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4-(Dimethylamino)pyridinium chlorosulfonate: A new ionic liquid exhibiting chlorosulfonic acid action as monoprotic Brönsted acid and no sulfonating reagent

Lia Zaharani [a], Mohd Rafie Johan [a], Salam Titinchi [b], Nader Ghaffari Khaligh [a,*]

[a] *Nanotechnology and Catalysis Research Center, Institute for Advanced Studies (IAS), University of Malaya, Kuala Lumpur 50603, Malaysia*
[b] *Department of Chemistry, University of the Western Cape, Cape Town, South Africa*

A B S T R A C T

Many papers considered chlorosulfonic acid as a sulfonating and sulfating agent, whereas our previous work and a few reports showed it acts as a monoprotic Brönsted acid. Therefore, in the present work, we decided to respond to this question by investigating the reaction between chlorosulfonic acid and DMAP. First, a new ionic liquid *viz.* 4-dimethylaminopyridinium chlorosulfonate was obtained, which its chemical structure was elucidated using different spectroscopic techniques. Another derivative, 4-dimethylaminopyridinium hydrogen sulfate, was also synthesized, which showed a similar NMR pattern. The NMR spectra analyses of reactants, the new ionic liquid, and 4-dimethylaminopyridinium hydrogen sulfate support the formation of 4-dimethylaminopyridinium chlorosulfonate. Therefore, the formation of *N*-sulfonic acid-4-dimethylaminopyridinium chloride or 4-dimethylaminopyridinium sulfate and the presence of an excess of chlorosulfonic acid and sulfuric acid were ruled out based on the spectroscopic results. Finally, the new ionic liquid's thermal behavior and thermal stability were investigated, and a possible mechanism was presented for its degradation based on a TGA/DTA analysis.

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1. Introduction

The chemical structure of chemical compounds plays a vital role in their physical and chemical properties. Therefore, there is a robust relationship between the chemical structure of compounds and their activity, which establishes a well-known concept in the organic chemistry and pharmaceutical field as Structure-Activity Relationship (SAR) [1]. The structure elucidation of chemical compounds is performed using various spectroscopic techniques, including nuclear magnetic resonance (NMR) spectroscopy, mass, infrared, and Raman spectroscopy [2].

Pyridine sulfur trioxide complex (**1**) was prepared by Sisler in 1946 through the treatment of pyridine with 0.42 equivalents of chlorosulfonic acid in dry chloroform at 0 °C [3]. This compound has been broadly used in organic chemistry; for example, convert of a hydroxyl group to sulfate monoester, which is an excellent leaving group [4], Swern type oxidation [5], and as a sulfating agent [6–8]. Sisler indicated that the final product, obtained in 62% yield, contained pyridinium sulfate; however, there was no evidence of spectroscopic (NMR and IR). Despite Sisler's claim,

pyridinium chloride cannot remain in the chloroform solution due to its ionic property. This fact was demonstrated by our experiments on the reaction of pyridine with HBr and HCl.
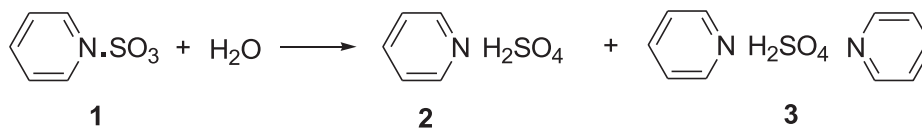
Pyridine sulfur trioxide (Py·SO$_3$) complex (**1**) has been prepared by direct reaction of liquid or solid SO$_3$ with the pyridine in different solvents or solvent-free conditions [9]. The commercial pyridine sulfur trioxide complex, >95% purity most vendors claim, very often contains large amounts of impurity including pyridine sulfuric acid salts with the ratio of 1:1 (**2**) and 2:1 (**3**) due to the reaction with moisture and water [10] (Scheme 1). The chemical structure of **1** has not been approved entirely by the spectroscopy techniques (NMR, Raman, and FTIR). Regarding salt ratio, at least two sets of proton signals with different chemical shifts were detected in the NMR spectrum of salt.

It is well known that sulfuric acid disassociates immediately in the water to hydronium cation (H$_3$O$^+$) and hydrogen sulfate or sulfate anions. Therefore, we proposed the chemical structure of (**2**) and (**3**) for the hydrolysis of the commercial pyridine sulfur trioxide complex (**1**) (Scheme 2).
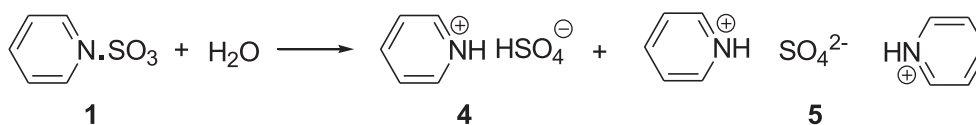
Py·SO$_3$ complex has been employed to prepare azido analogs of pregnanolone, sulfate esters of morphine derivatives, and the reaction of sulfur trioxide and its adducts with organic compounds [9]. It was employed in the total synthesis of sesquiterpenes to trans-

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Scheme 1. Hydrolysis of the commercial pyridine sulfur trioxide complex.

Scheme 2. The chemical structure of the possible products after the hydrolysis of the commercial pyridine sulfur trioxide complex.

form the allylic or benzylic hydroxyl groups in geraniol, farnesol, and 1-indanol into sulfate monoester as an excellent leaving group [4]. As a sulfating agent, the Py·SO$_3$ complex was used for the preparation of sulfated-chitins [6], sulfated hyaluronan derivatives [7], and sulfated starch [8].

Very recently, 1*H*,4*H*-piperazine-*N*,*N*′-diium dichlorosulfonate was synthesized, and the presence of chlorosulfonate anion was approved [11]. A few works indicated that the ClSO$_3$H acts as a strong protic acid [12,13], whereas many reports consider it a sulfonating agent [14,15]. Very recently, a similar salt-containing imidazolium cation was reported [16]. When amines or *N*-heteroaromatic compounds are treated with ClSO$_3$H (CSA), the formation of chlorosulfonate anion or sulfamic acid moiety and chloride anion depends on base nature and reaction conditions such as solvent, temperature, stoichiometry, etc. FTIR and Raman spectroscopy can prove the presence of [N–SO$_3$H] moiety and [Cl–SO$_3$]$^-$ anions through their fundamental vibration frequencies [11]. The ^{1}H NMR technique can also be employed to distinguish acid protons in an appropriate dry deuterated solvent. However, the presence of [N–SO$_3$H] in the compounds cannot be often demonstrated by ^{1}H NMR due to many parameters' influence on the chemical shift and signal intensity of acidic protons. Some effective parameters include the nature of the deuterated solvent, sample solubility and water content in the deuterated solvents, hydrogen bonding, and proton exchange rate [17].

In extending our previous works on synthesis and characterization of the molten salts and ionic liquids containing –SO$_3$H moiety and chlorosulfonate anion [18–21], herein, the action of chlorosulfonic acid (CSA) as a sulfonating agent or a monoprotic inorganic acid in reaction with 4-dimethylaminopyridine (DMAP), an *N*-heteroaromatic organic base, in CH$_2$Cl$_2$ was investigated. A new ionic liquid with melting points 98–99 °C was obtained [22,23]. Protonated DMAP was proved by FTIR spectrum and LC-ESI-MS technique in the positive mode, whereas [DMAP–SO$_3$H]Cl structure was excluded. Furthermore, the NMR spectra and LC-ESI-MS of the product obtained from the reaction of equimolar DMAP and sulfuric acid (100%) were analyzed, which confirmed the chemical structure containing [DMAPH]$^+$ cation. Also, the absence of chloride anion was approved due to the lack of white precipitate formation after adding pure crystalline AgNO$_3$ and 0.1 M aqueous solution of AgNO$_3$ into 100 mg of ionic liquid in 2 mL ultrapure water. The chemical structure was supported by the absence of S–OH stretching mode in the FTIR spectrum, while the Raman spectrum showed S–Cl stretching mode. The pH, a defined concentration of the new ionic aqueous solution, was reported. In addition, the water content and melting point of the new ionic liquid were measured and reported. Finally, the thermal phase transitions and thermal stability of new ionic liquid were studied and documented.

2. Results and discussion

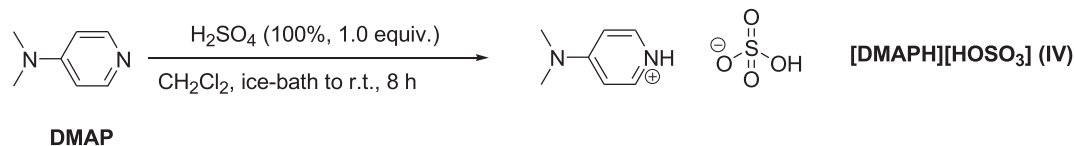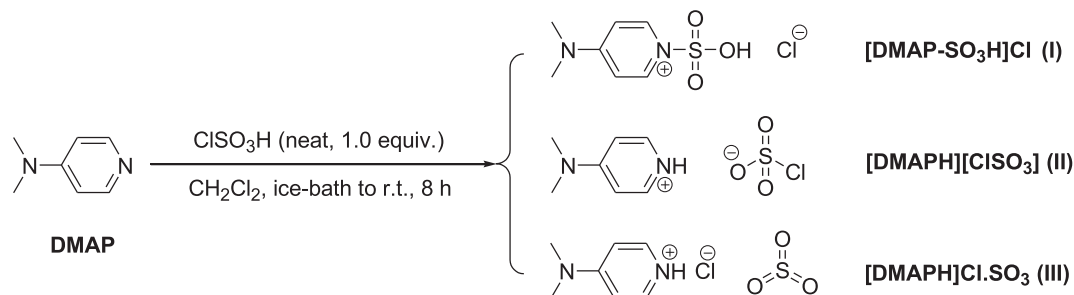### 2.1. Synthesis and characterization of 4-(dimethylamino)pyridinium chlorosulfonate [DMAPH][ClSO$_3$]

The ^{1}H NMR of 4-dimethylaminopyridine (DMAP) exhibited two doublet–doublet at 8.09, 6.56 with constant coupling 5.0 and 1.4 Hz and one sharp singlet 2.93 ppm. These signals were attributed to ten protons of DMAP, including four CHs of pyridine ring and two methyl groups, respectively. The ^{13}C NMR spectrum of DMAP showed four signals at 153.93 ppm for C-4, 149.35 ppm for C-2 and C-6, 106.69 ppm for C-3 and C-5, and 38.55 ppm for C-7 (See supplementary information, Figure S1).

DMAP was treated with one equivalent of chlorosulfonic acid (CSA) to investigate three expected chemical structures of the product based on the Brönsted acid or *N*-sulfonating agent property of ClSO$_3$H (Scheme 3).

One equivalent of CSA was slowly added into a solution of DMAP in dichloromethane at ice-bath within 20 min. Then, the mixture was stirred at room temperature for eight hours, giving a white solid characterized by the ^{1}H NMR, ^{13}C NMR, FTIR, Raman's spectra, and LC-MS analysis in positive and negative modes. The ^{1}H NMR of the DMAP-CSA (1:1) in DMSO d_6 showed two doublets at 8.17 and 6.84 ppm with the constant coupling of 7.0 Hz and one sharp singlet at 3.10 ppm, which are assigned to CH-2 and CH-6, CH-3 and CH5, and methyl groups, respectively. The ^{13}C NMR of the DMAP-CSA (1:1) showed four peaks at 155.92, 142.81, 106.90, and 39.28 ppm (See supplementary information, Figure S2).

To further support the chemical structure of the DMAP-CSA (1:1), DMAP was also treated with sulfuric acid (SA), another derivative of CSA having an acidic proton instead of a chlorine atom. One equivalent of SA (100%) was added dropwise over 30 min to a solution of DMAP in dichloromethane at an ice bath. After stirring the mixture for eight hours at room temperature, the solvent was removed by a rotary evaporator. The residue was washed with dichloromethane several times, and its chemical structure was elucidated after drying (Scheme 4) (See supplementary information, Figure S3).

In addition, the ^{1}H NMR of neat **SA** and **CSA** were recorded in DMSO d_6, the same deuterated solvent used for NMR recording of DMAP-CSA (1:1) and DMAP-SA (1:1). The ^{1}H NMR of SA (100%) showed a sharp singlet at 7.13 ppm, and a multiplet was detected at a range of 7.33–7.24 ppm for CSA (neat) (See supplementary information, Figures S4 and S5). These results showed that the hydrogen bonding network of SA is more labile than that of CSA in DMSO d_6. On the other hand, the ^{1}H NMR spectrum of DMAP-SA (1:1) did not show any sharp or broadened peak at a range of 8.0–7.0 ppm and above 8.30 ppm; therefore, an excess of sulfuric

Scheme 3. The synthesis conditions and three proposed structures of new ionic liquid.

Scheme 4. Synthesis conditions and the chemical structure of DMAP-SA (1:1).

acid was obviated. It is worth mentioning that the strong hydrogen bonding in DMSO d_6, an excellent hydrogen-bond acceptor, along with a fast proton exchange rate, led to a broadening of the peaks at 4.10 and 4.45 ppm in ^{1}H NMR of the DMAP-CSA (1:1) and DMAP-SA (1:1), respectively. This data indicates that the hydrogen bonding network of DMAP-SA (1:1) is more robustst than that of DMAP-CSA (1:1). Moreover, the unqualified water content in DMSO d_6, even after storing in molecular sieves overnight, influences displaying the downfield signal for the acid proton of $[HSO_4]^-$ in the ^{1}H NMR spectrum of the TMDP-SA (1:1). The characteristic peak of $[HSO_4]^-$ can be undetectable owing to the fast proton exchange rate between $[HSO_4]^-$ and residual water content in DMSO d_6 [24].

The proton and carbon chemical shifts of pyridine ring and methyl groups and the constant coupling of the pyridine ring of DMAP-CSA (1:1) and DMAP-SA(1:1) are different, as shown in Tables 1 and 2. These differences can be due to the effect of different anions or the existence of different chemical structure of pyridine ring. As shown in Table 1, the replacement of CSA by SA resulted in a negligible downfield shift of the CH-2 and CH-6 protons from 8.17 ppm to 8.19 ppm ($\Delta\delta H$ = 0.02). In contrast, a larger downfield shift was observed for the signals of CH-3 and CH-5 from 6.84 ppm to 6.97 ppm ($\Delta\delta H$ = 0.13), and methyl protons shifted from 3.10 ppm to 3.17 ppm ($\Delta\delta H$ = 0.07). Also, the coupling constant of CH-2 and CH-6 with CH-3 and CH-5 increased from 7.0 Hz in DMAP-CSA (1:1) to 7.6 Hz in DMAP-SA(1:1). Hence, it

is indicated that the interaction between cation and anion in DMAP-SA (1:1) is more robust than DMAP-CSA (1:1).

The triplet determination of pH exhibited an average pH of 3.02 ± 0.02 for 50 mg of DMAP-CSA (1:1) into 25 mL ultrapure water at 33.0 ± 0.1 °C. The same concentration of DMAP-SA (1:1) showed a pH of 2.27 ± 0.02 at 33.0 ± 0.1 °C.

The test for chloride ion based on precipitation of an insoluble chloride salt was also conducted for 50 mg of DMAP-CSA (1:1) into 2.0 mL of ultrapure water by adding 5 mg of AgNO₃ or 0.2 mL of 0.1 M solution of AgNO₃. Again, no precipitate of silver chloride formed, whereas a white precipitate formed for a blank test containing 50 mg of HCl (37% in water).

The further study was performed through FTIR and Raman's spectra analysis of DMAP-CSA(1–1). The infrared spectrum of neat DMAP-CSA (1:1) was studied in the range of 4000–450 cm^{-1} (See supplementary information, Figure S6). The stretching vibration of C = C and C–C is generally observed at the region 1625–1400 cm^{-1}. In the same vein, the C–C vibration appeared at 1558 cm^{-1}, and the week intensity peak at 1446 cm^{-1} was assigned to C = C stretching vibrations. The medium stretching vibrations of C–N in the pyridinium ring are estimated in the range 1685–1580 cm^{-1} [27]. The strong band at 1640 cm^{-1} and a shoulder at 1618 cm^{-1} were attributed to the C–N–H bending vibration [28]. A weak peak at 982 cm^{-1} was assigned to the C–H out-of-the-plane bending vibration. The N–H stretching vibrations occur in the region of 3600–3200 cm^{-1} in amines. The N–H stretching mode

Table 1
The ^{1}H NMR data of DMAP, DMAP-SA(1:1), DMAP-CSA (1:1), and [DMAP-1-pentyl]$^+$F$^-$ in DMSO d_6 as well as DMAP-HBr(1:1) in D₂O.
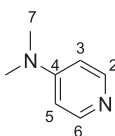
Compound	CH-2 and CH-6 δ^{1}H (ppm)	CH-3 and CH-5 δ^{1}H (ppm)	CH₃-7 δ^{1}H (ppm)	HOD peak δ^{1}H (ppm)
DMAP	8.11 (dd, J = 5.0 and 1.4 Hz, 2H)	6.58 (dd, J = 5.0 and 1.4 Hz, 2H)	2.93 (s, 6H)	3.45 (s)
DMAP-CSA (1:1)	8.17 (d, J = 7.0 Hz, 2H)	6.84 (dd, J = 7.1 Hz, 2H)	3.10 (s, 6H)	4.10 (br s)
DMAP-SA (1:1)	8.19 (d, J = 7.6 Hz, 2H)	6.97 (d, J = 7.6 Hz, 2H)	3.17 (s, 6H)	4.45 (br s)
DMAP-HBr (1:1)(400 MHz, D₂O)[a]	7.99 (d, J = 7.6 Hz, 2H)	6.85 (d, J = 7.6 Hz, 2H)	3.18 (s, 6H)	4.79 (s) (D₂O)
[DMAP-1-pentyl]$^+$F$^-$(400 MHz, DMSO d_6)[b]	8.28 (d, J = 7.6 Hz, 2H)	7.02 (d, J = 7.6 Hz, 2H)	3.17 (s, 6H)	3.35 (s)

Table 2

The ^{13}C NMR data of DMAP, DMAP-SA(1:1), DMAP-CSA (1:1), and [DMAP-1-pentyl]$^+$F$^-$ in DMSO d_6 as well as DMAP-HBr(1:1) in D$_2$O.

Compound	C-2 and C-6	C-3 and C-5	C-4	C-7
	δ ^{13}C (ppm)	δ ^{13}C (ppm)	δ ^{13}C (ppm)	δ ^{13}C (ppm)
DMAP	149.35	106.69	153.93	38.55
DMAP-CSA (1:1)	142.81	106.90	155.92	39.28
DMAP-SA (1:1)	139.46	107.08	157.00	39.69
DMAP-HBr (1:1)[a]	138.16	106.79	157.46	39.43
(400 MHz, D$_2$O)				
[DMAP-1-pentyl] + F−(400 MHz, DMSO d_6)	141.94	107.64	155.79	39.68

[a] NMR data are based on reference [25]

[b] NMR data are based on reference [26]

was observed at 3236 cm^{-1} as a weaker peak than the band at 3422 cm^{-1}, attributed to the physically adsorbed humidity. The pyridinium ring's N–H stretching band was observed at a range of 2800–2668 cm^{-1} [29]. The symmetric and asymmetric stretching vibrations of two CH$_3$ groups appear around 3083 and 2928 cm^{-1}. The pyridinium ring's bending out–plane vibrations occur at a medium sharp peak at 810 and 742 cm^{-1} [30]. Our result and the previous reports of the IR vibrational assignment of the SO$_3$Cl anion are shown in Table 3. The symmetric and asymmetric stretching vibrations of SO$_2$ were observed as a strong band at 1129 cm^{-1} with two weak shoulders at 1215 and 1196 cm^{-1}, respectively. The SO$_2$ bending, S–C1 stretching, and SO$_2$ wagging modes were observed at a range of 566–470 cm^{-1} [31].

As a result, the neat FTIR spectrum demonstrated the existence of the strong hydrogen bonds in new ionic liquid. Nevertheless, ^1H NMR did not show strong hydrogen bonding, probably due to the preferential hydrogen bond formation with DMSO d_6, a strong hydrogen bond acceptor.

Figure S7 shows a Raman spectrum of DMAP-CSA (1:1) (See supplementary information). The N–H stretch and bend vibrations appeared at 3098 and 1640 cm^{-1}, and our results and Dhanuskodi [30] are exhibited in Table 4.

Raman spectrum of DMAP-CSA (1:1) showed two bands at 412 and 177 cm^{-1} assigned to S–Cl stretch and wag vibrations, respectively. Our results and those of Gillespie [36], Steger [37], Stufkens [37,38], Khaligh [11,21] are exhibited in Table 5.

Stufkens and Gillespie assigned the bands at 312 cm^{-1} and 220 cm^{-1} to the S–Cl bend vibrations; in comparison, these bands were not detected in the Raman spectrum of both liquid and solid NO·SO$_3$Cl [38]. As seen in Figure S7 (See supplementary information), the depolarized S–Cl wag vibration can be assigned to weak and medium bands at 199 and 177 cm^{-1}.

The mass spectrum of DMAP-CSA (1:1) showed [C$_7$H$_{11}$N$_2$]$^+$ and [C$_{14}$H$_{21}$N$_4$]$^+$ at m/z 123.0923 (calcd. 123.0922) and 245.1761 (calcd. 245.1766) in positive ion mode by LC-ESI-MS analysis (See supplementary information, Figure S8). Also, the fragment cation peak of [C$_6$H$_7$N$_2$]$^+$ was detected at m/z 107.0610 (Calcd.

Table 4

The Raman vibrational assignment of the vibrations of the 4-dimethylaminopyridinium cation (3200–100 cm^{-1}).

Approximate description	Dhanuskodi [30] (cm^{-1})	Our result (cm^{-1})
C–H or N–H stretch	3104	3098
C–H stretch	2941	2954
N–H bend	1641	1640
C = C stretch	1556	1561
C–H bend	1309, 1252, 1211	1280, 1216
C–H bend out-of-plane	743	747

107.0609) in positive ion mode, respectively. The isotopic analysis and chemical structure of cations are shown in Table 6.

The existence of many negative ions could be attributed to sulfuric acid and its fragments, and these ions had very low intensities. The hydrolyzation of chlorosulfonate anion can produce sulfuric acid and hydrochloride acid clusters in the presence of water under LC-MS conditions.

Based on the above results, chlorosulfonic acid cannot be a sulfonating agent in the reaction with DMAP. It was a monoprotic Brönsted acid; thus, the chemical structure (**II**) or (**III**) can be indicated for the DMAP-CSA (1:1), while the structure (**I**) is excluded. The melting point of DMAP-CSA (1:1) was 89–99 °C. The average water content of DMAP-CSA (1:1) was determined 3.11 ± 0.02 wt % by Karl Fisher (KF) titration at relative local humidity and room temperature.

2.2. The thermal behavior of DMAP-CSA (1:1)

The differential scanning calorimetry (DSC) was recorded in three cycles at 25–150, 25–200, and 25–300 °C under nitrogen atmosphere to study the thermal behavior of new ionic liquid (see supplementary Information, Figure S9). One sharp exothermic peak was displayed at 95 °C in the first cooling cycle. TGA did not show a weight loss at a range of 95–100 °C; thus, this sharp peak at 95 °C was indicated as the crystallization point of DMAP-CSA (1:1) with a crystallization enthalpy of 45.9 J g^{-1}. There are two relatively sharp exothermic peaks at 115 and 148 °C in the second

Table 3

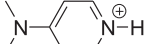Our result and the previous reports of the IR vibrational assignment of the SO$_3$Cl anion.

Approximate description	Waddington [32]	Ciruna [33]	Paul [34]	Hanai [35]	Khaligh [11]	Khaligh [21]	Our result
	> 500 cm^{-1}	1500–400 cm^{-1}	> 500 cm^{-1}	> 200 cm^{-1}	> 450 cm^{-1}	> 450 cm^{-1}	> 450 cm^{-1}
SO$_3$ sym. stretch	1044	1035–1077	1044	1171	1135, 996	1044	1108
S–Cl stretch	565	376–417[a]	562	533, 491	442, 419	488	471
SO$_3$ sym. bend	540	529–554	540	533, 491	574	610	527, 512
SO$_3$ asym. stretch	1275	1240–1270	1250	1366	1332, 1135	1320	1338
SO$_3$ asym. bend	583	566–599	580	533, 491	574	578	566
S–Cl wagor ClSO$_3$ deformation	–	233–251[a]	–	372	–	–	–

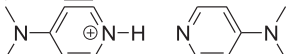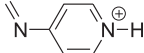[a] Predicted based on a combination of the S–C1 stretch and the S–Cl wag vibration to give the frequencies at a range of 600 and 640 cm^{-1}.

Table 5
The Raman assignment of the vibrations for the chlorosulfonate anion.

Approximate description	Raman (3200–100 cm^{-1})					
	Gillespie [36]	Steger [37]	Stufkens [38]	Khaligh [11]	Khaligh [21]	Our result
SO$_3$ sym. stretch	1050	1062	1042	1041	1040	1058
S–Cl stretch	416	392	381	420, 439	440	412
SO$_3$ sym. bend	535	600, 640	601	578	799	646
SO$_3$ asym. stretch	1195	1250–1312	1300	1320	1355	1280, 1216
SO$_3$ asym. bend	585	531–559	553	588,613	581	489
S–Cl wag or ClSO$_3$ deformation	220	220	312	202	193	199, 177

Table 6
Mass spectrum analysis of DMAP-CSA (1:1) in positive mode.

Chemical structure	Cation peak	Found	Calculated
	[M + H]$^+$	123.0923 (100.0%) 124.0950 (8.1%)	123.0922 (100.0%) 124.0956 (7.8%)
	[2 M + H]$^+$	245.1761 (100.0%) 246.1800 (16.3%)	245.1766 (100.0%) 246.1800 (17.1%)
	[M − CH$_3$ + H]$^+$	107.0610 (100.0%) 108.0649 (5.8%)	107.0609 (100.0%) 108.0643 (6.7%)

and third cooling with the crystallization enthalpies of 4.0 and 25.8 J g^{-1}, respectively. They can be indicated to the crystallization points of a new compound due to the removal of HCl and SO$_2$ gas at higher temperatures. In the third heating, there is one endothermic peak onset and endset at 194 and 212 °C, respectively. The melting point of sulfur trioxide pyridine complex (≥45% SO$_3$ basis) is 160 °C (Sigma Aldrich); and the formation of an N-methylimidazole sulfur trioxide has been previously described [39]. Thus, we indicate a melting point of 194 °C for a new compound of DMAP·SO$_3$ with a fusion enthalpy of − 28.6 J g^{-1} (Scheme 5). In addition, the dehydration and degassing led to some weak endothermic peaks in DSC.

The thermogravimetric analysis/differential thermal analysis (TGA/DTA) curve of DMAP-CSA (1:1) was recorded at a range of 25–800 °C under nitrogen atmosphere to determine thermal stability and degradation mechanism (see supplementary Information, Figure S10). The TGA curve displayed a three-step degradation pattern with the first weight loss at a range of 50 to 180 °C, corresponding to the removal of physically absorbed water (16.24%). The second weight loss occurred between 200 °C and 290 °C, and it corresponds to the desulfonation process, which involves the release of SO$_x$ (22.5%). Finally, the third weight loss above 325 °C is related to DMAP decomposition (56.5%) (Table 7), and the thermal decomposition is mainly completed at 380 °C.

The thermal study indicated that DMAP-CSA (1:1) is stable thermally up to 296 °C at a nitrogen atmosphere.

3. Experimental

3.1. The synthesis of DMAP-CSA (1:1)

A solution of chlorosulfonic acid (99%, 0.466 g, 0.26 mL, 4.0 mmol) in dry dichloromethane (2 mL) was added dropwise

Table 7
Weight loss analysis of TGA/DTA spectrum of DMAP-CSA (1:1).

Chemical	Molecular Mass	Weight loss (%)	
		Found	Calculated
DMAP-CSA (1:1)	238.7	16.4	15.3
DMAP. SO$_3$	202.2	22.5	26.8
DMAPO	138.2	56.5	57.8

and slowly to a solution of DMAP (0.488 g, 4.0 mmol) in dry CH$_2$-Cl$_2$ (2 mL) over 20 min. then, the mixture was stirred for eight hours, affording two phases. After decanting upper solution, the residual white solid was washed with dichloromethane several times (5 × 5 mL). The solvent removal by a rotary evaporator gave a white solid (0.897 g, 94%).

4. Conclusions

In conclusion, 4-(dimethylamino)pyridinium chlorosulfonate was prepared from the reaction chlorosulfonic with 4-dimethylaminopyridine. This work showed that chlorosulfonic in the reaction with DMAP acts as a Bronsted acid no a sulfonating or sulfating agent. The different spectroscopy techniques were applied for the structure elucidation of new ionic liquid. After structure elucidation of the new ionic liquid DMAP-CSA (1:1), some properties were determined, including melting point, pH, and water content. The thermal behavior and thermal stability of DMAP-CSA (1:1) were also investigated, and a degradation mechanism was presented. The crystallization enthalpy + 45.9 J g^{-1} was recorded for the new ionic liquid by DSC analysis. Furthermore, a

$C_7H_{11}ClN_2O_3S$
M = 238.7

$C_7H_{10}N_2O_3S$
M = 202.2

$C_7H_{10}N_2O$
M = 138.2
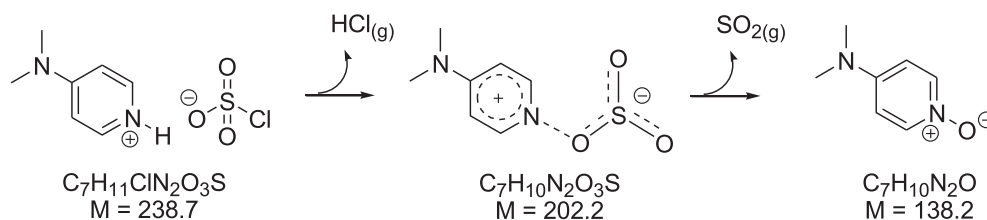
Scheme 5. A proposed thermal degradation of DMAP-CSA (1:1) at nitrogen atmosphere.

new compound of DMAP·SO₃ with a fusion enthalpy of $-28.6\,\mathrm{J\,g^{-1}}$ has been detected using TGA/DTA analysis. This compound can be an alternative for Py·SO₃, and our group is working to isolate and characterize this new compound.

CRediT authorship contribution statement

Lia Zaharani: Methodology, Investigation, Data curation. **Mohd Rafie Johan:** Project administration, Resources, Supervision. **Salam Titinchi:** Validation, Writing – original draft, Writing – review & editing. **Nader Ghaffari Khaligh:** Conceptualization, Investigation, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.118261.

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