

A SYNTHESIS OF XENON DIFLUORIDE NOT INVOLVING USE OF ELEMENTAL FLUORINE

Sir:

Although the existence of noble gas fluorides has excited intense interest in recent months, each of the preparative methods¹⁻⁴ heretofore described has involved manipulation of elemental fluorine. This Laboratory is engaged currently in the exploration of new approaches to the synthesis of noble gas compounds by techniques involving neither fluorine handling nor high pressure or high temperature instrumentation.

Among the pathways to xenon fluoride synthesis currently being explored here are the use of high voltage electric and microwave powered discharges in mixtures of xenon and a variety of perfluorinated species, and the vacuum ultraviolet photolysis of these mixtures using xenon and krypton resonance lamps. Among the fluorination reagents being evaluated are CF₄ and SiF₄.

These approaches were suggested by a considerable volume of literature pertaining to noble gas photosensitized reactions,⁵ and by the frequent observation of ionic species containing xenon in mass spectrometric studies.⁶

Abstraction reactions involving various ionic and electronically excited species of xenon, and simple perfluorinated species, seemed a promising route to the formation of xenon difluoride. The well known 1470 Å line of xenon, for example, corresponds to an available energy of 194.5 kcal. An estimate of the C-F bond dissociation energy in CF₄, for example, is 121 kcal.⁷ and the stripping of a second fluorine atom, to produce CF₂, would be expected to require substantially less energy. Further, CF₂ appears to be a relatively stable species capable, however, of elimination by polymerization.^{5,8}

We wish to report, at this stage, the demonstrated possibility of routinely successful syntheses of XeF₂ using a high voltage discharge in approximately equimolar mixtures of xenon and CF₄.

The apparatus consisted of a simple U-tube immersed in a refrigerant bath, and equipped with neon-sign electrodes, appropriate flow regulating valves and a high vacuum sampling train. The discharge was powered by a commercial neon-sign transformer operated near, or somewhat above, its rated capacity of 6000 v. at 120 ma.

The Pyrex discharge tube, having an approximate diameter of 25 mm. and a distance between electrodes of 360 mm., was refrigerated with Dry Ice and acetone, thus maintaining the walls of the reaction zone at temperatures above the boiling points of the reactants.

In a typical experiment, two l.-atm. of reaction mixture are permitted to flow through the discharge zone over periods of 1-2 hr. Upon terminating the discharge, a white microcrystalline or amorphous material is found, collected largely in the bottom of the U-tube.

After distillation, a white, nonvolatile organic residue remains in the discharge region. The volatile component, condensed in the sampling train, appears to contain at least two fractions condensable at -78°. The more volatile of these can be removed by flash evacuation at room temperature. The amounts of this material have been insufficient for physical characterization.

(1) C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962).

(2) J. H. Holloway and R. D. Peacock, *Proc. Chem. Soc. (London)*, **389** (1962).

(3) J. L. Weeks, C. L. Chernick and M. S. Matheson, *J. Am. Chem. Soc.*, **84**, 4612 (1962).

(4) A. V. Grosse, A. D. Kirshenbaum, A. G. Streng and L. V. Streng, *ibid.*, **85**, 360 (1963).

(5) See, for example: J. R. Dacey and J. W. Hodgins, *Can. J. Res.*, **28**, 173 (1950).

(6) See, for example: M. S. B. Munson, F. H. Field and J. L. Franklin, *J. Chem. Phys.*, **37**, 1790 (1962).

(7) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1958, p. 275.

(8) W. Mahler, *Inorg. Chem.*, **2**, 230 (1963).

The remaining fraction on standing undergoes spontaneous distillation with recrystallization at room temperature, forming clear, colorless, well formed crystals adhering to the walls of the storage vessel. Typical yields have been 50-150 mg. It must be emphasized that no serious effort has been made to optimize discharge conditions or to prefluorinate the sampling train.

Mass spectrographic analysis of these crystals was performed with a Consolidated Electrodynamics Model 21-103C instrument. The mass spectrum demonstrated conclusively that the crystals were the expected XeF₂. Peaks corresponding to XeF₂⁺, XeF⁺, Xe⁺ and Xe⁺⁺ were observed, having the correct isotopic distribution. Trace quantities corresponding to still higher masses were observed also.

It is noteworthy that the first injection of vapor into the mass spectrograph sampling manifold resulted merely in deactivation of interior surfaces and contaminants, producing as a consequence the mass spectrum of xenon in correct isotopic distribution. Analogous phenomena had been observed earlier, typically in distillation of the XeF₂ in the un-prefluorinated glass vacuum system.

The infrared spectrum of the vapor phase in equilibrium with these crystals was recorded at approximately 24°, using a 10-cm. gas cell equipped with KBr windows. A Beckman IR-4 spectrometer employing CsBr optics was used for these measurements. The vapor spectrum was found to exhibit a band with P and R components centered at 549 cm.⁻¹ and 564 cm.⁻¹, respectively. The previous observation by D. F. Smith⁹ that greater intensity is associated with the R branch is confirmed. In addition, an extremely weak absorption was observed at 520 cm.⁻¹. It may be significant to note that Smith has estimated a frequency of 515 cm.⁻¹ for the infrared inactive fundamental, ν_1 , on the basis of an apparent combination band at 1070 cm.⁻¹.

Acknowledgment.—We wish to thank Professor G. J. Mains for the mass spectrographic analysis.

(9) D. F. Smith, *J. Chem. Phys.*, **38**, 270 (1963).

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NON-CHLOROPHYLLOUS PIGMENTS OF *CHLOROBIVUM THIOSULFATOPHILUM* CHLOROBIVUMQUINONE

Sir:

The anaerobic, photosynthetic bacterium, *Chlorobium thiosulfatophilum*, differs from all other known photosynthetic systems in having several unique chlorophylls.¹ This induced us to examine other pigments of this bacterium which may be related to its photosynthetic and oxidative phosphorylating systems, *viz.*, the carotenes and the quinones.

This organism had been reported² to contain γ -carotene, pro- γ -carotene, and rubixanthin. Also, Fuller, *et al.*,³ reported that *C. thiosulfatophilum* (strain L) is devoid of coenzyme Q and plastoquinone, but detected a substance, λ_{\max} 254 m μ , which they suggested was related to plastoquinone.

We have extracted¹ dried cells of *C. thiosulfatophilum* (strain PM) and chromatographed the non-chlorophyllous pigments on Decalco. A carotene fraction was eluted with isoöctane and established as γ -carotene, identical with an authentic sample⁴ by its visible

(1) J. H. Mathewson, W. R. Richards and H. Rapoport, *J. Am. Chem. Soc.*, **85**, 364 (1963), and references therein.

(2) T. W. Goodwin and D. G. Land, *Biochem. J.*, **62**, 553 (1956).

(3) R. C. Fuller, R. M. Smillie, N. Rigopoulos and V. Yount, *Arch. Biochem. Biophys.*, **95**, 197 (1961).

(4) We are indebted to Dr. G. McKinney for this sample.

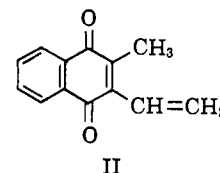
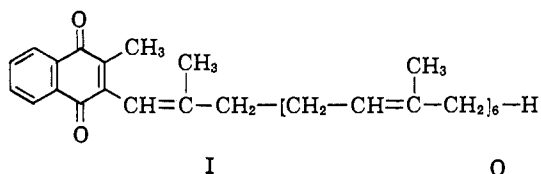
TABLE I
REVERSED-PHASE PAPER CHROMATOGRAPHY^a OF CHLOROBIIUM-
QUINONE AND SOME OTHER NATURAL QUINONES

Quinone	R _F ^b	Ultraviolet fluorescence ^c
Chlorobiumquinone	0.46	Blue
Vitamin K ₂₍₃₀₎	.44	Violet
Vitamin K ₂₍₃₅₎	.34	Violet
Coenzyme Q ₁₀ ^d	.24	Red
Plastoquinone ^d	.17	Red

^a On Whatman 3MM paper impregnated with silicone 550.
^b Descending technique with propanol:water, 4:1. ^c Seen with an ultraviolet lamp. On subsequent development with neotetrazolium chloride each spot became blue-violet. ^d Generously provided by Dr. K. Folkers.

absorption spectra and by circular paper chromatography on alumina paper.⁵ Elution with isoöctane-5% ether gave a vitamin K which was identical with an authentic sample⁶ of vitamin K₂₍₃₅₎ by m.p. (54°),

Structure I has been assigned to chlorobiumquinone on the basis of the following evidence



Chlorobiumquinone has the molecular formula C₄₅H₆₂O₂ by element analysis (found, C, 84.6; H, 9.3) and spectrophotometric molecular weight determina-

TABLE II
N.M.R. ABSORPTION^a OF CHLOROBIIUMQUINONE, VITAMIN K₂₍₃₀₎, PLASTOQUINONE AND COENZYME Q₁₀

Structural element	Chlorobiumquinone	Vitamin K ₂₍₃₀₎	Plastoquinone	Coenzyme Q ₁₀
	7.9(m) ^b [4] ^c	7.9(m)
	6.2(b) [1]
-CH=C< (chain)	5.1(b) [6]	5.1(b)	5.1(b)	5.1(b)
	...	3.4(d)	3.1(d)	3.2(d)
	2.3(d)
	2.1(s) [30]	2.2(s)	2.0(b)	2.0(b)
	2.0(b)	2.0(b)		
	1.7(d), 1.6(b) [21]	1.8(d), 1.6(b)	1.6(b)	1.7(d), 1.6(b)

^a As δ -values in deuteriochloroform, referred to internal tetramethylsilane ($\delta = 0$). ^b Letters in parentheses refer to singlet(s), doublet(d), multiplet(m), broad(b). ^c Numbers in brackets refer to number of protons obtained by integration for chlorobiumquinone (H₆₂).

mixture m.p., paper chromatography and infrared and ultraviolet absorption.

Continued elution with isoöctane-5% ether gave another quinone fraction. The yield was low, but was improved substantially when the cells were extracted with 70% acetone-30% water, 0.03 M in ferricyanide. This material has $\lambda_{\text{max}}^{\text{EtOH}}$ 254 m μ (sh 263 m μ) which, with sodium borohydride, disappears into a broad inflection at 251 m μ .⁷ Chromatography on powdered polyethylene and crystallization from acetone and petroleum ether gave this new quinone, chlorobiumquinone, m.p. 50-51°⁸, clearly distinguished from other natural quinones by paper chromatography (Table I).

(5) Procedure of Dr. E. A. Shneour, for whose assistance we are grateful.

(6) O. Isler, R. Ruegg, L. H. Chopard-dit-Jean, A. Winterstein and O. Wiss, *Helv. Chim. Acta*, **41**, 786 (1958). We thank Dr. Isler for samples of vitamins K₂₍₃₀₎ and K₂₍₃₅₎.

(7) Cf. reference 3.

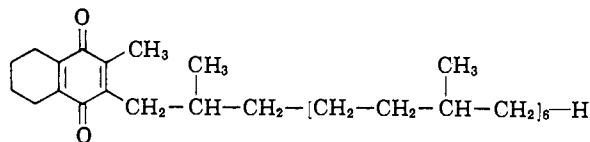
tions (see below). In the infrared (KBr), it shows absorption essentially identical with that of vitamin K₂₍₃₅₎, plastoquinone, and coenzyme Q₁₀ at 1660 and 1610 cm.⁻¹, characteristic of a 1,4-quinone, and at 875, 795, and 755 cm.⁻¹, characteristic of the all-*trans*-polyisoprenoid chains. Also, peaks at 700 and 690 cm.⁻¹, corresponding to those in vitamin K₂₍₃₅₎ at 720 and 690 cm.⁻¹, are assigned to the four adjacent aromatic protons. These infrared assignments indicated a 1,4-naphthoquinone with a polyisoprenoid side-chain. However, the ultraviolet spectrum [$\lambda_{\text{max}}^{\text{isoöctane}}$ 249 m μ (ϵ 16,300)] is different from that of the various vitamins K. The new chromophore was established as a vinyl-1,4-naphthoquinone by comparison with a synthetic sample of 2-methyl-3-vinyl-1,4-naphthoquinone (II),⁸ $\lambda_{\text{max}}^{\text{isoöctane}}$ 249 m μ (ϵ 16,200). Comparison of extinc-

(8) G. Manecke and W. Storck, *Ber.*, **94**, 300 (1961).

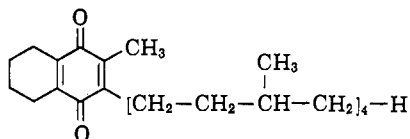
tion coefficients supports the molecular formula of chlorobiumquinone.

All these structural assignments were confirmed and further features established by a detailed study of chlorobiumquinone's n.m.r. spectrum in comparison with those of vitamin K₂₍₃₀₎, plastoquinone and coenzyme Q₁₀, presented in Table II. Thus structure I is uniquely defined for chlorobiumquinone.

Further confirmation was found in a comparison of octadecahydrochlorobiumquinone (III) (C₄₅H₈₀O₂; Found, C, 82.9; H, 11.8) with hexahydrovitamin K₁ (IV).⁹ In the ultraviolet, III has $\lambda_{\text{max}}^{\text{isoctane}}$ 260 m μ (ϵ 16,000) 268 (20,100), 335 (250); IV absorbs at 260 m μ



III



IV

(ϵ 15,900), 268 (20,000), 335 (250). Both compounds have identical n.m.r. absorption¹⁰ at δ 1.6 for the C₆, C₇ methylenes; δ 2.3 for the C₅, C₈ methylenes; δ 2.0 for the C₂-CH₃; δ 1.2 for the side-chain methylenes and methenes; and δ 0.8 for the side-chain methyls.

Chlorobiumquinone (I) is unique among natural vitamins K in having a double bond conjugate with the quinone¹¹ and one carbon less than the normal multiple-of-five carbons in the side chain. Although a vinyl naphthoquinone has not been found previously, it has been postulated as an intermediate in oxidative phosphorylation.¹²

The absence of coenzyme Q and plastoquinone in *C. thiosulfatophilum* is of interest, as is the fact that addition of a mild oxidizing agent during the extraction substantially increases the yield of chlorobiumquinone. This is not the case for the accompanying vitamin K₂₍₃₅₎, and suggests that chlorobiumquinone is present mostly in a reduced form.

(9) M. Tishler, L. F. Fieser and N. L. Wendler, *J. Am. Chem. Soc.*, **62**, 2866 (1940).

(10) In deuteriochloroform with internal tetramethylsilane.

(11) A quinone recently detected spectrophotometrically in *Sarcina lutea* may be of this type [D. H. L. Bishop, K. P. Pandya and H. K. King, *Biochem. J.*, **83**, 606 (1962)].

(12) I. Chmielewska, *Biochim. Biophys. Acta*, **39**, 170 (1960).

(13) Fellow of the Consejo Nacional de Investigaciones Cientificas y Técnicas de la Republica Argentina, 1962.

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BOND ENERGIES AND IONIC CHARACTER OF INERT GAS HALIDES¹

Sir:

Much interest has been aroused by the recent demonstration²⁻⁵ that at least some of the so-called inert gases are able to form true chemical compounds. It is

(1) Acknowledgment is made to the National Science Foundation for support of this research.

(2) H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

(3) C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962).

(4) P. R. Fields, L. Stein and M. H. Zirin, *J. Am. Chem. Soc.*, **84**, 4164 (1962).

(5) J. L. Weeks, C. L. Chernick and M. S. Matheson, *ibid.*, **84**, 4612 (1962).

very important that there be available a theoretical approach capable of treating such compounds and semi-quantitatively predicting their stabilities. We wish to report that an adaptation of the simple molecular orbital theory is applicable to the problem, and to give the results of calculations of the stabilities of some inert gas halides.

The energy of an electron in a localized two-center molecular orbital, $\psi = N(\phi_A + \lambda\phi_G)$, is given by the equation⁶

$$W = \frac{1}{2}(1+x)q_A + (1-x^2)^{1/2}\beta + \frac{1}{2}(1-x)q_G \quad (1)$$

where $x = (1 - \lambda^2)/(1 + \lambda^2)$ is defined as the bond ionicity, q_A and q_G are coulomb integrals for the halogen and the central atom, respectively, and β is the exchange integral; $2W$ measures the energy of the process $1/nGA_n \rightarrow 1/nG^{n+} + A^+ + 2e^-$. From W and data available in the literature, the energy of formation of gaseous GA_n from the elements is calculated. The coulomb integrals are approximated by expressions containing the bond ionicity, the ionization potentials and the valence state preparation energy (v.s.p.e.) of the inert gas atom, the ionization potential and electron affinity of the halogen, the G-A bond distance, and a geometric factor.⁶ The G-A exchange integral is approximated by the β for the appropriate interhalogen compound, using the equation of Pauling and Sherman,⁷ and correcting for v.s.p.e. of the inert gas atom and van der Waals repulsion.

Xenon tetrafluoride has a square planar configuration,^{8a} and XeF₂ is linear.^{8b} The same geometries were assumed for other possible inert gas halides GA₄ and GA₂. The experimental values⁸ of R were used for the Xe compounds. Bond lengths of the other inert gas halides were estimated from the Pauling covalent radii⁹ of the halogen A and of the halogen adjacent to the inert gas in the periodic table. Other estimates were obtained from the known bond lengths¹⁰ of the halides of elements immediately preceding the inert gas in the periodic table. Since for the tetrahalides the calculation is rather sensitive to the exact value assumed for R , calculations were made for a range of reasonable values. The valence states were assumed to be p²ds for the tetrahalides and ps for the dihalides, and the v.s.p.e. values were estimated from spectroscopic data.¹¹

Best values of the energies and ionicities are shown in Table I. The model predicts considerable stability for the known compound XeF₄, and somewhat lower stability for XeF₂. Krypton tetrafluoride is expected to exist, while KrF₂, XeCl₄ and ArF₄ are marginal.

The method predicts the intuitively expected increase in stability of the halides with increasing atomic number of the inert gas, and greater stability for fluorides than for the corresponding chlorides. More quantitatively, a change in the central atom from xenon to krypton or even argon is expected to entail a smaller decrease in stability than a change of ligand from fluorine to chlorine. Calculations were not made for bromides and iodides, since the trends in the calculated results strongly suggest that none of these would be stable.

A fluoride of radon has been prepared.⁴ Insufficient information about the ionization potentials of radon is

(6) R. G. Pearson, S. Yamada and H. B. Gray, *Proc. 7th ICCG*, 65 (1962); R. G. Pearson and H. B. Gray, *Inorg. Chem.*, in press.

(7) L. Pauling and J. Sherman, *J. Am. Chem. Soc.*, **59**, 1450 (1937).

(8) (a) J. A. Ibers and W. C. Hamilton, *Science*, **139**, 106 (1963); (b) H. Levy and P. A. Agron, *J. Am. Chem. Soc.*, **85**, 241 (1963); we thank Dr. W. C. Hamilton for communicating these results to us prior to publication.

(9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 224.

(10) "Interatomic Distances," The Chemical Society, London, 1958.

(11) C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Washington, D. C., 1949, 1952, 1958.