the rate constants of Bell and Linschitz,[2] is 1.74 ± 0.20 under our conditions. The inclusion of reaction 9

$$\text{dye–H}\cdot + (C_6H_5)_2\dot{C}OH \longrightarrow \text{dye} + (C_6H_5)_2CHOH \quad (9)$$

would accommodate any quantum yield for dye loss which is less than half the quantum yield of ketyl radical formation. A mechanism similar in many respects that just given has been proposed by Van Beek, Heertjes, and Visscher[6] for the photoreduction of an azo dye in the presence of *dl*-mandelic acid and photoexcited sodium 9,10-anthraquinone-2-sulfonate.

Acknowledgment. The authors wish to thank Professor Henry Linschitz for his helpful discussions.

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Wendell F. Smith, Jr., Bryant W. Rossiter
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650
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t-Butylsulfenic Acid

Sir:

We wish to report the characterization of *t*-butylsulfenic acid (I) as produced by the thermolysis of *t*-butyl sulfoxide.[1] Although sulfenic acids have been postulated as intermediates in various reactions,[2] only four are known; all four are mono- or diacids of anthraquinone.[3]

The nmr[4] spectra of partially decomposed (80°) solutions of *t*-butyl sulfoxide in various solvents exhibit a *t*-butyl absorption in addition to those assigned to the starting material and the final product in the reaction, the thiolsulfinate (II). This absorption is assigned

$$(CH_3)_3\overset{\overset{O}{\uparrow}}{C}SC(CH_3)_3 \xrightarrow{80°} (CH_3)_3CSOH + (CH_3)_2C{=}CH_2$$
I

$$2(CH_3)_3CSOH \longrightarrow (CH_3)_3C\overset{\overset{O}{\uparrow}}{S}SC(CH_3)_3 + H_2O$$
II

to the previously[1] postulated sulfenic acid intermediate. Plots of concentration *vs.* time are typical of a reaction with two consecutive steps. The decomposition of the sulfoxide gives good first-order kinetics. The rate of decomposition decreases with increasing solvent polarity, which is consistent with a *cis*-elimination mechanism.[1,5]

The sulfenic acid was observable in all solvents used. In nonaromatic solvents, the *t*-butyl absorption occurred about 2 cps upfield from the sulfoxide absorption and 7–20 cps downfield when aromatic solvents were employed. The diamagnetic shift with aromatic solvents could be attributed to π complexation between the acid and the solvent, causing the *t*-butyl group to be deshielded. Attempts to date have failed in the location of the acid proton in the nmr spectra.

The stability of the acid in various solvents at room temperature decreases in the order polar > aromatic > nonpolar.[6] There is an order of magnitude difference between each of the groups. Indications are that the acid could not be isolated in pure form.

The infrared spectra of solutions of the sulfenic acid exhibit up to three regions of absorption (Table I). Absorptions A and B can be assigned to the O–H and S–H stretching modes of the two tautomers, Ia and Ib, repeatedly postulated for sulfenic acids, but never before demonstrated. Anthraquinone-1-sulfenic acid has

$$(CH_3)_3CSOH \rightleftharpoons (CH_3)_3\overset{\overset{O}{\uparrow}}{C}SH$$
Ia Ib

a sharp absorption at 3510 cm^{-1} in dilute $CHCl_3$ solution which shifts to a broad band at 3125 cm^{-1} in the solid state.[7] It does not exhibit an absorption in the 2600-cm^{-1} region, but neither does anthraquinone-1-thiol. Sulfinic acids show 2600-cm^{-1} absorptions, but there is still controversy over assignment of this to the $RS(O_2)H$ tautomer.[8] The sulfenic acid absorptions in region C are assigned to S–O stretch. *t*-Butyl thioperoxide exhibits bands at 845 and 780 cm^{-1}.

Table I. Infrared Absorptions of *t*-Butylsulfenic Acid[a]

Solvent	ν, cm⁻¹[b] A[c]	B	C
Benzene-d_6	3050[d]	2610	880
n-Heptane	3160	...	875,780
CCl_4	3175	...	880
Cyclooctatetraene	3175	2600	865
Dioxane	3270	...	775
DMSO	3350	...	765
Acetonitrile	3360	...	780

[a] 0.5 *M* solutions of *t*-butyl sulfoxide at 80° for 1 hr. [b] Obtained on a Perkin-Elmer 237 calibrated to polystyrene film. [c] All absorptions are broad and intense. [d] A/B = 6.

The increase in wavelength of the O–H band when going from polar to nonpolar solvents could indicate a change of hydrogen bonding with the solvent to dimer or polymeric structures.[9] However, a nonbonded absorption does not appear for the acid in *n*-heptane as the concentration of the acid is decreased. The low frequency in benzene-d_6 again suggests formation of a complex between the sulfenic acid and benzene.

t-Butylsulfenic acid was found to add readily to electrophilic olefins at room temperature. The adducts could be obtained uncontaminated with thiosulfinate by employing the olefin as solvent for the sulfoxide decomposition. With ethyl acrylate, an oil was obtained after 24 hr at 80°; infrared: ν 1093 cm^{-1} (S→O); ultraviolet: $\lambda_{max}^{heptane}$ 217 mμ (log ε 3.23) (S→O); nmr in benzene: τ 8.8 (singlet, nine protons), 8.75 (triplet, three protons, J = 7 cps), 7.0–7.5 (multiplet, four protons), 5.88 (quartet, two protons, J = 7 cps).

(1) T. Colclough and J. I. Cunneen, *Chem. Ind.* (London), 625 (1960).
(2) (a) N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, **39**, 276 (1946); (b) T. C. Bruice and A. B. Sayigh, *J. Am. Chem. Soc.*, **81**, 3416 (1959).
(3) (a) K. Fries, *Ber.*, **45**, 2965 (1912); (b) T. C. Bruice and P. T. Markiw, *J. Am. Chem. Soc.*, **79**, 3150 (1957); (c) W. Jenny, *Helv. Chim. Acta*, **41**, 317, 326 (1958).
(4) A Varian A-60 spectrometer was employed.
(5) C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960).
(6) The half-life of a 0.1 *M* solution of the acid in DMSO is on the order of 1 week.
(7) J. A. Barltrop and K. J. Morgan, *J. Chem. Soc.*, 4245 (1956).
(8) H. Bredereck, G. Brod, and G. Hoschele, *Ber.*, **88**, 438 (1955).
(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 6.

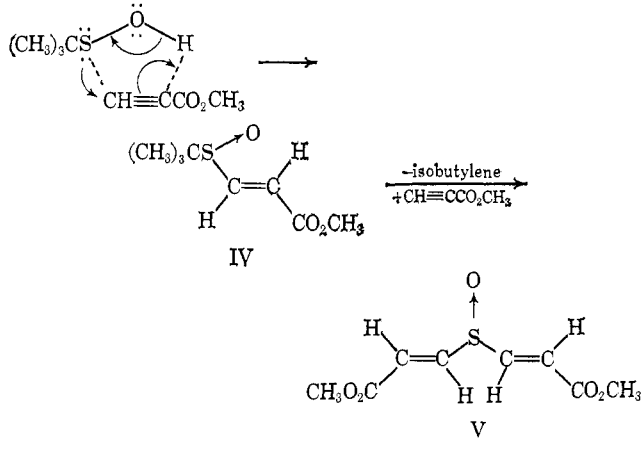
The adduct was identified as ethyl β-(2-methylpropyl-2-sulfinyl)propionate (III) and was identical with the material prepared by standard methods. The adduct

III

was stable to elimination of isobutylene, but the propionate group could be thermally exchanged with other olefins such as acrylonitrile, presumably through the sulfenic acid intermediate.

The sulfenic acid also adds to methyl propiolate to give the diadduct (V), β,β′-bis(*trans*-carbomethoxy)-divinyl sulfoxide, by a double elimination–addition reaction; mp 105–106° from ethanol. *Anal.* Calcd for $C_8H_{10}SO_5$: C, 44.04; H, 4.59; S, 14.67. Found:[10] C, 43.84; H. 4.43; S, 14.51. The infrared spectrum in KBr showed absorptions at 1092 (S→O) and 962 cm^{-1} (*trans*-disubstituted olefin). The nmr spectrum in C_6D_6 had peaks at τ 6.63 (singlet, six protons) and two AB doublets centered at τ 3.18 and 2.88 (four protons, J = 15 cps). The diadduct thus has both double bonds in the *trans* configuration. Studies with corresponding compounds possessing the *cis*/*cis* (J = 15 cps) and *cis*/*trans* (J_{cis} = 10 cps, J_{trans} = 15 cps) configurations showed they were stable toward rearrangement under the reaction conditions.

The stereochemistry of the adduct points to a *cis* addition of the sulfenic acid. The intermediate adduct,



IV

V

IV, can be observed in low concentration during the reaction. The stereoselectivity remains unchanged when polar solvents such as DMSO are employed; in no case was any *cis* product obtained.

The characterization of *t*-butylsulfenic acid by nmr and infrared spectral data and the demonstration of its presence by addition reactions with electrophilic olefins and acetylenes confirm the formation of this compound in the thermolysis of *t*-butyl sulfoxide. This is the first instance in which the existence of an aliphatic sulfenic acid has been demonstrated.

(10) Analysis by Galbraith Laboratories.
(11) National Science Foundation Cooperative Fellow, 1965–1967.

J. Reid Shelton, Kirk E. Davis[11]

Department of Chemistry, Case Institute of Technology
Cleveland, Ohio 44106

Received December 8, 1966

Chloroperoxidase. IV. Evidence for an Ionic Electrophilic Substitution Mechanism[1,2]

Sir:

Chloroperoxidase catalyzes the peroxidative formation of the carbon–halogen bond according to eq 1, where X^- represents an oxidizable halogen anion (chloride, bromide, or iodide) and HA represents an acceptor molecule with a replaceable proton.[3] We have directed our efforts toward resolving the question

$$H_2O_2 + X^- + HA \longrightarrow AX + OH^- + H_2O \qquad (1)$$

of whether this reaction proceeds *via* a free-radical or ionic substitution mechanism. Firstly, several lines of evidence indicate that an initial step in the halogenation reaction involves the oxidation of the halogen anion by hydrogen peroxide rather than the oxidation of the halogen acceptor. For example, it has been established that crystalline chloroperoxidase preparations catalyze the peroxidation of iodide[3d] to form elemental iodine. This reaction, in which the halogen anion serves both as donor and acceptor, clearly indicates that chloroperoxidase can catalyze the oxidation of the halogen anion. In contrast, there are numerous compounds which can serve as acceptors in reaction 1, *i.e.*, tyrosine and monochlorodimedone, but are nevertheless completely resistant to oxidation by chloroperoxidase and hydrogen peroxide.[3d] Collectively, these results provide strong evidence for the hypothesis that chloroperoxidase catalyzes the oxidation of the halogen anion to an activated state prior to the reaction with the acceptor molecule. Secondly, chloroperoxidase exhibits a broad specificity with respect to halogen acceptors. A wide diversity of compounds, ranging from β-keto acids,[3b] cyclic β-diketones,[3d] phenol and substituted phenols,[3d] related aromatic compounds,[4] sulfides, and compounds containing the thiouracil grouping,[2] all serve in an acceptor capacity in the chloroperoxidase reaction. It occurred to us that we could utilize this nonspecificity of chloroperoxidase with respect to halogen acceptor in designing an experiment which could aid in resolving the mechanism question. If enzyme specificity is eliminated from playing a determinant role in the reaction of the oxidized halogen (presumably enzyme-bound) donor with the acceptor molecule, the products of the enzyme reaction should be strictly comparable to chemical halogenation by a free-radical or an ionic electrophilic substitution mechanism. Formally, the chloroperoxidase-catalyzed oxidation of the halogen anion could involve a one-electron oxidation ($X^- \rightarrow X\cdot + e$) to form a halogen radical species, or an over-all two-electron oxidation to the halogenium ion ($X^- \rightarrow X^+ + 2e$). These two halogenating species have quite different properties and yield different products with aromatic substrates. Therefore, we have compared the enzymatic chlorination of anisole with the halogenation of anisole by using hypochlorous acid as a prototype for the ionic reaction and

(1) This work was supported by a grant from the National Science Foundation (GB-2786).
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(4) F. S. Brown and L. P. Hager, unpublished experiments.