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Molecular Beam Kinetics: Reactions of Alkali Atoms with NO_2 and CH_3NO_2

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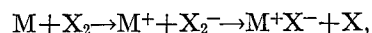
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Magnetic and electric deflection analysis of the scattering of $\text{Cs}+\text{NO}_2$ shows that the principal product is a paramagnetic, polar molecule. Magnetic analysis of the $\text{K}+\text{NO}_2$ system indicates that the scattered signal is paramagnetic; a similar study of $\text{Na}+\text{NO}_2$ shows a small yield of diamagnetic product. For the analogous reactions with CH_3NO_2 , 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 $\text{Cs}+\text{NO}_2$, a ${}^2\Sigma$ electronic state of CsO ; for $\text{Na}+\text{NO}_2$, probably a ${}^2\Pi$ state of NaO ; for $\text{M}+\text{CH}_3\text{NO}_2$, almost certainly MNO_2 in a singlet state. The NO_2 results indicate that the ground state of the MO molecule changes from ${}^2\Pi$ for LiO (the only species which had been previously observed) to ${}^2\Sigma$ for CsO . The usual differential surface ionization detection fails for $\text{Cs}+\text{NO}_2$ and consequently only a very rough estimate of the scattering is obtained; this indicates that the total reaction cross section is $\sim 100 \text{ \AA}^2$. For the CH_3NO_2 reactions differential surface ionization is applicable. Again the reaction cross sections are $\sim 100 \text{ \AA}^2$ and increase as $\text{Na} \rightarrow \text{K} \rightarrow \text{Cs}$. 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 $\text{R}'\text{ONO}_2$ (with $\text{R} = i\text{-C}_5\text{H}_{11}$ and $\text{R}' = \text{C}_2\text{H}_5$), which give diamagnetic products with yields very similar to CH_3NO_2 , and N_2O and $\text{R}''\text{OOR}''$ (with $\text{R}'' = i\text{-C}_4\text{H}_9$), 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.¹ 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.² 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.³ 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 NO_2 , CH_3NO_2 , 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 NO_2 is high, perhaps higher than that of a diatomic halogen molecule X_2 , but the electron affinities of the O atom and of NO are much lower than that of an X atom.⁴ 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,



the analogous NO_2 reactions are nearly thermoneutral and the ion-pair $\text{M}^+ + \text{NO}_2^-$ 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_2^- 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 $\text{Cs}+\text{NO}_2$ nonreactive scattering.⁵ Another special feature considered here is

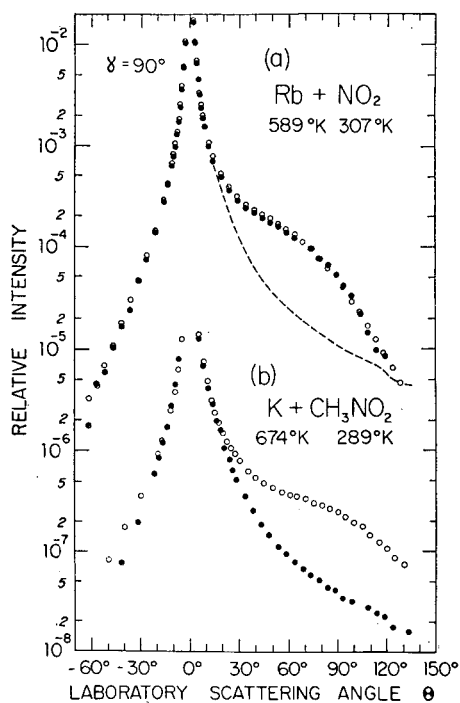


FIG. 1. Scattering of (a) $\text{Rb} + \text{NO}_2$ and (b) $\text{K} + \text{CH}_3\text{NO}_2$ measured on W (O) and Pt (●) surface-ionization filaments. The extrapolated, dashed curve in (a) has the same shape as the Pt signal of (b) and the ordinate scale for (b) is shifted downwards by two decades.

the possible participation of excited electronic states, particularly spin-triplet states. The CH_3NO_2 reaction offers a formal analogy with CH_3I . However, the electronic structure is much different, and if the reaction forms MNO_2 the alkali atom must attack a central rather than a peripheral bond.

An early Na flame experiment⁶ appears to be the only previous study of these reactions. The product was assumed to be NaO in each case and the rate constants were found to be comparable for NO_2 and CH_3NO_2 and about an order of magnitude less than that for Cl_2 . The results presented here indicate that the NO_2 and CH_3NO_2 reactions yield different products and the cross sections are comparable to those for Cl_2 .

EXPERIMENTAL RESULTS

The apparatus and experimental procedures have been described in previous work.^{3,7} In these experiments the scattering was measured in the plane of the reactant beams, which intersected at right angles ($\gamma = 90^\circ$). Figure 1 shows results obtained with a two-filament (W, Pt) surface ionization detector. The relative intensity scale gives the ratio of the measured signal to the attenuation of the parent alkali beam. The Pt readings are normalized to those for W at small angles.

For the $\text{Rb} + \text{NO}_2$ system the readings taken on the W and Pt filaments coincide.⁸ This cannot be taken as evidence for lack of reaction since in the presence of

O_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 $\text{K} + \text{CH}_3\text{NO}_2$ 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 hydrocarbons⁹ or alkyl iodides¹⁰ render the Pt filament insensitive to alkali halides; CH_3NO_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 $\text{Cs} + \text{NO}_2$ 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 scattering¹³ of the incident atoms were to occur for $\text{Cs} + \text{NO}_2$, 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

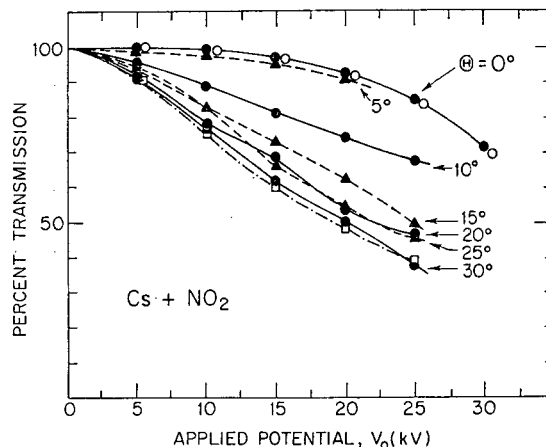


FIG. 2. Electric deflection analysis for scattering of $\text{Cs} + \text{NO}_2$ at various laboratory angles (●, ▲). Beam temperatures: $T(\text{Cs}) = 633^\circ\text{K}$, $T(\text{NO}_2) = 295^\circ\text{K}$. Results obtained with thermal calibrating beams of Cs atoms (O, 630°K) and CsCl molecules (□, 850°K) are included to indicate the deflecting power of the analyzing field.

that the reaction cross section is probably larger than $\sim 100 \text{ \AA}^2$.

An electric deflection analysis of the product from the Cs+CH₃NO₂ reaction has been reported elsewhere.¹² At $\Theta=40^\circ$ this shows very strong attenuation of the transmission at low voltage (25% at $<3 \text{ kV}$!), 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 paramagnetic alkali atoms, although there remains a residual transmission arising from the high-velocity atoms in the thermal distribution and from the small fraction of diamagnetic alkali dimer molecules in the parent beam.⁷

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 contribution 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

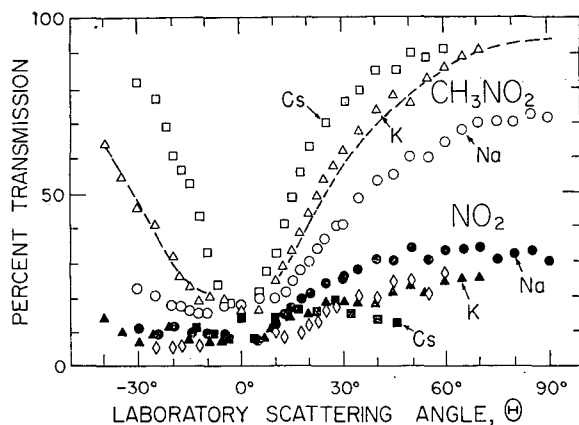


FIG. 3. Magnetic deflection analysis for scattering of Cs (\square), K (Δ), and Na (\circ) atoms from CH₃NO₂ (open symbols), NO₂ (solid symbols), and for scattering of Na from propane (\diamond). The dashed curve gives the transmission ratio calculated for K+CH₃NO₂ from the two-filament data of Fig. 1. Beam temperatures (in $^\circ\text{K}$): $T(\text{Cs})=595$, $T(\text{K})=670$; $T(\text{Na})=740$, $T(\text{CH}_3\text{NO}_2)=295$, $T(\text{NO}_2)=310$, $T(\text{C}_3\text{H}_8)=294$.

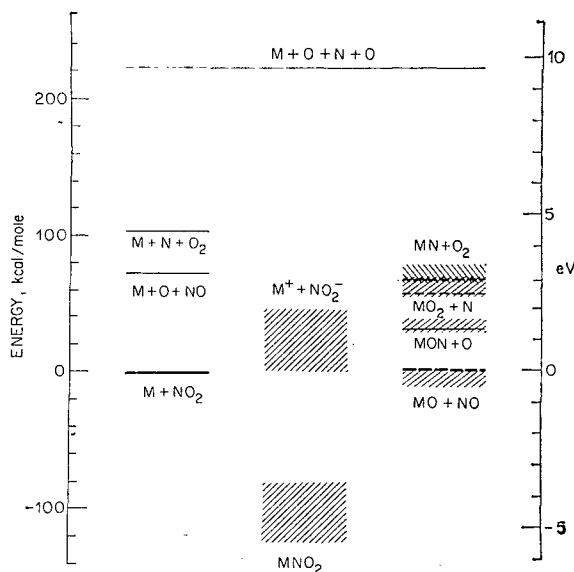


FIG. 4. Location of asymptotic energy states (corresponding to infinite separation of the species indicated) for possible products (at right) and some transient intermediates (middle) in reactions of Cs atoms with NO₂. Solid lines refer to accurately known energies, dashed lines to estimates or bounds based on assumption of ionic bonding; shading suggests probable direction and nominal extent of uncertainty.

the transmission are observed, indicating a large yield of 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 calculation 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^{3,7} indicates that the reaction cross section is $\lesssim 50 \text{ \AA}^2$ for Na+CH₃NO₂ and $\lesssim 100 \text{ \AA}^2$ 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 correlation. 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.¹⁴

Of the MO molecules, only LiO has been observed in the gas phase.¹⁵⁻¹⁷ The best available thermochemical data indicates $D_0(\text{LiO})=83\pm 4 \text{ kcal/mole}$.¹⁵ Two sets of $D_0(\text{MO})$ estimates found in the literature^{18,19} 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

TABLE I. Estimates of D_0 (kilocalories/mole) for MO molecules.

LiO	NaO	KO	RbO	CsO	Ref.
<83	71	81	79	80	a
77	71	70			b
82 ± 4	67 ± 3	71 ± 3	68 ± 3	70 ± 3	c

^a Reference 18.

^b Reference 19.

^c This work.

empirical correlation of alkali-halide data^{20,21} 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 atom 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.⁴ 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 affinity⁴ of 34 kcal/mole by assuming $r_e(MO) = r_e(MF) + 0.05$ Å. The increment of 0.05 Å is suggested by the r_e values for KOH and CsOH found in recent microwave work,²² since we expect $r_e(MO) = r_e(M-OH)$. Also, the estimate of $r_e(LiO)$ obtained from the LiO vibration frequency¹⁶ 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, $E(F) - E(O) \approx 47$ kcal/mole. Since the dipole moment data²² 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, $E(OH) = 42$ kcal/mole is accurately known.⁴ 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.²³ These values are higher than the estimates of $D_0(M-OH)$ we obtain, by 11, 2, 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, MO_2 , MN, or MNO_2 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,^{24,25} but if not the true D_0 presumably will be smaller than that estimated for ionic bonding. Of these molecules, only $NaNO_2$ has been observed in the gas phase.²⁴ The vibrational spectrum of LiON has been obtained in a matrix isolation study.²⁵ This indicates the molecule is bent ($\angle LiON = 110^\circ \pm 10^\circ$) with the LiO distance (1.65 ± 0.04 Å) longer by ~ 0.05 – 0.13 Å than $r_e(LiF)$. 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 experiment²⁶ gives 2.0 kcal/mole for the electron affinity of NO, considerably below the value of 20 kcal/mole cited in current reviews.⁴ Thus, $D_0(M-ON)$ is expected to be less than $D_0(MO)$ by at least $E(O) - E(NO) \sim 32$ kcal/mole. The corresponding lower limit for the endoergicity for production of $MON + O$ is indicated in Fig. 4; the actual endoergicity is probably considerably larger since the separation of charge centers in $M^+(ON)^-$ is substantially larger than in M^+O^- . Similarly, from $E(O_2) = 10$ kcal/mole,⁴ we estimate

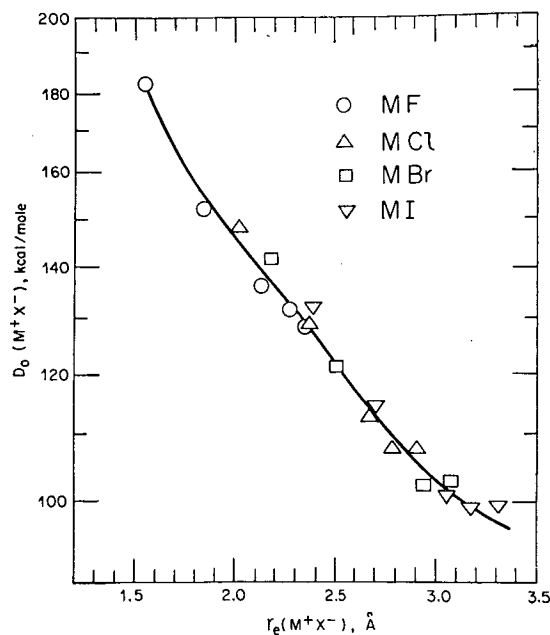


FIG. 5. Correlation between equilibrium bond length and energy required to dissociate alkali-halide molecules to ions. Ordinate scale is logarithmic.

$D_0(M-O_2)$ to be less than $D_0(MO)$ by at least 24 kcal/mole. From $E(N) \approx 0$, which is now well established,²⁷ and from bond-length estimates²⁵ which indicate $r_e(MN) \approx r_e(MO)$, we estimate $D_0(MN)$ to be less than $D_0(MO)$ by about 30 kcal/mole. Much higher estimates²⁸ of $D_0(MN)$ are cited in tabulations,^{18,19} 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 NO₂ is large, at present its magnitude is quite uncertain. Values between about 45 and 90 kcal/mole have been derived from various surface-ionization²⁹ and charge-transfer experiments.³⁰⁻³⁴ 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, $M^+ + NO_2^-$.

The ON-O dissociation energy is 72 kcal/mole³⁵ and the mean thermal energy available in relative translation and in rotational excitation of NO₂ is only ~ 2 kcal/mole. The large reaction cross section for Cs+NO₂ indicated by the data of Fig. 2 therefore requires that $D_0 \gtrsim 70$ 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.³⁶ The lowest-lying electronic states of an MO molecule must be $^2\Pi$ and $^2\Sigma$, in order to correlate with the ion-pair configuration $M^+(^1S) + O(^2P)$ as well as with $M(^2S) + O(^3P)$. A second-order Stark effect, as observed, is expected for a $^2\Pi$ as well as for a $^2\Sigma$ electronic state, because even for quite modest rotational energy the rotational angular momentum is large (e.g., $J \sim 30\hbar$ for ~ 1 kcal/mole, typical in other alkali reactions^{11,12}). However, the observed paramagnetic behavior of the product from Cs+NO₂ indicates a $^2\Sigma$ state. For a $^2\Pi$ state, the $^2\Pi_{1/2}$ component is diamagnetic and even for the $^2\Pi_{3/2}$ component the electronic magnetic moment would be expected to couple strongly to the internuclear axis and hence to exhibit a weak rotation-averaged interaction with the deflecting field.

Thus, we conclude that Cs+NO₂ produces a large yield of CsO in a $^2\Sigma$ state. In view of the small reaction exoergicity, this is quite likely the ground state. In contrast, for LiO deflection experiments^{17,37} have shown the ground state to be $^2\Pi$. An electronic structure calculation for LiO gives a $^2\Pi$ ground state but also predicts a $^2\Sigma$ state lying only ~ 8 kcal/mole higher.³⁸ The diamagnetic contribution found in Fig. 3 for Na+NO₂ indicates the reaction produces NaO in a $^2\Pi$ 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 $^2\Sigma$ and $^2\Pi$ states are of

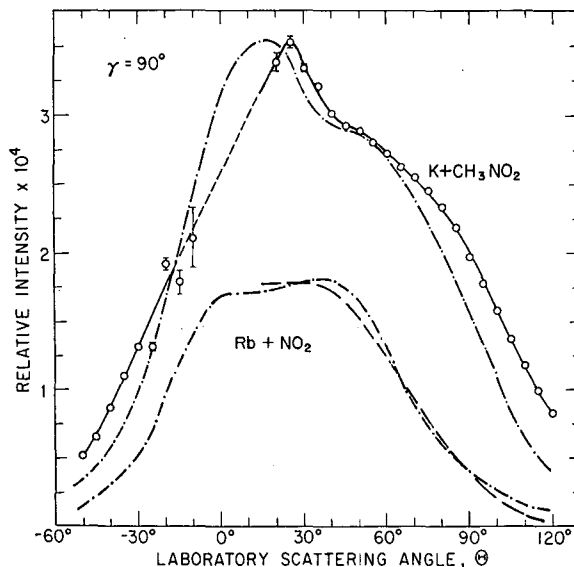


FIG. 6. Angular distribution (Lab system, data from Fig. 1) of reactive scattering for K+CH₃NO₂ (—) and Rb+NO₂ (---, rough estimate, probably an upper limit) compared with curves (---) calculated for isotropic scattering (c.m. system) and averaged over parent beam velocity distributions. Ordinate scale for CH₃NO₂ case has been amplified by a factor of 10.

comparable stability for NaO. Although this remains an open question, it seems likely that the diamagnetic component represents most of the NaO yield, as Table I indicates the reaction is probably somewhat endoergic. For K and Rb+NO₂, 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 $^2\Sigma$ state for KO.

For the M+CH₃NO₂ reactions our deflection data clearly indicate that MNO₂ is the product and thereby imply a lower limit for $D_0(M-NO_2)$ of 54 kcal/mole, the H₃C-NO₂ bond dissociation energy.³⁵ This is indicated in Fig. 4. Reaction to form MO offers the only other exoergic path. The observed pseudo-first-order Stark effect¹² and diamagnetic behavior are incompatible with either the $^2\Sigma$ or $^2\Pi$ states of MO, however, whereas these properties are expected for MNO₂, which is a near-symmetric-top rotor and should have a 1A ground state.

KINEMATIC ANALYSIS

In Fig. 1, the prominent bulge in the Rb+NO₂ scattering curves on the positive angle side suggests that in the region $\Theta \sim 30^\circ - 100^\circ$ 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-

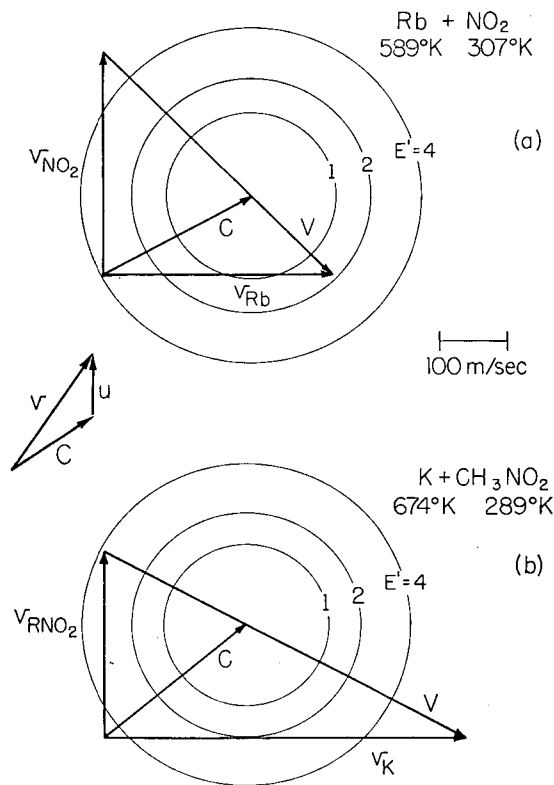


FIG. 7. Kinematic diagrams corresponding to the most probable velocities in the parent beams for the experiments of Fig. 1. The center-of-mass velocity vector is denoted by C and the relative velocity vector by V . The circles indicate the length of recoil velocity vectors for (a) RbO or (b) KNO_2 produced with various amounts of final relative translational kinetic energy E' (kilocalories/mole).

angle scattering from $Rb+NO_2$ 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 I). 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 $RbNO_2$, 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.³⁹

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

$$G(u, v, \delta) = (u/v)^2 \cos \delta$$

and δ is the angle between u and v . The Jacobian factor G takes account of the variation in the ratio of solid-angle elements in the two systems.⁴⁰ This factor has a pronounced influence on the LAB distribution when the c.m. velocity of the detected particle is low ($u < C$) or directed more or less orthogonally to its LAB velocity ($\cos \delta$ small). The variation of $1/G$ with LAB angle, averaged over the parent beam velocity distributions, is shown in Fig. 6. This curve is very similar in shape to the observed bulge. Although the kinematics for reactive or sticky scattering differ somewhat from the elastic case, for this system the Jacobian enhancement should be much the same, since the mass ratios and the available energy confine Rb and RbO to the low-velocity region. We conclude that even a qualitative interpretation of the angular distribution data cannot be made without velocity analysis of the scattering, which so far has been forestalled by the detection problem.⁸

The product angular distribution for the $K+CH_3NO_2$ reaction, also given in Fig. 6, was obtained as usual by subtracting the nonreactive scattering (Pt signal) from the total scattering (W signal). For this system, the kinematic analysis is again handicapped by the Jacobian weighting and by the large value of the KNO_2/CH_3 mass ratio, which makes the KNO_2 distribution rather insensitive to the relative motion of the products. However, a significant qualitative feature is apparent, from comparison with Fig. 7. The center of the product distribution coincides with the direction of the center of mass of the system, in marked contrast to the CH_3I reactive scattering.¹⁰ A curve calculated assuming an isotropic distribution of KNO_2 in the c.m. system and a fixed final relative kinetic energy of $E' = 7$ kcal/mole is shown in Fig. 6, to illustrate the shape arising from the Jacobian factor alone. Comparable or better agreement with the data is found assuming symmetrical forward-backward peaking of $I_{c.m.}(\theta, u)$ of the form expected for a long-lived complex.³⁹ From such comparisons, it is clear that the product distribution in the c.m. system must be quite broad, with about the same intensity in the forward and backward hemispheres, but velocity analysis will be required to resolve the shape of the distribution.

The c.m. angular distribution for nonreactive scattering of K from CH_3NO_2 was derived from the Pt data of Fig. 1 by the approximate transformation used in previous work.^{3,10} The resulting curve lies well below that for nonreactive scattering from CH_3I at wide angles (factor of 2 to 3 below at 90° – 150°) and has practically the same shape as found for the CCl_4 system.³ Since the intensity of nonreactive scattering at wide angles is attenuated by the presence of reactive scattering, this indicates that the reaction cross section for CH_3NO_2 is appreciably larger than for CH_3I and about the same as for CCl_4 , in agreement with our estimates from the magnetic deflection analysis.

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,⁶ 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 10⁻⁵ torr. The data indicate that at least within the range $\Theta = 0^\circ - 30^\circ$ 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 R₁NO₂ 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.³⁵ 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 alcohols³⁵). Thus, in the nitrate reaction, the likely products are MNO₂ and the alkali alkoxide, MOR₂; in the nitrite reaction, MON or MOR₃. The alkoxide salt is the more likely product in the nitrite case since $D_0(\text{M-ON})$ is probably less than 35-40 kcal/mole. Activation energies for reactions of Na with alcohols indicate $D_0(\text{Na-OR}) \sim 95$ kcal/mole.^{41,42} In this context, it is of interest that the scattering, particularly for Cs, is more closely similar for R₁NO₂ and R₂ONO₂ than for R₃ONO, as this suggests R₂ONO₂ may give MNO₂ as the principal product and R₃ONO may give MOR₃. A brief magnetic deflection study of K+*t*-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 $\Theta = 0^\circ - 30^\circ$, 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

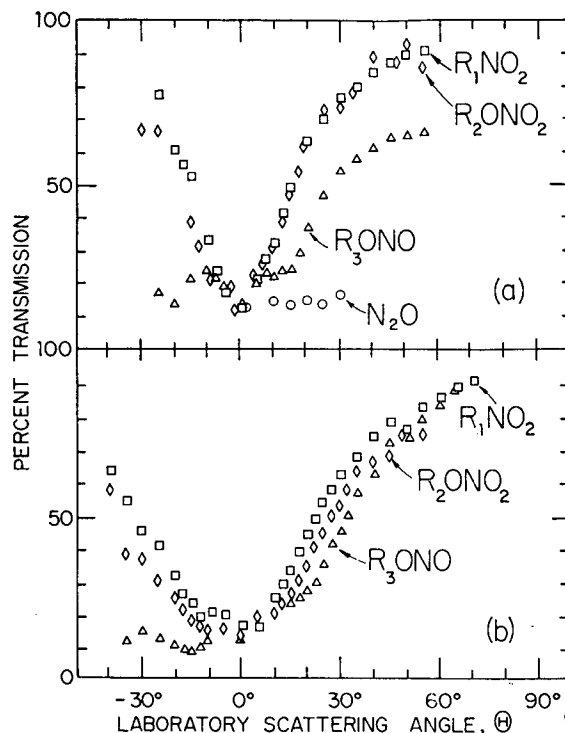
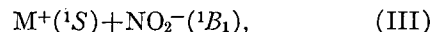
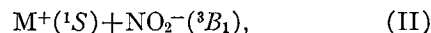
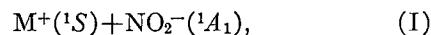


FIG. 8. Magnetic deflection analysis for scattering of (a) Cs and (b) K atoms from nitromethane (\square , R₁=CH₃, data from Fig. 3), ethyl nitrate (\diamond , R₂=C₂H₅), *i*-pentyl nitrite (Δ , R₃=C₅H₁₁), and nitrous oxide (\circ). Beam temperatures: $T(\text{Cs}) = 600^\circ\text{K}$, $T(\text{K}) = 670^\circ\text{K}$, $T(\text{gas}) = 300^\circ\text{K}$.

encountered with other reactions: the possible role of excited electronic states of the NO₂⁻ ion and participation of spin-triplet as well as spin-singlet configurations. The initial "covalent" configuration, M(²S)+NO₂(²A₁), can interact with at least three ionic configurations,

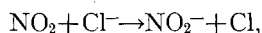


all of which can correlate with the product configuration, MO(²Σ or ²Π)+NO(²Π). Route I involves the ground electronic state of NO₂⁻, derived from the 6a₁ molecular orbital that contains the odd electron in the NO₂ ground state.^{43,44} Route III involves the lowest singlet excited state, derived from the 2b₁ molecular orbital, the lowest unoccupied orbital in NO₂. From spectra of nitrite compounds in solution and solid phase, this ¹B₁ state of NO₂⁻ is known to lie ~74 kcal/mole above the ground state.⁴⁵ Route II involves the corresponding ³B₁ state, which is expected to be the lowest-lying triplet state of NO₂⁻. This state has not been reported but it should lie below the known ¹B₁ state by ~10-15 kcal/mole.⁴⁶ The deep potential-energy basin corresponding to formation of the MNO₂ ground state almost certainly correlates only with Route I.

However, the reactants $M+\text{NO}_2$ approach in a triplet configuration in $\frac{3}{4}$ of the collisions. In these triplet collisions, electron transfer to form singlet NO_2^- 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 NO_2 reaction dynamics: (1) At least for Cs, the reaction cross section is very large, $Q_r \lesssim 100 \text{ \AA}^2$. 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 Q_r can probably also be accounted for by ordinary van der Waals forces, as in some other reactions,³⁹ 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 $r_c \simeq e^2 \Delta$ with Δ the asymptotic energy of the $M^+ + \text{NO}_2^-$ ion pair (see Fig. 4 for Route I), can become extremely large if the NO_2 electron affinity is very high. Thus, e.g., for $E(\text{NO}_2) = 83 \text{ kcal/mole}$, $r_c \sim 50 \text{ \AA}$ for Cs and $\sim 20 \text{ \AA}$ for K; $\sim 9 \text{ \AA}$ for Na and $\sim 1.8 \text{ \AA}$ for Li. The electron transfer in such a case is expected to be severely inhibited⁴⁷ for the Cs, Rb, K reactions unless use is made of an excited electronic state, as in III, for which Δ and r_c become much smaller. This curious situation was the original motivation⁴⁸ for our study, as the charge-transfer process



had been reported to occur rapidly at very low collision energies, implying that $E(\text{NO}_2) \lesssim E(\text{Cl}) = 83 \text{ kcal/mole}$.³⁰ 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 $\sim 90 \text{ kcal/mole}$ obtained from the surface ionization method remains provisional, pending identification of the negative ions formed.²⁹ For a time, a value decidedly below 83 kcal/mole but probably above about 45 kcal/mole was indicated by experiments involving titration of NO_2 by various negative-ion species.^{32,33} However, the most recent study of this kind has shown that the charge-transfer cross section increases rapidly with decreasing ion velocity.³⁴ Consequently, it appears now that $E(\text{NO}_2) \lesssim 83 \text{ kcal/mole}$ may hold after all, although a definitive result has to await experiments with well-defined ion velocity. If $E(\text{NO}_2) \sim 45 \text{ kcal/mole}$, r_c would be small enough ($\sim 8 \text{ \AA}$) to allow even the Cs reaction to proceed via the ground state, as in Route I.

Ironically, the question whether $M+\text{NO}_2$ 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 resonance⁴⁹ or matrix isolation²⁵ experiments.

The electronic structure of the MO molecules is of interest³⁸ since these are simple open-shell systems and can be compared with the extensively studied alkali fluorides and alkaline-earth oxides (which have one more valence electron).^{49,50} Our finding that the ground state appears to change from $^2\Pi$ for LiO to $^2\Sigma$ for CsO is anomalous according to the simplest ionic model. The electron donated by the alkali atom might be expected to enter the $2p\sigma$ oxygen orbital along the internuclear axis, leaving a hole in the $2p\pi$ orbital and hence giving a $^2\Pi$ ground state ($\sigma^2\pi^3$ 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 $2p\pi$ orbital, which is much more polarizable than the $2p\sigma$ orbital⁵¹; this would provide a $^2\Sigma$ ground state ($\pi^4\sigma$ configuration). Another viewpoint is suggested by inspection of the SCF-MO calculations.⁵⁰ In $\text{LiF} \cdots \text{RbF}$, the uppermost filled σ orbital is predicted to lie below the uppermost filled π orbital ($\cdots\sigma^2\pi^4$ configuration), but the energy difference is small even for LiF (0.033 a.u. = 20 kcal/mole) and decreases rapidly from 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.⁵² 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 ($\sigma^2\pi^3$) is predicted to be the same as in LiF, the energy difference has decreased threefold (to ~ 0.01 a.u.).³⁸ A similar trend is discernable in the $\text{BeO} \cdots \text{SrO}$ series, although obscured by the shorter internuclear distance and other effects.⁴⁹ A $\pi^4\sigma^2$ ground-state configuration is predicted⁵⁰ for MgO and SrO.

Beyond a formal analogy, reactions of alkali atoms with CH_3NO_2 and CH_3I are comparable in terms of the energy available. The strength of the bonds broken is the same (54 kcal/mole) and that of $M-\text{NO}_2$ is probably quite close to MI (76 kcal/mole). However, in addition to the steric difference, CH_3NO_2 probably presents a qualitatively different case for the electron-jump process. The bonding in CH_3NO_2 evidently involves overlap of an sp^3 orbital on C with an sp^2 orbital on N (derived from the $6a_1$ orbital of NO_2). This is consistent with the microwave spectrum,⁵³ which shows the C-N bond is coplanar with the NO_2 group. The electron affinity of CH_3NO_2 thus should be much smaller than for NO_2 , as the C-N bond utilizes the orbital

which receives the last electron in NO₂⁻. Accordingly, the alkali reaction is expected to involve only the ground electronic state as in the CH₃I case. In CH₃NO₂, 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 2*b*₁ orbital of NO₂). 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 CH₃I molecule.⁴⁸ If so, the repulsive interaction which appears to dominate the CH₃I reaction dynamics⁵⁴ should be much weaker or absent from CH₃NO₂. The electron affinity may even be large enough (perhaps ~10 kcal/mole) to enable the alkali atom to form a charge-transfer collision complex.

For the CH₃NO₂ reaction we find: (1) The product angular distribution (c.m. system) puts comparable intensity in the forward and backward hemispheres, whereas CH₃I gives strongly backward recoil. (2) The product is almost certainly KNO₂ in a ¹A₁ state, as expected if the reaction involves the ground electronic state of CH₃NO₂. (3) The reaction cross section *Q_r* is definitely larger by a factor of about 2 or 3 than for CH₃I. (4) The magnitude of *Q_r* decreases as Cs→K→Na, the same trend found for the CH₃I case.⁵⁵ At present, these properties appear to be compatible with either a direct reaction mechanism of the sort that accounts for the CH₃I reaction dynamics or with a collision complex mechanism.

In the direct regime, as demonstrated by Monte Carlo trajectory calculations for the CH₃I case,⁵⁴ the product angular distribution tends to become isotropic as *Q_r* increases. For CH₃NO₂, 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 CH₃I, due to the statistical predominance of broadside collisions in experiments with randomly oriented target molecules. Elegant experiments with CH₃I molecules aligned in an electric field have shown that the reaction probability strongly favors end-on collisions in that case.⁵⁶ A preference for broadside reaction of CH₃NO₂ 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.⁵⁷

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,^{5,39} the nonreactive scattering of K+CH₃NO₂ 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 CH₃NO₂ case, and both promote reactive decay of the complex.

The CH₃NO₂ 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 technique⁵⁶ appears particularly promising for CH₃NO₂, 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.⁵³

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