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Molecular Beam Kinetics: Reactions of Alkali Atoms with NO₂ and CH₃NO₂

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Magnetic and electric deflection analysis of the scattering of Cs+NO₂ shows that the principal product is a paramagnetic, polar molecule. Magnetic analysis of the K+NO₂ system indicates that the scattered signal is paramagnetic; a similar study of Na+NO₂ shows a small yield of diamagnetic product. For the analogous reactions with CH₃NO₂ the product is diamagnetic and has a pseudo-first-order Stark effect. From these data and thermochemical arguments the principal alkali-containing products are identified as: for Cs+NO₂, a 2Σ electronic state of CsO; for Na+NO₂, probably a 2Π state of NaO; for M+CH₃NO₂, almost certainly MN₂O in a singlet state. The NO₂ results indicate that the ground state of the MO molecule changes from 2Π for LiO (the only species which had been previously observed) to 2Σ for CsO. The usual differential surface ionization detection fails for Cs+NO₂ and consequently only a very rough estimate of the scattering is obtained; this indicates that the total reaction cross section is \( \sim 100 \text{ Å}^2 \). For the CH₃NO₂ reactions differential surface ionization is applicable. Again the reaction cross sections are \( \sim 100 \text{ Å}^2 \) and increase as Na-+K-+Cs.

The c.m. product angular distribution is broad, with about the same intensity in the forward and backward hemispheres. These results are discussed in terms of the electronic structure of the reactant and product molecules and contrasted with reactions of alkali atoms with halogen-containing molecules. Scattering of related molecules has also been studied briefly, including RONO and R'ONO₂ (with \( R=\text{t-C₅H₁₁} \) and \( R'=\text{C₂H₅} \)), which give diamagnetic products with yields very similar to CH₃NO₂ and N₂O and R"OOR" (with \( R"=\text{t-C₄H₉} \)), for which only paramagnetic species were observed.

In the development of molecular beam kinetics, the dominant theme has been the elucidation of prototype modes of reaction dynamics by more and more detailed studies of a few simple reactions. However, this is now accompanied by a complementary theme which employs "chemical scanning" in relatively primitive experiments to pursue the fundamental goal of correlating the dynamics with electronic structure. The large family of reactions of alkali atoms with halogen-containing molecules has been much studied and the beam results generally confirm the chemical systematics mapped out in the early Polanyi flame experiments. The reaction cross sections, preferred direction of recoil of the products, attenuation of the elastic scattering, and other features of the reaction dynamics are found to be strongly correlated with the electrophilic character of the target molecule.

This paper describes an exploratory study of reactions of alkali atoms with NO₂, CH₃NO₂, and some related molecules. These systems appeared likely to be of special interest for comparison with some of the favorite halogen reactions. The electron affinity of NO₂ is high, perhaps higher than that of a diatomic halogen molecule \( x₂ \), but the electron affinities of the \( O \) atom and of NO are much lower than that of an \( X \) atom. Accordingly, whereas the diatomic halogen reactions are strongly exothermic and can proceed by a long-range electron transfer followed by almost immediate separation of the products,

\[ M+X₂→M^++X₂^{-}→M^+X^-+X, \]

the analogous NO₂ reactions are nearly thermoneutral and the ion-pair \( M^++NO_2^- \) corresponds to a "vibrationally activated" stable compound which undergoes unimolecular decay to form the products. Since the potential-energy surface is expected to contain a rather deep basin with a relatively restricted exit channel, the \( M^+NO^- \) complex can persist for times long compared to its vibrational and rotational periods. Evidence consistent with a "sticky" collision complex has indeed been found in a recent study of Cs+NO₂ nonreactive scattering. Another special feature considered here is
as evidence for lack of reaction since in the presence of NO$_2$ the Pt filament ionizes alkali compounds and alkali atoms with comparable efficiency,$^9$ just as W does, and NO$_2$ is likely to have the same effect. For the K+CH$_3$NO$_2$ system, the two filaments clearly show differential detection. This is interpreted in the usual way (W sensitive to both alkali compounds and atoms, Pt only to alkali atoms). Previous work has shown that hydrocarbons$^9$ or alkyl iodides$^{10}$ render the Pt filament insensitive to alkali halides; CH$_3$NO$_2$ may have a similar effect and at least it does not render Pt sensitive to the salt.

Electric Deflection

The electric deflection analysis$^{11,12}$ shown in Fig. 2 proves that there is a large yield of polar molecules in Cs+NO$_2$ scattering. The apparatus was the same as in Ref. 11. The ratio of the signals transmitted to the detector (W filament) with and without the field on is plotted versus the potential applied to the electrodes. If only nonreactive scattering$^{11}$ of the incident atoms were to occur for Cs+NO$_2$, the transmission at all angles would be similar to that observed at $\Theta=0^\circ$-$5^\circ$. The much lower transmissions observed at larger scattering angles can only be due to a polar molecule (which must contain Cs in order to be detected). The variation with the applied potential resembles that for the calibrating salt beam and thus indicates the product has a second-order Stark effect.$^{12}$ Since the deflection depends on the dipole moment and the mean translational velocity of the product molecules, both of which are unknown, only a rough estimate of the yield can be made. However, at $\Theta=30^\circ$ the product must comprise at least 40%-50% of the scattered signal. Comparison with results obtained for reactive scattering of alkali atoms from halogen compounds (assuming similar dipole moment and velocity distribution) suggests

![Electric Deflection Analysis](image)

**FIG. 2.** Electric deflection analysis for scattering of Cs+NO$_2$ at various laboratory angles ($\Theta$). Beam temperatures: $T$ (Cs) = 633 K, $T$ (NO$_2$) = 295 K. Results obtained with thermal calibrating beams of Cs atoms (O, 630 K) and CsCl molecules (□, 850 K) are included to indicate the deflecting power of the analyzing field.
that the reaction cross section is probably larger than
\(\sim 100\ \text{Å}^2\).

An electric deflection analysis of the product from the
Cs+CH₃NO₂ reaction has been reported elsewhere. At \(\Theta = 40^\circ\) this shows very strong attenuation of the
transmission at low voltage (25% at <3 kV), which indicates that the product has a pseudo-first-order
Stark effect.

**Magnetic Deflection**

Figure 3 shows the results of a magnetic deflection
analysis of the scattering of Na, K, Cs from NO₂ and
CH₃NO₂. The apparatus was the same as in Ref. 7; the magnet current used was 84 A, corresponding to a
field \(B = 11\ \text{kG}\) and gradient \(\nabla B = 28\ \text{kG/cm}\). The
ordinate in Fig. 3 gives the ratio of the signal at the
detector (W filament) with the magnet current on to
that with it off. As illustrated by the data included for
Na+propane, when only elastic scattering is possible
most of the signal can be deflected since it is due to
diamagnetic alkali dimer molecules in the
parent beam. For K+NO₂ and Cs+NO₂ practically the entire scattered signal must be paramagnetic, as the magnetic
analysis shows only the expected residual transmission. In view of the evidence for a large reaction yield from
Cs+NO₂ (Fig. 2), the magnetic moment of the product
molecule (or molecules) must be large, comparable to
that of an alkali atom. For Na+NO₂ the magnetic
analysis definitely shows a small diamagnetic contribu­
tion in excess of the residual transmission. Again, there
may also be a much larger yield of paramagnetic
product.

For Na, K, or Cs+CH₃NO₂ much higher values of
the transmission are observed, indicating a large yield
diamagnetic product. Good agreement is found (dashed curve in Fig. 3) with the transmission ratio calculated from the two-filament measurements assum­ing that the product is entirely diamagnetic. This calcu­
lation employs Eq. (13) of Ref. 7. The reaction yield
decreases in the order Cs > K > Na. Comparison with
similar results found for reactions of alkali atoms with
halogen compounds indicates that the reaction cross
section is \(\gtrsim 50\ \text{Å}^2\) for Na+CH₃NO₂ and \(\gtrsim 100\ \text{Å}^2\) for
Cs+CH₃NO₂.

**IDENTITY OF PRODUCTS**

The magnetic and electric deflection analyses clearly show that the principal alkali-containing products in
NO₂ and CH₃NO₂ reactions are different molecules. The identification of the products and determination of the reaction exothermicities is handicapped by uncer­tainties concerning the bond dissociation energies
and electronic structures of the products. However, it
is instructive to examine pertinent thermochemical
information and an empirical bond-strength–bond-length
relation. As shown in Fig. 4, this indicates that
MO+NO is the only product channel accessible in the
thermal energy, single-collision M+NO₂ reaction.

Of the MO molecules, only LiO has been observed in the
gas phase. The best available thermochemical data indicates \(D_0(\text{LiO}) = 83 \pm 4\ \text{kcal/mole}\). Two sets of
\(D_0(\text{MO})\) estimates found in the literature are
given in Table I (rows a and b); these are of obscure
origin and the uncertainty assigned to them is not
specified. Estimates we have obtained by use of an

![Fig. 3. Magnetic deflection analysis for scattering of Cs (□), K (Δ), and Na (○) atoms from CH₃NO₂ (open symbols), NO₂ (solid symbols), and for scattering of Na from propane (○). The dashed curve gives the transmission ratio calculated for K+CH₃NO₂ from the two-filament data of Fig. 1. Beam temperatures (in °K): \(T(\text{Cs}) = 95,\ \ T(\text{K}) = 670,\ \ T(\text{Na}) = 740,\ \ T(\text{CH₃NO₂}) = 295,\ \ T(\text{NO₂}) = 310,\ \ T(\text{C₂H₆}) = 294\).](image-url)
empirical correlation of alkali-halide data are also included in Table I (row c). This procedure assumes that the bonding in MO molecules is predominantly ionic, M+O⁻.

As shown in Fig. 5, the energy required to dissociate an alkali-halide molecule into ions, \( D_0(M^+X^-) \), correlates very well with the equilibrium bond length, \( r_e \). This energy is related to the dissociation energy to atoms, ionization potential of the alkali atom, and electron affinity of the halogen by

\[
D_0(M^+X^-) = D_0(MX) + I(M) - E(X).
\]

The data were taken from Ref. 21, and corrected to correspond to more recent values of the halogen-atom-electron affinities. The correlation of Fig. 5 indicates that the dissociation energy of an alkali halide can be estimated from its bond length to within about ±2 kcal/mole, which is about the same as the uncertainty in the \( D_0(MX) \) data.

Our estimates of \( D_0(MO) \) given in Table I were obtained from Fig. 5 and the O-atom-electron affinity of 34 kcal/mole by assuming \( r_e(MO) = r_e(MF) + 0.05 \text{ Å} \). The increment of 0.05 Å is suggested by the \( r_e \) values for KOH and CsOH found in recent microwave work, since we expect \( r_e(MO) = r_e(M-OH) \). Also, the estimate of \( r_e(LiO) \) obtained from the LiO vibration frequency suggests an increment of 0.07±0.03 Å. From Fig. 5, a variation of ±0.02 Å in the value adopted for \( r_e(MO) \) produces an uncertainty of ±2 kcal/mole in \( D_0(MO) \) for LiO and ±1 kcal/mole for the other MO molecules; this is included in the nominal limits given in Table I.

With our assumptions, the principal factor which decreases \( D_0(MO) \) below \( D_0(MF) \) is simply the electron affinity difference, \( E(F) - E(O) \approx 47 \text{ kcal/mole} \). Since the dipole moment data for alkali hydroxides again indicates ionic bonding, and since we expect \( r_e(MO) \approx r_e(M-OH) \), the same procedure predicts

\[
D_0(M-OH) = D_0(MO) + E(OH) - E(O).
\]

From photodetachment work, \( E(OH) = 42 \text{ kcal/mole} \) is accurately known. Thus, we expect \( D_0(M-OH) \) should be about 8 kcal/mole larger than the corresponding \( D_0(MO) \) values listed in Table I. Values of \( D_0(M-OH) \) have been derived by application of the third law to alkali-seeded flames, assuming thermal equilibrium between M, H, MOH, and HOH in the flame. These values are higher than the estimates of \( D_0(M-OH) \) we obtain, by 11, 2, 7, and 13 kcal/mole, respectively, for M=Li, Na, K, Rb, and Cs. The discrepancy for the Li and Cs cases is large enough to be significant and deserves further study.

Since no thermochemical data are available for MON, MO₂, MN, or MNO₂ molecules, we again invoke the correlation of Fig. 5 in order to place rough bounds on the location of channels involving these species. The bonding may not be dominantly ionic in all cases, but if not the true \( D_0 \) presumably will be smaller than that estimated for ionic bonding. Of these molecules, only NaNO₂ has been observed in the gas phase. The vibrational spectrum of LiON has been obtained in a matrix isolation study. This indicates the molecule is bent (\( \angle \text{LiON} = 110°±10° \)) with the Li-O distance (1.65±0.04 Å) longer by ~0.05–0.13 Å than \( r_e(\text{LiF}) \). The fact that the O-N stretching frequency is only 20% higher than that expected for the nitroso ion, NO⁻, suggests that the bonding is predominantly ionic, Li⁺(ON)⁻. A recent photodetachment experiment gives 2.0 kcal/mole for the electron affinity of NO, considerably below the value of 20 kcal/mole cited in current reviews. Thus, \( D_0(M-ON) \) is expected to be less than \( D_0(MO) \) by at least \( E(O) - E(NO) \approx 32 \text{ kcal/mole} \). The corresponding lower limit for the endothermicity for production of MON+O is indicated in Fig. 4; the actual endothermicity is probably considerably larger since the separation of charge centers in M⁺(ON)⁻ is substantially larger than in M⁺O⁻. Similarly, from \( E(O_2) = 10 \text{ kcal/mole} \), we estimate

\[
D_0(M-OH) = D_0(MO) + E(OH) - E(O).
\]

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\[
D_0(M-OH) = D_0(MO) + E(OH) - E(O).
\]
$D_0(M-O_2)$ to be less than $D_0(MO)$ by at least 24 kcal/mole. From $E(N)\approx 0$, which is now well established, and from bond-length estimates which indicate $r_e(M-N)\approx r_e(MO)$, we estimate $D_0(MN)$ to be less than $D_0(MO)$ by about 30 kcal/mole. Much higher estimates of $D_0(MN)$ are cited in tabulations but these were based on the assumption that $E(N)$ was comparable to $E(O)$ and on bond-length estimates which now appear too small. Finally, Fig. 4 includes a rough estimate of the likely range for $D_0(M-NO_2)$. Again the charge separation was merely taken equal to $r_e(MO)$, which probably overestimates $D_0$. Although there is abundant evidence showing that the electron affinity of NO$_2$ is large, at present its magnitude is quite uncertain. Values between about 45 and 90 kcal/mole have been derived from various surface-ionization and charge-transfer experiments. Thus, there is a corresponding wide range in our estimate of $D_0(M-NO_2)$ and in the location of the asymptote for the ion-pair state, $M^+\cdot NO^-_2$.

The ON–O dissociation energy is 72 kcal/mole and the mean thermal energy available in relative translation and in rotational excitation of NO$_2$ is only $\sim 2$ kcal/mole. The large reaction cross section for Cs+NO$_2$ indicated by the data of Fig. 2 therefore requires that $D_0\geq 70$ kcal/mole for the Cs-containing reaction product. According to Fig. 4, the product must be CsO and the reaction exoergicity is small, probably less than 5–10 kcal/mole. Both the electric and magnetic deflection analyses are consistent with CsO as the product. The lowest-lying electronic states of an MO molecule must be $\Pi$ and $\Sigma$, in order to correlate with the ion-pair configuration $M^+(1S)+O^-(2P)$ as well as with $M^*(2S)+O^*(2P)$. A second-order Stark effect, as observed, is expected for a $\Pi$ as well as for a $\Sigma$ electronic state, because even for quite modest rotational energy the rotational angular momentum is large (e.g., $J\approx 30h$ for $\sim 1$ kcal/mole, typical in other alkali reactions). However, the observed paramagnetic behavior of the product from Cs+NO$_2$ indicates a $\Sigma$ state. For a $\Pi$ state, the $\Pi_{1/2}$ component is diamagnetic and even for the $\Pi_{3/2}$ component the electronic magnetic moment would be expected to couple strongly to the internuclear axis and hence to exhibit a weak rotational-averaged interaction with the deflecting field.

Thus, we conclude that Cs+NO$_2$ produces a large yield of CsO in a $\Sigma$ state. In view of the small reaction exoergicity, this is quite likely the ground state. In contrast, for LiO deflection experiments have shown the ground state to be $\Pi$. An electronic structure calculation for LiO gives a $\Pi$ ground state but also predicts a $\Sigma$ state lying only $\sim 8$ kcal/mole higher. The diamagnetic contribution found in Fig. 3 for Na+NO$_2$ indicates the reaction produces NaO in a $\Pi$ state. At present, we have no way to determine whether the larger paramagnetic component found for this system also arises in part from reactive scattering; if so, it would indicate that the $\Sigma$indicates the reaction is probably somewhat endoergic. For K and Rb+NO$_2$, our data does not reveal whether any of the scattering is reactive. From Table I we expect that these systems may also give substantial yields of KO and RBO, and if so the paramagnetic behavior again corresponds to a $\Sigma$ state for KO.

For the M+CH$_3$NO$_2$ reactions our deflection data clearly indicate that MNO$_2$ is the product and thereby imply a lower limit for $D_0(M-NO_2)$ of 54 kcal/mole, the H$_2$C–NO$_2$ bond dissociation energy. This is indicated in Fig. 4. Reaction to form MO offers the only other exoergic path. The observed pseudo-first-order Stark effect and diamagnetic behavior are incompatible with either the $\Sigma$ or $\Pi$ states of MO, however, whereas these properties are expected for MNO$_2$, which is a near-symmetric-top rotor and should have a $\Pi$ ground state.

**KINEMATIC ANALYSIS**

In Fig. 1, the prominent bulge in the Rb+NO$_2$ scattering curves on the positive angle side suggests that in the region $\Theta\sim 30°–100°$ there is a large extra contribution, with intensity up to 5 times greater than the ordinary elastic scattering. If this bulge is assumed to be due solely to reaction product, the corresponding product angular distribution can be roughly evaluated by deducting an extrapolated contribution from elastic scattering. A curve obtained in this way is included in Fig. 6. However, a marked enhancement of the wide-
angle scattering from Rb+NO₂ is expected even if reaction does not occur (i.e., if the RbO bond strength proves to be on the low side of our estimate in Table 1). If a “sticky” collision complex is formed with lifetime long compared to its rotational period, nonreactive as well as reactive decay of the complex will enhance the intensity in the backward hemisphere of the center-of-mass system. This indeed corresponds to the bulge region in the laboratory system, as seen in Fig. 7. If the reactive channel is significantly endoergic, as it may be for RbNO₂, nonreactive decay will be dominant. Studies of several three- and four-atom collision complex systems have found that even when the reactive channel is fairly exoergic, nonreactive decay remains competitive.

There is also a purely kinematic effect which contributes to the bulge, whether or not complex formation occurs. The transformation of intensity between the center-of-mass (θ, u) and laboratory (Θ, v) systems for ordinary elastic scattering is given by

$$I_{LAB}(\Theta) = I_{c.m.}(\theta)/G(u, v, \delta),$$

where

$$G(u, v, \delta) = \frac{(u/v)^2 \cos \delta}{\cos \alpha}.$$
OTHER REACTIONS

Figure 8 gives magnetic analysis results for some other nitrogen oxides, including nitrous oxide, ethyl nitrate (R₂ONO₂), and iso-pentyl nitrite (R₃ONO). These were chosen because they had been studied in the early sodium flame work, in which NaO was assumed to be the product in each case.

For N₂O only a few measurements were made since the vapor pressure was too high for the present apparatus and the background pressure rose to about 10⁻⁸ torr. The data indicate that at least within the range Θ=0°-30° the scattering of Cs+N₂O gives only paramagnetic species. This may be due to lack of reaction or, as with NO₂, to formation of paramagnetic CsO.

The results for the alkyl nitrate and nitrite are similar to those for nitromethane (labeled R₂ONO₂ in Fig. 8), and again indicate a large yield of diamagnetic product. Attempts to carry out two-filament measurements of the scattering for these compounds failed due to severe poisoning of both the W and Pt filaments. The alkyl nitrite was especially bad; e.g., a brief exposure of the W filament to this gas would render it insensitive to both alkali atoms and alkali salts and the effect persisted for hours. The poisoning did not cause difficulty in the magnetic deflection experiments because the additional collimation and cold trapping used provided good shielding of the detector.

The identity of the products remains an open question in the nitrate and nitrite reactions. For both these compounds the reaction is likely to proceed by rupture of the alkoxide-nitrogen bonds (R₂O-NO₂ or R₃O-NO), as the dissociation energies are only ~35-40 kcal/mole. Rupture of the C-O bond is less likely since the dissociation energy in these compounds is probably about 90 kcal/mole (in analogy to alcohols⁵⁰). Thus, in the nitrate reaction, the likely products are MNO₂ and the alkali alkoxide, MOR₂; in the nitrite reaction, MON or MOR₄. The alkoxide salt is the more likely product in the nitrite case since Dₛ(M-O-R) is probably less than 35-40 kcal/mole. Activation energies for reactions of Na with alcohols indicate Dₛ(Na-OR)~95 kcal/mole.⁴⁴ In this context, it is of interest that the scattering, particularly for Cs, is more closely similar for R₂ONO₂ and R₃ONO₂ than for R₂ONO, as this suggests R₃ONO₂ may give MNO₂ as the principal product and R₂ONO may give MOR₄. A brief magnetic deflection study of K+2-butyl peroxide scattering was also made, to look for evidence of an alkali–alkoxide product formed directly by rupture of the weak oxygen–oxygen bond. The data covered only the region Θ=0°-30°, but showed no evidence of a diamagnetic product, in contrast to the alkyl nitrate and alkyl nitrite systems.

DISCUSSION

In the context of the electron-jump model for alkali-atom reactions, the NO₂ case has some aspects not yet encountered with other reactions: the possible role of excited electronic states of the NO₃⁻ ion and participation of spin-triplet as well as spin-singlet configurations. The initial "covalent" configuration, M(S) + NO₃(2A¹), can interact with at least three ionic configurations,

\[ \text{M}^+(5S) + \text{NO}_3^-(4A_1), \quad (I) \]
\[ \text{M}^+(5S) + \text{NO}_3^-(4B_1), \quad (II) \]
\[ \text{M}^+(5S) + \text{NO}_3^-(4B_2), \quad (III) \]

all of which can correlate with the product configuration, MO(Σ) or Π) + NO(Π). Route I involves the ground electronic state of NO₃⁻, derived from the 6a₁ molecular orbital that contains the odd electron in the NO₃ ground state.⁴⁷ Route III involves the lowest singlet excited state, derived from the 2b₁ molecular orbital, the lowest unoccupied orbital in NO₃. From spectra of nitrite compounds in solution and solid phase, this 1B₁ state of NO₃⁻ is known to lie ~74 kcal/mole above the ground state.⁴⁸ Route II involves the corresponding 1B₁ state, which is expected to be the lowest-lying triplet state of NO₃⁻. This state has not been reported but it should lie below the known 1B₁ state by ~10-15 kcal/mole.⁴⁹ The deep potential-energy basin corresponding to formation of the MNO₂ ground state almost certainly correlates only with Route I.
However, the reactants M+NO₂ approach in a triplet configuration in 3/4 of the collisions. In these triplet collisions, electron transfer to form singlet NO₂⁻ is strongly forbidden and only Route II or some other excited triplet path is available.

Our rather limited experimental results bring out two significant features of the NO₂ reaction dynamics: (1) At least for Cs, the reaction cross section is very large, Q₀ ≈ 100 Å². For Na it is probably smaller, although still substantial, whereas for K and Rb our data give no definite evidence whether or not reaction occurs. (2) For the Cs case, more than 50% of the scattering near 30° is due to reaction (as shown by the electric deflection analysis of Fig. 2). Property (1) can be reasonably attributed to the electron-transfer process. However, because of the large polarizability of Cs, the large Q₀ can probably also be accounted for by ordinary van der Waals forces, as in some other reactions, provided that the triplet collisions can lead to reaction. Property (2) implies that a substantial fraction of the triplet collisions do indeed produce reaction rather than nonreactive scattering.

At present, the role of the singlet Routes I and III cannot be assessed, although one or both are likely to contribute to reaction. The covalent-ionic curve-crossing radius, given by r₉,αΔ with Δ the asymptotic energy of the M⁺+NO₂⁻ ion pair (see Fig. 4 for Route I), can become extremely large if the NO₂ electron affinity is very high. Thus, e.g., for E(NO₂) = 83 kcal/mole, r₉ ≈ 50 Å for Cs and ~20 Å for K; ~9 Å for Na or 18 Å for Li. The electron transfer in such a case is expected to be severely inhibited for the Cs, Rb, K reactions unless use is made of an excited electronic state, as in III, for which Δ and r₉ become much smaller. This curious situation was the original motivation for our study, as the charge-transfer process

\[ \text{NO}_2^+ + \text{Cl}^- \rightarrow \text{NO}_2^- + \text{Cl} \]

had been reported to occur rapidly at very low collision energies, implying that \( E(\text{NO}_2^-) \geq E(\text{Cl}^-) = 83 \text{ kcal/mole} \). As noted in Fig. 4, the value of \( E(\text{NO}_2^-) \) is now far more uncertain than it appeared to be a few years ago. A value of ~90 kcal/mole obtained from the surface ionization method remains provisional, pending identification of the negative ions formed. For a time, a value decidedly below 83 kcal/mole but probably above about 45 kcal/mole was indicated by experiments involving titration of NO₂ by various negative-ion species. However, the most recent study of this kind has shown that the charge-transfer cross section increases rapidly with decreasing ion velocity. Consequently, it appears now that \( E(\text{NO}_2^-) > 83 \text{ kcal/mole} \) may hold after all, although a definitive result has to await experiments with well-defined ion velocity. If \( E(\text{NO}_2^-) \sim 45 \text{ kcal/mole}, r₉ \) would be small enough (~8 Å) to allow even the Cs reaction to proceed via the ground state, as in Route I.

Ironically, the question whether M+NO₂ forms a collision complex remains unanswered. It calls for mass spectroscopic detection and spin selection. In any case, these reactions may find application as a means to generate MO molecules for spectroscopic studies in electric resonance or matrix isolation experiments.

The electronic structure of the MO molecules is of interest since these are simple open-shell systems and can be compared with the extensively studied alkal fluorides and alkaline-earth oxides (which have one more valence electron). Our finding that the ground state appears to change from II for LiO to Σ for CsO is anomalous according to the simplest ionic model. The electron donated by the alkali atom might be expected to enter the 2π oxygen orbital along the inter-nuclear axis, leaving a hole in the 2π orbital and hence giving a Σ ground state (πσ⁹ molecular orbital configuration). The anomaly can be plausibly attributed to a size or polarization effect. For Li or Na, the ionic radius of M⁺ is less than that of O⁻, whereas for K, Rb, Cs the opposite holds. When M⁺ is the larger ion, the Coulombic interaction might actually be maximized with the alkali-valence electron in the 2π orbital, which is much more polarizable than the 2π orbital; this would provide a Σ ground state (πσ configuration). Another viewpoint is suggested by inspection of the SCF-MO calculations. In LiF...RbF, the uppermost filled σ orbital is predicted to lie below the uppermost filled π orbital (πσ⁹ configuration), but the energy difference is small even for LiF (0.033 a.u.) to NaF (0.014 a.u.) to KF (0.008 a.u.) to RbF (0.001 a.u.). The trend correlates with orbital composition. The uppermost π and σ in LiF are almost entirely 2p orbitals of F, whereas in RbF they contain a much larger admixture of Rb orbitals, particularly the 4p orbital. The decreased nuclear charge of O as compared to F will enhance such mixing in the MO molecules. In LiO, although the order of orbitals (σπ⁹) is predicted to be the same as in LiF, the energy difference has decreased threefold (to ~0.01 a.u.) A similar trend is discernible in the BeO...SrO series, although obscured by the shorter internuclear distance and other effects. A πσ⁹ ground-state configuration is predicted for MgO and SrO.

Beyond a formal analogy, reactions of alkali atoms with CH₃NO₂ and CH₃I are comparable in terms of the energy available. The strength of the bonds broken is the same (54 kcal/mole) and that of M-NO₂ is probably quite close to MI (76 kcal/mole). However, in addition to the steric difference, CH₃NO₂ probably presents a qualitatively different case for the electron-jump process. The bonding in CH₃NO₂ evidently involves overlap of an sp³ orbital on C with an sp³ orbital on N (derived from the 6a₁ orbital of NO₂). This is consistent with the microwave spectrum which shows the C-N bond is coplanar with the NO₂ group. The electron affinity of CH₃NO₂ thus should be much smaller than for NO₂, as the C-N bond utilizes the orbital...
which receives the last electron in NO$_2^\cdot$. Accordingly, the alkali reaction is expected to involve only the ground electronic state as in the CH$_3$I case. In CH$_3$NO$_2$, however, there is a low-lying vacant orbital formed from constructive overlap of the out-of-plane $p$ orbitals of the N atom and the two O atoms (derived from the $2b_1$ orbital of NO$_2$). It seems likely that this orbital can accept an electron from an attacking alkali atom without causing dissociation of the molecule, in contrast to the situation expected for the CH$_3$I molecule.\(^{48}\) If so, the repulsive interaction which appears to dominate the CH$_3$I reaction dynamics\(^{44}\) should be much weaker or absent from CH$_3$NO$_2$. The electron affinity may even be large enough (perhaps $\sim$10 kcal/mole) to enable the alkali atom to form a charge-transfer collision complex.

For the CH$_3$NO$_2$ reaction we find: (1) The product angular distribution (c.m. system) puts comparable intensity in the forward and backward hemispheres, whereas CH$_3$I gives strongly backward recoil. (2) The product is almost certainly KNO$_2$ in a $1^4A_1$ state, as expected if the reaction involves the ground electronic state of CH$_3$NO$_2$. (3) The reaction cross section $Q_r$ is definitely larger by a factor of about 2 or 3 than for CH$_3$I. (4) The magnitude of $Q_r$ decreases as Cs $\rightarrow$ K $\rightarrow$ Na, the same trend found for the CH$_3$I case.\(^{48}\) At present, these properties appear to be compatible with either a direct reaction mechanism of the sort that accounts for the CH$_3$I reaction dynamics or with a collision complex mechanism.

In the direct regime, as demonstrated by Monte Carlo trajectory calculations for the CH$_3$I case,\(^{44}\) the product angular distribution tends to become isotropic as $Q_r$ increases. For CH$_3$NO$_2$, a special effect may also operate, since presumably the need to attack a central bond rather than a peripheral bond makes the reaction much more probable for “broadside” collisions (M atom approaching more or less perpendicular to the C–N bond) than for “end-on” collisions. This steric effect alone might enhance $Q_r$ considerably as compared with CH$_3$I, due to the statistical predominance of broadside collisions in experiments with randomly oriented target molecules. Elegant experiments with CH$_3$I molecules aligned in an electric field have shown that the reaction probability strongly favors end-on collisions in that case.\(^{48}\) A preference for broadside reaction of CH$_3$NO$_2$ would be expected to foster sideways peaking or isotropy in the product angular distribution. In broadside collisions, the angular momentum associated with the initial impact parameter will go primarily into rotation about the C–N bond direction. In a direct reaction, that tends to be the direction of separation of the products, and hence in broadside orientations the collisional angular momentum will not go primarily into the relative motion of the products, as usual. This situation fosters sideways or isotropic scattering because it offsets the “glory form factor” associated with the azimuthal distribution of impact parameters, which ordinarily enhances the intensity forward or backward with respect to the initial relative velocity vector.\(^{47}\)

If the reaction proceeds via a collision complex with lifetime long compared to its vibration–rotation periods, the product angular distribution must show forward–backward symmetry. Although the cross section for complex formation may well depend on the orientation of the target molecule, this will not show up in the product angular distribution, which is determined solely by the partitioning of angular momentum between relative motion and rotation.\(^{39}\) The product distribution would be expected to show fairly strong forward–backward peaking, as a consequence of the large magnitude of $Q_r$ which implies the angular momentum of the complex is large. Unlike the collision complex systems previously studied,\(^{39},\)\(^{50}\) the nonreactive scattering of K$+\text{CH}_3\text{NO}_2$ does not display a “bump” at wide angles from decay of the complex to reform the reactants. This cannot be taken as evidence against a complex mechanism, as the exoergicity and the number of degrees of freedom are substantially larger for the CH$_3$NO$_2$ case, and both promote reactive decay of the complex.

The CH$_3$NO$_2$ reaction merits further study. The form of the product angular distribution can be resolved by velocity analysis and it should reveal whether the mechanism is direct (with isotropic or sideways scattering) or complex (symmetric forward–backward scattering). The orientation technique\(^{56}\) appears particularly promising for CH$_3$NO$_2$, by virtue of the large $Q_r$, the expected preference for broadside reaction, and the strong Stark effect arising from a very large dipole moment and from the presence of free internal rotation.\(^{48}\)

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1 For recent reviews, see (a) J. P. Toennies, Ber. Bunsenges. Physik. Chem. 72, 927 (1968); (b) E. F. Greene and J. Ross, Science 159, 587 (1968); (c) J. C. Polanyi, Discussions Faraday Soc. 44, 293 (1967).


Accordingly, in the magnetic deflection analysis clearly indicates a paramagnetic product large reaction cross section ever, at the source pressures used (dimerized, large deflections seen in Fig. 2.

If multiple collisions occurred or if the NO beam were dimerized, MNO and MNO2 would be possible products. However, at the source pressures used (0.5 torr), multiple scattering should be negligible and NO should be a minor constituent of the NO2 beam (21%). The observed reactive scattering (Fig. 2) could not be attributed to NO2, without postulating a ridiculously large reaction cross section (~10^8 A^2). Furthermore, the magnetic deflection analysis clearly indicates a paramagnetic product and thus excludes MNO2 and MNO.


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