ratio for inversion (1.1) because the most efficient retention process requires only *one* pseudorotation, whereas the most efficient inversion process requires *two*. The configurational assignments for **2a** and **2b** are tentatively determined by their ^{1}H nmr spectroscopic behavior. The methyl protons of the *trans* isomer (**2b**) would be expected to be deshielded by the oxide oxygen [found: for **2b** δ 0.99 (J = 4.5 Hz); for **2a** δ 0.89 (J = 1.0 Hz).[7] Such nmr evidence has been used to assign configurations for cyclic phosphorus[8] and sulfur[9] systems and is consistent with X-ray data.[1h] Additionally, of known geometrically isomeric pairs of phosphine oxides, the melting points of the *trans* isomers are almost always observed to be higher than those of the *cis*.[10] Our melting point data are therefore consistent with the nmr assignment, as are the solubility and chromatographic characteristics of the oxides. The configurations of phosphonium salts **1a** and **1b** and the oxides **2a** and **2b** were related by the Wittig reaction.[2] Isomers **1a** and **1b** were prepared by stereospecific reduction (retention of configuration)[11] of the corresponding oxides with phenylsilane[1f,12] and quaternization of the resulting configurationally stable phosphine with benzyl bromide.[13] Both **2a** and **2b** are configurationally stable under conditions of base cleavage.

Acknowledgment. This work was supported by National Science Foundation Grant No. GP-7407.

---

[7] The ^{1}H nmr spectra were measured at 60 MHz in methylene chloride with a JEOL C-60H spectrometer, using tetramethylsilane as an internal standard.

[8] D. Z. Denney and D. B. Denney, *J. Amer. Chem. Soc.*, **88**, 1830 (1966); H. E. Shook, Jr., and L. D. Quin, *ibid.*, **89**, 1841 (1967); C. Bodkin, *Chem. Commun.*, 829 (1969).

[9] J. G. Pritchard and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 2105 (1961); E. Jonsson, *Ark. Kemi*, **26**, 357 (1967); P. B. Sollman, R. Nagarajan, and R. M. Dodson, *Chem. Commun.*, 552 (1967); K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, *ibid.*, 759 (1966); A. B. Foster, J. M. Druxbury, T. D. Inch, and J. M. Webber, *ibid.*, 881 (1967); E. Jonsson and S. Holmquist, *Ark. Kemi*, **29**, 301 (1968); A. B. Foster, T. D. Inch, M. H. Qadir, and J. M. Webber, *Chem. Commun.*, 1086 (1968); K. Kondo, *Tetrahedron Lett.*, 2461 (1969); C. R. Johnson and W. O. Siegl, *J. Amer. Chem. Soc.*, **91**, 2796 (1969).

[10] See ref 6b, p 6.

[11] Reoxidation of the phosphine with *t*-butyl hydroperoxide in each case regenerated the original oxide. *t*-Butyl hydroperoxide oxidations of phosphines are known to occur with retention of configuration (D. B. Denney and J. W. Hanifin, Jr., *Tetrahedron Lett.*, 2177 (1963)).

[12] H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **97**, 1988 (1964).

[13] The results of elemental analyses of all new compounds were within acceptable limits.

Kenneth L. Marsi, Roger T. Clark
Department of Chemistry, California State College, Long Beach
Long Beach, California 90801

Received January 22, 1970

Absorption Spectrum and Decay Rate of the Ascorbic Acid Radical

Sir:

The autoxidation and enzymatic oxidation of ascorbic acid have been found to proceed through a free radical, the electron spin resonance spectrum of which has been observed.[1–3] Ascorbic acid has been found to be oxidized very rapidly by OH radicals formed in aqueous solutions by radiolysis.[4,5] We have observed the optical absorption spectrum of a radical formed by pulse radiolysis of an aqueous solution of ascorbic acid and have determined its rate of decay.

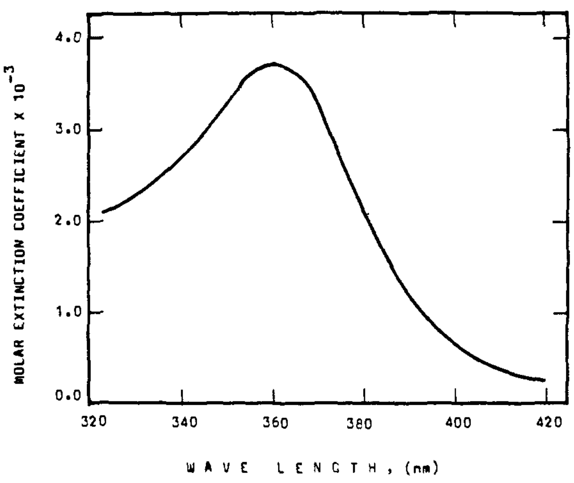

Figure 1. Absorption spectrum of the ascorbic acid radical.

Pulses of 1.9-MeV electrons of 20–30-μsec duration were delivered from a Van de Graaff generator to a 5 mM solution of ascorbic acid at the natural pH 3.3, saturated with nitrous oxide to convert solvated electrons to OH radicals. A transient absorption was found at wavelengths greater than those at which the ascorbic acid and its permanent reaction products absorb. With doses of about 800 rads, the optical densities observed at the end of the pulse were determined at a series of wavelengths, and the resulting spectrum is shown in Figure 1. The same spectrum was obtained in an argon-saturated solution containing equal concentrations (1 mM) of ascorbic and dehydroascorbic acids (pH 3.6). We see no reason to doubt that this transient is a radical intermediate in oxidation level between ascorbic and dehydroascorbic acids.

In order to determine more precisely the maximum extinction coefficient and decay kinetics of the radical N_2O-saturated solutions, 10 mM in ascorbic acid, adjusted to pH 4.1 with NaOH, were pulsed at 23° with doses ranging from 280 to 1310 rads. For each run the optical density per centimeter light path was determined as a function of time, and in every case plots of the reciprocal of the optical density against time were linear, showing good second-order decay of the radical. Setting the rate of disappearance of the radical $-d(R)/dt$ equal to $2k(R)^2$ the slope of these plots equals $2k/\epsilon$, where ϵ is the molar extinction coefficient at the wavelength used, 360 nm. From five runs, $k/\epsilon = 2.58 \pm 0.13 \times 10^4$ cm sec^{-1}. To determine ϵ, it was necessary to estimate the specific yield for formation of the radical. We assumed that every radical formed by irradiation of the water, whether e_{aq}^-, OH, or H, would result in formation of one oxidized ascorbic acid radical. The solvated electrons would, of course, react with the N_2O to form O^-, which would be converted into OH and would react

---

[1] I. Yamasaki, H. S. Mason, and L. Piette, *J. Biol. Chem.*, **235**, 2444 (1960).

[2] I. Yamasaki and L. H. Piette, *Biochem. Biophys. Acta*, **50**, 62 (1961).

[3] C. Lagercrantz, *Acta Chem. Scand.*, **18**, 562 (1964).

[4] N. F. Barr and C. G. King, *J. Amer. Chem. Soc.*, **78**, 303 (1956).

[5] G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael in "Pulse Radiolysis," M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Ed., Academic Press, New York, N. Y., 1965, p 131.

rapidly[5] with ascorbic acid to form the radical. Hydrogen atoms react only slowly with N_2O and we supposed that they should abstract a labile H atom from the ascorbic acid to form H_2. In support of this assumption, some rough measurements of the yield of H_2 gas were made from γ-ray irradiations of N_2O-saturated solutions of ascorbic acid. The results indicated hydrogen yields of 0.7–1.0, considerably greater than the yield of hydrogen coming directly from the water and hence supporting the assumption of abstraction by H. The total yield of radicals in nearly pure water is $G = 6.05$,[6] and is about 0.4 higher in nitrous oxide saturated solutions,[7] so that it was assumed here that the yield of ascorbic acid radicals was $G = 6.45$. The optical densities observed at the end of the pulse were proportional to the magnitude of the dose, and assuming this value of G we determined that the extinction coefficient ϵ is 3700 at 360 nm. Then $k = 9.5 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. Yamasaki and Piette[2] found values for this constant ranging from 6.3 to $10.0 \times 10^7\ M^{-1}\ \text{sec}^{-1}$.

Transient spectra of radicals formed by OH attack on a large number of aliphatic acids and alcohols have been seen in pulse radiolysis;[8] in every case, the unpaired electron is believed to reside on carbon. In the ascorbic acid radical produced by enzyme action or autoxidation the unpaired electron is believed to reside on oxygen.[1,3] We are continuing studies designed to determine the point of radical attack on ascorbic acid and the nature and properties of the radical formed at various pH.

Acknowledgment. It is a pleasure to acknowledge the invaluable assistance of Mr. David Comstock in the experimental work. This study was supported by the U. S. Atomic Energy Commission.

(6) B. H. J. Bielski and A. O. Allen, *Int. J. Radiat. Phys. Chem.*, **1**, 153 (1969).

(7) A. Appleby and H. A. Schwarz, *J. Phys. Chem.*, 73, 1937 (1969).

(8) M. Simic, P. Neta, and E. Hayon, *ibid.*, 73, 3794, 4207, 4214 (1969).

B. H. J. Bielski, A. O. Allen
Chemistry Department, Brookhaven National Laboratory
Upton, New York 11973

Received March 19, 1970

A New Fundamental Type of Inorganic Complex: Hybrid between Heteropoly and Conventional Coordination Complexes. Possibilities for Geometrical Isomerisms in 11-, 12-, 17-, and 18-Heteropoly Derivatives

Sir:

This paper reports establishment of a new fundamental class of complexes, of broad potential scope. Transition metal heteroatoms, M^{m+}, are polycoordinated within heteropoly complex structures, as integral parts thereof both electronically and with respect to atomic positions, while the same M^{m+} atoms are simultaneously coordinated to discrete conventional ligands such as NH_3, H_2O, pyridine, pyrazine, halide ion, etc. The existence of such complexes, which should involve a wide variety of ligands and of metals, will add a considerable new dimension to the field of heteropoly electrolytes and perhaps to the chemistry of complexes in general.

Background. In 1966 our group reported[1,2] an investigation in depth, centered on five complexes, which established unequivocally a large new general structural category of heteropoly anions, formulated

$$[H_hM^{m+}O_6X^{x+}O_4W_{11}O_{30}]^{(14-m-x-h)-}$$

It was indicated that a wide variety of metal ions might function as octahedrally coordinated M^{m+}, and a wide variety of nonmetals and transition metals, as well as $H_2{}^{2+}$, could function as X^{x+}.

The structure was shown[1,2] to be a modification of the well-known 12-tungsto "Keggin" structure.[3–7] Octahedrally coordinated M^{m+} replaces just 1 of the 12 octahedral W atoms of the conventional Keggin structure, and X^{x+} occupies the Keggin unit's central tetrahedral cavity.[8]

Subsequently, Weakley and Malik[10–12] and then the Tournés[13,14] reported preparation of a large number of 11-tungsto and 11-molybdo complexes (various M's and X's) which they formulated according to the above. Although the data they reported would be insufficient, standing alone, to establish the formulas and structures, there can be little doubt, in view of the whole body of evidence, that most and probably all of their materials do in fact belong to that new class of heteropoly complexes.[1,2]

Ripan and Puscasu,[15] also in 1968, reformulated, on the above-stated basis, three compounds which they had earlier interpreted differently.[16] They added convincing evidence to substantiate their new assignment.

The New Complexes. The work reported below unambiguously establishes that the formula for the above-described complexes can be rewritten on a still more general basis

$$[(Y^{y-})M^{m+}O_5X^{x+}O_4(\text{W or Mo})_{11}O_{30}]^{(12-m-x+y)-}$$

wherein Y^{y-} is a monodentate ligand which occupies the M's one unshared coordination position (which points toward the exterior of the heteropoly part). See Figure 1. It appears evident that for most of the many complexes heretofore reported[1,10–15] Y is a water molecule, but in some of those cases it is presumably merely an oxide ion. The present work indicates that a great variety of other ligands can also function as Y.

(1) L. C. W. Baker, *et al.*, *J. Amer. Chem. Soc.*, 88, 2329 (1966).

(2) L. C. W. Baker, *et al.*, *Proc. Int. Conf. Coord. Chem.*, *9th*, *1966*, 421 (1966).

(3) J. F. Keggin, *Proc. Roy. Soc.*, *Ser. A*, **144**, 75 (1934).

(4) R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 1076 (1934).

(5) L. C. W. Baker and V. E. Simmons, *J. Amer. Chem. Soc.*, 81, 4744 (1959).

(6) N. F. Yannoni, Ph.D. Dissertation, Boston University, 1961.

(7) L. C. W. Baker in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 608.

(8) The derivative wherein $X = Si^{4+}$ and $M = Co^{2+}$ had been the first heteropoly anion proven to contain two different elements as heteroatoms.[1,9]

(9) V. E. Simmons and L. C. W. Baker, *Proc. Int. Conf. Coord. Chem.*, *7th*, *1963*, 195 (1962).

(10) T. J. R. Weakley and S. A. Malik, *J. Inorg. Nucl. Chem.*, **29**, 2935 (1967).

(11) S. A. Malik and T. J. R. Weakley, *Chem. Commun.*, 1094 (1967).

(12) S. A. Malik and T. J. R. Weakley, *J. Chem. Soc.*, *A*, 2647 (1968).

(13) C. Tourné, *C. R. Acad. Sci.*, *Ser. C*, **266**, 702 (1968).

(14) C. Tourné and G. Tourné, *ibid.*, *Ser. C*, **266**, 1363 (1968); *Bull. Soc. Chim. Fr.*, 1124 (1969).

(15) R. Ripan and M. Puscasu, *Z. Anorg. Allg. Chem.*, **358**, 83 (1968).

(16) R. Ripan, A. Duca, D. Stanescu, and M. Puscasu, *ibid.*, **347**, 333 (1966).