



Sulfonation of arylamines

Part 14. Kinetics of thermolysis of dichloroanilinium hydrogensulfate salts

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Abstract

Three dichloroanilinium hydrogensulfate (DCAHS) and two dichloroanilinium sulfate salts were formed while treating corresponding amines with excess amount of conc. sulfuric acid. These DCAHS salts were characterized by elemental analysis and spectral data. Thermolysis of these salts has been studied by using various thermo-analytical techniques under different conditions. All the salts on heating produce corresponding dichloroaminobenzene sulfonic acids (DCABSA) as intermediate product, which on further heating decomposes into gaseous products. The DCABSA were isolated and characterized by elemental and spectral analyses. Conventional model fitting methods and a model free isoconversional method were used to evaluate kinetic parameters for isothermal TG data and an attempt has been made to compare merits and demerits of both ways of kinetic approaches. The thermal decomposition pathway has also been suggested for DCAHS salts via solid-state sulfonation involving proton transfer as primary step.

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1. Introduction

Sulfonation of arylamines has been conventionally achieved by 'baking process' [1–4], more recently by microwave heating [5,6] which involves multi-step reactions and use of organic solvents [2,3,7]. The aminobenzene sulfonic acid (ABSA) is usually obtained after heating the intermediate compound [8] at high temperatures for very long periods [2,3]. Singh and Kapoor [9] have introduced a simple, easy, convenient, and direct process named, 'solid-state

sulfonation'. In this process, sulfate [9,10] or hydrogensulfate [11] salts of arylamines are subjected to thermal energy to get the corresponding ABSA. ABSAs have wide range of applications [12,13] in the field of organic synthesis, dyestuffs, sulfa drugs, detergents and tanneries. Extensive studies have been made on the solid-state sulfonation and a large number of ring substituted (mono- and di-) arylammonium sulfates (RSASs) [10,11,14–17] having electron-donating or demanding substituents were prepared, characterized and their thermal decomposition was investigated using various thermo-analytical techniques. Some substituted anilinium hydrogensulfate [11] salts were also prepared and their thermolysis has been undertaken. Proton transfer process

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[18,19] was proposed to be the primary step, which is followed by sulfonation in the condensed phase. A few sulfate salts [20] and hydrogensulfate salts [11] were not found to give corresponding ABSA during solid-state sulfonation. In comparison to sulfate salts, study on thermal decomposition and kinetics of the ring substituted aniliniumhydrogen sulfate salts are inadequate. So the basis of present investigation is to study the thermal decomposition of dichloroanilinium hydrogensulfate (DCAHS) salts using various thermo-analytical techniques.

In our earlier studies, the kinetics of thermolysis of different salts were analyzed using conventional model fitting methods [21,22]. The conventional model fitting methods yield a single value of activation energy and frequency factor. Thus the conventional method over simplifies the complex multi-step reactions during solid-state thermal decomposition. Recently, use of model free isoconversional methods [23–25], which yield activation energy as a function of temperature as well as extent of conversion has been suggested [26] to have a realistic kinetic description of the solid-state thermal decomposition reactions. Such a kinetic analysis has never been attempted in the case of thermal decomposition of sulfate or hydrogensulfate salts. Hence in the present study, we have evaluated kinetic parameters using both conventional method as well as a model free isoconversional [27] method.

2. Experimental

2.1. Materials

2,3-, 2,4-, 2,5-, 2,6- and 3,4-dichloroanilines (DCA, E. Merck, LR grade) were purified by distillation and recrystallization methods. Conc. H_2SO_4 , silica gel TLC grade (Qualigens) and barium chloride were used as received.

2.2. Preparation and characterization of dichloroanilinium hydrogensulfate (DCAHS) salts

In all cases, white salts were obtained by mixing the DCA with excess conc. sulfuric acid and pouring the reaction mixture on ice cubes. The precipitates were washed with ethyl acetate and recrystallized with methanol.

The purity was checked by HPLC (DATA LAB 3103 UV-Vis detector with a 3101 pump and Alltech Econosil C-18 5U column (250 mm \times 4.60 mm)) and all the compounds were found to be more than 98% pure. Thin layer chromatography (TLC) analyses were performed and retention factor (R_f) values are reported in Table 1 along with physical parameters and results of microanalysis. Fourier transform infrared spectroscopy (FTIR, KBr pellets) and fast atom bombardment (FAB) mass spectral analyses [28] are also summarized in Table 1.

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

Name of compound	Crystal structure	R_f^a	mp/d (K)	Elemental analysis			m/z	IR frequency
				C (%)	H (%)	N (%)		
2,3-DCAHS·4H ₂ O	White amorphous	0.567 a:b:c	448 (d)	21.88 (21.69)	4.80 (4.52)	3.25 (4.22)	161, 137, 99	3350, 2900 ν (C–H), 1450 ν (N–H), 700 ν (C–Cl), 600 ν (HSO ₄ [–])
2,4-DCAHS·2H ₂ O	White solid	0.431 a:b:c	413 (d)	24.55 (24.32)	5.58 (5.06)	3.26 (4.73)	162, 154, 137	3370, 2950 ν (C–H), 1540 ν (N–H), 700 ν (C–Cl), 610 ν (HSO ₄ [–])
2,6-DCAHS	White needle	0.555 a:b:c	443	27.60 (27.69)	2.69 (2.69)	5.30 (5.38)	161, 137, 99	3400, 2950 ν (C–H), 1450 ν (N–H), 760 ν (C–Cl), 600 ν (HSO ₄ [–])
2,3-DCABSA	Light brown needles	0.66 c:b:d	>523 (d)	28.75 (29.75)	2.71 (2.06)	5.27 (5.78)	–	1390 ν (C–Cl), 1636 ν (N–H), 1190 ν (C–N), 1029 ν (C–SO ₃ H)
2,4-DCABSA	Light orange needles	0.56 c:b:d	>523 (d)	27.13 (29.75)	2.57 (2.06)	5.25 (5.78)	–	1392 ν (C–Cl), 1615 ν (N–H), 1175 ν (C–N), 1038 ν (C–SO ₃ H)
2,6-DCABSA	Dirty white amorphous	0.46 c:b:d	>523 (d)	29.31 (29.75)	2.00 (2.06)	5.12 (5.78)	–	1397 ν (C–Cl), 1616 ν (N–H), 1180 ν (C–N), 1053 ν (C–SO ₃ H)

R_f , retention factor; mp, melting point; d, decomposition temperature; m/z , mass of the ion.

^a Eluent, ethylacetate (a), acetic acid (b), chloroform (c), methanol (d), locating reagent, iodine; a:b:c = c:b:d = 1.5:0.5:0.5.

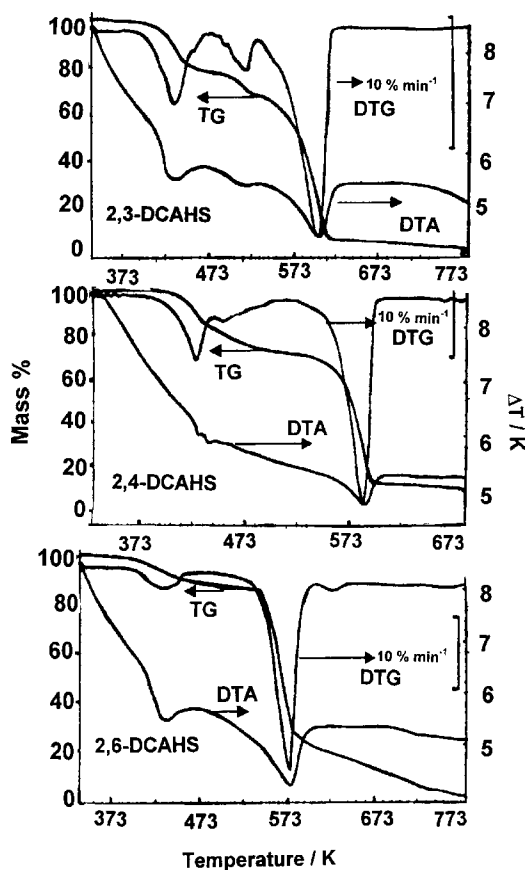


Fig. 1. TG–DTG–DTA thermograms of dichloroanilinium hydrogensulfate (DCAHS) salts under inert atmosphere.

2.3. Thermolysis of DCAHS salts

Thermal decomposition of the salts were investigated as follows.

2.3.1. Simultaneous TG–DTG–DTA studies

Simultaneous TG–DTG–DTA studies on the salts (heating rate = 5 K min^{-1} , weight $\sim 5 \text{ mg}$, 100–200 mesh) were undertaken in N_2 atmosphere. The corresponding thermograms are given in Fig. 1 and data are summarized in Table 2.

2.3.2. Non-isothermal TG and DTA in static air

To determine whether the atmosphere has any role on the thermolysis of the samples, non-isothermal TG

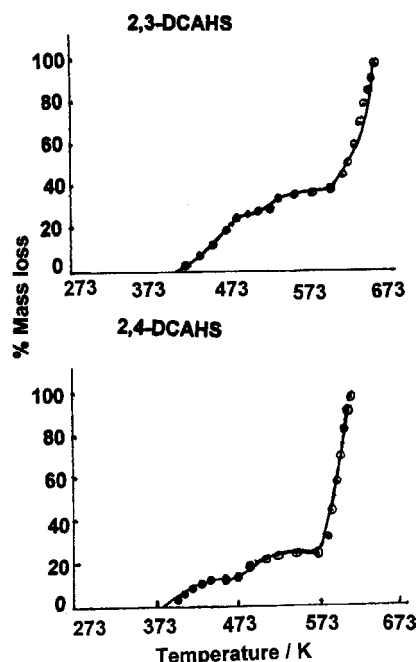


Fig. 2. Non-isothermal TG of dichloroanilinium hydrogensulfate (DCAHS) salts under static air atmosphere.

and DTA analyses were done under static air atmosphere. Non-isothermal TG studies on the salts (weight $\sim 20 \text{ mg}$, 100–200 mesh) were undertaken at a heating rate of 10 K min^{-1} using indigenously fabricated TG apparatus [29]. The thermograms are given in Fig. 2 and the phenomenological data are summarized in Table 3. The non-isothermal TG thermogram for 2,6-DCAHS was reported earlier [30] and hence it is not included in Fig. 2. DTA analyses of the samples were carried out in flowing air (60 ml min^{-1}) atmosphere at a heating rate of 10 K min^{-1} , using a DTA apparatus by Universal Thermal Analysis Instruments, Mumbai. Sample mass was kept as 30 mg for each sample and all thermograms are given in Fig. 3 and the phenomenological data are reported in Table 3.

2.3.3. Isothermal TG studies

Isothermal TG thermograms of all salts (mass = 42 mg , 100–200 mesh) are given in Fig. 4, which were done in the range of temperature where sulfonation takes place.

Table 2
TG–DTG–DTA phenomenological data on DCAHS salts

Compound	TG data				DTA peak temperature	
	T_i (K)	T_s (K)	T_f (K)	Mass loss (%)	Endo (K)	Peak area (K ²)
2,3-DCAHS-4H ₂ O	420	438	453	20.13	437	615.4
	504	522	526	7.57	516	237.3
	582	607	616	55.58	608	441.2
2,4-DCAHS-2H ₂ O	418	432	436	13.98	433	20.3
	460	462	479	5.60	444	498.3
	574	591	597	55.80	592	134.1
2,6-DCAHS	400	432	446	7.34	433	517.2
	553	570	579	49.30	578	223.4

T_i , onset temperature; T_s , inflection temperature; T_f , endset temperature.

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

Compound	TG data			DTA peak temperature (K)
	SDT	FDT	Mass loss (%)	Endo
2,3-DCAHS-4H ₂ O	408	520	23	453
	583	613	93	520
				625
2,4-DCAHS-2H ₂ O	403	473	20	440
	573	593	90	604
2,6-DCAHS [30]	408	483	12	448
	508	593	92	590

SDT, starting decomposition temperature; FDT, final decomposition temperature.

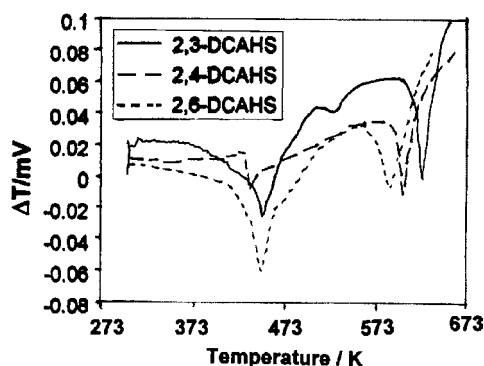


Fig. 3. DTA thermograms of dichloroanilinium hydrogensulfate (DCAHS) salts under flowing air atmosphere.

2.4. Kinetic analysis of isothermal TG data

2.4.1. Model fitting methods

The equation generally used for kinetic evaluation of thermal decomposition of solids is the well-known expression for rate, which is

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α is the extent of conversion, t represents time, T the absolute temperature, $k(T)$ the temperature dependent rate constant and $f(\alpha)$ is a function called the reaction model. Various forms of $f(\alpha)$ are summarized in Table 4. The temperature dependency of rate constant is assumed to obey Arrhenius expression

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where A is pre-exponential (Arrhenius) factor, E the activation energy and R is gas constant. Eq. (1) is often used in its integral form, which for isothermal conditions become

$$g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha = k(T)t \quad (3)$$

where $g(\alpha)$ is the integrated form of the reaction model (Table 4). Substituting a particular reaction model into Eq. (3) results in evaluating the corresponding rate constant, which is found from the slope of the plot of $g(\alpha)$ against t . For each reaction model selected, the rate constants are evaluated at several temperatures and the Arrhenius parameters are obtained from logarithmic form of Arrhenius equation

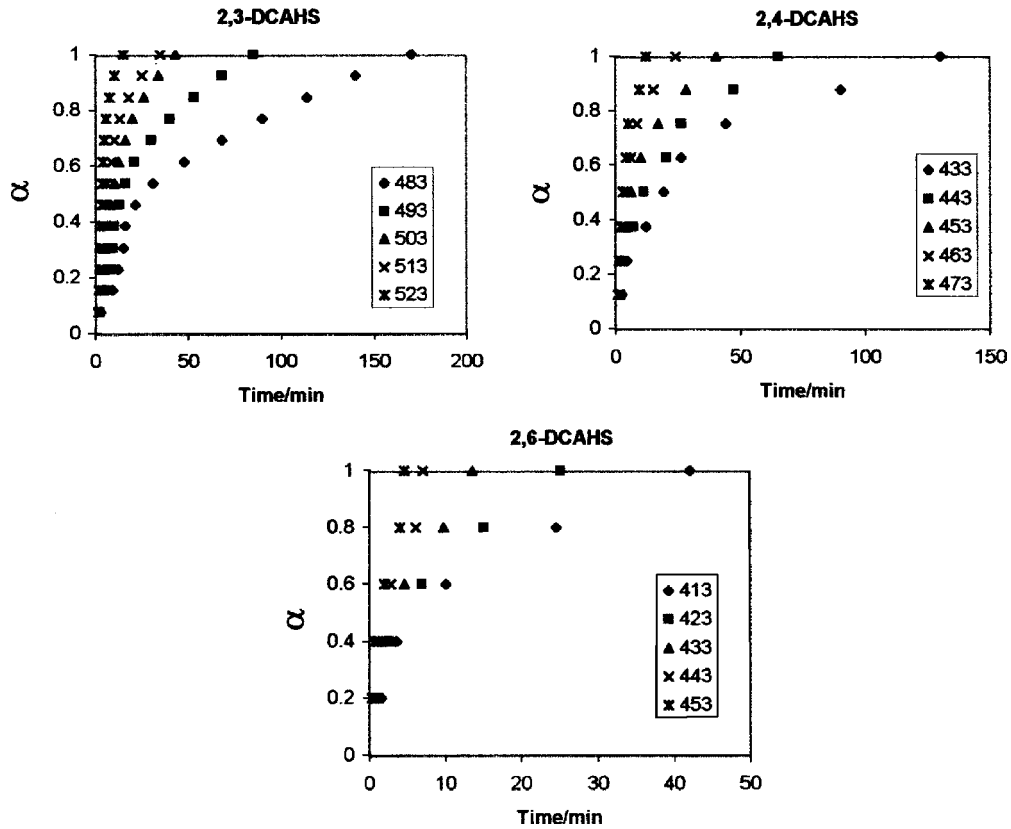


Fig. 4. Isothermal TG thermograms of dichloroanilinium hydrogensulfate (DCAHS) salts in the temperature range where sulfonation takes place.

Table 4

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

Sl. no.	Model	$f(\alpha)$	$g(\alpha)$
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	Mampel (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	Contracting cylinder	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
13	Prout-Tomkins	$\alpha(1 - \alpha)$	$\ln(\alpha/1 - \alpha)$
14	Ginstling-Brounshtein	$3/2[(1 - \alpha)^{-1/3} - 1]^{-1}$	$[1 - (2\alpha/3)] - (1 - \alpha)^{2/3}$

Table 5

Kinetic parameters for isothermal decomposition of 2,3-DCAHS salt from mechanism based kinetic models

Model ^a	E_{α} (kJ mol ⁻¹)	ln(A min ⁻¹)	-r
1	123	29	0.9931
2	123	29	0.9932
3	123	29	0.9934
4	120	29	0.9942
5	119	29	0.9946
6	124	33	0.9976
7	116	28	0.9943
8	115	28	0.9943
9	114	28	0.9945
10	116	28	0.9947
11	117	28	0.9952
12	118	28	0.9945
13	112	30	0.9945
14	115	26	0.9951

^a Enumeration of models is as given in Table 4.

$$\ln k(T) = \ln A - \frac{E}{RT} \quad (4)$$

Kinetic parameters obtained for the isothermal decomposition of all salts are given in Tables 5–7, respectively. The correlation coefficient (r) is usually used as a parameter for choosing the best fit model and the values of which are also reported in Tables 5–7.

2.4.2. Isoconversional method

In isoconversional method, it is assumed that the reaction model in Eq. (1) is not dependent on temper-

Table 6

Kinetic parameters for isothermal decomposition of 2,4-DCAHS salt from mechanism based kinetic models

Model ^a	E_{α} (kJ mol ⁻¹)	ln(A min ⁻¹)	-r
1	102	23	0.9986
2	101	23	0.9986
3	101	23	0.9987
4	100	23	0.9989
5	100	23	0.9990
6	100	26	0.9987
7	100	24	0.9984
8	100	24	0.9988
9	100	24	0.9988
10	100	23	0.9990
11	100	23	0.9989
12	100	23	0.9990
13	100	26	0.9987
14	100	22	0.9991

^a Enumeration of models is as given in Table 4.

Table 7

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

Model ^a	E_{α} (kJ mol ⁻¹)	ln(A min ⁻¹)	-r
1	93	22	0.9991
2	93	22	0.9991
3	93	22	0.9991
4	90	22	0.9993
5	88	21	0.9994
6	75	20	0.9973
7	82	20	0.9992
8	81	20	0.9991
9	79	20	0.9987
10	82	20	0.9993
11	77	19	0.9982
12	86	21	0.9994
13	77	21	0.9982
14	82	19	0.9993

^a Enumeration of models is as given in Table 4.

ature. Under isothermal conditions, we may combine Eqs. (3) and (4) to get

$$-\ln t_{\alpha,i} = \ln \left[\frac{A}{g(\alpha)} \right] - \frac{E_{\alpha}}{RT_i} \quad (5)$$

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

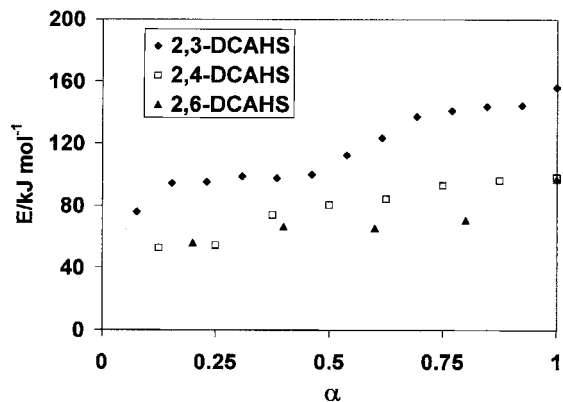


Fig. 5. Dependencies of activation energies (E_{α}) on extent of conversion (α) for the isothermal decomposition of dichloroanilinium hydrogensulfate (DCAHS) salts.

3. Results and discussion

It is clearly evident from the elemental and IR analysis that out of five samples, only three (2,3-, 2,4- and 2,6-DCA) form the DCAHS salts when arylamines were reacted with excess of conc. H_2SO_4 . The reaction may be represented by Scheme 1. Rest two salts, namely 2,5-DCA and 3,4-DCA form dichloroanilinium sulfate whose preparation, characterization, thermal studies and kinetics were reported earlier [30]. The non-formation of the hydrogen sulfate salts in above said amines even with excess of H_2SO_4 might be due to the position and the steric effect [31,32] of the chloro group.

The C, H, N data also shows that 2,3-DCAHS and 2,4-DCAHS crystals formed in hydrated form and their molecular formula is 2,3-DCAHS·4 H_2O and 2,4-DCAHS·2 H_2O . In our earlier study [30] it was found that 2,6-DCA form the corresponding DCAHS salt even in the condition where sulfate salts are formed (2:1 molar ratio of amine and H_2SO_4). The elemental and spectral data for 2,6-DCAHS, reported in Table 1 is same as reported earlier [30].

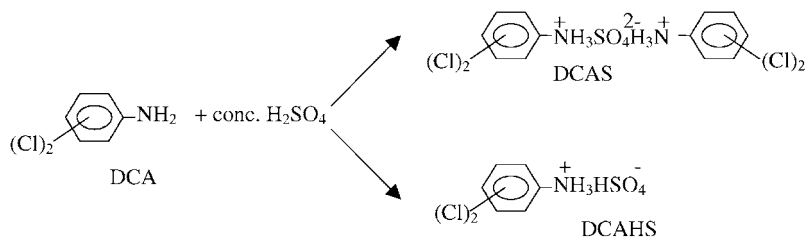
Table 2 shows that mass loss occur in three steps for 2,3- and 2,4-DCAHS whereas it occurs in two steps for 2,6-DCAHS. All the steps are endothermic in nature according to DTA, irrespective of atmosphere. As per our previous studies [11], on the thermolysis of RSAHS, the first step is sulfonation with the release of a molecule of water. Thus, for the DCAHS salts, a mass loss of 6.92% is expected for the sulfonation process. For 2,6-DCAHS there is 7.34% mass loss in the first step, which is clearly indicating that sulfonation is the first step for this case. However, for the other two salts, namely, 2,3- and 2,4-DCAHS, there are 20.13 and 13.98% mass loss in the first step, respectively. This mass loss is due to the evolution of

water of crystallization in these salts. The mass loss in the second step for these salts agrees with the expected mass loss for sulfonation. The plateau regions in TG thermograms (Fig. 1) for 2,3-DCAHS in the temperature region 516–608 K, for 2,4-DCAHS 444–592 K and for 2,6-DCAHS 448–553 K are showing the stability of the corresponding ABSA. The final step in all the three salts is the decomposition of corresponding DCABSA by deamination, desulfonation followed by ring rupture.

DTA thermogram shown in Figs. 1 and 3 and the corresponding data given in Tables 2 and 3 reveal that atmosphere has no effect in the mechanism of thermolysis of these salts. There are three endotherms in the case of 2,3-DCAHS and 2,4-DCAHS in the thermograms corresponding to DTA run under inert atmosphere. The nature of DTA thermogram recorded under inert atmosphere for 2,3-DCAHS is the same as that recorded under air atmosphere. But for 2,4-DCAHS there are only two endotherms in the thermogram recorded under air atmosphere. This is evidently due to overlapping of the first two endotherms, which are at slightly differing temperatures in inert atmosphere.

3.1. Mechanism of sulfonation

It has been reported [33,34] that basicity of the anion (HSO_4^-) increases with rise in temperature until it reaches the base strength of DCA. At this temperature, the anion base removes the proton from dichloroanilinium cation to form DCA and H_2SO_4 molecule. Therefore DCAHS salts seem to dissociate into corresponding DCA and H_2SO_4 molecules via proton transfer. H_2SO_4 formed in situ sulfonates the amine with the release of a molecule of water, which is also proved here by thermo-analytical

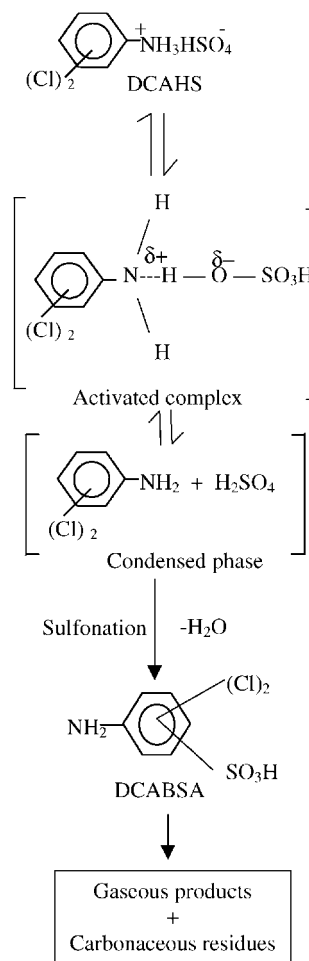


Scheme 1. The formation of DCAS and DCAHS.

techniques. FAB-MS data also confirm the formation of dichloroanilinium cation ($m/z = 161$) during decomposition of these salts. Cross-sulfonation studies [15–17,35] have been proved to be an effective tool to confirm the proton transfer reactions, during sulfonation. The cross-sulfonation studies were performed by heating each sample separately in tube furnace [36] with small amount of aniline under vacuum for about 30 min. The sulfanilic acid was obtained in each case along with the corresponding sulfonic acid (formed from salts). It indicates the formation of H_2SO_4 and amine molecules in situ and H_2SO_4 might have sulfonated aniline. In order to do cross-sulfonation, the samples 2,3-, 2,4- and 2,6-DCAHS were heated with aniline at temperature 483, 473 and 453 K with 30 min, respectively. In each case sulfanilic acid was formed along with the corresponding DCABSA and this was proved by TLC. The overall mechanism of thermolysis of DCAHS salts is given in Scheme 2.

Since all the above studies prove beyond doubt that sulfonation of DCAs takes place on giving thermal stimulus to DCAHS salts, we have prepared the DCABSAs from all the three DCAHS. The samples of 2,3-, 2,4- and 2,6-DCAHS were heated, respectively, at 483, 463, 453 K in glass tubes for 35, 30 and 35 min, respectively, under reduced pressure 13328 ± 267 Pa to get the corresponding DCABSA. Each residue was washed with ethylacetate and recrystallized from double distilled water. Its purity was checked by TLC and HPLC. These compounds were found to decompose during melting point determinations. The physical parameters, elemental and IR data analysis are also reported in Table 1. All DCABSA gave dye test and effervescence with $NaHCO_3$.

Kinetic parameters for solid-state sulfonation are of practical interest as the data may be helpful for prediction of conditions for manufacture and storage. Thermo-analytical techniques can provide important measure of kinetics of thermally stimulated reactions, which permit a deeper insight into the mechanism of solid-state decomposition reactions. The values of ' r ' reported in Tables 5–7 are very close to each other, so that choosing 'best fit' based on it is not possible. The values of activation energy are close to each other for a sample irrespective of the equation used. Thus for 2,3-, 2,4- and 2,6-DCAHS average values of ~ 118 , ~ 100 and ~ 84 $kJ\ mol^{-1}$, respectively, were obtained as activation energy. As the isothermal TG thermograms



Scheme 2. Thermal decomposition pathway of DCAHS salts.

were recorded in the temperature range where sulfonation takes place, the mass loss accounts for two different processes for 2,3- and 2,4-DCAHS salts and hence a single set of kinetic parameters may not adequately describe the whole process. In the first step, evolution of water of hydration takes place and then sulfonation follows it. However the mass loss in both steps is due to evolution of water, which may be diffusion-controlled; since the reaction is occurring in the solid-state. The second step involves proton-transfer to regenerate the corresponding amine and H_2SO_4 and subsequent sulfonation. Thus the mechanism of this step in particular may not be simple so that a single set of kinetic parameters could be able to describe it.

The variation of E_α on α is evident in Fig. 5. Values of E_α increase with increase in extent of conversion for all the three salts. For 2,6-DCAHS, $E_\alpha = 56 \text{ kJ mol}^{-1}$ at lowest α , which increases to $E_\alpha = 98 \text{ kJ mol}^{-1}$ at $\alpha = 1$. This variation of E_α clearly shows that there are more than one competing reaction channels during sulfonation step itself. The contribution of different paths to the value of E_α changes with values of α . However, the scenario is much more complicated during decomposition of the other two salts. Since evolution of water of hydration takes place at a reasonably lower temperature range than sulfonation and the isothermal TG thermograms were recorded at higher temperatures, it may be assumed that the processes are taking place separately in succession and not simultaneous in 2,4-DCAHS. Thus the values of E_α for 2,4-DCAHS at lower values of α must be corresponding to the loss of water of hydration. E_α has a value of $\sim 100 \text{ kJ mol}^{-1}$ at $\alpha = 0-0.5$, which then increases up to $\sim 150 \text{ kJ mol}^{-1}$ at $\alpha = 1$. Thus almost a constant value of activation energy during the first step shows that the rate-limiting step in this case is same during the whole process. However, the sulfonation process in the second step is complicated for 2,3-DCAHS also, which is evident from the variation of E_α with α . For 2,4-DCAHS, E_α varies from an initial value of $\sim 52-98 \text{ kJ mol}^{-1}$ at $\alpha = 1$. In this case, as the temperature range for first step and second step are closer and hence there is a chance of overlapping of both steps.

4. Conclusions

Only three out of five DCA gave corresponding DCAHS salts even in the presence of excess sulfuric acid. Out of the three salts 2,3- and 2,4-DCAHS were formed in the hydrated form, whereas 2,6-DCAHS was obtained anhydrous. Removal of water of hydration is the first step for the hydrated salts followed by sulfonation step. Proton transfer process seems to be the primary process when hydrogen sulfate salts were subjected to thermal stimulus and the H_2SO_4 formed in situ sulfonates the DCA with the evolution of a molecule of water. The conventional model fitting methods over simplifies the thermal decomposition process as they give a single value for kinetic parameters for the entire process. However the iso-

conversional methods show that there are many competing reaction channels even during the sulfonation step.

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