
2,4-DCABr	368	541	96	498
2,5-DCABr	389	559	95	525
2,6-DCABr	379	513	99	464
3,4-DCABr	425	594	94	531

SDT= Starting decomposition temperature, FDT= Final decomposition temperature

Table 4 Various mechanisms based kinetic models generally used to describe thermal decomposition of solids

S. No.	Model	$f(\alpha)$	g(α)
1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	$(2/3)\alpha^{-1/2}$	$\alpha^{3/2}$
5	one-dimensional diffusion	$(1/2)\alpha^{-1}$	α^2
6	Manpel (first order)	$1-\alpha$	$-\ln(1-\alpha)$
7	Avrami-Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
8	Avrami-Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9	Avrami-Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
10	Contracting sphere	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
11	Three-dimensional diffusion	$2(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$	$3/4[1-(1-\alpha)^{1/3}]^2$
12	Conctracting cylinder	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13	Prout-Tomkins	$\alpha(1-\alpha)$	$\ln(\alpha/1-\alpha)$
14	Ginstling-Brounshtein	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$	$[1-(2\alpha/3)]-(1-\alpha)^{2/3}$

samples. All DTA peaks fall in between the range of 466 to 483 K. Beside these, 2,6-DCABr having the endotherm at 432 K has comparatively low value. In the air atmosphere, all DTA peak temperatures also follow the same trend. Among all the salts, 2,6-DCABr has shown the peculiar behaviour may be due to the steric hindrance and ortho-ortho position of the chloride group. Thus the thermal stability of the salts as indicated by TG, decreases in the order:

$$3,4 > 2,3\text{-} > 2,4\text{-} \approx 2,5\text{-} > 2,6\text{-}$$

It also recorded that the endothermic peak temperature in DTA decreases in the same order.

During DTA runs under a flowing air atmosphere we observed white deposits near the lower and relatively colder region of the glass tube, covering the sample and thermocouples. The deposits gave the same R_f values as the parent compounds on TLC analysis. This indicates that sublimation takes place dur-

Table 5 Kinetic parameters for isothermal decomposition of 2,3-DCABr salts from mechanism based kinetic models

Model*	E_α/kJ mol^{-1}	Ln(A/min)	$-r$
1	87	17.60	0.9933
2	87	17.73	0.9933
3	87	17.84	0.9935
4	84	17.47	0.9942
5	83	17.19	0.9946
6	77	17.24	0.9972
7	83	17.14	0.9950
8	82	17.24	0.9928
9	81	17.29	0.9980
10	82	16.49	0.9954
11	78	15.16	0.9969
12	83	16.98	0.9948
13	81	18.59	0.9960
14	80	15.14	0.9958

*Enumeration of models is as given in Table 4

Table 6 Kinetic parameters for isothermal decomposition of 2,4-DCABr salts from mechanism based kinetic models

Model*	E_α/kJ mol^{-1}	Ln(A/min)	$-r$
1	76	14.83	0.9801
2	76	15.01	0.9804
3	76	15.21	0.9810
4	75	15.32	0.9840
5	74	15.24	0.9850
6	73	15.58	0.9889
7	75	15.24	0.9844
8	75	15.48	0.9851
9	75	15.81	0.9863
10	74	14.83	0.9859
11	74	14.29	0.9887
12	73	15.06	0.9848
13	75	17.22	0.9864
14	74	13.73	0.9871

*Enumeration of models is as given in Table 4

Table 7 Kinetic parameters for isothermal decomposition of 2,5-DCABr salts from mechanism based kinetic models

Model*	E_α/kJ mol^{-1}	Ln(A/min)	$-r$
1	78	15.02	0.9986
2	78	15.18	0.9986
3	78	15.34	0.9987
4	76	15.26	0.9989
5	75	15.10	0.9990
6	73	16.16	0.9987
7	76	15.09	0.9984
8	75	15.29	0.9988
9	74	15.55	0.9988
10	75	14.61	0.9990
11	73	13.86	0.9989
12	75	14.91	0.9990
13	74	16.94	0.9987
14	74	13.42	0.9991

*Enumeration of models is as given in Table 4

Table 8 Kinetic parameters for isothermal decomposition of 2,6-DCABr salts from mechanism based kinetic models

Model*	E_α/kJ mol^{-1}	Ln(A/min)	$-r$
1	73	16.06	0.9919
2	72	15.32	0.9901
3	73	16.01	0.9900
4	71	15.00	0.9920
5	72	15.89	0.9923
6	72	15.58	0.9903
7	72	15.06	0.9905
8	73	16.08	0.9914
9	73	16.01	0.9912
10	73	16.29	0.9918
11	72	15.32	0.9913
112	73	16.67	0.9920
13	72	15.85	0.9907
14	73	16.03	0.9909

*Enumeration of models is as given in Table 4

ing heating. However sublimation is not the only process occurring during heating because some carbonaceous residues are left behind in the crucible. Thus the sublimation observed may be dissociative in nature. It seems that sublimation takes place initially and as the temperature rises, oxidative decomposition also takes place in the condensed state [14, 15]. In order to confirm the sublimation process further, we have recorded DTA thermograms under vacuum and the curves for 2,3-DCABr are given as a representative (Fig. 6). Shifting of the onset temperature for the endothermic peaks showed that sublimation occurs predominantly under the favourable condition of vacuum. In our earlier studies on RSABr salts it has been proposed that proton transfer takes place initially and thus the parent amine and HBr are formed in the condensed phase. We have recorded DTA curves of mixtures of the salt (~30 mg) and the corresponding

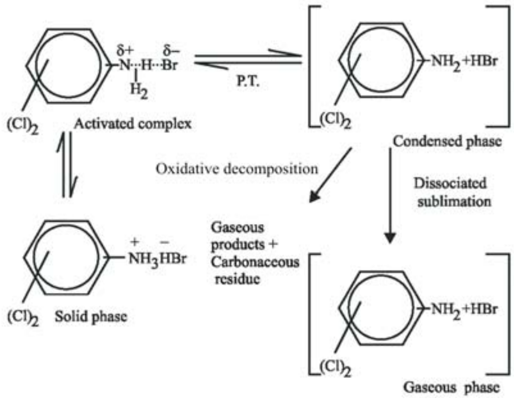
Table 9 Kinetic parameters for isothermal decomposition of 2,4-DCABr salts from mechanism based kinetic models

Model*	E_α/kJ mol^{-1}	Ln(A/min)	$-r$
1	116.40	21.69	0.9929
2	116.04	21.81	0.9929
3	115.35	21.90	0.9928
4	111.94	21.50	0.9925
5	110.96	21.21	0.9923
6	103.97	21.41	0.9975
7	111.13	21.22	0.9915
8	96.29	17.99	0.9999
9	108.58	21.39	0.9906
10	19.36	20.57	0.9915
11	105.11	19.33	0.9896
12	110.78	21.03	0.9921
13	108.16	22.70	0.9898
14	107.88	19.24	0.9915

*Enumeration of models is as given in Table 4

arylamine (~10 mg) under flowing air atmosphere at a heating rate of 10 K min^{-1}. The DTA curves of 2,3-DCABr and 2,3-DCA mixtures are shown in Fig. 6 as representative of all other mixtures. We observed that the onset temperature for the endothermic process shifts to higher temperature when parent arylamine is present. This supports our argument based on a proton transfer mechanism [27, 28] and subsequent dissociative-sublimation. Thus the overall thermal decomposition process may be summarized as shown in Scheme 2.

The model fitting-methods gave almost the same value of activation energy (E_a) for each salt irrespective of the model used (Tables 4–9). Thus for 2,3-; 2,4-; 2,5-; 2,6- and 3,4-DCABr, the average values of the activation energy were ~ 83, 75, 75, 72 and 109 kJ mol^{-1}, respectively.



Scheme 2 Thermal decomposition pathway of DCABr (P.T. – Proton transfer)

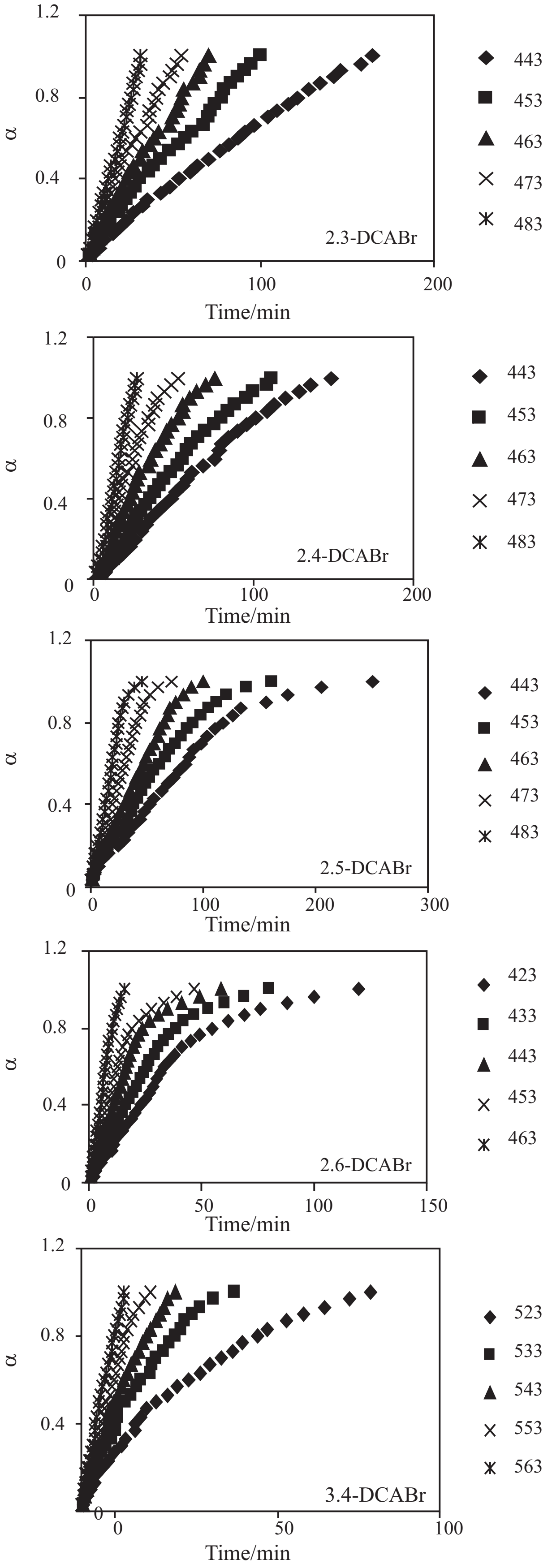


Fig. 4 Isothermal TG of DCABr salts in static air

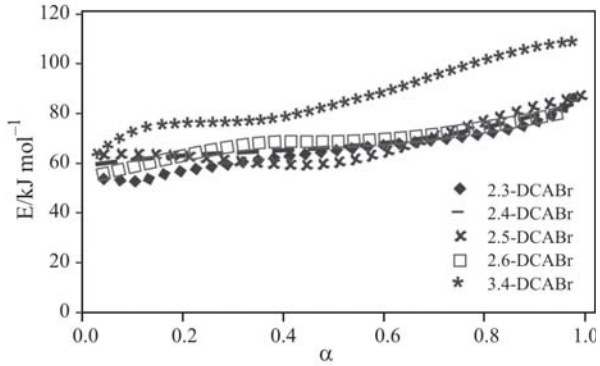


Fig. 5 Dependencies of E_α on extent of conversion (α) of DCABr salts

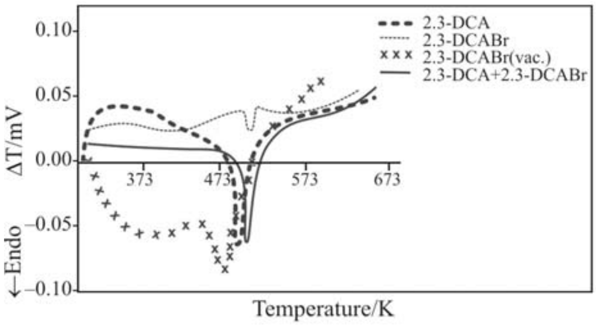


Fig. 6 DTA curves of 2,3-DCABr under different conditions

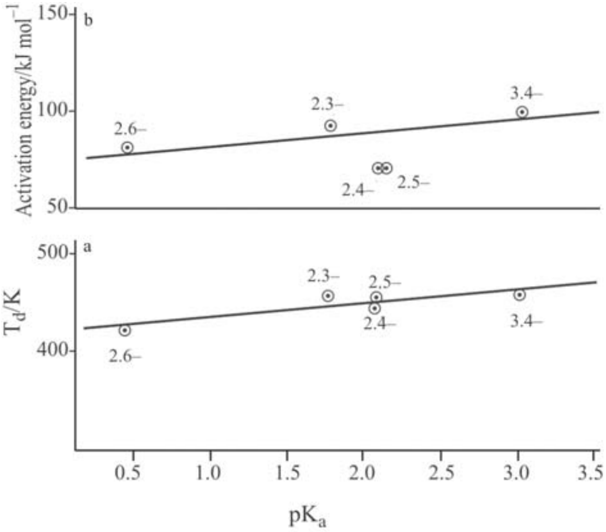


Fig. 7 a – T_d (K) *vs.* pK_a plot for DCABr; b – activation energy (kJ mol^{-1}) *vs.* pK_a plot for DCABr

The acid dissociation constant (pK_a) values [29, 30] shown linear plots *vs.* average activation energy and decomposition temperature (T_d) which are given in Fig. 7a and b. Low pK_a (higher acidity) of the amine cause easy removal of the proton from $-NH_3^+$ and, consequently, T_d (°C) will be lowered. All these factors clearly indicate that thermal stability of the bromide salts depend upon pK_a value of the corresponding amine.

However it is not possible to attribute the average activation energy values to any physical or chemical processes because the statistical parameter '*r*' has similar values for all the various models. Thus, for conventional method of deriving mechanism of thermolysis from the model, giving best statistical fit to the experimental data, fails here. Moreover as discussed earlier, it is evident from our thermal analysis, that there are multiple competing reaction pathways during the course of thermolysis. As the various models may represent the experimental data mathematically, support for mechanistic conclusions of thermoanalytical data is not provided by the kinetic parameters obtained from model fitting.

The isoconversional method used shows that the activation energy varies with the extent of conversion (Fig. 5). Values of E_α increase with increase in extent of conversion for all of the five salts. For 2,3-; 2,4-; 2,5-; 2,6- and 3,4-DCABr, E_α=61, 57, 60, 48 and 64 kJ mol^{-1} at lowest α, which increases to E_α=86, 90, 85, 74 and 113 kJ mol^{-1} at α=1 respectively. 3,4-DCABr gave the highest and 2,6-DCABr gave the lowest value of E_α at lowest and highest α. This may be attributed to the low pK_a value, more steric hinderence and (–I) of the chloride groups (both –Cl groups are ortho-ortho to $-^+NH_3$) for 2,6-DCABr which weakens the N–H bond better than 3,4-DCABr (in this both chloride groups are meta and para positions to $-^+NH_3$). Thus the variation in E_α supports the results of our thermal analysis. We have suggested initial dissociative sublimation followed by oxidative decomposition as the mechanism of thermolysis (Scheme 2). However as E_α is steadily increasing (Fig. 5), it is more likely that sublimation and decomposition are competitively occurring, in the condensed phase [12, 14, 15]. However it is reasonable to think that the value of E_α at the initial stage of reaction corresponds to sublimation. As the reaction progresses, contribution from decomposition process having higher activation energy increases and hence the observed steady increment of E_α. The value of activation energy obtained from conventional model fitting method and value of E_α at *a*=1, for each salt are nearly the same.

Conclusions

The kinetic parameters and decomposition temperatures for the thermal decomposition of DCABr have been found to be related pK_a of arylamines. Thermal decomposition of DCABr occurs principally by dissociation into HBr and the corresponding dichloroaniline. The regenerated parent compounds may then further go into vapour phase (dissociative sublimation) and/or undergo oxidative decomposition in the condensed phase. Conventional model fitting approach fails to describe any change in the mechanism of isothermal decomposition of these salts. Isoconversional analysis shows that activation energy is slightly dependent on the extent of conversion and as the reaction progresses, E_α increases steadily for all the salts. Thus the mechanisms of two competing reaction pathways suggested by thermal analysis get support from the kinetic parameters derived from isoconversional method.

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