Since each of the parallel curves plotted in Figure 2 of ref 13 constitutes a reaction series with HA varying and the hydroxide base remaining constant, it might be expected that α_1 contributes to the total Brønsted coefficient. It should be noted that if the weak acid were maintained constant and the base varied, eq 5 predicts that if $\Delta G^{\circ\prime} \ll 4\Lambda$, the limits on α are 0–0.5 for the reaction in one direction and 0.5–1 for the reaction in the opposite direction, since the sign of $\Delta G^{\circ\prime}$ determines whether the term in parentheses is greater or less than unity. It is only when $\Delta G^{\circ\prime} \sim 4\Lambda$ that α can approach the limits of 0 or 1 in the case of constant Λ.

Marcus' theory has, to date, been shown to be consistent with a large number of experimental results for both normal and carbon acids, both when the base is varied and when the acid is varied. This does not, however, constitute a critical test of the theory, since the parameters involved (Λ, ΔG^*, $d\Lambda/d\Delta G^{\circ\prime}$) are themselves calculated from the experimental data. It would be particularly desirable to be able to calculate Λ from other data. Since Λ in eq 3 is assumed to be the arithmetic mean of the intrinsic barriers for the two exchange reactions[10]

$$\mathrm{RAH} + \mathrm{RA}^- \rightleftharpoons \mathrm{RA}^- + \mathrm{RAH} \qquad \text{(b)}$$

$$\mathrm{BH} + \mathrm{B}^- \rightleftharpoons \mathrm{B}^- + \mathrm{BH} \qquad \text{(c)}$$

determination of the exchange rates *via* nmr would allow Λ to be calculated for reaction a. Λ is also the sum of the reorganizational energies for the outer (Λ_o) and inner (Λ_i) coordination spheres. The Λ_o and Λ_i values for the exchange reaction (a) are assumed also to be the arithmetic mean of the cross-reaction terms.[20] Since Marcus has derived equations for these terms, Λ_o and Λ_i could conceivably be calculated for each exchange reaction, if the equilibrium values of the bond coordinates and reduced force constants were known. Unfortunately, such calculations apparently cannot be readily performed at the present time.

Acknowledgment. This investigation was supported by the Division of General Medical Sciences, Public Health Services, in the form of Research Grant No. GM 13116.

Photodissociation of the CH_3Cl^+ and N_2O^+ Cations

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Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received October 2, 1970*

Abstract: The ion cyclotron resonance technique was used to observe the photodissociation of the cations CH_3Cl^+ and N_2O^+ in the gas phase. Ions were trapped in the icr cell for periods of the order of seconds, which permitted the photodissociation process to be observed with wavelength-selected light. A cyclotron resonance ejection technique was employed to show that CH_3Cl^+ ions were being dissociated rather than the CH_3ClH^+ ions which were also present. The photodissociation cross section for N_2O^+ was found to be roughly 0.25×10^{-18} cm^2 without strong wavelength dependence between 4000 and 6500 Å. The cross section for CH_3Cl^+ showed a large peak at 3150 Å, having a value at that wavelength of 7.8×10^{-18} cm^2. Possible assignments of this peak are considered, and it is suggested that photodissociation occurs through an ion excitation involving a change in occupation of the bonding or antibonding orbitals of the C–Cl bond.

The dissociation of positive ions by photon impact, apart from its intrinsic interest as a basic photochemical process, has potential importance to several areas of interest. (1) Approximate theoretical calculations can be made of photodissociation cross sections in simple systems, and such studies would benefit from having experimental data for comparison. (2) In the event that a well-defined threshold were observed, the energy of the photodissociation threshold would provide bond dissociation energies of a precision far greater than is presently available for most ions. (3) The possibility of depositing a precisely known quantum of energy in an ion and observing the subsequent competitive unimolecular dissociation processes offers a stringent test of unimolecular dissociation theories. (4) If the photodissociation process could be observed at sufficiently high resolution, the assignment of vibrational structure could provide new information on the symmetries and bonds of simple ions. (5) As the results of the present study suggest, the determination even of the broad features of the wavelength dependence of the dissociation process can give interesting information about the upper electronic levels of ionic species.

In view of the potential interest which such processes have in terms of characterizing ions, the almost total absence of experimental data must be attributed to the lack of a sensitive and convenient means of observing them. The present study is intended to show that ion cyclotron resonance spectroscopy (icr) may provide such a technique, and also that the photodissociation cross sections of some simple cations are sufficiently large to make such investigations quite feasible.

Several other experimental techniques provide information about cation dissociation, of which the most important are uv optical spectroscopy, electron impact mass spectroscopy, and photoionization mass spectroscopy.[1] All of these methods examine processes in

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(1) See, for example, V. H. Dibeler, J. A. Walker, and K. E. McCulloh, *J. Chem. Phys.*, 51, 4230 (1969); T. A. Walter, C. Lifshitz, W. A. Chupka, and J. Berkowitz, *ibid.*, 51, 3531 (1969).

which dissociation immediately follows ionization of a neutral molecule, and thus differ from photodissociation in which the ion dissociation process is observed directly.

Several calculations and measurements have been made of the cross section and wavelength dependence of the H_2^+ photodissociation,[2,3] and this process has a cross section in the neighborhood of 10^{-18} cm^2 with well-resolved vibrational structure. Dunn[3] has also observed the photodissociation of N_2^+ near the limits of sensitivity of his instrument, and found a value of about 1.7×10^{-20} cm^2. He also obtained an upper limit of 10^{-20} cm^2 for the dissociation cross section of H_3^+.

No other cation photodissociation processes appear to have been investigated in the gas phase. It seemed of interest to examine larger ions of lower symmetry in the hope that their cross sections would be larger, and several such dissociations have been observed using the icr technique.

Use of the Icr Spectrometer in Photodissociation Measurements

The ion cyclotron resonance spectrometer has been described previously,[4] and Brauman and Smyth have applied the spectrometer to photodetachment measurements.[5] In observing a photodissociation process, the primary ions are generated by electron bombardment and trapped in the icr cell by the applied magnetic and electric fields. Monochromatic light from filters or a monochromator is passed down the length of the icr cell, dissociating a small fraction of the trapped primary ions. The secondary ions produced by the photodissociation process are observed by the marginal oscillator detector as a function of incident light wavelength. Figure 1 shows a spectrum obtained for the wavelength dependence of the process

$$CH_3Cl^+ \xrightarrow{h\nu} CH_3^+ + Cl \qquad (1)$$

The analysis of data such as that shown in the figure to obtain a cross section for the dissociation process involves a detailed analysis of the processes occurring in the icr cell, as outlined below.

The icr cell may be visualized as an ion trap containing both primary ions (CH_3Cl^+) and secondary ions (CH_3^+). Both primary and secondary ions are being fed into the trap from the source region of the cell following their production by electron bombardment of neutral molecules (the CH_3^+ ions produced by the electron beam are not distinguished from those produced by photodissociation, and all are referred to as "secondary" ions here). Ions are removed from the trap by ion-loss mechanisms, and primary ions are converted to secondary ions by photon impact. To formalize these ideas, the following quantities may be defined: P and S are the concentrations of primary and secondary ions in the cell; $k_{\mathrm{loss}}(\mathrm{P})$ and $k_{\mathrm{loss}}(\mathrm{S})$ are the rate constants for loss of primary and secondary ions from the cell; $C(\mathrm{P})$ and $C(\mathrm{S})$ are the rates of formation of primary and secondary ions at the electron beam; and k_{phot} is the rate constant for photodissociation of primary ions into secondary ions.[6]

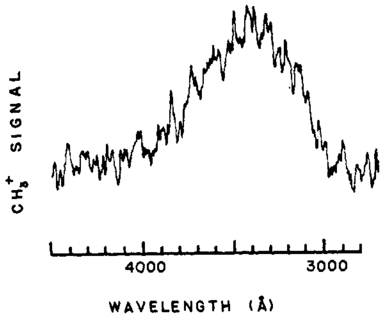

Figure 1. Production of CH_3^+ by photodissociation of CH_3Cl^+. The concentration of CH_3^+ in the icr cell is continuously monitored while the wavelength of the irradiating light from the monochromator is swept. The wavelength resolution (FWHM of the irradiating light) is 140 Å.

The kinetic equations governing the ion concentrations in the cell take the form

$$\begin{aligned} \mathrm{d}P/\mathrm{d}t &= (-k_{\mathrm{loss}}(\mathrm{P})P) - (k_{\mathrm{phot}}P) + C(\mathrm{P}) \\ \mathrm{d}S/\mathrm{d}t &= (-k_{\mathrm{loss}}(\mathrm{S})S) + (k_{\mathrm{phot}}P) + C(\mathrm{S}) \end{aligned} \qquad (2)$$

The steady-state solution of these equations gives the relation

$$(S - S_0)/P = k_{\mathrm{phot}}/k_{\mathrm{loss}}(\mathrm{S}) \qquad (3)$$

where S_0 is the concentration of secondary ions with the light source turned off. The photodissociation rate constant is related to the photon flux $\phi(\lambda)$ and the photodissociation cross section $\sigma(\lambda)$ by

$$k_{\mathrm{phot}} = \int_0^\infty f(\lambda')\phi(\lambda')\sigma(\lambda')\mathrm{d}\lambda' \qquad (4)$$

where $f(\lambda)$ is a normalized photon distribution function. For the purposes of this work, the form of (4) for monochromatic photons[7] is

$$k_{\mathrm{phot}} = \phi(\lambda)\sigma(\lambda) \text{ sec}^{-1} \qquad (5)$$

This gives the photodissociation cross section in terms of measurable quantities as

$$\sigma(\lambda) = k_{\mathrm{loss}}(\mathrm{S})(1/\phi)[(S - S_0)/P] \qquad (6)$$

Experimental Section

The photodissociation of methyl chloride ions was carried out at a gas pressure of about 2×10^{-8} with ion trapping times of approximately 1 sec. A standard icr cell having dimensions $2.54 \times 2.54 \times 13$ cm which has been previously described[4] was used in a Varian ICR-9 icr spectrometer. Ion trapping times of up to perhaps 15–30 sec have been observed with this cell, but for this experiment the trapping time was kept at around 1 sec to reduce ion–molecule reactions. The trapping voltage was 3.0 V; the (+) and (−) analyzer drift voltages were zero; the (+) source drift voltage was zero; and the (−) source drift voltage was 0.75 V. The magnetic field was always 7500 G, and the marginal oscillator frequency varied in the range 200–750 kHz depending on the ion observed. The radiofrequency field peak amplitude was about 25 mV. The ionizing beam voltage was 12.5 with a current of 5 μA. Comparable conditions were used for N_2O.

Since the experiments were performed at constant field, the results must be corrected for the variation of marginal oscillator

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(2) See, for instance, C. B. Richardson, K. B. Jefferts, and H. G. Dehmelt, *Phys. Rev.*, **165**, 80 (1968).

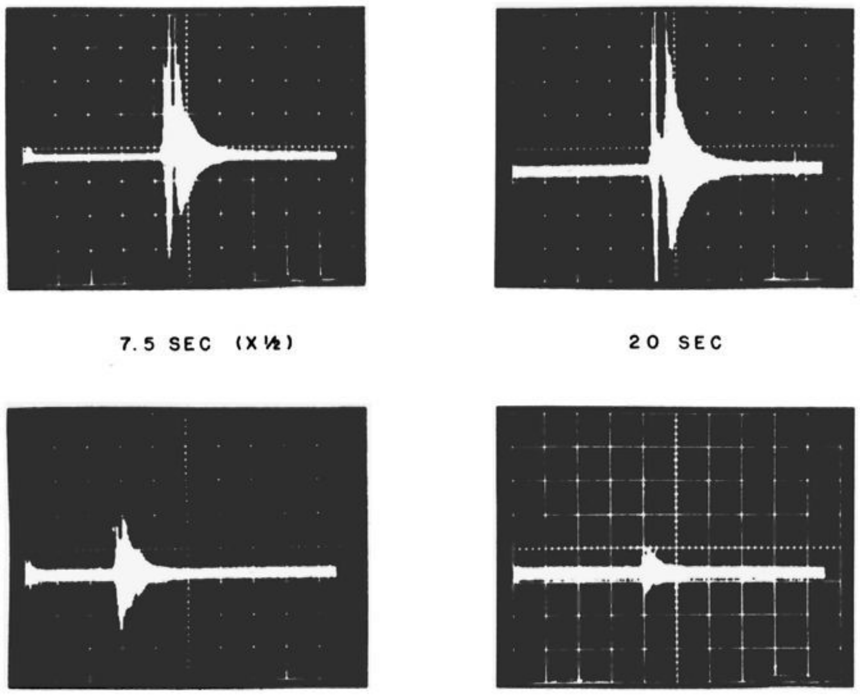
(3) G. H. Dunn in "Atomic Collision Processes," M. R. C. McDowell, Ed., North Holland Publishing Co., Amsterdam, 1964, p 997.

(4) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

(5) J. I. Brauman and K. C. Smyth, *J. Amer. Chem. Soc.*, **91**, 7778 (1969).

(6) k_{phot} is a first-order rate constant such that the number of particles per cubic centimeter dissociated in 1 sec is $k_{\mathrm{phot}}n$, where n is the number density of target particles. A similar definition applies to the pseudo-first-order $k_{\mathrm{loss}}(\mathrm{P})$ and $k_{\mathrm{loss}}(\mathrm{S})$.

(7) For monochromatic radiation, $f(\lambda') = \delta(\lambda - \lambda')$.



7.5 SEC (X½) 20 SEC

30 SEC 60 SEC

Figure 2. Ion trapping. The trapping of H_3O^+ ions under conditions of extremely long trapping is shown. The traces shown indicate a trapping time of about 30 sec for H_3O^+.

Figure 3. Resonance ejection results for methyl chloride. The height of each peak gives the extent of production of CH_3^+ ions when the light source is switched on. The first spectrum shows the CH_3^+ photoproduction without any ejection field and the second and third spectra show the effect on the process of ejecting from the cell the ions at mass 50 (CH_3Cl^+) and 51 (CH_3ClH^+), respectively.

sensitivity with frequency. This was done by taking a low-pressure spectrum of CH_3Cl at 50 eV, using normal icr potential settings (residence time of the ions is a few milliseconds), and comparing the spectrum with published (API Tables) mass spectrometer data for the ionization pattern of methyl chloride.

Ion Lifetimes. Methyl Chloride. The CH_3^+ signal was too weak for measurement of the lifetime of this ion, so the lifetime of CH_3Cl^+ was measured and corrected for reaction effects to obtain an estimate of the CH_3^+ lifetime. The procedure used for lifetime measurement involved detuning the marginal oscillator to minimize its effects on the ion lifetime, since the marginal oscillator field rapidly drives the ions from the cell. Each experiment was initiated by terminating the production of ions; after waiting for the appropriate time, the marginal oscillator was rapidly tuned into resonance, giving a signal whose height is proportional to the number of ions still remaining in the cell. In Figure 2 a series of oscilloscope traces is reproduced from H_3O^+ ion measurements which illustrate the method used and also show the extremely long trapping times which can be obtained with the standard icr cell. The decay curve for CH_3Cl^+ gave a satisfactory fit to an exponential decay function with a lifetime $\tau_{CH_3Cl^+} = 0.86$ sec.

It seems reasonable to assume that at constant field, the rate of loss of ions from the cell is approximately independent of ionic mass. However, to obtain the CH_3^+ lifetime from the CH_3Cl^+ lifetime, the effect of the two reactions

$$CH_3Cl^+ + CH_3Cl \xrightarrow{k_1} CH_3ClH^+ + CH_2Cl$$

and

$$CH_3^+ + CH_3Cl \xrightarrow{k_2} CH_4 + CH_2Cl^+$$

on the lifetimes of the reactant ions must be considered. A detailed kinetic analysis shows that only the ratio of the two reaction rates is necessary to make this correction, and gives for the CH_3^+ lifetime the expression

$$\tau_{CH_3^+} = \tau_{CH_3Cl^+}\frac{1 + [CH_3Cl^+]/[CH_3ClH^+]}{k_2/k_1 + [CH_3Cl^+]/[CH_3ClH^+]}$$

where the ratio of ion concentrations $[CH_3Cl^+]/[CH_3ClH^+]$ can be taken as equal to the ratio of the icr peak heights. Beauchamp, *et al.*,[8] have recently determined the ratio $k_2/k_1 = 0.67$, which gives a lifetime of 1.16 sec for the CH_3^+ ion.

Nitrous Oxide. The lifetime of N_2O^+ was measured by an approximate method using direct observation of the signal decay with the marginal oscillator after abrupt termination of ion production by turning off the electron beam. No reactive corrections are necessary in this case, and the NO^+ lifetime was taken to be about 200 msec.

Light Source. The light source was a Hanovia 1-kW xenon arc whose output was passed through a Schoeffel GM250 monochromator with a grating blazed at 3000 Å in first order. Matched 4.4-mm slits were used, giving a bandpass of 140 Å. The calculations were performed assuming that all the light traversed the cell and that the photon flux was constant over the volume of the cell.

The power output from the monochromator was measured with two instruments, an Optics Technology Model 615 power meter and a thermopile, and was corrected for the transmission function of the glass viewing port. At 3500 Å, the flux was 3.8×10^{15} photons/(cm² sec).

Because the photodissociation cross section in nitrous oxide is much lower than that for methyl chloride, the monochromator could not be used. Instead, the output from the arc was wavelength selected with a set of Optics Technology variable-bandpass interference filters, used in pairs to provide 500-Å pass bands between 4000 and 6500 Å. The power meter was used to calibrate the light intensity for the 6000–6500-Å wavelength band, yielding a value for the flux of 6.2×10^{17} photons/(cm sec).

Cyclotron Resonance Ejection. While it has been assumed above that the CH_3^+ ions result from photodissociation of CH_3Cl^+, it is possible that some of them come from CH_3ClH^+, which was present in the cell with about the same abundance as CH_3Cl^+. This possibility was tested with a cyclotron resonance ejection experiment which showed that CH_3Cl^+ accounts for most of the dissociation product.

In the cyclotron resonance ejection technique, the ions to be ejected from the cell are ejected with a radiofrequency field in the plane of their cyclotron motion. When the ejecting field is precisely at the cyclotron frequency of the ions, the ion cyclotron orbits increase in radius until the ions strike the drift plates and are removed from the cell. The amplitude of the ejecting field must be chosen large enough so that the ions are ejected soon after their arrival in the cell, but not so large that ions at nearby masses are also ejected. The cyclotron resonance ejection technique is similar to the continuous-wave mode of ion cyclotron double resonance; since the instrument used in these experiments was equipped with a double-resonance oscillator, the ejection experiment was performed without instrumental modification, the only variation from the usual double-resonance procedure being the higher rf field amplitude required for efficient ejection.

The requirements of efficient ion ejection and high mass resolution conflict, and the ejecting-field amplitude must be chosen to fit the particular needs of the experiment. As compared with the trapping field ejection method,[9] the cyclotron method appears to be capable of higher mass resolution, and in cases such as the present experiments, where relatively long ejection times can be tolerated but high mass resolution is imperative, it appears to be the method of choice.

In this case, the extremely long lifetimes of the ions in the cell made it a simple matter to eject ions in a time short compared with

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(8) J. L. Beauchamp, D. Holz, S. Woodgate, and S. Patt, manuscript in preparation.

(9) J. L. Beauchamp and J. T. Armstrong, *Rev. Sci. Instrum.*, **40**, 123 (1969).

their lifetimes while achieving sufficient mass resolution to discriminate between CH_3Cl^+ and CH_3ClH^+. The photoproduction of CH_3^+ was monitored while each of the two possible precursors was ejected, as shown in Figure 3. The photoproduction actually increased slightly when CH_3ClH^+ was ejected, probably due to space charge effects on ion lifetimes, but ejection of CH_3Cl^+ resulted in a 55% reduction, as compared with a theoretical maximum reduction of 75% (the other 25% being due to the ^{37}Cl isotope). From this it seems clear that most or all of the photoproduction of CH_3^+ ions is from CH_3Cl^+ parent ion.

Results

Methyl Chloride. Based on the results of the cyclotron resonance ejection experiment, it is reasonable to suppose that the curve in Figure 1 relates to the process of eq 1. Measurements were made with the monochromator set at 3500 Å of P, S, and S_0, which in this case are $[CH_3Cl^+]$, $[CH_3^+]$, and $[CH_3^+]_0$. Using eq 6 and applying the light-intensity corrections discussed above, the data of Figure 1 can be corrected and referred to absolute cross sections to obtain the absolute cross section *vs.* wavelength curve which is shown as Figure 4.

Nitrous Oxide. The process

$$N_2O^+ \xrightarrow{h\nu} NO^+ + N$$

took place over the full range of wavelengths used and declined slowly with increasing wavelength, so that with photon energy centered at 6250 Å the cross section was about two-thirds of its value at 4250 Å. Since the threshold for this process lies at about 9000 Å, the experiment did not give any information about the interesting region near the threshold. A rough estimate of the cross section was made using eq 6, and it was calculated that $\sigma(6250) = 0.25 \times 10^{-18}\ cm^2$.

Discussion

The cross section for CH_3Cl^+ dissociation is quite large and is comparable to many cross sections obtained for other photon-induced processes of small molecules, such as photoionization and photodissociation of neutrals and photodetachment of negative ions.[10] The calculated threshold for this dissociation lies at about 5500 Å, whereas these experiments detected no dissociation for wavelengths beyond 4500 Å, so it is clear that the rise of the cross section from threshold is very gradual. It is anticipated that improvements in sensitivity will make possible the observation of the direct dissociation near threshold.

It is reasonable to suppose that the CH_3Cl^+ dissociation observed in these experiments proceeds through an excited state of the CH_3Cl^+ ion lying about 3.9 eV above the ground state. It is interesting to note that the CH_3S radical, which is isoelectronic with CH_3Cl^+, has been reported[11] as having a strong absorption at 3700 Å (3.3 eV), which can very readily be associated with the postulated excited state of CH_3Cl^+.

While the low resolution and intensity of the curve obtained for methyl chloride cation dissociation rule out any definitive assignment of the observed peak, some comments may be made on its possible significance. Adopting a simple molecular orbital picture, the occupied orbitals of methyl chloride are [core, $3a_1^2$, $2e^4$], and the lowest ionization potential corresponds to removal of a (2e) nonbonding electron to give a ^2E ion ground state. There are no symmetry restrictions on optical transitions from this ground state to excited states of any symmetry in C_{3v}. Photoelectron spectra[12] show a second ionization potential with its band maximum at about 3.2 eV above the 0–0 transition of the first ionization potential, probably corresponding to removal of the ($3a_1$) bonding electron. The energy of onset of this band agrees well with the photoionization efficiency curve for CH_3^+ production,[13] which can reasonably be assumed to proceed through this same excited state. The broad bands associated with excitations to this state suggest either a purely repulsive potential curve or Franck–Condon factors making only the inner portion of the potential curve accessible in vertical ionization. The photoelectron spectrum also shows a poorly defined peak lying 4.1 eV above the ground state.[12]

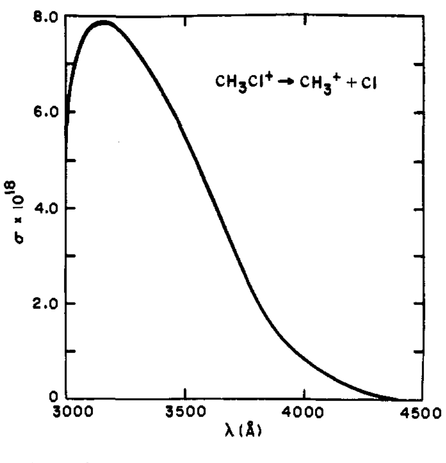

Figure 4. Photodissociation curve for CH_3Cl^+. The data of Figure 1 are shown after correction for the various effects discussed in the text. The curve gives the cross section *vs.* wavelength for the process $CH_3Cl^+ \rightarrow CH_3^+ + Cl$, with a resolution of 140 Å.

The broad peak of Figure 4 can be satisfactorily fitted to a Gaussian line shape, which suggests that it reflects vertical excitation from a low vibrational state of the ^2E ion ground state to a steeply rising approximately linear portion of a higher potential curve. Such a curve could belong to a state with a purely repulsive potential curve or it could be the inner portion of the potential curve of a bound state with a sharply displaced equilibrium geometry. Either of these situations could arise from excitation of an electron out of a ($3a_1$) bonding orbital or from excitation of a (2e) electron into a ($3a_1^*$) antibonding orbital. It seems reasonable to suppose that the peak in Figure 4 involves a change in occupation of the ($3a_1$) bonding or antibonding orbitals, which are the orbitals most likely to affect the bond strength and bond distance of the C–Cl bond.

It is possible that Figure 4 reflects excitation of the ($3a_1$) bonding electron into the (2e) orbital, and this interpretation is supported by the fact that the onset of the peak of Figure 4 at about 2.8 eV is close to the onset of 2.6 eV which is expected for this process based on both the photoelectron and photoionization results. However, it is difficult to understand why the band

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[10] G. V. Marr, "Photoionization Processes in Gases," Academic Press, New York, N. Y., 1967.

[11] P. Goldberg, *J. Chem. Phys.*, 40, 427 (1964).

[12] J. L. Ragle, I. A. Stenhouse, D. C. Frost, and C. A. McDowell, *ibid.*, 53, 178 (1970).

[13] M. Krauss, J. A. Walker, and V. H. Dibeler, *J. Res. Nat. Bur. Stand., Sect. A*, 72, 281 (1968).

maximum in Figure 4 is displaced by about 0.7 eV from the band maximum for the photoelectron peak, and in fact the peak at 3.9 eV in Figure 4 might more reasonably be identified with the photoelectron peak at 4.1 eV. It is hoped that further photodissociation studies at higher resolution and sensitivity will resolve this uncertainty and clarify the nature of the primary process in methyl chloride cation photodissociation.

If the photodissociation of cations turns out to proceed commonly *via* the low-lying excited electronic states of the ions, then the icr photodissociation technique may be a precise and convenient indirect method for obtaining optical absorption spectra of cations for levels lying above the dissociation threshold. While the cross-section value obtained for N_2O is probably uncertain within a factor of 2, and that for CH_3Cl is probably $\pm 30\%$, it is still significant that the cross sections for these two processes are different by at least an order of magnitude. This indicates that the cross sections are strongly related to the chemical properties of the ions, and suggests that the systematic study of cation photochemistry will reveal varied and chemically interesting photodissociation patterns for cations.

Acknowledgments. The author wishes to express his appreciation to Mr. Kermit Smyth for his invaluable help and suggestions and for providing the transmission curve of the window, to Professor Bube for the loan of his thermopile, and to Professor John D. Baldeschwieler for his enthusiastic support and encouragement.

This work was supported in part by a grant from the National Science Foundation (No. NSF GP 4924-X), in part by a grant from the National Aeronautics and Space Administration (No. NGL-05-020-250), and in part by the Center for Materials Research, Stanford University, Stanford, Calif.

Nitrogen Dioxide Catalyzed Cis–Trans Isomerization of *cis*-2-Butene

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Abstract: Nitrogen dioxide has been found to catalyze the cis–trans isomerization of *cis*-2-butene in the gas phase. At room temperature, for nitrogen dioxide pressures of 0.1–3.0 Torr and *cis*-2-butene pressures of 1.0–30 Torr, the reaction is first order in both reactants and appears to be homogeneous. At room temperature the reaction has a second-order rate constant of 0.148 ± 0.003 l. mol^{-1} sec^{-1}. Over the temperature range 298–338°K, the Arrhenius parameters of the reactions are $\log A$ (l. mol^{-1} sec^{-1}) = 8.1 ± 0.2 and $E_a = 12.1 \pm 0.3$ kcal mol^{-1}. Thermochemical calculations show that these Arrhenius parameters are consistent with a free-radical isomerization mechanism.

Because it is a major pathway for olefin consumption in photochemical smog, photoinitiated oxidation of olefins by NO_2 has been extensively studied.[1] In solution NO_2 is known to react thermally with olefins to form α,β-nitronitrosoalkanes.[2] If this thermal reaction proceeds at a significant rate under atmospheric conditions, it would constitute an important new pathway for atmospheric olefin consumption. Accordingly, we have begun a study of the gas-phase reactions of NO_2 with olefins.

Early in this study we observed that *cis*-2-butene was being isomerized to *trans*-2-butene. Gas-phase thermal cis–trans isomerization of *cis*-2-butene is well known.[3] The reaction has an activation energy of 62.8 kcal mol^{-1}.[4] The isomerization has been shown to be catalyzed by free radicals such as NO,[3a] I,[5] S,[6] HS,[7] and RS.[8] The activation energies of the NO and I catalyzed isomerizations have been measured[3a,5b] and are 26.2 and 9.4 kcal mol^{-1}, respectively.

The ground state of NO_2 has doublet spin multiplicity and, therefore, free-radical character. NO_2 catalyzed cis–trans isomerization of unsaturated fatty acid esters[9] and of poly(*cis*-butadiene) and *cis*-2-butene[10] has been studied in the liquid phase. However, no kinetic data were reported. We here report the results of our gas-phase kinetic study of the NO_2 catalyzed isomerization of *cis*-2-butene to *trans*-2-butene.

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