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Stabilization of the Primary Products of O(^{1}D) Reactions with CO, CO$_2$, CH$_4$, and Other Hydrocarbons in Cryogenic Matrices

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Broad-band UV–visible irradiation of argon matrices containing 2% N$_2$O and 10% of either CO, CO$_2$, methane or ethane resulted in the formation of CO$_2$, CO$_3$, CH$_3$OH, or CH$_3$CH$_2$OH as the dominant photoproducts of O(^{1}D) reactions, as observed by FTIR absorption spectroscopy. With methane, no significant production of formaldehyde or methyl or hydroxyl radicals was observed, in contrast with previous work on this system in liquid argon. Similar irradiation of argon matrices containing 2% N$_2$O and 10% propane or isobutane gave rise to mixtures of 1-propanol and 2-propanol or 2-methyl-1-propanol and 2-methyl-2-propanol. The latter reaction showed an essentially statistically determined product ratio, indicating indiscriminate attack of O(^{1}D) on the different C–H bonds of isobutane, as has been found in previous gas- and liquid-phase studies. Matrix-isolated NO, *cis*-ON–NO, ON–NO$_2$, and NO$_2$ were also observed as side products of the reactions of O(^{1}D) with all precursor molecules. In all cases, no other major photoproducts or decomposition fragments were observed, indicating the occurrence of very efficient quenching of the highly energized primary reaction products.

Introduction

The kinetics and dynamics of the reactions of O(^{1}D) with hydrocarbons have been extensively studied over the past three decades. The gas-phase kinetics of O(^{1}D) reactions with numerous molecules such as H$_2$, CO, CO$_2$, CH$_4$, and various saturated and unsaturated hydrocarbons have been studied in detail, chiefly by Cvetanović and co-workers[1-5] and also by DeMore and co-workers.[6] Three major reaction pathways have been proposed[2] for the interactions of O(^{1}D) with hydrocarbons in the gas phase, namely, (1) exoergic C–H bond insertion to form a highly energized alcohol intermediate which, depending on its complexity and the pressure at which the reaction takes place, may be stabilized or decompose by fragmentation to form radical products, (2) H atom abstraction to give direct formation of alkyl and hydroxyl radicals, and (3) elimination of H$_2$. Recent dynamics studies of O(^{1}D) reactions with CH$_4$ have shown that only atomic hydrogen is formed in the gas phase,[7] suggesting that the observation of molecular hydrogen in earlier gas- and solution-phase work may be due to hydrogen atom abstraction or recombination reactions.

The reactivity of O(^{1}D) with H$_2$, CH$_4$, and several small hydrocarbons in liquid argon has been studied by DeMore[8,9] and DeMore and Raper.[10] The reactions of O(^{1}D) with ethane, propane, and isobutane[8] resulted in the formation of alcohols as the major products. The products of these three reactions were completely stabilized in the liquid argon environment, allowing the initial insertion product ratios to be determined directly by gas chromatographic techniques. The insertion reaction was found to proceed statistically, indicating no selectivity for the type or strength of C–H bond. In the case of methane, dissociation of the methanol product occurred to the extent of about 30%,[10] while in the case of H$_2$, only fragments of the presumed H$_2$O intermediate were observed.[9] Formation of H$_2$ and formaldehyde from the reaction of O(^{1}D) with methane was also observed, indicating a minor side reaction which accounted for about 10% of the reactivity.

Several reactions between O(^{1}D) and small molecules in cryogenic matrices have been observed by Appelman *et al.*,[11]

who produced O(^{1}D) from photolysis of HOF in solid Ar, CO, CH$_4$, NO, and other matrix materials. In particular, production of methanol in solid methane and CO$_2$ in solid CO was observed. Hawkins and Andrews[12] have observed production of vinyl alcohol, ethylene oxide, acetaldehyde, and ketene, following broad-band excitation of ozone in matrices containing ethene. Several groups[13-15] have observed carbon trioxide formation in solid CO$_2$ and argon matrices, following the reaction of O(^{1}D) with CO$_2$. Sodeau and Withnall[16] have characterized the photoproducts formed following 184.9-nm photolysis of N$_2$O aggregates in argon matrices, observing the formation of *cis*-ON–NO following reaction of O(^{1}D) with N$_2$O. The photochemistry of matrix-isolated ON–NO has also been studied by Hawkins and Downs,[17] who observed the formation of NO$_2$. Both NO$_2$ and ON–NO are observed side products in the present studies.

Chemical dynamics studies involving the reaction of O(^{1}D) with many of the molecules involved in the present study have been done. Studies of O(^{1}D) reactions with molecular hydrogen and various alkanes are all in accord with direct insertion processes, followed by decomposition of the primary insertion products.[18-24]

The present work is a study of the reactivity of O(^{1}D) formed following broad-band UV–visible irradiation of nitrous oxide in argon matrices. For all reactions studied, one or more stable addition or insertion products were observed, with no significant evidence for secondary fragmentation processes. The study illustrates the complementary role of the matrix-isolation technique with respect to gas- and solution-phase reactivity and kinetics studies of excited-state atom chemistry with respect to identification of the primary reaction product(s). The results also show that nitrous oxide is a feasible source of metastable O(^{1}D) atoms when a conventional xenon arc lamp is employed.

Experimental Approach

The matrix-isolation apparatus used was similar to that described earlier.[25] Matrices containing 2% nitrous oxide (CP) and 10% of either CO (CP), CO$_2$ (Bone Dry), methane (UHP), ethane (CP), propane (CP), or isobutane (CP) in research-grade argon were formed by condensing a premixed gas sample on a CsI window cooled to 12 K with a closed-cycle helium refrigeration unit (APD Cryogenics Displex Model 202). Gas flow rates were controlled by a mass-flow meter, typically set to 1.2 cm^3/min. Other combinations of gases were as noted in the text below. All
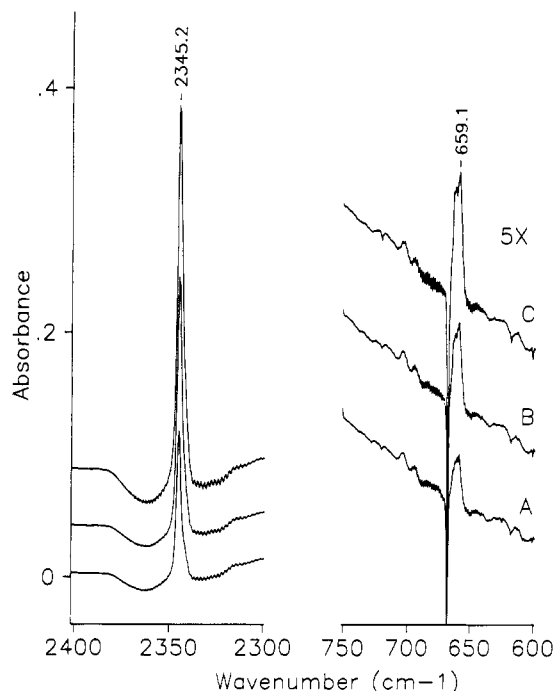
Figure 1. FT-infrared absorption spectra of a matrix formed by condensing argon containing 2% N$_2$O and 10% CO over the 2400–2300 and 750–600-cm^{-1} ranges (A) on deposition, (B) following 1 h of broad-band irradiation, and (C) following 2 h of irradiation. Wavenumber markers indicate features associated with CO$_2$ that grew in intensity following irradiation.
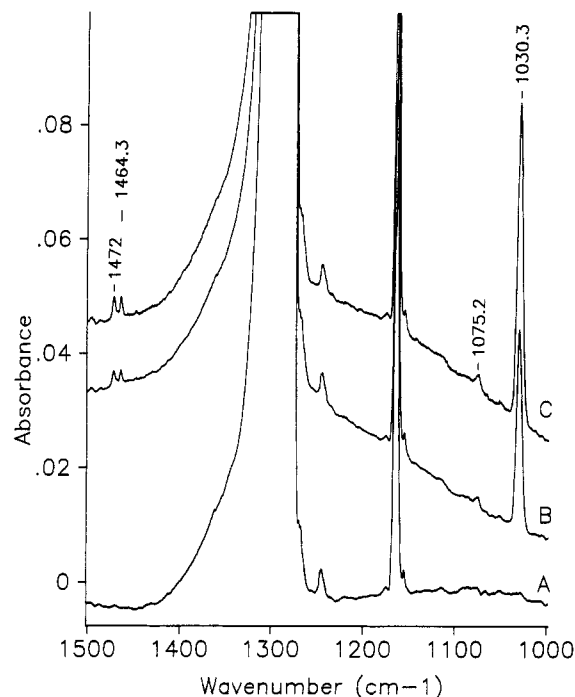

Figure 2. FT-infrared absorption spectra of a matrix formed by condensing argon containing 2% N$_2$O and 10% CH$_4$ over the 1500–1000 range (A) on deposition, (B) following 1 h of broad-band irradiation, and (C) following 110 min of irradiation. Wavenumber markers indicate features associated with methanol that grew in intensity following irradiation.

gases were supplied by Matheson of Canada and were used without further purification. Single-beam infrared absorption spectra of the matrices following deposition and following subsequent irradiation were recorded at 1-cm^{-1} resolution with a Bomem MB-102 FTIR spectrometer and ratioed against the single-beam spectrum of the cold window. Samples were irradiated by focusing the full output of a high-pressure 150-W xenon arc lamp through a dry N$_2$ purged cylinder and quartz window. Sample irradiation time periods were between 1 and 2 h, unless otherwise noted. Under the conditions of these experiments, product molecule spectra are expected to be somewhat perturbed due to the presence of the reactant molecules, with respect to spectra of fully matrix-isolated molecules.

Results

N$_2$O. Irradiation of a matrix formed by condensing a 2% mixture of N$_2$O in argon for 3 h resulted in a 3% decrease in absorptions associated with N$_2$O (2222.2, 1282.9, 588.2 cm^{-1}) as well as the appearance of features assigned in previous work to NO$_2$[26] (1611.8, 1606.5 cm^{-1}), *cis*-ON–NO[16] (1863.5, 1775.7 cm^{-1}), NO[27] (1872.7 cm^{-1}), and N$_2$O$_3$[28] (1835.0, 1689.0, 1629.7 cm^{-1}). No other new absorptions were observed. Product bands were observed to grow in monotonically with irradiation time. Production of NO, NO$_2$, *cis*-ON–NO, and N$_2$O$_3$ as minor products was observed along with the major products noted in all subsequent experiments described below.

N$_2$O/CO. Irradiation of a matrix formed by condensing argon containing 2% N$_2$O and 10% CO resulted in the appearance of new bands at 2345.2, and 659.1 cm^{-1}, corresponding to the IR-active fundamental absorptions of matrix-isolated CO$_2$,[29] illustrated in Figure 1. The slight red shift of the bending mode vibrational frequency from the usual value of 668 cm^{-1} is most likely a reflection of a perturbation associated with the 10% CO in the matrix.

N$_2$O/CO$_2$. Irradiation of a matrix formed by condensing argon containing 2% N$_2$O and 10% CO$_2$ resulted in a decrease in N$_2$O absorptions, and the appearance of a new band at 2041.9 cm^{-1},

corresponding to one of the previously reported IR-active fundamental absorptions of CO$_3$.[13–15] Irradiation of a CO$_2$ matrix containing 2% N$_2$O resulted in the growth of features at 2045.7, 1880.0, 972.0, and 568.0 cm^{-1}, again due to CO$_3$. An approximately 4-fold increase in yield was observed when compared with irradiation of an Ar matrix containing 2% N$_2$O and 10% CO$_2$.

N$_2$O/CH$_4$. Irradiation of a matrix formed by condensing argon containing 2% N$_2$O and 10% CH$_4$ resulted in the growth of new absorptions at 3661.0, 2950.7, 2841.7, 1471.9, 1464.2, 1332.6, 1030.3 cm^{-1} (and others), associated with the infrared absorptions of matrix-isolated methanol.[30] The growth of features in the 1000–1500-cm^{-1} region is illustrated in Figure 2.

N$_2$O/Ethane. Irradiation of a matrix formed by condensing argon containing 2% N$_2$O and 10% ethane resulted in the growth of features associated with matrix-isolated ethanol[31] at 3655.6, 1239.5, 1088.6, 1026.0, 889.6, and 421 cm^{-1} (and others).

N$_2$O/Propane. Irradiation of a matrix formed by condensing argon containing 2% N$_2$O and 10% propane resulted in the growth of features associated with matrix-isolated 1-propanol (1232.2, 1221.2, 1023.1, 968.6 cm^{-1}, and others) and 2-propanol (1250.7, 1077.5, 952.7 cm^{-1}, and others). Product identification was done by spectral comparison with matrices containing only one of 1-propanol or 2-propanol in argon containing 2% N$_2$O and 10% propane. The 1-propanol and 2-propanol yields were found to be similar, although it was not possible to obtain an internally consistent measure of the relative yields of the two products.

N$_2$O/Isobutane. Irradiation of a matrix formed by condensing argon containing 2% N$_2$O and 10% isobutane resulted in the growth of new features associated with matrix-isolated 2-methyl-1-propanol (1005.8, 992.7, 813.9, 488.9 cm^{-1}, and others) and 2-methyl-2-propanol (1213.5 cm^{-1} and others). Product identification was done by spectral comparison with matrices containing only one of 2-methyl-1-propanol and 2-methyl-2-propanol in argon containing 2% N$_2$O and 10% butane. The relative yield of 2-methyl-1-propanol to 2-methyl-2-propanol was found to be approximately 9:1, as determined by peak area ratio comparisons with spectra of standard mixtures of these two
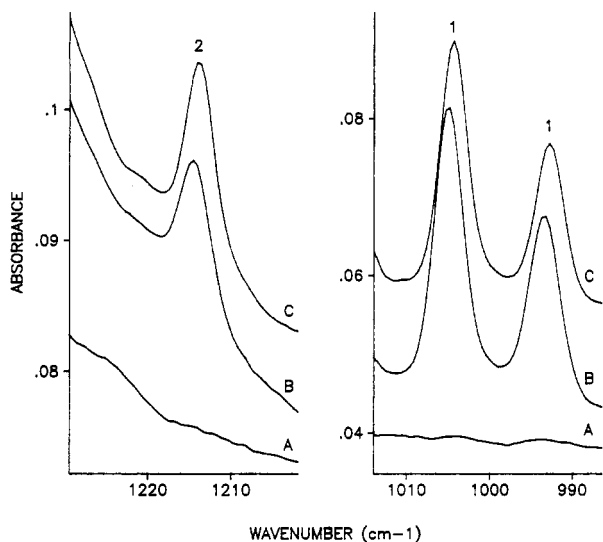
Figure 3. FT-infrared absorption spectra of a matrix formed by condensing argon containing 2% N_2O and 10% isobutane over the 1230–1200- and 1015–985-cm^{-1} range (A) on deposition, (B) following 715 min of broadband irradiation. Features associated with 2-methyl-1-propanol (denoted 1) to 2-methyl-2-propanol (denoted 2) that grew in intensity following irradiation are marked. Spectrum C illustrates the observed intensity ratio for a 9:1 mixture of 2-methyl-1-propanol (0.12%) to 2-methyl-2-propanol (0.013%) in an argon matrix containing 2% N_2O and 10% isobutane, for comparison.

chemicals in argon containing 2% N_2O and 10% isobutane. The calculated ratio is approximately the value anticipated for a random insertion process (9.0:1), in which no selectivity for type or strength of bond is present. Figure 3 illustrates the growth of features associated with 2-methyl-1-propanol and 2-methyl-2-propanol following irradiation, with the spectrum of a 9:1 standard reference mixture of 2-methyl-1-propanol and 2-methyl-2-propanol for comparison.

Discussion

The results of this study show that $O(^1D)$ is produced in cryogenic matrices, following irradiation of N_2O with light from a focused xenon arc lamp. This follows since (1) $O(^1D)$ is known to be the major primary product of N_2O photolysis in the high-energy limit of the wavelength region utilized in the experiments[32] and (2) the primary products created following N_2O photolysis are known to be formed from the reactions of $O(^1D)$ atoms with the substrate molecules studied here. N_2O is therefore a viable source of $O(^1D)$ in cryogenic matrices when a xenon arc lamp is used as a radiation source. An important reason for using N_2O as a source of $O(^1D)$ over the more commonly used ozone source is that $O(^1D)$ is the only major product of N_2O photodissociation in the UV range, while UV photodissociation of ozone leads to production of both $O(^1D)$ and $O(^3P)$.[32] Moreover, the photolysis byproduct, N_2, is relatively inert as a matrix constituent, while the product of ozone photolysis, molecular oxygen, is photoactive in the wavelength region utilized in the present study, where it is a source of ground-state $O(^3P)$ atoms.[32]

The absence of absorptions associated with hydroxyl or alkyl radicals following $O(^1D)$ reactions with methane and other hydrocarbons suggests that the efficiency of energy transfer from the initially formed "chemically activated" alcohol molecule is sufficiently high to quench essentially all subsequent decomposition processes. The observation of methanol as the only major product in the reaction of $O(^1D)$ with methane suggests that the rate of energy transfer is significantly greater than is present in liquid argon, where the same reaction leads to partially fragmented products such as methoxy radicals and hydrogen atoms as well as methanol.[10] Thus, the solid matrix environment appears to be substantially better suited for the stabilization of primary products of excited-state $O(^1D)$ reactions than liquid argon.

The question of a very highly efficient matrix cage recombination process in which primary product decomposition fragments such as alkyl and hydroxyl radicals recombine with unit efficiency must be addressed to evaluate the present work in terms of its significance with respect to gas-phase reaction intermediate stabilization. The ability of photodecomposition fragments such as methyl radicals, hydrogen atoms, and other small radicals to escape the matrix cage in which they are initially formed and to be trapped subsequently in high yield in a nearby cage is well-established.[33] The reactions studied in the present work are all highly exoergic, when considered as insertion processes. For example, the reaction of $O(^1D)$ with methane to form methanol has a reaction exoergicity of about 600 kJ mol^{-1}. Therefore, a highly efficient radical recombination process brought about by the matrix cage effect is not likely in the present system, given the highly energized state in which the primary products would be formed, which is comparable to that involved in a typical photoinduced fragmentation process. We feel that the present results are best understood as reflecting the stabilization of initially formed reaction products which, in the absence of third-body collisional stabilization, would be transient intermediates in the analogous gas-phase reactions.

Abstractive reaction mechanisms have been suggested in studies of the kinetics and dynamics of $O(^1D)$ reactions with hydrocarbons.[2,23,24] Such abstraction processes are considerably less exoergic than the corresponding insertion processes but are believed nevertheless to have no significant activation energy barriers. As the abstractive process occurs without formation of a long-lived intermediate, energy transfer to the surrounding matrix is much less probable for an abstractive than for an insertive process. On this basis, it seems reasonable to assume that hydroxyl and alkyl radicals formed in an abstractive mechanism would have as great or greater probability of escaping the matrix cage in which they are initially formed and therefore of being trapped and observed spectroscopically. Thus, the absence of such radical fragments in the present work is also taken as evidence that an abstractive mechanism is not appropriate for the reactions of $O(^1D)$ with hydrocarbons in a solid matrix and perhaps in other media as well.

The observation of CO_2 as a product of the reaction of $O(^1D)$ with CO is of interest with respect to the interpretation of the mechanism for collisional quenching of $O(^1D)$ by CO to form $O(^3P)$. The gas-phase kinetics studies of Paraskevopoulos and Cvetanović[1] have shown that CO is a very efficient deactivator of $O(^1D)$, forming $O(^3P)$ on every collision. DeMore has shown that the relatively complex pressure dependence of the kinetics of this reaction is, however, indicative of deactivation of $O(^1D)$ via a CO_2 intermediate.[34] Cvetanović has also noted that there is no long-range attractive character to the triplet surface for the approach of $O(^3P)$ to CO, and a significant barrier[35] must be surmounted before access to the ground-state singlet surface of CO_2 is possible. This strongly suggests that formation of CO_2 from $O(^3P)$ + CO is not possible at the very low temperatures at which the present studies were done. Therefore, the appearance of CO_2 as a product in the present study is best interpreted by considering the collisional deactivation of $O(^1D)$ by CO as proceeding through the initial formation of an energized CO_2 intermediate which decomposes to $O(^3P)$ and CO in the gas phase, but which leads to the formation of CO_2 in a matrix. Such an interpretation is consistent with the previous gas-phase kinetics and dynamics studies noted above.

The production of CO_3 following reaction of $O(^1D)$ with CO_2 in cryogenic matrices has been known for some time.[13-15] As noted above, the production of CO_3 was enhanced by about 4-fold on passing from an argon matrix containing 10% CO_2 and 2% N_2O to a CO_2 matrix containing 2% N_2O. This enhancement may be attributable to the higher probability of the $O(^1D)$ encountering a CO_2 molecule in a pure CO_2 matrix before being

deactivated to $O(^3P)$ in the matrix. However, it may also reflect the greater availability of vibrational and rotational energy states of CO_2 which act as additional sinks for the excess energy with which the initially formed CO_3 would be found. This would then suggest that the efficiency with which CO_3 is stabilized in an argon matrix containing 10% CO_2 is less than about 25% and that a substantial portion of the interactions of $O(^1D)$ with CO_2 result in deactivation and formation of $O(^3P)$, the dominant process in the gas phase.[3] This is the only evidence in the present study that suggests a less than complete efficiency in the stabilization of the primary reaction product. However, it is difficult to distinguish between the two possible explanations, and therefore no conclusion can be reached to explain the CO_3 yield enhancement in pure CO_2.

The observed distribution of isomeric products in the reactions of $O(^1D)$ with isobutane confirms the statistical nature of the insertion process, given that the product distribution observed is that which would be anticipated in a random process in which no selectivity is present. This in turn strongly suggests that the reaction efficiency is near unity for this reaction, which is consistent with very high absolute quenching cross sections for the gas-phase reactions of $O(^1D)$ with all molecules studied in the present work.[36] It is highly unlikely that indiscriminate insertion would occur if a significant fraction of the $O(^1D)$ atoms were deactivated following interaction with a hydrocarbon precursor molecule. It would be necessary for the efficiency of such deactivation to be independent of the particular aspect of the molecule encountered by the $O(^1D)$ for a statistically determined product distribution to be observed. Note that subsequent reactions with hydrocarbons of any $O(^3P)$ formed in such a scheme would not be expected to occur at 12 K, given the significant activation energy barriers to C–H insertion.[37] Therefore, the statistical product distribution could not be interpreted as resulting from a combination of $O(^1D)$ and $O(^3P)$ reactions, both occurring with very high efficiency. The product distribution observed also strongly suggests that there is no favored orientation of the N_2O photolytic precursor molecule with respect to the hydrocarbon substrate, since such a prealignment would also be expected to result in the observation of a nonstatistical product distribution.

Summary

$O(^1D)$ is produced in argon matrices following irradiation of N_2O with a xenon arc lamp. The products of the reactions of $O(^1D)$ with CO, CO_2, methane, ethane, propane, and isobutane have been observed spectroscopically and correspond to the anticipated primary reaction products CO_2, CO_3, methanol, ethanol, and isomers of propanol and 2-methylpropanol. In all cases, highly efficient quenching of the excess energy associated with a "hot" primary reaction product is believed to occur, since no decomposition products such as alkyl and hydroxyl radicals were observed. The absence of radical fragments also suggests that an abstraction mechanism is not appropriate for the reaction of $O(^1D)$ with hydrocarbons in the matrix environment. The statistical product distribution observed in the reaction of $O(^1D)$ with isobutane reflects a highly efficient, indiscriminate insertion process, without a significant contribution from deactivation processes leading to production of $O(^3P)$.

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