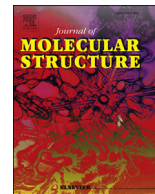




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Matrix isolation study of the red light-induced reaction of triethylborane with ozone

Bruce S. Ault

Department of Chemistry, University of Cincinnati, Cincinnati, OH, 45221-0172, USA

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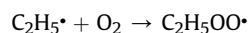
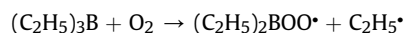
ABSTRACT

The thermal and red photochemical reaction of triethylborane and ozone has been explored in argon matrices with infrared detection. Using both twin jet and merged jet deposition, no significant thermal reaction was observed. In contrast, red light irradiation of the twin jet-deposited matrix led to the formation of the novel $\text{H}_5\text{C}_2\text{BO}$ species, ethyloxoborane. A strong, broad absorption was observed at 1963 cm^{-1} after irradiation and assigned to the $^{11}\text{B}=\text{O}$ stretching mode, with a ^{10}B counterpart at 2027 cm^{-1} . Two additional bands of lower intensity were also assigned to $\text{C}_2\text{H}_5\text{BO}$. Band assignments for this species were supported by ^{18}O isotopic labeling experiments. Computational studies further supported the band assignments and confirmed that $\text{H}_5\text{C}_2\text{BO}$ plus butane is the thermodynamically favored reaction pathway. Kinetic considerations for this reaction are also presented.

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1. Introduction

Triethylborane, $(\text{C}_2\text{H}_5)_3\text{B}$, is widely used as a radical initiator in synthetic organic reactions [1–3], following radical formation through the autoxidation reaction of $(\text{C}_2\text{H}_5)_3\text{B}$ with O_2 :



A recent theoretical study [4] found evidence that this reaction is autocatalytic, helping to account for the high yield of radicals produced even at relatively low temperatures. A kinetic study [5] recently explored the elementary steps and rate constants for this reaction sequence to identify the known challenges to working with this system. Overall, the importance of the $(\text{C}_2\text{H}_5)_3\text{B}/\text{O}_2$ system for radical reactions is well known.

Given this importance, it is interesting to note that there are no reports of the reaction of $(\text{C}_2\text{H}_5)_3\text{B}$ with ozone in the literature, and very little is known about the reaction of $(\text{C}_2\text{H}_5)_3\text{B}$ with oxygen atoms. One early report [6] studied the chemiluminescent reaction of O atom with $(\text{C}_2\text{H}_5)_3\text{B}$ in the gas phase flow reactor and noted

fluorescence from BO and BO_2 . However, this study gave no indication of a mechanism by which these species would form and what intermediates might have been formed during the reaction. Along these lines, the reactions of the heavier group IIIA trialkyls with ozone and/or O atoms have not been reported in the literature either.

To provide insights as to the mechanism of reaction of trialkyl compounds of the group IIIA elements, we have employed the matrix isolation technique to study the thermal and photochemical reactions of $(\text{CH}_3)_3\text{Al}$, $(\text{CH}_3)_3\text{Ga}$ and $(\text{CH}_3)_3\text{In}$ with ozone [7–9]. The matrix isolation technique has proven exceptionally valuable for the study of reactive intermediates and the determination of (at least) partial reaction mechanisms [10–12]. Both twin jet and merged jet techniques were employed, to study initial intermediates and “later” products of these reaction. At short times using twin jet deposition in each of these systems, the initial product was the O atom insertion product, forming $(\text{CH}_3)_2\text{MOCH}_3$, $\text{M} = \text{Al}, \text{Ga}$ and In . Later products, using merged jet deposition, included H_2CO , CH_3OH and C_2H_6 . A mechanism was developed to account for all of the observed products. The present manuscript reports a similar matrix isolation and computational study of the thermal and photochemical reactions of ozone with triethylborane (chosen since it is less hazardous to handle than trimethylborane). However, as described below, this reaction follows a very different, novel pathway compared to the previous $(\text{CH}_3)_3\text{M}$ studies, yielding

E-mail address: bruce.ault@uc.edu.

an unexpected borane intermediate.

2. Experimental

All experiments in this study were conducted using a standard matrix isolation system that has been previously described [13,14]. Triethylborane (Strem Chemical) was introduced into the vacuum system from a gas cylinder and was subjected to a freeze-pump-thaw cycle at 77 K prior to sample preparation. Ozone was produced by the Tesla coil discharge of O_2 in a discharge tube cooled to 77 K. Residual O_2 was pumped off before the ozone was warmed to room temperature. Isotopically labeled $^{18}O_3$ was produced in the same manner from ^{18}O -labeled O_2 (94%, Cambridge Isotope Laboratories). A known amount of reactant vapor was diluted with argon to the desired ratio in each sample manifold. Argon (Wright Brothers) was used as the matrix gas in all experiments, without further purification.

Both twin jet and merged jet deposition methods were used to explore different time scales of the thermal reaction. In twin jet deposition, the two gas reactants were deposited onto CsI window from two separate nozzles simultaneously, allowing only a very short mixing time prior to matrix condensation. In merged jet deposition [14], a 24-cm merged jet reaction region (reaction zone) was used. The gas samples combined at a tee and flowed together through the merged or reaction zone to the cold window. Samples were deposited on the window for about 20 h before a final spectrum was recorded. In most experiments, the matrix was irradiated with a near infrared diode ($\lambda = 880$ nm), a red-emitting diode ($\lambda = 625$ nm) or an unfiltered Hg pen lamp after which additional spectra were recorded. All the spectra were recorded on a Perkin Elmer Spectrum One Fourier transform infrared spectrometer from 450 to 4000 cm^{-1} at 1 cm^{-1} resolution.

Theoretical calculations were carried out on a number of likely intermediates in this study, using the Gaussian 03 and 03 W suite of programs [15]. Density functional theory (DFT) using the hybrid functional B3LYP along with 6–311++G(d, 2p) basis set was used for geometry optimization, to locate energy minima and calculate vibrational spectra.

3. Results and discussion

Separate experiments were conducted on each of the reagents alone in argon prior to any codeposition experiments. The experimentally obtained blank spectra of ozone in solid argon were in good agreement with literature spectra [16] and with blanks run previously in this laboratory. While there were no matrix spectra of $(C_2H_5)_3B$ available in the literature, the spectra recorded here were in good agreement (within about 1%) of the spectra that we calculated theoretically. Both blank experiments were also irradiated, in sequence, with the 880 nm near infrared diode, the 625 nm red diode and the Hg pen lamp. No changes occurred as a result of any of these irradiation processes.

3.1. Twin jet

When a sample of $Ar/(C_2H_5)_3B = 1000$ was deposited with a sample of $Ar/O_3 = 250$ in the twin jet mode only one very weak product band was observed, at 1726 cm^{-1} . This matrix sample was then annealed to 27 K, recooled and a spectrum recorded. No changes were observed as a result of annealing. The matrix was then irradiated with the output of the 880 nm near infrared diode for 1 h and no changes were observed. Lastly, the matrix was irradiated with the 625 nm light from a red diode for 1 h and distinct changes were detected. The most significant was the growth of a somewhat broad (10 cm^{-1} width at half maximum),

somewhat asymmetric peak at 1963 cm^{-1} . Additional very weak bands were seen at 528, 744 and 2027 cm^{-1} along with slight growth in the 1726 cm^{-1} band. Fig. 1a and b shows spectra of this experiments.

In several subsequent experiments, similar samples were deposited and again only the weak 1726 cm^{-1} band was observed upon initial deposition. Then, these matrixes were irradiated for a longer time (4 and 5 h) with the red diode. The same product bands reported above were observed with a somewhat higher yield. In addition, the weak product band was again noted at 2027 cm^{-1} with the same general band shape as the 1963 cm^{-1} band but with about 20% of the intensity. This suggests that it might be due to a ^{10}B counterpart of the more intense ^{11}B band at 1963 cm^{-1} . This shift, 64 cm^{-1} , is of the magnitude expected for a boron atom vibration. Moreover, the lack of one or more intermediate peaks between 1963 and 2027 cm^{-1} would indicate that the product species responsible for the 1963 cm^{-1} contains a single boron atom. These twin jet results were reproducible over multiple experiments.

A similar experiment was conducted in which the matrix was irradiated for 4 h with the full output of a mercury pen lamp instead of the red diode. In this case, some growth of the band at 1726 cm^{-1} was observed. The 1963 cm^{-1} band was observed as well but in lower amount than with red diode irradiation. This indicates that somewhat different photochemical processes are occurring with the two different irradiation methods.

To further understand the species responsible for the new absorptions reported above, a sample of $Ar/(C_2H_5)_3B = 1000$ was deposited with a sample of isotopically labeled $Ar/^{18}O_3 = 250$ (94 atom % ^{18}O). Before irradiation, a new weak band was observed at 1693 cm^{-1} , while after red irradiation, weak product bands were observed at 526 and 744 cm^{-1} as well as a broad, somewhat asymmetric band at 1929 cm^{-1} . These are all clear counterparts of the ^{16}O bands at 528, 744 and 1963 cm^{-1} . Finally, one experiment was conducted with a sample of $Ar/(C_2H_5)_3B = 1000$ and a sample of scrambled $Ar/^{16,18}O_3$ (approximately 40% ^{18}O). The 1693 and 1726 cm^{-1} bands appeared as a weak doublet upon initial deposition. After red diode irradiation, the 1929, 1963 cm^{-1} bands appeared as a distinct doublet with no intermediate bands while the weak 744 cm^{-1} band was present, unshifted. The mixture of isotopes made the very weak bands around 528 cm^{-1} too indistinct to clearly resolve. The appearance of a doublet at 1929, 1963 cm^{-1} in the scrambled isotopic experiment strongly indicates that the absorbing species contain a single oxygen atom. Fig. 2 shows spectra of this scrambled isotopic experiment.

The experimental data presented above strongly suggest that the species responsible for the 1726 cm^{-1} band seen prior to red irradiation contains a single O atom. More, this band is in the region of a carbonyl, C=O, stretching mode. Based on comparison to the earlier work with the trimethyl metal compounds, acetaldehyde is a likely product. In fact, the weak 1726 cm^{-1} band with its ^{18}O counterpart at 1693 cm^{-1} matches nearly exactly the band position of the intense C=O stretch of matrix isolated acetaldehyde [17]. Since this band was very weak, no other bands of acetaldehyde are likely to be detectable. The 528 and 744 cm^{-1} bands grew in on irradiation and do not match any bands of acetaldehyde. Thus, based on the match between an authentic matrix spectrum of acetaldehyde and the 1726 cm^{-1} band in the present study, assignment to acetaldehyde is made.

Of more interest is the one or more species formed after red light irradiation. Red light irradiation of ozone has been shown in many studies to produce O atoms in the 3P state through an n to π^* transition on O_3 [18,19]. Further, this transition is often intensified and slightly shifted when ozone is weakly complexed to another molecule. This is consistent with the observation that the product(s) formed on red light irradiation contain a single O atom. Based

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