Collisionally activated dissociation of *N*-acylpyridinium cations

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Relative fragmentation energies of a variety of *N*-acylpyridinium cations have been measured in the gas phase by electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS). *N*-Aroyl- and *N*-heteroaroyl-pyridinium cations dissociated to give free $ArCO^+$ ions with activation energies which are strongly decreased/increased by stabilizing/destabilizing electron-donor/acceptor substituents in the aroyl group. *N*-Alkylcarbonyl- and *N*-phenoxycarbonyl-pyridinium cations fragment *via* ion molecule complexes which dissociate to pyridinium cation and ketene or CO_2 + aryne. *N*-Alkoxycarbonylpyridinium cations form pyridinium cations *via* detectable *N*-carboxypyridinium cations. The propensity of those cations to undergo S_N1 or S_N2 reactions is discussed.

Introduction

Acyl cations are important reaction intermediates in both solution and gas phase chemistry. Salts of simple acyl cations with non-nucleophilic anions (RCO^+X^-) have been prepared in solution[1–3] (*e.g.* in FSO_3H–SbF_5–SO_2 or oleum) and isolated.[4] Gas phase dissociation energies for CH_3COBr (151.1 kcal mol^{-1}) and Bu^{t}Br (148.7 kcal mol^{-1}) indicate that CH_3CO^+ is of comparable stability to the *tert*-butyl cation.[5] Acyl cations are stabilized by a canonical form containing a triple bond $R{-}C^+{=}O \longleftrightarrow R{-}C{\equiv}O^+$ and are linear; however, much of the positive charge is located on the carbon atom.[6]

Acyl transfer reactions in solution have been extensively investigated and reviewed.[7,8] Experimental work up to 1960 was satisfactorily interpreted in terms of a carbonyl addition–elimination mechanism proceeding through a covalently bound tetrahedral intermediate.[7] Later, Williams[9] and Jencks[10] and their co-workers found concerted bimolecular acyl transfer between substituted phenolate anions and nitrophenyl acetates and formates. Such concertedness has been demonstrated in the solvolysis of acyl chlorides in aqueous media[11] and in alcoholic media.[12] More recent evidence was interpreted in terms of an S_N2–S_N1 mechanistic spectrum for these reactions.[13]

Previous gas-phase studies of acyl transfer

The mechanism of acyl group transfer in the gas phase has been controversial. Early workers[14] suggested a loose adduct for the $CF_3CO_2^-\cdot(CF_3CO)_2O$ system that implied a single minimum potential energy surface with a stable covalently-bound tetrahedral intermediate analogous to the solution phase results. Riveros and co-workers suggested that the tetrahedral adduct $HC(OMe)(OH)O^-$ in the reaction of OH^- + HCOOMe was a local transition state rather than a stable intermediate.[15] Kinetic acyl transfer rates measured by Asubioji and Brauman[16] [reaction (1)], where X = F, Cl, CH_3O, CN, SH; R = CH_3, C_2H_5,

$$X^- + RCOY \longrightarrow Y^- + RCOX \qquad (1)$$

$(CH_3)_2CH$, $(CH_3)_3C$, C_6H_5, CF_3; Y = Cl, Br, were considerably slower than the corresponding predicted collision rates, implying that the potential energy surface contains at least two minima separated by a barrier, estimated to be *ca.* 7 kcal mol^{-1} from RRKM (Rice, Ramsberger, Kassel, Marcus) calculations. Gas phase S_N2 reactions at saturated carbon atoms disclose unsymmetrical complexes as energy minima in which the ionic nucleophile is electrostatically bound by the induced dipole of the neutral substrate.[17] However, Kim and Caserio *et al.*[18] concluded that acyl transfer between protonated acyl substrates (*e.g.* $AcOH_2^+$) and oxygen or sulfur nucleophiles frequently occurs by the formation of acyl cation complexes rather than tetrahedral intermediates. Theoretical calculations support a double-well separated by a barrier potential energy surface for these reactions but disagree as to whether the intermediate state is tetrahedral[19] or not.[20] Park *et. al.*[21] suggest a mechanistic change from rate-limiting formation to breakdown of the anionic intermediate in the gas phase. Recently, Wilbur and Brauman[22] found for the reaction Cl^- + CH_3OCOCl unsymmetrical ion–molecule intermediates, but did not distinguish between tetrahedral intermediates or transition states. Carbanion additions to esters in the gas phase were shown to occur by an addition–elimination–deprotonation mechanism just as in the familiar solution Claisen condensation.[23,24]

Most gas phase studies to date, and all those discussed above, have involved acyl transfer reactions between neutral substrates and anionic nucleophiles. Only a few examples of acyl transfer reactions between protonated acyl substrates and neutral nucleophiles leading to acyl cation reaction intermediates have appeared[18] and these involve protonated substrates in which the position of protonation is sometimes uncertain. In previous gas phase[25] and theoretical work,[26] we have studied the mechanism of nucleophilic substitution at saturated carbon atoms using charged pyridinium substrates of type $R{-}Py^+$. Such species have neutral leaving groups which allow both S_N1 and S_N2 reactions to occur in media of low relative permittivity.[27] Utilizing Fourier transform ion cyclotron resonance (FTICR) mass spectrometry, *N*-substituted pyridinium cations are easily generated in the gas phase and appearance energies for fragmentation have been measured.[25a,b] Most recently, we have achieved intramolecular nucleophilic substitution reactions (S_N2) using pyridinium cations in the gas phase.[28]

These previous findings have provided motivation for the present study of the collisionally activated dissociation (CAD) of substituted pyridinium cations and acyl transfer reactions with neutral nucleophiles in the gas phase. We first set out to determine the relative fragmentation energies of the CAD of various *N*-acylpyridinium cations in the gas phase, a good understanding of which is necessary before examining the corresponding bimolecular reactions.

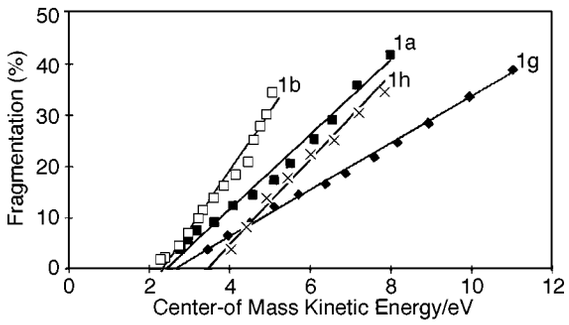


Fig. 1 Percentage fragmentation of *N*-(aroyl)-4-(dimethylamino)-pyridinium cations (**1a**,**b**,**g**,**h**) to aroyl cations and DMAP plotted *vs*. nominal center-of-mass kinetic energy (eV) to yield the observed threshold fragmentation energies E_{obs}

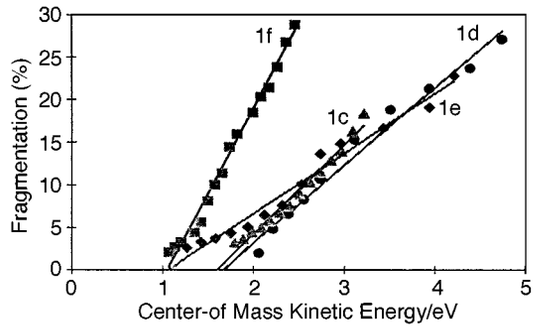


Fig. 2 Percentage fragmentation of *N*-(aroyl)-4-(dimethylamino)pyridinium cations (**1c**–**f**) to aroyl cations and DMAP plotted *vs*. nominal center-of-mass kinetic energy (eV) to yield the observed threshold fragmentation energies E_{obs}

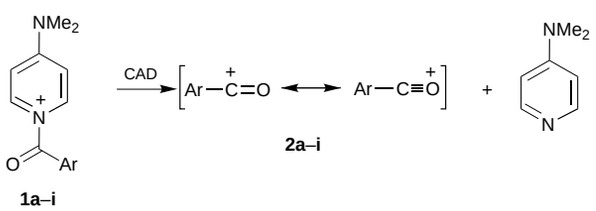
Table 1 E_{obs} for the fragmentation of *N*-aroyl-4-(dimethylamino)-pyridinium cations to aroyl ions

		m/*z*		
Compound	Ar	**1a**–**i**	**2a**–**i**	E_{obs}/kcal mol^{-1}
a	Ph	227	105	56
b	*p*-MeC_6H_4	241	119	54
c	Naphthyl	279	157	39
d	*o*-MeC_6H_4	241	119	37
e	*p*-$MeOC_6H_4$	257	135	25
f	*p*-$Me_2NC_6H_4$	270	148	24
g	*p*-FC_6H_4	245	123	61
h	*p*-$CF_3C_6H_4$	295	173	80
i	2-Thienyl	233	111	<24

Results and discussion

Fragmentation of *N*-(aroyl)-4-(dimethylamino)pyridinium cations

N-Benzoyl-4-(dimethylamino)pyridinium cation (**1a**) was subjected to CAD experiments utilizing electrospray ionization FTICRMS. Compound **1a** was first introduced and then isolated in the FTICR analyzer cell, and the intact parent ion was detected (*m*/*z* 227). Following resonant radiofrequency (RF) excitation of the parent ion to high kinetic energies in the presence of argon, two major ions were detected: the precursor ion **1a** at *m*/*z* 227 and the product benzoyl cation **2a** at *m*/*z* 105 (Scheme 1). The observed fragmentation energy (E_{obs}) for the



Scheme 1 CAD patterns for compounds **1a**–**i** (see Table 1)

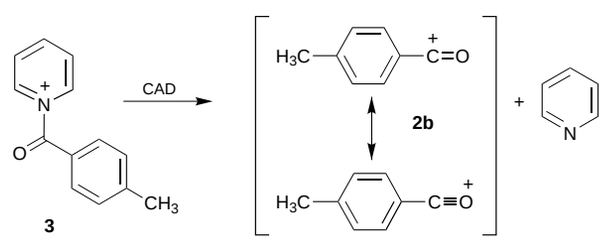
benzoyl cation **2a** was estimated (56 kcal mol^{-1}) as described in previous work (see Experimental section).[25a,b] The nominal center-of-mass energy (E_{cm}) was plotted *vs*. the percentage fragmentation observed (I/I_o), and the straight line portions of this plot were extrapolated to zero fragmentation to give the observed fragmentation energy (Fig. 1).

Seven other *N*-aroyl-4-(dimethylamino)pyridinium cations (**1b**–**h**) (see Table 1) with various electron-donating or electron-withdrawing groups at the benzene ring were studied under similar CAD conditions. Formation of the corresponding aroylium ions (**2b**–**h**) was observed in all cases as shown in Scheme 1. The observed fragmentation energies (E_{obs}) were estimated as shown in Figs. 1 (**1a**,**b**,**g**,**h**) and 2 (**1c**–**f**), and the results are summarized in Table 1.

N-(2-Thienoyl)-4-(dimethylamino)pyridinium cation (**1i**) followed the same fragmentation pattern as compounds **1a–h**. However, we were not able to measure its fragmentation energy since this compound underwent instantaneous fragmentation and attempts to isolate the parent ion led only to formation of fragment ion.

From Table 1, the E_{obs} values for this series of *N*-(aroyl)-4-(dimethylamino)pyridinium cations (**1a**–**i**) increase as follows: **1i** < **1f** < **1e** < **1d** < **1c** < **1b** < **1a** < **1g** < **1h**. These trends are expected since aroyl cations are stabilized by electron-donating groups and destabilized by electron-withdrawing groups. Thus, the greater electron-donating ability of the *p*-methoxy and *p*-dimethylamino groups lowered the E_{obs} of cations **1e** and **1f** significantly ($\Delta E_{obs} = 31$ and 32 kcal mol^{-1}, respectively, compared to cation **1a**). Compared with cation **2a**, the naphthalenyl-substituted cation **2c** has a larger conjugated π system, which also resulted in a lower E_{obs} value for cation **1c**. In the case of the *o*-methyl-substituted cation **1d**, a steric effect is likely to be the main driving force in the energetically favorable dissociation of cation **1d** to form the aroylium ion **2d**. The observed lowest fragmentation energy for the heterocyclic cation **2i** reflects the high electron-donating ability of the 2-thienyl group. The strong electron-withdrawing effect of the trifluoromethyl substituent increases the E_{obs} value of cation **1h** to 80 kcal mol^{-1}. When a fluorine atom is directly connected to the benzene ring (cation **1g**, fragmentation energy estimated to be 61 kcal mol^{-1}), this effect is much less pronounced since the fluorine atom acts both as a σ electron-withdrawing and p–π electron-donating group.

When *N*-(*p*-methylbenzoyl)pyridinium cation (**3**) was employed as a substrate in the CAD experiment, the same product *p*-methylbenzoyl cation **2b** was detected as from cation **1b** (Scheme 2). However, no extra RF energy is needed to dissociate cation **3** to the benzoyl cation **2b**, while the measured E_{obs} for the cation **1b** is 54 kcal mol^{-1}. These results reflect the stronger (acyl)C–N bond of cation **1b** because of the electron-donating *p*-dimethylamino group.



Scheme 2 CAD pattern for compound **3**

Fragmentation of *N*-(alkylacyl)-4-(dimethylamino)pyridinium cations

Four *N*-(alkylcarbonyl)pyridinium cations (**4a**–**d**) were investigated by the method described above. A novel fragmentation

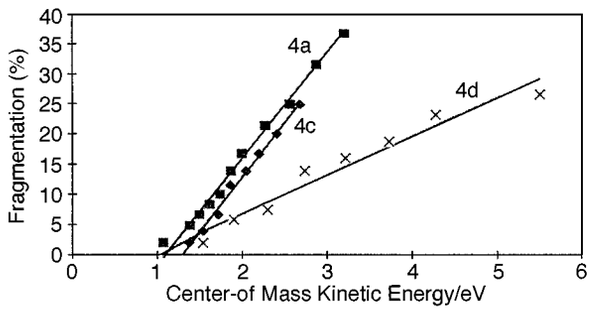
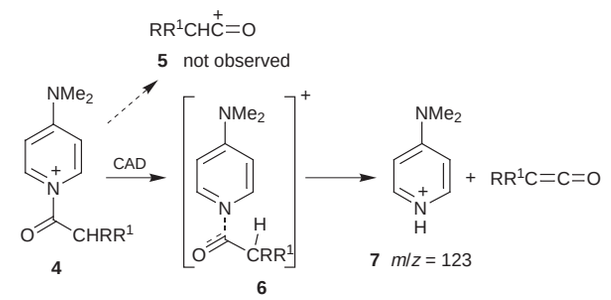


Fig. 3 Percentage fragmentation of *N*-(acyl)-4-(dimethylamino)pyridinium cations (**4a**,**c**,**d**) to acyl cations and DMAP plotted *vs*. nominal center-of-mass kinetic energy (eV) to yield the observed threshold fragmentation energies E_{obs}

pathway was found in these studies. After the parent ion, *N*-acetyl-4-(dimethylamino)pyridinium cation (**4a**), was isolated and energized in the analyzer cell, the only fragment ion observed was protonated *N*,*N*-dimethylaminopyridine DMAP (**7**) (Scheme 3) and the acetyl cation **5** which would come from



4a R = R^1 = H, *m*/*z* = 175
b R = *n*-C_7H_{15}, R^1 = H, *m*/*z* = 259
c R, R^1 = -$(CH_2)_2$-, *m*/*z* = 191
d R, R^1 = PhCH=, *m*/*z* = 253

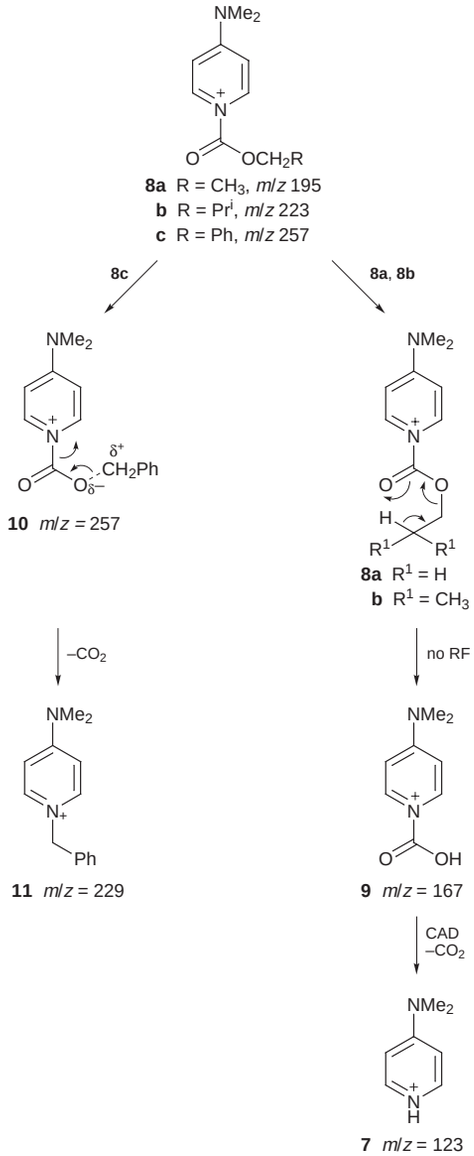
Scheme 3 CAD patterns for compounds **4a**–**d**

simple S_N1 dissociation was not detected. From plots of the observed percentage fragmentation *vs*. the center-of-mass kinetic energy (Fig. 3), E_{obs} for the protonated DMAP was estimated to be 25 kcal mol^{-1}. When *N*-octanoyl-4-(dimethylamino)pyridinium cation (**4b**), *N*-(cyclopropanecarbonyl)-4-(dimethylamino)pyridinium cation (**4c**) and *N*-cinnamoyl-4-(dimethylamino)pyridinium cation (**4d**) were used as substrates, protonated DMAP (**7**) was again the only fragment ion observed. The fragmentation energies were estimated to be 30 kcal mol^{-1} for cation **4c** and 24 kcal mol^{-1} for cation **4d**. The fragmentation energy for cation **4b** was not measured since the reaction proceeded with no additional activation energy. On the basis of the other experimentally measured fragmentation energies, we estimated E_{obs} for cation **4b** to be less than 24 kcal mol^{-1}.

In our previous work,[29] we demonstrated that ion–molecule pair complexes are involved in fragmentation pathways of *N*-alkylpyridinium cations. Most likely, ion–molecule pairs are involved in the reactions of cations **4a**–**d**. The first step proceeds *via* a C–N bond cleavage of *N*-(acyl)pyridinium cations **4a**–**d** to form an ion–molecule pair **6** (Scheme 3) from which protonated DMAP **7** is formed *via* β-H elimination together with a neutral ketene. The preparation of such ketenes from *N*-(acyl)-benzotriazoles has been previously reported.[30]

Fragmentation of *N*-(alkoxycarbonyl)-4-(dimethylamino)-pyridinium cations

N-(Ethoxycarbonyl)pyridinium cation **8a** was studied under nearly identical CAD experimental conditions. The fragment ions observed were *N*-carboxy-4-(dimethylamino)pyridinium cation (**9**) at *m*/*z* 167 and protonated DMAP (**7**) at *m*/*z* 123

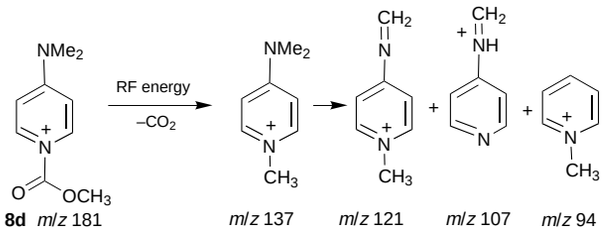


Scheme 4 CAD patterns for compounds **8a**–**c**

(Scheme 4). Cation **9** was formed without introducing any RF energy to the precursor ion, while additional energy was required for the formation of cation **7**. When the ion at *m*/*z* 167 was continuously ejected from the cell in a double resonance experiment, the ion at *m*/*z* 123 was not observed, proving that cation **7** was formed only from cation **9** (*via* loss of carbon dioxide) and not from the parent ion **8a**. Additionally, when the ion at *m*/*z* 167 was isolated in the cell and further subjected to CAD, as expected, the ion at *m*/*z* 123 was formed. Similarly, only cations **9** and **7** were formed when *N*-(isobutoxycarbonyl)pyridinium cation (**8b**) was investigated under the same CAD conditions. However, when the *N*-(benzyloxycarbonyl)-4-(dimethylamino)pyridinium cation (**8c**) was first isolated and then energized in the analyzer cell, immediate elimination of CO_2 took place and the only product observed was the corresponding fragment **11** (Scheme 4).

A probable explanation for the formation of **9** and **11** is shown in Scheme 4. In the case of cations **8a** and **8b**, β-H elimination of the esters led to the formation of intermediate **9** and, presumably, a neutral alkene *via* a concerted mechanism. The intermediate **9** is relatively unstable and it can easily lose CO_2 when RF energy is applied. When the β-H was not available, as in the case of ion **8c**, an ion–molecule complex **10**, which has the same *m*/*z* ratio as the starting pyridinium cation, was formed *via* a C–O instead of a C–H bond cleavage. Elimination of carbon dioxide was directly observed as a result of an intra-

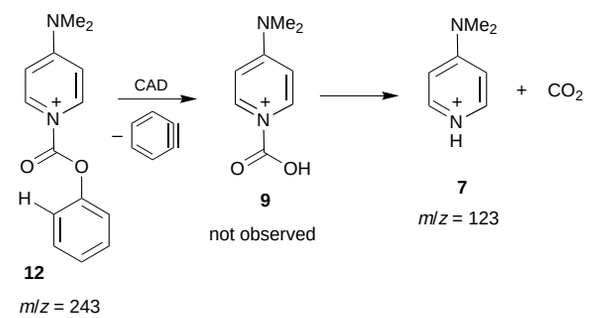
molecular nucleophilic substitution reaction (S_Ni) presumably from the ion–molecule complex **10** (Scheme 4). To test the proposed mechanism we chose to investigate the *N*-(methoxycarbonyl)pyridinium cation **8d**, which does not have a β-H. Cation **8d** was extremely stable when subjected to CAD; only after the application of high RF energy, did elimination of carbon dioxide take place to form the fragment ion at *m*/*z* 137, which further fragmented to give the ions at *m*/*z* 121, 107 and 94 (see Scheme 5). As expected, fragment ion **9** at *m*/*z* 167 was not



Scheme 5 CAD pattern for compound **8d**

detected, which confirms that when there is no β-H (cations **8c**,**d**) and that the dissociation proceeds *via* immediate elimination of carbon dioxide and not through a six-membered ring transition state as is the case for cations **8a**,**b**.

N-(Phenoxycarbonyl)-4-(dimethylamino)pyridinium cation (**12**) was also very stable under the same CAD conditions. Only the parent ion was observed until very high RF energy (E_{obs} = 72 kcal mol^{-1}) was applied. No fragmentation *via* either of the routes shown in Scheme 4 was observed. However, cation **9** is still the likely intermediate as outlined in Scheme 6. There

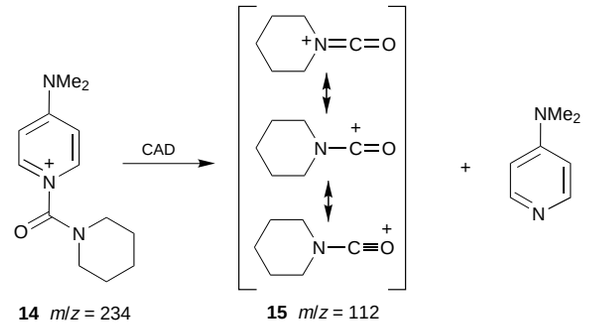


Scheme 6 CAD pattern for compound **12**

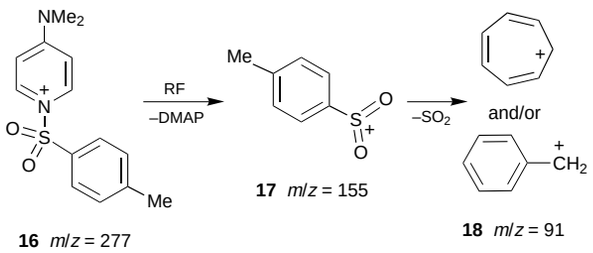
are major differences between the pyridinium cations **8a**,**b** and cation **12**: both the sp^2 C–O bond and the sp^2 C–H of pyridinium cation **12** are stronger than the corresponding sp^3 C–O and sp^3 C–H bonds in cations **8a**,**b**. When cation **12** was accelerated to high kinetic energies in the CAD process, resulting in high internal excitation after collision with the neutral argon gas and subsequent cleavage of the sp^2 C–O and C–H bonds, the neutral molecules carbon dioxide and benzyne (Scheme 6) are lost simultaneously on the millisecond timescale of this experiment, forming ion **7**, and therefore no intermediate **9** could be detected.

N-(Piperidinocarbonyl)-4-(dimethylamino)pyridinium cation (**14**) was examined under similar CAD conditions. Although **14** is structurally different from cations **1a**–**i**, cation **14** behaved similarly with the piperidinocarbonyl cation **15** being the only fragment ion observed during the CAD experiment (Scheme 7). The fragmentation energy was 67 kcal mol^{-1}.

N-(Toluene-*p*-sulfonyl)-4-(dimethylamino)pyridinium cation (**16**) was studied using the CAD conditions described above. The parent ion was isolated in the analyzer cell, and when the RF energy was applied, it gave two fragment ions at *m*/*z* 155 (toluene-*p*-sulfonyl cation **17**, Scheme 8) and at *m*/*z* 91 (tropylium ion and/or benzyl cation **18**).[31,32] To verify the dissociation sequence of this reaction, cation **17** was continuously ejected from the cell and as a result, the product ion at *m*/*z* 91



Scheme 7 CAD pattern for compound **14**

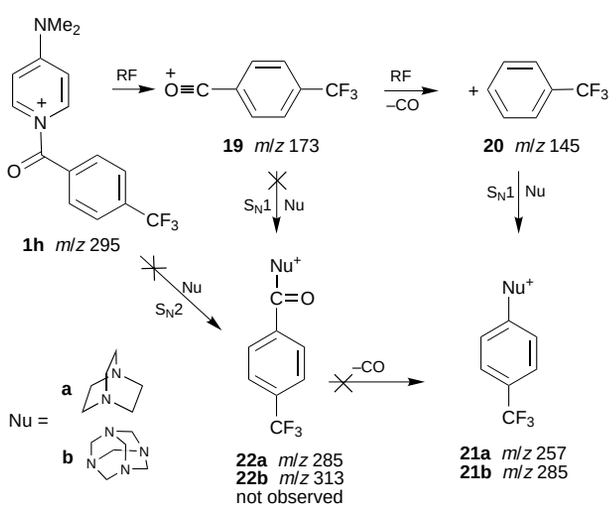


Scheme 8 CAD pattern for compound **16**

disappeared. This confirms that the starting cation **16** dissociated to cation **17**, which can dissociate further to cation **18** as shown in Scheme 8. E_{obs} was measured to be 38 kcal mol^{-1}. Compared to 54 kcal mol^{-1} for *N*-acyl cation **1b**, the significantly lower E_{obs} value for *N*-sulfonyl cation **16** suggests that the N–C (acyl) bond is stronger than the N–S bond in these pyridinium cations.

Attempts to induce S_N2 processes by ion–molecule reactions

Cation **1h** was chosen for its high relative stability (E_{obs} = 80 kcal mol^{-1}), and triethylenediamine and hexylmethylenetetramine were selected as the neutral substrates. The neutral species were introduced into the cell *via* a leak valve as described elsewhere.[33] In both cases no reactions were observed unless additional RF energy was imparted to the precursor ion. The product ion **19** at *m*/*z* 173, formed *via* loss of a neutral DMAP from the parent ion **1h**, was observed after applying a RF pulse. This ion underwent further loss of CO to give a fragment ion at *m*/*z* 145 possibly of structure **20** (see Scheme 9). In both

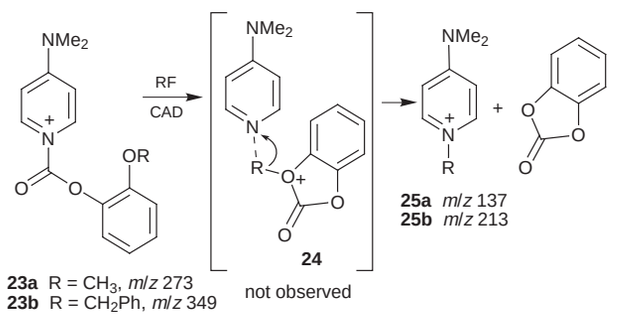


Scheme 9 Ion–molecule reactions of cation **1h**

cases product ions **21a**,**b** at *m*/*z* 257 and 285, respectively, were generated and observed, while the expected adducts **22a**,**b** at *m*/*z* 285 and 313, respectively, were not detected. Cations **21a**,**b** could be formed *via* S_N1 type reactions between cation **20** and

the corresponding nucleophile or between cation **19** and the corresponding nucleophile to form cations **22a**,**b** (not observed) followed by an immediate loss of CO. Alternatively, cations **21a**,**b** could be formed *via* S_N2 reactions which proceed *via* direct formation of the adduct ions **22a**,**b** followed by immediate loss of CO. To distinguish between these reaction mechanisms, cation **20** was completely ejected from the cell with the result that cations **21a**,**b** also disappeared, thus proving that the reaction proceeded *via* the S_N1 pathway on **20** as outlined in Scheme 9. Similar S_N1 reaction pathways in the gas phase were previously reported by us.[33]

In another study we have observed intramolecular S_N2 reactions at a saturated sp^3-carbon under similar reaction conditions.[28] For the present study compounds **23a**,**b** were synthesized and subjected to CAD using argon as the collision gas (Scheme 10). In both cases transfer of the R group to the



Scheme 10 CAD patterns for compounds **23a,b**

DMAP molecule was observed, where, as expected, transfer of the benzyl group was easier (fragment ion **25b** was observed in higher relative intensity than fragment ion **25a**, under the same reaction conditions). Protonated DMAP was also detected. The reaction most likely proceeded *via* formation of the cyclic intermediate **24** (not observed), followed by an immediate transfer of the R group to the DMAP molecule.

Conclusions

N-Aroyl- and *N*-heteroaroyl-pyridinium cations dissociate cleanly to form $ArCO^+$ cations in a process which is governed mainly by the stabilization of the $ArCO^+$ group by electron donor substituents and to a lesser extent by the acceleration from *ortho* substituents in the aryl group. By contrast, *N*-alkylcarbonyl- and *N*-phenoxycarbonyl-pyridinium cations dissociate to yield the corresponding pyridinium cation. The process must involve the transfer of a proton from the acyl cation fragment to the pyridine nitrogen atom within an ion–molecule complex intermediate; presumably the accompanying neutral product is a ketene or CO_2 + aryne. A third pathway is taken up by *N*-alkoxycarbonylpyridiniums $ROCOPy^+$ which yield detectable *N*-carboxypyridinium cations, evidently by R–O cleavage.

We previously demonstrated[25a,27d] unimolecular heterolysis for compounds of type RR′CHX by using positively charged substrates with a neutral leaving group. The present results show that unimolecular heterolysis also occurs for compounds of type RCOX of similar charge strutures. The absence of charge generation in the process $RCOPy^+ \longrightarrow RCO^+ + Py$ allows it to occur readily in the gas phase. Indeed, in the present work all the reaction studies have involved unimolecular processes.

Although our initial attempts to induce S_N2 processes, either by ion–molecule or by intramolecular processes have failed, we believe that further study of $RCOPy^+$ substrates in both the gas phase and in non-nucleophilic solvents should help define the mechanistic spectrum of aryl transfer reactions in general.

Experimental

Mass spectrometry techniques

All experiments were performed on a Bruker Apex 4.7 tesla Fourier transform ion cyclotron resonance mass spectrometer (Bruker Analytical Systems, Billerica, MA), equipped with an external ion source. The ions were introduced from an Analytica Electrospray Ionization source (Analytica, Branford, CT). The acylpyridinium salts, dissolved in dry acetonitrile (0.1 mM concentration), were sprayed at a flow rate of 60 μl h^{-1}. The experimental set-up is described in detail elsewhere.[34]

Broadband detection was utilized in these experiments covering a mass range of 50 to 2500 amu. During detection, 20 spectra were acquired and co-added prior to the Fourier transformation to provide signal-to-noise ratios greater than 500 : 1. Typically 32K data points were collected and for more accurate determination of the relative intensities of the parent and fragment peaks, the data were zerofilled twice to improve peak quantification.

Determination of fragmentation energies

The fragmentation energies for the formation of the acylium ions or protonated DMAP (depending on the fragmentation pathway) were determined by a procedure which was previously explained in detail.[25a]

In these calculations, no attempts have been made to account for the vibrational energies of the individual acylpyridiniums because of the strong structural similarities between all of the compounds studied. The calculated values for fragmentation energies previously determined by CAD experiments in our group[25a] vary from literature values for the same system by 0.35 eV (8 kcal mol^{-1}). Since fragmentation energies have not been reported for the systems we have investigated in the present study, we cannot report the estimated errors with the same certainty, however for our present calculations we have used the same conditions as described previously[25a] and therefore the error limits should be similar. Relative errors should be less and thus trends in the data provide extremely useful information as to the relative stability of various acylpyridiniums. In addition, much insight may be gained regarding the effect of various functional groups upon acylium ion stability.

Preparation of compounds

Compounds **1a**, **1f** and **14** were made following previously published methods,[35] and characterized by ^1H and ^{13}C NMR spectroscopy (*J* values are given in Hz) and electrospray FTICRMS. All of the other *N*-acyl-4-(dimethylamino)pyridinium salts (**1a**–**e**, **3**, **4**, **8**, **12**) and *N*-(toluene-*p*-sulfonyl)-4-(dimethylamino)-pyridinium salt (**16**) were prepared in solution by mixing the 4-dimethylaminopyridine (DMAP) and the corresponding acyl chloride in acetonitrile at room temperature for 15 min; the resulting acetonitrile solutions were directly used in the CAD experiments without isolation and purification. The cation structures were all characterized by electrospray FTICRMS.

General procedure for the synthesis of *N*-acyl-4-(dimethylamino)pyridinium tetraphenylborate salts (1f, 14)

An anhydrous CH_3CN (5 ml) solution of DMAP (2 mmol) was added dropwise into a stirred, cooled (0–4 °C) solution of an appropriate acid chloride (2 mmol) and sodium tetraphenylborate (2 mmol) in CH_3CN (10 ml) under a nitrogen atmosphere. The reaction mixture was stirred for 30 min after the amine addition was complete, then the white precipitate (NaCl) was allowed to settle and to pack at the bottom of the reaction flask. The supernatant was transferred by decanting and then evaporated to dryness to give a solid, which was recrystallized from CH_2Cl_2–diethyl ether or CH_2Cl_2–hexanes.

***N*-[4-(Dimethylamino)benzoyl]-4-(dimethylamino)pyridinium tetraphenyl borate (1f).** A yellow solid, 73% yield, mp 140–142 °C (CH_2Cl_2–diethyl ether); δ_H(300 MHz; [$^2H_6$]DMSO) 8.48

(2H, d, *J* 8.0), 7.64 (2H, d, *J* 9.1), 7.17–7.22 (8H, m), 7.08 (2H, d, *J* 8.0), 6.91–6.96 (8H, m), 6.86 (2H, d, *J* 9.3), 6.77–6.82 (4H, m), 3.31 (6H, s), 3.10 (6H, s); δ_C(75 MHz; [$^2H_6$]DMSO) 166.7, 163.3 (q, *J* 49.3, ^{11}BC), 157.6, 154.4, 139.2, 135.5, 133.7, 125.2 (q, *J* 2.7, ^{11}BC), 121.4, 111.2, 106.7, 40.4, 39.6. [HRMS (FTICR for the cation) $C_{16}H_{20}N_3O$ required 270.1606. Found: 270.1618.]

***N*-Piperidinocarbonyl-4-(dimethylamino)pyridinium tetraphenylborate (14).** A white solid, 82% yield, mp 146–148 °C (CH_2Cl_2–hexanes); δ_H(300 MHz; [$^2H_6$]acetone) 8.08 (2H, d, *J* 8.0), 7.33–7.39 (8H, m), 6.91–6.96 (8H, m), 6.77–6.83 (6H, m), 3.40–3.48 (4H, m), 3.18 (6H, s), 1.62–1.68 (6H, m); δ_C(75 MHz; [$^2H_6$]acetone) 164.8 (q, *J* 49.4, ^{11}BC), 158.4, 152.4, 139.6, 136.9, 126.0 (q, *J* 2.7, ^{11}BC), 122.3, 108.0, 48.45, 48.4, 40.8, 26.0, 24.4. [HRMS (FTICR for the cation) $C_{13}H_{20}N_3O$ required 234.1606. Found: 234.1600.]

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Paper 7/06086F
Received 19*th August* 1997
Accepted 19*th January* 1998