Doubly Charged Ion Mass Spectra of Alkyl-substituted Furans and Pyrroles

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Doubly charged ion mass spectra of alkyl-substituted furans and pyrroles were obtained using a double-focusing magnetic mass spectrometer operated at 3.2 kV accelerating voltage. Molecular ions were the dominant species found in doubly charged spectra of lower molecular weight heterocyclic compounds, whereas the spectra of the higher weight homologues were typified by abundant fragment ions from extensive decomposition. Measured doubly charged ionization and appearance energies ranged from 22.8 to 47.9 eV. Ionization energies were correlated with values calculated using self-consistent field-molecular orbital techniques. A multichannel diabatic curve-crossing model was developed to investigate the fundamental organic ion reactions responsible for development of doubly charged ion mass spectra. Probabilities for Landau-Zener type transitions between reactant and product curves were determined and used in the collision model to predict charge-transfer cross-sections, which compared favorably with experimental cross-sections obtained using time-of-flight techniques.

INTRODUCTION

Ever-increasing numbers of investigations have been devoted to experimental and theoretical studies of gas-phase carbocations.¹⁻⁵ Likewise, the amount of research dealing with carbocations in solution^{6,7} has been increasing as methods have improved for producing and characterizing stable doubly charged ions. Most of the gas-phase studies have employed the techniques of charge stripping^{1,2} or doubly charged ion mass spectrometry.^{4,5} Charge-stripping methods involve the removal of an electron from AB^+ in kilo-electron-volt collisions to form AB^{2+} product ions, whereas doubly charged ion mass spectral techniques start with AB^{2+} ions which collide with target molecules to form AB^+ products.

We employ the latter method to study doubly charged ions of some of the smallest heterocyclic aromatic compounds: furan, pyrrole and their alkyl-substituted homologues. Doubly charged ions, produced in the ion source of a mass spectrometer of Nier-Johnson geometry, are accelerated into the first field-free drift/collision region of the mass spectrometer, where they may undergo charge-transfer reactions of the type

Little momentum is transferred in this reaction, and fast AB^+ product ions have twice the kinetic energy of all singly charged ions formed in the ion source. The fast AB^+ product ions are then passed by an electrostatic sector operated at twice the normal operating voltage ($2E$). These product ions are then momentum analysed in the magnetic sector and appear at an apparent mass m^* given by $(AB^+/z)^2/(AB^{2+}/2z)$ which unambiguously identifies both the reactant and product ions of reaction (1).

The aims of this study are as follows:

(i) to obtain and interpret the doubly charged ion mass spectra of alkyl-substituted furans and pyrroles;

(ii) to determine the ionization/appearance energies of abundant ions in these spectra and correlate energetic information with that obtained from self-consistent field-molecular orbital (SCF-MO) theoretical methods;

(iii) to measure the absolute reaction cross-section for a fundamental electron-transfer process from the neutral reactant to the incident doubly charged ion;

(iv) to develop a model to explain these gas-phase carbocation reaction dynamics responsible for doubly charged ion mass spectra.

RESULTS AND DISCUSSION

Doubly charged ion mass spectra

Stable doubly charged ions were produced by electron impact (EI) ionization of alkyl-substituted furans and pyrroles. Fully accelerated doubly charged ions underwent charge-transfer reactions to produce stable singly charged product ions which were transmitted through the electrostatic sector operated at twice the voltage ($2E$) normally required to pass singly charged ions formed in the source. The product ion mass distributions, termed the $2E$ mass spectra, of alkyl-substituted furans are presented in Table 1. All product ions from these alkyl-substituted furans having a relative abundance greater than 1% are tabulated. Doubly charged alkyl-substituted furans fragmented in the source readily to form a variety of stable doubly charged fragment F^{2+} ions, which were accelerated and underwent charge-transfer reactions of the type (1) to form singly charged F^+ product ions of the same mass. The intensity distribution of product fragment ion peaks in the $2E$ spectra given in this table is correlated with the number of carbons in the alkyl substituent. The $2E$ spectrum of furan is dominated by the molecular ion in contrast with the $2E$ spectrum of 2-propylfuran which is composed of 28 product fragment ion peaks, more than half of which had greater

Figure 1. Relative abundance of $[C_nH_2]^+$ product ions from the $2E$ spectra of alkyl-substituted furans. The dashed line illustrates the abundance of all product ions with the formula $[C_nH_2]^+$ ($n=3-8$) as a function of number of carbon atoms in the alkyl substituent. The solid line shows the relative abundance of only $[C_5H_2]^+$ product ions plotted as a function of number of carbon atoms in the alkyl substituent.

than 10% relative intensity. Many of the intense product ion peaks in the substituted furan spectra contain only carbon and hydrogen.

The $[C_nH_2]^+$ product ions are abundant in the $2E$ mass spectra of a wide range of compounds, and these ions are also prevalent in the $2E$ spectra of alkyl-substituted furans shown in Table 1. The $[C_nH_2]^+$ product ion abundances range from 11 to 35% of the total ion abundance. The dashed line in Fig. 1 illustrates the isotopically corrected relative abundances of $[C_nH_2]^+$ ($n=3-8$) product ions as a function of the number of carbon atoms in the alkyl substituent. The $[C_5H_2]^+$ product ion has been found to be dominant in the $2E$ spectra of other hydrocarbons,⁵ and its abundance has been rationalized on the basis of its stability.^{8,9} The solid line in Fig. 1 shows the relative abundance of $[C_5H_2]^+$ product ions which maximizes at 2-ethylfuran. The maximum in the solid line corresponds to the $[C_5H_2]^+$ product ion abundance from reactions of $[C_5H_2]^{2+}$ incident ions which are derived from loss of one carbon and oxygen as well as extensive hydrogen ejection from the molecular ion.

The relative abundance of $[M-nH]^+$ product ions decreases as the alkyl chain length increases; whereas the abundance of product ions resulting from C—C and C—O bond scission increases. A graphical display of these trends is provided in Fig. 2, where the relative abundances of $[M-nH]^+$ ($n=0-6$) product ions are given as a function of both the number of carbon atoms

Table 1. Relative intensities of product ion peaks in the $2E$ mass spectra of alkyl-substituted furans

<i>m/z</i>	Furan (68 u)	2-Methyl- furan (82 u)	2-Ethyl- furan (96 u)	2-Propyl- furan (110 u)	2-Butyl- furan (124 u)	2,5-Dimethyl- furan (96 u)
36		1.8				
38	11.4	13.3		6.4		
39	2.0					
48		3.2				
49		2.5				
50	2.2	40.5				11.1
51		72.8	6.8			25.7
52		100.0	6.0			39.7
53		5.7				3.2
60		2.0				3.3
61		4.9				3.2
62		36.4	100.0	48.7	38.5	100.0
63		3.7	20.3	11.5	9.8	19.9
64			17.3	8.7	13.3	19.5
65	2.1		37.1	11.2	6.7	15.1
66	1.8		5.9	2.7	3.9	7.2
67			8.5	3.3		7.3
68	100.0				1.7	
69	4.7					
71					2.5	
73				3.2		2.4
74				39.6	20.2	11.1
75				25.4	10.3	2.9
76		6.9	2.5	28.7	22.7	1.9
77		3.6		20.7	14.4	
78		5.1	6.3	91.9	53.1	3.9
79				100.0	86.1	3.9
80		8.7		13.3	9.3	
81		82.1	7.6	4.9		2.5
82		53.0				
85				1.7	1.7	
86				17.4	83.9	
87				2.4	11.3	
88				2.4	9.7	
89					14.7	
90			6.3		100.0	
91					54.8	
92			7.4		34.8	
93					8.5	
94			56.7	4.6	7.7	58.4
95			9.4	1.9	3.6	48.6
96						74.7
97						7.8
98					9.1	
102					2.9	
103					5.0	
104				30.3	4.0	
105				16.5	22.2	
106				24.0	3.9	
107				19.0	27.2	
108				1.8	4.1	
110					3.6	
115					5.9	
118					21.2	
119					5.5	
120					23.9	
121					2.1	
122					3.2	

in the alkyl substituent and the number of hydrogen atoms removed. As the length of the alkyl substituent increases, greater numbers of hydrogens are readily

Figure 2. Relative abundance of all product ions from alkyl-substituted furans, with the formula $[M - nH]^+$ ($n=0-6$) is displayed as a function of number of carbon atoms in the alkyl substituent.

removed from the molecular ion. For example, in the case of 2-butylfuran, the highest-mass product ion in the spectrum corresponds to the loss of two hydrogens, and the relative abundances of the $[M - 4H]^+$ and $[M - 6H]^+$ product ions are greater than those obtained from either ethyl- or methylfuran.

Several features observed in the 2E spectrum of 2,5-dimethylfuran are found to be intermediate between those observed for 2-methyl- and 2-ethylfuran. Abundant fragment F^+ product ions in the spectra of both 2-methyl- and 2-ethylfuran are abundant also in the spectrum of 2,5-dimethylfuran. The small number of hydrogens lost from 2,5-dimethylfuran is a characteristic of furans with small hydrocarbon substituents. The 27.2% relative abundance of $[C_nH_2]^+$ product ions from 2,5-dimethylfuran falls between the 21 and 35% determined for methyl- and ethyl-substituted furan. The $[C_5H_2]^+ / \sum(\text{product ions})$ ratio for 2,5-dimethylfuran is between the values observed for 2-methyl- and 2-ethylfuran.

The 2E mass spectra of product ions with abundances greater than 1% from alkyl-substituted pyrroles are presented in Table 2. In most cases, the only significant fragmentation route is hydrogen elimination from the molecular ion. The only compound to undergo extensive fragmentation, 2,4-dimethyl-3-ethylpyrrole, possesses a base peak at m/z 108 corresponding to the loss of a methyl group. Another intense fragment peak appears in this spectrum at m/z 93 and corresponds to loss of two methyl groups. The relative abundance of ions due to hydrogen elimination from the substituted pyrrole molecular ions is plotted in Fig. 3 as a function of the number of hydrogens lost. The relative intensity of the molecular ion peak decreases as the number of carbons in the compound is increased. Distinct maxima occur in Fig. 3 for removal of two hydrogens, which may indicate elimination of molecular hydrogen by a low-energy decomposition pathway. As illustrated in Fig. 3, the relative abundance of $[M - nH]^+$ product ions increases relative to the molecular product ion $[M]^+$ as the degree of substitution is increased.

Table 2. Relative intensities of product ion peaks in the 2E mass spectra of alkyl-substituted pyrroles

m/z	Pyrrole (67 u)	Methylpyrrole (81 u)	2,5-Dimethyl- pyrrole (95 u)	2,4-Dimethyl- 3-ethylpyrrole (123 u)
62			2.5	
64	4.4			
65	13.8			
67	100.0			
68	4.1			
76		12.9	1.0	
77		1.7		
78		1.2		
79		5.4		
80		16.4	2.9	
81		100.0		
82		6.3		
91			6.2	3.5
92			1.1	
93			100.0	37.5
94			22.4	3.0
95			11.5	1.7
103				2.7
104				20.9
105				14.7
106				42.3
107				40.8
108				100.0
109				7.3
117				56.7
118				12.4
119				8.8
120				4.9
121				32.4
122				5.7

Figure 3. Relative abundance of $[M - nH]^+$ ($n=0-6$) product ions of alkyl-substituted pyrroles plotted as a function of number n of hydrogen atoms removed from molecular ion.

In order to determine the total quantity of product ions formed in the $2E$ spectra of furan and pyrrole systems, total product ion abundances have been obtained for each compound. The total product ion abundance for each system was compared with a reference standard: the well-known $2E$ ion mass spectrum of benzene. These total product ion abundances relative to product ion abundances in the benzene system are presented in Table 3. In general, the $2E$ total ion abundances of the pyrroles are larger than the furans. These total ion abundances relative to benzene range from 1.3 to 25% for the furans and from 5.4 to 87% for the pyrroles. Although the total $2E$ ion abundances of these compounds are lower than that of benzene, the molecular ion of pyrrole is twice as abundant as the benzene molecular ion.

Data in Table 3, which show a progressive decrease in total $2E$ product ion abundance as the molecular weight M increases, suggest that either the formation of long-lived doubly charged ions in EI ionization decreases as a function of increasing M or that electron-transfer cross-sections decrease as M increases. A detailed consideration of the cross-section for charge-transfer reactions involving doubly charged ions is given below. Although there is a decrease in the product ion abundance as molecular weight increases, the ion abundances are sufficiently high to enable ionization efficiency curves to be measured and appearance energies to be obtained.

Ionization and appearance energies of doubly charged ions

Appearance energies for abundant ions in the $2E$ mass spectra of both furans and pyrroles have been determined. The results for a typical system, the m/z 93 product ion from 2,5-dimethylpyrrole, are given in Fig. 4. The data points in this figure illustrate the linear dependence of the square root of product ion abundance as a function of ionizing electron energy. It has been suggested,¹⁰ and found in other systems,^{5,11,12} that the probability of forming a doubly charged ion is a function of the square of the ionizing electron energy in excess of the ionization energy. As a result, a plot of the square root of doubly charged ion abundance is expected to be linear as a function of electron energy and extrapolate to the ionization energy at zero ion abundance. Product ions which form the doubly charged ion mass spectra reflect the behavior of their doubly charged primary ion

Table 3. Total product ion abundances in $2E$ mass spectra of alkyl-substituted furans and alkyl-substituted pyrroles relative to total product ion abundance in the benzene $2E$ spectrum

Furans		Pyrroles	
Compound	Relative abundance	Compound	Relative abundance
Furan	2.5×10^{-1}	Pyrrole	8.7×10^{-1}
2-Methylfuran	8.1×10^{-2}	Methylpyrrole	2.8×10^{-1}
2-Ethylfuran	1.3×10^{-1}	2,5-Dimethylpyrrole	5.4×10^{-2}
2-Propylfuran	4.0×10^{-2}	pyrrole	5.4×10^{-2}
2-Butylfuran	1.3×10^{-2}	2,4-Dimethylpyrrole	1.4×10^{-1}
2,5-Dimethylfuran	1.3×10^{-1}	3-ethylpyrrole	1.4×10^{-1}

Figure 4. Variation of square root of m/z 93 ion peak intensity from 2,5-dimethylpyrrole as a function of ionizing electron energy.

precursors with ionizing electron energy. Results similar to those displayed in Fig. 4 were observed for ions in the $2E$ spectra of both furans and pyrroles. Appearance energies of abundant ions in the spectra of furans are given in Table 4. Values range from 24.2 eV for forming the doubly charged molecular ion of 2-methylfuran to 47.9 eV for forming a fragment of mass 50 u from this compound. Ionization energies to form stable doubly charged molecular ions as well as doubly charged fragment ions in the pyrrole and substituted pyrrole systems are presented in Table 5. Values range from 22.8 eV, for

Table 4. Appearance energies of abundant ions in the $2E$ mass spectra of alkyl-substituted furans

Compound	Ion mass (u)	Appearance energy (eV)	Relative abundance (%)
Furan	68	25.8	100.0
2-Methylfuran	50	47.9	40.5
	52	31.0	100.0
	80	27.7	8.7
	81	29.1	82.1
	82	24.2	53.0
2-Ethylfuran	62	39.7	100.0
	63	40.7	20.3
	64	35.9	17.3
	65	35.4	37.1
	94	28.4	56.7
2-Propylfuran	95	26.4	9.4
	78	27.3	91.9
	79	26.7	100.0
2,5-Dimethylfuran	51	42.3	25.7
	52	36.3	39.7
	62	37.7	100.0
	94	25.6	58.4
	95	27.7	48.6
	96	24.8	74.7

Table 5. Appearance energies of abundant ions in the 2E mass spectra of alkyl-substituted pyrroles

Compound	Ion mass (u)	Appearance energy (eV)	Relative abundance (%)
Pyrrole	65	31.5	13.8
	67	25.6	100.0
	81	24.2	100.0
Methylpyrrole	93	24.1	100.0
	94	26.5	22.4
	95	22.8	11.5
2,4-Dimethyl-3-ethylpyrrole	93	24.7	37.5
	106	26.4	42.3
	107	26.1	40.8
	108	24.5	100.0
	121	23.0	32.4

the production of doubly charged 2,5-dimethylpyrrole molecular ions, to 31.5 eV, for forming mass 65 u doubly charged ions from pyrrole. Energies required to form doubly charged molecular ions in the furan and pyrrole systems are approximately three times higher than energies required for producing the respective singly charged ions.

Computed energies and structures of doubly charged ions

In order to gain insight into the energetics of doubly charged ion formation and mechanisms that control the reactions which produce 2E spectra, we have employed a quantum mechanical SCF-MO treatment to determine ion structures and energies. These ionic properties have been obtained from the MNDO semiempirical treatment¹³ using techniques previously outlined.¹⁴ Vibrational frequencies were determined⁹ for the geometry-optimized structures to ensure that minimum energy, rather than transition state structures, were obtained. Computed vertical ionization energies are

given in Table 6 along with experimental values. Vertical ionization energies have been determined from differences in heats of formation computed for neutral molecules and doubly charged ions frozen in the configuration of the respective molecules. As indicated in this table, there is reasonable accord between measured and computed energies. Geometry-optimized, minimum-energy, doubly charged ion structures presented in Table 6 are illustrated by the three-dimensional representations of Fig. 5, in which bond distances are given in angstroms. Identical bonds are labeled only once. Charge-transfer collisions involving these ions at 6.4 keV translational energy occur in time periods short compared to internal motion. As a consequence, an electron is transferred from the stationary target molecule to the fast doubly charged reactant ion in a vertical Franck-Condon process to form a fast singly charged product ion in the configuration of the incident 2+ ion. Doubly charged ion recombination energies liberated in such vertical 2+ → 1+ processes are given in Table 6 for molecular ions shown in Fig. 5. Ion recombination energies of approximately 15 eV displayed in this table are significantly larger than organic molecule ionization energies and, as a result, doubly charged ion reactions of the type given by (1) are very exothermic.

Theoretical model of doubly charged ion collisions

Aided by information on organic ion recombination energies, we have employed a diabatic curve-crossing model to examine the fundamental basis of doubly charged ion mass spectra. This model has been used¹⁵ successfully to describe the interactions of doubly charged atomic ions with neutral atoms, and we extend this treatment to the pyrrole ion-molecule system as a typical example. Transitions from reactant to product states are assumed to occur near the intersection of reactant and product potential energy curves. The reactant potential energy curves are dominated at long range

Table 6. Energetics of pyrrole and furan dication systems

	Heat of formation (eV) for geometry-optimized structure	Heat of formation in eV (Franck-Condon) of 2+ ion in configuration of neutral	Computed vertical ionization energy (eV)	Measured ionization energy (eV)	Heat of formation in eV (Franck-Condon) of 1+ product ion in configuration of 2+ reactant	Recombination energy (eV)
Pyrrole (compound 1)	1.42	24.76	23.34	25.6		
Pyrrole ²⁺	24.33				9.49	14.84
Pyrrole (T) ²⁺	24.41				9.68	14.73
1-Methylpyrrole (2)	1.41	24.36	22.95	24.2		
1-Methylpyrrole ²⁺	23.88				9.36	14.52
1-Methylpyrrole(T) ²⁺	23.97				9.54	14.43
2,5-Dimethylpyrrole (3)	0.45	22.68	22.23	22.8		
2,5-Dimethylpyrrole ²⁺	22.29				8.29	14.00
2,5-Dimethylpyrrole(T) ²⁺	22.65				8.49	14.16
Furan (4)	-0.39	24.33	24.72	25.8		
Furan ²⁺	23.84				8.36	15.48
Furan(T) ²⁺	24.06				8.57	15.49
2-Methylfuran (5)	-0.85	23.09	23.94	24.2		
2-Methylfuran ²⁺	22.62				7.73	14.89
2-Methylfuran(T) ²⁺	23.03				8.22	14.81
2,5-Dimethylfuran (6)	-1.32	21.97	23.29	24.8		
2,5-Dimethylfuran ²⁺	21.53				7.10	14.43
2,5-Dimethylfuran(T) ²⁺	22.07				7.31	14.76

Figure 5. ORTEP plots of doubly charged ion structures for pyrroles and furans. Bond distances are given in angstroms.

by ion-induced dipole interactions of the form

$$V = -(Ze)^2\alpha/2R^4 \quad (2)$$

where e is the electronic charge, α the molecular polarizability ($7.94 \times 10^{-24} \text{ cm}^3$ for pyrrole) and R the ion-molecule separation distance. Long-range product ion interactions described by Coulombic repulsion are given by the relation

$$V = e^2/R - \Delta E \quad (3)$$

where ΔE is the energy defect of the reaction. The reaction energy defect is the difference between energy liberated in the charge reduction $2+ \rightarrow 1+$ 'half reaction' and the ionization energy of the neutral pyrrole molecule. Thermoneutral reactions correspond to 0 eV interaction energies at infinite separation distances. Interaction energies of product and reactant systems given by Eq. (2) and (3) are shown as the solid curves in Fig. 6. Although there is only one attractive curve describing the reactant interaction, there are near infinite numbers of repulsive curves which describe possible product states. Three such product curves are joined

Figure 6. Interaction energies (eV) of doubly charged pyrrole ions with neutral pyrrole molecules. Diabatic reactant and product potential energy curves are presented as a function of ion-molecule reactant and ion-ion product separation distances. Product channels terminate at asymptotic energy defect values ΔE . The lowest product curve corresponds to removal of an electron from $\text{C}_4\text{H}_5\text{N}$ to form ground state $[\text{C}_4\text{H}_5\text{N}]^+$. The vertical Franck-Condon envelope for single-electron ionization of pyrrole is presented by the photoelectron data of Eland¹⁶ on the right-hand side of the figure.

asymptotically to the vertical Franck-Condon envelope for ionization of C_4H_5N to $[C_4H_5N]^+$ which was obtained from the photoelectron spectroscopy measurements of Eland.¹⁶ Franck-Condon factors give a measure of probability for the various ionizing transitions in isolated species. Since the relative velocity of our reactant species is approximately 10^7 cm s^{-1} , corresponding to an ion-molecule interaction time of 10^{-14} – 10^{-15} s , the nuclear configuration of the target molecule remains essentially frozen during electron transfer. Thus, Franck-Condon factors obtained from photoionization experiments have application in electron-transfer kilo-electron-volt ion-molecule reactions.

Crossing of diabatic potential energy curves provides a possible mechanism for electron transitions to occur from reactant to product systems; however, because of the non-crossing rule these intersections become avoided crossings. In this case, the reactant curve, which is dominated by $(M^{2+} + M)$ character at long range, passes over smoothly to one dominated by $(M^+ + M^+)$ character at short range. This behavior is illustrated by the adiabatic dotted curves in Fig. 7 which gives an expanded view of the crossing region for two possible product channels with energy defects of 3.66 and 6.16 eV. As reactants approach one another, following the uppermost adiabatic curve from large distances, transitions to the lower adiabatic curve can occur at approximately 4.6 Å.

The probability of transition at an avoided crossing may be computed using the Landau-Zener model.¹⁷ Realizing that the existence of an avoided crossing signals a mixing of wavefunctions for the two states, and that the interaction is time dependent, the relevant form of the wavefunction for the system is

$$\Psi = C_1(t)\Phi_1(t, r) + C_2(t)\Phi_2(t, r) \quad (4)$$

where Φ_1 and Φ_2 are the time-dependent wavefunctions for the two states with 'mixing' coefficients C_1 and C_2 . The absolute square of the asymptotic value of each coefficient gives the probability of finding the system in

Figure 7. Expanded view of the potential energy curve crossing region. Energies in electron-volts are given as a function of separation distance in angstroms. The attractive diabatic potential for the $[C_4H_5N]^{2+} + C_4H_5N$ reactant system is given by the solid curve. Two repulsive diabatic potential energy curves for $[C_4H_5N]^+ + [C_4H_5N]^+$ products of reaction with energy defects of 3.66 and 6.16 eV are given by dashed lines. Dotted curves illustrate adiabatic potential energy curves near avoided crossings.

each state, thus giving the transition probability. The solution^{17,18} of the time-dependent Schrödinger equation gives the following expression for the transition probability:

$$p_j = \exp(-2\pi V_{ij}^2 / \hbar v_{Rj} \Delta S_j) \quad (5)$$

in which $2V_{ij}$ is the energy separation of the two adiabatic curves at the avoided crossing, v_{Rj} is the relative velocity at the avoided crossing and ΔS_j is the difference in adiabatic curve slopes at the avoided crossing. These last two quantities may be expressed as

$$v_{Rj} = v_0[1 - V_1(R_j)/E_0 - b^2/R_j^2]^{1/2} \quad (6)$$

and

$$\Delta S_j = \frac{d}{dR} (V_1 - V_j)|_{R=R_j} \quad (7)$$

in which v_0 is the initial relative velocity and V_1 and V_j denote diabatic potential energy functions for reactants and products, respectively. The critical radius R_j corresponds to the radial distance between reactants at an avoided crossing of diabatic curves 1 and j , and E_0 is the initial relative kinetic energy.

Following the approach of Child and Baer,^{19,20} the probability of remaining on an adiabatic curve is given by the product of the Franck-Condon probability F and the Landau-Zener probability $1 - p$:

$$P = F(1 - p) \quad (8)$$

The probability of making a transition from one adiabatic curve to another is the Landau-Zener probability p .

A general expression relating the probability of a curve-crossing event to an electron-transfer cross-section will be developed by starting with the simplest case: one diabatic reactant curve crossing one diabatic product curve. The probability of transition from the reactant curve to the product curve is p , and the probability of remaining on the reactant curve is $(1 - p)F$. As the two species approach one another, the radial separation decreases to a minimum and then increases as they separate. During separation the critical radius is again reached. The probability of the reactants traversing the crossing point twice and emerging unchanged is

$$P = p^2 + (1 - p)^2 F^2 \quad (9)$$

Similarly, the probability of reactants exiting as products is

$$P = 2p(1 - p)F \quad (10)$$

The somewhat more complicated case of two product curves intersecting a reactant curve is shown in Fig. 7. The solid line was generated from Eqn (2), and the dashed curve obtained from Eqn (3) using energy defects of 3.66 and 6.16 eV. The dotted lines represent individual sixth-degree polynomial least-squares approximations of the appropriate adiabatic potential energy curves. The calculated adiabatic curve represents a good fit to the reactant curve and given individual product curves up to within $\sim 0.5 \text{ Å}$ of the crossing region and results in a smooth extrapolation through the crossing region. This extrapolated region was symmetric about the crossing point, and was sufficiently small to ensure correlation

Figure 8. Schematic representation of charge-transfer processes. The upper portion illustrates potential energy curves for reactant (solid) and product (dashed) pathways. The reactant curve (1) crosses the product curves (2) and (3) giving products separating from collision on curves B or C. The transition probability at R_2 is labeled p_2 and that at R_3 by p_3 . The lower portion of the figure gives the trajectory of the incident ion relative to the target molecule for an impact parameter b .

coefficients greater than 0.995 in the sixth-order polynomial fitting routine.

The collision process is illustrated in Fig. 8. The probabilities of exiting on each of the curves, 1, 2 and 3 are symbolized by A, B and C, respectively. The bottom portion of Fig. 8 illustrates how two identical crossing points occur during a single collision event as the ion approaches and recedes from the neutral target molecule. The expressions for these exit channel probabilities are developed beginning with channel 3. This exit channel C is populated via two paths. The first consists of two consecutive transitions at R_2 and R_3 , followed by the retraversal of R_3 with no transition as the particles separate. The second path is reaction at R_2 , no transition at R_3 , followed by transition at R_3 as the species depart. Combining these gives the following probability for reactants to exit on curve 3:

$$C = p_2 p_3 (1 - p_3) F_3 + p_2 (1 - p_3) F_3 p_3 \quad (11)$$

The probability B of exiting along product curve 2 reflects the fact that there are three possible paths leading to that exit channel. The simplest path is that of no transition at R_2 as reactants approach, followed by reaction at R_2 when the species recede. This path contributes $(1 - p_2) F_2 p_2$ to B. The next path is that of reaction at R_2 , no reaction at R_3 and none at the second encounter of R_3 or of R_2 . The probability of following this path is $p_2 (1 - p_3)^2 F_3^2 (1 - p_2) F_2$. The third path consists of two successive transitions at R_2 and R_3 , an additional reaction at the second encounter of R_3 but then failure to react at R_2 which results in a probability of $p_2 p_3 p_3 (1 - p_2) F_2$. The total probability B, which is the sum of these

three possibilities, is given by the expression

$$B = p_2 (1 - p_2) F_2 + p_2 (1 - p_3)^2 F_3^2 (1 - p_2) F_2 + p_2 p_3^2 (1 - p_2) F_2 \quad (12)$$

Finally, the probability A of emerging on the reactant curve is given by

$$A = (1 - p_2)^2 F_2^2 + p_2^2 (1 - p_3)^2 F_3^2 + p_2^2 p_3^2 \quad (13)$$

This development is extended to give a general formula for the case of N product curves crossing a reactant curve. The probability that reactants start on curve 1 and exit on curve j is given by

$$\begin{aligned} P_{1j} &= p_2 p_3 p_4 \cdots p_j (1 - p_j) \{ 1 + (p_{j+1} p_{j+2} p_{j+3} \cdots p_N)^2 \\ &\quad + (1 - p_{j+1})^2 + [p_{j+1} (1 - p_{j+2})]^2 + [p_{j+1} p_{j+2} (1 - p_{j+3})]^2 \\ &\quad + \cdots + [p_{j+1} p_{j+2} p_{j+3} \cdots p_{N-1} (1 - p_N)]^2 \} \\ &= (1 - p_j) \left(\prod_{i=2}^j p_i \right) \left[1 + (1 - p_{j+1})^2 + \left(\prod_{k=j+1}^N p_k \right)^2 \right. \\ &\quad \left. + \sum_{l=j+2}^N (1 - p_l)^2 \left(\prod_{m=j+1}^{l-1} p_m \right)^2 \right] \quad (14) \end{aligned}$$

Inclusion of appropriate Franck-Condon probabilities F_j in the above equation results in

$$\begin{aligned} P_{1j} &= (1 - p_j) F_j \left(\prod_{i=2}^j p_i \right) \left[1 + (1 - p_{j+1})^2 F_{j+1}^2 \right. \\ &\quad \left. + \left(\prod_{k=j+1}^N p_k \right)^2 + \sum_{l=j+2}^N (1 - p_l)^2 F_l^2 \left(\prod_{m=j+1}^{l-1} p_m \right)^2 \right] \\ &\quad (j < N) \quad (15a) \end{aligned}$$

For the special case $j = N$, we have

$$P_{1N} = 2(1 - p_N) F_N \prod_{i=2}^N p_i \quad (15b)$$

The total cross-section is given as a sum of the individual cross-sections:

$$\sigma = \sum \sigma_j \quad (16)$$

Individual cross-sections σ_j are computed from the relation

$$\sigma_j = 2\pi \int_0^{b_j} b P_{1j} db \quad (17)$$

in which b_j is the limiting impact parameter for the distance of closest approach R_j . This impact parameter is determined from the relation

$$b_j = R_j [1 - V_{11}(R_j)/E_0]^{1/2} \quad (18)$$

The above curve-crossing model is readily applied to exothermic reactions in which the incident ion recombination energy is greater than the target molecule ionization energy. Products of such reactions possess a lower potential energy than reactants, as shown in Figs 7 and 8. Application of this model to the pyrrole prototype system requires that the pyrrole target molecule ionization energy be less than the 14.84 eV recombination energy of doubly charged incident pyrrole ions (Table 6). The photoelectron spectrum of pyrrole shows two distinct ionization bands at 8.2 and 9.2 eV¹⁶ corresponding to formation of $1a_2(\pi)$ and $2b_1(\pi)$ states. There is

also an unresolved series which ranges from roughly 12.5 to 14.6 eV at which point it decreases to the baseline at 16.5 eV. The vibrational fine structure of the first two ionization bands shows ionic levels with spacings of approximately 0.1 eV. However, the Franck-Condon envelopes (Fig. 6) for these electronic states are only ~ 0.6 eV wide, indicating that only the lower vibrational levels are populated to a significant extent. We have taken nine vibrational levels of the $1a_2(\pi)$ and $2b_1(\pi)$ states observed in the photoelectron spectrum of pyrrole as possible product channels. The vibrational envelope of higher excited $[C_4H_5N]^+$ states is relatively flat over 2 eV and indicates similar transition moments for formation of $6a_1(\sigma)$, $4b_1(\sigma)$ and $1b_1(\pi)$ state ions. We have considered that 13 different product channels are possible in which $[C_4H_5N]^+$ product ions are formed in these higher excited states with reaction energy defects ranging from 2.2 to 0.2 eV. As illustrated in Figs 6 and 7, charge-transfer product channels with small energy defects cross the reactant channel curve at relatively large separation distances, but we note this does not automatically lead to large cross-section values. The energy difference $2V_{ij}$ of adiabatic curves at avoided crossing points decreases as R increases and is expected to result in larger values of p_j from Eqn. (5); but this is partially compensated by a decrease in ΔS_j , the difference in curve slopes. Reaction channels that dominate the total cross-section are those with energy defects less than 1 eV, although all channels contribute to the total calculated cross-section of $55.8 \text{ \AA}^2$.

Comparison of theoretical model with experimental data

In order to confirm the applicability of the multistate curve-crossing model, we have measured the absolute value of the total cross-section for single-electron-transfer reactions between $[C_4H_5N]^{2+}$ and C_4H_5N in reaction (1). Time-of-flight techniques were employed to determine the flux of fast singly charged $[C_4H_5N]^+$ reaction products. Reactant ions were produced by 100 eV EI ionization of pyrrole, accelerated to terminal velocities and reacted with neutral target molecules. Unreacted ions and fast neutral products proceeded through a first drift region and were retarded by a deceleration voltage placed on a final drift region prior to collection. Application of a deceleration voltage to the final drift region resulted in longer arrival times for $[C_4H_5N]^{2+}$ reactants than for $[C_4H_5N]^+$ products entering this region with the same initial mass and velocity. The flux of fast $[C_4H_5N]^+$ products i_p is related to the primary reactant $[C_4H_5N]^{2+}$ ion flux i_R by the equation

$$i_p = i_R n l \sigma \quad (19)$$

where l is the path length over which reactions occur, n the pyrrole target concentration and σ the reaction cross-section. The total cross-section we measure for the $[C_4H_5N]^{2+} + C_4H_5N$ reaction is $48.6 \text{ \AA}^2$ for 4.6 keV energy incident ions. This measured value is in reasonable accord with the computed value of $55.8 \text{ \AA}^2$ and lends support to our use of multistate curve crossing to model doubly charged ion reactions.

Additional evidence that charge-transfer channels with small energy defects dominate the reaction comes

from comparisons of fast product AB^+ and reactant AB^{2+} ion translational energies. It was noticed in early work and subsequent studies of polyatomic doubly charged ions that fast product ion peak shapes were very similar to those of the reactant ions, and product ions possessed translational energies associated with reaction channels having energy defects close to zero.²¹ We observe this also for the $[C_4H_5N]^{2+} + C_4H_5N$ interactions. Although reactions of doubly charged atomic ions with atoms leads generally to fast product ions with velocities different from the reactant ion,²² the cross-sections are typically small.²³ Substitution of organic for atomic species increases the density of internal states so that close energy balance exists between reactant and product reaction channels. As a consequence, products of reaction are internally excited and velocities are essentially identical for reactant ions and fast product ions.

Also present in the $2E$ spectrum of pyrrole shown in Table 2 is a product ion appearing at m/z 65 with a relative abundance of 13.8%. This ion results from reactions of dehydropyrrole $[C_4H_3N]^{2+}$ ions for which there exist several geometry-optimized minimum-energy, stable configurations. Ionic recombination energies, heats of formation and structural parameters for $[C_4H_3N]^{2+}$ ions are presented in Table 7. Recombination energies for these structures range from 14.9 to 15.3 eV. These values are close to that for pyrrole (14.84 eV) and the energy defects, as well as the corresponding long-range interaction potentials for $[C_4H_3N]^{2+} + C_4H_5N$ charge-transfer reactions, are very similar to those shown in Fig. 6. As a consequence, the cross-sections computed for charge-transfer reactions of dehydropyrrole doubly charged ions are identical to those computed for pyrrole.

Table 7. Structure parameters of dehydropyrrole dications

	2,4-Dehydro-pyrrole	3,4-Dehydro-pyrrole	2,5-Dehydro-pyrrole	2,3-Dehydro-pyrrole
$H_f(\text{eV})$	30.558	30.851	30.761	30.826
$RE(\text{eV})$	15.002	14.893	15.269	15.281
Bond lengths ($\text{\AA}$)				
N_1-H_1	1.030	1.027	1.031	1.030
C_2-H_2	—	1.104	—	—
C_3-H_3	1.095	—	1.094	—
C_4-H_4	—	—	1.094	1.097
C_5-H_5	1.039	1.104	—	1.102
N_1-C_2	1.407	1.411	1.375	1.335
C_2-C_3	1.454	1.466	1.484	1.458
C_3-C_4	1.421	1.379	1.443	1.426
C_4-C_5	1.494	1.467	1.483	1.472
C_5-N_1	1.375	1.411	1.376	1.457
Bond angles (deg)				
$C_2-N_1-H_1$	123.64	122.95	127.89	126.72
$H_2-C_2-N_1$	—	124.58	—	—
$C_3-C_2-N_1$	114.68	103.24	113.64	109.48
$H_3-C_3-C_2$	129.87	—	126.12	—
$C_4-C_3-C_2$	97.78	109.71	104.22	109.04
$H_4-C_4-C_3$	—	—	129.62	128.47
$C_5-C_4-C_3$	115.78	109.71	104.20	104.55
$H_5-C_5-C_4$	130.81	132.16	—	130.79

Similar charge-transfer cross-sections for reactions involving different incident ions is a necessary condition for associating product ion distributions measured in $2E$ spectra with doubly charged primary ion precursor distributions. Direct measurement of the $[\text{C}_4\text{H}_5\text{N}]^{2+}$, $[\text{C}_4\text{H}_3\text{N}]^{2+}$ and $[\text{C}_4\text{H}_2\text{N}]^{2+}$ ion intensities yields a normalized distribution of 100.0, 24.0 and 6.6. Measurements were carried out with sufficient resolution to separate $[\text{C}_4\text{H}_2\text{N}]^{2+}$ from oxygen background. Comparison of these values with relative product ion abundances given in the $2E$ spectrum of pyrrole reveals that the $[\text{C}_4\text{H}_3\text{N}]^+$ product ion relative abundance is abnormally low by a factor 1.7. Product $[\text{C}_4\text{H}_3\text{N}]^+$ ions from $[\text{C}_4\text{H}_3\text{N}]^{2+} + \text{C}_4\text{H}_5\text{N}$ interactions are expected to possess internal excitation energy since the $2+$ ion recombination energies are more than 7 eV larger than target ionization energies. It is not unexpected that a fraction of the electron-transfer collisions lead to $[\text{C}_4\text{H}_3\text{N}]^+$ product ions with more than sufficient internal energy to undergo unimolecular decomposition after their formation in electron-transfer reactions but prior to energy analysis by the electrostatic sector. Ions from such electron capture induced decompositions are rejected by the sector operated in the $2E$ mode, but can be measured by variation of the electrostatic sector from $2E$ to E while scanning the magnetic sector.²⁴ We find product ions from the electron capture induced decomposition processes appearing with mass 39 and 38 corresponding to $([\text{HC}_2\text{N}]^+, [\text{C}_3\text{H}_3]^+)$ and $([\text{C}_2\text{N}]^+, [\text{C}_3\text{H}_2]^+)$, respectively. The total abundance of these products is 1.5 times as large as the intensity of their undecomposed $[\text{C}_4\text{H}_3\text{N}]^+$ precursor which accounts for the low abundance of $[\text{C}_4\text{H}_3\text{N}]^+$ product ions as compared with that of the $[\text{C}_4\text{H}_3\text{N}]^{2+}$ primary reactant ion.

The ability of other doubly charged ions to undergo charge-transfer reactions and form product ions efficiently is controlled in large measure by their recombination energies. Abundant ions appearing at m/z 50, 51, 62, 74 and 86 in the $2E$ spectra of furans in Table 1 result from reactions of $[\text{C}_4\text{H}_2]^{2+}$, $[\text{C}_4\text{H}_3]^{2+}$, $[\text{C}_5\text{H}_2]^{2+}$, $[\text{C}_6\text{H}_2]^{2+}$ and $[\text{C}_7\text{H}_2]^{2+}$ ions. Ions of the type $[\text{C}_n\text{H}_2]^{2+}$ are quite stable,⁹ possess high recombination energies and are expected to react readily to form singly charged products shown in Table 1. The m/z 52 ion is also a prominent product in Table 1 and a number of stable doubly charged precursor ions are possible. Heats of formation and recombination energies for these isomers are given in Table 8. These recombination energies, which extend from 14 to 16 eV, lead to reaction energy defects in the range of 5–7 eV which result in favorable reactant/product curve crossings at large separation distances.

CONCLUSION

Doubly charged ions are readily formed by EI ionization of alkyl-substituted furans and pyrroles. The $2E$ spectra of these compounds are intense, indicating efficient charge-transfer reactions. Recombination energies of abundant doubly charged ions are typically 15 eV which lead to reaction energy defects of approximately 6 eV for many reactions. The fundamental collision processes giving rise to doubly charged ion mass spectra have been

Table 8. Recombination energies of doubly charged ion precursors to m/z 52 product ions

Dication structure	Dication heat of formation (eV)	Franck-Condon heat of formation of 1 + product in configuration of 2 + reactant (eV)	Recombination energy (eV)
$[\text{H}_2\text{CCCCH}_2]^{2+}$	25.83	11.78	14.05
$[\text{H}_2\text{CCHCCH}]^{2+}$	26.82	12.87	13.95
$[\text{H}_3\text{CCCCH}]^{2+}$	26.97	12.28	14.69
$\text{CH}-\text{CH}^{2+}$	26.98	11.96	15.02
$\text{CH}-\text{CH}$			
$[\text{H}_2\text{CCCHCH}]^{2+}$	27.46	12.91	14.55
$[\text{HCCHCHCH}]^{2+}$	27.56	11.96	15.60
$[\text{H}_2\text{CCHCHC}]^{2+}$	29.50	15.12	14.38
$[\text{H}_3\text{CCCHC}]^{2+}$	29.97	15.45	14.52
$[\text{CCCO}]^{2+}$	31.34	14.82	16.52
$[\text{H}_3\text{CCHCC}]^{2+}$	32.01	16.50	15.51

examined using a multistate curve-crossing model which is consistent with large cross-sections and suggests products are formed in a variety of internally excited states.

EXPERIMENTAL

Doubly charged ion mass spectra were obtained using an Hitachi RMU-7L mass spectrometer. Spectra were obtained using previously documented experimental conditions.⁵ Spectra were obtained using the compound under investigation as both the source gas and collision target gas. Ionization efficiency curves were determined from 100 eV to the energetic thresholds of the individual ions. The absolute energy of the ionizing electron beam was determined using known ionization/appearance energies of doubly charged ions from reference standards.^{11,25} Appearance energy reproducibilities were within 0.5 eV; however, absolute uncertainties may have been as large as 1.0 eV.

A time-of-flight system was employed to measure the absolute cross-section for charge transfer. Use of this calibrated system to measure charge-transfer processes of singly and doubly charged ions has been described.^{23,26} Doubly charged ions were produced by controlled EI ionization and drawn out of the source by a fast-rising pulse and accelerated to terminal velocities. The fully accelerated ion beam entered a static gas-collision region where charge-transfer reactions occurred. Unreacted ions and fast productions from charge-transfer reactions proceeded through a 1 m drift region and were collected on the cathode of a gated electron multiplier. The final 0.2 m segment of the drift region was insulated from the first segment in order to retard the ions as they passed from the first drift region to the second. Application of a deceleration voltage to the second region resulted in longer arrival times for the $[\text{C}_4\text{H}_5\text{N}]^{2+}$ reactants than for the $[\text{C}_4\text{H}_5\text{N}]^+$ products and enabled both reactant and product fluxes to be determined. This system was particularly clean and free of organic background ion contamination. The value of the $1/(nl)$ term used in Eqn (19) was typically $6.5 \times 10^{-14} \text{ cm}^2$.

Normal mass spectrometry of the distilled samples possessing high purity showed the compounds to be free of contamination.

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