intermediates in the biological action of pyridoxal and some of the chemistry of the nicotinamide nucleotides.[6] Our postulated mechanism for its formation and hydrolysis requires initial addition of OH^- to I to form the pseudo-base V. This hemiacetal derivative can then undergo ring scission with elimination of pyridine to yield the isolated intermediate VI. Hydrolysis of this Schiff base takes place in the usual manner, but the enamine VII which is now generated (or the precursor carbinolamine) can cyclize to the pseudo-base VIII and then undergo dehydration to pyridine. In the total process, then, one pyridine ring is torn asunder and then later reconstituted in a surprisingly clean reaction.

Acknowledgment. This research was supported by a grant from the U. S. Public Health Service (GM 13980).

(6) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1966.

(7) Alfred P. Sloan Foundation Fellow, 1965–1967.

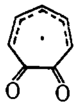
R. A. Olofson,[7] D. M. Zimmerman
Chemistry Department, The Pennsylvania State University
University Park, Pennsylvania 16802

Received July 5, 1967

α-Keto Radicals[1,2]

Sir:

The oxidation of phenols by ceric ion and the detection of the resulting phenoxy radicals in a flow system by esr spectroscopy have been described in the pioneering work of Stone and Waters.[3] We now describe the application of this technique to a variety of enols. Extension of the technique to stable enols, such as the tropolones or hydroxypyridines, is obvious. Thus, reaction of α-tropolone (0.01 *M* in water) with an equal volume of a 0.01 *M* solution of ceric sulfate in 1 *M* sulfuric acid yields radical **1**, a^H = 10.3, 7.1, 7.1, 2.5, and 2.5 gauss, detected ~0.1 sec after mixing.



1

About 3 l. of solution was required to record the spectrum.[4] Ketones that exist with an appreciable enol content, such as cyclohexane-1,3-dione or acetylacetone, are readily converted to a single radical ($RCO\dot{C}HCOR$). Substrates with a low enol content, such as 3-cyano-2-butanone or methyl acetoacetate, give negligible concentrations of radicals under the standard conditions. However, reaction of a solution of these ketones containing 0.1 *M* aqueous potassium hydroxide with the 1 *M* acidic solution of ceric ion yielded appreciable concentrations of the α-keto radicals (Figure 1). In a similar fashion 2-nitropropane in basic solution yields the 1-nitro-1-methylethyl radical upon acidification and oxidation by ceric ion.

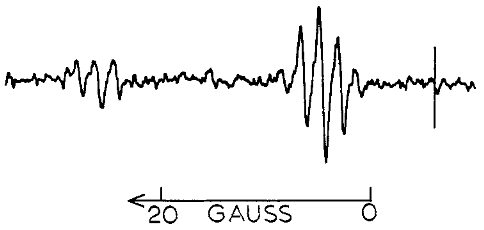
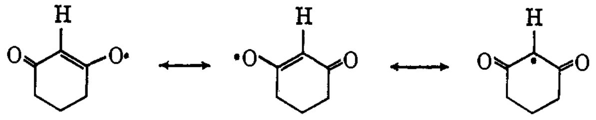


Figure 1. High field of the first-derivative esr spectrum of 1-methyl-2,5-cyclopentanedione radical prepared by reaction of 2-methyl-1,3-cyclopentanedione in basic solution with acidic ceric sulfate. Two of the four 1:4:6:4:1 multiplets are shown; $a_{CH_3}{}^{H}$ = 20.4, $a_{CH_2}{}^{H}$ = 1.72 gauss.

The formation of α-keto radicals by the reaction of ketones with hydrogen peroxide and titanous ion[5] suffers from adverse directive effects[6–8] and from the possibility of hydroxyl radical addition to the enol.

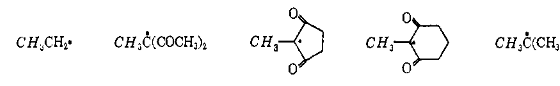
Functionally substituted alkyl radicals are of interest because of the question of spin delocalization.[9] We originally investigated the tropolone radical and β-diketone radicals because of the expectation of unusual stability due to resonance stabilization. However,



resonance stabilization of the type shown appears to be of little importance. Using a value of *Q* of 26 gauss[10] for the α-tropolone radical enables us to predict that more than 75% of the unpaired spin resides on the carbon atoms ((10.3 + 2(7.1) − 2(2.5))/26).[11] Similarly, in the series $CH_3\cdot$, $CH_3COCH_2\cdot$, $CH_3CO\dot{C}HCOCH_3$, the value of a^H decreases only slightly from 23 to 19.3 to 18.6 gauss. Fischer emphasizes that empirical spin densities in the system $(X)(Y)\dot{C}CH_3$ can be estimated by eq 1.[9,12,13] Again, the value of $a_{CH_3}{}^{H}$ decreases only

$$a_{CH_3}{}^{H} = 29.3\rho^{C} \qquad (1)$$

20% as the ethyl radical is substituted by two acetyl groups. This effect is comparable to methyl substitution.[12]



The data of Table I stress the relative unimportance of resonance interactions such as those shown in Scheme I.

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(1) Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. X.

(2) This work was supported by grants from the National Science Foundation (GP-6402X) and the National Institutes of Health (IGM-13000).

(3) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 213 (1964).

(4) Flow rates of ~2–3 ml/sec through Varian Associates cell V-4548.

(5) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

(6) W. T. Dixon, R. O. C. Norman, and A. L. Buley, *ibid.*, 3625 (1964).

(7) J. T. Pearson, P. Smith, and T. C. Smith, *Can. J. Chem.*, **42**, 2002 (1964).

(8) P. Smith, P. B. Wood, and T. C. Smith, *J. Chem. Phys.*, **43**, 1535 (1965).

(9) H. Fischer, *Z. Naturforsch.*, **19a**, 866 (1964); **20a**, 428 (1965).

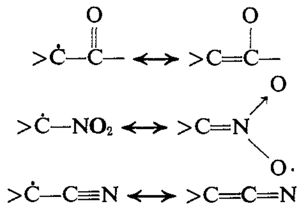
(10) A value of *Q* = 26.25 at 96° is measured for the tropenyl radical: G. Vincow, M. L. Morrell, W. V. Volland, H. J. Dauben, and F. R. Hunter, *J. Am. Chem. Soc.*, **87**, 3527 (1965).

(11) Similarly, T. J. Stone and E. A. Waters, *J. Chem. Soc.*, 4302 (1964), concluded that >82% of the spin of *m*-semiquinone radical anion resides on the carbon atoms.

(12) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(13) G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 744 (1964).

Scheme I



$$>\dot{C}-\overset{O}{\overset{\|}{C}}- \longleftrightarrow >C=\overset{O}{\overset{|}{C}}-$$

$$>\dot{C}-NO_2 \longleftrightarrow >C=N(\to O)(O\cdot)$$

$$>\dot{C}-C\equiv N \longleftrightarrow >C=C=N\cdot$$

Table I. Hyperfine Splitting Constants and Spin Densities for Alkyl Radicals in Water at 300°K

R	$a_{CH_3}^H$	a_{CH}^H	a^N	ρ^C
		A. $CH_3CO\dot{C}(CH_3)R$		
H[a,b]	22.6	18.5		0.77
NO_2	22.5		4.0	0.77
$COCH_3$	22.3, 0.5			0.76
CN	21.8		3.0	0.75
OH[c]	17			0.58
		B. $CH_3CO\dot{C}(H)R$		
H[a]	1.2	19.3 ($a_{CH_3}^H$)		~0.80[d]
CN		19.1	2.8	~0.79[d]
CO_2CH_3	1.1, 0.2	19.1		~0.79[d]
$COCH_3$	0.3	18.6		~0.77[d]
CH_3[a,b]	22.6	18.5		~0.77[d]
		C. $(CH_3)_2\dot{C}R$		
H[e]	24.7	21.1		0.84
CH_3[f]	22.7			0.78
CN[a,g]	21.5		3.6	0.74
CO_2H[a,h]	21.3			0.73
CO_2CH_3[a,h]	21.3			0.73
OH[a,i]	20.0			0.68
NO_2	19.8		3.9	0.68

[a] Prepared by the reaction of the substrate with hydrogen peroxide and titanous ion.[4] [b] For $CH_3CH_2CO\dot{C}HCH_3$.[9] The alternative structure $CH_3CH_2\dot{C}(OH)CH(OH)CH_3$ is excluded. [c] J. R. Steven and J. C. Ward, *J. Phys. Chem.*, **71**, 2367 (1967). [d] Calculated by the expression $a_{CH}^H = |24|\rho^C$. [e] At 188°K in liquid propane.[12] [f] At 128°K in liquid isobutane.[12] [g] Reference 7. [h] Reference 8. [i] Reference 6.

Resonance stabilization of free radicals is more important when the functional substituent is electron supplying, for example, alkoxy, thioalkyl, or amino.[6,14]

(14) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

(15) National Institutes of Health Postdoctoral Fellow, 1967.

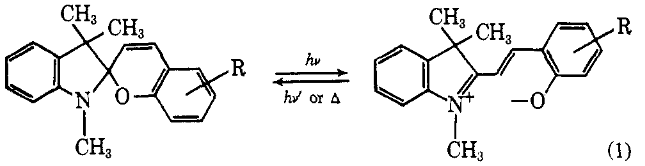
Glen A. Russell, Jerrold Lokensgard[15]
Department of Chemistry, Iowa State University
Ames, Iowa 50010

Received July 17, 1967

Medium Effects on Photochromism. Reversible Photobleaching of a Spiropyran on Silica Gel[1]

Sir:

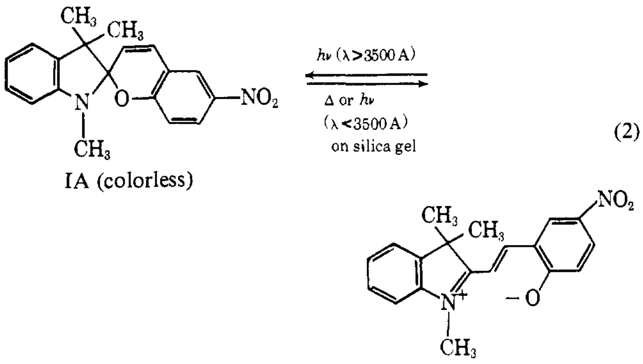
Photochromism in spiropyrans involving the reversible process A $\rightleftarrows$ B (eq 1) is adequately documented and has been treated in recent reviews.[2,3] The most exhaustive research in these compounds has been that of Hirshberg and Fischer[4] who have shown that the closed form A which is normally colorless undergoes photochemical ring opening to the open, colored modification B. B reverts thermally and photochemically to A, the rate of which is solvent dependent since the open, polar form B is relatively stabilized in polar solvents.[4,5]



A (colorless) B (colored) (1)

In general, most photochromic materials of various types behave in the above manner; *i.e.*, the colorless form is converted by ultraviolet irradiation to a metastable colored form. A well-known exception to this general behavior has been the system 15,16-dimethyldihydropyrene (colored) which may be transformed to the isomeric colorless metacyclophane by visible radiation, the latter isomer reverting in the dark to the more stable dihydropyrene.[6]

We should now like to report that this same "inverse photochromism" is observed in the spiropyran series when the medium is a cyclohexane–silica gel matrix; that is, in this matrix the open or colored tautomer of 1,3,3-trimethylindolino-6′-nitrobenzopyrylospiran (IB) is the stable form which, upon irradiating with wavelengths greater than 3500 A, is rapidly photobleached to the colorless tautomer IA (eq 2). The latter reverts in the dark to the intensely colored IB ($t_{1/2}$ = 41 min measured at either 373 or 525 mμ) and partially reverts to IB in a few seconds with 2537-A light (all irradiations with ultraviolet light lead to wavelength-dependent photostationary mixtures of IA and IB).



IA (colorless)

IB (colored)

Solutions 5 × 10^{-4} *M* in I in cyclohexane or methanol solvent are colorless in the dark but become intensely blue upon irradiation for 10 sec with light from an unfiltered 500-w PEK high-pressure mercury arc lamp. Upon standing in the dark the cyclohexane solution bleaches rapidly while the methanol solution bleaches much more slowly, as expected. The unimolecular rate constant for bleaching in ethanol[5] has been determined as 4.3 × 10^{-5} sec^{-1} at 6°, and our qualitative observations indicate that bleaching in nonpolar solvents is about 100 times faster.

Addition of silica gel[7] to a colorless 5 × 10^{-4} *M* solution of I in cyclohexane produces a bright red matrix

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(1) Electronic Spectra and Photochemistry of Adsorbed Organic Molecules. V. Part IV: P. A. Leermakers, H. T. Thomas, L. D. Weis, and F. C. James, *J. Am. Chem. Soc.*, **88**, 5075 (1966).

(2) R. Dessauer and J. P. Paris, *Advan. Photochem.*, **1**, 288 (1963).

(3) R. Exelby and R. Grinter, *Chem. Rev.*, **65**, 254 (1965).

(4) R. Heiligman-Rim, Y. Hirshberg, and E. Fischer, *J. Phys. Chem.*, **66**, 2465, 2470 (1962), and preceding papers in this series.

(5) E. Berman, R. E. Fox, and F. D. Thomson, *J. Am. Chem. Soc.*, **81**, 5605 (1959).

(6) V. Boekelheide *et al.*, *ibid.*, **89**, 1695, 1704, 1709 (1967), and references therein.

(7) The silica gel was Fisher 60–200 mesh, heated to 200° then partially hydrated by contact with the atmosphere for several hours. Rigorously dried silica gel was less effective in promoting IA → IB thermal conversion.