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Gas Phase Reactions between Carbon Tetrachloride and Mass Analyzed Ions of Nitrogen between 3 and 200 E.v.¹

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A tandem mass spectrometer has been constructed to study ion-molecule and charge-transfer reactions. A primary ion beam is generated and mass analyzed in the first mass spectrometer. An ion lens system adjusts the beam acceleration to a desired value between 3 and 200 v. and focuses it into a reaction chamber containing a target gas. Secondary ions formed in the reaction chamber are extracted at right angles to the primary beam, through an exit slit into the second mass spectrometer where they are mass analyzed. Z-Direction deflection plates in the second spectrometer permit the observation of secondary ions possessing momentum in the direction of the primary ion beam. Thus, reactions involving momentum transfer as well as charge transfer may be studied. The reactions of N^+ , N_2^+ , N_2^{2+} , and Ar^+ with CCl_4 have been examined as a function of the ion energy. The Ar^+ reactions appear to be entirely due to charge transfer. In the reactions with the nitrogen ions, atom exchange produces significant amounts of the secondary ions NCl^+ and $NCCI^+$ as well as ionic fragments of CCl_4 . The dependence of the reaction cross sections on nitrogen ion energy indicates that a collision complex is formed between the ion and the molecule at ion energies below about 30 e.v. At higher energies, head-on collisions dominate the reactions.

Introduction

The study of gas phase ion-molecule reactions in mass spectrometers can yield information about the elementary steps involved in high energy reactions of gas discharges and irradiated systems. For this purpose, it is desirable to observe reactions which are endothermic or have activation energies as well as those which occur spontaneously. The large body of literature on ion-molecule reactions which has arisen in the last ten years deals mainly with spontaneous reactions. Talrose^{2a} and Hasted^{2b} have given useful reviews of this work. Recently, Giese and Maier³ have described an instrument which is not limited to spontaneous reactions.

The results of mass spectrometer experiments indicate that the reactions proceed from the formation of a collision complex, the exchange of charge between the ion and molecule, or a combination of these interactions. Both mechanisms are sensitive to the relative velocity of the collision. The tandem mass spectrometer arrangement used for the experiment described here allows a specific ion to be directed into a target gas with controlled energy between about 3 and 200 e.v. Both spontaneous reactions and those initiated by momentum transfer are observed.

In earlier work at this laboratory,⁴⁻⁶ several alkyl halides and alcohols were irradiated with deuterons from a Van de Graaff accelerator. The N^{13} produced by the $C^{12}(d,n)N^{13}$ process reacted with the target gas to give stable compounds containing nitrogen. It was speculated that the charged and energetic nitrogen atom emerging from the nuclear reaction probably did not react until it had slowed down to near bond energies. The tandem mass spectrometer was constructed to investigate the elementary ion-molecule reactions of such systems and to examine their energy dependence.

Experimental

Apparatus.—The apparatus is presented schematically in Fig. 1. The primary ion beam is generated by a 180° magnetic mass spectrometer having a 1 cm. radius of curvature (manufactured by Consolidated Electrodynamics Corp. under the trade name Eiatron). The ion beam from this primary mass spectrometer (PMS) passes between deflection plates and enters an ion lens

which focuses it into a reaction chamber. This lens also adjusts the ion acceleration to any value between 2 and 200 v. This voltage is measured by a voltmeter connected between the PMS ionization chamber and the reaction chamber, with a correction for the contribution of the PMS repeller potential to the primary ion acceleration.

The ion lens consists of a series of seven plates with slit apertures arranged electrically to provide either a unipotential lens followed by a field-free drift space or a series of three "unipotential lenses"; see Fig. 2. The latter arrangement is best with primary ions of mass 28 or higher. The final aperture of the primary ion lens is at the potential of the PMS exit slit. Primary beam energy changes are made in a single step between the last lens aperture and the reaction chamber.

A permanent magnet is attached to the PMS within the main vacuum envelope. Its field is small enough to allow mass 14 ions to pass through the PMS exit slit with an acceleration of about 7 v. Under these conditions the mass resolution, $m/\Delta m$, of the PMS is about 5. Since the primary ion beams are generated with a small initial energy, they can be further retarded to around 2 e.v. with little difficulty. The low PMS resolution was not a handicap in this experiment.

The primary ion beam crosses the reaction chamber at right angles to the direction in which secondary ions are extracted through the exit slit. The reaction chamber repeller potential is applied continuously. To minimize the spread in primary ion energies caused by the repeller field, all of the primary ions are introduced into the reaction chamber at approximately the same distance from the repeller plate. This geometry requires that, in the reaction chamber, the wide dimension of the primary ion beam ribbon lie between, and parallel to, the planes containing the exit slit and the repeller plate. Such an arrangement decreases the sensitivity, since many secondary ions are not formed above the exit slit, and electron multiplier detection is necessary. The energy spread caused by the repeller field has been held to less than 15% of the measured primary ion energy.

After extraction from the reaction chamber, secondary ions are accelerated to 2 or 3 kev. and mass analyzed in an 8 in. radius, 60° magnetic sector mass spectrometer. In order to detect secondary ions from momentum transfer reactions, Z-direction deflectors have been added to the secondary mass spectrometer (SMS) ion accelerating lens; see Fig. 1. These deflectors can be adjusted to counteract the Z-direction momentum transferred from primary ions to secondary ions permitting the secondary ions to reach the electron multiplier detector.

For maximum sensitivity, the SMS was always operated with wide slits giving a mass resolution of approximately 150. The ability of the Z-deflectors to cancel the Z-direction momentum of the secondary ions is demonstrated by the fact that the primary beam itself can be focused on the SMS detector, for energies up to about 40 e.v., by using the Z-deflectors along with higher than usual repeller voltages in the reaction chamber. The resulting primary ion peaks are flat-topped and undistorted. The long slits used in the SMS accelerating lens to increase the sensitivity make the energy resolution of the Z-deflectors too low to be of much value for measuring the Z-momentum carried by a particular ion. However, further improvements in the sensitivity of the instrument may make such measurements possible.

Procedure.—Since the experiment was rather insensitive to small amounts of impurities, oil-pumped tank N_2 and CCl_4 of C.P. grade were adequate. The N_2 flow into the PMS was adjusted so that the source manifold pressure rose to 2×10^{-6} torr from its "empty" pressure of about 10^{-7} torr. Then CCl_4 was admitted to the reaction chamber through a variable leak at a rate which raised the source manifold pressure further to about

(1) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract No. AF 49(638)-481.

(2) (a) V. L. Talrose, *Pure Appl. Chem.*, **5**, 455 (1962); (b) J. B. Hasted in "Advances in Electronics and Electron Physics," Vol. 13, Academic Press, Inc., New York, N. Y., 1960, p. 1.

(3) C. F. Giese and W. B. Maier, II, *J. Chem. Phys.*, **39**, 739 (1963).

(4) H. Schmied and W. S. Koski, *J. Am. Chem. Soc.*, **82**, 4766 (1960).

(5) W. S. Koski, H. Schmied, and W. C. Perkins, "Chemical Effects of Nuclear Transformations," Intern. Atomic Energy Agency, Vienna, 1961, p. 217.

(6) W. C. Perkins and W. S. Koski, *J. Phys. Chem.*, **66**, 474 (1962).

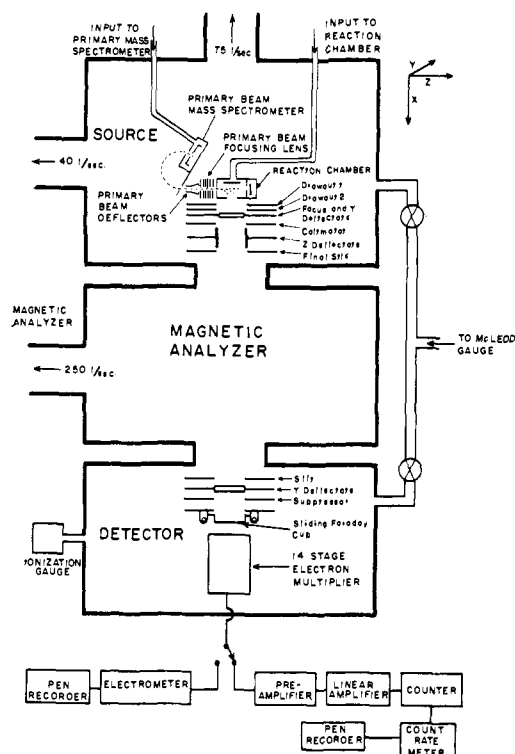


Fig. 1.—Diagram of the ion-molecule reaction apparatus.

1×10^{-5} torr. The PMS filament was generally operated at about 240 μa . trap current. The PMS accelerating voltage was set for mass 14 or 28. Mass 14 consisted of N^+ and N_2^{++} if the ionizing voltage were greater than 43.5 v., which is the appearance potential of N_2^{++} .⁷ Therefore, an N^+ beam was generated by using an ionizing voltage of 40 v. and a beam containing both N^+ and N_2^{++} was made by raising the ionizing voltage to 100 v. An ionizing voltage of 80 v. gave the most intense mass 28 beam.

At low primary beam energies (less than 15 e.v.), the reaction chamber repeller field necessary to extract the secondary ions also deflects the primary ion beam away from its collector. For this reason, the primary beam could not be monitored accurately during measurements, and separate measurements of its intensity were necessary. The primary ion lens transmission characteristics were determined by measuring the current to the primary ion collector in the reaction chamber as a function of primary ion energy. This measurement was made with the repeller at 0 v. and no CCl_4 in the reaction chamber. Over a period of several months, the primary ion lens transmission curves were consistent to within 5% on separate measurements.

The reaction chamber repeller field creates a further ambiguity at low primary ion energies. The repeller field required to extract a given secondary ion depends on the amount of Z-direction momentum transferred to that ion. A primary ion entering the reaction chamber enters a region between the repeller and exit slit which is more positive than the reaction chamber entrance slit by an amount about one-third of the repeller voltage. Thus the primary beam loses Z-direction energy and receives an acceleration toward the exit slit. In practice, the repeller was adjusted to give a maximum secondary peak intensity whenever possible. At primary ion energies above 30 e.v., the secondary beam intensity could always be maximized with repeller settings of 9 v. or less. However, at primary beam energies below about 30 e.v., where the reaction cross section usually was increasing rapidly with decreasing primary ion energy (see Fig. 7-10), the secondary ion intensity often would not saturate as the repeller voltage was raised. This is expected, since at low energies the decrease in primary ion energy due to the repeller field increases the reaction probability markedly. Where secondary ion saturation could be achieved at low primary energies, with N_2^+ and Ar^+ primary ions, the required repeller voltage was less than 3 v. This would decrease the primary ion energy by 1 v. or less. At low primary energies, repeat measurements often showed a 1- or 2-v. uncertainty in the primary ion energy required to produce a given secondary ion intensity. For our measurements, the repeller either saturated the secondary peak or else its potential was limited to a value which changed the primary ion energy not more than 15%. Data taken at primary energies less than 3 e.v. were unreliable. It is possible that for

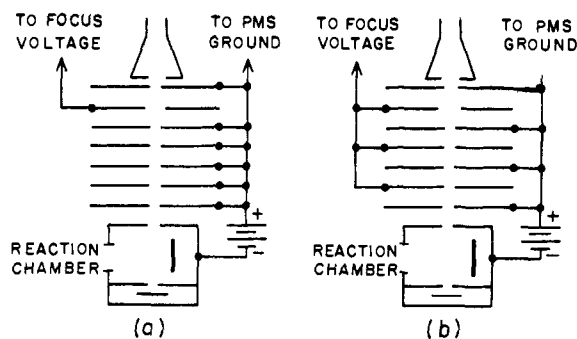


Fig. 2.—Alternate primary ion lens arrangements. The simple unipotential lens followed by a field-free drift region (a) worked best for ions lighter than mass 28. The lens shown in (b) worked better for masses 28 and higher.

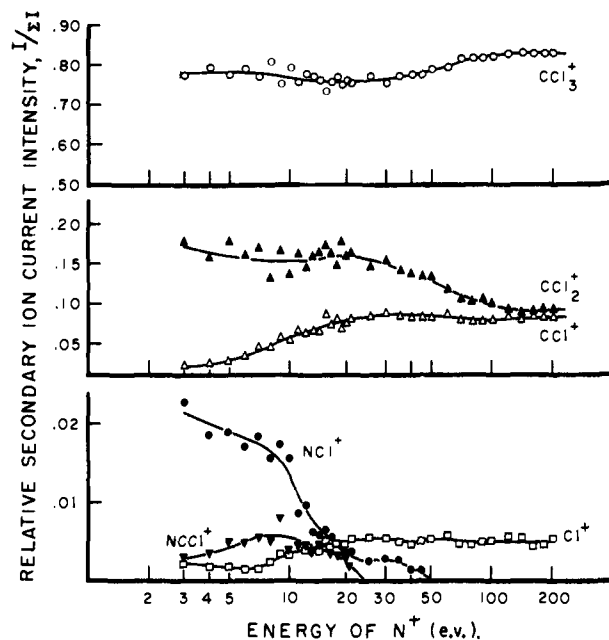


Fig. 3.—Relative yields of various secondary N^+ ions as a function of N^+ ion energy for the reaction $\text{N}^+ + \text{CCl}_4 \rightarrow \text{products}$.

N^+ and N_2^{++} primary ions, the decrease in slope of the cross section curves below about 5 e.v. ion energy is at least partly instrumental in origin. That this effect was not noted for N_2^+ primary ions could be due to the fact that the N_2^+ primary beam was about 100 times more intense than the N^+ beam. The relative reaction cross section for a given secondary ion was determined by $\sigma = C(S/P)$, where S is the measured secondary ion current, P is the primary ion current obtained from the primary ion lens transmission characteristics, and C is a normalization constant. The cross section for CCl_3^+ from $\text{N}^+ + \text{CCl}_4 = \text{CCl}_3^+ + \text{products}$, was arbitrarily set equal to 100 and all other cross sections were normalized with reference to this value. The secondary ion intensities used were isotopically corrected. Each point in Fig. 3-12 represents an average of four to six measurements. The relative cross sections and fractional abundances of each secondary ion abundant enough to yield reliable data were determined at primary ion accelerating voltages between 3 and 200 v. Negative ions were not examined.

Results

The collected data from the nitrogen primary ion reactions are summarized in Fig. 3-10. These curves show that the nitrogen atom transfer products NCl^+ and NCCl^+ were always present in restricted primary ion energy ranges. CN^+ and NCCl_2^+ were observed also, but their intensities were too low to allow reliable measurements.

A primary beam of Ar^+ was used for comparison purposes. Here, charge transfer is expected to be the dominant reaction. Figures 11 and 12 show that the reaction $\text{Ar}^+ + \text{CCl}_4 = \text{products}$ gives an energy depend-

(7) F. H. Dorman and J. D. Morrison, *J. Chem. Phys.*, **35**, 575 (1961).

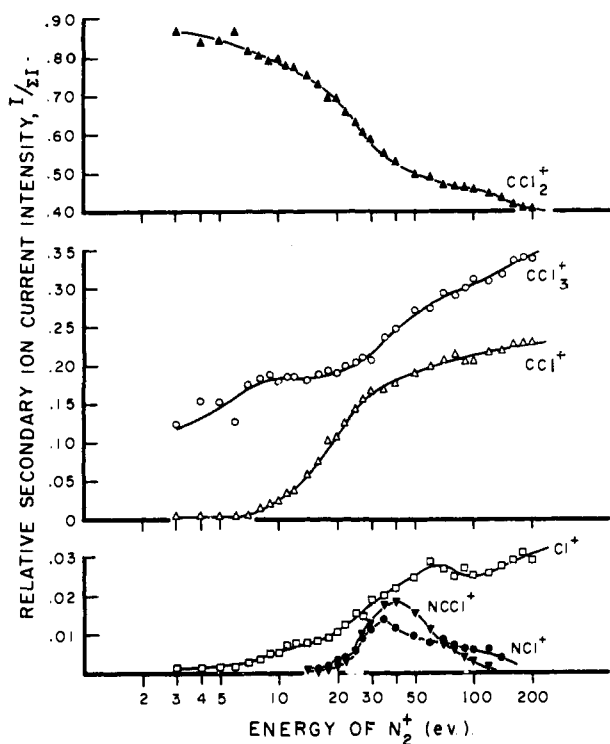


Fig. 4.—Relative yields of various secondary ions as a function of N_2^+ ion energy for the reaction $N_2^+ + CCl_4 \rightarrow$ products.

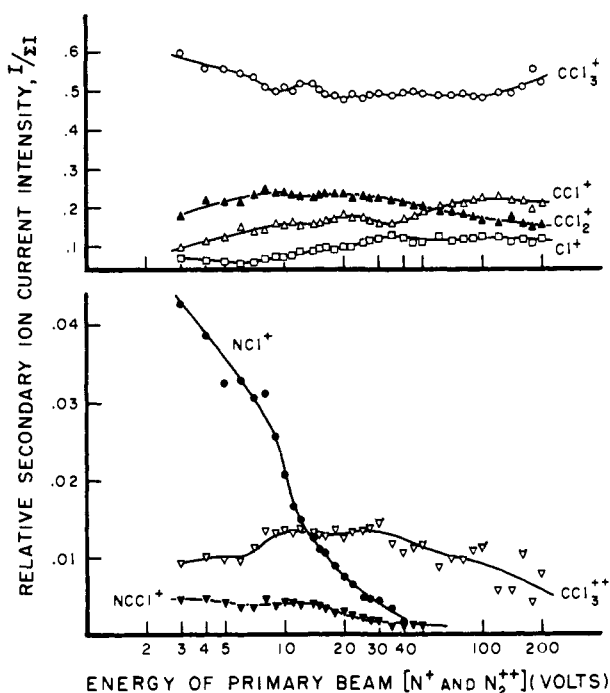


Fig. 5.—Relative yields of various secondary ions as a function of ion energy for the reaction $[N^+ + N_2^{++}] + CCl_4 \rightarrow$ products.

ence and distribution of products which are very different from the reactions between nitrogen ions and CCl_4 .

$Ar^+ + CCl_4 =$ Products.—Figure 12 shows a general agreement with Massey's adiabatic hypothesis,⁸ indicating that the charge transfer reaction predominates. Massey's hypothesis predicts that a given cross section should decrease monotonically with increasing Ar^+ energy after passing through a maximum value. In Fig. 12, the curves for CCl_2^+ and CCl^+ appear to be

(8) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Clarendon Press, Oxford, 1962, p. 441.

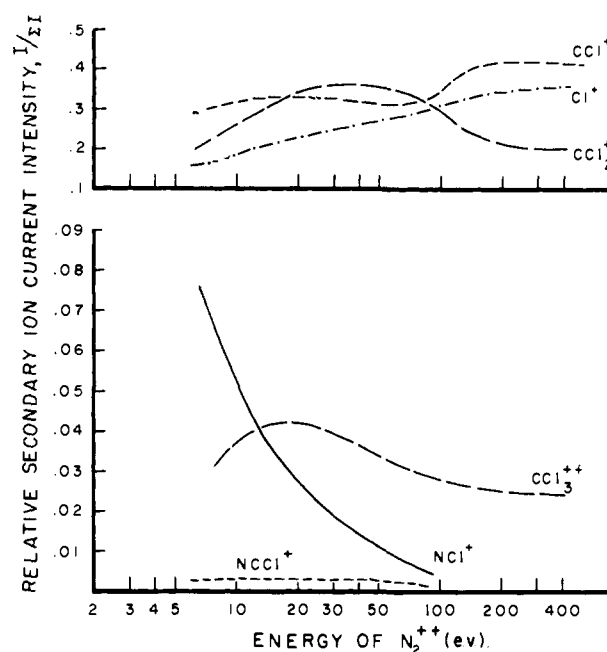


Fig. 6.—Relative yields of various secondary ions as a function of N_2^{++} ion energy for the reaction $N_2^{++} + CCl_4 \rightarrow$ products.

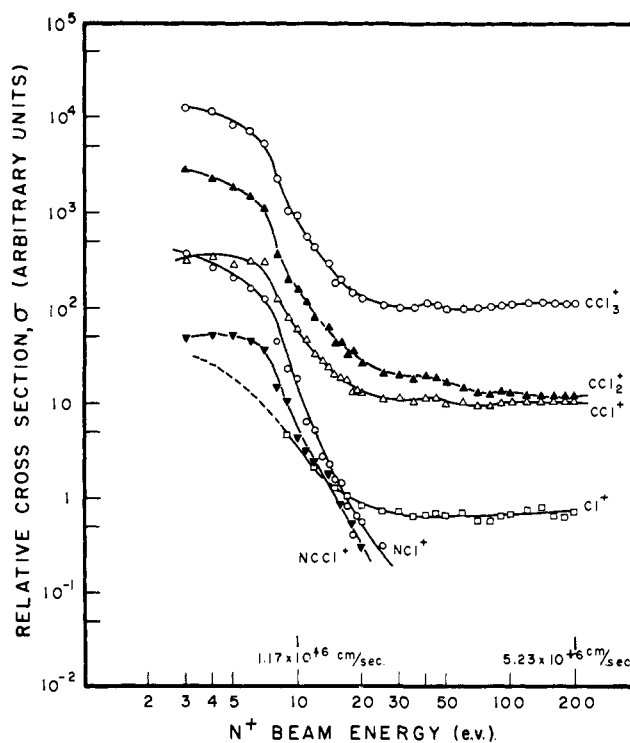


Fig. 7.—Relative cross sections for production of various ions as a function of N^+ ion energy for the reaction $N^+ + CCl_4 \rightarrow$ products.

approaching a region where the cross section is nearly independent of ion energy. This probably may be attributed to the dominance at higher Ar^+ energies of reactions induced by direct head-on collisions. Boelrijck and Hamill⁹ have observed this effect in a standard mass spectrometer.

Nitrogen Ion + $CCl_4 =$ Products.—The cross section curves, Fig. 7–10, clearly do not resemble those expected from charge transfer reactions. The presence of the secondary ions NCl^+ and $NCCl^+$ demonstrates that a collision complex is formed between the incident ion and the target molecule. As the relative energy

(9) N. Boelrijck and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 730 (1962).

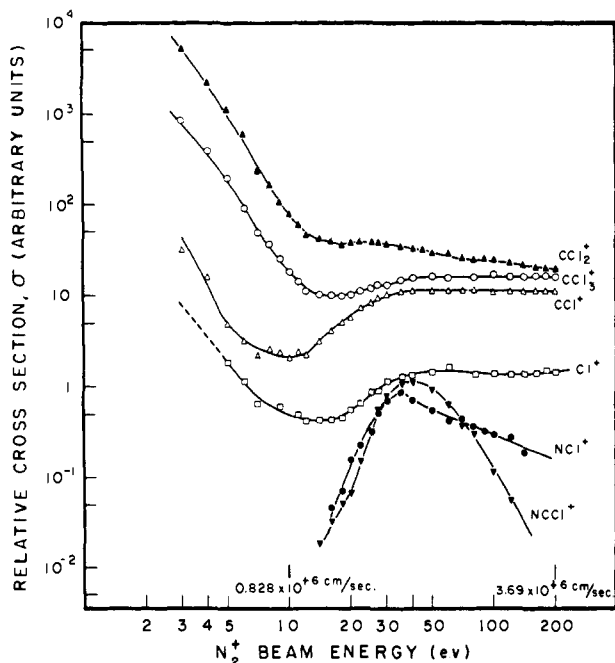


Fig. 8.—Relative cross sections for production of various ions as a function of N₂⁺ ion energy for the reaction N₂⁺ + CCl₄ → products.

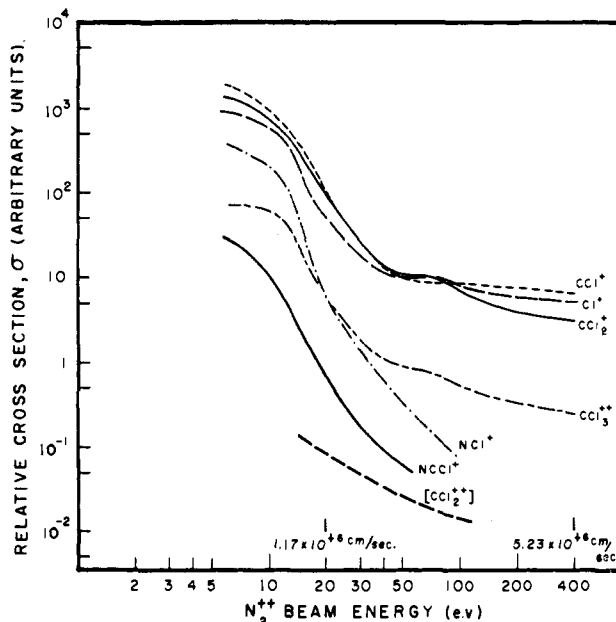


Fig. 10.—Relative cross sections for the production of various ions as a function of N₂⁺⁺ ion energy for the reaction N₂⁺⁺ + CCl₄ → products.

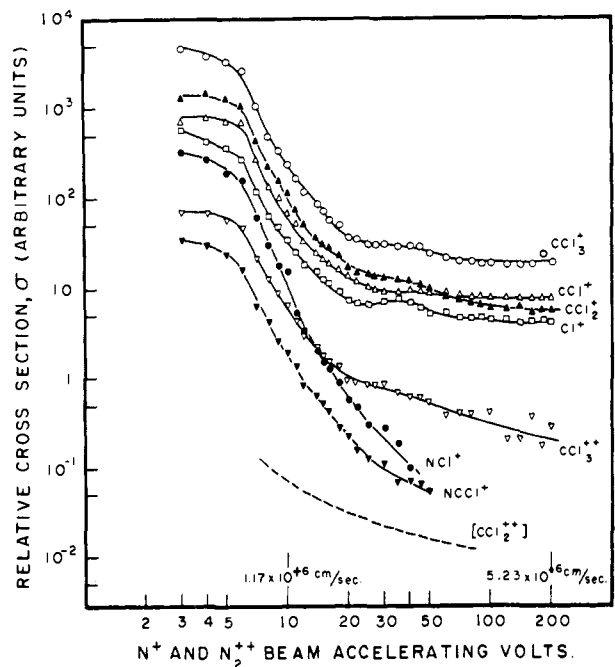


Fig. 9.—Relative cross sections for the production of various ions as a function of [N⁺ + N₂⁺⁺] ion energy for the reaction [N⁺ + N₂⁺⁺] + CCl₄ → products.

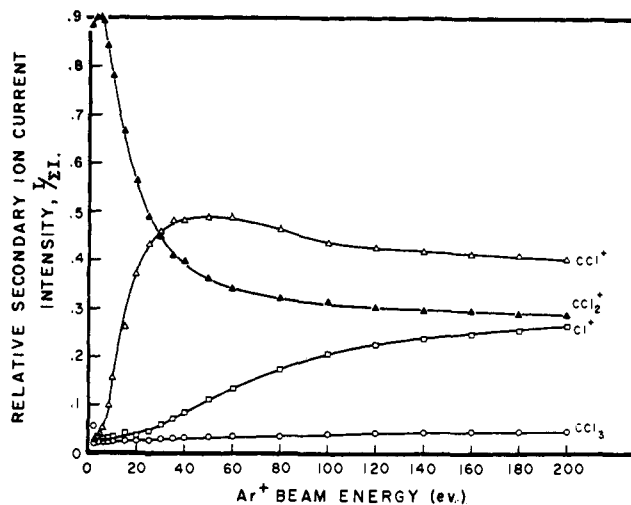


Fig. 11.—Relative yields of various secondary ions as a function of Ar⁺ ion energy for the reaction Ar⁺ + CCl₄ → products.

increases, the flattening of the cross section curves for CCl₄ fragment ions and the disappearance of the nitrogen-containing secondary ions shows that the reactions become dominated by head-on collisions in which complex formation is increasingly improbable.

In general, more than one reaction may be written down to account for any particular secondary ion. As the incident ion energy is raised and more internal energy must be dissipated, increasingly endothermic reactions will be favored. Since there are no obvious systematic trends in the curves of Fig. 3-6, the general structure is believed to be due to competing reactions, although instrumental factors may play a role.

N⁺ Primary Ions.—Below 30 e.v., the cross sections for all of the secondary ions decrease sharply with increasing primary ion energy, paralleling the decrease in the probability of complex formation. Around 30 e.v., the cross sections for NCl⁺ and NCCl⁺, $\sigma(\text{NCl}^+)$ and $\sigma(\text{NCCl}^+)$, become too small to measure while $\sigma(\text{CCl}_3^+)$, $\sigma(\text{CCl}^+)$, and $\sigma(\text{Cl}^+)$ become velocity independent; $\sigma(\text{CCl}_2^+)$ continues to show a small velocity dependence at the higher energies.

If the recombination energy (R.E.) of N⁺ is taken as 14.54 e.v.,¹⁰ the reactions forming CCl₂⁺, CCl⁺, and Cl⁺ are endothermic. The reactions forming CCl₃⁺ and NCCl⁺ and probably the reaction yielding NCl⁺ are exothermic. It is of interest to note that the relative abundance of CCl₃⁺ remains essentially constant over the entire energy range, while the relative abundance of CCl⁺ and Cl⁺ increase, seemingly at the expense of CCl₂⁺.

A literature search failed to reveal any information concerning the heat of formation of NCl⁺. Our data permit the very qualitative estimates of $\Delta H_f(\text{NCl}^+) \leq$

(10) E. Pettersson and E. Lindholm, *Arkiv Fysik*, **24**, 49 (1963).

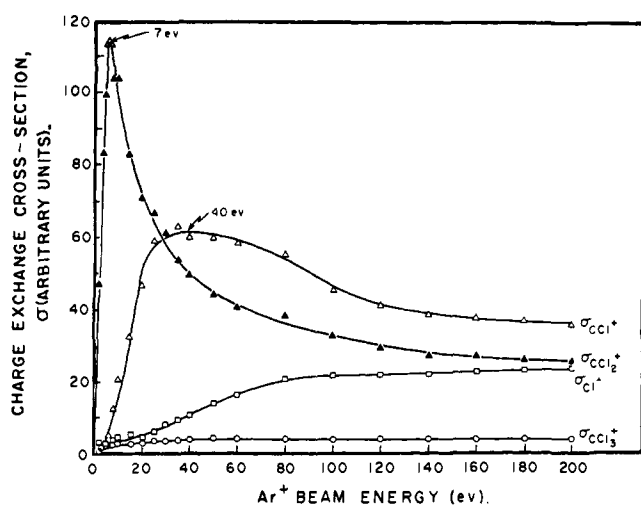
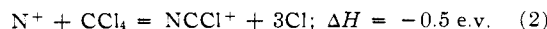


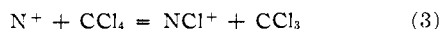
Fig. 12.—Relative cross sections for the production of various ions as a function of Ar^+ ion energy for the reaction $\text{Ar}^+ + \text{CCl}_4 \rightarrow \text{products}$.

14.6 e.v. and $\Delta H_f(\text{NCl}) \leq 1.6$ e.v. from the following observations.

The formation of NCCl^+ very likely proceeds by either $\text{N}^+ + \text{CCl}_4 = \text{NCCl}^+ + \text{Cl}_2 + \text{Cl}$; $\Delta H = -3.1$ e.v.¹¹ (1) or



or both. At the lowest N^+ energies, reaction 1 should be favored. Figure 7 shows that the cross section for NCl^+ is increasing as the primary ion energy decreases. Thus, the important reactions forming NCl^+ do not require momentum transfer. The most probable reaction would be



Since the cross section for NCl^+ is larger than that for NCCl^+ over the same energy range, reaction 3 might be expected to be exothermic like reactions 1 and 2. If ΔH of reaction 1 is taken as the smallest possible exothermicity for reaction 3 then

$$\Delta H_f(\text{NCl}^+) \leq \Delta H_f(\text{N}^+) + \Delta H_f(\text{CCl}_4) - \Delta H_f(\text{CCl}_3) - 3.1 \text{ e.v.} \leq 14.6 \text{ e.v.}^{11}$$

The ionization potential of many simple molecules containing a chlorine atom in an exposed position is about 13 e.v., which is just I.P.(Cl).¹² If this were the case for NCl , then $\Delta H_f(\text{NCl}) \leq 1.6$ e.v. The energy of dissociation of NCl^+ to N and Cl^+ would be, then, ≥ 4.6 e.v., if the products carry no kinetic energy. In this connection, it is interesting to note that two reported values for the dissociation energy of NS , which is isoelectronic with NCl^+ , are similar to the estimate for NCl^+ , being 5.0 and 5.9 e.v.¹³

N_2^+ Primary Ions.—No secondary ions containing nitrogen appear until the ion energy reaches about 14 e.v. The cross section curves indicate that the $(\text{N}-\text{N})^+$ bond breaks at this energy and that this stabilizes the collision complex so that NCl^+ and NCCl^+ are observed up to 150 e.v. primary energy.

(11) ΔH_f for N^+ , CCl_4 , Cl_2 , NCCl_2 , and Cl were taken as 19.4, -1.1, 0, 1.4, and 1.3 e.v., respectively, from F. D. Rossini, *et al.*, *Natl. Bur. Standards Circ. No. 500* (1952), and J.A.N.A.F. Thermochemical Data Tables, prepared by Dow Chemical Co., Thermal Laboratory (1960); $\Delta H_f(\text{CCl}_3) = 0.58$ e.v. from J. B. Farmer, *et al.*, *J. Chem. Phys.*, **24**, 348 (1956), and $\Delta H_f(\text{NCCl}^+) = \Delta H_f(\text{NCCl}) + \text{I. P.}(\text{NCCl}) = 13.9$ e.v. using data from J. T. Herron and V. H. Dibeler, *J. Am. Chem. Soc.*, **82**, 1555 (1960).

(12) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957.

(13) T. I. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths Publications Ltd., London, 1958.

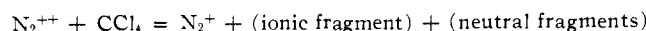
Giese and Maier¹⁴ have shown that the onset energy of the cross section curve for a secondary ion from an endothermic reaction, will, in certain cases, correspond closely to the activation energy for the formation of that ion. The breaking of the $(\text{N}-\text{N})^+$ bond requires 8.7 e.v. and, therefore, requires at least a measured primary ion kinetic energy of $\text{K.E.} = 8.7$ (total mass/target mass) = 10.3 e.v., if we assume that the CCl_4 molecule contains the normal isotopic distribution. The apparent onset of the curves for NCl^+ and NCCl^+ in Fig. 8 agrees reasonably with this required energy. Our curves do not rise so sharply from onset as the examples of Giese and Maier, and this must be attributed to the more complicated nature of our reaction.

No secondary ions containing two nitrogen atoms were observed. The stabilization of the collision complex allows the cross sections for the CCl_4 fragment ions to increase with higher primary ion energies until they reach the velocity independent region at about 40 e.v.; $\sigma(\text{CCl}_2^+)$ is not particularly sensitive to the breaking of the $(\text{N}-\text{N})^+$ bond and characteristically exhibits a small velocity dependence up to 200 e.v. The energy dependence of CCl_2^+ may be interpreted¹⁵ as indicating that CCl_2^+ is made when there is a transfer of charge at the very onset of complex formation. This competes less favorably with other reactions as the relative velocity of the collision partners increases. This would occur also when N^+ or N_2^{++} is the primary ion.

N_2^{++} Primary Ions.—Figures 5 and 9 are the relative abundance and cross section curves for the reactions of CCl_4 with a primary beam containing both N^+ and N_2^{++} . N_2^{++} has an R.E. of 43.5 e.v. for double charge exchange and R.E.'s around 27.9 and 15.6 e.v. for successive single charge transfers. This greatly increases the energy which can be transferred to internal energy of the collision complex and its effect is seen in the presence of CCl_3^{++} and CCl_2^{++} and also in the enhanced abundance of Cl^+ . The amount of CCl_2^{++} produced was too small to permit accurate cross section measurements and its curve in Fig. 9 is estimated.

It was evident from our data that, between 2 and 200 e.v., the cross section for producing CCl_3^+ from the reaction between N_2^{++} and CCl_4 was too small to be measured.¹⁵ Consequently, we were able to separate the reactions of N^+ and N_2^{++} which are combined as shown in Fig. 5 and 9. The results to be expected in reactions of CCl_4 with only N_2^{++} are shown in Fig. 6 and 10. The breaking of the $(\text{N}-\text{N})^{++}$ bond, which Hurley¹⁶ has predicted should require less than 2.5 e.v., occurs at the lowest primary ion energy measured. CCl_3^+ is absent and the cross sections for CCl_2^+ , CCl^+ , and Cl^+ are very similar over the entire energy range, although $\sigma(\text{CCl}_2^+)$ typically decreases faster in the higher energy range than does $\sigma(\text{CCl}^+)$ or $\sigma(\text{Cl}^+)$.

Because $\Delta H_f(\text{N}_2^{++})$ is so large (~ 43.5 e.v.), most reactions of N_2^{++} with CCl_4 are exothermic. A small N_2^+ secondary ion current was seen when the primary beam contained N_2^{++} , showing that some of the products were produced by the reaction



Conclusions

Both charge transfer and atom transfer products are observed in the reactions of nitrogen ions with carbon tetrachloride within the energy range 3–200 e.v. The dependence of the cross sections on the energy of the bombarding ion suggests that the reaction products were formed by two mechanisms. In the lower energy

(14) C. F. Giese and W. B. Maier, II, *J. Chem. Phys.*, **39**, 197 (1963).

(15) E. R. Weiner, Dissertation, The Johns Hopkins University, 1963.

(16) A. C. Hurley, *J. Mol. Spectry.*, **9**, 18 (1962).

region, the rapid increase of the cross sections for all of the product ions with decreasing energy is best accounted for by assuming complex ion formation. The presence of atom transfer product ions in this region confirms this assumption. In the higher energy region, it is believed that the products arise as a result of an exchange of charge and kinetic energy during direct head-on collisions between the incident ions and the CCl_4 molecules.

One of the reasons for undertaking this investigation was to learn more about the role of ion-molecule reactions in chemical reactions of energetic species produced as a result of nuclear transformation. In the deuteron bombardment of compounds containing carbon, N^{13} is formed as a multiply charged positive ion. Recent work⁶ on the deuteron bombardment of methanol, to which various rare gases were added, has indicated that the hot reactions involved ionic species, at least in part. Furthermore, the proposed mechanism involved CN ions and probably CN radicals as intermediates.

The ion-molecule reaction studied here which has the most direct bearing on such hot atom reactions is the one involving N^+ primary ions. The presence of significant amounts of NCCl^+ as a product of the N^+ reactions in the present experiment suggests an ionic mechanism to explain the NCCl obtained as a final product in the deuteron bombardment experiment mentioned above. The production of CN^+ in the N^+ reactions with CCl_4 is also compatible with the proposed

mechanism in the case of deuteron-irradiated methanol. Of course the relative roles of ionic and neutral species in the over-all chemistry of reactions initiated by nuclear transformations cannot be evaluated without knowledge of the relative cross sections for reactions involving both species. However, it should be noted that, in Fig. 7, the cross sections are rising rapidly as the incident ion energy decreases in the 10-e.v. region. The flattening of the curves in the 5-e.v. region is believed to be largely instrumental since it is not observed in the case of the more intense N_2^+ primary beam. The probability of an ion-molecule reaction before the ion is neutralized depends on its cross section for reaction relative to that for neutralization and the steady-state concentrations of ions, electrons, and gas molecules. The behavior of the reaction cross section as the ion kinetic energy approaches bond energies suggests that the probability of reaction before the ion is neutralized may become significant under some conditions. For example, if the electron concentration is small relative to the ion concentration owing to the presence of gases with high electron attachment coefficients, ion-molecule reactions might be expected to play an important role in chemical effects of nuclear transformation.

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[CONTRIBUTION FROM THE BIOPHYSICS DIVISION, SAHA INSTITUTE OF NUCLEAR PHYSICS, CALCUTTA-9, INDIA]

Measurement of the Diffusion Coefficients of Sucrose in Very Dilute Aqueous Solutions Using Jamin Interference Optics at 25°

BY AMALA CHATTERJEE

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Diffusion coefficients of sucrose in very dilute solutions have been measured at 25° as a function of concentration with the help of the Jamin interference optics and a microdiffusion cell. The details of the method have been described and the results compared with those obtained by Gosting and Morris with the help of the Gouy method at 25°. A very satisfactory agreement has been obtained.

Gosting and Morris¹ measured the diffusion coefficient of sucrose in aqueous solutions (25°) in the concentration range 0.75 to 5.25% (g./100 ml.) with the help of the Gouy method. On the other hand, English and Dole² performed the same experiments with supersaturated solutions of sucrose using a newly designed diffusion cell and observed that their data and those of Gosting and Morris fitted excellently on the same straight line when plotted in the same scale. The latter authors further observed that the schlieren method was far less consistent than the Gouy method in the measurement of the diffusion coefficient. The object of the present investigation is (1) to measure the diffusion coefficient of sucrose with the help of Jamin interference optics using a microdiffusion cell and to compare the results with those obtained by Gosting and Morris with the help of Gouy method, and (2) to extend the measurements to comparatively more dilute solutions of sucrose at 25°.

Experimental

Materials and Methods.—The diffusion experiments were carried out in a Tiselius type of microdiffusion cell (widths along and perpendicular to the light path are 5 and 1 mm., respectively) provided in the Antweiler microelectrophoresis diffusion equipment, where the quantity of the sample required was about 0.3

ml. A source of white light produced the interference fringes and the color sensitivity of the eye was used to detect the change in the solute concentration at any level of the cell occurring in the course of the diffusion process. A minimum concentration difference of about 10^{-5} g./ml. of sucrose can be easily detected with this system. The details of the optical arrangements and the sensitivity of the equipment have been described by Antweiler^{3,4} elsewhere.

In the present method, different points along the height of the cell can be scanned in steps of 0.1 mm. The refractive increment Δn or the corresponding change in concentration ΔC compared to a reference channel is obtained directly as a function of x . This leads to a curve given by the well known diffusion equation

$$C_x = C_0/2 \left[1 - 2/\sqrt{\pi} \int_0^{x/\sqrt{4Dt}} \exp(-x^2/4Dt) d(x/\sqrt{4Dt}) \right] \quad (1)$$

where C_x is the concentration at a distance x from the initial boundary at an instant after the formation of the boundary. Equation 1 may be written as

$$C_x/C_0 = 1/2 \int_{x/\sqrt{4Dt}}^{\infty} 2/\sqrt{\pi} \exp(-x^2/4Dt) d(x/\sqrt{4Dt}) \quad (2)$$

Since the values of the probability integral

$$2/\sqrt{\pi} \int_{hx}^{\infty} \exp(-h^2x^2) d(hx), \quad h = 1/\sqrt{4Dt}$$

are tabulated in standard texts for different hx one can prepare a table relating $x/2\sqrt{Dt}$ with any measured value of C_x/C_0 and this

(1) L. J. Gosting and M. S. Morris, *J. Am. Chem. Soc.*, **71**, 1998 (1949).
 (2) A. C. English and M. Dole, *ibid.*, **72**, 3261 (1950).

(3) H. J. Antweiler, *Chem. Ing. Tech.*, **5**, 284 (1952).
 (4) H. J. Antweiler, *Mikrochim. Acta*, **36**, 561 (1951).