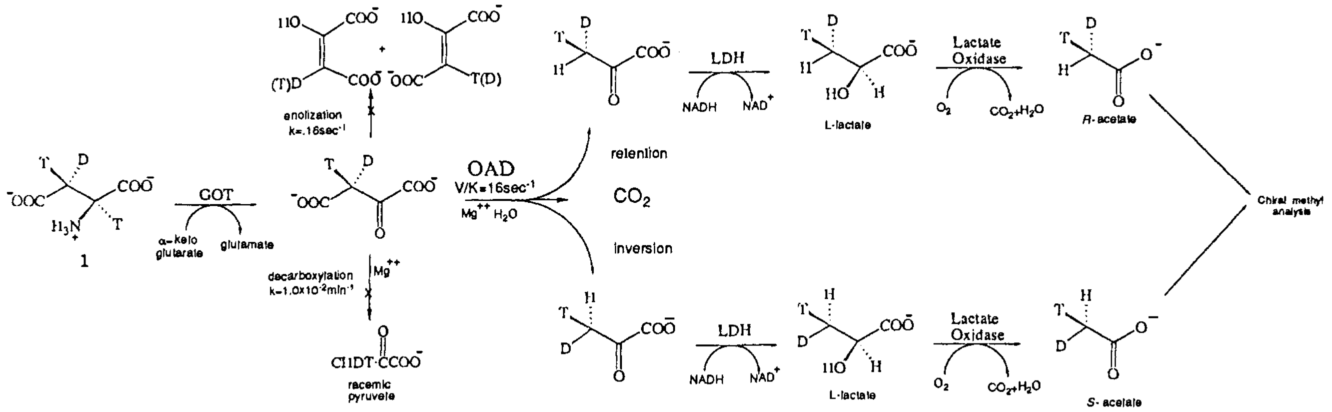
Scheme II



acid (**1**), stereospecifically labeled at C-3 with deuterium and tritium (Scheme II).[17] Incubation of **1** with glutamate–oxaloacetate transaminase (GOT) and α-ketoglutarate resulted in generation of $(3S)$-[^{2}H,^{3}H]oxaloacetate, which was decarboxylated in situ by OAD to yield [^{2}H,^{3}H]pyruvate. Pyruvate was reduced in situ to lactate with NADH and lactate dehydrogenase to prevent loss of chirality via enolization. Chiral lactate was isolated by anion exchange chromatography (Dowex-1 formate),[18] oxidized to acetate with lactate oxidase, and analyzed for chirality.[19] (S)-[^{1}H,^{2}H,^{3}H]acetate was formed from $(3S)$-oxaloacetate, showing that decarboxylation was with inversion. This conclusion was confirmed by the production of (R)-acetate starting with $(3S)$-[3-^{1}H,^{3}H]aspartate.[20]

An OAD that produces inversion violates the correlation in Table I. Indeed, the result is inconsistent with any functional explanation for stereospecificity in decarboxylases based on a property intrinsic in the substrate, as OAD from *Klebsiella aerogenes* (biotin dependent),[21] pyruvate carboxylase (biotin dependent),[7] and malic enzyme all produce retention.[7] In the last case, the enzyme-producing retention appears to operate via the same mechanism as the one reported here producing inversion.[22] Therefore, mechanistic diversity does not appear to accompany stereochemical diversity. However, the result is also inconsistent with "historical" explanations that presume common ancestry for enzymes catalyzing analogous reactions.[11] Such explanations are prominent in the analysis of stereospecificity in many enzymatic reactions and are weakened by the results presented here.

The enzyme class "β-ketoacid decarboxylases" thus displays a full range of stereochemical diversity: retention, inversion, and racemization. This result is consistent with the emerging notion that enzymatic distinctions between diastereomeric transition states often reflect functional adaptation, while distinctions between enantiomeric transition states do not.[23]

However, for β-decarboxylases, three explanations must be considered for these results: (a) Several independent pedigrees of decarboxylases descendent from several ancestral decarboxylases, where stereospecificity is nonfunctional but highly conserved; (b) stereospecificity as a nonfunctional trait capable of facile neutral "drift" as homologous enzymes diverge; or (c) stereospecificity as a functional trait, where a mechanistic imperative is hidden in the details of the individual reactions or environments of the organism.

Acknowledgment. We thank David Berkowitz for helpful discussion. This research was supported by the Swiss National Science Foundation, Sandoz, Ciba-Geigy, Hoffmann-La Roche, the Searle Foundation, and the National Institutes of Health.

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[17] The presumed stereospecificity of the aspartase reaction was confirmed by converting aspartate to malate with use of glutamate–oxaloacetate transaminase, malate dehydrogenase, and NADH. Incubation of the radiolabeled malate with fumarase showed 97% of the label to be in the pro-*S* position of C-3.

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Charge-Transfer Photooxygenation of Sulfides in a Cryogenic Oxygen Matrix: IR Spectroscopic Observation of Persulfoxides

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The oxygenation of organic sulfur compounds with molecular oxygen continues to yield fascinating results.[1-8] Much attention

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[1] For reviews, see: (a) Ando, W. *Sulfur Report* **1981**, *1*, 143. (b) Ando, W.; Takata, T. In *Singlet O₂*; Frimer, A. A., Ed.; CRC Press: Florida, 1985; Vol. 3, Chapter 1, p 1.

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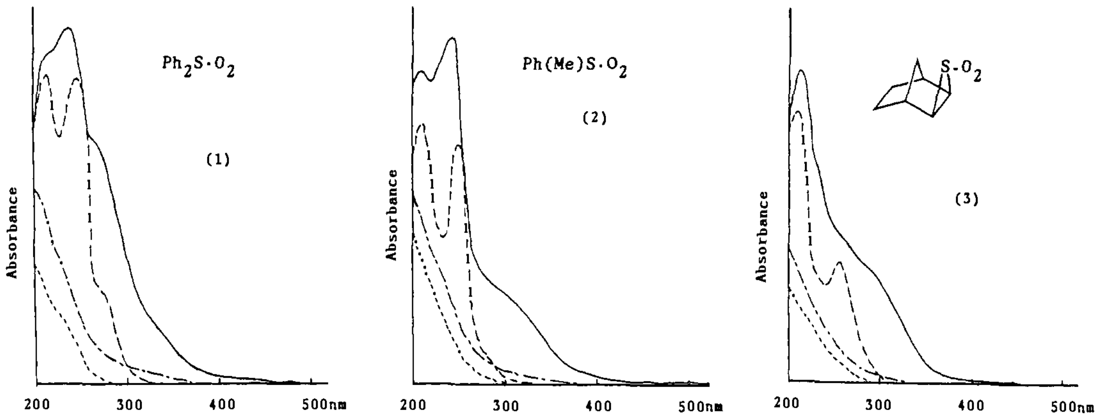
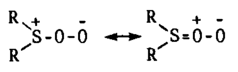


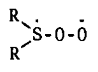
Figure 1. UV spectra, (1)–(3), of sulfides **4**–**6** isolated in oxygen matrices at 13 K, respectively. Each spectrum was recorded individually: background on a sapphire plate (---), after deposition of oxygen (— — — —), after deposition of sulfide (---), and after deposition of both sulfide and oxygen (—).

has been devoted to the reactivities of initially formed peroxidic intermediates for which persulfoxide **1**, diradical **2**, or dioxirane **3** structures have been suggested.[1-8] However, since no direct observation of the intermediates[9] has been achieved so far, their structures are still controversial.[1] Our approach to the direct spectroscopic observation of such intermediates is based on the direct charge-transfer (CT) photochemical reaction of sulfides with molecular oxygen.[7] The photochemical oxygenations of sulfides (diphenyl sulfide (**4**),[7b] methyl phenyl sulfide (**5**),[7b] and 3-thiatricyclo[3.2.1.0^{2,4}]octane (**6**))[10,11] have been investigated in oxygen matrices at 13 K. We report here the first observation of the matrix-isolated intermediates by FT-IR spectroscopy. The IR spectra suggest that these species are best formulated as the persulfoxide zwitterions **1**.



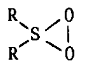
$R_2\overset{+}{S}-O-\overset{-}{O} \longleftrightarrow R_2S=\overset{+}{O}-\overset{-}{O}$

1

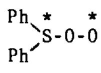


$R_2\overset{\cdot}{S}-O-\overset{-}{O}$

2

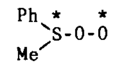


3



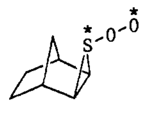
$Ph_2\overset{*}{S}-O-\overset{*}{O}$

7



$Ph(Me)\overset{*}{S}-O-\overset{*}{O}$

8



9

* = +/- or •

The UV absorption spectra of sulfides **4**, **5**, and **6** in solid oxygen matrices[12] reveal contact CT bands with broad maxima at ca. 310, 315, and 295 nm, respectively (Figure 1).[14] The main continuum

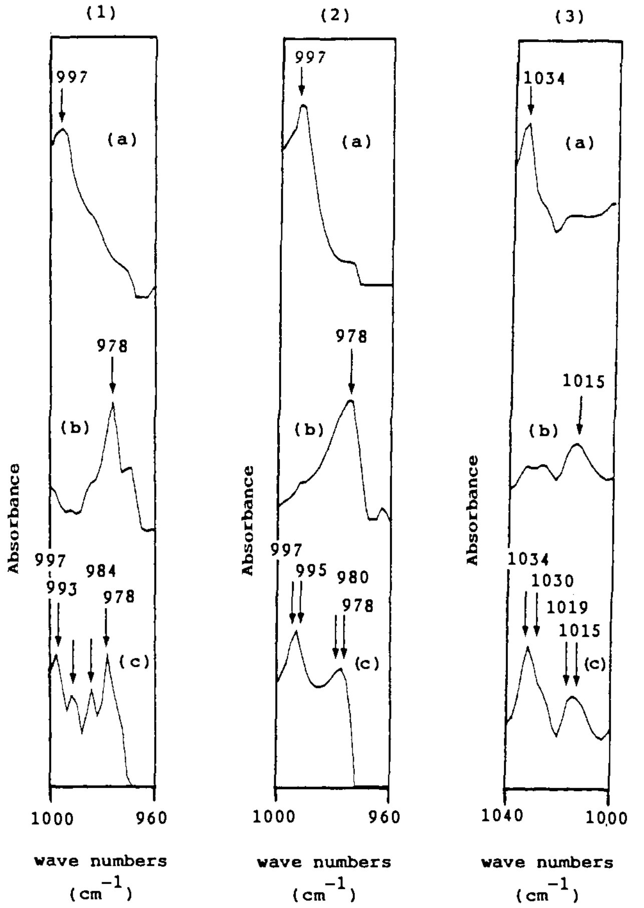


Figure 2. Difference IR spectra, (1)–(3), obtained upon photolysis of sulfides **4**–**6** isolated in oxygen matrices at 13 K, respectively. The following isotopic mixtures were used: (a) $^{16}O_2$, (b) $^{18}O_2$, and (c) $^{16}O_2$, $^{18}O_2$, and $^{16}O-^{18}O$.

at ca. 300 nm is similar to the sulfide–O_2 contact CT band reported in the liquid phase.[7] The reaction intermediates resulting from UV irradiation (300–400 nm)[17] of the contact CT band were studied by FT-IR spectroscopy.[18]

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(11) When a benzene solution of the sulfide was irradiated with a high pressure mercury lamp through a Pyrex filter with bubbling oxygen, the corresponding sulfoxide was detected by means of NMR spectral analyses.

(12) The cryostat system used is the same one reported by Chapman et al.[13] For UV–vis measurement, sulfide and oxygen gas were deposited on the sapphire plate cooled to 13 K by an Air Products Displex refrigerator. The spectra were recorded through the quartz windows on a Shimazu UV-265 spectrophotometer. The spectral range measured was 200–800 nm.

(13) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.

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(15) Ellis, J. W.; Kneser, H. O. *Z. Phys.* **1933**, *86*, 583.

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Irradiation of the sulfides (**4**–**6**) isolated in oxygen matrices at 13 K gave new species, adducts **7**, **8**, and **9**, respectively, with intense IR bands at 997, 997, and 1034 cm^{-1}, respectively (Figure 2–1a ~ 3a). Each product behaves as a single chemical entity (i.e., the IR bands appear and disappear simultaneously at the initial stage of irradiation). Subsequent annealing[19] (at temperatures up to 40 K) did not change the IR absorption.[20] These intense bands may result from the characteristic S–O stretching mode and are consistent with the calculated value (1019 cm^{-1})[21] for a persulfoxide.[3h] It is significant that these stretching frequencies are very close to the S–O frequency (ca. 1050 cm^{-1}) in normal sulfoxide compounds. Isotopic labeling experiments show that the IR bands for **7**–**9** shift by 19 cm^{-1} to lower wavenumber with $^{18}O_2$ (95% doubly labeled).[23] These shifts are similar to the 28 cm^{-1} decrease in stretching frequency observed in going from PhS(^{16}O)Me to PhS(^{18}O)Me.[24] The absence of a band at 700–900 cm^{-1} ion the IR spectra, which can be assigned to the S–O single bond stretching vibration,[26] may eliminate diradical **2** as a possible intermediate. We can conclude that these bands derive from the S–O stretching vibration in the persulfoxide **1**.

We also generated the sulfide–oxygen adducts in matrices with ^{16}O–^{18}O[27] to show which of the intermediates **1** and **3** participates in the oxidation.[28] Figure 2 shows the IR spectra in the region 1040–960 cm^{-1} from three experiments in which different isotopic mixtures of O_2 were used. In the ^{16}O–^{18}O adduct, S–O stretching vibration bands were split into two additional absorption bands.[29] Such splitting for the mixed isotope indicates that two oxygen atoms are not equivalent in the intermediate and therefore rules out the dioxathiirane structure **3** and sulfoxides. The IR results also rule out alternative intermediates, such as dimer structures (which may show more complicated isotopic shifts) and a sulfide cation radical–superoxide anion radical pair. We therefore conclude that the labile intermediate formed in sulfide photooxidation is a persulfoxide and that structure **1** best represents this molecule.[30]

Since diphenyl sulfide is known to be inert to oxidation by singlet oxygen,[2,3b] it is unlikely that these reactions involve it. A probable pathway to persulfoxide **1** is direct reaction from the excited donor–acceptor complex of the sulfide and oxygen, similar to the case of photooxidation of tetramethylethylene in a cryogenic oxygen matrix[16] and sulfides in solution.[7]

After this paper was submitted, Foote et al.[31] reported a theoretical study of products of reaction of singlet oxygen with H_2S and Me_2S. The infrared frequencies and intensities of a persulfoxide intermediate and the effect on the frequencies of substituting either one or both of the oxygens in a persulfoxide with ^{18}O were calculated. The calculated values agree with experimental data reported here.

Acknowledgment. We are indebted to Professor C. S. Foote for his valuable comments and discussion.

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(18) For IR measurement, sulfide and oxygen gas were deposited on a CsI plate at 13 K. IR absorption spectra were recorded on as Shimazu FT-IR 4000 spectrophotometer with 2 cm^{-1} resolution and 50 accumulations. The spectral range measured was 400–4000 cm.$^{-1}$ UV irradiation was carried out by means of a 500-W high pressure mercury lamp (USHIO). A water cell (20 cm) with quartz windows and a sharp-cut optical filter (Toshiba UV-D35 filter) were used at all times to remove the infrared radiation and to select exciting wavelengths (300–400 nm).

(19) Td, mp, and bp of oxygen are 26, 54, and 90 K, respectively: *Cryochemistry*; Moskovits, M., Ozin, G. A., Eds.; John Wiley & Sons: New York, 1976; p 24.

(20) At temperatures higher than 40 K, the intense bands at ca. 1000 cm^{-1} disappeared and the oxygen matrix became very cloudy. Product analysis at room temperature shows the formation of diphenyl and methyl phenyl sulfoxide by means of mass and nmr spectral analysis.

(21) The stretching vibrations of the S–O bond can be calculated simply by the following equation,[22] by using the values 1.538 Å[3h] for the S–O bond length in unsubstituted thiirane persulfoxide: $\nu = {}^1/_2\, \pi c(f/(M_s \cdot M_o/M_n + M_s))^{1/2}, f = 1.86 \times 10^5/(r - 0.88)^3$, where ν = the stretching frequency (cm^{-1}); c = the velocity of light (cm/s); f = the force constant of bond (dyn/cm); r = the bond length (Å); M_s and M_o = the mass of sulfur atom and oxygen atom, respectively (g).

(22) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128.

(23) $^{18}O_2$ labeled oxygen was obtained from Amersham International.

(24) ^{18}O Labeled methyl phenyl sulfoxide (^{18}O content 30 atom %) was prepared by a literature method.[25] The IR absorption bands at 1050 and 1022 cm^{-1} are assigned to the stretching vibrations due to S–^{16}O and S–^{18}O group, respectively.

(25) Hojo, M.; Masuda, R. *Tetrahedron Lett.* **1978**, 1121.

(26) Nakanishi, K. *IR Absorption Spectroscopy—Practical*; Nankodo: Tokyo, 1968.

(27) Scrambling to give a near-statistical mixture of $^{16}O_2$, ^{16}O–^{18}O, and $^{18}O_2$ was achieved by electrolysis of a 55:45 mixture of $H_2{}^{16}O$ and $H_2{}^{18}O$ (Amersham International).

(28) For a discussion of isotopic labeling experiments in the related structural problem of carbonyl oxide and dioxirane intermediate, see: (a) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213. Dunkin, I. R.; Shileds, C. J. *J. Chem. Soc., Chem. Commun.* **1986**, 154. (b) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517.

(29) It has been known that the isotope effect for an α substituent is generally small compared to the bond frequency: Halford, J. O. *J. Chem. Phys.* **1956**, *24*, 830.

(30) A proposed rearrangement of a persulfoxide intermediate **1** to a dioxathiirane intermediate[3g] **3** was not observed under the reaction condition.

(31) Jensen, F.; Foote, C. S., submitted for publication. We thank Prof. Foote for a prepublication copy of their manuscript.

Proton Transfer from Metal Hydrides to Metal Alkynyl Complexes. Remarkable Carbon Basicity of $(C_5H_5)(PMe_3)_2Ru—C{\equiv}C—CMe_3$

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The reactions of transition-metal hydrides with metal alkynyl compounds are virtually unexplored. The only previous systematic study is Lukehart's[1] synthesis of bridging vinylidene complexes from formal addition of a Pt–H bond across the carbon–carbon triple bond of several metal alkynyl compounds. Davison and Selegue[2] have shown that unsaturated carbon ligands bonded to late transition metals generally undergo β-attack by electrophiles and α-attack by nucleophiles. This suggested that metal vinylidene complexes might be formed by proton transfer from metal hydrides to metal alkynyl complexes. This communication reports the first kinetic and thermodynamic measurements on this type of reaction and provides evidence that certain ruthenium alkynyl complexes are remarkably strong carbon-centered bases.

The ruthenium methylvinylidene/metal anion complexes[3] (**1**$^+$) precipitate from solution as yellow powders when toluene solutions of $(C_5H_5)(PMe_3)_2Ru—C{\equiv}C—CH_3$[4] and $(C_5H_5)M(CO)_3H$ (M = Cr, Mo, W) are combined. Thermolysis of the PF_6^- salt of **1**$^+$ in acetonitrile at 95 °C results in release of the methylvinylidene ligand as propyne, with clean formation of the acetonitrile complex[3,5] $(C_5H_5)(PMe_3)_2Ru(CH_3CN)^+PF_6^-$ (**2**$^+$). In contrast, thermolysis of metal anion salts of **1**$^+$ produces cyclobutenylidene complex **3**$^+$ in addition to **2**$^+$. The formation of **3**$^+$ can be accounted for by partial deprotonation of **1**$^+$ by the metal anion base, thus regenerating the ruthenium alkynyl complex from which it was formed. The alkynyl complex and the methylvinylidene complex then combine to form **3**$^+$ (as the $(C_5H_5)M(CO)_3^-$ salt). Independent synthesis[3] and isolation (73% yield) of the intensely colored orange complex **3**$^+PF_6^-$ ($\epsilon = 1.9 \times 10^4$ M^{-1} cm^{-1} at λ_{max} = 428 nm) was accomplished by reaction of **1**$^+PF_6^-$ with

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(1) (a) Afzal, D.; Lukehart, C. M. *Organometallics* **1987**, *6*, 546–550. (b) Afzal, D.; Lenhert, P. G.; Lukehart, C. M. *J. Am Chem. Soc.* **1984**, *106*, 3050–3052.

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(3) Spectroscopic and analytical data are provided in the Supplementary Material.

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