$$\left[\frac{-\mathrm{d}(\mathrm{NO_2}^-)}{\mathrm{d}t}\right]_t \Big/ \left[\frac{+\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t}\right]_t = a + b(\mathrm{NO_2}^-)_t/(\mathrm{H_2O_2}) \tag{A}$$

The values of a and b are summarized in Table I.

Table I. Summary of Values of Slopes and Intercepts from Plots of $[-\mathrm{d}(\mathrm{NO_2})/\mathrm{d}t]_t/[+\mathrm{d}(\mathrm{O_2})/\mathrm{d}t]_t$ *vs.* $(\mathrm{NO_2}^-)_t/(\mathrm{H_2O_2})$ and Values of k_5/k_6 and f Calculated from (B)[a]

$[\mathrm{H_2O_2}]$, M	Temp, °C	a	b	k_5/k_6	f
1.13	15.0	5.7 ± 0.4	910 ± 60	136 ± 9	0.30 ± 0.02
	25.0	4.9 ± 0.5	660 ± 70	112 ± 12	0.34 ± 0.03
	35.0	5.6 ± 0.5	510 ± 40	77 ± 6	0.30 ± 0.03
1.87	15.0	4.8 ± 0.4	920 ± 80	158 ± 13	0.34 ± 0.03
	25.0	5.2 ± 0.4	560 ± 40	90 ± 6	0.32 ± 0.03
	35.0	5.2 ± 0.4	340 ± 30	55 ± 5	0.32 ± 0.03

[a] Uncertainties calculated from standard errors of estimate from least-squares treatment of the data.

A reaction scheme consistent with this expression is the following

$$\mathrm{H^+ + NO_2^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HNO_2} \tag{1}$$

$$\mathrm{HNO_2 + H^+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{NO^+ + H_2O} \tag{2}$$

$$\mathrm{NO^+ + H_2O_2} \xrightarrow[k_3]{} \mathrm{HOONO + H^+} \quad \text{(slow)} \tag{3}$$

$$\mathrm{HOONO} \xrightarrow{fk_4} \mathrm{HO\cdot + NO_2} \tag{4}$$

$$\mathrm{HO\cdot + NO_2^-} \xrightarrow{k_5} \mathrm{HO^- + NO_2} \tag{5}$$

$$\mathrm{HO\cdot + H_2O_2} \xrightarrow{k_6} \mathrm{H_2O + HO_2\cdot} \tag{6}$$

$$\mathrm{2HO_2\cdot} \xrightarrow{k_7} \mathrm{H_2O_2 + O_2} \tag{7}$$

$$\mathrm{2NO_2 + H_2O} \xrightarrow{k_8} \mathrm{HNO_3 + HNO_2} \tag{8}$$

where f represents the fraction of pernitrous acid which yields hydroxyl radical and nitrogen dioxide. Utilizing a steady-state assumption for HO·, $\mathrm{HO_2}$·, HOONO,[10] and $\mathrm{NO_2}$[11]

$$\frac{-\mathrm{d}(\mathrm{NO_2}^-)}{\mathrm{d}t} = k_4(\mathrm{HOONO}) - {}^1\!/_2 fk_4(\mathrm{HOONO}) + {}^1\!/_2 k_5(\cdot\mathrm{OH})(\mathrm{NO_2}^-)$$

$$\frac{+\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t} = {}^1\!/_2 k_6(\cdot\mathrm{OH})(\mathrm{H_2O_2})$$

And since

$$(\cdot\mathrm{OH}) = \frac{fk_4(\mathrm{HOONO})}{k_5(\mathrm{NO_2}^-) + k_6(\mathrm{H_2O_2})}$$

we may write

$$\frac{-\mathrm{d}(\mathrm{NO_2}^-)}{\mathrm{d}t} \Big/ \frac{+\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t} = \left(\frac{2}{f} - 1\right) + \left(\frac{2}{f}\right)\frac{k_5}{k_6}\frac{(\mathrm{NO_2}^-)}{(\mathrm{H_2O_2})} \tag{B}$$

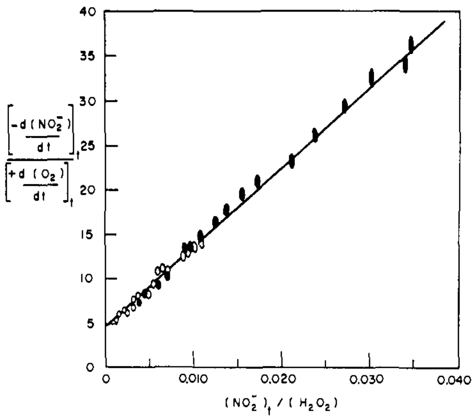

Figure 1. A plot of $[-\mathrm{d}(\mathrm{NO_2}^-)/\mathrm{d}t]_t/[+\mathrm{d}(\mathrm{O_2})/\mathrm{d}t]_t$ *vs.* $(\mathrm{NO_2}^-)_t/(\mathrm{H_2O_2})$ at 15° and pH 4.80 for solutions containing 1.87 M $\mathrm{H_2O_2}$, 2 × 10^{-5} M EDTA, and 0.5 M phosphate buffer, with initial concentrations of $\mathrm{NaNO_2}$ of (●) 0.72 and (○) 0.024 M.

The literature values obtained from pulse radiolysis experiments at or slightly above room temperature vary for k_5 from 2.5 × 10^9 to 3.5 × 10^9 M^{-1} sec^{-1} and for k_6 from 1.2 × 10^7 to 4.0 × 10^7 M^{-1} sec^{-1}.[12] The values of the ratio k_5/k_6 calculated from eq B and our experimental results (Table I) are therefore consistent with those calculated from the literature values. Moreover, the temperature coefficient for the experimental ratio varies in a manner which would be anticipated for a hydrogen atom transfer from a solvated O-H bond, reaction 6, compared to a diffusion-controlled electron transfer, reaction 5.

Further support for the homolytic decomposition of pernitrous acid is obtained from the following analysis. Consider the cycle

$$\begin{tikzcd}
\mathrm{HO{-}NO_2(aq)} \arrow[d, "\Delta H_1"] & \mathrm{HO\cdot(aq) + NO_2(aq)} \arrow[l, "\Delta H_4"'] \\
\mathrm{H^+(aq) + O^-{-}ONO(aq)} \arrow[r, "\Delta H_2"] & \mathrm{HOONO(aq)} \arrow[u, "\Delta H_3"']
\end{tikzcd}$$

On the assumption that ΔH_4 in aqueous solution is equal to the gas-phase value, −49.0 kcal/mol, and utilizing the reported value of ΔH_1, +38.8 ± 2.0 kcal/mol,[13] a value of $\Delta H_2 + \Delta H_3$ = 10.0 ± 2.0 kcal/mol is calculated. This value compares favorably with the value of 12.5 kcal/mol[14] reported for the activation energy for the isomerization of pernitrite anion to nitrate anion, which proceeds *via* pernitrous acid[6,7,14] and therefore corresponds to $\Delta H_2 + \Delta E_3^{\ddagger}$.

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[10] The half-life of pernitrous acid is extremely short[5-7] compared with the duration of the experiments.

[11] M. Grätzel, A. Henglein, J. Lelie, and G. Beck, *Ber. Bunsenges. Phys. Chem.*, **73**, 627 (1969). From the values reported in the work it is also possible to show that the rate of reaction 5 is at least 10^5 times greater than the secondary recombination reaction of hydroxyl radicals with nitrogen dioxide.

[12] *Cf.* J. K. Thomas, *Advan. Radiat. Chem.*, **1**, 138 (1969).

[13] J. D. Ray, *J. Inorg. Nucl. Chem.*, **24**, 1159 (1962).

[14] M. N. Hughes and H. G. Nicklin, *J. Chem. Soc. A*, 451 (1968). The authors mistakenly assumed that the -O-O bond energy of pernitrous acid should be equal to the value for a typical organic peroxide, *i.e.*, 30–40 kcal/mol. As a result they argued that the homolytic decomposition did not occur, owing to the low value they observed for the activation energy.

Lee R. Mahoney
Chemistry Department, Scientific Research Staff
Ford Motor Company, Dearborn, Michigan 48121

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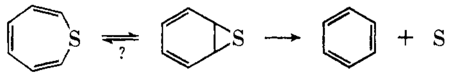
The Synthesis of a Stable 8-π-Electron Thiepin

Sir:

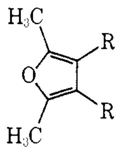
The electronic description of heterocyclic systems which do not satisfy the Hückel rule has long been a topical problem in organic chemistry. Although numerous studies have been reported for azepines and oxepins,[1] nothing is known about simple thiepins. Indeed, only recently have sophisticated calculations for thiepin become available.[2] These calculations predict the heterocycle to be antiaromatic and thus to be of considerable experimental interest.

In considering the synthesis of 8-π-electron thiepin systems, we took cognizance of the fact that a number of annulated thiepins are known to thermally undergo a facile sulfur extrusion reaction.[3] This transformation presumably occurs by valence isomerization of the thiepin ring into its corresponding benzene sulfide isomer followed by ready loss of sulfur from the latter.[4] Thus, unlike oxepin, an equilibrium between thiepin (**1**) and its valence isomer **2** did not seem likely, and it appeared necessary to prevent this type of valence isomerization if nonannulated thiepins were to be studied as other than transient species. In the latter regard, we wish to describe the synthesis of a sterically hindered and remarkably stable 8-π-electron thiepin.

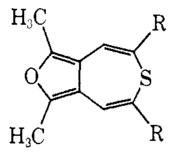


1 **2**

Oxidation of furan **3**[5] with manganese dioxide in benzene solution gave in 65% yield the furan dialdehyde **4**, mp 77–78°.[6] The dialdehyde was then condensed with the dimethyl ester of thiodiglycolic acid (sodium hydride in glyme) to give the furanothiepin diacid **5** which was converted without isolation into its dimethyl ester **6** (60% overall yield). Compound **6** (golden yellow needles, mp 188°, from methylene chloride) gives absorption maxima at $\lambda_{\max}^{\mathrm{CH_3OH}}$ 294 (ϵ 33,000) and 337 nm (4250) with tailing to 510 nm. In addition, **6** shows a parent peak at 294 in the mass spectrum, and exhibits singlet proton resonance at δ 2.21 (CH_3), 3.80 (OCH_3), and 7.31 (thiepin ring protons).

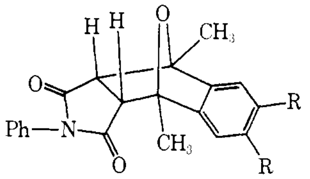


3, R = CH_2OH
4, R = CHO

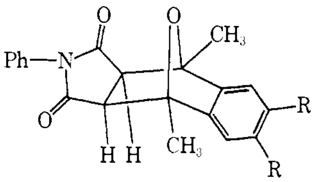


5, R = CO_2H
6, R = CO_2CH_3
9, R = $COH(CH_3)_2$

We have previously shown that annulated thiepins like **6** undergo the Diels–Alder reaction on the furan residue to ultimately give adducts which have lost sulfur.[7] Thiepin **6** is no exception, for when it was heated at 120° with *N*-phenylmaleimide there was formed a 7:3 mixture (95% yield) of the endo and exo adducts **7** and **8**, respectively. The structural assignments for **7** and **8** are based on their nmr spectra. Endo adducts like **7** show resonance for the protons α to the imide carbonyl groups at lower field values than their corresponding exo isomers.[8] Thus, **7** shows resonance for these protons at δ 3.62 while adduct **8** gives resonance for the same protons at δ 2.93. The endo adduct also exhibits singlet resonance at δ 2.07 (bridgehead methyl groups), 3.88 (OCH_3), and 7.54 (benzene ring protons). Complex multiplets were observed for the imide phenyl group of **7** at δ 6.38–6.50 (2 H, ortho protons) and 7.10–7.50 (3 H, meta and para protons).[9] Adduct **8** gives singlet resonance at δ 1.99 (bridgehead methyls), 3.92 (OCH_3), and 7.59 (benzene ring protons) as well as a single complex multiplet for the imide phenyl group at 7.10–7.50 (5 H).



7, R = CO_2CH_3



8, R = CO_2CH_3

These adduct-forming reactions have been shown to involve nonannulated thiepins as transient reaction intermediates.[10] Thus, by introducting bulky R groups on **6**, and then carrying out the Diels–Alder reaction, we felt it might be possible to prepare a stable 8-π-electron thiepin system. To this end, **6** was converted with methylmagnesium bromide into the highly reactive pale yellow furanothiepin diol **9**.[11] Diol **9** shows singlet proton resonance at δ 1.52 (isopropyl groups), 2.24 (furan ring methyl groups), and 6.80 (thiepin protons), along with broad singlet resonance at δ 3.00 (OH groups). When methylene chloride solutions of **9** were treated with *N*-phenylmaleimide at room temperature, a rapid reaction occurred followed by spontaneous crystallization of the bright yellow 8-π-electron thiepin **10** (65% overall yield from **6**).

Thiepin **10** is a highly crystalline compound which is thermally quite stable melting with decomposition at 180°. Interestingly, only the endo form of **10** arises from the Diels–Alder reaction. The structure of **10** follows from its nmr spectrum which shows singlet proton resonance at δ 1.40 and 1.50 (nonequivalent methyls of the isopropyl groups), 1.85 (bridgehead methyl groups), 3.50 (protons α to the imide carbonyl groups),[8] and 6.50 (thiepin protons). In addition, **10** shows broad singlet resonance at δ 2.50 (OH) along with complex multiplet resonance for the imide phenyl protons at 6.70–7.00 (2 H, ortho protons) and 7.15–7.40 (3 H, meta and para protons).[9] Thiepin **10** also gives the correct parent peak at *m/e* 467 in the mass spectrum

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(1) For an excellent review of azepines and oxepins, see E. Vogel and H. Gunther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967).

(2) M. J. S. Dewar and N. Trinajstic, *J. Amer. Chem. Soc.*, **92**, 1453 (1970).

(3) J. D. Loudon in "Organic Sulfur Compounds," Vol. 1, N. Kharasch Ed., Pergamon Press, Elmsford, N. Y., 1961, p 299.

(4) B. P. Stark and A. J. Duke, "Extrusion Reactions," Pergamon Press, Elmsford, N. Y., 1967, p 91.

(5) K. Y. Noritski, Y. K. Yurev, V. N. Zhingareau, and K. Gresl, *Zh. Obshch. Khim.*, **34**, 2568 (1964).

(6) Satisfactory spectral and analytical data were obtained on all new compounds.

(7) R. H. Schlessinger and G. S. Ponticello, *Tetrahedron Lett.*, 4361 (1969).

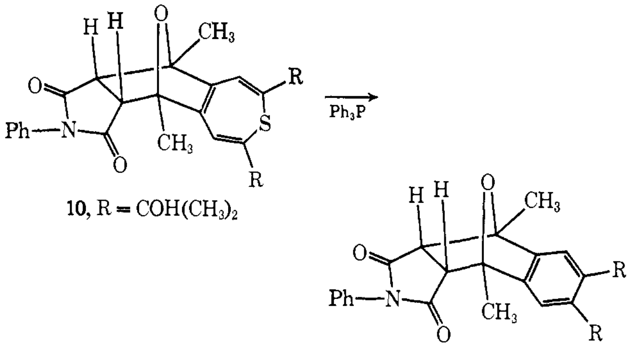
(8) For a leading reference, see M. P. Cava and N. M. Pollack, *J. Amer. Chem. Soc.*, **89**, 3639 (1967).

(9) Nmr spectra were recorded on a Jeolco Model C-60-HL. For a more complete discussion of the nmr spectra of similar adducts, see G. S. Ponticello, Ph.D. Thesis, The University of Rochester, Rochester, N. Y., 1969.

(10) R. H. Schlessinger and G. S. Ponticello, *Tetrahedron Lett.*, 3017 (1968), and references cited therein.

(11) Diol **9** was found to be extremely sensitive to handling. Thus, an accurate melting point and analysis for **9** could not be obtained. Nmr, mass spectral, and infrared data do confirm the structure of **9**, however.

and shows only a single absorption maximum at $\lambda_{\max}^{CH_3OH}$ 381 nm (ϵ 444) as well as strong end absorption and tailing to 500 nm in the visible.



10, R = COH(CH$_3$)$_2$

11, R = COH(CH$_3$)$_2$

Solutions of thiepin **10** in dimethylformamide or chloroform may be heated for prolonged periods without noticeable decomposition. When triphenylphosphine is added, however, rapid decolorization of these solutions occurs and the sulfur-free endo adduct **11**, mp 275°, is formed in 93% yield along with triphenylphosphine sulfide (87% yield). Adduct **11** exhibits singlet proton resonance at δ 1.60 and 1.70 (methyls of the isopropyl groups), 2.03 (bridgehead methyl groups), 3.56 (protons α to the imide carbonyl groups), and 7.10 (benzene ring protons). Broad singlet resonance for the hydroxyl group occurs at δ 5.52 and complex multiplets for the imide phenyl protons appear at 6.20–6.45 (2 H, ortho protons) and 7.20–7.55 (3 H, meta and para protons).

Paramagnetic ring current properties have been observed for annulated thiepins similar to **6** and **9**.[12] The thiepin ring protons of **10** occur at higher field values (δ 6.50) than the corresponding protons of the furanothiepin **9** (δ 6.80). In addition, the ortho protons of the imide phenyl group in heterocycle **10** occur at lower field values (δ 6.70–7.00) than the comparable protons of adduct **11** (δ 6.20–6.45). This behavior is consistent with the supposition that thiepin **10** might possess a paramagnetic ring current.[12]

Further work on heterocycle **10**, including an X-ray crystal-structure determination, is in progress.

Acknowledgment. We are grateful for support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation.

[12] For a more detailed discussion of this phenomenon, see ref 7 and 10.

[13] National Science Foundation Trainee Fellow, 1969–1970.

[14] Alfred P. Sloan Fellow; to whom correspondence should be addressed.

J. M. Hoffman, Jr.,[13] **R. H. Schlessinger**[14]
Department of Chemistry, University of Rochester
Rochester, New York 14627

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Electron Spin Resonance Identification of Oxygen Adducts of Cobalt(II) Complexes[1]

Sir:

Cobaltous complexes of simple amines such as triethylenetetramine bind molecular oxygen reversibly.

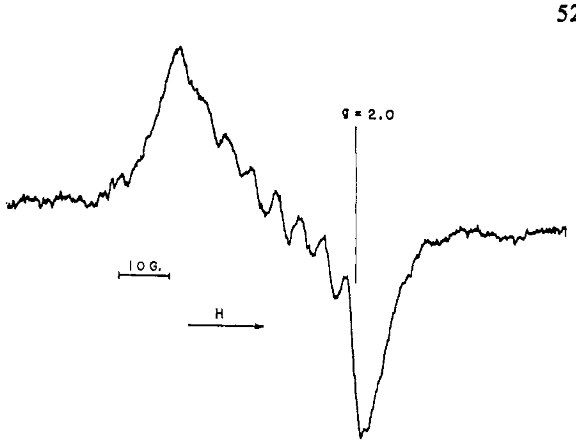

Figure 1. Esr spectrum of oxygenated aqueous solution (pH 5.6) of cobalt(II) and polyethylenimine (0.4%). The spectrum was taken 45 sec after oxygenation.

During the oxygenation process free radicals are produced, as indicated by the initiation of polymerization of vinyl monomers.[2] The initiating species was proposed to be a peroxy cobalt radical. Peroxy metal species appear to be the initial intermediates in metal-catalyzed autoxidation such as occurs in biochemical systems.[3,4]

In the present communication we wish to report the identification by electron spin resonance of the free radical species produced by the addition of molecular oxygen to a variety of cobalt–amine complexes. Esr spectra have been obtained previously for the cobalt compounds vitamin B$_{12r}$ and cobaloximes(II)[5] and for some specific cobalt Schiff bases[6] in organic solvents at low temperatures when oxygen is introduced. Our systems, on the other hand, involve aqueous solutions of simple amines at room temperature.

Aqueous solutions of diethylenetriamine, triethylenetetramine, tetraethylenepentamine, polypropylenimine, and polyethylenimine (number-average molecular weight, 40,000), each at a concentration of 0.4%, were adjusted to pH 5.6 and deoxygenated by purging with helium. The acidification was carried out with the noncomplexing perchloric acid. Cobaltous nitrate was then added to give a final concentration of 10^{-3} *M*. The solutions were subsequently oxygenated by bubbling oxygen through for 15 sec. Esr measurements were performed with a Varian E-3 spectrometer, using an aqueous cell, 45 sec after the oxygenation.

A typical esr spectrum is illustrated in Figure 1. It was found that the larger was the ligand in the homologous series the greater was the signal. All solutions exhibited at room temperature a characteristic spectrum consisting of a well-resolved eight-line hyperfine structure with an isotropic splitting constant of 13.1 G, which is very close to that found for the monomeric oxygen adducts of cobalt(II) Schiff bases.[6] This corresponds to the interaction of an unpaired electron with a single ^{59}Co nucleus of spin $^7/_2$ and demonstrates that the para-

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[1] Supported by the Ford Foundation on Grant No. 690-0106.

[2] N.-L. Yang and G. Oster, *J. Polym. Sci., Part B*, 7, 861 (1969).

[3] S. Fallab, *Angew. Chem.*, 79, 500 (1967).

[4] A. H. Mehler in "Oxygenases," O. Hayaishi, Ed., Academic Press, New York, N. Y., 1962, p 123.

[5] J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.*, 91, 2775 (1969); G. N. Schrauzer and L. P. Lee, *ibid.*, 92, 1551 (1970).

[6] B. M. Hoffman, D. L. Siemente, and F. Basolo, *ibid.*, 92, 61 (1970).