zation step, but rather to rearrangement of the ion pair *after* the ionization step.[10,12]

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Infrared Spectrum of Matrix-Isolated HBO

Sir:

Boroxine ($H_3B_3O_3$), a trimer of HBO, has been observed as a product in a number of high temperature (or high energy) reactions including (a) the reaction of H_2O with elemental boron at temperatures above 1000°,[1] (b) explosive reactions of B_2H_6–O_2[2] and B_5H_9–O_2[3] mixtures at low pressures, and (c) the photolysis of $H_2B_2O_3$–B_2H_6 mixtures with radiation in the vacuum-ultraviolet.[4] These experimental results have suggested that a simple monomeric species, HBO, is a short-lived chemical intermediate. We have now identified the HBO molecule as one of the photolysis products of $H_2B_2O_3$ in a low-temperature argon matrix.

The matrix-isolation apparatus has been described.[5] Manometrically prepared gas mixtures of Ar and $H_2B_2O_3$ were metered into the vacuum system and deposited on a cooled (5°K) CsI target window. Residual pressure in the system was maintained at 5×10^{-6} Torr or lower during deposition. The photolysis source was a low-pressure (0.5 mm) Xenon lamp[6] with a LiF window. The body of lamp was extended through a sealed flange into the vacuum system to place the lamp window within 4 cm of the target window. Microwave power for the lamp was provided by a Raytheon 2450-MHz unit. Radiation reaching the target has a wavelength of 1480 Å with a half-width of about 10 Å. In a typical experiment, a gas sample containing Ar + $H_2B_2O_3$ was simultaneously deposited and photolyzed for 5 hr with a total deposition of $10\text{–}15 \times 10^{-6}$ mol of $H_2B_2O_3$. The dewar was then rotated and the absorption infrared spectrum (4000–250 cm^{-1}) was recorded on a Perkin-Elmer 521 spectrometer calibrated with NH_3 and HCl. Essentially identical spectra were obtained from the following experiments: (1) variation of the molar ratio of $Ar/H_2B_2O_3 = 250$ to a ratio of 1000, (2) photolysis during or after deposition, and (3) photolysis with a low-pressure xenon lamp or a medium-pressure mercury lamp (1849-Å radiation). Samples of $H_2B_2O_3$ with the natural isotopic composition were prepared from B_5H_9 and O_2.[7] Isotopically labeled samples, $D_2B_2O_3$, $H_2{}^{10}B_2O_3$, and $D_2{}^{10}B_2O_3$, were prepared from the appropriately labeled diborane and oxygen.[4]

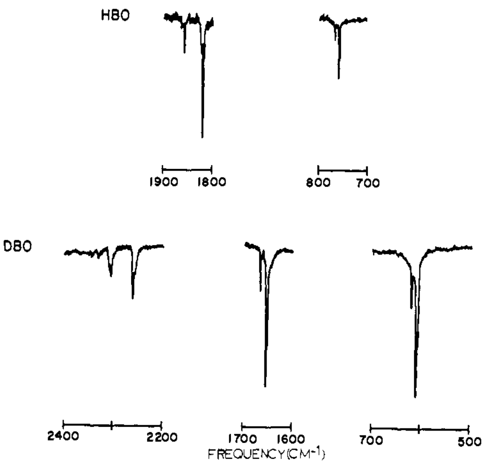

Figure 1. Infrared spectra of matrix-isolated HBO and DBO.

Products of the photolysis of $H_2B_2O_3$ in an argon matrix exhibit strong ir absorption in the region 2000–2130 cm^{-1}; moderately strong bands at 3685 and 3635 (OH stretching region), 1382 and 1425 (^{11}B–O and ^{10}B–O stretch), 1398 and 1440 cm^{-1} (^{11}B–O and ^{10}B–O stretch); a relatively broad band centered at 3367 cm^{-1} which shifts to 2505 cm^{-1} on deuterium substitution; and a group of line-like bands that will be discussed subsequently. Two of the strongest bands at 2062 and 2130 cm^{-1} that also appear when $D_2B_2O_3$ is photolyzed are readily identified with the molecule B_2O_3.[8]

In Figure 1 is shown the band structure associated with the molecule HBO and in Tables I and II are listed fundamentals and results of product rule calculations based on a linear molecule with $C_{\infty v}$ symmetry. There is very good agreement between the experimental and calculated results in Table II. Force constants calculated by assuming a simple valence force model[9] for

Table I. Frequencies (cm^{-1}) Observed for HBO in an Argon Matrix

	Isotopic species			
	$H^{11}BO$	$H^{10}BO$	$D^{11}BO$	$D^{10}BO$
ν_1	(2849)[a]	(2874)[a]	2259	2303
ν_2	754	764	606	617
ν_3	1817	1855	1648	1663

[a] Calculated.

Table II. Product Rule Calculations for HBO

Vibration species	Isotope pair X/X′	$(\nu_1\nu_3)/(\nu_1'\nu_3')$ Obsd	$(\nu_1\nu_3)/(\nu_1'\nu_3')$ Calcd	ν_2/ν_2' Obsd	ν_2/ν_2' Calcd
Σ^+	$D^{10}BO/D^{11}BO$	1.029	1.031		
π	$H^{10}BO/H^{11}BO$			1.013	1.013
π	$H^{11}BO/D^{11}BO$			1.244	1.243
π	$D^{10}BO/D^{11}BO$			1.018	1.019

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[9] G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, p 173.

Table III. Force Constants Calculated for HBO

Fundamentals and frequencies, cm^{-1}	Force constants $\times 10^5$ dyn/cm k_1	k_2	k_σ/l_1l_2
ν_3 ($H^{11}BO$), ν_3 ($D^{11}BO$) (1817, 1648)	4.27	13.86	
ν_3 ($H^{11}BO$), ν_3 ($H^{10}BO$) (1817, 1855)	4.45	13.83	
ν_1 ($D^{11}BO$), ν_3 ($D^{11}BO$) (2259, 1648)	4.10	14.32	
ν_2 $H^{11}BO$ (754)			0.233
ν_2 $D^{11}BO$ (606)			0.233

HBO with H—B and B—O bond distances of 1.18[10] and 1.20 Å,[11] respectively, are summarized in Table III. Values of the B—O stretching force constants (Table III) are close to that found in B_2O_2 (13.86×10^5 dyn/cm).[8] The ^{11}B-H stretching frequency in HBO, which was too weak for detection, is calculated from the DBO force constants to be 2849 cm^{-1} and is probably reliable to within ± 10 cm^{-1}. This is higher than any B-H stretching frequency known and is close to that reported for BH_3.[5]

The photodecomposition of $H_2B_2O_3$ in an argon matrix must involve at least one reaction path in addition to those leading to HBO and B_2O_3. The band of a photolysis product at 3367 cm^{-1} is interesting because it can most reasonably be assigned to a hydrogen-bonded OH stretching vibration. This band, the weaker bands in the normal OH stretching regions, and the bands between 1380 and 1440 cm^{-1} may be associated with a hydrogen-bonded complex formed by intramolecular transfer of H atoms from boron to oxygen sites.

Acknowledgment. We are grateful for financial support from the Advanced Research Projects Agency through the Materials Science Center, Cornell University, and the Army Research Office-Durham.

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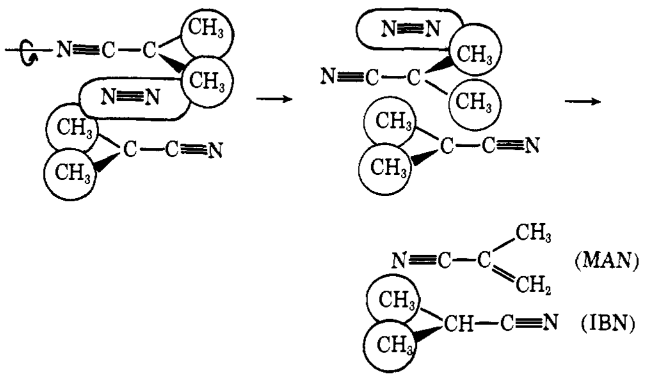
Rotational Diffusion Control of Radical Disproportionation in the Solid-State Photolysis of Azobisisobutyronitrile

Sir:

For some time we have been studying the chemistry of the cyanoisopropyl radical pair and the nitrogen molecule generated in crystalline azobisisobutyronitrile (AIBN) by photolysis.[1] Disproportionation to methacrylonitrile (MAN) and isobutyronitrile (IBN) accounts for only 5% of the radical-radical reactions in fluid solution but for 95% in the crystal.[2] From epr studies and dynamic computer simulations we suspected that disproportionation of the nitrogen-separated radical pair was limited in rate by rotational diffusion about a C—C≡N axis which brings a methyl group into the position formerly occupied by the nitrogen molecule. We show below that the rate of disproportionation is limited not by atom transfer but, presumably, by this diffusion.[3]



Two deuterated samples of AIBN were prepared. One from exchanged acetone 2-cyano-2-propylhydrazone was 75 mol % AIBN-d_6 with one pair of geminal methyls labeled and 25 mol % of roughly equal parts of AIBN-d_0 and AIBN-d_{12}.[4] In deuterated positions labeling was 94% complete.[4] The other from partially exchanged acetone contained 73 atom % deuterium randomly distributed.[4]

Samples recrystallized three times from methanol were sealed in nmr tubes at 10^{-3} Torr and photolyzed in a Dry Ice-acetone bath for 10-15 hr with a Pyrex-filtered Hanovia L mercury arc. Products were analyzed by nmr after opening the tube, adding solvent, and resealing. The AIBN-d_6 sample was 79% decomposed to give 94% disproportionation and 6% tetramethylsuccinodinitrile (TMSN). The randomly labeled AIBN was about 72% decomposed to give a ratio of disproportionation to TMSN of about 9.

Integrals for AIBN-d_6 products based on 3 for MAN methyl were: MAN vinyls, 1.06 and 1.05; IBN methyl, 6.64.[5] Crude calculation of an apparent k_H/k_D from the excess of IBN-d_0 + IBN-d_1 over MAN-d_0 gives 0.85 or 0.92 based on MAN methyl and MAN vinyl, respectively.[6] These values are nearly within experimental error of unity. Neglecting isotopic differences, pathways for atom donation by the two radicals are equivalent by symmetry in the centrosymmetric reaction

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[1] A. B. Jaffe, D. S. Malament, K. J. Skinner, and J. M. McBride, papers presented at the Second International Symposium on Organic Solid-State Chemistry, Rehovot, Israel, Sept 1970, Abstract Ic, and at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN-118.

[2] Previous work[1] leaves no doubt that this is a true solid-state reaction under the conditions used here.

[3] Product determination during an initial photolytic holocaust, bypassing the vibrationally equilibrated, centrosymmetric, nitrogen-separated radical pair, seems unlikely from our epr studies.[1]

[4] Analysis was from m/e 119 to 131 in the mass spectrum of TMSN from thiol-scavenged thermolysis. The presence of equal amounts of AIBN-d_0 and AIBN-d_{12} suggests reversible HCN elimination and hydrolysis to acetone hydrazone during addition of cyanide to the exchanged compound. A synthesis through α-chloro-α'-cyanoazoisopropane may avoid this complication.

[5] As expected from the isotopic impurity of the starting material 36% of the IBN methyl signal was in a doublet (J = 7 Hz, methine proton) and 64% in a triplet (J = 1 Hz, methine deuteron). The 5% excess in the vinyl positions of MAN is probably due to experimental error.

[6] AIBN-h_{12} runs have shown that polymerization of MAN does not occur under these conditions. The observations are consistent with a detailed calculation assuming that the d_0 radical moves 0.85 or 0.94 times as fast as the d_6 radical. The sense of this difference is reasonable.[7,8]

[7] The unit cell sides of AIBN-d_{12} are uniformly 0.1% shorter than for AIBN-h_{12}; A. B. Jaffe, to be published.

[8] K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *J. Amer. Chem. Soc.*, **86**, 1733 (1964).