stirred at −70° under a nitrogen atmosphere and phenyllithium[10] (16 ml, 1.5 *N* in ether, 4 equiv) was added over a 5-min period, forming a dark red solution. After quenching with an excess of cold aqueous ammonium chloride, a red-brown organic layer was formed to which 25 ml of benzene was added. The two layers were filtered to remove 0.347 g of an insoluble dark brown solid, and the organic layer was then separated and washed with cold distilled water. The dark brown oily residue left on evaporation was taken up in 100 ml of dry benzene and filtered to remove insoluble material. After drying over sodium sulfate and evaporating, the residual brown oil was dried overnight at 0.004 mm and 18.4 mg of biphenyl distilled over into the trap. Anhydrous ether (20 ml) was added to the oily residue. The red solution was filtered from some insoluble material and cooled in an ice-water bath before adding 100 ml of cold petroleum ether (bp 30–60°). The brown solid which precipitated was collected by filtration, washed with petroleum ether, and then freeze dried from benzene to yield 121.5 mg (14%) of 1-phenylthiabenzene, softening point 68–73°.

1-Phenylthiabenzene (VI) was also prepared[2] by treating 1.0 g of VII[11] suspended in 50 ml of ether under nitrogen in a separatory funnel capped with a rubber serum cap with 15 ml of 2 *M* phenyllithium in ether-benzene (Lithium Corp. of America, New York, N. Y.) added by a syringe slowly with shaking. After 15 min additional shaking, it was worked up as above to give 72 mg of a brown solid, softening point 68–72°.

Anal. Calcd for $C_{11}H_{10}S$: C, 75.81; H, 5.78; S, 18.40; mol wt, 174. Found: C, 75.71; H, 5.92; S, 18.22; mol wt, 173 (Rast method).

The nmr showed only a single absorption centered at τ 2.8. The ultraviolet spectrum in ethanol showed λ_{max} (log ϵ) 202 (4.01) and 246 mμ (3.64), and major infrared absorption bands occurred at 3050 (35), 3020 (45), 1600 (40), 1580 (45), 1474 (35), 1437 (30), 1020 (40), 740 (60), and 685 cm^{-1} (65) (% abs).

The dipole moment and molecular refractivity were measured at 30 ± 0.002° using a General Radio Co. frequency capacitance bridge, oscillator, and null detector[12] to measure the dielectric constant of various concentrations of VI in benzene. The corresponding refractive indices were measured by a Pulferich refractometer. The Halverstadt-Kumler[13] equation was then used to calculate the molar polarization (142.67 cc), the molar refraction (130.28 cc), and the dipole moment (0.79 ± 0.2 D).

Mass Spectra of VI run at various inlet temperatures showed very low intensity parent peaks at 174 amu. The major peak at temperatures above 100° was biphenyl (154 amu), while at 90°, the major peak was the thiopyrylium ion (97 amu). In all spectra, there was a moderately intense peak at 186 amu, corresponding to diphenyl sulfide. These observations indicate that VI is very unstable to electron impact, decomposing readily to phenyl radical and thiopyrylium ion. The phenyl radical (or ion) must then rapidly attack another molecule of VI to form diphenyl sulfide and a $C_5H_4^+$ fragment, also very abundant in all the mass spectra. We believe the biphenyl is formed mainly by thermal decomposition in the inlet.

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Evidence and Hypothesis for a "Taube Bridge Electron Transfer" Propagating to a Remote Site through σ Bonding. The Formation of Ethylene from Monoethyl Sulfate

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Abstract: Ethylene has been produced from monoethyl sulfate by a reaction with a free radical or oxygen in the presence of a reduced metal ion, ferrous. A "Taube Bridge" mechanism involving electron activity at a remote site is proposed for this process.

The requirement for the close physical location of nuclei within molecular dimensions for redox processes was elegantly and conclusively taught by Westheimer[2a] in his ester mechanism for the two-electron chromic acid oxidation of alcohols, and this same kind of spatial requirement was established by Taube[2b] for many inorganic one-electron transfer reactions. This type of molecular arrangement can now be taken as a model frame of reference from which one should view all redox processes and is understood as a consequence of the molecular orbitals needed to transmit electrons across space.[3] The conduction of

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[1] Predoctoral Fellow, National Institute of Health Training Grant 1-T01-ES-84 from Division of Environmental Sciences.

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electron activity to remote regions of a molecule over extended π systems[4,5] has been reported, and the involvement of σ bonds, where an adjacent bond is broken and a π bond formed between the center carbon atom and the oxygen atom directly attached to the oxidizing chromate species has been shown; but there has been no suggestion that electron activity could be transmitted to a remote region of a molecule through several σ bonds. The simplest mechanism that we can propose for the generation of ethylene from the ferrous cation, the ethyl sulfate anion, and a radical species is a concerted process where a hydrogen atom is abstracted from a site that is remote from the expected point of ligand attachment to the ferrous ion.

Experimental Section

Reagents. Eastman White Label ethylsulfuric acid potassium salt was dried *in vacuo* before use. Mallinckrodt analytical reagent ferrous sulfate heptahydrate, and practical grade *t*-butyl hydroperoxide from Matheson Coleman and Bell were used directly.

Generation of Ethylene. For this study, two methods of addition of ferrous ion and peroxide were used.[6] A typical experiment was made up with 0.30 g of ferrous sulfate and 1.00 g of potassium ethyl sulfate dissolved in 10.0 ml of H_2O in a 50-ml erlenmeyer flask. The atmosphere was purged with nitrogen and the flask stoppered with a serum cap. A gas-collection buret was connected by means of a large hypodermic needle and the hydroperoxide injected with a hypodermic syringe while the flask was magnetically stirred. The generated gas volume was measured directly and its composition determined by gas chromatography on a Beckman GC-4. In the cases where ferrous sulfate was added to the flask, a stock solution was first prepared. Ferrous sulfate, 16.00 g, was placed in a 50-ml erlenmeyer flask and 30 ml of distilled water was added; the flask was closed with a serum cap and connected to a water leveling bulb system by means of a hypodermic needle and rubber tubing. A stream of nitrogen was then blown into the erlenmeyer flask *via* a second hypodermic needle, punctured through the serum cap and allowed to bubble through the gas-collection system. After purging for approximately 5 min, vigorous magnetic stirring was begun. The stirring and nitrogen purge was continued for 2 hr. A solution thus prepared will keep its blue-green color for approximately 6 hr. After that, gradual formation of yellow-brown precipitate will occur. Aliquots (3 ml) of the fresh solution were withdrawn with a nitrogen-purged syringe and injected into a serum cap stoppered, previously N_2-purged, 50-ml erlenmeyer flask containing 7.0 ml of water, 0.10 ml of peroxide, and 1.00 g of $KEtOSO_3$, while stirring vigorously on a magnetic stirrer.

Results

The ferrous ion decomposition of *t*-butyl hydroperoxide has been shown to give *t*-butoxy radicals[7,8] which subsequently cleave to yield methyl radicals.[9] The analyses of gaseous products from the reactions of these radicals with ethyl sulfate are shown in Table I and Figures 1, 2, and 3.

In the control experiments without peroxide a very slow evolution of ethylene from ferrous sulfate and ethyl sulfate was observed which is dependent on oxygen. Degassing samples with only a Duo-Seal oil pump reduced the rate of this production by a factor of around 28. Experiments substituting equivalent amounts of hydrogen peroxide for *t*-butyl hydro-

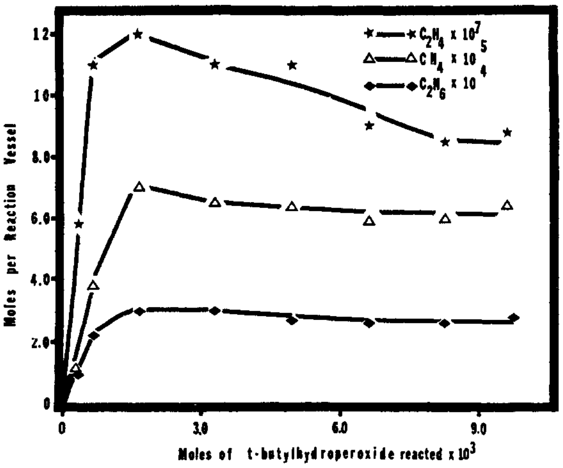

Figure 1. Gaseous products when varying amounts of *t*-butyl hydroperoxide are added to 0.30 g of ferrous sulfate and 1.00 g of potassium ethyl sulfate in 10 ml of water.

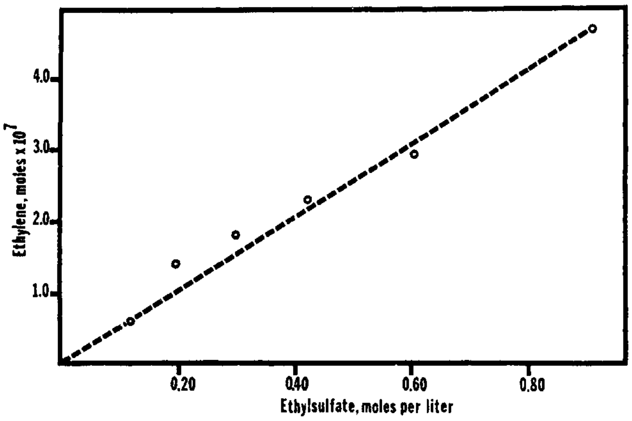

Figure 2. The yield of ethylene when 0.10 ml of *t*-butyl hydroperoxide is added to 1.60 g of ferrous sulfate and varying amounts of potassium ethyl sulfate in 10 ml of water.

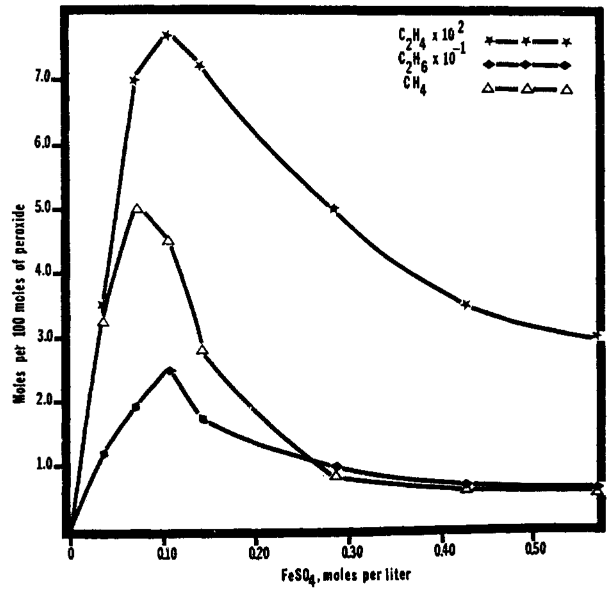

Figure 3. Moles of gaseous products when 0.10 ml of *t*-butyl hydroperoxide is added to 1.00 g of potassium ethyl sulfate and varying concentrations of ferrous sulfate in 10 ml of water.

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Table I. Gaseous Products from the Reaction of *t*-Butyl Hydroperoxide with Ferrous Sulfate and Ethyl Sulfate

	—Moles/100 mol of peroxide reacted—			
	A[a]	B[b]	A	B
$KEtOSO_3$	0	0	910	910
Methane	3.0	23	5.6	27
Ethane	37	42	35	38
Ethylene	0.008	0.01	0.15	0.08
Propane	0.30	0.42	0.28	0.25

[a] A, the peroxide, 0.1 ml, was added to the ferrous sulfate (0.30 g) with and without ethyl sulfate. [b] B, the ferrous sulfate (0.30 g) was added to the 0.1 ml of peroxide with and without ethyl sulfate.

peroxide in a typical experiment produces ethylene in somewhat higher yields. These systems are under further investigation.

Discussion

Although trace amounts of ethylene are formed during the simple decomposition of the *t*-butyl hydroperoxide with ferrous ion, our interest and discussion is focused on a large increase of this product that is observed when ethyl sulfate is present. A simple first order dependence of the yield of ethylene on the ethyl sulfate concentration is shown in Figure 2. In the control experiments with oxygen and in the analogous reaction substituting hydrogen peroxide for *t*-butyl hydroperoxide there can be no doubt that ethyl sulfate is the precursor for ethylene because it is the only carbon source in the system. The actual dependence on the ferrous ion is complicated as shown by the graph in Figure 3. Ferrous ion appears to be serving two functions in this system. The first is in the expected fast reaction for the formation of *t*-butoxy radicals from its reaction with *t*-butyl hydroperoxide and the second is in the complex redox system which generates ethylene. The variation in the yield of ethylene with changing amounts of peroxide added is shown in Figure 1, and a plot of ethylene *vs.* $(C_2H_6)^{1/2}$ indicates that there is a first-order dependence on radicals, Figure 4, because the ethane can be used as an internal monitor for free-radical formation.[10] Evidence that ferrous is the important oxidation state of the iron in the reaction is indicated by the fact that ethylene is generated by the analogous reaction of oxygen with ferrous ion but not with ferric ion. Since essentially the same amount of propane is observed in the control as well as in the ethylene-forming reactions, and a total absence of *n*-butane is noted, the possibility that ethyl free radicals can be an intermediate for the formation of ethylene is eliminated.[11,12]

A simple mechanism to explain these observations is a remote attack by a radical on a ligand bridge of the metal ion. In such a concerted process where the attacking radical abstracts a hydrogen atom while the metal ion is oxidized, sufficient free energy becomes available from the redox process to permit the formation of ethylene, *i.e.*

$$[\mathrm{R{\cdots}HCH_2CH_2OSO_2O^-{\cdots}Fe^{+2}}] \longrightarrow \mathrm{RH} + \mathrm{CH_2{=}CH_2} + \mathrm{SO_4^{2-}} + \mathrm{Fe^{3+}}$$

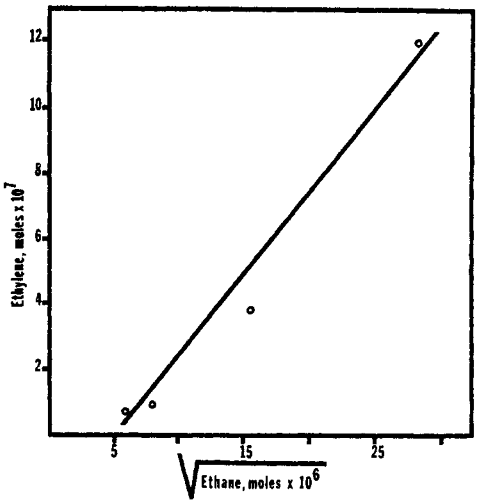

Figure 4. The yield of ethylene plotted using the square root of the yield of ethane as an internal monitor for the free-radical concentration when varying amounts of *t*-butyl hydroperoxide are added to 1.60 g of ferrous sulfate and 0.33 g of potassium ethyl sulfate.

A close variation of this mechanism would involve a bidentate ligand formation by the sulfate anion where the alcohol oxygen is one of the dentae. The attacking radicals in this reaction are either a methyl or *t*-butoxy.

The proposed mechanism suggests that a large variety of organic ligands can be expected to produce ethylene when they are exposed to a one-electron reducing agent such as ferrous or cuprous ion and coupled with a one electron-oxidizing agent such as a free radical or oxygen. Preliminary experiments show that methionine, monoethyl phosphate, diethyl phosphate, butyric acid, ethyliodide, ethanol, and methional can be made to produce some ethylene.

Conclusion

While the yield of ethylene is very poor with respect to synthetic organic chemistry, the mechanism proposed above is important for examples where the faster competing reactions can be controlled such as in the study of ethylene as a plant hormone and the molecular mechanism for its biological action.[13] This is an example of how free energy stored in redox couples can be utilized to perform chemistry in biological systems. The formation of ethylene can be thought of as arising from a concerted radical elimination reaction (RE_2) which accompanies a one electron redox reaction and this is a special case of an outer sphere reaction such as has been suggested for the very reactive sulfate radical ion with chromous ion.[14] Studies of the action of two one-electron oxidizing agents acting in concert[15] or in a two-step oxidative process *via* an

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intermediate[16] have been reported and the "enzymatic oxidation of a quinol phosphate"[17] reported recently may be another example of a concerted oxidative process. The possibility that ethyl sulfate is an intermediate in the formation of ethylene from the reaction of ethyl radicals with cupric sulfate[18,19] is suggested by these results. If this is the case, the reaction with the hypothetical cuprous ethyl sulfate must be a more efficient process.

Acknowledgment. We wish to thank Mr. Paul Bigelow for his enthusiastic help as a National Science Foundation Summer Science Trainee.

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Stereochemistry of Nucleic Acids and Their Constituents. V. The Crystal and Molecular Structure of a Hydrated Monosodium Inosine 5′-Phosphate. A Commonly Occurring Unusual Nucleotide in the Anticodons of tRNA[1]

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Abstract: The crystal structure of hydrated monosodium inosine 5′-phosphate has been determined from 1420 observed reflections recorded with a Picker four-circle automatic diffractometer using the 2θ scan mode and Ni-filtered Cu radiation. The crystal belongs to the orthorhombic space group $C222_1$ with eight formula units in the unit cell of dimensions $a = 8.682 \pm 0.003$, $b = 23.216 \pm 0.009$, and $c = 21.917 \pm 0.007$ Å. The structure was determined by three-dimensional Patterson and Fourier methods, and was refined by anisotropic full-matrix least-squares to an R value of 0.10. The occupancy parameters of the water molecules were varied during the isotropic refinement, but were held fixed during the anisotropic refinement. The nucleotide assumes the preferred *anti* conformation about the glycosidic linkage with the ribose ring showing the C(2′)-*endo* pucker. The torsion angle around the C(5′)–O(5′) bond is 176°. The sugar phosphate assumes the extended conformation. The sodium ion is not directly coordinated to the phosphate oxygens but is coordinated to both the ribose hydroxyls and to four water molecules. There are close contacts between O(1′) of the ribose and the base of a symmetry-related molecule as found in other similar structures. The waters are distributed over nine sites, four of which are disordered. A plausible hydrogen-bonding scheme is suggested.

The triplet anticodon of tRNA (transfer ribonucleic acid) is often found to contain one unusual nucleotide besides the common ribotides. Inosine is present in four of the tRNAs, alanine tRNA, serine tRNA 1, serine tRNA 2, and valine tRNA, whereas 2′-O-methylguanosine and pseudouridine are present in tyrosine tRNA and phenylalanine tRNA, respectively. We are currently investigating the detailed crystal structures of several unusual nucleic acid constituents occurring in the anticodon loops of tRNAs in order to gain information concerning their function. The detailed stereochemical and hydrogen-bonding properties of inosine 5′-phosphate are presented here. A brief account of the structure has already been published.[3] The occurrence of a large number of waters of crystallization and a sodium ion provides also some indication of the manner in which water and alkali metal ions interact with nucleic acids.

Experimental Section

The monosodium salt of inosine 5′-phosphate (IMP), which was obtained from Sigma Biochemical Co., St. Louis, Mo., gave well-formed needles on recrystallization from water. Oscillation and Weissenberg photographs established the crystal system to be orthorhombic with the systematic absences hkl, $h + k = 2n + 1$, and $00l$, $l = 2n + 1$, thus indicating that the space group is $C222_1$. The cell constants were determined from medium- and high-angle reflections measured on a Picker automatic diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) and were found to be $a = 8.682 \pm 0.003$, $b = 23.216 \pm 0.009$, and $c = 21.917 \pm 0.007$ Å. The density of the crystal, 1.576 g cm^{-3}, obtained by the method of flotation using a mixture of chloroform and bromoform, is in agreement with the calculated density of 1.580 g cm^{-3} assuming eight formula units of $C_{10}N_4O_8H_{12}P \cdot Na \cdot 8H_2O$ in the unit cell. However, it will be seen that the structure determination can account for only about six water molecules. Presumably the remaining crystal waters slowly effloresced before and during the recording of the data. The crystal used in the experimental work was not enclosed in a capillary. The chemical formula of IMP and the atom numbering scheme are shown below.

Complete three-dimensional intensity data up to $2\theta = 134°$ were collected on the Picker automatic diffractometer with Ni-filtered Cu radiation employing the 2θ scan technique. About 2200 independent reflections were thus recorded. On the basis of the counting statistics derived from the systematically absent reflections, a reflection was considered observed if $I > 1.5\sigma(I)$ where

$$\sigma(I) = [I_{\text{scan}} + I_{\text{bkg}}]^{1/2}$$

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