Direct Observation of the Crossed Beam (Bimolecular) Reaction of Atomic Nitrogen with Halogens

Sir:

Using a recently developed beam source of atomic nitrogen,[1] it has now been possible to observe directly the products of a number of elementary biomolecular reactions of N atoms with halogen molecules: $N + XY \rightarrow NX + Y$ (where X, Y ≡ Cl, Br, I).

Despite extensive literature[2] on gas phase reactions of "active" nitrogen, there appear to be no experimental studies of N atom reactions under single-collision conditions. Questionable are the apparent bimolecular rate constants extracted from complex overall kinetic data acquired in these flowing afterglow, flame, or gas discharge experiments which involve ionic, excited, and metastable species.

The present experiments make use of the crossed molecular beam scattering technique.[3] An intense supersonic beam of nitrogen atoms is crossed at right angles with a thermal beam of halogen molecules; the NX product is observed over a range of scattering angles.

The apparatus is a modified version of the three-chamber differentially pumped beam machine previously described.[1] An arc-heated (~7000–15 000 K) supersonic nozzle beam source in the first chamber produces the "primary" beam, atomic nitrogen in an argon carrier. Dissociation of admixed N_2 (~5%) in the Ar arc is typically 50–70%.[4] The primary beam is collimated with a fired "lava" skimmer cone between the first and second chambers, followed by a 4.8-mm-diameter collimator in chamber 2. The distance between skimmer and crossed beam intersection zone is 35.4 cm. Chamber 3 contains the cross beam source and scattering detector. The thermal halogen beam is introduced (at a pressure of ~10 Torr upstream) through a heated 2.5-mm-diameter multichannel array source (with cryogenic shielding). The detection system (rotatable in the plane of the crossed beams) consists of an electron-bombardment ionizer, quadrupole mass filter (Extranuclear), and an ion counter (Channeltron multiplier). The ionizer entrance (9.1-mm diameter) is located ~7.6 cm from the scattering center; so the angular aperture of the detector is 6.9° (solid angle 0.012 sr).

The primary beam is square-wave modulated by a chopper in chamber 2. Synchronous counting techniques[5] extract the product signal from the "DC" background. The "AC" background, caused by a small fraction of metastable N_2 and Ar in the chopped primary beam, is minimized by placing the ion multiplier off axis from the quadrupole rods.

Typical N beam velocities, based on earlier measurements,[1] are ~3500 m s^{-1}. The average halogen velocity, calculated from the source temperature, ranges from 360 m s^{-1} for Cl_2 to 211 m s^{-1} for IBr. Thus the average relative translational energy of the reactants in the center-of-mass system is ~72, 79, and 81 kJ mol^{-1}, respectively, for $N + Cl_2$, Br_2 (and ICl), and IBr.

Figure 1 shows the results of two reactive scattering experiments, presented in the form of product mass spectra, i.e., counting rates for the specified mass filter (*m/e*) settings, with the detector at 7° with respect to the primary beam. The signal level "DIFF" is the readout of the synchronous counter, i.e., the difference between primary beam "on" and "off", expressed as a net counting rate. The error bars merely denote one standard deviation of the count rate.[6]

The product yield is proportional to the nitrogen atom flux in the primary beam and unrelated to the molecular N_2 content, implying bona fide N atom reactions (not due to excited N_2 molecules in the primary beam). Since the yield is also proportional to the intensity of the halogen beam the reactions are believed to be bimolecular.

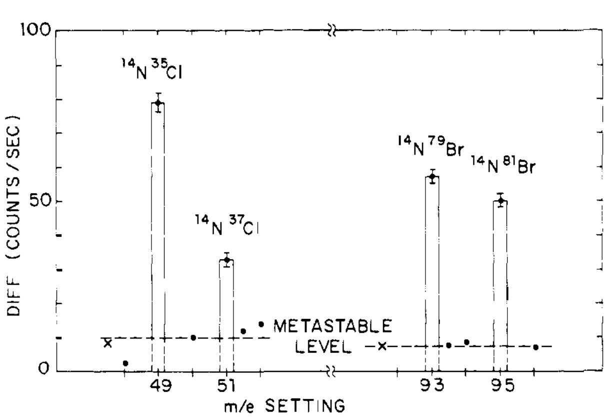

Figure 1. Early observations of NX product signal levels. Dots indicate the synchronous ion count rate ("DIFF"); × denotes the signal with ionizer off; dashed horizontal lines display the metastable level. The net, bona fide NX signal is that above the dashed lines. The NCl and NBr were, respectively, products of the reactions with ICl (June 1, 1977) and Br_2 (May 23, 1977).

Table I

Reaction	ΔE_0, kJ mol^{-1} [a]
$N + Cl_2 \rightarrow NCl + Cl$	−150
$N + Br_2 \rightarrow NBr + Br$	−80
$N + ICl \rightarrow NCl + I$	−180
$N + ICl \nrightarrow NI + Cl$ (not detected)	+50
$N + IBr \rightarrow NBr + I$ (>99%)	−100
$N + IBr \rightarrow NI + Br$ (<1%)	+20

[a] Estimated; literature bond dissociation energies for NX compounds are extremely uncertain (e.g., by tens of kJ mol^{-1}).

Using the value previously determined[1] for the N atom beam flux and a reasonable estimate of the halogen number density at the scattering center, assuming an overall detection efficiency of 10^{-5}, one calculates from the product count rate that the reaction cross sections are of the order of 10 Å^2, close to gas kinetic.

Listed in Table I are the reactions observed.

It is noted that the two NI-forming reactions are endoergic, requiring utilization of collision energy to reach thermodynamic threshold. Although observations of the angular distribution of the NX products are not yet fully analyzed, the most intense product signal levels are in the "forward" scattering direction, implying either a stripping mechanism or a long-lived complex decay route.[7] Electronic state correlation diagrams[8] support the latter; i.e., $N + XY \rightarrow [XNY] \rightarrow NX + Y$. The related reaction of atomic oxygen, $O + Br_2 \rightarrow Br + OBr$, is known to proceed via the complex mode.[9] The NX molecules are of intrinsic theoretical interest (e.g., isoelectronic with oxygen) and may be of practical importance in the field of chemical lasers. Further experimental[10] and theoretical[11] work on these and other N atom reactions is in progress.

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References and Notes

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(2) A. N. Wright and C. A. Winkler, "Active Nitrogen", Academic Press, New York, N.Y., 1968.
(3) D. R. Herschbach, *Pure Appl. Chem.*, **47**, 61 (1976).
(4) It is believed that the N atom beam consists primarily of ground-state (^4S) atoms, but it may contain[1] ≲25% of the low-lying metastable states (^2D and ^2P).

(5) J. A. Haberman, Ph.D. dissertation, University of Wisconsin, Madison, Wis., 1975.

(6) Although the apparent isotope ratio $^{14}N^{35}Cl/^{14}N^{37}Cl$ is close to the normal 3:1, that for the NBr deviates somewhat from the expected 1:1 owing to slight *m/e* "mistuning" of the mass filter, here operating at very high resolution. (There were experiments where the discrepancy was reversed and others where the proper 1:1 ratio was observed.)

(7) R. D. Levine and R. B. Bernstein, "Molecular Reaction Dynamics", Clarendon Press, Oxford, 1974.

(8) M. B. Faist, private communication.

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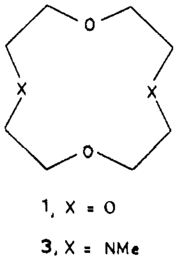
Complexation of Primary Alkylammonium Salts and Secondary Dialkylammonium Salts by *N,N*-Dimethyl-1,7-diaza-4,10-dioxacyclododecane

Sir:

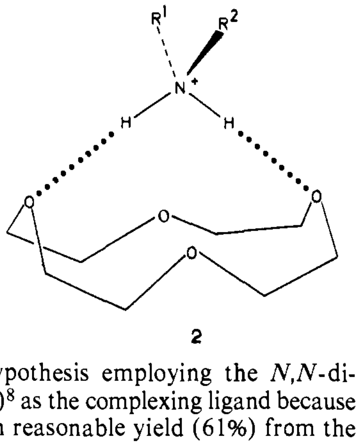
Since the discovery by Pedersen[1] that dibenzo-18-crown-6 forms complexes with ammonium and primary alkylammonium cations, as well as with metal ions, the design of highly structured molecular complexes has attracted the attention of several groups of investigators.[2-6] Recently, our own interests have been directed toward the search for a ligand which will form strong complexes with secondary dialkylammonium cations. Examination of Corey-Pauling-Koltun (CPK) molecular models led us to the belief that 12-crown-4 (**1**)[7] should bind secondary dialkylammonium cations through participation of their two acidic hydrogens on nitrogen in hydrogen bonding with a pair of diametrically opposed oxygens in **1** leaving the other two oxygens of **1** to act efficiently in the stabilization of the positive charge on nitrogen. Thus, the two-point binding model we propose for the cationic complex can be visualized to have structure **2**.



1, X = O

3, X = NMe

4, X' = NH



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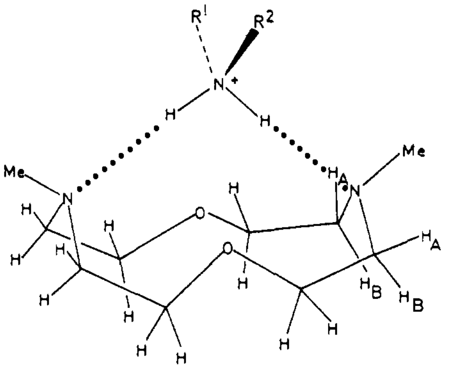
We have tested our hypothesis employing the *N,N*-dimethyldiaza-12-crown-4 (**3**)[8] as the complexing ligand because (i) it is easily obtainable in reasonable yield (61%) from the known[9] macrocyclic diamine (**4**) on, treatment (100 °C, 16 h) with $HCHO-HCO_2H$;[10] (ii) it contains suitable probes for rapid ^1H NMR spectroscopic investigation; and (iii) nitrogen containing crowns of large ring size are known[5,11] to form strong complexes with primary alkylammonium cations. We now report that **3** does indeed complex in organic solvents with secondary dialkylammonium perchlorates and thiocyanates[8] derived from Me_2NH (**5**), $(Me_2CH)_2NH$ (**6**), $(PhCH_2)_2NH$ (**7**), and piperidine (**8**). Moreover, the primary alkylammonium perchlorates and thiocyanates[8] derived from $MeNH_2$ (**9**), $MeCH_2NH_2$ (**10**), Me_2CHNH_2 (**11**), Me_3CNH_2 (**12**), $PhCH_2NH_2$ (**13**), and (*S*)-$PhCHMeNH_2$ ((*S*)-**14**) are also complexed by **3** in organic solvents.

Formation of 1:1 complexes with the amine salts **5**-(*S*)-**14**·$HClO_4$ and **5**-(*S*)-**14**·HSCN in CD_2Cl_2 was accompanied by significant chemical shift changes[12] in the ^1H NMR spectrum of **3** which exhibits a singlet at δ 2.42 for the NMe protons and triplets at 2.54 and 3.53 for the NCH_2 and OCH_2 protons, respectively. We have examined (Table I) the temperature dependences of the ^1H NMR spectra of all of these 1:1 complexes[12] as well as the "2:1 complexes" [13] formed between **3** and the amine salts **7**·$HClO_4$, **7**·HSCN, **12**·$HClO_4$, (*S*)-**14**·$HClO_4$, and (*S*)-**14**·HSCN. The kinetic and thermodynamic data obtained from these two sets of experiments have been interpreted in terms of two exchange processes: (i) the exchange of cations between opposite faces of **3** (examination of CPK space-filling molecular models indicates that such an exchange process must involve ring inversion of **3** as well as inversion at both nitrogens;[14] complete or partial dissociation of the complex must also occur; this exchange process is measured by the temperature-dependent ^1H NMR spectra for 1:1 complexes (see Table I) leading to $\Delta G^{\ddagger}_c$ values which we equate with free energies of activation ($\Delta G^{\ddagger}_{d+rni}$) for a face-to-face equilibration involving both dissociative and conformational inversion components); (ii) the exchange of cations with a single face of **3** in a process which must involve complete or partial dissociation of the complex (this exchange process may be measured by the temperature-dependent ^1H NMR spectra for "2:1 complexes" [13] leading to $\Delta G^{\ddagger}_c$ values which we equate with free energies of activation ($\Delta G^{\ddagger}_d$) for dissociation of complexes).

The temperature-dependent ^1H NMR spectra of the 1:1 complexes formed between **3** and the $R^1R^2NH_2^+X^-$ salts **5**-**8**·HX are consistent with complexes having C_{2v} symmetry as represented by the general structure **15**. At low temperatures, the signal (A_2) for the NCH_2 protons in all of these complexes separates into two signals (AB) of equal intensity reflecting the diastereotopic nature of the protons in the face-to-face complex **15**. The fact that the OCH_2 protons remain isochronous despite their diastereotopicity suggests that the hydrogen bonding in the complexes involves the nitrogens of **3** leaving the more electronegative oxygens free to participate in electrostatic stabilization of the charge on nitrogen in the cation. The two NMe groups are homotopic in **15** and so, not surprisingly, resonate as a singlet at low temperatures. However, the singlet for the NMe protons separates into two equal intensity singlets at low temperatures in the "2:1 complexes" involving **3** and **7**·HX reflecting equimolar proportions of complexed and uncomplexed **3**.



C_{2v} symmetry

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