Sensitivity of Charge Transfer Reactions to Hydrocarbon Ion Structures

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Charge transfer reactivities of hydrocarbon ions have been measured with time-of-flight techniques, and results correlated with theoretical structures computed by self-consistent field molecular orbital methods. Recombination energies, ion structures, heats of formation, reaction energetics and relative charge transfer cross-sections are presented for molecular and fragment ions produced by electron bombardment ionization of CH_4 , C_2H_4 , C_2H_6 , C_3H_8 and C_4H_{10} molecules. Even-electron bridged cations have low ion recombination energies and relatively low charge transfer cross-sections as compared with odd-electron hydrocarbon cations.

INTRODUCTION

Numerous investigations of hydrocarbon ions have been undertaken, but much remains to be learned about their structures. Theoretical molecular orbital computations have predicted the structures of many hydrocarbon ions.¹⁻⁴ High-resolution spectroscopic experiments, which would validate detailed molecular orbital calculations, have been performed for gaseous ions composed of only a few atoms.^{5,6} Low-temperature electron spin resonance (ESR) studies⁷⁻⁹ have characterized geometrical structures and identified unpaired electron orbitals of several matrix-isolated hydrocarbon ions.

Photoelectron spectra¹⁰ have yielded important energetic information on various ion states which have been correlated¹¹ with computed energy level assignments. Photoelectron-photoion coincidence measurements¹²⁻¹⁵ have provided valuable data on ionic fragmentation processes. This technique permits the study of ions with selected internal energies. Experimentally measured ionic heats of formation comprise the bulk of available data¹⁶⁻²¹ for comparison with theoretical calculations. Mass spectrometric collisional activation techniques have begun to provide information on structural features of ions.²²⁻²⁶ A recent article²⁷ reviews experimental methods of assigning structures to gas phase organic positive ions.

This paper reports results of hydrocarbon ion charge transfer reactions utilizing time-of-flight techniques. These reactions are sensitive functions of ionic recombination energies, which in turn are controlled by hydrocarbon ion structure. Recombination energies are computed using self-consistent field molecular orbital methods to facilitate understanding of the trends in charge transfer cross-sections. Relevant theoretical and experimental data are discussed along with our results.

EXPERIMENTAL

Time-of-flight techniques were utilized to measure fast neutral products resulting from keV charge transfer reactions. The apparatus and techniques had been used previously to investigate the formation of fast neutral products from charge transfer reactions of singly²⁸ and doubly²⁹ charged ions. Reactant molecular ions and their characteristic fragment ions were produced by controlled electron impact ionization of high purity gases. Ionizing electrons were emitted from a directly heated filament and accelerated into the ion source by a voltage controllable from 2 to 100 V. A regulated filament current supply ensured that the electron beam intensity was kept constant during each measurement.

Reactant molecular and fragment ions produced by electron impact were drawn out of the source by a fast rising pulse and accelerated to terminal velocities. The fully accelerated ion beam next entered a static gas collision region where ion-molecule interactions took place. Unreacted ions and fast neutral products from charge transfer proceeded through a one meter drift region and were collected on the cathode of a gated electron multiplier. The final 0.2 m segment of drift region was insulated from the first segment so that it was possible 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 ions than for fast neutral products with the same initial mass and velocity. For each ion peak present in a mass spectrum, a corresponding neutral peak from charge transfer was detected as well.

The number of secondary electrons emitted from metal surfaces by high-energy particle bombardment was found to be equivalent for both the ion $[\text{M}]^+$ and the charge transfer neutral product $[\text{M}]^0$.^{30,31} Equal emission coefficients resulted in equivalent electron multiplier response for both the incident ion and its

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corresponding neutral product at 3 keV energy. We measured the fast neutral product mass spectrum of N_2 , O_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_8 and C_4H_{10} .

RESULTS

Most studies of charge transfer reactions have measured slow charged products because of the convenient experimental methods available for ion analysis, while fast neutral products of these reactions have gone undetected. However, both reactant ions and their fast neutral products from keV reactions can be monitored with high sensitivity using an electron multiplier detector^{30,31} and time-of-flight techniques. Relationships between neutral product and incident ion intensities are discussed for N_2 and O_2 calibration systems where absolute cross-section data are available, and then for hydrocarbon molecular and fragment ions in the CH_4 , C_2H_4 , C_2H_6 , C_3H_8 and C_4H_{10} systems. Relative rather than absolute cross-section values have been obtained for each different hydrocarbon system which permits intra-system rather than inter-system comparisons.

Nitrogen. Electron bombardment of N_2 results in the formation of N_2^+ molecular ions and N^+ fragment ions which are simultaneously accelerated by a 3.00 kV potential difference and undergo charge transfer reactions:

Charge transfer cross-sections for reaction (1) are approximately $21 \times 10^{-16} \text{ cm}^2$.³²⁻³⁴ The corresponding cross-section³⁵ for chemical activation processes involving ground state N_2^+ ions which form fast N^0 products is $1 \times 10^{-16} \text{ cm}^2$. These fast N^0 products give rise to a slight broadening³⁶ at the base of the neutral molecular charge transfer peak. Dissociative neutral products comprise less than 5% of the charge transfer product peaks and do not interfere with measurements of relative charge transfer cross-sections.

The reactant ion time-of-flight mass spectra at 30, 50, 80 and 100 eV electron impact ionization are shown in Fig. 1 along with their respective neutral time-of-flight mass spectra from reactions (1) and (2). The secondary neutral product signal, i_s , is related to the primary reactant ion signal, i_p , by the equation

$$i_s = i_p n l \sigma \quad (3)$$

where l is the path-length over which reactions occur and σ is the reaction cross-section. The ratio of neutral N^0/N_2^0 products is related to the N^+/N_2^+ primary ion ratio through the relation

$$\frac{i_{sN^0}}{i_{sN_2^0}} = \frac{i_{pN^+}(nl\sigma_2)}{i_{pN_2^+}(nl\sigma_1)} = \frac{i_{pN^+} \sigma_2}{i_{pN_2^+} \sigma_1} \quad (4)$$

As shown in Fig. 1 the N^0/N_2^0 ratio is one-third the magnitude of the N^+/N_2^+ ratio which indicates that

Figure 1. Mass spectra of nitrogen formed by 100, 80, 50 and 30 eV electron impact ionization are presented, along with the mass spectra of neutral products formed by charge transfer reactions.

the cross-section for forming fast N^0 products in reaction (2) is approximately one-third that of reaction (1). Since the measured cross-section for reaction (1) is $21 \times 10^{-16} \text{ cm}^2$ at 3 keV,³² we estimate σ_2 to be $7 \times 10^{-16} \text{ cm}^2$, a value identical to that measured in Ref. 37.

Oxygen. The corresponding reactions in the oxygen system are

The 3 keV charge transfer cross-section measured³⁸ for reaction (5) is $8 \times 10^{-16} \text{ cm}^2$ while that for reaction (6) is $13 \times 10^{-16} \text{ cm}^2$.³⁹ The ion and fast neutral spectra obtained in the oxygen system are presented in Fig. 2. In this figure the O^0/O_2^0 ratio is approximately 40% greater than the O^+/O_2^+ ratio which indicates that the cross-section for reaction (6) is larger than that for reaction (5), a result in harmony with the aforementioned experimental values.^{38,39} The relative O^0/O^+ signal remains constant as the ionizing electron energy decreases from 100 to 50 eV, but at 30 eV this ratio is lower by 15%. A similar 17% decrease in the efficiency of reaction (6) has been observed previously³⁹ and shown to result from a decrease in O^+ reactivity, as electronically excited states are depleted in the O^+ reactant ion beam.

Figure 2. Mass spectra of oxygen formed by 100, 80, 50 and 30 eV electron impact ionization are presented, along with the mass spectra of neutral products formed by charge transfer reactions.

Figure 4. Mass spectra of ethylene formed by 100, 80, 50 and 30 eV electron impact ionization are presented, along with the mass spectra of neutral products formed by charge transfer reactions.

Methane. The ionic and neutral product spectrum of methane is presented in Fig. 3 for several ionizing electron energies. The two spectra are very similar and would indicate that charge transfer cross-sections for interactions of CH_4^+ , CH_3^+ , CH_2^+ and CH^+ ions with CH_4 molecules are identical. This observation is somewhat surprising and suggests that the recombination energies (the energies liberated in the $[\text{M}]^+ \rightarrow [\text{M}]^0$ neutralization 'half-reactions') for each of these reactant ions are similar. The implications of these results will be examined further in the discussion section.

Ethylene. Ionic and neutral spectra for the ethylene system are presented in Fig. 4. The C_2H_4^0 product forms the largest peak in the neutral spectrum while C_2H_4^+ is the base peak for the ionic spectrum. The neutral spectrum differs significantly from the ion spectrum in that the C_2H_3^0 intensity is low compared with the C_2H_3^+ ion intensity and the C_2H^0 intensity is high relative to the C_2H^+ intensity.

Ethane. Figure 5 presents the ionic and neutral spectra for the ethane system. The largest peaks in each spectrum result from C_2H_4^+ and C_2H_4^0 produced

Figure 3. Mass spectra of methane formed by 100, 80, 50 and 30 eV electron impact ionization are presented, along with the mass spectra of neutral products formed by charge transfer reactions.

Figure 5. Mass spectra of ethane formed by 100, 80, 50 and 30 eV electron impact ionization are presented, along with the mass spectra of neutral products formed by charge transfer reactions.

Figure 7. Mass spectra of butane formed by 100, 80, 50 and 30 eV electron impact ionization are presented, along with the mass spectra of neutral products formed by charge transfer reactions.

from $C_2H_4^+ - C_2H_6$ charge transfer interactions. The relative abundances of $C_2H_5^0$ and $C_2H_3^0$ product peaks are low when compared with the respective ion peaks.

Propane. In the propane system (Fig. 6) the largest peak in the ionic spectrum is $C_2H_5^+$, while $C_2H_4^0$ is the dominant peak in the neutral spectrum. The relative $C_2H_5^0/C_2H_5^+$ and $C_2H_4^0/C_2H_4^+$ ratios indicate that the cross-section for production of $C_2H_5^0$ is approximately half that for $C_2H_4^0$. Similarly, the relative $C_3H_7^0/C_3H_7^+$ and $C_3H_8^0/C_3H_8^+$ ratios show that the reactivity of $C_3H_7^+$ ions is one half that of $C_3H_8^+$ ions.

Butane. The neutral product and reactant ion mass spectra in the butane system are illustrated in Fig. 7. The general features of the neutral and ionic spectra are similar. It can be seen that the $C_4H_{10}^0/C_4H_{10}^+$, $C_4H_9^0/C_4H_9^+$, $C_3H_6^0/C_3H_6^+$ and $C_2H_4^0/C_2H_4^+$ ratios are approximately two, whereas the $C_3H_7^0/C_3H_7^+$, $C_3H_5^0/C_3H_5^+$, $C_2H_5^0/C_2H_5^+$ and $C_2H_3^0/C_2H_3^+$ ratios are close to unity. These ratios and the results shown in Figs 3–6 indicate a low probability for charge transfer when reactions involve even-electron ions of

Figure 6. Mass spectra of propane formed by 100, 80, 50 and 30 eV electron impact ionization are presented, along with the mass spectra of neutral products formed by charge transfer reactions.

the type $C_2H_{3,5}^+$ and $C_3H_{5,7}^+$ relative to the corresponding odd-electron ions $C_2H_{4,6}^+$, $C_3H_{4,6,8}^+$ and $C_4H_{10}^+$.

DISCUSSION

In order to understand the trends in charge transfer cross-sections for even- and odd-electron ions, it is necessary to examine factors that influence charge transfer processes. Among numerous factors⁴⁰ which affect charge transfer reaction efficiencies, the energy defect (Q) exerts a controlling influence at low keV incident ion energies. This quantity Q is the energy difference between the reactant ion recombination energy⁴¹ and neutral target ionization potential ($Q = RE - IP$). The recombination energy is the energy liberated in the neutralization of the incident ion $[M]^+$ to form neutral $[M]^0$ in a vertical Franck-Condon transition. When $Q \sim 0$ for a particular reaction, the recombination energy of the reactant ion balances the ionization potential of the neutral target and cross-sections for charge transfer are large,^{40,42} of the order of 10^{-14} – 10^{-15} cm². Recombination energies, which are dependent on ion structure, can be computed using self-consistent field molecular orbital (SCF-MO) methods.

SCF-MO computations of ion recombination energies

Energies of ions formed in the CH_4 , C_2H_4 , C_2H_6 , C_3H_8 and C_4H_{10} systems have been computed using the MINDO/3 semiempirical SCF-MO approach developed by Dewar and coworkers.^{43–47} Molecular energies, structures and reactivities are determined in a reasonably accurate and reliable manner with

MINDO/3. In this quantum-mechanical method, valence electrons are assumed to move in a fixed core of nuclei and inner-shell electrons, and are treated using a minimum basis set simplified by neglecting certain electron repulsion integrals involving differential overlap. The remaining integrals are then equated to parametric functions containing numeric parameters which have been adjusted^{43–47} to fit experimental data. MINDO/3 calculations have been performed for several hundred hydrocarbon species^{44–49} with an average deviation of ~ 0.3 eV between experimental and calculated energies.

In this investigation, lowest energy geometries for each ion have been determined by minimizing the energy with respect to all geometric variables using the Davidon-Fletcher-Powell method.⁵⁰ Recombination energies have been determined by calculating the energy difference between the minimized reactant ion structure and the neutral, 'frozen' in the geometry-optimized minimum energy configuration of the reactant ion. Tables 1–3 contain the MINDO/3 recombination energies along with the minimized geometric structures, ionization potentials, heats of formation (ΔH_f), energy defects (Q) and relative charge transfer cross-sections for reactant ions shown in Figs 3–7. Ion structures 1–19 appearing in Tables 1–3 are illustrated separately by three-dimensional representations where bond distances are given in Å. Bonds of identical magnitude are only labelled once. Recombination energies are illustrated for ion structures suggested from previous experimental investigations and theoretical computations. The MINDO/3 calculations for both ion and neutral have been employed to obtain recombination energies and energy defects in a computationally efficient, accurate and reliable manner. Other experimental and theoretical information relevant to the individual ions are discussed in the next section.

Table 1. Recombination energies and charge transfer cross-sections for hydrocarbon ions

Source gas	IP(eV)	Ion	Ion structure	ΔH_f (eV)	Q (eV)	Recombination energy (eV)	Relative charge transfer cross-section
CH ₄	13.6	CH ₄ ⁺	1	11.444	−3.984	9.616	1.00
		CH ₃ ⁺	2	11.287	−4.197	9.403	1.00
		CH ₂ ⁺	3a	13.657	−4.998	8.602	1.00
			3b	13.902	−5.922	7.678	
		CH ⁺	4	15.244	−4.349	9.251	1.00
		C ₂ H ₄ ⁺	5a	10.550	−1.546	8.954	3.22
C ₂ H ₄	10.50		5b	10.956	−3.226	7.274	
		C ₂ H ₃ ⁺	6a	10.767	−4.808	5.692	1.00
			6b	10.998	−2.534	7.966	
			6c	12.576	−2.725	7.775	
			6d	12.401	−2.647	7.853	
		C ₂ H ₂ ⁺	7	12.909	−0.321	10.179	3.22
		C ₂ H ⁺	8a	16.938	0.036	10.536	6.45
			8b	15.276	−1.206	9.294	
		C ₂ H ₆ ⁺	9	10.038	−2.731	9.259	1.92
		C ₂ H ₅ ⁺	10a	8.921	−5.689	6.301	0.96
C ₂ H ₆	11.99		10b	9.268	−3.740	8.250	
		C ₂ H ₄ ⁺	5a		−3.036	8.954	1.92
		C ₂ H ₃ ⁺	6a		−6.298	5.692	1.00
		C ₂ H ₂ ⁺	7		−1.811	10.179	2.63
		C ₂ H ⁺	8a		−1.454	10.536	3.85

Table 2. Recombination energies and charge transfer cross-sections for hydrocarbon ions

Source gas	<i>I</i> <i>P</i> (eV)	Ion	Ion structure	ΔH_f (eV)	<i>Q</i> (eV)	Recombination energy (eV)	Relative charge transfer cross-section
C ₃ H ₈	11.51	C ₃ H ₈ ⁺	11	9.193	-2.658	8.852	1.98
		C ₃ H ₇ ⁺	12a	8.012	-3.811	7.699	1.01
			12b	8.316	-6.026	5.484	
		C ₃ H ₆ ⁺	13a	9.786	-2.755	8.755	1.70
			13b	9.456	-2.992	8.518	
		C ₃ H ₅ ⁺	14a	9.626	-3.796	7.714	1.04
			14b	9.259	-4.182	7.328	
			14c	10.308	-3.612	7.898	
		C ₃ H ₄ ⁺	15a	10.612	-3.312	8.198	1.90
			15b	11.197	-2.044	9.466	
			15c	11.290	-3.420	8.090	
		C ₃ H ₃ ⁺	16a	10.426	-5.583	5.927	0.90
			16b	11.135	-3.733	7.777	
		C ₃ H ₂ ⁺	17a	14.179	-2.865	8.645	1.51
			17b	13.107	-4.596	6.914	
			17c	12.740	-3.702	7.808	
		C ₂ H ₅ ⁺	10a		-5.209	6.301	0.90
		C ₂ H ₄ ⁺	5a		-2.556	8.954	1.88
		C ₂ H ₃ ⁺	6a		-5.818	5.692	1.00
		C ₂ H ₂ ⁺	7		-1.331	10.179	2.95

Hydrocarbon ion structural information and recombination energies

Methane. Ionic methane, CH₄⁺, has a MINDO/3 computed C_{2v} symmetry and a H—H bond distance of 1.025 Å. These results are in harmony with the *ab initio* results of Meyer⁵¹ and Bouma *et al.*,² the MINDO/3 calculation of Dewar and Rzepa⁴ and the ESR experiments of Knight *et al.*⁸ The computed recombination energy of 9.6 eV, shown in Table 1, is in agreement with the experimental recombination energy of 9.0 or 9.5 to 12.0 eV reported by Lindholm.⁵² Our calculated value of 11.44 eV for the CH₄⁺ heat of formation is close to the experimental value¹⁸ of ≤11.92 eV. The MINDO/3 structure for CH₃⁺ is planar D_{3h}, corresponding to the *ab initio* minimum energy structure reported by Raghavachari *et al.*³ Lindholm⁵² has reported a recombination energy of 9.0 or 9.5 to 10.5 eV for the CH₃⁺ ion, in

good agreement with our calculated value of 9.4 eV. The experimental CH₃⁺ ground state heat of formation value¹⁸ of 11.32 eV compares well with our value of 11.29 eV. We have calculated two structures for CH₂⁺, a bent (**3a**) and linear (**3b**) structure, with the bent ion more stable by 0.245 eV. The experimental¹⁸ ΔH_f for CH₂⁺ is 14.49 eV, approximately 0.6 eV above the MINDO/3 linear structure and 0.85 eV above that computed for the bent structure. Lindholm⁵² reports a CH₂⁺ recombination energy of 10.4 eV or lower. Szabo⁵³ reports that for electron impact ionizing energies greater than 20 eV, CH₂⁺ is produced primarily in an excited state with a recombination energy larger than our computed values. Thus, for electron impact ionization in a mass spectrometer, we would expect CH₄⁺, CH₃⁺, CH₂⁺ and CH⁺ to have similar recombination energies, in the range of 9 eV. This MINDO/3 data is in harmony with the results presented in Fig. 3, as equal

Table 3. Recombination energies and charge transfer cross-sections for hydrocarbon ions

Source gas	<i>I</i> <i>P</i> (eV)	Ion	Ion structure	ΔH_f (eV)	<i>Q</i> (eV)	Recombination energy (eV)	Relative charge transfer cross-section
C ₄ H ₁₀	11.09	C ₄ H ₁₀ ⁺	18	8.845	-1.567	9.523	2.08
		C ₄ H ₉ ⁺	19a	7.428	-3.647	7.443	2.06
			19b	7.666	-3.475	7.615	
			19c	8.443	-3.162	7.928	
		C ₃ H ₇ ⁺	12a		-3.391	7.699	1.04
			12b		-5.606	5.484	
		C ₃ H ₆ ⁺	13a		-2.335	8.755	2.35
			13b		-2.572	8.518	
		C ₃ H ₅ ⁺	14a		-3.376	7.714	1.14
			14b		-3.762	7.328	
			14c		-3.192	7.898	
		C ₃ H ₃ ⁺	16a		-5.163	5.927	1.22
			16b		-3.313	7.777	
		C ₂ H ₅ ⁺	10a		-4.789	6.301	0.97
		C ₂ H ₄ ⁺	5a		-2.136	8.954	2.42
		C ₂ H ₃ ⁺	6a		-5.398	5.692	1.00

12a

14c

12b

15a

13a

13b

15b

14a

15c

14b

16a

16b

17a

17b

17c

18

19a

19b

19c

recombination energies for these ions should result in similar ion and neutral spectra.

Ethylene. The MINDO/3 calculations for $C_2H_4^+$ predict an open structure (5a) with a 45° twist and a bridged (5b) structure 0.4 eV higher in energy, in agreement with calculations by Dewar and Rzepa.⁴ Shiotani *et al.*⁹ have reported that their ESR results confirm the 45° twist of the open $C_2H_4^+$ structure predicted by MINDO/3. Lindholm⁵² reports a recombination energy 'somewhat lower than 10.5' eV, closer to the computed recombination energy of the open rather than the bridged structure. Table 1 shows the four structures calculated for $C_2H_3^+$. The bridged structure 6a is the most stable, in agreement with the best *ab initio* calculations.¹ Lindholm⁵² assigns a recombination energy 'much lower than 10.5' eV for $C_2H_3^+$. Szabo⁵⁴ reports the relative cross-section of $C_2H_3^+$ charge transfer reactions to be much lower than for $C_2H_4^+$ and $C_2H_2^+$, a result he attributes to the low relative recombination energy for the $C_2H_3^+$ ion. Our results shown in Fig. 4 where the $C_2H_3^0$ product peak is low relative to other product peaks, agree with the work of Szabo, and favor a significant population of the bridged (6a) structure (recombination energy = 5.69 eV) in our reactant ion beam. For $C_2H_2^+$, the MINDO/3 C—C bond distance of 1.258 Å compares well with the 1.255 Å value deduced from photoelectron spectroscopy by Hollas and Sutherley.⁵⁵ The experimental $C_2H_2^+$ recombination energy value obtained by Lindholm⁵² is 11.4 eV, 1.2 eV higher than our calculated value. Our computations predict a linear (8a) and bridged (8b) structure for C_2H^+ , with heats of formation of 16.94 and 15.28 eV, respectively. The experimental value¹⁸ is 16.9 eV. Lindholm⁵² reports a recombination energy of 11.4 eV for C_2H^+ and we obtain values of 10.54 and 9.29 eV for the linear and bridged structures. The high recombination energy for the linear structure leads to a relatively large C_2H^0 product peak from $C_2H^+-C_2H_4$ interactions. In summary, the 5.69 eV recombination

energy of bridged $C_2H_3^+$ is considerably lower than energies for $C_2H_4^+$, $C_2H_2^+$ and C_2H^+ ions. This results in a significantly lower $C_2H_3^0$ peak as compared with other product peaks in the ethylene neutral spectrum.

Ethane. The structure depicted in Table 1 for $C_2H_6^+$ has C_s symmetry with one close H—H bond distance of 1.095 Å, and is the same as the structure calculated by Dewar and Rzepa.⁴ Lindholm⁵² has obtained a recombination energy of 9.0 or 9.5 eV in good agreement with our value of 9.26 eV. This C_s structure is different from the predicted ground state, $^2A_{1g}(D_{3d})$, of Bouma *et al.*² and both of these theoretical structures are at odds with the interpretation of the ESR spectrum of Toriyama *et al.*⁷ which is consistent with a C_{2h} symmetry. The MINDO/3 heat of formation is 10.04 eV, less than the experimental estimate¹⁸ of 10.8 eV. The MINDO/3 heats of formation for bridged (**10a**) and open (**10b**) structures of $C_2H_5^+$ are 8.92 and 9.27 eV, respectively. The experimental values^{17,56,57} range from 9.34 to 9.5 eV, and *ab initio* calculations¹ also favor the bridged structure by 0.39 eV. Houle and Beauchamp⁵⁶ base their value on the heats of formation of the neutral radicals and on the assumption that the ion and neutral structures are sufficiently similar that an adiabatic ionization energy can be obtained from photoelectron spectroscopy. Baer⁵⁷ uses the PIPECO technique,¹² and suggests that since discrepancies in the heats of formation are far beyond the experimental uncertainties, the structures of C_2H_5 and $C_2H_5^+$ are probably different. Our calculated recombination energies are 6.30 eV for the bridged structure and 8.25 eV for the open structure. The $C_2H_5^0$ product peak height, shown in Fig. 5, is relatively low for $C_2H_5^+-C_2H_6$ interactions and can be rationalized by invoking a bridged $C_2H_5^+$ structure **10a** in our reactant beam. The $C_2H_3^0$ product peak is significantly lower than the $C_2H_4^0$, $C_2H_2^0$ and C_2H^0 product peaks, a result which follows the same pattern as the ethylene system. This indicates that the $C_2H_4^+$, $C_2H_3^+$, $C_2H_2^+$ and C_2H^+ ions have the same structures as discussed previously.

Propane. Ions, ion structures, energies and relative charge transfer cross-sections for the C_3H_8 system are presented in Table 2. Our calculated heat of formation for $C_3H_8^+$ is 9.19 eV, less than the experimental estimate¹⁷ of ≤ 9.88 eV. Bouma *et al.*² predict a C_s symmetry for the ground state ion, while Toriyama *et al.*⁷ interpret their $C_3H_8^+$ ESR results in terms of a C_{2v} symmetry. The lowest energy MINDO/3 $C_3H_7^+$ ions have 2-propyl (**12a**) and edge-protonated (**12b**) cyclopropane structures, with heats of formation separated by 0.3 eV. All *ab initio* calculations¹ and previous MINDO/3 results⁴⁸ agree that 2-propyl is the most stable structure of $C_3H_7^+$. Gas phase studies^{1,58,59} suggest that the most stable form for $C_3H_7^+$ is the 2-propyl cation with a second isomer 0.3–0.39 eV higher in energy. The low recombination energies of both of these structures are consistent with the small $C_3H_7^0$ product peak observed for $C_3H_7^+$ ions. The first $C_3H_6^+$ structure (**13a**) in

Table 2 corresponds to a cyclopropane ion with a long C—C bond of 1.70 Å and a heat of formation of 9.79 eV. The second $C_3H_6^+$ structure (**13b**) resembles the propene ion, with a heat of formation of 9.46 eV, which is 0.5 eV lower than the experimental value of Rosenstock *et al.*¹⁷ McLafferty *et al.*²² have used collisionally activated dissociation of $C_3H_6^+$ ions to show that the two long-lived and stable $C_3H_6^+$ isomers have propene and cyclopropane structures. The computed MINDO/3 structures for allyl (**14a**), 2-propenyl (**14b**) and cyclopropenyl (**14c**) $C_3H_5^+$ cations have heats of formation of 9.63, 9.26 and 10.31 eV respectively. The recombination energies for these structures are all low, consistent with the low $C_3H_5^0$ product peak intensity observed in Fig. 6. *Ab initio* calculations¹ performed on the $C_3H_5^+$ system indicate that the allyl structure is more stable than 2-propenyl. Aue *et al.*⁶⁰ have proposed heats of formation of 9.8, 10.30 and 10.32 eV for the three possible isomers and later work has indicated⁶¹ that the allyl and 2-propenyl cations are long-lived. Bowen *et al.*⁶² and Lay and Gross²⁶ have both confirmed the existence of allyl and 2-propenyl cations in the gas phase. Traeger⁶³ has obtained a 9.84 eV heat of formation for the allyl cation in a recent photoionization mass spectrometry experiment. Three isomers of $C_3H_4^+$ have been studied experimentally^{13,64–67} and our calculated heats of formation are approximately 1 eV higher than the experimentally derived values in all three cases. The four $C_3H_3^+$ isomers predicted to be stable by *ab initio* methods¹ have been detected by Burgers *et al.*²⁴ The most stable two structures are the cyclopropenyl (**16a**) and propargyl (**16b**) cations, shown in Table 2. Our calculated structures have geometries close to the *ab initio* results,¹ and heats of formation 0.7 eV and 1 eV lower than the experimentally derived values⁶⁸ for cyclopropenyl and propargyl respectively. The presence of the cyclopropenyl structure in our reactant ion beam, with its low recombination energy of 5.93 eV, is in harmony with the small relative $C_3H_3^0$ peak height observed for $C_3H_3^+-C_3H_8$ interactions. We have computed three structures for the $C_3H_2^+$ ion, with heats of formation of 14.18, 13.11 and 12.74 eV and recombination energies of 8.64, 6.91 and 7.81 eV, respectively. The MINDO/3 linear structure **17a** with a ΔH_f of 14.18 eV supports the experimental value of 14.3 eV estimated for linear ions.⁶⁹ Figs 5 and 6 illustrate that the relative product peak heights formed from reactions of $C_2H_5^+$, $C_2H_4^+$, $C_2H_3^+$ and $C_2H_2^+$ ions are similar for both the propane and ethane systems.

Butane. Ions, ion structures, recombination energies and relative charge transfer cross-sections for butane are listed in Table 3. The MINDO/3 $C_4H_{10}^+$ structure has C_{2h} symmetry, a heat of formation of 8.84 eV and a recombination energy of 9.52 eV. The ESR results of Toriyama *et al.*⁷ and the *ab initio* computations of Bouma *et al.*² also indicate a C_{2h} symmetry for $C_4H_{10}^+$. For $C_4H_9^+$, we have calculated *tert*-butyl, 2-butyl and 1-butyl isomers to be stable structures. The experimental¹⁹ heats of formation known for *tert*-butyl (**19a**) and 2-butyl (**19b**) cations are within 0.2–0.4 eV of our MINDO/3 results. A comparison of

Figs 5-7 shows that the relative product peak heights produced from reactions of $C_3H_7^+$, $C_3H_6^+$, $C_3H_5^+$, $C_3H_3^+$, $C_2H_5^+$, $C_2H_4^+$ and $C_2H_3^+$ with butane follow previously discussed trends.

Relative charge transfer cross-sections and reaction energy defects

Reaction energy defects Q exert a controlling influence on the magnitudes of charge transfer cross-sections. For each particular ion structure, Q changes as the target molecule (and IP) changes. Therefore, correlations are made between relative cross-sections and Q for the family of ions produced from each individual target molecule system. Although Tables 1 and 2 list thermodynamic quantities for a range of possible structures, not all of the structures are expected to be produced in electron impact ionization or anticipated to live long enough to be important in ion beam experiments. Consequently we rely on other experimental measurements to suggest the predominant structures in our reactant ion beam. These preferred structures allow a correct selection of energy defects for the various reactions.

Relative charge transfer cross-sections are given as functions of energy defects in Fig. 8 for the C_2H_4 and C_2H_6 systems. Different reactant ion structures in each possible reaction system are represented by the open and closed circles. A straight line connects the possible reactant ion structures, each of which has its own distinct value of Q . Closed circles represent structures for which there is experimental verification.

Methane system. The values of Q for reactions of CH_4^+ , CH_3^+ , CH_2^+ and CH^+ ions in the methane system are large and similar in magnitude. This results in an identical relative charge transfer cross-section for each reaction.

Ethylene system. Table 1 depicts the two MINDO/3 calculated structures for the $C_2H_4^+$ ions, with Q values of -1.5 and -3.2 eV and a relative charge transfer cross-section of 3.22. The open structure **5a** has been confirmed by the ESR results of Shiotani *et al.*⁹ as well as the ion beam recombination energy measurements of Lindholm.⁵² Thus, the closed circle at $Q = -1.5$ (Fig. 8) represents the $C_2H_4^+$ structure for which there is experimental validation, and this structure **5a** is expected to be predominant in our reactant ion beam. Likewise the closed circle for C_2H^+ represents Q for the linear ion **8a** which has an experimental¹⁸ heat of formation of 16.9 eV, in agreement with the calculated value of 16.94 eV.

Only one structural configuration is calculated for $C_2H_2^+$. However, ion beam experiments of Lindholm⁵² indicate that the actual recombination energy of $C_2H_2^+$ is 1.2 eV higher than the calculated ground state value listed in Table 1, leading to a corrected value of Q shown by the open arrow. The energy defect Q for $C_2H_3^+$ of -4.8 eV corresponds to the minimum-energy bridged structure **6a** favored by both *ab initio*¹ and MINDO/3 calculations. Furthermore, the experimental recombination energy of

Figure 8. Relative charge transfer cross-sections as a function of energy defect for C_2H_4 and C_2H_6 systems. For a given ion, open circles depict energy defects for calculated ion structures while solid circles represent energy defects for calculated structures that have been confirmed in previous experiments. Solid lines connect Q values for ion structures of a given mass.

$C_2H_3^+$ is reported^{52,54} to be much lower than those for $C_2H_4^+$ and $C_2H_2^+$, a fact which supports the bridged structure **6a** with $Q = -4.8$ eV. This structure is represented by the closed circle in Fig. 8.

Ethane system. The calculated structure for $C_2H_6^+$ differs in symmetry from the ESR interpretation⁷ and the experimental¹⁸ heat of formation is 0.76 eV higher than the calculated value. Therefore, this ion has been represented by an open circle. Baer has suggested⁵⁷ that the structures of C_2H_5 (open) and $C_2H_5^+$ are much different, based on the fact that discrepancies in the experimental heats of formation using different techniques are far beyond experimental uncertainties. This evidence indicates that the bridged structure **10a** of $C_2H_5^+$, with $Q = -5.7$, is predominant. The structures of the remaining reactant ions in the top portion of Fig. 8 have been described above.

The dashed curves illustrate approximate variations of relative cross-sections with Q for reactant ions of experimentally verified structures. Both dashed curves in Fig. 8 show that cross-sections decrease significantly as the magnitude of Q increases.

Propane system. Electron impact of propane results in

formation of $C_3H_x^+$ ions existing in different isomeric structures. The overall Q for reaction of an isomeric ion mixture should be represented by an average Q value determined by weighting Q for each individual ion structure by its population distribution in the ion beam. Accurate values for these distributions are not available, but the overall Q should lie on the horizontal line connecting values of Q for the isomeric structures in Fig. 9. The $C_3H_8^+$ calculated structure is represented by an open circle since the ESR results⁷ do not confirm the calculated symmetry and the experimental heat of formation¹⁷ is 0.79 eV higher than the calculated value. Gas-phase studies^{1,58,59} have confirmed the existence of two $C_3H_7^+$ structures, with one of the isomers possessing a ΔH_f 0.3–0.39 eV higher in energy than the 2-propyl structure. Table 2 shows that the computed edge-protonated cyclopropane structure **12b** is 0.3 eV higher than the 2-propyl structure **12a**, and for both of these structures Q values are represented by closed circles in Fig. 9. McLafferty *et al.*²² have shown that propene (**13b**) and cyclopropane (**13a**) $C_3H_6^+$ structures are long-lived and Q values for these structures are denoted by closed circles. The three calculated structures of $C_3H_5^+$ have been found to exist in the gas phase,^{26,60,62} as have the three isomers of $C_3H_4^+$.^{13,64–67} Four $C_3H_3^+$ isomers have been detected²⁴ and the two most stable forms are given in Table 2 and denoted by closed circles in Fig. 9. Calculated energies for the $C_3H_2^+$ structures are shown in Table 2 where the straight-chain isomer **17a** with Q equal to -2.9 eV is in harmony with the experimental evidence of Refs 66 and 69.

Butane system. The ESR symmetry⁷ for the $C_4H_{10}^+$ molecular ion agrees with the calculated symmetry, but the state of this species is uncertain. The butane energy distribution obtained by Ref. 70 suggests that $C_4H_{10}^+$ ions possess considerable internal energy which results in a corresponding uncertainty in the calculated Q value. The *tert*-butyl (**19a**) and 2-butyl (**19b**) $C_4H_9^+$ cations have experimentally determined heats of formation¹⁹ that are within 0.2–0.4 eV of the MINDO/3 heats. These two structures have Q values of -3.5 and -3.6 which are represented by the closed circles. The remaining ions in Fig. 9 have been discussed previously.

Although there are many possible isomeric ion structures in the C_3H_8 and C_4H_{10} systems, the dashed lines in Fig. 9 reflect the general decrease in relative charge transfer cross-sections with increasing magnitude of Q .

Figure 9. Relative charge transfer cross-sections as a function of energy defect for C_3H_8 and C_4H_{10} systems. For a given ion, open circles depict energy defects for calculated ion structures, while solid circles represent energy defects for calculated structures that have been confirmed in previous experiments. Solid lines connect Q values for ion structures of a given mass.

CONCLUSION

Relative probabilities for charge transfer have been measured by time-of-flight techniques for molecular and fragment ions produced by electron impact ionization of CH_4 , C_2H_4 , C_2H_6 , C_3H_8 and C_4H_{10} molecules. Charge transfer probabilities are sensitive to the recombination energies of the incident ions which have been computed using the MINDO/3 method. Low recombination energies of even-electron bridged cations lead to low values of Q and are responsible for the low charge transfer reactivities observed for these ions.

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