

product isolated (63%) was a mixture of 8-allylguanine and 8-propenylguanine (**4c**). When the sodium salt of **1c** was heated in diglyme for 24 hr at 150°, **4c** was also produced in 65% yield. The structure of the **4c** mixture was established by hydrogenation over palladium on charcoal to 8-propylguanine (**4g**) (82% yield) and comparison with a sample synthesized (45%) in a procedure similar to that for **4f** but employing butyryl chloride and 6-hydroxy-2,4,5-triaminopyrimidine. Since the rearrangement of **1c** without added base required a higher temperature (170°, triglyme) and gave a mixture which contained *ca.* 50% of **4c** plus four other products, it is apparent that the rearrangement is favored by proceeding through anionic species.

The crotyl case gave results intermediate between those for allyl and dimethylallyl in ease of rearrangement. The reaction of 2-amino-6-chloropurine (**2**) with sodium 2-buten-1-oxide (2 equiv) at 100° in either 2-buten-1-ol or dioxane yielded a mixture of *O*⁶-(2-buten-1-yl)guanine (**1d**) and 8-(2-buten-1-yl)guanine (**4d**). The ratio of products was sensitive to the time of heating (**1d**:**4d** = 80:20 (74% yield) for 5 hr to 10:90 (59% yield) for 48 hr) and the temperature (0:100 (70% yield) for 5 hr at 150°). The sodium salt of **1d** was converted at 150° in diglyme in 73% yield⁷ during 5 hr to **4d** as the only isolated product. The arrangement is thus facilitated by methyl groups at the γ position. No allylic inversion products, *i.e.*, 8- α -methylallylic products, were formed in the rearrangement of the crotyl and dimethylallyl compounds.

The sodium salts of both *O*⁶-methylguanine and *O*⁶-ethylguanine (**1a**)⁶ were stable at 162° in diglyme for 24 hr. The sodium salt of *O*⁶-benzylguanine (**1e**) was likewise stable under these conditions. The reaction of **2** with sodium benzyloxide (3 equiv) in benzyl alcohol at 130° for 5 hr followed a different course from the allyl types in that the product was not the expected *O*⁶-benzylguanine, but *N*²-benzylguanine (**5**), mp 275–276°. The formation of *N*²-benzylguanine requires at least 3 equiv of sodium benzyloxide and a trace of benzaldehyde to be present.^{19–21} *O*⁶-Benzylguanine (**1e**), mp 202–203°, prepared from **2** using 2 equiv of sodium benzyloxide with the exclusion of benzaldehyde, was convertible to *N*²-benzylguanine when heated with 2 equiv of sodium benzyloxide and a trace of benzaldehyde, while *N*²-benzylguanine was stable to such treatment.

This study has disclosed an allylic rearrangement from the *O*⁶ to the C-8 position of guanine that occurs without overall allylic inversion, is partially controlled by the degree of methyl substitution on the allylic group and by the temperature, and proceeds with

greatest facility through anionic species. Investigation of the mechanistic details is in progress.

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Photoelectron Spectrum of HBS

Sir:

Molecular photoelectron spectroscopy provides information on the electronic structures of ions and molecules.¹ Intercomparison of a series of isoelectronic species enhances the general usefulness of photoelectron spectra and facilitates their interpretation. However, many interesting members of such series are unstable or reactive and require specialized conditions for observation. Here we report the spectrum of one such species, the HBS molecule. HBS is a linear triatomic molecule with ten valence electrons.²

The 127° sector photoelectron spectrometer with electron retardation used in this work has been described previously.³ By reducing the length of the analyzer entrance slit to 1 cm and by placing a grounded 1 × 4 mm slit between the ionization chamber slit and the analyzer entrance slit, the resolution was improved and the scattered electron intensity reduced. The resolution and sensitivity deteriorated somewhat in the presence of HBS although both could be restored by cleaning the ionization chamber. The spectra reported here were obtained with a resolution of *ca.* 40 meV for argon (FWHM) during the production of HBS.

HBS was continuously prepared by flowing H₂S (Matheson) over pure boron (Koch-Light) in an 8-mm i.d. quartz tube heated to a temperature ranging between 1100 and 1150° as described by Kirk and Timms.⁴ The efflux of the reactor was admitted directly to the collision chamber of the spectrometer *via* a 1-cm length of 1-mm i.d. tubing. The pressure in the reactor was estimated to be 0.1 Torr while that in the analyzer was less than 5 × 10⁻⁵ Torr. Calibration was carried out using Ar, H₂, and H₂S as internal standards.

Typical photoelectron spectra observed as a function of boron temperature are illustrated in Figure 1. At the higher temperature the production of hydrogen is evidenced by the band beginning at 15.42 eV. In addition, at least two new bands appear. These bands increase with increasing boron temperature and depend on the H₂S mass flow. The ratio of the intensities of the two new bands at lowest ionization potential is independent of temperature and mole fraction of H₂S. As it has been shown previously that HBS and H₂ are the major constituents of the reactor efflux,^{2,4} we assign

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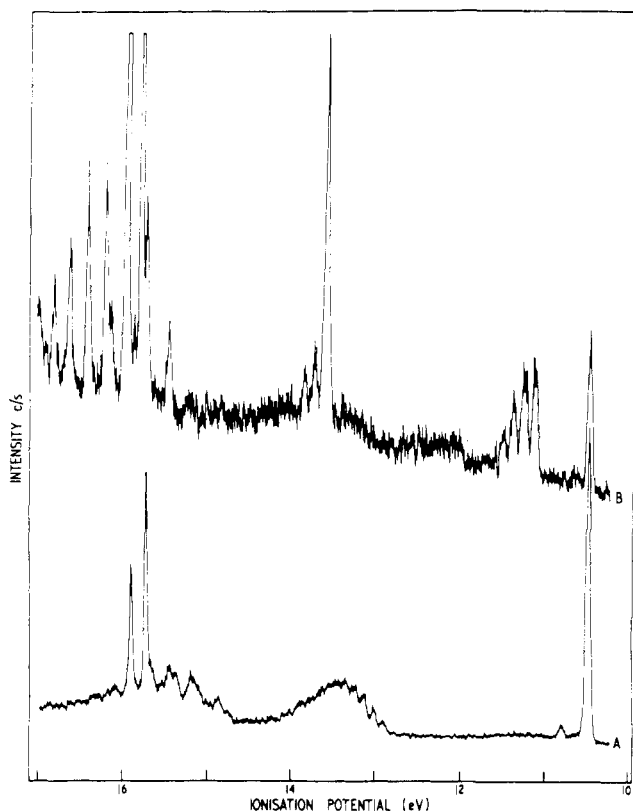


Figure 1. Photoelectron spectra of $\text{H}_2\text{S} + \text{B(s)}$ as a function of boron temperature with Ar as calibration gas: A, $T \approx 670^\circ$; B, $T \approx 1150^\circ$.

these new bands to the HBS molecule. This interpretation is supported by the simple and sharp nature of the bands themselves. The ionization potentials and observed vibrational frequencies are listed in Table I.

Table I. Ionization Potentials of HBS and Vibrational Frequencies Excited in the Electronic States of HBS^+

Photo-electron band	Adiabatic IP, eV	Vibrational frequencies, cm^{-1}		
		ν_1^a	ν_2^b	ν_3^c
First	11.12			990
Second	13.57			1090
Third ^d	15.86 (?)	2200 (?)		
Fourth ^d	17.9 (?)			

^a BH stretching mode. ^b Bending mode. ^c BS stretching mode. ^d Identity uncertain.

The shape of the first photoelectron band indicates that ionization involves the removal of an electron from a bonding or antibonding orbital. If it is the former the observed vibrational frequency in this ionic state along with a previous correlation between change in vibrational frequency produced upon ionization and the difference between adiabatic and vertical ionization energies⁵ suggests that the vibrational frequency in the molecule should be about 1100 cm^{-1} . For comparison ν_1 (B-H stretching mode) has recently been measured as 2735.80 cm^{-1} ⁶ for $\text{H}^{11}\text{B}^{32}\text{S}$, and an estimate of 680 cm^{-1} for ν_2 (bending mode) is available.² In the iso-

electronic molecule HCP,⁷ ν_3 (CP stretching mode) = 1278 cm^{-1} and ν_3 has been calculated to be about 1200 cm^{-1} in HBS.⁸ It is clear then that the vibrational mode excited in this state of the ion is the BS stretching frequency. Finally, the vibrational bands of this state have larger width (full width at half mean height (fwhm) = 90 meV) than do those for the first ionic state of H_2S (fwhm = 60 meV) or the second ionic state of HBS (fwhm = 60 meV). The observed peak width suggests a splitting of *ca.* 300 cm^{-1} which we attribute to spin-orbit coupling. It is 440 cm^{-1} in the $2\pi_g$ state of CS_2^+ for almost 100% S localization. Thus this band corresponds to ionization from the π molecular orbital of HBS which is partially localized on sulfur.

In the second band, the relative intensity of the (0, 0, 0) component suggests ionization from a nonbonding molecular orbital. The fine structure lines indicate either two vibrational modes are excited with frequencies of 1110 and 2140 cm^{-1} or a single mode with a frequency of 1090 cm^{-1} . In either case it is clear that the lower frequency relates to the BS stretching vibration, ν_3 , and here should have a value close to that in the molecule. Comparison with the value of this frequency estimated from the first photoelectron band of HBS supports the conclusion that the first band involves the removal of a bonding electron. Although the relative intensities of the fine structure lines would suggest the excitation of two modes, the frequency of 2140 cm^{-1} is not compatible with the nonbonding character of the orbital and the observed BH stretching frequency in the molecule. Thus, the second fine structure line is attributed to $2\nu_3$. This band, then, corresponds to ionization from a nearly nonbonding σ molecular orbital of HBS.

There is also evidence for two additional bands at higher ionization potential. The third band listed in Table I is badly overlapped by the spectrum of H_2 . The two unambiguous lines present are reproducible and may well be due to HBS. The fourth band consists of a single line of low intensity and cannot be definitely attributed to HBS.

It is of interest to briefly compare the partial spectrum of HBS with those of two isoelectronic species. The first two bands in the spectrum of CS are remarkably similar to those of HBS, in both energy and Franck-Condon envelope except that the order of σ and π orbitals is reversed.⁸ In CS the first band at 11.33 eV results from ionization from a nonbonding σ orbital, while the second at 12.79 eV results from ionization from a bonding π orbital. On the other hand, the highest π and σ orbital of HCN appear to be of nearly the same energy.¹ Both HBS and CS can be related to HCP by the movement of one nuclear charge unit, CS by its transfer from the terminal position into the P nucleus, and HBS by its transfer from C to P. In the first-row compounds (CO, HCN, HBO) the CO-HCN difference is mainly one of reduced π orbital ionization energy. The HBO-HCN difference is unknown; however, by reference to the methyl derivatives of HCN where the π ionization is hardly affected, the difference may be expected to be mainly in reduced σ ionization energy. Thus we might expect HCP to behave in sim-

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ilar fashion having nearly the same σ and π ionization energies near 11.2 eV.

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Comparison of Photochemical and Temperature-Jump Perturbations. The Rate of Interconversion of Planar and Octahedral Configurations of a Nickel(II) Complex¹

Sir:

Pulsed neodymium lasers are finding increasing application in the study of fast chemical reactions. One such application is the temperature-jump technique in which the laser is used to raise the temperature of a solution containing the system of interest by several degrees within a very short time; this is conveniently accomplished by using a laser wavelength that is absorbed strongly by the solvent, but not the solutes.²⁻⁴ In a less common application, the laser is used to rapidly photochemically dissociate a reactant or convert it into a product of the reaction; in this case, the laser frequency is chosen so that solvent absorption is at a minimum but solute absorbance is high.^{5,6} Following these perturbations, the rate of adjustment of the system to its new equilibrium position (relaxation rate) is followed. This rate provides information about the kinetics obtaining in the system. We wish to report the results of a rather novel kinetic study in which a neodymium laser was used to produce predominantly either temperature increases or concentration jumps in the same equilibrium system depending upon whether the wavelength of the laser radiation was 1.06 or 1.41 μ and the solvent H₂O or D₂O. In each case the subsequent relaxation of the system was followed spectrophotometrically.

The system chosen for study is the nickel(II) complex of the quadridentate ligand NH₂(CH₂)₂NH(CH₂)₃NH(CH₂)₂NH₂ (*N,N'*-bis(2-aminoethyl)-1,3-propanediamine).⁷ The nickel complex exists as an equilibrium mixture of low-spin planar (¹A_{1g}) and high-spin octa-

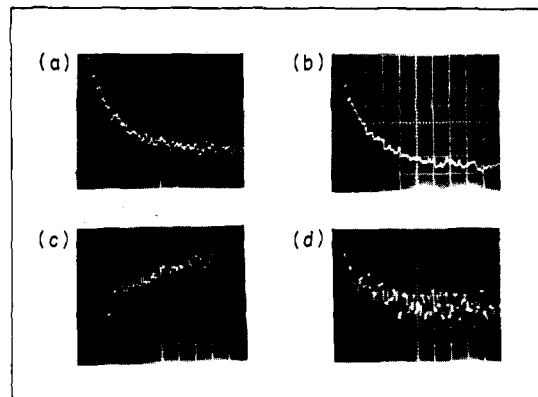


Figure 1. Absorbance at 440 nm as a function of time for solutions of NiLCl₂ (L = NH₂(CH₂)₂NH(CH₂)₃NH(CH₂)₂NH₂), with initial temperature 23°. The initial light intensity level was one major division above the bottom of the photograph, and the absorbance increases along the vertical axis. (a) 1.06 μ radiation, solvent H₂O, initial 440 nm absorbance is 0.32 ([Ni(II)] = 0.38 M, pathlength 0.08 cm), horizontal scale 0.2 μ sec per major division, vertical scale 2% absorbance change per major division; (b) 1.06 μ radiation, solvent D₂O, initial 440 nm absorbance is 0.21 ([Ni(II)] = 0.13 M, pathlength 0.16 cm), horizontal scale 0.2 μ sec per major division, vertical scale 3% absorbance change per major division; (c) 1.41 μ radiation, solvent H₂O, initial 440 nm absorbance is 0.32 ([Ni(II)] = 0.38 M, pathlength 0.08 cm), horizontal scale 0.1 μ sec per major division, vertical scale 2% absorbance change per major division; (d) 1.41 μ radiation, solvent D₂O, initial 440 nm absorbance is 0.32 ([Ni(II)] = 0.38 M, pathlength 0.08 cm), horizontal scale 0.2 μ sec per major division, vertical scale 0.6% absorbance change per major division.

hedral (³A_{2g}) forms in aqueous solution at room temperature.^{7,8}



This reaction was previously found to be too rapid for study by conventional temperature jump techniques.³ The system's relaxation times were, however, obtained in a study employing the neodymium laser radiation (1.06 μ) to rapidly perturb the above equilibrium by electronic excitation of the octahedral nickel complex ($\epsilon_{1.06 \mu} \sim 2.0 M^{-1} \text{ cm}^{-1}$).⁵ Following this perturbation, the return of the system to equilibrium was monitored by the absorbance decrease at 440 nm (an absorbance maximum for the planar complex). We have repeated these measurements on solutions 0.1–0.4 M in the chloride salt (both in H₂O and D₂O) using cells with path lengths of 0.08 and 0.16 cm. A typical relaxation is shown in Figure 1(a). It should be noted that there is a very rapid increase in the absorbance at 440 nm (rise time 30 nsec, the laser pulse width). This is followed by a slower absorbance decrease. The relaxation time for this decrease is $0.30 \pm 0.02 \mu\text{sec}$ at 23° and independent of the concentration of the nickel complex, in accord with the previously reported results.⁵ Also noteworthy is the observation that the "infinite time" absorbance is greater than the initial absorbance. This is due to a small displacement of the equilibrium resulting from the heating of the system. This effect is smaller, but not absent, in D₂O (Figure 1(b)). The temperature increase of the D₂O solution is primarily caused by the heat stemming from the non-radiative decay of the nickel excited state.

The interpretation of the observed relaxation de-

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