Previous warnings concerning the explosive nature of difluoramine itself and of organic difluoramino derivatives should be heeded.

[12] This research was conducted under Army Ordnance Contract DA-01-021 ORD-5135.

[13] Address correspondence to the Department of Chemistry, University of Notre Dame, Notre Dame, Ind.

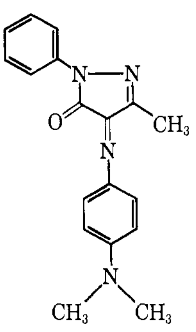
W. H. Graham,[12] J. P. Freeman[13]
Rohm and Haas Company, Redstone Research Laboratories
Huntsville, Alabama 35807

Received June 25, 1966

Photoreduction of a Pyrazolone Azomethine Dye by Benzophenone Ketyl Radicals. Dependence on Light Intensity

Sir:

We have been investigating the reaction in degassed benzene solution of benzophenone ketyl radicals with the pyrazolone azomethine dye I. We generate our ketyl radicals by reaction of photoexcited benzophenone with benzhydrol, a reaction (1) which has been investigated in other laboratories.[1-3] An obvious complication in such a system could be reaction 2, whereby



I

$$(C_6H_5)_2CO^* + (C_6H_5)_2CHOH \longrightarrow 2(C_6H_5)_2\dot{C}OH \tag{1}$$

$$(C_6H_5)_2CO^* + \text{dye} \longrightarrow (C_6H_5)_2CO + \text{dye}^* \tag{2}$$

energy is transferred from the benzophenone triplet ($(C_6H_5)_2CO^*$) to dye I. Assuming the latter reaction to be diffusion controlled and using the rate constants of Bell and Linschitz for reactions 1 and 3, we calculated

$$(C_6H_5)_2CO^* \longrightarrow (C_6H_5)_2CO \text{ (all deactivation steps)} \tag{3}$$

that no more than 4-5% of the benzophenone triplets should react by path 2 in a system in which $[(C_6H_5)_2CHOH] = 0.5\ M$ and $[\text{dye}] = 10^{-5}\ M$. These are the concentrations which we have used in most of our experiments. In all cases the benzophenone concentration was 0.02 *M*.

Irradiations were performed with a Hanovia utility ultraviolet quartz lamp No. 30600. This is a medium pressure, mercury arc lamp rated at 100 w. The 3660-A emission was isolated by passing the light through a $^1/_8$-in. thickness of plate glass and a Corning No. 7-37 filter. At a benzophenone concentration of 0.02 *M*, virtually all radiation at 3660 A is absorbed by the benzophenone. Samples were prepared by degassing 3-ml aliquots in 18 × 156 mm Pyrex glass culture tubes and sealing them. Actinometry was performed in identical tubes, but the degassing step was omitted. Potassium ferrioxalate actinometry[4] was used throughout.

The reaction of benzophenone ketyl radicals with dye I results in bleaching of the dye; the disappearance of dye is readily followed by spectrophotometry in the visible region. Approximately 85% of the dye loss results in the formation of a leuco dye which is quantitatively oxidized to starting dye upon admission of air to the tubes. In air-saturated benzene, the oxidation of the leuco dye follows first-order kinetics with $k = 1.3 \times 10^{-2}\ \text{sec}^{-1}$.

With regard to the reaction between benzophenone ketyl radicals and dye, the following facts are pertinent. (1) The rate of dye loss is precisely first order in light intensity over a 100-fold range (Table I). A log-log plot of the data in Table I gives a line with unit slope.

Table I. Rate of Dye Loss as a Function of Light Intensity

$10^8 \times$ rate, $M\ \text{sec}^{-1}$	$10^8 \times I$, einstein $\text{l.}^{-1}\ \text{sec}^{-1}$
0.419	0.542
4.23	5.28
40.2	52.0

The data fit the expression, rate = $0.78I$, or equivalently $\phi = 0.78$. Under our conditions, then, quenching of benzophenone triplets by benzophenone ketyl radicals does not occur.[5] (2) The reaction is zero order in dye. This was determined by a fivefold variation in dye concentration, the two rates being within 3% of each other. It was thought that an increase in dye concentration beyond $5 \times 10^{-5}\ M$ could lead to complications from the incursion of reaction 2.

These data may be accommodated by the following mechanism.

$$(C_6H_5)_2CO \xrightarrow{h\nu} (C_6H_5)_2CO^* \tag{4}$$

$$(C_6H_5)_2CO^* \longrightarrow (C_6H_5)_2CO \text{ (all deactivation steps)} \tag{3}$$

$$(C_6H_5)_2CO^* + (C_6H_5)_2CHOH \longrightarrow 2(C_6H_5)_2\dot{C}OH \tag{1}$$

$$(C_6H_5)_2\dot{C}OH + \text{dye} \longrightarrow (C_6H_5)_2CO + \text{dye-H}\cdot \tag{5}$$

$$\text{dye-H}\cdot + (C_6H_5)_2\dot{C}OH \longrightarrow (C_6H_5)_2CO + \text{dye-H}_2 \tag{6}$$

$$2\text{dye-H}\cdot \longrightarrow \text{dye} + \text{dye-H}_2 \tag{7}$$

Chain transfer of dye-H· with benzhydrol to yield leuco dye and a ketyl radical is precluded by the first-order dependence on light intensity (and/or the zero-order dependence on dye), as is also termination by combination of two ketyl radicals to yield benzpinacol. These steps predict half-order or mixed half- and first-order dependence on light intensity. The fact that the quantum yield for dye loss is <1 indicates that termination by reaction 8 to form a leuco dimer is unimportant. The proposed mechanism predicts a

$$2\text{dye-H}\cdot \longrightarrow (\text{dye-H})_2 \tag{8}$$

quantum yield of dye loss equal to half the quantum yield of ketyl radical formation. The latter, by using

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[1] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

[2] J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

[3] C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

[4] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956)

[5] N. C. Yang and S. Murov, *J. Am. Chem. Soc.*, **88**, 2852 (1966).

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

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

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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(6) H. C. A. Van Beek, P. M. Heertjes, and F. M. Visscher, *J. Soc. Dyers Colourists*, **81**, 400 (1965).

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

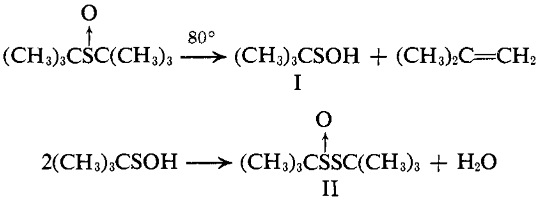
Received July 28, 1966

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 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]



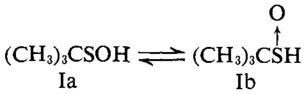
$$(CH_3)_3C\overset{\overset{O}{\uparrow}}{S}C(CH_3)_3 \xrightarrow{80^\circ} \underset{\text{I}}{(CH_3)_3CSOH} + (CH_3)_2C{=}CH_2$$

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

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 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}.



$$\underset{\text{Ia}}{(CH_3)_3CSOH} \rightleftharpoons \underset{\text{Ib}}{(CH_3)_3C\overset{\overset{O}{\uparrow}}{S}H}$$

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: $\lambda_{\max}^{\text{heptane}}$ 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).

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(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.