(PRF 1619-A1 and 1700-G1), administered by the American Chemical Society, for support of this research.

William S. Johnson, Lucius Werthemann, William R. Bartlett
Timothy J. Brocksom, Tsung-tee Li
Department of Chemistry, Stanford University
Stanford, California 94305

D. John Faulkner, Michael R. Petersen
Scripps Institution of Oceanography
La Jolla, California 92037

Received December 11, 1969

Nuclear Magnetic Resonance Spectroscopy. Carbon-13 Spectra of the Silver(I) Complexes of Cyclopentene and Cyclohexene[1]

Sir:

In recent years, proton magnetic resonance spectroscopy has been utilized to investigate the nature of the species arising when alkenes are dissolved in solutions containing either silver(I)[2] or mercury(II)[3] ions. We report here on the use of high-resolution nmr spectra of ^{13}C (cmr) in natural abundance[4] in examining such complexes.

The cmr spectra of cyclopentene and cyclohexene in aqueous silver nitrate solution[5] reveal that the unsaturated carbon resonances in both compounds are shifted to higher fields by 4.4 ppm, relative to those of the free cycloalkenes (see Table I). The remaining carbon resonances are shifted downfield slightly. These shifts seem best rationalized on the basis of a small increase in the σ character of the bonds at the unsaturated carbons,[6] although steric interactions[2c] with the silver ion cannot be definitely ruled out. As with the proton chemical shifts of silver–alkene complexes,[2b] there is no significant concentration effect on the ^{13}C chemical shifts.

The downfield shift of vinyl protons on formation of a silver(I) complex is usually explained as resulting from proton deshielding arising from π-electron donation from the alkene to the silver(I) ion.[2] Dewar[7] has proposed that the complexes are formed as the result of σ overlap between the bonding alkene π orbital with a vacant s or sp hybrid orbital on the silver(I) ion and π overlap of an occupied d orbital on the ion with an antibonding alkene π orbital. The net effect appears to be that the π-electron density decrease at carbon is not balanced by the d-electron contribution, thus making σ bonding more important than π bonding.[2c] Thus, an increase in the σ character of the bonds at the alkene carbons is expected and the ^{13}C results tend to bear this out. An increase in the σ character of the bonds to the unsaturated carbons would be expected to decrease the couplings between alkenic carbons and the directly attached hydrogens, but actually there is very little change upon complexation. The lack of appreciable change in the ^{13}C–H coupling constants suggests an alternative explanation of the chemical-shift changes, namely that the π-orbital energy of the alkene is reduced by coordination with silver ion, so as to produce small changes in the excitation energy.

Table I. Carbon Chemical Shifts of Cycloalkene–Silver Nitrate Complexes in Aqueous Solution at 15.1 MHz

	δ (CS_2)[a]	δ (CS_2)[a]	$\Delta\delta$
		Cyclopentene–$AgNO_3$ Complex	
Cyclopentene			
C1, C2	62.2	66.6	+4.4
C3, C5	160.2	158.3	−1.9
C4	169.7	168.3	−1.4
		Cyclohexene–$AgNO_3$ Complex	
Cyclohexene			
C1, C2	65.6	70.0	+4.4
C3, C6	167.3	165.8	−1.5
C4, C5	169.7	169.4	−0.3

[a] In parts per million relative to carbon disulfide.

With regard to interaction of mercury(II) ion with alkenes, evidence has been presented[3b,c] and challenged[3a] for direct observation of proton resonances of mercurinium ions. We have found that the cmr spectra of methanol solutions containing equimolar amounts of cyclopentene or cyclohexene and mercury(II) acetate gave no resonances corresponding to alkenic carbons and, indeed, were best explained as arising from 1-acetoxymercuri-2-methoxycyclopentane or 1-acetoxymercuri-2-methoxycyclohexane.

Richard G. Parker, John D. Roberts
Contribution No. 3921, Gates and Crellin
Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109

Received September 22, 1969

---

(1) Supported by the National Science Foundation.

(2) (a) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960); (b) J. Schug and R. J. Martin, *J. Phys. Chem.*, **66**, 1554 (1962); (c) H. W. Quinn, J. S. McIntyre, and D. J. Peterson, *Can. J. Chem.*, **43**, 2896 (1965).

(3) (a) W. Kitching, A. J. Smith, and P. R. Wells, *Aust. J. Chem.*, **21**, 2395 (1968); (b) Y. Saito and M. Matsuo, *Chem. Commun.*, 961 (1967); (c) V. Sokolov, U. Yustynyuk, and O. Reutov, *Dokl. Akad. Nauk SSSR*, **173**, 1103 (1967).

(4) (a) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967); *ibid.*, **90**, 3543 (1968); (b) F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **60**, 1152 (1968); (c) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, in press.

(5) The samples were prepared by saturating either a 2 *M* or saturated silver nitrate solution with cycloalkene. Cyclopentene and cyclohexene were chosen for study because of their high solubility in silver nitrate solutions (H. J. Taufen, M. J. Murray, and F. F. Cleveland, *ibid.*, **63**, 3500 (1941)).

(6) It is well known that there is a large chemical shift difference between sp^2- and sp^3-hybridized carbons, the sp^3 carbons being upfield by about 100 ppm (J. B. Stothers, *Quart. Rev.* (London), **19**, 144 (1965)).

(7) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).

Isoporphyrins

Sir:

The discovery of phlorins and the recognition of their stability prompted Woodward[1] to suggest that tautomeric structures of porphyrin with a saturated bridging carbon atom [isoporphyrin (**1**)] might exist. We report here the synthesis of a metalloisoporphyrin.

Controlled-potential oxidation of zinc *meso*-tetraphenylporphyrin (ZnTPP), at 1.1 V *vs.* sce, in dichloromethane–tetrapropylammonium perchlorate brings about two successive reversible one-electron oxidations. The first step generates a π cation radical[2] which is stable in nucleophilic solvents[3] and can be isolated in

---

(1) R. B. Woodward, *Ind. Chim. Belge.*, **27**, 1293 (1962).

(2) R. H. Felton, D. Dolphin, D. C. Borg, and J. Fajer, *J. Amer. Chem. Soc.*, **91**, 196 (1969).

(3) Stable cations of metallooctaethylporphyrins have been reported by J.-H. Fuhrhop and D. Mauzerall, *ibid.*, **91**, 4147 (1969).