MASTER

ABSTRACT

The angular and energy distribution of ionic products from the reaction of $B^+(^1S_g)$ with D_2 was studied over a projectile energy range of 10-50 eV in the laboratory system. The product states as determined from the limiting values of the translational exoergicity were $BD^+(^2\Sigma^+)$ and $BD^+(^2\Pi)$. The experimental measurements and theoretical considerations suggest that both of these reactions are proceeding through a persistent complex.

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REACTIVE SCATTERING OF $B^+(^1S_g)$ BY MOLECULAR DEUTERIUM

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In a previous study¹ the angular and energy distribution of the ionic products from the reaction of B^+ in its first excited state, 3P_u with molecular deuterium was studied over a projectile energy range of 1 to 40 eV in the laboratory system. The product states $BD^+(^2\Sigma^+)$ and $BD^+(^2\Pi)$ were determined from the limiting values of the translational exoergicities. The experimental velocity contour maps indicated that $BD^+(^2\Pi)$ was being produced by a direct mechanism in the energy range studied. At the high range of the energy covered, $BD^+(^2\Sigma^+)$ was also being produced by a direct mechanism; however, at low energies (0.34 eV c.m.), the process showed evidence of proceeding through a persistent complex mechanism. These observations were supported by spin and symmetry restrictions as well as orbital fillings.

In this study we extend the investigation to include the reactions of B^+ in the ground state, 1S_g , with molecular deuterium. The reactions expected in the energy domain that were studied are:

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Both of these are endothermic and have small cross sections.² They are, however, interesting ion-molecule reactions to investigate since considerations of the spin and symmetry restrictions coupled with orbital fillings indicate that it is not unreasonable for both of these reactions to proceed through a persistent complex. It should also be noted that mass spectrometric studies³ of the boron hydrides show that BD_2^+ is a long-lived ion and consequently represents a deep potential well in the $\text{B}^+ + \text{D}_2$ system. The accessibility of this potential well to this colliding system is of interest both dynamically and mechanistically.

The results of this study appear to be consistent with the conjecture that both of these reactions are proceeding through a persistent intermediate although we were not able to obtain a velocity contour map for the reaction of ground state projectile to produce ground state products at energies close to the threshold because of the small cross section of the reaction. Velocity contours at higher energies for this reaction and for the reaction of ground state B^+ to produce $\text{BD}^+(^2\Sigma^+)$ were readily realized. Two limiting values of the translational exoergicity were observed and their values were consistent with the production of $\text{BD}^+(^2\Pi)$ and $\text{BD}^+(^2\Sigma^+)$.

EXPERIMENTAL

The apparatus used in this study has been described previously.⁴ Briefly, the instrument consists of two quadrupole mass filters and two hemispherical electrostatic energy analyzers in tandem. The 180° electrostatic analyzers are similar in type to those described in the

literature.^{5,6}

The B^+ ions are formed by electron bombardment of BF_3 . The ions are extracted and focussed into the primary quadrupole mass filter and then decelerated into the first electrostatic analyzer and then accelerated and focussed into the reaction cell. The cell consists of two concentric cylinders, with the inner cylinder being able to rotate through $\pm 45^\circ$. The reaction cell is the center of the axis for the angular movement of the detection system. The detection system moves in a planar direction, pivoting the inner cylinder as the system is moved by a mechanical feed-through.

The detection system is similar to the primary ion beam section. The ions leaving the reaction cell are energy analyzed by another 180° electrostatic analyzer and are mass analyzed by the secondary quadrupole mass filter and then they are detected by a continuous channel electron multiplier. Pulse counting techniques are used. The data for the angular and energy distributions for the reactant and product runs are collected, stored and processed using a PDP-8/E minicomputer.

RESULTS AND DISCUSSION

The results of this study are presented by means of product ion velocity contour maps and by the behavior of the translational exoergicity (Q) with projectile ion kinetic energy. Q is the difference between the translational energy of the products and the reactants.

The raw data from which the Q 's and the contour maps are obtained are the energy spectra and a typical one is illustrated in Fig. 1. This spectrum is produced with a composite B^+ ion beam containing states

$1S_g$ and $3P_u$. The broad peak (a) on the left arises from $B^+(1S_g)$ reactions to produce $BD^+(2\Pi)$. The peak (b) in the center of the tracing is a composite peak with contributions from $B^+(1S_g)$ to give $BD^+(2\Sigma)$ and $B^+(3P_u)$ to give $BD^+(2\Pi)$. These two peaks overlap at the B^+ energy used here (25.1 eV), but are separated at other energies. The broader (c) of the two peaks at the right side of the tracing arises from $BD^+(2\Sigma^+)$ produced by $B^+(3P_u)$. Peak d is due to the B^+ projectile.

Fig. 2 shows the variation of the translational exoergicity (Q) as a function of projectile ion kinetic energy. Alternatively, Fig. 3 presents the data in the form of velocity contour maps. The translational exoergicity, Q, is obtained in the following manner.⁴ Conservation of energy and linear momentum permit one to obtain a relation between Q, masses of colliding particles, energies of projectile and product ions and the angle made by the product ion beam with the direction of the primary ion beam. Q is then obtained from the known masses and the measured energies of the projectile and product ions for some measured value of the angle which is generally set at zero for this purpose. Conservation of energy also permits one to relate the internal energies and the heat of reaction:

$$T_R + U_R - \Delta H = T_P + U_P$$

$$Q = T_P - T_R = U_R - U_P - \Delta H$$

where T and U represent the translational and internal energies of the reactants (R) and products (P), respectively, and ΔH is the heat of reaction. Knowledge of the thermodynamic properties of the products and reactants permits one to put limits on the value of Q. These are

designated as $Q_{\max}$ and $Q_{\min}$ in the figure. $Q_{\max}$ then is the value of Q when the products are in their ground states and $Q_{\min}$ is the value of Q when the product ion has reached its dissociation limit, i.e., when $U_p = D_0$, the dissociation energy. In the cases reported here, the neutral product is in its ground state.

Fig. 2 gives the Q curves for the two reactions resulting from ground state B^+ reactions with D_2 . The inclined lines represent the expected behavior for the persistent complex mechanism and for the stripping mechanism. The horizontal lines for $Q_{\max}$ and $Q_{\min}$ are obtained from the known thermodynamic data. It will be noted that for the reaction producing ground state products for energies close to the threshold the observed points fall on the complex line. For the reaction involving the excited product ion again the points fall close to the complex line but are consistently somewhat forward of it. These behaviors suggest that the projectile ion is interacting with both atoms of the target molecule.

The second point to notice is that the curves flatten out close to the expected thermodynamic limit consistent with the indicated electronic states of BD^+ . It would have been preferable to be able to obtain more points on the flat portion of the curves; however, at those energies the cross-sections of both of these reactions are very small, making the signal to noise ratio unfavorable for accurate measurements.

The flattening of the Q curve to a value approximating a thermodynamic limit indicated by the dissociation energy of the product diatomic ion and the heat of reaction is an interesting one since it has

been pointed out that this is not the expected behavior. It can be easily shown⁷ that for a reaction following the ideal spectator stripping mechanism that Q should decrease until a dissociation limit is reached and at this point the diatomic ion would no longer exceed its dissociation energy. Muckerman⁸ has carried out some trajectory calculations for the neutral-neutral reaction, $F + HD$ and has determined Q as a function of F atom kinetic energy. In the low energy region the Q curves approximate the behavior of Q for the ideal spectator stripping mechanism in which the "spectator" or non-reacting atom does not participate in the collision process. As the energy increases, however, the Q curve departs from the spectator stripping model curve and then goes through a maximum before once again declining. At no time does the Q curve reach the dissociation limit. This has been interpreted as indicating that an additional (high energy) mechanism is operating and becomes dominant at energies which are too high for the spectator stripping mechanism to allow formation of ionic molecular product. If this additional mechanism were characterized by a less negative Q value, one then would expect the Q curve to go through a maximum. This type of behavior has not yet been reported for ion molecule reactions and in all cases where attention was paid to instrumental resolution, the minimum value of Q closely approximated the thermodynamic limit.^{4,9,10} Clearly this point deserves further study and we plan to address ourselves to this matter in the near future.

Fig. 3d gives the velocity contour maps for the ground state ionic product, $BH^+(^2\Sigma^+)$, formed by reaction 1. The map corresponds to a B^+

ion energy of 18.5 eV. At this energy it is clear that the peak of the product distribution is ahead of the c.m. and that the reaction is proceeding by a direct mechanism. Conditions were unfavorable for obtaining a contour map at energies close to the threshold for this reaction. The reason for this is that the cross section is small² and falling with decreasing kinetic energy and the products are being spread over a larger laboratory scattering angle. These two factors result in contributing to a small signal to noise ratio, preventing the realization of an acceptable contour map. However, Fig. 2 at 0° in which Q is plotted vs. B⁺ kinetic energy shows that the low energy points are close to the line representing a persistent complex mechanism. This shows that the peak of the product distribution has the velocity of the center of mass, suggesting that the reaction is proceeding by long lived complex formation. Fig. 3 (a,b,c) gives the contour maps at three B⁺ ion kinetic energies for the reaction of ground state reactants to give the excited product BH⁺(²Π) as represented by equation 2. It will be noted that in the higher B⁺ velocity the peak of the BH⁺ ion velocity distribution is well forward of the center of mass, indicating a direct reaction. As the B⁺ kinetic energy decreases, the difference between the velocities of the peak of the BH⁺ distribution and the c.m. decreases, and at the lowest barycentric energy the distribution exhibits a high degree of symmetry about the line $\pm 90^\circ$ to the beam direction and passing through the center of mass. The symmetry of the contour is not perfect and the peak is somewhat forward of the c.m.; however, it does indicate a high degree of interaction between the B⁺ and both atoms of the target, suggesting

a lifetime for the complex of about one rotational period (10^{-12} sec) at the projectile ion kinetic energy indicated. Although the symmetry of the product ion velocity distribution about the line $\pm 90^\circ$ is a necessary criterion for complex formation, it is not a sufficient condition. For example, for endothermic reactions one would expect a symmetrical distribution of products at the reaction threshold. Another example is that hard sphere scattering is isotropic, so reactions that approximate such collisions may give product velocity distribution showing a high degree of symmetry about $\pm 90^\circ$. This type of reasoning has been applied in interpreting the results of the $\text{Kr}^+(\text{D}_2, \text{D})\text{KrD}^+$ reaction.¹¹

Supportive information that would be very illuminating would be a trajectory calculation using reliable potential energy surfaces. In the absence of such calculations, we have found that qualitative considerations of spin and symmetry restrictions coupled with orbital fillings frequently give one an insight into the situation.

In a previous discussion,¹ spin and symmetry restrictions on the intermediate $(\text{BD} \cdots \text{D})^+$, which could be formed from the various electronic states of the reactants $\text{B}^+ + \text{D}_2$ (or $\text{B} + \text{D}_2^+$) and the products $\text{BD}^+ + \text{D}$ (or $\text{BD} + \text{D}^+$), plus spin, symmetry and molecular orbital filling considerations of the BD^+ states arising from $\text{B}^+ + \text{D}$ (or $\text{B} + \text{D}^+$), led to the conclusion that while $\text{BD}^+(^2\Pi)$ could arise by direct mechanism, $\text{BD}^+(^2\Sigma^+)$ can arise only from an intermediate complex. The tables (Tables 1 and 2) of spin and symmetry restrictions for $\text{B}^+ + \text{D}_2$ (or $\text{B} + \text{D}_2^+$) reactants and $\text{BD}^+ + \text{D}$ (or $\text{BD} + \text{D}^+$) products going to and arising from intermediates are reproduced here again in order to facilitate the discussion of the

reaction of $B^+\tilde{X}(^1S_g) + D_2(^1\Sigma_g^+)$.

The reactions of $B^+(^1S_g) + D_2$ to form both $BD^+(\tilde{X}^2\Sigma^+)$ and $BD^+(^2\Pi)$ are endothermic. The correspondence of the endothermicity to the thermochemical value observed here implies that there are no activation barriers higher than the thermochemical ones. Furthermore, the reactions to form $BD^+(\tilde{X}^2\Sigma^+)$ and $BD^+(^2\Pi)$ both appear to proceed through a persistent complex formation.

We shall first discuss the product $BD^+(\tilde{X}^2\Sigma^+)$. While $B^+(^1S_g) + D_2(^1\Sigma_g^+)$ combine to form $(B^+---D_2) [^1\Sigma_{(g)}^+ (\text{linear}); ^1A' (C_s \text{ symmetry}); ^1A_1 (C_{2v} \text{ symmetry})]$ at the reaction asymptote, the $(B^+---D_2) (^1\Sigma_{(g)}^+; ^1A'; ^1A_1)$ intermediate does not connect smoothly to the lowest electronic state of $(B^+---D_2) [^1\Sigma_{(u)}^+; ^1A'; ^1B_2]$. The lowest $^1\Sigma^+$ electronic state of the intermediate must arise diabatically from the much higher lying reaction asymptote $B^+(^1P_u) + D_2$. The reactants $B^+\tilde{X}(^1S_g) + D_2$ combine along what must be a repulsive surface of a $(B^+---D_2)(^1\Sigma_{(g)}^+; ^1A'; ^1A_1)$ state, the repulsiveness of which could be somewhat mitigated due to the long range ion-induced dipole attraction $\frac{\alpha e^2}{2r^4}$ until it crosses the $(B^+---D_2)(^1\Sigma_{(u)}^+; ^1A'; ^1B_2)$ surface arising from $B^+(^1P_u) + D_2$ where there could be an adiabatic transition from the surface arising at the asymptote from $B^+(^1S_g) + D_2$ to the equilibrium region intermediate surface arising from $B^+(^1P_u) + D_2$. There is another pair of reactants $B\tilde{X}(^2P_u) + D_2(^2\Sigma_g^+)$ which can also combine to give $(B---D_2^+)(^1, ^3\Sigma_{(u)}^+ + ^1, ^3\Pi_{(u)}; ^1, ^3A + ^1, ^3A' + ^1, ^3A''; ^1, ^3B_2 + ^1, ^3A_1 + ^1, ^3B_1)$. However, it seems probable to assume little or no involvement of this latter surface since the products $BD^+\tilde{X}(^2\Sigma^+)$ and $BD^+(^2\Pi)$ arise from $B^+ + D$, and it seems to be a general phenomena that for these

types of ion-molecule reactions the charge remains with the atom on which it started, provided this atom had the lower ionization potential.

In the case of the $BD^+(^2\Pi)$ product the most probable intermediate $(BD---D)^+$ from which this product arises is the $(^3\Pi_{(u)}; ^3A' + ^3A''; ^3A_1 + ^3B_1)$ component of $(B---D_2)^+(^3\Sigma_{(u)}^+ + ^3\Pi_{(u)}; ^3A' + ^3A' + ^3A'')$; $^3B_2 + ^3A_1 + ^3B_1) \leftrightarrow (BD---D)^+(^1, ^3\Pi_{(u)}; ^1, ^3A' + ^1, ^3A''; ^1, ^3A_1 + ^1, ^3B_1)$ or $^1, ^3A_2 + ^1, ^3B_2)$ which arises from $B^+(^3P_u) + D_2$. While both $(B---D_2)^+(^1\Sigma_{(u)}^+ + ^1\Pi_{(u)}; ^1A' + ^1A' + ^1A''); ^1B_2 + ^1A_1 + ^1B_1)$ intermediates can arise from the higher reaction asymptotes $B^+(^1P_u) + D_2$ both of these surfaces would be expected to be considerably higher in energy than the (B^+---D_2) arising from $B^+(^3P_u) + D_2$. Since the experimentally observed endothermicity to form $BD^+(^2\Pi)$ from $B^+(^1S_g) + D_2$ is equivalent to the thermochemical endothermicity, this implies that the repulsive (B^+---D_2) $(^1\Sigma_{(g)}^+; ^1A'; ^1A_1)$ surface arising from $B^+(^1S_g)$ cuts the (B^+---D_2) $(^3\Pi; ^3A' + ^3A''; ^3A_1 + ^3B_1)$ surface at a point less than or equal to the thermochemical endothermicity. A surface crossing occurs with a change in spin from the singlet to the triplet surface and the $BD^+(^2\Pi) + D(^2S_g)$ arises from the corresponding $(BD---D)^+(^3\Pi; ^3A' + ^3A''; ^3A_1 + ^3B_1)$ or $^3B_2 + ^3A_2)$ surface.

Although this type of consideration cannot predict that the lifetime of the complex will be greater than the rotational period of the system, resulting in a velocity contour map with a symmetry about $\pm 90^\circ$, it does indicate that the collision complex undergoes rehybridization and extensive electronic rearrangement with all three atoms of the colliding species interacting strongly.

In addition to reactions of $B^+ + D_2$ which give rise to $D(^1S_g)$, we have also observed at higher energies reactions in which the deuterium atom was produced in excited states; however, studies of these reactions were not pursued.

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FIGURE CAPTIONS

Fig. 1 Energy spectrum of the BD^+ ions produced in the reaction $\text{B}^+(^1\text{S}_g) + \text{D}_2$: (a) $\text{BD}^+(^2\Pi)$, (b) $\text{BD}^+(^2\Sigma)$ and $\text{BD}^+(^2\Pi)$, (c) $\text{BD}^+(^2\Sigma^+)$ and (d) B^+ projectile.

Fig. 2 Variation of translational exoergicity (Q) vs. projectile ion translational energy for the reaction $\text{B}^+(^1\text{S}_g) + \text{D}_2$.

Fig. 3 $\text{BD}^+(^2\Pi)$ ion velocity distributions in cartesian coordinates in the center of mass system for barycentric energies: (a) 6.8 eV, (b) 8.1 eV, (c) 11.4 eV, and (d) $\text{BD}^+(^2\Sigma^+)$ at 4.9 eV. (x) indicates the most probable velocity of the ideal spectator stripping product at 0° and (+) indicates velocity of the center of mass of the system.

TABLE I. Spin and Symmetry Restrictions

Energy relative to
separated neutral
atoms (eV)

Reactants

TABLE I. (continued)

Products

$BH^+ + H$ (or $BH + H^+$)

Energy relative to
separated neutral
atoms (eV)

TABLE II. Spin and symmetry restrictions BH^+ .

Energy relative to
separated neutral
atoms (eV)

B^+ $1S_g$ $\downarrow C_{\infty V}$ $1\Sigma^+$	+	$H \longrightarrow BH^+$ $2S_g$ $\downarrow C_{\infty V}$ $2\Sigma^+$	$2\Sigma^+$ $\downarrow C_{\infty V}$ $2\Sigma^+$	8.296
B^+ $3p_u$ $\downarrow C_{\infty V}$ $3\Sigma^+$ 3Π	+	$H \longrightarrow BH^+$ $2S_g$ $\downarrow C_{\infty V}$ $2\Sigma^+$	$2,4\Sigma^+$ $\downarrow C_{\infty V}$ $2,4\Pi$	12.924
B $2p_u$ $\downarrow C_{\infty V}$ $2\Sigma^+$ 2Π	+	$H^+ \longrightarrow BH^+$ $1S_g$ $\downarrow C_{\infty V}$ $1\Sigma^+$	$2\Sigma^+$ $\downarrow C_{\infty V}$ 2Π	13.595
B^+ $1p_u$ $\downarrow C_{\infty V}$ $1\Sigma^+$ 1Π	+	$H \longrightarrow BH^+$ $2S_g$ $\downarrow C_{\infty V}$ $2\Sigma^+$	$2\Sigma^+$ $\downarrow C_{\infty V}$ 2Π	17.396

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CHARGE DISTRIBUTION IN ^{13}N IONS PRODUCED BY THE $^{12}\text{C}(\text{d},\text{n})^{13}\text{N}$ REACTION

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ABSTRACT

The short half life of ^{13}N requires that processing and synthesis steps be least time consuming as possible. A knowledge of the history of the ^{13}N from the time of its creation until its ultimate fate can frequently be of help in shortening the preparation time. In this study we have examined the charge distribution of ^{13}N produced by deuteron bombardment of carbon foils. The energy range covered was 8 MeV to 14 MeV. The ^{13}N ions produced were collimated, magnetically analyzed, and collected on a catcher foil which was scanned for activity with a Geiger counter. The peak of the charge distribution was at +3 to +4. Such energetic, highly charged ions rapidly lose their charge as they slow down by collision and do not undergo interesting chemical reactions until they reach epithermal energies and a charge of +1 or zero. Some of the ion-molecule reactions that take place as ^{13}N recoils through various gaseous materials and the ultimate products are discussed.

I. Introduction

In designing chemical syntheses incorporating nuclear recoils, one would like to know as much as possible about the creation and fate of those recoils. To this end we have measured the ionic charge state distribution of ^{13}N recoiling from the $^{12}\text{C}(\text{d},\text{n})^{13}\text{N}$ reaction. The energetic intermediates formed following this nuclear reaction depend on the state of the recoil. These intermediates in turn determine the ensuing kinetics and radiolysis in the synthetic medium.

A fast atomic ion travelling through matter picks up and loses electrons as dictated by its velocity-dependent charge-changing cross sections in that material. A beam of such ions displays a distribution of charges which attains equilibrium after passing through a number of atomic layers, on the order of $100^{(1)}$, that number depending on the ions' initial charge state and velocity. After attainment of equilibrium, all memory of the initial charge state is lost. Using heavy-ion accelerators, a number of workers have determined equilibrium charge state distributions for ^{14}N in various materials as a function of velocity.^(2,3,4,5) Charge state distributions of nuclear recoils have received relatively little attention, few studies having been reported to date,^(6,7,8,9) two of those dealing with recoils from simple elastic scattering,^(8,9) and none dealing with nitrogen. It is then still pertinent to ask whether the charge state distribution of recoils immediately after the nuclear reaction, the "instantaneous" distribution, is appreciably different from the equilibrium distribution. The present study attempts to shed some light on that question.

As recoils pass through matter, they lose kinetic energy through electronic excitation and ionization. Only when they have slowed to

about 1 keV or less do they begin to form stable molecular bonds. At this point, the most probable charge state is, in general, either +1 or 0. Accordingly, we have included a brief discussion of the chemical fate of ^{13}N recoils by considering literature data on reactions of N and N^+ .

II. Experimental

These experiments were carried out at the Tandem Van de Graaff facility at Edgewood Arsenal, Aberdeen Proving Grounds, Maryland. The accelerator provided up to 5 μA of deuteron beam current at the target after final beam shaping and collimation. The targets were self-supporting carbon foils mounted over 9 mm apertures. Their thicknesses were determined to within 10% by optical transmittance at 5460 $\text{\AA}$.⁽¹⁰⁾ As shown in figure 1, the deuteron beam passed straight ahead to a Faraday cup. The ^{13}N recoils were accepted at 22.5° to the deuteron beam, so the target was turned to this same angle to minimize the recoils' path through the target. The recoils were collimated and then passed into a dispersing magnetic field provided by an electromagnet and maintained at 3.3 kG as measured with a Hall effect gaussmeter. The recoils came to rest on a tantalum catcher strip, successive charge state peaks being separated by about 15 mm. After a 30 minute irradiation, the catcher was immediately removed and scanned with a properly shielded Geiger tube mounted on a carriage which could be advanced in precise steps along the catcher strip to measure the ^{13}N charge state spectrum. Maximum count rates at charge state peaks were about 400 cpm. Based on the 9.96 minute half-life of ^{13}N , these count rates were extrapolated back to a common time, zero, to normalize the spectra.

Because all excited nuclear states of ^{13}N are unstable to proton emission, only the ground state is detected in our experiments. This simplifies the kinematics associated with the charge state spectra, since for a given deuteron energy, only one ^{13}N energy results in the center-of-mass reference frame, this energy dictated by the 281 keV endothermicity of the $^{12}\text{C}(d,n)^{13}\text{N}$ reaction and momentum and energy conservation. However, the ^{13}N center-of-mass angle and thus its lab energy are double-valued functions of lab angle. For the deuteron energy range employed here and 22.5° ^{13}N lab angle, we observe ^{13}N corresponding to center-of-mass angles of 58° and 168° . The 168° group is unimportant here because it is of very low energy (less than 250 keV) and is slowed to such an extent by the target⁽¹¹⁾ that it is removed from our detection zone by the magnetic field and thus does not interfere with spectral resolution of the 58° group. The lab energies and differential cross sections for the 58° group and total reaction cross sections are listed in table 1 for deuteron energies employed in this work.

III. Results and Discussion

Examples of experimental results are shown in figure 2 for deuteron energies of 8, 10, and 14 MeV. The fraction of ^{13}N recoils of a given charge state, i.e., the probability of a recoil having that charge state, is plotted as a function of charge state. All charge states, 0-7, were sought, but charges 1, 6, and 7 were not detected, and, if present, constituted fractions of less than 0.05 each. Small amounts of neutrals detected are attributed to the slow group of recoils (168° center-of-mass angle). The shapes of these distributions resemble those reported for equilibrium distributions, because these particular runs employed relatively thick carbon targets, $30\ \mu\text{g}/\text{cm}^2$ or $1250\ \text{\AA}$; whereas

approximately $5 \mu\text{g}/\text{cm}^2$ is more than sufficient for charge equilibration at these energies. ^(1,16)

Our results at 10 MeV deuteron energy are plotted in figure 3 as a function of target thickness. On the right are included the literature ⁽¹⁶⁾ equilibrium charge state fractions. Because of low count rates, there is considerable statistical scatter; however, agreement with the equilibrium values is good, except for the thinnest target, $16 \mu\text{g}/\text{cm}^2$, where the increased fraction of N^{+5} may reflect an "instantaneous" average charge higher than the equilibrium value. These and other data are tabulated in table 2, where agreement with the equilibrium values is good at all deuteron energies for the thicker targets, but not the thinnest target at 10 MeV.

The average recoil charge calculated from the charge state fractions reported in table 2 are plotted as a function of ^{13}N recoil velocity in figure 4. The solid line represents the equilibrium values. ⁽¹⁶⁾ The values for $30 \mu\text{g}/\text{cm}^2$ targets (O) agree well with the equilibrium values. The only significant deviation from equilibrium is again in the data for the thinnest target (X).

Wolke and coworkers have observed nearly "instantaneous" non-equilibrium charge state distributions of ^{12}C ⁽⁸⁾ and ^{11}B ⁽⁹⁾ elastically scattered by deuterons by using extremely thin targets of carbon and boron, respectively. The average instantaneous charge was higher by 0.09 for ^{12}C recoiling at 4.4 MeV and by 0.31 for ^{11}B recoiling at 7 MeV. The difference in average charge was thought to be due to loss of electrons accompanying the sudden energetic recoil of the nucleus and passage of the fast deuteron through the electron cloud of the recoil. Those effects will also be present in our study but with an additional charge

of +1 due to the abrupt increase in atomic number resulting from pick-up of a proton by ^{12}C . We might then expect the average instantaneous charge on ^{13}N to be about 5, i.e., 1-1.5 units higher than the average equilibrium charge.

In our experiments, recoils originate over the entire thickness of the target, so that non-equilibrated instantaneous recoils originating near the exit side of the target are included in those we detect, regardless of the target thickness. The target thicknesses used in Wolke's work⁽⁸⁾, charge-changing cross sections^(17,18), and other considerations⁽¹⁾ lead to the conclusion that charge equilibration requires approximately $4\text{ }\mu\text{g}/\text{cm}^2$ of carbon for nitrogen ions in the velocity range pertinent to this study. Thus the last $4\text{ }\mu\text{g}/\text{cm}^2$ of our targets supply recoils not equilibrated upon exiting the target, and in sufficient quantities to be detected in our system judging from count rates observed per $\mu\text{g}/\text{cm}^2$ of target thickness. If the instantaneous charge of the recoils were +6 or +7, peaks for those charge states should have been observed. Their absence implies that the average instantaneous charge of ^{13}N recoils in these experiments is no greater than +5, in agreement with the conclusion reached above based on Wolke's work with elastic scattering.

As a recoil travels through matter it initiates a multitude of chemical reactions by ionization and charge transfer which also serve to slow the recoil to thermal energies. This process is very fast, on the order of 10^{-12} second in solids and 10^{-9} second in gases at atmospheric pressure based on published stopping power data.^(19,20) At the higher energies and charge states, relative collision energies are too great to permit formation of chemical bonds between recoils and atoms of the stopping medium. As the recoil slows its charge decreased (see

figure 4) until the average charge becomes +1 at about 200 keV. ^(2,4)
 Below about 1 keV kinetic energy, the recoil may begin to undergo atom transfer reactions, forming stable chemical bonds. Thus the primary species involved in labelling reactions are N^{+1} and N^0 .

We have reviewed the literature to gather a collection of reactions which N^{+1} and N^0 undergo, and these are listed in tables 3 and 4, respectively. These lists are by no means exhaustive but are intended to illustrate the general characteristics of these reactions and to provide starting points for understanding product distributions in specific media.

Each reactant in table 3, including N_2 , undergoes charge transfer as well as atom transfer reactions with N^+ . The formation of H_2^+ from H_2 and CCl_2^+ , CCl^+ , and Cl^+ from CCl_4 are endothermic for ground state N^+ (3P). These channels as well as many of the exothermic ones probably involve excited N^+ , specifically N^+ (1D) with 1.9 eV excitation energy and 300 second lifetime and N^+ (1S) with 4.1 eV excitation energy and 0.9 second lifetime. Many of the products, e.g. NH^+ from H_2 ⁽²²⁾, are probably excited as well.

Extensive reviews of N atom reactions do exist. ^(26,27,28,29) Much of the data in table 4 was obtained using "active" nitrogen and may involve electronically excited N atoms as is the case of reaction with N_2O where only excited N (2D) is reactive, not ground state N (4S). Atom transfer with N_2 proceeds only with excited N (2D) (excitation energy 2.38 eV, lifetime 26 hours) or with N (2P) (excitation energy 3.57 eV, lifetime 12 seconds), or with hot N (4S), but not thermalized N (4S). N atoms are apparently unreactive toward H_2 , NH_3 , SO_2 ⁽²⁷⁾, CO_2 ⁽³⁰⁾, and $COCl_2$ ⁽³¹⁾, reactions reported with these molecules having been due to contaminant gases adsorbed on vessel walls or excited

molecular nitrogen. Products are listed in the general order of decreasing abundance for the reactions with alkanes, alkenes, and alkynes.

Reactions such as those in tables 3 and 4 ultimately lead to ^{13}N -labelled products such as those listed in table 5 for ^{13}N recoils reacting with various media. Products are listed in order of decreasing abundance. Again, the list is not intended to be comprehensive. ^{13}N was produced by the reaction $^{12}\text{C}(\text{d},\text{n})^{13}\text{N}$ in the studies on NO , CO , CO_2 , CH_4 , CH_3OH , CH_3Cl , and CCl_4 . ^{13}N from $^{14}\text{N}(\text{n},2\text{n})^{13}\text{N}$ was used in the studies on NaNO_3 , NH_4F , $(\text{NH}_4)_2\text{SO}_4$, and NH_4NO_3 . ^{13}N from $^{16}\text{O}(\text{p},\alpha)^{13}\text{N}$ as well as ^{16}N from $^{16}\text{O}(\text{n},\text{p})^{16}\text{N}$ was used in studies on H_2O . As for the primary reactions, impurities are also expected to be extremely important here as made clear by detection of $^{13}\text{N}^{14}\text{N}$ and $^{13}\text{N}^{14}\text{NO}$ after recoil reactions in CO and CO_2 . To fully understand the entries in table 5, we must first gather more detailed information concerning reactant and product quantum states and velocity-dependent cross sections for the primary reactions and all radiolytic side reactions, particularly through the use of beam experiments. It may then become possible to design precise clean syntheses of radio-labelled products from first principles.

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FIGURE CAPTIONS

- Figure 1. Experimental arrangement used to observe the ^{13}N recoil charge state distribution.
- Figure 2. Examples of ^{13}N recoil charge state distributions from 30 g/cm^2 targets. Charge state fractions (probabilities) are plotted versus charge state for the three deuteron energies employed in this work.
- Figure 3. ^{13}N recoil charge state fractions versus carbon target thickness for 10 MeV deuteron energy. The equilibrium values (16) are shown on the right for charge states +2(O), +3(X), +4(+), and +5(@).
- Figure 4. Average ^{13}N recoil charge versus recoil velocity for 30 g/cm^2 targets (O) and 16 g/cm^2 targets (X). The solid line represents the equilibrium value (16) for ^{14}N in carbon.

TABLE 1 -- Reaction Parameters for $^{12}\text{C}(\text{d},\text{n})^{13}\text{N}$

Deuteron Energy (MeV)	^{13}N Recoil Energy At 58 ⁰ CM (MeV)	Differential (12-14) Cross Section At 58 ⁰ CM (mb/ster)	Total ⁽¹⁵⁾ Cross Section (mb)
8.0	2.31	5	110
10.0	2.90	4	90
14.0	4.08	1	60

TABLE 2 -- ^{13}N Charge State Distributions

Deuteron Energy (MeV)	^{13}N Charge State	Charge State Fraction for 30 $\mu\text{g}/\text{cm}^2$ Target	Equilibrium ⁽¹⁶⁾ Charge State Distribution	Charge State Fraction for 16 $\mu\text{g}/\text{cm}^2$ Target
8	2	0.190	0.115	
	3	0.397	0.432	
	4	0.330	0.383	
	5	0.083	0.069	

10	2	0.083	0.045	0.094
	3	0.317	0.322	0.193
	4	0.439	0.494	0.385
	5	0.162	0.140	0.328

14	3	0.176	0.151	
	4	0.462	0.523	
	5	0.362	0.326	

TABLE 3 -- Reactions of N^+

		<u>References</u>
H_2	---- $NH^+ + H, H_2^+ + N$	21, 22
N_2	---- $N_2^+ + N$	23
O_2	---- $NO^+ + O, O_2^+ + N, O^+ + NO$	21, 24
NO	---- $NO^+ + N, N_2^+ + O$	21
CO	---- $CO^+ + N, O^+ + C$	21
CO_2	---- $CO_2^+ + N, CO^+ + NO$	21
H_2O	---- $H_2O^+ + N, NO^+ + H_2$	21
NH_3	---- $NH_3^+ + N, NH_2^+ + NH, N_2H^+ + H$	21
CH_4	---- $CH_4^+ + N, CH^+ + NH, CHN^+ + H, HCN^+ + H + H$	21
CCl_4	---- $CCl_3^+, CCl_2^+, CCl^+, Cl^+, NCCl^+, NCl^+, CN^+,$ $NCCl_2^+$	25

TABLE 4 -- Reactions of N atoms.

		Reference
NO	----- $N_2 + O$	32
O_2	----- $NO + O$	33
N_2	----- $N + N + N$	30
SO	----- $NO + S$	27
X_2	----- $NX + X$ ($X = Cl, Br, I$)	34
HX	----- $NH + X$ ($X = Br, I$)	35
NO_2	----- $N_2O + O, 2NO, N_2 + 2O, N_2 + O_2$	36
O_3	----- $NO + O_2$	37
N_2O	----- $N_2 + NO$	38
SO_3	----- $SO_2 + NO$	27
PH_3	----- $NH + PH_2$	39
Alkanes	----- $HCN, NH_3, (CN)_2, CH_3CN, \text{Hydrocarbons}$	27
Alkenes	----- $HCN, CH_3CN, (CN)_2, NH_3, \text{Hydrocarbons}$	27
Alkynes	----- $(CN)_2, HCN, NH_3, NC_3H, \text{Hydrocarbons}$	27
$CHCl_3, CH_2Cl_2, CH_3Cl$	----- HCl, HCN	40
CCl_4	----- $ClCN, Cl_2$	40
CH_3OH, C_2H_5OH	----- HCN, H_2O	

TABLE 5 -- Products of ^{13}N Recoiling in Various Media

		Reference
NO	---- ^{13}NN , ^{13}NO	42
CO	---- ^{13}NN , ^{13}NNO	30
CO ₂	---- ^{13}NN , ^{13}NNO	30, 43
H ₂ O (l)	---- $^{13}\text{NH}_4^+$, $^{13}\text{NO}_3^-$, $^{13}\text{NH}_2\text{OH}$, $^{13}\text{NO}_2^-$ ^{13}NO , ^{13}NN	44, 45
NaNO ₃ (s)	---- $^{13}\text{NO}_3^-$, $^{13}\text{NO}_2^-$	45
NaNO ₃ (aqu)	---- $^{13}\text{NH}_4^+$, $^{13}\text{NO}_3^-$, $^{13}\text{NO}_2^-$	45
NH ₄ F (s)	---- $^{13}\text{NH}_4^+$, $^{13}\text{NH}_2\text{NH}_2$	45
NH ₄ (aqu)	---- $^{13}\text{NH}_4^+$, $^{13}\text{NO}_3^-$, $^{13}\text{NO}_2^-$, $^{13}\text{NH}_2\text{NH}_2$	45
NH ₄ NO ₃ (s)	---- $^{13}\text{NO}_3^-$, $^{13}\text{NH}_4^+$, $^{13}\text{NO}_2^-$, ^{13}NNO	46
(NH ₄) ₂ SO ₄ (s)	---- $^{13}\text{NH}_2\text{OH}$, $^{13}\text{NH}_2\text{NH}_2$, $^{13}\text{NH}_4^+$, $^{13}\text{NO}_3^-$	47
CH ₄	---- HC^{13}N , $^{13}\text{NH}_3$, $\text{CH}_3^{13}\text{NH}_2$, $\text{C}_2\text{H}_5^{13}\text{NH}_2$, $\text{CH}_3\text{C}^{13}\text{N}$, ^{13}NN	48, 49
CH ₃ OH	---- HC^{13}N , $\text{CH}_3\text{C}^{13}\text{N}$, ^{13}NN	49, 50
CH ₃ Cl	---- HC^{13}N , ^{13}NN , $^{13}\text{NO}_2$	50, 51
CCl ₄	---- ClC^{13}N	50, 51