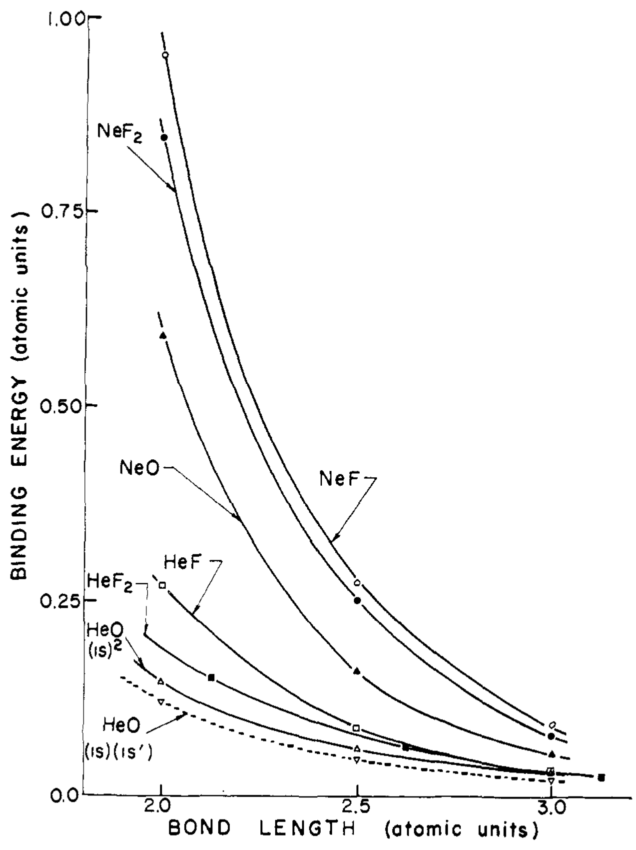

Figure 1. Average bond energies *vs.* bond length.

inclusion of all the electrons. A complete configuration interaction over the occupied atomic orbitals was carried out for each molecule with a Hartree-Fock atomic basis set. Thus the NeO wave function includes the chemical structures NeO, Ne^+O^-, $Ne^{2+}O^{2-}$, and is composed of 16 states made up from twenty-four 18 × 18 determinants. The curves of Figure 1 are all singlets with the oxygen atoms going to a ^1D configuration at infinite separation. Triplet states for the oxides were calculated. For these the free oxygen atom is in its ground-state ^3P configuration (calculated to be 0.0805 au lower than the ^1D), but the molecular potential energy curves lie even higher than the corresponding fluorides. Table I displays the chemically significant terms in the wave functions for the various species. The fact that the neon-associated species lie above those with helium can be attributed simply to the relative size of these atoms, although it is difficult to assign an effective radius to helium or bond length for HeO or HeF (the leading term in the wave functions effectively represents two neutral atoms repelling one another, and its coefficient measures the extent to which they have achieved a free atom-like behavior). As would be expected, the triatomic bifluorides lie below the diatomic fluorides because their extra symmetry element leads to resonance. The particularly interesting result showing the oxides to lie lower in energy than the fluorides arises from three factors which together override the greater electronegativity of fluorine. In the *neutral* states 2s–2p hybridization, favored in oxygen over fluorine because of the smaller orbital energy separation, together with the existence of half-filled π orbitals in the oxygen-containing species permits an energy lowering charge redistribution. Hybridization in these states allows the charge to move away from the between atom-repulsive region. Among the *singly ionized* states there are three in NeO and one in HeO which significantly lower the energy through formation of electron-pair bonds between open shells on each atom. Hybridization in the ionic states has the opposite sense to that in the neutral states, favoring the pair bonds by building up the charge between atoms. Purely ionic contributions are almost identical for both the fluorides and oxides, and the doubly ionized states, possible for the oxides but not the fluorides, make such an insignificant contribution that they have been omitted from the approximate wave function tabulation in Table I. In general, binding is discouraged because in the dominant states one of the atoms always has a closed-shell configuration. Since HeO exhibited the least repulsion, an even more elaborate configuration interaction, including different orbitals for different spins on helium, was carried out with the result shown by the dotted curve in Figure 1.

Table I. Wave Functions at 2.0 au (1.06 A)

HeO	$\Psi \cong +0.714\mathrm{HeO}(2s)^2(2p_\pi)^4 - 0.072\mathrm{HeO}(2s)(2p_\sigma)(2p_\pi)^4 - 0.071\mathrm{HeO}(2p)^6 - 0.051\mathrm{HeO}(2s)^2(2p_\sigma)^2(2p_\pi)^2 + 0.377\mathrm{He^+O^-}(2s)^2(2p_\sigma)(2p_\pi)^4$
NeO	$\Psi \cong +0.600\mathrm{NeO}(2s)^2(2p_\pi)^4 - 0.157\mathrm{NeO}(2s)(2p_\sigma)(2p_\pi)^4 - 0.037\mathrm{NeO}(2p)^6 - 0.031\mathrm{NeO}(2s)^2(2p_\sigma)^2(2p_\pi)^2 - 0.364\mathrm{Ne^+}(2s)^2(2p_\sigma)(2p_\pi)^4\mathrm{O^-}(2s)^2(2p_\sigma)(2p_\pi)^4 - 0.107\mathrm{Ne^+}(2s)(2p)^6\mathrm{O^-}(2s)^2(2p_\sigma)(2p_\pi)^4 + 0.043\mathrm{Ne^+}(2s)^2(2p_\sigma)(2p_\pi)^4\mathrm{O^-}(2s)(2p)^6$
HeF	$\Psi \cong +0.848\mathrm{HeF}(2s)^2(2p_\sigma)(2p_\pi)^4 + 0.282\mathrm{He^+F^-}$
NeF	$\Psi \cong +0.770\mathrm{MeF}(2s)^2(2p_\sigma)(2p_\pi)^4 - 0.360\mathrm{Ne^+}(2s)^2(2p_\sigma)(2p_\pi)^4\mathrm{F^-} + 0.104\mathrm{Ne^+}(2s)(2p)^6\mathrm{F^-}$

For argon the one-electron orbital energies of the 3p and 3s are remarkably close to degeneracy with the O 2p and O 2s, respectively. This renders simple electronegativity arguments ineffective, but our quantitative numerical experience with neon and helium suggests that the strong mixing of these states may produce minima in the potential energy surfaces for ArO_3 and ArO_4. For these and the fluorides ArF_2, and ArF_4, it is decidedly a border-line case as to whether or not they will show potential minima, and from a theoretical viewpoint it will require wave functions of the present degree of sophistication to provide a convincing answer. Such calculations are under way in this laboratory. The present massive synthesis effort for helium, neon-, and argon-containing species will provide a rigorous experimental test of the theory.

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Received September 28, 1965

Crystal Structure Studies of Some Unusual Antimony Bromide Salts[1]

Sir:

The group of salts of the type R_2SbX_6 ($R = NH_4^+$, Rb^+, or Cs^+; $X = Cl$ or Br) has been the subject of con-

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(1) Contribution No. 1808. This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

siderable investigation over the past 30 years.[2–7] The interest has arisen primarily from the fact that they are jet black in color and appear to contain tetravalent antimony. They have been shown[2] to be diamagnetic and so contain no unpaired electrons. The presence of a mixture of Sb(III) and Sb(V) has thus been assumed, although unconfirmed experimentally.

Several years ago Rundle, who also doubted the existence of the tetravalent state, predicted[8] that if the R_2SbX_6 salts contain the mixed Sb(III) and Sb(V) states, they would necessarily give rise to weak reflections in the reciprocal lattice and thus render themselves amenable to a detailed single crystal X-ray structure determination. In an attempt to settle the question concerning the actual existing oxidation state(s) of antimony in these salts, we thus decided to solve the crystal structure of one of these salts, $(NH_4)_2SbBr_6$, by single-crystal X-ray diffraction techniques. We wish to report that the final results of this investigation have confirmed the presence of the mixed states. The predicted weak reflections were observed (a total of 252 out of 621 observed reflections) and were disposed in such a manner as to give rise to the space group $I4_1/amd$ (D_{4h}^{19}) for a unit cell of dimensions $a = 10.66 \pm 0.02$ A and $c = 21.52 \pm 0.02$ A ($c/a = 2.02$). Three-dimensional X-ray scintillation counter data were refined by a full matrix anisotropic least-squares analysis. The refinement of all atoms, except hydrogen, yielded a final unweighted reliability index of 10.5% for the 621 observed reflections.

The structure is a distorted K_2PtCl_6 structure. The unit cell may be described as two K_2PtCl_6-type cells stacked one above the other. The entire cell contains four formula units of $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$ with the 16 ammonium ions occupying tetrahedral holes formed by four undistorted $Sb^{III}Br_6{}^{3-}$ ions (with O_h symmetry[9]) and four distorted $Sb^{V}Br_6{}^{-}$ ions (with D_{2d} symmetry, Br_e–Sb–Br_a = 93.67 ±0.15°), arranged as shown in Figure 1. The average Sb(III)–Br and Sb(V)–Br bond lengths, after correction for thermal motion assuming a librating ion, were found to be 2.795 ± 0.006 and 2.564 ± 0.006 A, respectively.

A recent study by Day[10] of the solid reflection spectra of several hexahalide complexes containing Sb(III) and Sb(V) has indicated that electron-transfer transitions from the ns^0 or $(n + 1)s^2$ shell of the trivalent ion to the ns^0 shell of the pentavalent ion are responsible for the abnormally deep color. However, it is not clear how such a transition could take place in this case. In order to obtain additional information on structural requirements for the existence of charge transfer in the solid state, we have prepared a wide variety of similar salts, $R_xSb_yBr_z$, through the introduction of nonspherical monovalent cations, R^+. The salts, a total of thirteen, were prepared by approximately the same method as was used in the preparation of the ammonium salt with the exception that the ammonium ion was replaced by the tetramethylammonium ion or the protonated form of one of the following amines: pyridine, α-picoline, β-picoline, γ-picoline, 4-ethylpyridine, γ-collidine, quinoline, pyrrolidine, 2-pyrrolidone, piperidine, morpholine, and quinuclidine.[11] The colors of the resulting salts ranged from violet-black to jet black.

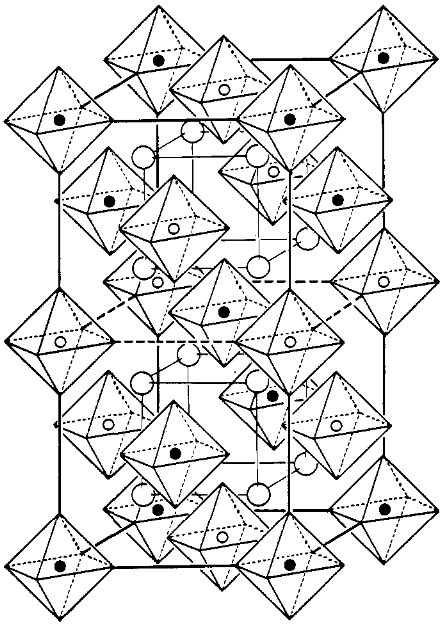

Figure 1. The unit cell of tetragonal] $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$, showing the relative distribution of Sb(III) (small black circles) and Sb(V) (small white circles). Each antimony atom is located at the center of an octahedron formed by six bromine atoms (distortions not shown). The ammonium ions, represented by large white circles, occupy the tetrahedral holes.

Preliminary single-crystal structure studies of nine of the thirteen salts, together with a knowledge of their crystal density, have produced three interesting results. First, three different moles ratios of R:Sb:Br were observed, namely (1) 3:2:11, (2) 3:2:14, and (3) 2:1:8, depending upon the cation used. (This dependence on R^+ was also observed by Petzold,[12] although the exact formulas he obtained differ from ours.) The ratio 4:2:12 was not observed. Second, the reciprocal lattice of each (except that of the piperidinium salt, which has four $R_4Sb_2Br_{16}$ per unit cell) was found to be completely void of weak reflections of the type observed for $(NH_4)_4Sb_2Br_{12}$. And third, in some cases (*i.e.*, R_2SbBr_8, except the piperidinium salt) X-rays indicate the presence of only *one* antimony atom per asymmetric unit, indicating that if the crystals are ordered there exists only one oxidation state for antimony instead of a mixture of III and V. The net oxidation state of this antimony atom is thus not immediately obvious. It does suggest, however, that these salts may exhibit physical properties not observed for the other black salts. For instance, a change in color has been noted with decrease in temperature but only for some of those salts having

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(2) N. Elliot, *J. Chem. Phys.*, **2**, 298 (1934).

(3) (a) K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **232**, 193 (1937); (b) K. A. Jensen, *ibid.*, **252**, 317 (1944).

(4) (a) J. Whitney and N. Davidson, *J. Am. Chem. Soc.*, **69**, 2076 (1947); (b) J. Whitney and N. Davidson, *ibid.*, **71**, 3809 (1949); (c) N. Davidson, *ibid.*, **73**, 2361 (1951).

(5) N. A. Bonner, *ibid.*, **71**, 3909 (1949).

(6) A. T. Jensen and S. E. Rasmussen, *Acta Chem. Scand.*, **9**, 708 (1955).

(7) G. Brauer and W. D. Schnell, *Z. Anorg. Allgem. Chem.*, **283**, 49 (1956).

(8) R. E. Rundle, private communication.

(9) The $Sb^{III}Br_6{}^{3-}$ ion contains a lone pair of electrons. For recent discussions on the proposed influence of the lone pair on both the stereochemistry and bonding in $:XL_6$ complexes, see (a) D. S. Urch, *J. Chem. Soc., Suppl. I*, 5775 (1964); (b) I. D. Brown, *Can. J. Chem.*, **42**, 2758 (1964).

(10) P. Day, *Inorg. Chem.*, **2**, 452 (1963).

(11) Details on the preparation of these salts will be reported later.

(12) W. Petzold, *Z. Anorg. Allgem. Chem.*, **215**, 92 (1933).

the formula R_2SbBr_8 and $R_3Sb_2Br_{14}$. At or near liquid air temperature, colors ranging from bright orange to red have been obtained. The color change is reversible and changes from black to red to orange as the temperature is lowered.

The preliminary investigations carried out on the $R_xSb_yBr_z$ salts confirm the need for additional extensive study. Further investigations into the color change with temperature and a study of their magnetic properties are planned. The detailed single crystal structure determinations of several of these salts by X-ray diffraction are currently in progress. More complete details concerning the crystal structure of $(NH_4)_4Sb_2Br_{12}$, as well as of those under current investigation, will be reported later.

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Received October 7, 1965

A New Acyclic Acid Metabolite in Camphor Oxidation

Sir:

Previous studies[1–3] revealed types of reactions and enzymes which oxygenate and cleave the carbocyclic rings of the bicyclic bornane nucleus. Figure 1 depicts the known intermediates, I → VII,[4,5] in a pathway of (+)-camphor [(+)-2-bornanone] oxidation by a soil diphtheroid, strain T_1.[6]

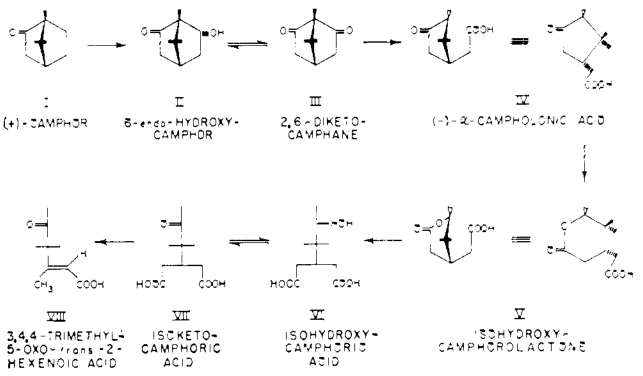

Figure 1. Oxidation pathway of (+)-camphor by bacterial strain T_1. The stereochemistry of the C-10 methyl has not been established rigorously [M. Harispe and D. Mea, *Bull. Soc. Chim. France*, 1340 (1962)]. Its depiction here does not indicate any stereochemical assignment.

This paper identifies a branched 9-carbon acid (3,4,4-trimethyl-5-oxo-*trans*-2-hexenoic acid, VIII) isolated from the medium and presumed to arise from the 10-carbon skeleton VII by decarboxylation following α,β-dehydrogenation, possibly as a coenzyme A thioester.[7]

The pathway outlined in Figure 1 was deduced from our identification[3,5] of the intermediates and their use in enzyme studies. The steps include direct 6-*endo*-hydroxylation of camphor to II, its DPN mediated dehydrogenation by an inducible dehydrogenase[2,8] to form 2,6-diketocamphane (III) and hydrolysis to (−)-α-campholonic acid (IV) by a stereospecific β-diketone hydrolase.[3] Cleavage of the second carbocyclic ring adjacent to the ketone, by a keto–lactonase system similar to the pseudomonad pathway,[9] is suggested by the analogous reaction on fenchone[10] and the presence of a specific inducible DPNH-coupled alcohol dehydrogenase,[11] which reduces isoketocamphoric acid (VII) to the hydroxy acid VI.

Experimental details have been described for growth of the organism and for extraction of the culture medium with methylene chloride to give neutral and acidic intermediates.[5] The crude acids were separated into ketonic and nonketonic acid fractions by Girard's reagent T. Separation of the unreacted "non-ketonic" components was effected on 2.1 g. of sample by preparative thin layer chromatography on silica gel plates prepared by the modified spreading techniques of Lees and DeMuria.[12] Separation of at least six distinct bands, as visualized by an ethanolic bromcresol green spray, was achieved by developing with acetic acid–chloroform (10:90 v./v.). The fastest moving band (R_f 0.74) was scraped from 35 chromatographic plates, 20 × 20 cm., and extracted with ether to yield 76 mg. of crystalline VIII, m.p. 123°, neut. equiv. 172 ± 2 (calcd. 170). Gas–liquid chromatography of the methyl ester gave a single peak; thin layer chromatography similarly showed only one component, detectable by ultraviolet absorption, acidic properties to ethanolic bromcresol green spray, and positive reaction with 2,4-dinitrophenylhydrazine reagent.[13]

This acid showed infrared absorption ($CHCl_3$) at 1691 cm.$^{-1}$ (carbonyl) and 1629 cm.$^{-1}$ (conjugated olefin), and an ultraviolet maximum, ϵ 9000 at 210 mμ (EtOH), which corresponds to an α,β-unsaturated acid.[14] The nuclear magnetic resonance spectrum ($CDCl_3$) assigns an olefinic methyl peak at C-3 (τ 7.92, doublet), *cis* to the carboxyl, and an olefinic proton peak at C-2 (τ 4.04, multiplet);[15] it also contains peaks at τ −1.75 (1H, singlet carboxyl proton), τ 7.92 (3H, acetyl singlet, overlapping with the doublet of the allylic methyl), and τ 8.70 (6H, two singlet methyl groups). The groups defined by the ultraviolet and nmr. spectra (CH_3—C═CH—COOH, $(CH_3)_3$ = $C_7H_{14}O_2$) account for 130 mass units. The equivalent weight indicated by titration agrees satisfactorily with the molecular formulas $C_9H_{14}O_3$ (mol. wt. 170) and $C_8H_{14}O_4$ (mol. wt. 174), but only the former can account for the nmr. spectrum

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[1] W. H. Bradshaw, H. E. Conrad, E. J. Corey, I. C. Gunsalus, and D. Lednicer, *J. Am. Chem. Soc.*, **81**, 5507 (1959).

[2] P. J. Chapman, J. F. Kuo, and I. C. Gunsalus, *Federation Proc.*, **22**, 296 (1963).

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[4] H. E. Conrad, E. J. Corey, J. Hedegaard, N. S. Paisley, and I. C. Gunsalus, Proceedings, Vth International Congress of Biochemistry, Vol. 29, Moscow, 1961, p 343.

[5] P. J. Chapman, I. C. Gunsalus, H. Uda, and E. J. Corey, in preparation.

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