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ON THE MECHANISM OF $M^+O_3^-$ AND $M^+NO_2^-$ FORMATION
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MECHANISM OF $M^+O_3^-$ FORMATION BY PHOTOLYSIS

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ABSTRACT

The species $M^+O_3^-$ and $M^+NO_2^-$ have been produced in matrix samples of alkali atoms, N_2O and O_2 or NO by mercury arc photolysis. In similar studies, Milligan and Jacox proposed a mechanism involving the diffusion and reaction of the O^- anion. However, energetic consideration rule out the production of a free O^- ion in these experiments. We believe that the observations are better explained by photolysis of N_2O in the presence of $M^+O_2^-$ with oxygen atom transfer to give $M^+O_3^-$ and the analogous reaction with M^+NO^- to give $M^+NO_2^-$.

INTRODUCTION

Matrix reactions between alkali metal atoms and oxygen (1,2,3,4) and alkali metal atoms and nitric oxide (5,6,7,8) have been thoroughly investigated; the primary products of these reactions are the $M^+O_2^-$ and M^+NO^- species, respectively. Milligan and Jacox (hereafter MJ) have shown that with N_2O added to the matrix gas, mercury arc photolysis causes N_2O decomposition producing NO_2^- or O_3^- from the respective alkali metal reactions with NO or O_2 (6,9). The mechanism MJ proposed for the production of NO_2^- and O_3^- was the photolytic decomposition of $M \cdots N_2O$ into M^+ , N_2 , and O^- with O^- diffusing to NO or O_2 and reacting to form NO_2^- or O_3^- . However, this mechanism fails to account for the pronounced alkali metal effect on the observed NO_2^- and O_3^- absorptions and it is energetically unreasonable for O^- to diffuse away from its M^+ counterion, even under the influence of mercury arc photolysis which, in the final analysis, is capable of electron photodetachment from O^- .

New results obtained in similar studies indicate that oxygen-atom transfer during photolysis from a lower to a higher oxide can better account for the spectral changes observed in these experiments.

EXPERIMENTAL

The cryogenic apparatus, chemicals, and experimental procedures used in these studies have been described in previous papers (2,3,7,10). Infrared spectra were recorded after sample deposition for 8-16 hours and again after mercury arc photolysis on a Beckman IR-12 spectrophotometer using expanded wavenumber scale and $8 \text{ cm}^{-1}/\text{min}$ scanning speeds. Frequency accuracy is $\pm 0.5 \text{ cm}^{-1}$.

RESULTS

First, the cesium atom reaction with N_2O was observed upon codeposition of cesium atoms with an $\text{Ar}/\text{N}_2\text{O} = 250/1$ sample. The major absorptions were Cs_2O at 457.3 cm^{-1} (0.32 O.D.), CsO at 320.5 cm^{-1} (0.25 O.D.) and CsO_2 at 236 cm^{-1} (0.30 O.D.) (4), the latter arising from a trace of O_2 impurity in the sample. Cs_2O and CsO have been observed previously at 457.1 and 321.7 cm^{-1} following Cs-O_3 reactions (10) and at 455.2 and 314.0 from the N_2O nitrogen-matrix reaction (11). Mercury arc photolysis of the sample was done for 20 min with a pyrex filter, (transmits $2800 \text{ \AA}$ to water cut-off), and for 10 additional min with a saturated CoSO_4 , NiSO_4 solution (transmits $2200\text{--}4000 \text{ \AA}$). The Cs_2O band at 457 cm^{-1} was reduced to 0.12 O.D. whereas the CsO band at 321 cm^{-1} was unchanged. The 1205 cm^{-1} intermediate, reported by MJ (6), appeared with an intensity 0.07 O.D.; the latter photolysis with the solution filter was clearly more effective in producing the 1205 cm^{-1} band. Photolysis change of the 236 cm^{-1} CsO_2 band could not be determined because of low background transmission in this region.

In order to ascertain the CsO_2 photolysis behavior in these experiments, a reaction was performed with 45% oxygen-18 enriched N_2O and a reduced

concentration of cesium. The CsO isotopic doublet was observed at 322 and 306 cm^{-1} (0.18 O.D.), Cs_2O was weak, and no absorption was detected at 236 cm^{-1} . Following mercury arc photolysis, a weak new band appeared at 229 cm^{-1} with weaker shoulders at 236 and 226 cm^{-1} and the CsO isotopic doublet was unchanged. Again, the results are not conclusive, but the weak new bands are appropriate in intensity and frequency for CsO_2 and its isotopic components (4).

The matrix reaction of O_2 and N_2O with cesium atoms is depicted in Figure 1. In this experiment, the most intense products of the cesium- O_2 reaction (4) were observed at 1001, 357 and 236 cm^{-1} along with the Cs_2O and CsO products of the cesium- N_2O reaction at 457 and 322 cm^{-1} . Weak new features at 803 (0.03 O.D.) and 789 cm^{-1} (0.01 O.D.) were observed in the combined experiment shown in Figure 1 and in the work of MJ (9). Following mercury arc photolysis for one hour the latter two bands grew to 0.08 and 0.10 O.D., respectively. Similar photolysis results were reported by MJ (9). The cesium- O_3 argon matrix reaction produced a very intense band at 802.4 cm^{-1} (1.1 O.D.) and a weaker band at 788.8 cm^{-1} which were assigned to ν_3 of the ozonide ion in the Cs^+O_3^- species (10).

An isotopic experiment was performed with O_2 and N_2^{18}O (86% enriched) reacting with cesium atoms using $\text{Ar}/\text{O}_2/\text{N}_2\text{O} = 500/1/1$. The cesium- O_2 reaction products were observed as are illustrated in Figure 1 for the previous experiment. The Cs_2O isotopic bands appeared as a 5/1 doublet at 432 and 457 cm^{-1} along with a similar CsO doublet at 306 and 322 cm^{-1} . The 236 cm^{-1} CsO_2 band was too broad to observe the possible photolytic growth of $\text{Cs}^{16,18}\text{O}_2$ or Cs^{18}O_2 . Weak bands were observed at 792 and 778 cm^{-1} in

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a 2/1 intensity ratio; these features, which grew on photolysis, correspond to the most intense bands of asymmetrical and symmetrical $\text{Cs}^{+16}_{18}\text{O}_2^-$, respectively (10).

The potassium matrix reaction with N_2O was studied using an $\text{Ar}/\text{N}_2\text{O} = 200/1$ sample. The spectrum revealed several very weak bands below 300 cm^{-1} along with a weak feature at 375 cm^{-1} . The most likely reaction products K_2O and KO , which have been observed at 502 and 384 cm^{-1} , respectively, in N_2 matrix reactions (11), were not produced in detectable quantities in the analogous argon matrix experiments. A reaction of potassium with a $\text{Ar}/\text{O}_2/\text{N}_2\text{O} = 400/1/1$ sample produced the KO_2 band at 307 cm^{-1} (0.23 O.D.) and the KO_2K 433 cm^{-1} (0.41 O.D.) feature in good yields along with a weak KO_4 band at 993 cm^{-1} (0.21 O.D.) (3). No absorptions were noted in the 800 cm^{-1} region. Mercury arc photolysis caused these three bands to decrease one-half in intensity and weak bands to appear at 800 and 788 cm^{-1} , these absorptions occur within 1 cm^{-1} of the features produced by MJ (9) upon photolysis and by Spiker and Andrews (10) from the potassium- O_3 matrix reaction.

The reaction of alkali metals with NO and N_2O was investigated; Figure 2 illustrates the sodium reaction with both nitrogen oxides. Intense bands were observed at 1359 and 361 cm^{-1} as found in the sodium- NO reaction. Photolysis of these samples in the absence of N_2O produced no spectral changes (8). An additional intense new feature was observed at 1227 cm^{-1} in the present study. Figure 2 shows the effect of photolysis which destroyed the sharp 1227 cm^{-1} band (presumably due to a less-stable M^+NO_2^- isomer), decreased the 1359 and 361 cm^{-1} bands to one-third and

produced a new completely absorbing band at 1221 cm^{-1} with a weak 1244 cm^{-1} shoulder.

Finally, an analogous experiment was conducted with cesium and an $\text{Ar}/^{15}\text{NO}/\text{N}_2\text{O} = 400/1/1$ sample. After sample deposition, new bands of interest were observed at 1219.4 (0.04 O.D.) and 1190 cm^{-1} (0.18 O.D.), due to $\text{M}^{+15}\text{NO}_2^-$ species, and 1350 cm^{-1} (0.29 O.D.) due to $\text{Cs}^{+15}\text{NO}^-$ (6,8). Photolysis produced marked growth of the 1219 cm^{-1} feature to 0.18 O.D. and decrease of the 1350 cm^{-1} band to 0.20 O.D. The N_2O band at 590 cm^{-1} sustained a loss of one-third of its intensity upon photolysis.

DISCUSSION

In earlier work, MJ ascribed the photolytic production of alkali ozonide species in alkali metal /O₂/N₂O matrix samples to the diffusion and reaction of O⁻ with O₂ (9). In spite of the marked alkali metal effect on the O₃⁻ wavenumbers, these workers did not explain the mechanism for alkali metal involvement with the ozonide ion. The direct matrix synthesis of the M⁺O₃⁻ species from alkali metal-ozone reactions by Spiker and Andrews (10) gave sharper and significantly more intense absorptions which were in good agreement with the wavenumbers from the photolysis work. Therefore, the product species clearly is M⁺O₃⁻ and not isolated O₃⁻ and the mechanism for the photolytic synthesis must involve the alkali metal in the product species. It is of interest to point out that isolated O₃⁻ has been recently observed at 804.3±0.2 cm⁻¹ following proton beam radiolysis of argon-oxygen samples (12).

Several alkali metal-oxygen species were produced during deposition of these matrix samples and their role in the photolytic reactions must be considered. In the case of cesium, a small yield of Cs⁺O₃⁻ was produced upon condensation of Ar/O₂/N₂O samples with cesium atoms in the present experiments (Figure 1) and those of MJ. Noteworthy is the fact that CsO was synthesized by the argon matrix reaction of N₂O with cesium atoms, reaction (1).

Also, no other alkali metal MO diatomic could be formed by direct reaction with N₂O during argon matrix deposition and no other alkali ozonides were formed during metal deposition with O₂ and N₂O. Clearly CsO is involved

in the synthesis of Cs^+O_3^- during sample deposition which is readily explained by the simple mechanism involving reactions (1) and (2).

CsO produced by (1) could contain a large fraction of the heat of reaction, approximately 30 kcal/mole (13,14), as internal energy which would be expected to aid reaction (2). A similar mechanism was suggested by Ault and Andrews (15) to account for the production of Ca^+O_3^- in the Ca-O_2 nitrogen matrix reaction.

It is clear that the reagents Cs , O_2 , and N_2O are all involved in the photolytic synthesis of Cs^+O_3^- ; the isotopic studies with N_2^{18}O and $^{16}\text{O}_2$ have demonstrated this. Since both Cs^+O_2^- and Cs^+O^- were produced as products of the cesium atom deposition reaction (236 and 322 cm^{-1} bands in Fig.1), these molecules are the carriers of cesium for cesium ozonide formation upon photolysis. The photolysis light could activate CsO and promote reaction (2) where "cold" CsO and O_2 molecules were trapped in adjacent matrix sites. On the other hand, Cs^+O_2^- and N_2O trapped in adjacent matrix sites could undergo oxygen atom transfer reaction (3).

Since cesium atoms react with N_2O and O_2 separately, it is reasonable to expect these reagents to aggregate about cesium in the matrix during deposition. In like manner, Cs^+O_2^- and N_2O should be attracted to each other by dipole-induced dipole forces and form a complex $\text{Cs}^+\text{O}_2^- \cdots \text{ON}_2$ reagent for (3). The great ozonide ν_3 intensity requires a relatively small yield to produce the observed spectrum.

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Although a decrease in the intense CsO_2 band could not be determined upon photolysis, the growth of the extremely intense ν_3 ozonide bands in Cs^+O_3^- was relatively small which would not require an appreciable change in CsO_2 intensity. Furthermore, additional CsO_2 may be produced upon photolysis by reaction (4).

The photolysis of $\text{N}_2^{16}\text{O}-\text{N}_2^{18}\text{O}$ samples containing Cs atoms produced a weak band appropriate for ν_2 of $\text{Cs}^{+16}\text{O}^{18}\text{O}^-$, suggesting reaction (4).

The photodecomposition of nitrous oxide in matrix samples containing alkali metal atoms is most effective for ultraviolet light in the 2200-4200 Å region (6,9, this work). The strong, allowed transitions for N_2O photolysis requires vacuum ultraviolet radiation; however, two very weak continuous spectra have been reported for singlet-triplet transitions which maximize at 2900 and 2730 Å (16). It is suggested that the latter transitions are responsible for the present N_2O photochemistry and that the spin conservation selection rule has been removed (i.e., the intensity increased) by the close association of alkali metal species with N_2O which immediately react with the photolysis products. Whereas photodecomposition of N_2O via the $\tilde{a}(^3\pi)$ state to give $\text{N}_2(^1\Sigma)$ and $\text{O}(^3\text{P})$ is a weak, spin-forbidden transition in the gas phase, reaction (3) photolysis involves the oxygen atom transfer between interacting molecules with spin conservation which gives a more strongly allowed transition.

Thermodynamic stability supports reaction (3). Using thermodynamic data given recently for O_3^- (17), the electron affinity for O_2 (10 kcal/mole) and the oxygen bond dissociation energy of N_2O (40 kcal/mole) (14),

reaction (5)

is exothermic by 20 kcal/mole. Reaction (3) should be exothermic by approximately the same amount which indicates that (3) is a favored reaction.

In the photolysis of N_2O -alkali metal matrix samples, a new intermediate species absorbing at 1205 cm^{-1} and $(\text{NO})_2$ have been observed (6). The present experiments confirm the observation and photolysis wavelength dependence of the 1205 cm^{-1} absorption.

MJ assigned the 1205 cm^{-1} band to an isolated N_2O_2^- ion formed by reaction of a diffusing O^- with N_2O ; these workers suggest that (NO_2) arises from photodetachment of the electron from N_2O_2^- followed by rearrangement to the chain $(\text{NO})_2$ structure (6). The presently proposed mechanism provides a better explanation, we believe, for these observations. Unreacted $\text{N}_2\text{O} \cdots \text{M}$ species are probably present in the deposited sample; the LiON_2 species has been observed in the spectrum of Li, N_2O argon matrix reaction products (18). Accordingly, we propose reaction (6) as a better explanation for the production of N_2O_2^- which most probably contains an alkali counterion.

Another possible spin allowed photochemical reaction is (7) or (7a) with lithium electronic excitation which was observed by mercury arc photolysis of lithium atoms and N_2O in argon during deposition (18).

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$\text{N}_2\text{O}_2^- \text{M}^+$ could be formed by the union of N_2O and $\text{O}^- \text{M}^+$ upon photolysis, reaction (8)

Reaction (6) may in fact be the result of reactions (7) and (8).

The photolysis data (6) on growth of $(\text{NO})_2$ and N_2O_2^- do not require that $(\text{NO})_2$ arise from photodecomposition of N_2O_2^- . The alkali metal atom could effect the aggregation of two N_2O molecules, as in (6), which photolyse via the $\tilde{\text{b}}(^3\pi)$ state (which produces $\text{NO}(^2\pi)$ and $\text{N}(^4\text{S})$ in the gas phase (16)) to give $(\text{NO})_2$ and N_2 , reaction (9). Again, aggregation around the "sticky" alkali

atom makes a spin-conserved photolysis process possible which has a greater transition probability than the weak, gas phase N_2O process.

For the potassium matrix reaction with O_2 and N_2O , no KO was formed by the potassium analog of reaction (1); however, $\text{K}^+ \text{O}_2^-$ was produced in good yield. In all of the lighter (except Cs) alkali metal argon matrix reactions with O_2 and N_2O , the majority of the alkali atoms form $\text{M}^+ \text{O}_2^-$ since the oxygen abstraction from N_2O does not proceed for these metals in argon matrices. Dipole-induced dipole attractions lead to aggregation of the superoxide species and N_2O during deposition and photolysis produces the ozonide, reaction (10).

In the case of NO, N₂O photolysis with alkali atoms present, Figure 2 clearly shows a major reduction of Na⁺NO⁻ (1359,360 cm⁻¹) and growth of Na⁺NO₂⁻ (1221 cm⁻¹) upon photolysis. MJ observed the loss of the 1359 cm⁻¹ band and the growth of the intense 1221 cm⁻¹ band and the weaker 1244 cm⁻¹ band upon photolysis (6). In experiments with alkali metal atoms present, the 1244 cm⁻¹ absorption is also due to M⁺NO₂⁻ (19). In a cesium experiment with ¹⁵NO and ¹⁴N₂O, photolysis created the pyramidal Cs⁺¹⁵NO₂⁻ species at the expense of Cs⁺¹⁵NO⁻. These results suggest the oxygen-atom transfer mechanism (11) which is analogous to reaction (3).

The Milligan and Jacox (6) explanation required the diffusion and reaction of O⁻ ions under photolysis by reaction (12).

For charge transfer between the lighter alkali atoms and N₂O, the M⁺ and N₂O⁻ must be within reasonable attractive coulomb distances of each other since hν is not sufficient to ionize isolated Li or Na and the electron affinity of N₂O is very small (20). Now with M⁺ and N₂O⁻ within an attractive coulomb range, any O⁻ produced from decomposition of N₂O⁻ must diffuse to M⁺ giving M⁺O⁻ and the net effect is our reaction (1) with hν activation. We believe that O⁻ ions cannot diffuse away from the M⁺ which supplied the electron and accordingly that isolated O⁻ cannot be the active reagent. Furthermore, the electron affinity of atomic oxygen is 33.7 kcal/mole, (21) an energy abundantly available in the mercury arc which would quickly photodecompose any O⁻ to neutral atomic oxygen, thus ruling out the possibility of producing free O⁻ by photolysis.

CONCLUSIONS

The evidence for the formation of cesium ozonide during the codeposition of Cs, O₂ and N₂O at high dilution in argon indicates that Cs⁺O₂⁻, produced by the direct reaction of cesium and N₂O, combines with O₂ to give Cs⁺O₃⁻. The best explanation for the synthesis of alkali ozonides by photolysis of M, O₂ and N₂O in solid argon is the photodecomposition of M⁺O₂⁻... ON₂ formed during reagent condensation to give oxygen atom transfer to the superoxide forming the ozonide. This mechanism accounts for the alkali metal dependent ozonide absorptions and does not require the diffusion of a charged species. The analogous production of alkali nitrites upon photolysis of M, NO and N₂O in solid argon involves oxygen-atom transfer in the species M⁺NO⁻... ON₂ to give M⁺NO₂⁻.

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FIGURE CAPTIONS

- Fig. 1. Infrared spectra in the 200-460 and 780-1020 cm^{-1} regions before (solid) and after (dotted) 60 minutes of high pressure mercury arc photolysis following the matrix reaction of an $\text{Ar}/\text{N}_2\text{O}/\text{O}_2 = 500/1/1$ sample with cesium atoms.
- Fig. 2. Infrared spectra in the 340-380 and 1200-1400 cm^{-1} regions before (solid) and after (dotted) 60 minutes of high pressure mercury arc photolysis following the matrix reaction of an $\text{Ar}/\text{N}_2\text{O}/\text{NO} = 250/1/1$ sample with sodium atoms.

Fig. 1

Fig. 2

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