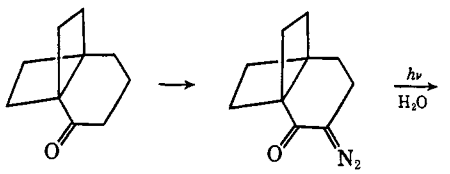
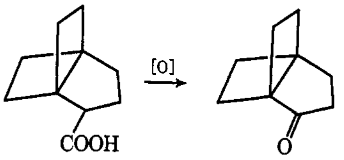
sponding *tert*-butyl peresters in 1,3,5-triisopropylbenzene at 160° gives **2**, [3.2.2]propellane, in 45% yield.[12] The pure hydrocarbon is a mobile liquid, fp 11°; the 100-MHz nmr spectrum of **2** is reproduced in Figure 1b.

The sequence from **7** works well and permits production of substantial amounts of the hydrocarbon **2**, yet it does not provide suitable intermediates for attempts at the preparation of the elusive [2.2.2]propellane system *via* another ring contraction.[13] Our second approach to [3.2.2]propellanes is without this subtle deficiency. Formylation of the [4.2.2]propellane **6** and subsequent reaction of the α-hydroxymethylene ketone with tosyl azide and diethylamine yields the α-diazo ketone **11**. Irradiation of **11** in aqueous dioxane gives (63%) the [3.2.2]propellane acid **12**, mp 79°. We have converted **12** to the ketone **13** [ir (CCl_4) ν 5.77 μ] and are trying now to bring about contraction of **13** to a [2.2.2]-propellane.

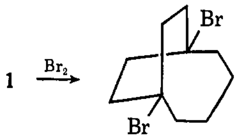


6 **11**



12 **13**

The [4.2.2]- and [3.2.2]propellane hydrocarbons are thermally stable to at least 160°. Neither reacts at a significant rate with hydrogen at atmospheric pressure over Adams catalyst. On the other hand, [4.2.2]- and [3.2.2]propellane react quantitatively with bromine[14] to give the tertiary dibromides **14**, mp 44–45°, and **15**, mp 143–143.5°, respectively, rare and useful examples of a bicyclo[4.2.2]decane and a bicyclo[3.2.2]nonane substituted at the bridgeheads.



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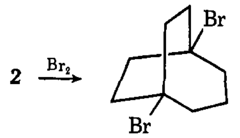

15

The propellane ketone **6** and the corresponding alcohol, mp 117.5–118.5°, are thermally stable, but both react very rapidly with acid.[15] We shall discuss these reactions in future reports along with the thermochemical and X-ray data now being gathered for the [4.2.2]- and [3.2.2]propellane systems.

Acknowledgments. Support of this work by the National Science Foundation and by the Institute for General Medical Sciences of the National Institutes of Health is recognized with gratitude. Badische Anilin-und-Soda-Fabrik AG was kind enough to provide generous gifts of bicyclo[3.3.0]oct-1(5)-en-2-one. We thank Mr. G. H. Temme for his help.

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(11) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958). See ref 8b and P. E. Eaton and T. W. Cole, Jr. (*ibid.*, **86**, 3157 (1964)) for examples of applications of this method.

(12) [3.2.2]Propell-6-ene is a minor product (*ca.* 5%).

(13) We have examined also a number of routes proceeding from relatives of 7 carrying functional groups on both five-membered rings, for example, from [3.3.2]propella-2,6-dione produced (*cf.* ref 3f) by way of photoaddition of ethylene to simple derivatives of bicyclo[3.3.0]oct-1(5)-ene-2,6-dione whose preparation will be described elsewhere. To date, these paths have offered no special advantages.

(14) The reactions were carried out at room temperature in carbon tetrachloride initially 1 *M* in each reactant and were complete in 10–20 min.

(15) An early, verbal report[1b] that halogen acids add across the central bond of 6 is in error; unfortunately, this interpretation has been quoted in the literature [W. F. Erman and T. W. Gibson, *Tetrahedron*, **25**, 2493 (1969)].

(16) Witco Chemical Co. Fellow, 1967–1968; American Chemical Society–Petroleum Research Fund Graduate Fellow, 1968–1969; National Institutes of Health Predoctoral Fellow, 1969–1970.

Discovery and Electron Spin Resonance Spectra of Matrix-Stabilized Hydronium Radicals H_3O and D_3O[1]

Sir:

Bernstein[2] was the first to publish on the possible existence of H atom adducts such as H_3O and NH_4. By estimations based on thermodynamic cycles and vibrational frequencies, he predicted the bond dissociation energies for such species in the gas phase to range from 7 to 33 kcal/mol. If so, H_3O would be stable relative to H + H_2O and should be observable. Further interest in the significance of H_3O was stimulated by Magee,[3] who proposed it as an intermediate in the radiolysis of water. Sworski[4] extended this view to argue that H_3O was the probable precursor of molecular hydrogen in water radiolysis. About this time, Martin[5] began to search for H_3O and NH_4 using a special palladium catalyst and mass spectrometer apparatus. He was encouraged in this effort by Soldano[6a] and Lossing.[6b] These experiments failed because the emission of spontaneous positive ions from the catalyst when exposed to either ammonia or water precluded using an electron beam of variable energy to detect transient free radicals. However, after witnessing

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(1) This work was made possible by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2825 and by Vanderbilt University. The esr apparatus used was purchased through Vanderbilt's Centers of Excellence Award sponsored by the National Science Foundation. We also thank Professor R. E. Rummel for adapting the photochemical apparatus for esr work and for drawing our figures. Parts of this study were first reported at the Ninth Informal Conference on Photochemistry, The Ohio State University, Columbus, Ohio, Sept 1–4 1970 and at the International Symposium on Atomic, Molecular and Solid-State Theory and Quantum Biology, University of Florida, Sanibel Island, Fla, Jan 18–23, 1971.

(2) H. J. Bernstein, *J. Amer. Chem. Soc.*, **85**, 484 (1963).

(3) J. L. Magee, *Radiat. Res. Suppl.*, **4**, 20 (1964).

(4) T. J. Sworski, *J. Amer. Chem. Soc.*, **86**, 5034 (1964).

(5) T. W. Martin, *J. Chem. Phys.*, **43**, 1422 (1965).

(6) (a) Dr. B. A. Soldano of the Oak Ridge National Laboratory predicted the existence and possible theoretical significance of the hydronium radical in private conversations with Martin during the summer of 1958. (b) Dr. F. P. Lossing of the National Research Council of Canada brought Bernstein's paper to his attention and independently suggested the catalyst experiments.

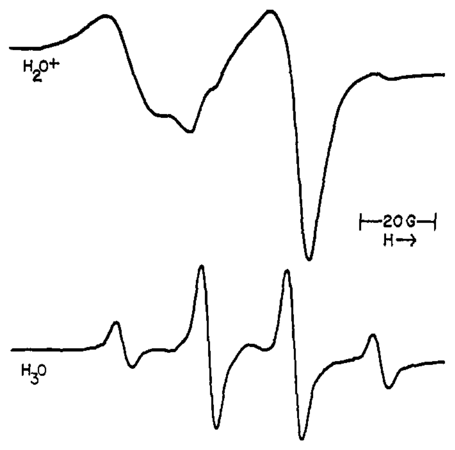

Figure 1 Esr spectra of H_2O^+ and H_3O at −180.°

these experiments, Melton later published several papers claiming mass spectrometric evidence for H_3O, D_3O, and HD_2O.[7,8] Unfortunately, mass spectrometry is an indirect and questionable method at best to prove the existence of H_3O because the neutral species must first be transformed to H_3O^+ to be detected and because unexplained and significant background peaks are often present which reduces one's confidence in the interpretations of the data. Furthermore, the experimental conditions are too severe and remote and the yields too low for useful chemistry.

In contrast, we publish here the first direct and unequivocal evidence for the hydronium radical. It was discovered after uv irradiation of 0.01 *M* aqueous ceric perchlorate-perchloric acid solutions frozen to form a glassy matrix at −180° in the cavity of an esr apparatus using light from 2800 to 3500 Å. Our equipment is described elsewhere.[9] In accord with the earlier work of Moorthy and Weiss,[10] we first observed the doublet esr spectrum of H_2O^+ (see Figure 1), which is formed by the photochemical reaction, $Ce^{IV}H_2O + h\nu \rightarrow Ce(III) + H_2O^+$. However, on annealing the matrix in the dark to −120° and recooling to −180°, the H_2O^+ spectrum disappears and is replaced by the H_3O quartet (see Figure 1). The H_3O spectrum is characteristic of a species that has axial symmetry with three equivalent hydrogens. Similar quartets could arise from such species as BH_3^-, CH_3, or NH_3^+, and special precautions and tests were made to eliminate them from consideration. The oxychloro radicals ClO, ClO_2, ClO_3, and ClO_4 could also give four-line spectra because Cl has a nuclear spin of $^3/_2$, but their line intensities should all be equal and not close to 1:3:3:1 as found for H_3O.

The most compelling evidence for assigning our quartet to H_3O came from successive spiking experiments with nitrate ion and acetic acid. These experiments show that we are not generating CH_3 radicals from some carbonaceous impurity which is resistant to our extensive purification procedures and provide an easy chemical way of distinguishing between H_3O and CH_3 radicals. They also allow us to make a detailed physical comparison of the esr spectra of these two very *similar* but *not identical* radicals. By adding 0.04–0.06 *M* $NaNO_3$ to an original solution containing about 0.01 *M* cerium(IV) perchlorate and 6–7.5 *M* perchloric acid in 80–85% D heavy water solvent, it is possible to inhibit the *simultaneous* formation of H_3O and H atoms normally recorded after 4 min of direct photolysis without annealing at −180°. Once the H_3O and H atom producing process is "turned off" by nitrate, the further addition of 0.04–0.06 *M* acetic acid and subsequent photolysis produces no H atoms but does yield an authentic CH_3 spectrum for comparison with the original H_3O quartet. Although we find the proton hyperfine splittings of H_3O and CH_3 to be remarkably close (within 1%), we do observe significant and reproducible differences in their band shapes and band widths with $\Delta H_{pp}(CH_3) > \Delta H_{pp}(H_3O)$ by 10–15%. These experiments clearly suggest that H_3O is formed from water molecules closely coupled to the Ce(IV) solvation shell

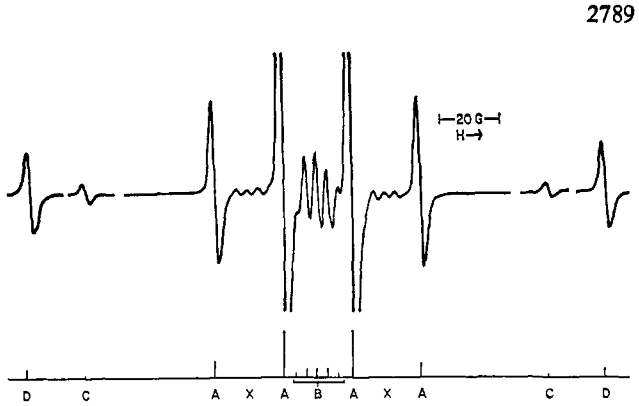

Figure 2. Composite (see text) esr spectra at −180° in 99.8% D heavy water solvent; $\bar{g}$ values are referenced to diphenylpicrylhydrazyl (DPPH). Lines A = H_3O (a_H = 22.84 G, $\bar{g}$ = 2.0035 ± 0.0003); lines B = D_3O (a_D = 3.65 G, $\bar{g}$ = 2.0035 ± 0.0003); lines C = D atom (a_D = 77.3 G, $\bar{g}$ = 2.0022 ± 0.0004); lines D = H atom (a_H = 504.3 G, $\bar{g}$ = 2.0020 ± 0.0004); and lines X = probably a triplet belonging to the H_2DO spectrum.

Further proof that we are observing hydronium radicals came from isotopic studies in 99.8% D heavy water. The analog D_3O should give a seven-line spectrum with relative intensities 1:3:6:7:6:3:1 having hyperfine splittings, a_D, reduced by a factor of 6.51 equal to the ratio of magnetic dipole moments μ_H/μ_D. Hence, the D_3O lines should be split by about 3.52 G when compared to $a_H(H_3O)$ = 22.84 G. These predictions are largely realized in Figure 2, where the three central D_3O lines (labeled B) have an intensity ratio of 6:7:6 with a_D = 3.65 G. The outer D_3O lines are masked by the H_3O quartet (labeled A). Additional proof for H_3O and D_3O comes from finding definite lines for H and D atoms in Figure 2. These atoms probably arise from the decomposition reactions $H_3O \rightleftharpoons H + H_2O$ and $D_3O \rightleftharpoons D + D_2O$. The heavy water studies are unusual in that H_3O, D_3O, H, and D are all observed on direct irradiation at −180° without annealing the matrix. On annealing in the dark to −120° and recooling to −180° the H and D atoms completely disappear, while the H_3O and D_3O lines increase in intensity. Figure 2 is a composite showing the maximum yields of each spectrum, and the relative intensities suggest that H_3O is stable relative to $H + H_2O$. This would be in accord with Bernstein's original prediction were this in gas phase rather than a matrix-

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(7) C. E. Melton and P. S. Rudolph, *J. Catal.*, **5**, 387 (1966).

(8) C. E. Melton and H. W. Joy, *J. Chem. Phys.*, **46**, 4275 (1967).

(9) T. W. Martin, L. L. Swift, and J. H. Venable, Jr., *ibid.*, **52**, 2138 (1970).

(10) P. N. Moorthy and J. J. Weiss, *ibid.*, **42**, 3127 (1965).

stabilized system. Hence, we believe the H_3O bond dissociation energy is probably less than Bernstein's lower limit of 7 kcal/mol.

Our assignment of neutral H_3O rather than $(H_3O)^{2+}$ is based on the following arguments. (1) We would predict $a_H(H_3O)^{2+}$ to be much greater than the 22.84 G observed because, in general, cation radicals display larger splittings than their corresponding anions. For example, $a_H(\text{anthracene})^+ > a_H(\text{anthracene})^-$.[11] This effect is also demonstrated by the isoelectronic series BH_3^-, CH_3, NH_3^+ shown in Table I to which $(H_3O)^{2+}$ would belong. (2) We would expect $(H_3O)^{2+}$ to be a strong oxidizing agent and H_3O a good reducing agent. Hence, the presence of H atoms is more easily correlated with H_3O. (3) We would expect $(H_3O)^{2+}$ to undergo isotopic exchange readily because of its repulsive double charge. However, we observe no enhancement of deuterated species upon continuous irradiation or annealing of the radicals in heavy water. It is remarkable that the esr and exchange properties of H_3O and CH_3 are so similar. If CH_3 is assumed to be planar as claimed,[12] this raises the question of whether H_3O is planar or tetrahedral or partially complexed to another species such as Ce(III).[13] (4) Lastly, we are able to produce H_3O in good yield in basic media, an environment surely more hostile to $(H_3O)^{2+}$ than H_3O.

Table I. Summary of Radicals with Three Equivalent Hydrogens

Radical	a_H or a_D, G	$\bar{g}$	Ref
BH_3^-	16.5	2.0013	*a*
CH_3	23.04	2.00255	*b*
NH_3^+	25.9	2.0035 ± 0.0003	*c*
	25.0	2.0034 ± 0.0001	*d*
H_3O	22.84	2.0035 ± 0.0003	*e*
D_3O	3.65	2.0035 ± 0.0003	*e*

[a] M. C. R. Symons and H. W. Wardale, *Chem. Commun.*, 758 (1967). See also E. D. Sprague and F. Williams, *Mol. Phys.*, **20**, 375 (1971), for interesting temperature effects on $\bar{g}$ and a_H. [b] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963). [c] T. Cole, *ibid.*, **35**, 1169 (1961). [d] J. S. Hyde and E. S. Freeman, *J. Phys. Chem.*, **65**, 1636 (1961). [e] This work, with $\bar{g}$ values referenced to diphenylpicrylhydrazyl (DPPH).

In conclusion, we have clearly demonstrated that matrix-stabilized hydronium radicals do exist, and we believe they may become as useful as H atoms and hydrated electrons in understanding water chemistry.

(11) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, 6, 273 (1963).
(12) T. Cole, H. O. Pritchard, N. R. Davidson, and H. M. McConnell, *ibid.*, 1, 406 (1958).
(13) Experiments with ^{17}O water may help resolve these structural questions.

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Hyperfine Interaction of Halide Ions with Metalloporphyrin Cation Radicals

Sir:

Numerous electron spin resonance studies have revealed interactions of diamagnetic cations with aromatic anion radicals.[1] We present here evidence of hyperfine interaction between halogen anions and the cation radical of a metalloporphyrin.

Oxidation of zinc tetraphenylporphyrin (ZnTPP) by controlled-potential electrolysis in CH_2Cl_2, with $(C_3H_7)_4NClO_4$ as carrier electrolyte, results in a stable π-cation radical, $ZnTPP\cdot^+ClO_4^-$. This radical is characterized[2-4] by its absorption spectrum and an esr spectrum of nine lines assigned to the four equivalent nitrogens.

Chemical oxidation of ZnTPP in CH_2Cl_2 or $CHCl_3$ with 0.5 mol of Br_2 is reversible[2] and produces a radical with the same absorption spectrum as $ZnTPP\cdot^+ClO_4^-$. The esr signal associated with the radical is not, however, the characteristic nine-line spectrum, but consists, instead, of the four lines shown in Figure 1. Similar spectra are obtained if $Co^{III}OEP\cdot^{2+}2Br^-$, the cation radical of cobaltic octaethylporphyrin,[3] is used as the oxidizing agent. Treatment of the bromine oxidation product with $AgClO_4$ causes AgBr to precipitate and regenerates the $ZnTPP\cdot^+ClO_4^-$ esr spectrum with no change in the absorption spectrum. The number of spins, determined by integration of the esr signals, is conserved within 10%. These facts are consistent with the following equation.

$$\text{ZnTPP} \xrightarrow{0.5Br_2} \text{ZnTPP}\cdot{}^+Br^- \xrightarrow{AgClO_4} \text{ZnTPP}\ {}^+ClO_4^- + AgBr\downarrow$$

The four-line spectrum is thus assigned to hyperfine interaction of the $ZnTPP\cdot^+$ radical with one bromide ion (nuclear spin, $I = {}^3/_2$). The experimental spectrum can be simulated assuming the splitting constants of Table I.

Table I. $ZnTPP\cdot^+X^-$ in $CHCl_3$

X^-	a_X, G[a]	a_N, G[a]	g value
^{79}Br	8.18[b]		
^{81}Br	8.82	1.60[c]	2.0059 (±0.0003)
^{35}Cl	1.66[b]		
^{37}Cl	1.38	1.62	2.0032 (±0.0001)
F	8.78	1.61	2.0027 (±0.0001)
ClO_4		1.46	2.0025 (±0.0001)

[a] Obtained from the computer simulations. [b] Determined by the magnetic properties of the isotopes. [c] From d_{20}-$ZnTPP\cdot^+Br^-$ (deuterated phenyl groups), where the nitrogens are partially resolved.

Oxidation of ZnTPP in CH_2Cl_2 or $CHCl_3$ by 0.5 mol of Cl_2, controlled-potential electrolysis with $(C_2H_5)_4NCl$ as supporting electrolyte, or treatment of $ZnTPP\cdot^+ClO_4^-$ with excess $(C_2H_5)_4NCl$ all yield a radical with the 12-line esr spectrum shown in Figure 2, but the absorption spectrum remains that of $ZnTPP\cdot^+ClO_4^-$. If the solvent, CH_2Cl_2 or $CHCl_3$, is pumped off and replaced by the more polar methanol, the optical spectrum does not change, while the esr spectrum shows the same nine lines as does that of ZnTPP $^+ClO_4^-$ The 12-line spectrum is satisfactorily simulated assuming hyperfine interaction of ZnTPP $^+$ with one chloride ion ($I = {}^3/_2$). As previously reported[2] for

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(1) M. C. R. Symons, *J. Phys. Chem.*, **71**, 172 (1967), and references therein.
(2) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Amer. Chem. Soc.*, **92**, 3451 (1970).
(3) R. H. Felton, D. Dolphin, D. C. Borg, and J. Fajer, *ibid.*, **91**, 196 (1969).
(4) A. Wolberg and J. Manassen, *ibid.*, **92**, 2982 (1970).