phenoxide-Sl occurs to the phenoxy oxygen and, other things being equal, one expects a larger negative charge density on this single charged atom than for the two oxygens of the NO_2 group of the nitrobenzene (radical) anions. Measurements of the other bond energies for the substituted phenoxides XPhO-Sl would have been of considerable interest. The nitrophenoxide anions were produced in the ion source by a reaction of NO_2^- or O_2^- with 2-CINB (or 4-CINB) described in earlier work.¹⁷ Unfortunately, the preparation of the other phenoxide anions, so far, is possible in our apparatus only by deprotonation of the corresponding phenols,¹⁶ and the presence of the strongly hydrogen-bonding XPhOH leads to the corresponding proton held dimers XPhO-HOPhX as the completely dominant species, precluding thus the observation of the XPhO-Sl.

While the phenoxide ions do not fall on the lines observed for the radical anions M^- in Figure 4, it is quite certain that the bond energies for XPhO-SI as a group by themselves will fall on an approximate straight line when plotted vs. EA(XPhO) or vs. the gas-phase acidity of XPhOH. An approximately linear inverse relationship is known to exist^{16,18,19} between the solvation energies of the phenoxides XPhO⁻ and the electron affinities of XPhO. This relationship has the same origin as the one observed for M⁻, i.e. the electron affinity of XPhO increases with increasing charge delocalization in XPhO⁻ and increasing charge delocalization decreases the bonding in XPhO-SI and the solvation energies of XPhO⁻.

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Registry No. DMF, 68-12-2; THF, 109-99-9; 2,3-Me₂NB⁻⁺, 35963-33-8; 3-MeONB⁻⁺, 42206-54-2; 4-MeONB⁻⁺, 34473-10-4; 2-MeNB⁻⁺ 34505-30-1; 3-MeNB⁻⁺, 34505-29-8; 4-MeNB⁻⁺, 34509-96-1; NB⁻⁺ 12169-65-2; 2-FNB-*, 34467-51-1; 3-FNB-*, 34470-17-2; 4-FNB-*, 34467-53-3; 2-CINB*, 34470-27-4; 3-CINB*, 34467-54-4; 4-CINB* 34473-09-1; 3-CF₃NB*, 34526-71-1; MaAn*, 51978-31-5; 2-CNNB*, 12402-45-8; 3-CNNB-, 12402-46-9; 4-CNNB-, 12402-47-0; 2-NO2NB⁻⁺, 34505-38-9; 3-NO2NB⁻⁺, 34509-56-3; 4-NO2NB⁻⁺, 34505-33-4; BQ⁻⁺, 3225-29-4; NpQ⁻⁺, 20261-01-2; 2,3-Cl₂NpQ⁻⁺, 22062-59-5; F₄BQ⁻⁺, 42439-31-6; MeOH, 67-56-1; MeCN, 75-05-8; Me₂SO₃, 67-68-5; 4-NO₂ phenoxide, 14609-74-6; 2-NO₂ phenoxide, 16554-53-3.

Thermal Energy Charge-Transfer Reactions of Ar⁺ and Ar₂⁺

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The rate coefficients for a number of thermal energy charge-transfer reactions are obtained with a recently completed selected ion flow tube (SIFT). The ion-molecule reactions studied involve Ar⁺ and Ar₂⁺ with a variety of neutral molecules including O₂, CS₂, CO₂, SO₂, H₂O, H₂S, NH₃, NO, SF₆, CH₄, N₂O, NO₂, and CO. The relative magnitudes of the observed rate coefficients are not in accord with an energy resonance model which requires favorable Franck-Condon factors. Furthermore, we find that the dimer ion reaction rate constant is not always greater than that of the monomer with a specific neutral although there is greater phase space in the case of the dimer where the dissociative channel leads to a three-body final state. However, the proximity of the recombination energy of Ar^+ and Ar_2^+ to a band in the photoelectron spectra of the neutral appear to explain the relative rates of the monomer and the dimer reactions with a specific neutral.

Introduction

Thermal energy charge-transfer reactions have been of longstanding interest in the field of gas-phase ion-molecule chemistry. Work has been prompted by both practical and fundamental considerations. For example, charge-transfer reactions are known to be one of the dominating processes in the ionosphere¹ and in interstellar chemistry.² Also, thermal energy charge-transfer reactions have been considered as possible sources of chemical lasers.^{3,4} The mechanism involved in a thermal energy chargetransfer reaction has yet to be definitively established, and much debate has appeared in the literature over this issue. The distribution of excess energy in the reaction into internal modes, translational energy, or dissociative channels has also been discussed.^{3,5-7} The subject of the present paper is to compare rate

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coefficients for atomic (Ar⁺) and molecular (Ar₂⁺) ions with a variety of polyatomic neutrals.

Two proposed mechanisms, the long-range electron jump mechanism and the collision complex formation mechanism, have dominated the literature over the past decade. The long-range electron jump mechanism is considered to occur over a relatively large distance by a nonorbiting collision⁸ on more than one potential surface. Early evidence for this mechanism at thermal energies included the observation of rate coefficients9,10 which were greater than the calculated collision rates from either the Langevin¹¹ or average dipole orientation $(ADO)^{12}$ theories, both of which imply orbiting collisions. Such long-range, nonadiabatic reactions were considered to occur by vertical transitions where Franck-Condon factors are significant.¹⁰ Laudenslager et al.¹³ have examined a number of charge-transfer reactions and have concluded that, in general, favorable Franck-Condon factors are necessary for a fast thermal energy charge-transfer reaction (k_{obsd} $\geq 0.10k_{calcd}$). Exceptions have been observed, notably reactions

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⁽¹⁹⁾ The relationship is actually between the gas-phase acidities and the solution acidities of the substituted phenols. From this relationship since the bond energies D(XPhO-H) are expected to change very little one can deduce a linear inverse relationship between the electron affinities EA(XPhO) and the solvation energies of XPhO⁻ ions.

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Ar⁺ and Ar₂⁺ Thermal Reactions

of Ar^+ with CO_2 and N_2O where both reactions are known to be fast and possess poor Franck-Condon factors.¹⁴ Some of the exceptions have been explained by a theory of "distorted" Franck-Condon factors where the vibrational wave functions of the neutral are perturbed by the approaching ion.9,10,15 More recently, Ausloos et al.¹⁶ reevaluated a number of the reported fast rate coefficients and concluded that evidence for a long-range electron jump mechanism is in question.

The collision complex formation mechanism occurs at relatively close proximity between the ion and the neutral on one potential surface. A long-lived intermediate is considered to be formed where the energy states of the products are randomized to a Boltzmann distribution. Lin et al.¹⁷ have recently observed a thermal energy charge-transfer reaction with a non-Boltzmann vibrational distribution. A diabatic mechanism forming an intermediate complex has been suggested where avoided crossings and nonadiabatic couplings of the potential energy surfaces of the reactant and product states become important. Determination of the actual mechanism clearly requires further study.

The method of energy deposition in thermal energy chargetransfer reactions is especially relevant in the case of polyatomic ions and molecules. Internal or translational excitation of the products and dissociative channels have all been considered to be responsible for the partitioning of the excess energy. $^{3,5-7}$ Where molecular ions are involved, interest is now turning to the role of vibrational excitation of the product ion.¹⁸ An energy resonance between the recombination energy of the reactant ion and an energy state of the product ion appears to be important.¹⁹ Further study of the energy dissipation processes is expected to lead to a clarification of the mechanisms involved.

In order to contribute to a further understanding of the factors governing rates of charge transfer for similar atomic and molecular systems, we undertook a study of thermal energy charge-transfer reactions of Ar⁺ and Ar₂⁺ with a variety of neutral polyatomic molecules. A number of physical parameters, including the energy difference between the recombination energy of the reactant ion and the adiabatic ionization potential of the neutral reactant, the dipole moment and the polarizability of the neutral, and Franck-Condon factors, were taken into consideration in selecting the systems for study. The rate coefficients for reactions of the monomer and the dimer argon cations are measured and compared with the calculated collision rates.

Experimental Section

The data reported here are obtained on a recently constructed selected ion flow tube (SIFT). Since these are the first measurements taken with this apparatus in our laboratory, a detailed description is given even though much of the general technique has been well documented by Smith and Adams.^{20,21} The present apparatus contains a number of subtle changes which will be detailed.

A schematic diagram of the system is shown in Figure 1. The apparatus, which is based on the flowing afterglow technique pioneered by Ferguson and co-workers,²² consists of five main components: an ion source, SIFT quadrupole mass filter, ion injector, flow tube, and a mass spectrometric detection system. Briefly, ions formed in an expansion source are focused into a quadrupole mass filter where they are mass selected. Thereafter,



Figure 1. A schematic of the selected ion flow tube (SIFT) used in this study. The break in the flow tube indicates a 90° rotation of the ion source for a more detailed view of the apparatus.

the selected ionic species of interest is injected into the flow tube. The ions are thermalized by collisions with the inert carrier gas which is helium in the present study. Neutral reactant gas is added through a reactant gas inlet (RGI) at an appropriate location downstream in the flow tube and allowed to react with the injected ions. Ions on the flow tube axis are sampled through a 1-mmdiameter orifice where they are mass analyzed by a second quadrupole mass spectrometer and detected. A large volume Stokes Pennwalt 1721 Roots blower with a pumping capacity of 1300 cfm at 0.1 torr is used to pump away the bulk of the gas in the flow tube.

The ions for this study, Ar^+ and Ar_2^+ , are produced with an expansion source. Argon is pressurized from 1 to 3 atm behind a 100- μ m-diameter orifice and expanded into a region where the pressure is ca. 2×10^{-4} Torr. An adiabatic expansion promotes clustering within a few nozzle diameters from the orifice.23 Electrons which are emitted from a tungsten filament (0.005-in. diameter) cross the expansion beam and electron impact ionization occurs. A current of 1.75-1.85 A and a potential of -16 to -25 Vdc are applied to the filament. A potential of +58 Vdc is typically applied to the orifice. Ion currents measured after mass selection with this source range from 1.0×10^{-7} to 6.0×10^{-7} A for Ar⁺ and from 0.5×10^{-9} to 9.0×10^{-9} A of Ar₂⁺.

An einzel lens is used to accelerate and focus the ions out of the source and into the SIFT quadrupole where the primary ionic species of interest is mass filtered. The enormous angles of divergence and spatial extent of the ion trajectories emerging from the quadrupole demand excellent focusing to ensure maximum ion injection into the flow tube. In our case, a two-lens system consisting of an electrostatic octapole and an einzel lens has been incorporated. Studies²⁴ have shown that the cross-sectional shape of the ion beam out of a quadrupole has extremities which point toward the quadrupole rods. The octapole has the ability to focus this beam in two planes simultaneously and create a more uniform circular cross section.²⁴ Addition of an einzel lens improves the focusing of this large circular cross section of ions to the 1-mmdiameter orifice of the injector.

The design of the injector used in the present work is based on a detailed study by Dupeyrat et al.²⁵ and is very similar to the NOAA 2 design. The injector walls slope away from the ion entrance orifice and form a 45° angle with the flow-tube axis so the plane containing the annular region is located 0.343 cm from the orifice. The carrier gas is introduced through an annular opening (0.025 mm wide at a diameter of 0.635 cm) around the injection orifice. The carrier gas first passes through a reservoir to eliminate any pressure differences in the annular region; it also functions to produce a uniform gas stream. Pressure builds up in the reservoir and the gas is forced through the annular region at a very high velocity parallel to the ion beam. A high impedance of the carrier gas flow is established at the annulus which enhances

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ion injection, reduces backstreaming, but also increases the distance of the turbulent flow in the flow tube. Ions are injected into the flow tube through a 1-mm-diameter orifice at a relatively low energy to prevent collisional fragmentation. The ion injection orifice is electrically insulated so that a small potential can be applied to attract ions. The orifice is constructed from 0.051mm-thick platinum plate.

The flow tube is 123 cm in length, 10.16 cm in diameter, and is constructed entirely of stainless steel. The pressure in the flow tube is typically 0.1 to 1.0 Torr. The carrier gas bulk flow velocity is approximately 10^4 cm/s and the ion number densities typically range from 10^3 to 10^4 cm⁻³. Space charge repulsion is essentially eliminated under these conditions, and normal field free diffusive-loss conditions are established. Therefore, compared to a flowing afterglow, smaller ion density gradients and smaller diffusive losses are observed in the SIFT.

Laminar flow of the carrier gas is desired for kinetic studies. It has been estimated by Dupeyrat et al.25 that the laminar region occurs approximately 30 cm downstream. Both stationary and movable reactant gas inlets (RGI) have been used in the instrument. The stationary inlet is located 51.7 cm downstream from the ion injector and 71.3 cm upstream from the sampling orifice. This distance before the addition of neutral reactant gas is also advantageous since it allows ample time for thermalization of the reactant ions to the temperature of the carrier gas. The RGI is constructed of 3.18 mm o.d. stainless steel tubing and is circular in shape. The outer diameter of the RGI is 3.50 cm which is approximately 3/8 the diameter of the flow tube. The reactant gas is distributed radially inward and outward from six equally spaced alternating holes each 0.0397 mm in diameter. This RGI had no apparent end correction and was determined to be the most effective and stable inlet for this flow tube.^{26,27} Uniform flow and distribution of the neutral reactant gas are maintained with a flush flow of the carrier gas through the RGI, approximately 1 to 2% of the total carrier gas flow rate.

Ions are sampled through a platinum orifice with a 1-mmdiameter hole located on the axis of the flow tube and mounted on the nose cone. The nose cone consists of the sampling orifice, the nose cone carrier, and the nose cone plate which are all insulated from one another so that a small potential ranging from -5 to +5 Vdc can be applied to improve the ion collection efficiency. The signal is extremely sensitive to the potentials on the sampling orifice and the nose cone carrier.

Ions which pass through the sampling orifice are focused by a series of electrostatic elements into a quadrupole mass spectrometer, where they are mass analyzed and detected with a channeltron electron multiplier (Model 4830 Galileo Electro-Optics). Pulse-counting techniques are incorporated for quantitative determination of the intensities; the data collected by repetitive scanning techniques are recorded with a Canberra 3100/e multichannel analyzer.

The gases used in this study are all commercial grade Union Carbide prepurified (99.9% minimum) and no further purification was needed. The vapors of distilled CS_2 and H_2O were used for their respective reactions. The carrier gas is purified by passing it through a sequence of three molecular sieves: Union Carbide type 13X, type 5A, and type 3A molecular sieve. When helium is used the sieves are placed in liquid nitrogen to condense out additional impurities.

Results and Discussion

Rate coefficients for charge-transfer reactions are obtained in the conventional manner.²⁰⁻²² Consider the reaction

$$A^{+} + B \xrightarrow{k_{f}} B^{+} + A \tag{1}$$

where A^+ designates the ion or ion cluster, B the neutral species, and k_f the forward rate coefficient.



Figure 2. Typical plot used to obtain the bimolecular charge-transfer rate coefficients. The decrease in the reactant ion with the addition of neutral reactant is linear for 2.5 to 3.0 decades.

When B is in great excess and assuming that the measured ion intensity I_{A^+} is directly proportional to the concentration of A^+ , pseudo-first-order kinetics lead to

$$I_{A^{+}} = I_{0A^{+}} \exp[-(C_2 k_f[\mathbf{B}] Z / V_p)]$$
(2)

Here I_{0A^+} is the measured intensity of A⁺ when no B is added, Z is the distance of reaction (this is the measured distance between the RGI and the sampling orifice with adjustments for the end correction²²), V_P is the flow velocity of the reactant ion and can be measured directly by creating a pulsed disturbance in the ion intensity, [B] is the concentration of the neutral reactant gas, and C_2 is the correction factor which considers the flow dynamics of the SIFT.²⁸

Therefore, a plot of $\ln I_{A^+}$ vs. [B] yields a slope of $-C_2k_1Z/Vp$, when I_{0A^+} is constant. C_2 , Z, and Vp are known, thereby enabling a direct determination of k_f . Three parameters can be varied to obtain a rate coefficient in a SIFT experiment: the concentration of the neutral reactant gas [B], the velocity of the reactant ion Vp, or the length of the reaction zone Z.

The rate coefficients for the thermal energy charge-transfer reactions in this study are obtained by monitoring the intensity of the primary ion of interest as a function of the concentration of the neutral reactant gas [B]. Figure 2 shows an example of typical plots used to obtain the rate coefficients. The concentration is monitored on a precalibrated MKS 254A mass flow controller with a MKS 1258 mass flow meter. [The calibration was confirmed in our laboratory.²⁶] Most of the rate coefficients are so fast that the neutral reactant gas has to be diluted with the inert carrier gas before being added to the flow tube.

Rate coefficients determined for a number of thermal energy charge-transfer reactions involving Ar^+ and Ar_2^+ are listed in Table I. Among these, new rate coefficients are reported for Ar^+ with H₂S, NO₂, and CS₂, and Ar₂⁺ with SF₆, NH₃, H₂O, H₂S, CS₂, CH₄, and NO₂. Repeated measurements on a few systems established the reproducibility of the apparatus and the technique to be within ±5%.

Where data from prior studies are available in the literature^{29,30} these are compared with the present results. Most of the rate coefficients compare within the accepted experimental system-to-system variation of $\pm 30\%$. The rate coefficients reported here

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TABLE	I
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	reactants → products	$k,^b \text{ cm}^3/\text{s}$	technique ^a	ref
1.	$Ar^+ + H_2S \rightarrow H_2S^+ + Ar$	1.3 × 10 ⁻⁹	SIFT	this work
2.	$Ar_2^+ + H_2^- S \rightarrow H_2^- S^+ + 2Ar$	1.2×10^{-9}	SIFT	this work
3.	$Ar^{+} + CS_{2} \rightarrow S^{+} (88 \pm 4\%), CS_{2}^{+} (12 \pm 4\%)$	2.6×10^{-10}	SIFT	this work
4.	$Ar_2^+ + CS_2^- \rightarrow CS_2^+ + 2Ar$	8.8×10^{-10}	SIFT	this work
5.	$Ar^{+} + NO_{2}^{-} \rightarrow NO^{+} (94 \pm 2\%), NO_{2}^{+} (6 \pm 2\%)$	4.6×10^{-10}	SIFT	this work
6.	$Ar_2^+ + NO_2^- \rightarrow NO^+ (85 \pm 2\%), NO_2^+ (15 \pm 2\%)$	9.2×10^{-10}	SIFT	this work
7.	$Ar^+ + SF_6 \rightarrow SF_5^+ + F + Ar$	9.3×10^{-10}	SIFT	this work
	\rightarrow SF ₅ ⁺ + F + Ar	1.2×10^{-9}	FA	31
8.	$Ar_2^+ + SF_6 \rightarrow SF_5^+ + F + 2Ar$	4.2×10^{-10}	SIFT	this work
9.	$Ar^+ + NH_3 \rightarrow NH_3^+ + Ar$	1.7×10^{-9}	SIFT	this work
	$\rightarrow \mathrm{NH_{3}^{+}} + \mathrm{Ar}$	1.3×10^{-9}	FA	32
10.	$Ar_2^{+} + NH_3 \rightarrow NH_3^{+} + 2Ar$	5.5×10^{-10}	SIFT	this work
11.	$Ar^{+} + CH_4 \rightarrow CH_2^{+} (11 \pm 2\%), CH_3^{+} (79 \pm 4\%), CH_4^{+} (10 \pm 2\%)$	8.2×10^{-10}	SIFT	this work
	$\rightarrow CH_2^+, CH_3^+, CH_4^+$	9.0×10^{-10}	FA	32
10	\rightarrow CH ₂ ' (17.3%), CH ₃ ' (82.5%)	1.10×10^{-10}		33
12.	$Ar_{2}^{\prime} + CH_{4} \rightarrow CH_{4}^{\prime} + 2Ar$	9.3 × 10 ¹	SIFI	this work
13.	Ar $+ H_2 \cup + H_2 \cup (00 \pm 5\%)$, ArH $(32 \pm 5\%)$	1.0×10^{-9}	SIFI	this work
	\rightarrow H ₂ O (79%), ATH (21%) \rightarrow H O A-U ⁺	2.1×10^{-9}		34
	\rightarrow H ₂ O, All \rightarrow H ₂ O ⁺ (100%)	1.43×10^{-9}		35
	\rightarrow products	1.61×10^{-9}	FA	37
14	$Ar_{2}^{+} + H_{2}O \rightarrow H_{2}O^{+} + 2Ar$	1.6×10^{-9}	SIFT	this work
15.	$Ar^+ + SO_2 \rightarrow SO_2^+ + Ar$	5.4×10^{-10}	SIFT	this work
	\rightarrow SO ₂ ⁺ + Ar	4.8×10^{-10}	FDT	38
16.	$Ar_2^+ + SO_2 \rightarrow SO_2^+ + 2Ar$	1.4×10^{-9}	SIFT	this work
	\rightarrow SO ₂ ⁺ + 2Ar	1.8×10^{-9}	SIDC	39
17.	$Ar^+ + N_2O \rightarrow N_2O^+ + Ar$	3.3×10^{-10}	SIFT	this work
	$\rightarrow N_2 O^+ + Ar$	2.2×10^{-10}	SIDC	39
	$\rightarrow N_2O^+ + Ar$	$2.4 \times 10^{-10} (^{2}P_{3/2})$	DT	40
	$\rightarrow N_2O^+ + Ar$	$6.5 \times 10^{-11} ({}^{2}P_{1/2})$	DT	40
18.	$Ar_2^+ + N_2O \rightarrow N_2O^+ + 2Ar$	8.2×10^{-10}	SIFT	this work
	$\rightarrow N_2O^+ + 2Ar$	7.0×10^{-10}	SIDC	39
	\rightarrow products	5.9×10^{-10}	PR	41
19.	$Ar^+ + CO \rightarrow CO^+ + Ar$	4.0×10^{-11}	SIFT	this work
	$\rightarrow CO^{+} + Ar$	9×10^{-11}	FA	42
	$\rightarrow CO^{+} + Ar$	$3.3 \times 10^{-11} (^{2}P_{3/2})$	DT	40
20	$\rightarrow CO^{+} + Ar$	$3.0 \times 10^{10} (^{2}P_{1/2})$		40
20.	$AI_2 + CO \rightarrow CO + 2AI$ $\rightarrow CO^{\dagger} + 2Ar$	0.1×10^{-10}	SIFI	this work
	$\rightarrow CO^+ + 2Ar$	4.8×10^{-10}	SIDC	43
	-> products	4.8×10^{-10}	PR	41
21	$Ar^+ + NO \rightarrow NO^+ + Ar$	2.7×10^{-10}	SIFT	this work
21.	$\rightarrow NO^+ + Ar$	$3.4 \times 10^{-11} (^{2}P_{1/2})$	DT	40
	$\rightarrow NO^+ + Ar$	$6.3 \times 10^{-11} (^{2}P_{1/2})$	DT	40
22.	$Ar_2^+ + NO \rightarrow NO^+ + 2Ar$	4.4×10^{-11}	SIFT	this work
	$\rightarrow NO^+ + 2Ar$	2.4×10^{-12}	FA	43
	\rightarrow products	$< 6.0 \times 10^{-10}$	PR	41
23.	$Ar^+ + CO_2 \rightarrow CO_2^+ + Ar$	4.4×10^{-10}	SIFT	this work
	$\rightarrow CO_2^+ + Ar$	7.6×10^{-10}	FA	42
	$\rightarrow CO_2^+ + Ar$	$5.5 \times 10^{-10} ({}^{2}P_{3/2})$	DT	40
• •	$\rightarrow CO_2^+ + Ar$	$7.5 \times 10^{-11} ({}^{2}P_{1/2})$	DT	40
24.	$\operatorname{Ar}_2^+ + \operatorname{CO}_2 \rightarrow \operatorname{CO}_2^+ + 2\operatorname{Ar}$	7.7×10^{-10}	SIFT	this work
	$\rightarrow CO_2' + 2Ar$	1.1×10^{-9}	FA	43
25	$- CO_2^{+} + 2Ar$	4.8 × 10 ⁻¹⁰	SIDC	39 Abia ana 1
25.	$A_1 + O_2 \rightarrow O_2 + A_1$	5.9×10^{-11}	SIFT	inis work
	$\rightarrow 0^+ + \Delta r$	3.2×10^{-11}	5161	20
	$\rightarrow 0_2^+ + Ar$	4.0×10^{-11}	SIFT	45
	$\rightarrow O_2^+ + Ar$	5.0×10^{-11}	SA	46
	$\rightarrow O_2^+ + Ar$	5.7×10^{-11}	ICR	13
	$\rightarrow 0_2^+ + Ar$	7×10^{-11}	ICR	47
	$\rightarrow O_2^+ + Ar$	$4.3 \times 10^{-11} ({}^{2}P_{1/2})$	DT	40
	$\rightarrow O_2^+ + Ar$	$2.9 \times 10^{-11} ({}^{2}P_{1/2})$	DT	40
26.	$Ar_2^+ + O_2 \rightarrow O_2^{\tilde{+}} + 2Ar$	7.4×10^{-11}	SIFT	this work
	$\rightarrow O_2^+ + 2Ar$	1.2×10^{-11}	FA	43
	$\rightarrow O_2^+ + 2Ar$	1.0×10^{-11}	SIDC	39
	\rightarrow products	1.2×10^{-11}	PR	41

^aSIFT, selected ion flow tube; FA, flowing afterglow, TI, ion trapping technique; ICR, ion cyclotron resonance; FDT, flow drift tube; SIDC, selected ion drift chamber; DT, drift tube. ${}^{b2}P_{3/2}$ or ${}^{2}P_{1/2}$ following a rate constant indicates that the two spin states of Ar⁺ are present and separable.

take into account recent findings in a diagnostic study of the flow dynamic effects associated with a SIFT.²⁶ Optimization of reactant gas injection and operating conditions have been made on this apparatus based on extensive studies of the flow dynamical effects and reactant gas inlet^{26,27} allowing an improved confidence limit for the quoted rate coefficients.

of the measured rate constant. In an attempt to determine any

The reactions given in Table II are listed in decreasing order

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TABLE II

	charge-transfer reactions	$k_{\rm obsd}, {\rm cm}^3/{\rm s}$	$k_{\rm calcd}, {\rm cm}^3/{\rm s}$	ΔE , eV	dipole moment, D	$\bar{\alpha}\gamma$, Å ³
1.	$Ar^+ + NH_3 \rightarrow NH_3^+ + Ar$	1.7×10^{-9}	1.9×10^{-9}	-5.5	1.47	2.20
2.	$Ar_2^+ + H_2O \rightarrow H_2O^+ + 2Ar$	1.6×10^{-9}	1.8×10^{-9}	-1.8	1.85	1.44
3.	$Ar_2^{+} + SO_2 \rightarrow SO_2^{+} + 2Ar$	1.4 × 10 ⁻⁹	1.3×10^{-9}	-2.1	1.63	3.70
4.	$Ar^{+} + H_2S^{-} \rightarrow H_2S^{+} + Ar$	1.3×10^{-9}	1.4×10^{-9}	-5.2	0.97	3.83
5.	$Ar_2^+ + H_2S \rightarrow H_2S^+ + 2Ar$	1.2×10^{-9}	1.2×10^{-9}	-3.9	0.97	3.83
6.	$Ar^{+} + H_2 O \rightarrow products$	1.0×10^{-9}	2.0×10^{-9}	-3.1	1.85	1.44
7.	$Ar_2^+ + CH_4 \rightarrow CH_4^+ + 2Ar$	9.3×10^{-10}	1.0×10^{-9}	-1.8	0.00	2.56
8.	$Ar^{+} + SF_6 \rightarrow SF_5^{+} + F + Ar$	9.3×10^{-10}	1.1 × 10 ⁻⁹	-1.1	0.00	6.54
9.	$Ar_{2}^{+} + NO_{2} \rightarrow products$	9.2×10^{-10}	7.6×10^{-10}	-4.6	0.316	3.02
10.	$Ar_2^+ + CS_2 \rightarrow CS_2^+ + 2Ar$	8.8×10^{-10}	1.1×10^{-9}	-4.3	0.00	8.73
11.	$Ar^{+} + CH_{4} \rightarrow products$	8.2×10^{-10}	1.1×10^{-9}	-3.1	0.00	2.56
12.	$Ar_2^+ + N_2O \rightarrow N_2O^+ + 2Ar$	8.2×10^{-10}	7.6×10^{-10}	-1.5	0.167	2.92
13.	$Ar_{2}^{+} + CO_{2} \rightarrow CO_{2}^{+} + 2Ar$	7.7×10^{-10}	7.2×10^{-10}	-0.7	0.00	2.65
14.	$Ar_2^+ + CO \rightarrow CO^+ + 2Ar$	6.1×10^{-10}	7.2×10^{-10}	-3.0	0.112	1.95
15.	$Ar_{2}^{+} + NH_{3} \rightarrow NH_{3}^{+} + 2Ar$	5.5×10^{-10}	1.7×10^{-9}	-4.2	1.47	2.20
16.	$Ar^{+} + SO_{2} \rightarrow SO_{2}^{+} + Ar$	5.4×10^{-10}	1.5×10^{-9}	-3.4	1.63	3.70
17.	$Ar^+ + NO_2 \rightarrow products$	4.6×10^{-10}	8.9×10^{-10}	-5.9	0.316	3.02
18.	$Ar^+ + CO_2^- \rightarrow CO_2^+ + Ar$	4.4×10^{-10}	8.3×10^{-10}	-2.0	0.00	2.65
19.	$Ar_{2}^{+} + SF_{6} \rightarrow SF_{5}^{+} + F + 2Ar$	4.2×10^{-10}	8.3×10^{-10}	~ 0	0.00	6.54
20.	$Ar^{+} + N_2O \rightarrow N_2O^{+} + Ar$	3.3×10^{-10}	8.8×10^{-10}	-2.8	0.167	2.92
21.	$Ar^+ + NO \rightarrow NO^+ + Ar$	2.7×10^{-10}	7.4×10^{-10}	-6.4	0.153	1.70
22.	$Ar^+ + CS_2 \rightarrow products$	2.6×10^{-10}	1.4×10^{-9}	-5.6	0.00	8.73
23.	$Ar_2^+ + O_2 \rightarrow O_2^+ + 2Ar$	7.4×10^{-11}	6.2×10^{-10}	-2.3	0.00	1.59
24.	$Ar_2^+ + NO \rightarrow NO^+ + 2Ar$	4.4×10^{-11}	6.6×10^{-10}	-5.1	0.153	1.70
25.	$Ar^{+} + CO \rightarrow CO^{+} + Ar$	4.0×10^{-11}	8.1×10^{-10}	-4.3	0.112	1.95
26.	$Ar^+ + O_2 \rightarrow O_2^+ + Ar$	3.9×10^{-11}	7.0×10^{-10}	-3.6	0.00	1.59

factors which may account for apparent trends, the observed rate coefficient k_{obsd} , the calculated collision rate coefficient k_{calcd} (Langevin or ADO), the energy difference (ΔE) between the recombination energy of the reactant ion and the adiabatic ionization potential of the neutral reactant, and the dipole moment and polarizability for each neutral reactant are tabulated. Consideration of these parameters does not indicate any trends in the observed rate coefficients.

A major objective of the present study is to compare rate coefficients for the atomic Ar⁺ reactions to those of the diatomic Ar_2^+ reactions. The results can be divided into three categories based on the ratio of the rate constant of the monomer over that of the dimer ion: (1) the dimer ion reaction is faster than that of the monomer for H_2O , SO_2 , CO_2 , O_2 , N_2O , CO, NO_2 , and CS_2 , (2) the monomer is faster than the dimer for SF_6 , NO, and NH_3 , and (3) the rate of the monomer is similar to that of the dimer for H_2S and CH_4 . The trends in the rate constants involving the atomic and dimer ion show that although dissociative channels are readily available in the dimer ion reaction (the dissociation energy of Ar_2 is only 0.01 eV⁴⁸), its reactions are not always faster in the charge-transfer process.

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TABLE III: Reactions in Which Franck-Condon Factors Are Favorable (Large in Magnitude) and Poor for the Reactant Neutral at the Recombination Energy of the Reactant Ion^a

	$k_{\rm obsd}/k_{\rm calcd}$			
Eavorable Reactions				
$Ar^+ + H_s S \rightarrow H_s S^+ + Ar$	0.93			
$Ar^+ + NH_2 \rightarrow NH_2^+ + Ar$	0.89			
$Ar_{2}^{+} + H_{2}O \rightarrow H_{2}O^{+} + 2Ar$	0.89			
$Ar_2^+ + CH_4 \rightarrow CH_4^+ + 2Ar$	0.93			
Poor Reactions				
$Ar^+ + CO_2 \rightarrow CO_2^+ + Ar$	0.53			
$Ar_2^+ + CO_2 \rightarrow CO_2^+ + 2Ar$	1.1			
$Ar^{+} + SO_{2} \rightarrow SO_{2}^{+} + Ar$	0.36			
$Ar_2^+ + SO_2 \rightarrow SO_2^+ + 2Ar$	1.1			
$Ar_{2}^{+} + H_{2}S \rightarrow H_{2}S^{+} + 2Ar$	1.0			
$Ar_{2}^{+} + NH_{3} \rightarrow NH_{3}^{+} + 2Ar$	0.32			
$Ar^{+} + O_2 \rightarrow O_2^{+} + Ar$	0.056			
$Ar_2^+ + \tilde{O_2} \rightarrow \tilde{O_2}^+ + 2Ar$	0.12			
$Ar_2^{+} + CS_2 \rightarrow CS_2^{+} + 2Ar$	0.80			
$Ar^{+} + NO^{-} \rightarrow NO^{+} + Ar$	0.36			
$Ar_2^+ + NO \rightarrow NO^+ + 2Ar$	0.066			
$Ar^{+} + N_2O \rightarrow N_2O^{+} + Ar$	0.38			
$Ar_2^+ + N_2O \rightarrow N_2O^+ + 2Ar$	1.1			
$Ar^{+} + CO^{-} \rightarrow CO^{+} + Ar$	0.049			
$Ar_2^+ + CO \rightarrow CO^+ + 2Ar$	0.85			

^a Interpreted at the recombination energies of the reactant ions $(Ar^+ = 15.7 \text{ eV and } Ar_2^+ = 14.4 \text{ eV}).$

All of the reactions studied excluding Ar⁺ with O₂ and CO and Ar_2^+ with NO are fast $(k_{obsd} \ge 0.10k_{calcd})$. Laudenslager et al.¹³ report that favorable Franck-Condon factors are necessary for a fast thermal energy charge-transfer reaction. The reported photoelectron spectra (PES)⁴⁹ for each neutral molecule has therefore been compared to the recombination energy of the reactant ion to determine relative magnitudes of the Franck-Condon factors for the ionization of the neutrals.

The reactions studied are categorized in Table III according to the magnitude of the Franck-Condon factors. The Franck-Condon factors for reactions which involve dissociation of the neutral reactant; Ar^+ with H_2O , SF_6 , CH_4 , NO_2 , and CS_2 , and Ar_2^+ with SF₆, and NO₂, are not evaluated from the PES of the

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Sulphur dioxide (full spectrum)

Figure 3. Photoelectron spectra of SO2. The arrows indicate the recombination energy of Ar⁺ (15.7 eV) and Ar₂⁺ (14.4 eV). Adapted from D. W. Turner (ref 49).

neutral reactant and therefore have not been included in this table. In agreement with the conclusion of Laudenslager et al.,¹³ four of the reactions, Ar⁺ with H₂S and NH₃, and Ar₂⁺ with H₂O and CH4, have Franck-Condon factors which are large and rates which are fast. However, poor Franck-Condon factors exist in the other cases and, accordingly, the rate coefficient should be considerably less than the calculated collision rate. Only three reactions, Ar⁺ with O_2 and CO and Ar_2^+ with NO, show such behavior. It is also interesting to note that the rate coefficients for the reactions of Ar_2^+ with CO₂, N₂O, and SO₂ are greater than the calculated collision rate. This observation has been previously interpreted as evidence for a nonorbiting collision which would therefore imply a long-range electron jump mechanism; however, this interpretation has been disputed in the literature.¹⁶ The remaining reactions all have $k_{obsd} > 0.1k_{calcd}$ even though Franck-Condon factors are poor. The relative rates of these reactions may be accounted for by either the possibility of vibrational distortion9,10 or by populating vibrational states which do have poor Franck-Condon overlap. From these results we conclude that the existence of favorable Franck-Condon factors is not the appropriate criterion for assessing the magnitudes of the charge-transfer reactions.

The relative proximity of the Ar⁺ and Ar₂⁺ recombination energies to the bands of the PES does seem to explain the relative rate coefficients of the monomer and dimer reactions with a specific neutral. We observe that the recombination energy of the ionic species which lies closer to the most probable vibrational state of the nearest energetically accessible electronic well indicated by the PES has the greater rate coefficient. Thus we can use the Franck-Condon factors to determine relative rate coefficients for specific ion-neutral interactions but not to evaluate the magnitudes of the rate coefficients. The recombination energies for Ar^+ (15.7) eV) and Ar_2^+ (14.4 eV) are shown relative to the PES of SO₂ in Figure 3. Due to the repulsive wall of the ground state of the neutral dimer and the ground vibrational state of the dimer ion, the recombination energy of Ar_2^+ may extend to lower energies over a range of approximately 1 eV.^{6,50,51} The recombination energy of Ar_2^+ within the broadening lies much closer to a probable vibrational state of the accessible electronic well of the SO₂⁺ product ion relative to Ar⁺ and we observe that the reaction of Ar_2^+ with SO₂ is approximately 2.5 times faster than the monomer rate. As another example, the reaction of Ar⁺ with NH₃ is significantly faster than the Ar2⁺ reaction. The recombination energy of Ar^+ is seen to lie within an electronic well of NH_3^+ , whereas the upper limit of recombination energy of Ar_2^+ is above the nearest accessible band by approximately 3 eV which is considerably more than the expected broadening (see Figure 4). The recombination energies of Ar^+ and Ar_2^+ (including the 1-eV broadening of Ar_2^+) fall between two bands for the ionization of The Journal of Physical Chemistry, Vol. 91, No. 10, 1987 2561



Figure 4. Photoelectron spectra of NH₃. The arrows indicate the recombination energy of Ar^+ (15.7 eV) and Ar_2^+ (14.4 eV). Adapted from D. W. Turner (ref 49).

 O_2 as indicated by the PES. The recombination energy for Ar_2^+ lies closer to an energetically accessible band and has a faster rate. For the reactions of NO, the recombination energy of Ar⁺ lies to the high-energy side of a PES which is energetically inaccessible to Ar_2^+ . The observed rate coefficient for the reaction of Ar^+ with NO is larger than the Ar_2^+ reaction and indicates that greater phase space does not necessarily account for faster reaction rates.

The product ion SF5⁺ has been identified from the reaction of Ar_2^+ with SF₆. In order for this reaction to be thermoneutral or slightly excergic this implies that the appearance potential of SF_5^+ from SF_6 is equal to or less than 14.4 eV. The recombination energy of Ar_2^+ (14.4 eV) was calculated from the literature values for the ionization potential of Ar⁵² and the bond energy of Ar₂^{+,53} This limit on the appearance potential of SF5⁺ agrees fairly well with the value of 14.6 eV determined in a recent study by Babcock and Streit.⁵⁴ These values are significantly lower than 15.3 eV obtained in earlier experiments.5

The reactions involving Ar^+ and Ar_2^+ with CS_2 show very different reaction paths. In agreement with the findings of Bowers,⁵⁶ the dominant primary product observed in the reaction of Ar^+ with CS_2 is S^+ at low concentrations of CS_2 . The branching ratio for the S^+ product is $88 \pm 4\%$ and $12 \pm 4\%$ for the charge transfer. The S^+ product undergoes a fast secondary reaction with CS_2 to form CS_2^+ . Only the charge-transfer product CS_2^+ is observed in the case of the dimer ion. This difference arises since the appearance potential of S^+ from CS₂ is 14.80 eV⁵² and the recombination energy of Ar^+ is 15.7 eV but only 14.4 eV for Ar_2^+ .

Addition of H₂O to Ar⁺ yields two ionic products (ArH⁺ and H_2O^+). The overall rate coefficient is $1.0 \times 10^{-9} \text{ cm}^3/\text{s}$ with approximately 35% ArH⁺ and 65% H_2O^+ . Both species undergo a rapid secondary reaction with H₂O to produce H₃O⁺ ($k = 2.0 \times 10^{-9} \text{ cm}^3/\text{s}^{57}$ and $1.8 \times 10^{-9} \text{ cm}^3/\text{s}^{58}$ for ArH⁺ and H₂O⁺, respectively). The reaction of Ar_2^+ with H_2O produces only H_2O^+ which once again rapidly forms H_3O^+ with H_2O . The formation of ArH⁺ as a product in this reaction is approximately 10.8 kcal/mol endothermic and therefore would not be expected.

Conclusions

To the authors' knowledge the rate coefficients for the thermal energy reactions of Ar^+ with H_2S , NO_2 , and CS_2 and Ar_2^+ with SF₆, NH₃, H₂O, H₂S, CS₂, CH₄, and NO₂ have not been pre-

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viously reported. An upper limit for the appearance potential of SF_5^+ from SF_6 of 14.4 eV is inferred from the reaction of Ar_2^+ with SF_6 . Rate coefficients are observed for which (1) the dimer reacts considerably faster than the monomer with H_2O , SO_2 , CO_2 , O_2 , N_2O , CO, NO_2 , and CS_2 , (2) the monomer reacts faster than the dimer with SF_6 , NO, and NH_3 , and (3) the monomer and dimer react at similar rates with H_2S and CH_4 . Thus the rate coefficient for the dimer reaction is not always greater than that of the monomer with a given neutral, although the dimer reaction has greater phase space due to the dissociative channel of the dimer neutral which leads to a three-body final state.

Most of the reactions in this study are classified as fast thermal energy charge-transfer reactions. The observation that many of these fast reactions involve unfavorable Franck-Condon factors suggests that the Franck-Condon factors are not a sufficient criterion to assess the magnitude of the rate coefficients. However, these factors can be used to obtain a qualitative evaluation of the relative rates between Ar^+ and Ar_2^+ if the relative proximity of the Ar^+ and Ar_2^+ recombination energies are compared to bands in the photoelectron spectra of a specific neutral. The larger rate coefficient is associated with the ionic species whose recombination energy is closer to the maximum of the nearest accessible band.

Although a number of observed rate coefficients are greater than the calculated collision rate, the relative magnitudes do not warrant conclusions for the electron jump mechanism. It is difficult to make detailed conclusions about the exact mechanism of the reactions in this study. The observation of a number of fast rate coefficients which involve unfavorable Franck-Condon factors leads one to speculate that such reactions may occur with mechanisms such as those suggested by Lin and co-workers,¹⁷ as opposed to a long-range electron jump. Kinetic data can provide information for the determination of charge-transfer reaction mechanisms; however, more efficient and detailed techniques¹⁷ are available and necessary to determine accurately these mechanisms. More extensive experimental or theoretical work is required to understand further the monomer/dimer behavior.

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Registry No. CS₂, 75-15-0; CO₂, 124-38-9; SO₂, 7446-09-5; H₂O, 7732-18-5; H₂S, 7783-06-4; NH₃, 7664-41-7; NO, 10102-43-9; SF₆, 2551-62-4; CH₄, 74-82-8; N₂O, 10024-97-2; NO₂, 10102-44-0; CO, 630-08-0; Ar₂⁺, 17596-58-6; O₂, 7782-44-7; Ar⁺, 14791-69-6.

Ion-Molecule Reactions within Methane Clusters Initiated by Photoionization

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Photoionization experiments using light from the Berlin synchrotron facility BESSY were performed with methane clusters. A number of ionic reaction products with masses m = k + 16n (k = 16, 17, 28, 29, 31, 40, and 57 and $n \ge 0$) were determined. These are interpreted as series of cluster ions of the form $[X \cdot (CH_4)_n]^+$ with $X = CH_4$, CH_5 , C_2H_4 , C_2H_5 , C_2H_7 , Ar, and Ar·CH₅. For all series except two (X = C_2H_4 , C_2H_7) analogue ion-molecule reactions in the gas phase were observed. The occurrence of these two exceptions is believed to be caused by the cluster environment which contains the reagents for a much longer time than that observed in gas-phase reactions. Some of the reactions ($X = CH_5$, C_2H_5 , Ar, Ar-CH₅) exhibit Ar interband transitions, which are believed to originate from neutral precursor clusters with an abundance of Ar atoms. Possible reaction schemes are discussed and compared with the analogue ion-molecule reactions in the gas phase.

Introduction

Cluster research has undergone a revival in the past years. The first experiments with gas-phase clusters were a product of the development and application of molecular beam techniques in the late 1950s and early 1960s to chemistry and physics.¹ Although a great number of basic problems had been addressed-and some of them solved—the majority could not be treated due to the lack of specific experimental techniques. During the early years clusters were regarded as an unwanted factor which had to be avoided at all costs. The advance of new experimental techniques prompted new attempts to resolve these questions and incited scientists of different backgrounds to compete for solutions in this difficult field of research.²

As in many developments in science it needed outstanding personalities to provide enough thrust to this second attempt to convince the scientific community that it was worthwhile to follow up this line of research. It is one of the merits of the late Gilbert Stein to be accredited partially with the renaissance of the nearly forgotten field of cluster research, especially in the application of newly developed electron diffraction techniques³ and the theoretical treatment of cluster formation by classical gas dynamic theory.⁴ In the early stages he distinguished between the cluster

of the gas phase and the condensed matter which he called the fifth state of matter-a term often quoted by subsequent researchers.⁵ The present experimental situation in the field of neutral clusters is characterized by two major deficiencies, namely the lack of generation methods for single size cluster beams and secondly the absence of a size specific detection technique for neutral clusters. In spite of many attempts no workable method

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