

# Notes

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## The Temperature Dependence of the Nuclear Magnetic Resonance Spectrum of Cyclopentamethylpentaarsine in Various Solvents

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While studying the novel synthesis of  $(\text{CH}_3\text{As})_5$  by the reaction of chloramine and dimethylchloramine with methylarsine,<sup>1</sup> the proton magnetic resonance spectrum of this compound was obtained. The spectrum of the neat liquid showed the presence of three magnetically nonequivalent methyl groups. This suggested that the structure of the polyarsine could possibly be determined by studying the temperature dependence and solvent dependence of the nuclear magnetic resonance parameters. Also, it was thought that these studies might give some insight into the comparative structures of this compound in solid<sup>2</sup> and liquid states. Finally, investigations in various solvents could suggest specific interactions between electron-donating solvents and the five-membered puckered arsenic ring.

The proton magnetic resonance spectrum of the pure liquid cyclopentamethylpentaarsine was obtained at sweep widths of 500, 100, and 50 cps. The spectrum shows three peaks in the approximate area ratios of 2:2:1, corresponding to the three magnetically nonequivalent types of methyl groups present in the compound. The average chemical shift was  $\tau$  8.36. A proton magnetic resonance spectrum was also obtained using  $\text{CDCl}_3$  as the solvent. The spectrum was identical with that of the neat liquid. The average chemical shift was  $\tau$  8.35. A proton magnetic resonance spectrum was obtained using  $\text{CCl}_4$  as the solvent and tetramethylsilane as the internal standard. The average chemical shift was  $\tau$  8.35. Therefore, the average chemical shift observed is independent of the solvent when deuterated chloroform and carbon tetrachloride are used.

A proton magnetic resonance spectrum was obtained using  $\text{C}_6\text{D}_6$  as the solvent. The spectrum shows three peaks in the area ratios of 2:1:2, corresponding to the three magnetically nonequivalent types of methyl groups present in the cyclopentamethylpentaarsine.

The average chemical shift was  $\tau$  8.48. The facts that the order of the methyl peaks is changed from 2:2:1 to 2:1:2 and that there is an upfield shift when the solvent is changed to hexadeuteriobenzene indicate that there exists a solvent-solute interaction.

A study of the temperature dependence of the nmr spectrum of the neat liquid was carried out over the temperature range of  $-20$  to  $180^\circ$ . Below  $20^\circ$  very broad and ill-defined methyl peaks resulted (at  $-20^\circ$ , the width of the signal was 75 cps), probably because of the increased viscosity of the liquid. The average chemical shift was unchanged with the change in temperature. Therefore, there is no self-association. The most upfield and downfield methyl peaks moved 0.5 cps closer together over the temperature range of  $40$  to  $180^\circ$ . This slight temperature dependence possibly results from the electronic environment of the methyls becoming more nearly equal through possible inversion about the ring as implied by Wells.<sup>3</sup>

A study of the temperature dependence of the nmr spectrum of the  $\text{C}_6\text{D}_6$ - $c$ - $(\text{CH}_3\text{As})_5$  solution was carried out over the temperature range of  $-20$  to  $140^\circ$  to determine the effect of temperature upon the relative positions of the methyl proton peaks and to detect any inversion of the methyl groups about the ring. The results are shown in Figure 1. As the temperature increased  $160^\circ$ , the average chemical shift value moved 7.3 cps downfield, the most upfield and downfield methyl peaks each moved approximately 1.7 cps toward the midpoint, and the middle methyl group peak moved upfield 0.75 cps relative to the midpoint. This middle methyl group peak could not be observed above  $90^\circ$ , since it moved under the most upfield methyl peak. The order of the area ratios of the methyl peaks remains 2:1:2 throughout the study. Figure 1 shows that there is a tendency toward a change in the order of the peaks from 2:1:2 to 2:2:1, as the temperature is increased, but, within the temperature range studied, this complete change does not occur. This may indicate that the tendency toward solvent-solute interaction decreases with increasing temperature.

The nmr spectra of cyclopentamethylpentaarsine obtained on the neat liquid and in deuterated chloroform, carbon tetrachloride, and hexadeuteriobenzene solutions all show the existence of three types of magnetically nonequivalent methyl groups having the area ratios 2:2:1 or 2:1:2. These studies indicate that the structure of the compound in the liquid state is possibly the same as that observed by Burns and Waser<sup>2</sup> in their X-ray crystal studies.

(1) L. K. Krannich and H. H. Sisler, submitted for publication.  
(2) J. H. Burns and J. Waser, *J. Am. Chem. Soc.*, **79**, 859 (1957).

(3) E. J. Wells, R. C. Ferguson, J. G. Hallett, and L. K. Peterson, *Can. J. Chem.*, **46**, 2733 (1968).

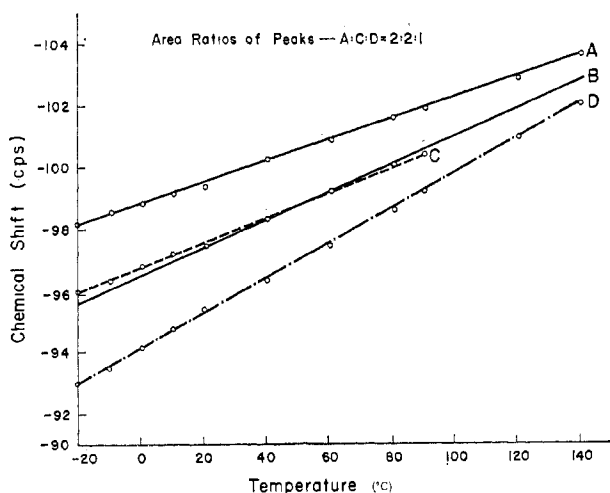


Figure 1.—Temperature dependence of chemical shifts of methyl groups in  $(\text{CH}_3\text{As})_2\text{-C}_6\text{D}_6$  solution: A, most downfield methyl; B, midpoint; C, middle methyl; D, most upfield methyl.

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### Rates of Reaction of Bis(8-mercaptoquinoline)nickel(II) with Alkyl and Aryl Halides

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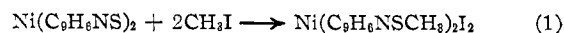
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The reactions occurring at metal-coordinated sulfur atoms have been well demonstrated.<sup>1-4</sup> It seems that these reactions with alkyl halide take place without the rupture of the metal-to-sulfur bond. The rates of reaction of some dimeric and trimeric nickel(II) complexes of  $\beta$ -mercaptoethylamine with alkyl and aryl halides have been measured. The Arrhenius parameters have low values compared with the data for reactions that conform to  $\text{S}_\text{N}2$  kinetic mechanisms.<sup>2</sup> These reactions have been shown to occur only at sulfur atoms bonded to one nickel ion; *i.e.*, the bridging sulfur atoms are inert to the organic halides.<sup>5</sup>

Recently it has been shown that chelated thioethers

undergo S-demethylation under mild conditions.<sup>3,6</sup> The demethylations of 8-methylthioquinoline and dimethyl-*o*-methylthiophenylarsine complexes have been studied more thoroughly. In the case of the latter ligand, the palladium and platinum complexes of a 2:1 ligand to metal ratio were also observed to undergo reaction with alkyl and aryl halides in chloroform solution to yield the thioether complexes. Again bridging sulfur atoms are unreactive.

It has been possible in the work reported here to methylate the nickel(II) complex of 8-mercaptoquinoline under room-temperature conditions in chloroform. The stoichiometry of the reaction is given in eq 1. The rates of reaction of this complex with



methyl iodide, benzyl chloride, benzyl bromide, and  $\alpha, \alpha'$ -dibromo-*o*-xylene have been determined spectrophotometrically as a function of temperature.

#### Experimental Section

**Bis(8-mercaptoquinoline)nickel(II)** was prepared by stirring nickel chloride hexahydrate with 8-mercaptoquinoline hydrochloride, supplied by K & K Laboratories, in a 3:1 ethanol-hypophosphorous acid solution. The acid served to prevent oxidation of the ligand to the disulfide and did not appreciably hamper the formation of the complex. A 2:1 mole ratio of metal ion to ligand was refluxed for 1 hr. The insoluble dark red precipitate was filtered on a sintered-glass funnel and washed successively with water, ethanol, and chloroform. Recrystallization from chloroform followed by air drying yielded bis(8-mercaptoquinoline)nickel(II) monohydrate. The analyses were performed by Galbraith Laboratories, Inc. *Anal.* Calcd for  $\text{Ni}(\text{C}_8\text{H}_6\text{NS})_2 \cdot \text{H}_2\text{O}$ : C, 54.58; H, 3.56; N, 7.25. Found: C, 54.55; H, 3.58; N, 6.80.

**Bis(S-methyl-8-mercaptoquinoline)nickel(II) iodide** was prepared in a manner analogous to that reported by Busch, *et al.*<sup>2</sup> Bis(8-mercaptoquinoline)nickel(II) was treated with an excess of methyl iodide in 250 ml of chloroform at room temperature overnight. The reaction of the dark red complex yielded a bright yellow solution when the reaction was complete. Reduction in solution volume under reduced pressure to 20 ml followed by addition of cold ethanol induced the precipitation of the yellow product. The precipitate was suction filtered, washed with chloroform, and air dried. *Anal.* Calcd for  $\text{Ni}(\text{C}_8\text{H}_6\text{NSCH}_3)_2 \cdot \text{H}_2\text{O}$ : C, 35.27; H, 2.96; N, 4.11. Found: C, 34.81; H, 2.92; N, 4.02.

**Kinetic measurements** were made on the reactions of bis(8-mercaptoquinoline)nickel(II) monohydrate with benzyl bromide, benzyl chloride, methyl iodide, and  $\alpha, \alpha'$ -dibromo-*o*-xylene in chloroform. Baker Analyzed reagent benzyl bromide and benzyl chloride were used. The benzyl chloride was redistilled and the fraction boiling from 178 to 180° was collected. Methyl iodide and  $\alpha, \alpha'$ -dibromo-*o*-xylene supplied by Eastman Organic Chemicals, as well as the benzyl bromide above, were used without further purification. Baker Analyzed reagent chloroform was used as the solvent.

The concentration of bis(8-mercaptoquinoline)nickel(II) was followed with a Beckman DU spectrophotometer. The visible absorption spectrum of the bis(8-mercaptoquinoline)nickel(II) shows bands at 539  $\text{m}\mu$  and at 390  $\text{m}\mu$ . The optical cells were thermostated to  $\pm 0.1^\circ$  with Beckman dual thermospacers by circulating water from a regulated bath. All solutions were brought to temperature before mixing the complex stock solution with the appropriate organic halide solution. A 10-1000-fold

- (1) R. G. V. Ewens and C. S. Gibson, *J. Chem. Soc.*, 431 (1949).
- (2) D. H. Busch, J. A. Burke, D. C. Jicha, M. C. Thompson, and M. L. Morris, *Advances in Chemistry Series*, No. 37, American Chemical Society, Washington, D. C., 1963, p 125.
- (3) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Inorg. Chem.*, **6**, 652 (1967).
- (4) E. L. Blinn and D. H. Busch, *ibid.*, **7**, 820 (1968).
- (5) D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *J. Am. Chem. Soc.*, **86**, 3642 (1964).

- (6) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Nature*, **211**, 519 (1966).