Molecular Charge-Transfer Cross Sections and Their Correlation with Reactant Ion Structures

G. C. Shields and T. F. Moran*

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332 (Received: April 18, 1985)

Charge-transfer cross sections have been obtained by using time-of-flight techniques, and results correlated with reaction energetics and theoretical structures computed by self-consistent field-molecular orbital methods. Ion recombination energies, structures, heats of formation, reaction energy defects, and 3.0-keV charge-transfer cross sections are presented for reactions of molecular and fragment ions produced by electron bombardment ionization of CH_3OCH_3 and CH_3Cl molecules. Relationships between experimental cross sections and reaction energetics involving different ion structures are discussed.

Introduction

Electron impact ionization of a molecule occurs by means of a vertical Franck-Condon transition in which the ion is formed with the nuclear configuration of the original molecule. This ion may then rearrange or relax to a more stable structure before charge-transfer collisions occur. Charge-transfer processes involving keV ions occur in time periods short compared to nuclear motion, and as a result fast neutrals formed in these interactions possess the structure of the incident ion. For a symmetric charge-transfer process of the type

in which both reactant ion and neutral product molecule have the same nuclear structure, the charge-transfer process is resonant, and relatively large cross sections are expected. In this special case, the energy released (recombination energy) by the ion to form a neutral exactly balances the ionization potential of the target molecule. However, if the initial ion relaxes to a structure with lower minimum energy prior to reaction, then the charge-transfer process

is no longer resonant, and smaller cross sections are anticipated. A nonresonant charge-transfer process has a nonzero energy defect, which is defined as the energy difference between the recombination energy of the incident reactant ion and the ionization potential of the target molecule. Since charge-transfer processes are sensitive functions of the energy defect, experimental charge-transfer cross sections provide an insight into molecular ion structures.

In this investigation time-of-flight techniques have been used to measure charge-transfer cross sections for reactant ions produced by electron impact ionization of CH_3OCH_3 and CH_3Cl . Reactant ion structures, recombination energies, and energy defects have been computed by using self-consistent field-molecular orbital methods, and this information has been correlated with the magnitudes of experimental charge-transfer cross sections.

Experimental Section

Time-of-flight techniques have been employed to measure fast neutral products resulting from keV charge-transfer reactions. The apparatus and techniques have been used before to monitor fast neutral products formed from charge-transfer reactions of singly¹ and doubly² charged ions. Reactant molecular ions and

their characteristic fragment ions have been produced by electron impact ionization of dimethyl ether and methyl chloride gases. Electrons have been emitted from a directly heated filament and accelerated into the ion source by a voltage controllable from 2 to 100 V. The electron beam intensity has been kept constant throughout each measurement with a regulated filament current supply.

Reactant molecular and fragment ions produced by electron impact have been drawn out of the source by a fast rising pulse and accelerated through a 3-kV potential. The fully accelerated ion beam then entered a static gas collision region, containing the parent molecule, where ion-molecule interactions could occur. Unreacted ions and fast neutral products from charge transfer 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 drift region has been 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 results 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 is detected as well.

The number of secondary electrons emitted from metal surfaces by high-energy particle bombardment has been found to be equivalent for both the ion M^+ and the charge-transfer neutral product M^0 .^{3,4} Equal emission coefficients result in equivalent electron multiplier response for both the incident ion and its corresponding neutral product at 3-keV energy.

Results and Discussion

Reactant ions and their fast neutral products from keV charge-transfer reactions can be monitored with high sensitivity by using an electron multiplier detector^{3,4} and time-of-flight techniques. The secondary neutral product signal, i_n , is related to the primary reactant ion signal, i_p , by the equation

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

where l is the path length over which reactions occur, n is the target molecule concentration, and σ is the reaction cross section. The cross section is a direct measure of charge-transfer reaction efficiencies, which vary with energy defect (Q) at low keV incident ion energies. This quantity Q is the energy difference between the reactant ion recombination energy⁵ and neutral target ionization potential ($Q = \text{RE} - \text{IP}$). The recombination energy is the energy liberated by 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

(2) G. C. Shields and T. F. Moran, *J. Phys. B*, **16**, 3591 (1983).

(3) H. W. Berry, *Phys. Rev.*, **74**, 848 (1948).

(4) H. Hayden and N. G. Utterback, *Phys. Rev. A*, **135**, 1575 (1964).

(5) E. Lindholm, *Z. Naturforsch., A: Astrophys., Phys. Phys. Chem.*, **9A**, 535 (1954).

(1) J. B. Wilcox, K. L. Harbol, and T. F. Moran, *J. Phys. Chem.*, **85**, 3415 (1981).

and cross sections for charge transfer are large,^{6,7} on the order of 10^{-14} – 10^{-15} cm².

Recombination energies of ions formed in the CH₃OCH₃ and CH₃Cl systems, which are dependent on ion structure, have been computed by using the MINDO/3 semiempirical SCF-MO approach developed by Dewar and co-workers.^{8–12} 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 constants which have been adjusted^{8–12} to fit experimental data. Lowest energy geometries for each ion have been obtained by minimizing the energy with respect to all geometric variables using the Davidson–Fletcher–Powell method.¹³ 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.

The primary reactant ion and secondary neutral product mass spectra are presented in Figures 1 and 2 for the dimethyl ether and methyl chloride systems. Cross sections are presented in Tables I and II, along with MINDO/3 minimum-energy geometry-optimized ion structures, heats of formation, recombination energies, and energy defects. All of the calculated ion structures in the tables are singlets or doublets unless otherwise noted. Magnitudes of observed cross sections can be rationalized by examining computed energy defects, thus allowing an insight into ion structure. Other experimental and theoretical information relevant to the individual ions are discussed in the next section.

CH₃OCH₃ System. The CH₃⁺ ion, formed from electron bombardment ionization and fragmentation of dimethyl ether, has a high probability for charge transfer in collisions with CH₃OCH₃ molecules. This is indicated in Figure 1, where the relative intensity of fast CH₃⁰ molecules is 2^{1/2} times the intensity of reactant CH₃⁺ ions. The charge-transfer section value of 64×10^{-16} cm² presented in Table I is a consequence of a close energy balance between the CH₃⁺ recombination energy and target CH₃OCH₃ ionization potential. The energy defect (*Q*) given in Table I is only –0.64 eV, a value characteristic of a near-resonant reaction. The MINDO/3 geometry-optimized minimum-energy structure for CH₃⁺ is planar *D*_{3h} and corresponds to the ab initio minimum-energy structure reported by Raghavachari et al.¹⁴ The experimental CH₃⁺ ground-state heat of formation value¹⁵ of 11.32 eV compares well with the MINDO/3 value of 11.29 eV. A reported¹⁶ CH₃⁺ recombination energy of 9.0 or 9.5 to 10.5 eV is in harmony with the calculated value of 9.4 eV and supports our estimation of *Q* for this near-resonant charge-transfer reaction which has a relatively large cross section.

Smaller charge-transfer cross sections for HCO⁺ ion reactions are indicated in Figure 1 where the relative intensity of the HCO fast neutral peak at mass 29 is approximately the same as that

for the HCO⁺ reactant ion. The HCO⁺ and COH⁺ ions have been studied by microwave spectroscopy in great detail.^{17,18} The HCO⁺ structure is much more prevalent than the COH⁺ structure in the methanol photoionization experiment of Berkowitz.¹⁹ Woods et al.²⁰ report that the ratio HCO⁺/COH⁺ is ~330 in interstellar molecular clouds. Illies et al.²¹ indicate both isomers can be detected by collision-induced dissociation fragmentation patterns and that the reaction between H₃⁺ + CO forms greater than 90% HCO⁺ products. The MINDO/3 minimized geometry of HCO⁺ is linear with a H–C bond distance of 1.094 Å and a C–O bond distance of 1.115 Å, consistent with the microwave spectroscopy values¹⁷ of 1.093 and 1.107 Å, respectively. The HCO⁺ ΔH_f value of 8.508 eV obtained from the photoionization mass spectrometric study of Guyon et al.²² is in reasonable accord with the MINDO/3 ΔH_f of 8.0 eV. The –3.01-eV energy defect *Q* for HCO⁺–CH₃OCH₃ interactions shown in Table I is significantly larger than that for the CH₃⁺–CH₃OCH₃ system and is consistent with a decrease in the cross section to a value of 29×10^{-16} cm² for reactions involving HCO⁺ ions.

The CH₂O⁺ ion peak at mass 30 is barely observable in Figure 1; however, the CH₂O neutral peak is clearly evident. This large (neutral product/reactant ion) ratio suggests very efficient charge-transfer reactions for CH₂O⁺ ions. The MINDO/3 computations indicate the CH₂O⁺ ion is planar with a relatively high recombination energy of 10.54 eV and *Q* = 0.50 eV. Thus, CH₂O⁺–CH₃OCH₃ charge-transfer interactions are near-resonant, and as a result this system with $\sigma = 87.5 \times 10^{-16}$ cm² exhibits the largest cross section in Table I.

Moderate size cross sections for reactions of mass 31 ions are evident in Figure 1 where the neutral/ion ratio is close to unity. Minimum-energy geometry-optimized structures for CH₂OH⁺ and CH₃O⁺ isomers are shown in Table I. The CH₂OH⁺ structure is much more stable than CH₃O⁺ in agreement with experimental work of Berkowitz¹⁹ and Dill et al.²³ and with theoretical calculations of Bouma et al.²⁴ and Dewar and Rzepa.²⁵ The MINDO/3 CH₃O⁺ singlet structure has a ΔH_f of 10.32 eV and is 1.37 eV more stable than the methoxy CH₃O⁺ structure calculated by Dewar and Rzepa.²⁵ This latter structure²⁵ was not a minimum on the CH₃O⁺ potential surface and was calculated by enforcing *C*_{3v} symmetry. The MINDO/3 triplet ground-state methoxy ion has a ΔH_f of 10.77 eV, in good agreement with the ab initio calculation²³ of 10.02 eV and the experimental value²⁶ of 10.7 eV, where the triplet-state ion was generated by collision-induced charge reversal of methoxy anions. Our charge-transfer cross section of 29×10^{-16} cm² for *m/e* 31 ions is in harmony with the *Q* value of –2.84 eV for the CH₂OH⁺ ion and agrees with previous results^{19,23–26} reporting the CH₂OH⁺ ion as the predominant isomer. We would expect a cross section higher than 29×10^{-16} cm² if the triplet methoxy ion was present to a significant extent in our reactant ion beam, since *Q* is only 0.13 for this species.

Reactions involving ground-state CH₃OCH₂⁺ ions have an energy defect of –5.79 eV, which is rather high to result in a cross section as large as 25×10^{-16} cm² (Table I). The data of Figure 1 suggest possible excited-state involvement in this reaction since the relative CH₃OCH₂ neutral product peak decreases as the

(6) R. D. Cannon, “Electron Transfer Reactions”, Butterworths, London, 1980.

(7) T. F. Moran in “Electron-Molecule Interactions and Their Applications”, Vol. 2, L. G. Christophorou, Ed., Academic Press, New York, 1984, pp. 1–64.

(8) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).

(9) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1294 (1975).

(10) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1302 (1975).

(11) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1307 (1975).

(12) M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *J. Am. Chem. Soc.*, **97**, 1311 (1975).

(13) W. C. Davidson, *Comput. J.*, **10**, 406 (1968); R. Fletcher, *Comput. J.*, **8**, 33 (1965); R. Fletcher and M. J. D. Powell, *Comput. J.*, **6**, 163 (1963).

(14) K. Raghavachari, R. A. Whiteside, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **103**, 5649 (1981).

(15) V. G. Anicich, G. A. Blake, J. K. Kim, M. J. McEwan, and W. T. Huntress, Jr., *J. Phys. Chem.*, **88**, 4608 (1984).

(16) E. Lindholm, in “Ion-Molecule Reactions in the Gas Phase”, R. F. Gould, Ed., American Chemical Society, Washington, D.C., 1966, pp. 1–19.

(17) R. C. Woods, R. J. Saykally, T. G. Anderson, T. A. Dixon, and P. G. Szanto, *J. Chem. Phys.*, **75**, 4256 (1981).

(18) C. S. Gudeman and R. C. Woods, *Phys. Rev. Lett.*, **48**, 1344 (1982).

(19) J. Berkowitz, *J. Chem. Phys.*, **69**, 3044 (1978).

(20) R. C. Woods, C. S. Gudeman, R. L. Dickman, P. F. Goldsmith, G. R. Huguenin, W. M. Irvine, A. Hjalmarsen, L.-A. Nyman, and H. Olofsson, *Astrophys. J.*, **270**, 583 (1983).

(21) A. J. Illies, M. F. Jarrold, and M. T. Bowers, *J. Am. Chem. Soc.*, **105**, 2562 (1983).

(22) P. M. Guyon, W. A. Chupka, and J. Berkowitz, *J. Chem. Phys.*, **64**, 1419 (1976).

(23) J. D. Dill, C. L. Fischer, and F. W. McLafferty, *J. Am. Chem. Soc.*, **101**, 6531 (1979).

(24) W. J. Bouma, R. H. Nobes, and L. Radom, *Org. Mass Spectrom.*, **17**, 315 (1982).

(25) M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **99**, 7432 (1977).

(26) P. C. Burgers and J. L. Holmes, *Org. Mass Spectrom.*, **19**, 452 (1984).

TABLE I: Charge-Transfer Cross Sections and Energy Defects for Depicted Ions Reacting with CH_3OCH_3 Target Molecules

m/e	Ion	Ion Structure	ΔH_f (eV)	Recombination Energy (eV)	Q (eV)	Charge Transfer Cross Section (10^{-16} cm^2)
15	CH_3^+		11.29	9.40	-0.64	64
29	HCO^+		8.00	7.03	-3.01	29
29	COH^+		7.31	6.41	-3.63	
30	CH_2O^+		9.46	10.54	0.50	87.5
31	CH_2OH^+		6.79	7.20	-2.84	29
	CH_3O^+		10.32	8.32	-1.72	
	CH_3O^+ Triplet		10.77	10.17	0.13	
45	$\text{CH}_3\text{OCH}_2^+$		6.44	4.25	-5.79	25
	$\text{CH}_3\text{OCH}_2^+$ Excited Singlet		9.57	9.71	-0.33	
	$\text{CH}_3\text{OCH}_2^+$ Triplet		9.22	9.42	-0.62	
46	$\text{CH}_3\text{OCH}_3^+$		7.85	9.45	-0.59	61
46	$\text{CH}_3\text{OHCH}_2^+$		7.51	6.53	-3.51	

electron energy is lowered from 100 to 30 eV. The two lowest excited states shown in Table I have reaction energy defects of -0.33 and -0.62 eV, respectively. A long-lived $\text{CH}_3\text{OCH}_2^+$ component in our reactant ion beam with a small energy defect

would be consistent with the magnitude of our measured charge-transfer cross section.

The dimethyl ether parent ion has a charge-transfer cross section of $61 \times 10^{-16} \text{ cm}^2$ which is in harmony with a MINDO/3 cal-

TABLE II: Charge-Transfer (CT) Cross Sections and Energy Defects for Depicted Ions Reacting with CH_3Cl Target Molecules

ion	ion structure	ΔH_f , eV	recombination energy, eV	Q , eV	CT cross section, 10^{-16} cm^2
CH_3^+		11.29	9.40	-1.89	20
CCl^+		12.55	8.08	-3.21	13
CHCl^+		11.74	8.06	-3.23	11
CH_2Cl^+		9.88	8.43	-2.86	16
CH_3Cl^+		9.75	9.23	-2.06	29

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

culated energy defect of $Q = -0.59$ eV. The geometry-optimized $\text{CH}_3\text{OCH}_3^+$ ion has C_{2v} symmetry, with both methyl groups eclipsing rather than staggering the neighboring C-O bonds, a result in agreement with *ab initio*²⁷ and ESR experimental results.²⁸ A value of $\Delta H_f = 8.11$ eV was obtained from the photoelectron-photoion coincidence spectrometric study of Butler et al.,²⁹ close to the calculated ΔH_f of 7.85 eV. The $\text{CH}_3\text{OHCH}_2^+$ isomer has

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

been predicted²⁷ to be slightly more stable than the parent dimethyl ether ion. Holmes et al.³⁰ report a ΔH_f of 7.6 eV for the $\text{CH}_3\text{OHCH}_2^+$ ion, in good agreement with the MINDO/3 calculation of 7.51 eV. It is not expected that a significant fraction of m/e 46 ions in our experiment have the $\text{CH}_3\text{OHCH}_2^+$ structure, as the Q value of -3.51 eV suggests that the charge-transfer cross section would be much smaller than the measured $61 \times 10^{-16} \text{ cm}^2$ value.

CH_3Cl System. Ionic and neutral product spectra for the CH_3Cl system are shown in Figure 2. The molecular ion and its

(27) W. J. Bouma, R. H. Nobes, and L. Radom, *J. Am. Chem. Soc.*, **105**, 1743 (1983).

(28) J. T. Wang and F. Williams, *J. Am. Chem. Soc.*, **103**, 6994 (1981).

(29) J. J. Butler, D. M. P. Holland, A. C. Parr, and R. Stockbauer, *Int. J. Mass Spectrom. Ion Processes*, **58**, 1 (1984).

(30) J. L. Holmes, F. P. Lossing, J. K. Terlouw, and P. C. Burgers, *J. Am. Chem. Soc.*, **104**, 2931 (1982).

neutral are the largest peaks in each individual spectrum. Intensities of neutrals formed from fragment ions are reduced in size relative to the corresponding ion intensities, in contrast to Figure 1. Data in Figure 2 are consistent with smaller charge-transfer cross sections in the CH_3Cl system. Cross sections for individual ions shown in Table II range from 11×10^{-16} to $30 \times 10^{-16} \text{ cm}^2$. Energy defects for reactions of all ions in the CH_3Cl system are approximately -2 to -3 eV, resulting in cross sections that are smaller than those given in Table I. For example, the cross section for $\text{CH}_3^+ - \text{CH}_3\text{Cl}$ charge-transfer reactions is $20 \times 10^{-16} \text{ cm}^2$ which is considerably smaller than the $\text{CH}_3^+ - \text{CH}_3\text{OCH}_3$ cross section. This small cross section is a consequence of the higher ionization potential of CH_3Cl .

Reactant ion structural and energetic information listed in Table II show CH_nCl^+ heats of formation to decrease with increasing n . Werner et al.³¹ derive a value of 10.44 eV for the ΔH_f of CH_2Cl^+ from their photoionization study, a result comparable with the MINDO/3 value of 9.88 eV. Nishimura et al.³² have calculated r_e to be 1.551 Å for the ground-state singlet CCl^+ ion,

a result close to our calculated value of 1.555 Å. Table II shows that the MINDO/3 calculated structure for CH_3Cl^+ has one bridged hydrogen atom. In contrast to the $\text{CH}_3\text{OCH}_3^+$ ionic structure, the geometry-optimized minimum-energy bridged CH_3Cl^+ ion structure is radically different from its ground-state neutral configuration. This structural change results in a significantly lower recombination energy. The corresponding large negative value of Q results in relatively small charge-transfer cross sections for the $\text{CH}_3\text{Cl}^+ - \text{CH}_3\text{Cl}$ reaction.

Conclusions

Charge-transfer cross sections have been measured by time-of-flight techniques for molecular and fragment ions produced by electron impact ionization of CH_3OCH_3 and CH_3Cl molecules. Charge-transfer probabilities are sensitive to energy defects Q and recombination energies of the incident ions, which have been computed by using SCF-MO methods. Low recombination energies result in large negative energy defects and relatively small charge-transfer cross sections.

Registry No. CH_3OCH_3 , 115-10-6; CH_3Cl , 74-87-3; CH_3^+ , 14531-53-4; HCO^+ , 17030-74-9; COH^+ , 97467-05-5; CH_2O^+ , 27837-46-3; CH_2OH^+ , 18682-95-6; CH_3O^+ , 58157-09-8; $\text{CH}_3\text{OCH}_2^+$, 23653-97-6; $\text{CH}_3\text{OCH}_3^+$, 38091-19-9; $\text{CH}_3\text{OHCH}_2^+$, 84602-74-4; CCl^+ , 69773-94-0; CHCl^+ , 89877-51-0; CH_2Cl^+ , 59000-00-9; CH_3Cl^+ , 12538-71-5.

(31) A. S. Werner, B. P. Tsai, and T. Baer, *J. Chem. Phys.*, **60**, 3650 (1974).

(32) Y. Nishimura, T. Mizuguchi, M. Tsuji, S. Obara, and K. Morokuma, *J. Chem. Phys.*, **78**, 7260 (1983).