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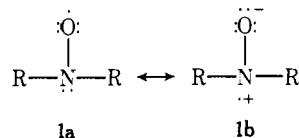
The Ease of Formation of Thionitroxide Radicals¹

Wayne C. Danen* and David D. Newkirk

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506. Received February 20, 1975

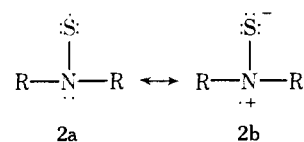
Abstract: The thermal decomposition of bis(pyrrolidyl-1) disulfide (**8**) was studied over the temperature range 45–68° by a radical scavenging technique utilizing Banfield's radical. The activation parameters obtained ($\Delta H^\ddagger = 30.8$ kcal/mol and $\Delta S^\ddagger = 6.5$ eu) indicated a relatively weak S–S bond in bis(dialkylamino) disulfides, $R_2NS-SNR_2$, and appreciable stability for thionitroxide radicals, $R_2NS\cdot$. The thermal and photolytic decompositions of several bis(dialkylamino) disulfides and bis(diphenylamino) disulfide were investigated by electron spin resonance spectroscopy and spectra of the corresponding thionitroxides observed. Phenyl radicals were found to react approximately twice as fast with bis(pyrrolidyl-1) disulfide as with cyclopentyl disulfide. The small difference in reactivity was interpreted in terms of a stepwise, addition-elimination displacement process with a rate-limiting formation of a metastable sulfur intermediate and little or no S–S bond homolysis in the transition state.

Most types of free radicals are transient species which are reactive with other compounds or are prone to self-reaction via dimerization or disproportionation. If, however, these self-reactions are prohibited by steric effects, or if the radical is stabilized by electronic effects, a free radical sufficiently stable to isolate and store may result. Several classes of such radicals are known,² with the nitroxides³, 1,



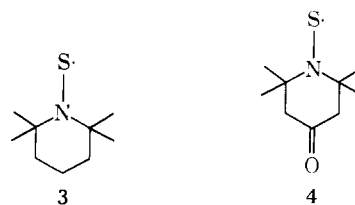
being one of the most common types of neutral radicals. Nitroxides have an inherently stable electronic arrangement about the oxygen and nitrogen atoms, and most organic nitroxides exhibit little tendency to dimerize at this center at room temperature.⁴

The remarkable stability of the nitroxide group has prompted us to investigate the sulfur analogue of these radicals, i.e., disubstituted aminothiyl radicals or thionitroxides, **2**. A priori, thionitroxides are expected to be less stable than the corresponding oxygen analogues because of the decreased importance of the charge-separated resonance **2b** relative to **1b** as a result of the lower electronegativity of



sulfur and the relatively long N–S bond. These expectations are borne out since, unlike nitroxides, thionitroxides exist as dimers at room temperature, as attested to by the fact that many bis(disubstituted amino) disulfides, R_2NSSNR_2 , have been synthesized and isolated.

The existence of the thionitroxides **3** and **4**, generated



from the corresponding disulfides by heating at 90–200°C, has been demonstrated by electron spin resonance (ESR) spectroscopy by Bennett, Sieper, and Tavs.⁸ Both **3** and **4** gave simple three-line ESR spectra: $a^N = 11.4$ G and 10.9 G; $g = 2.0173$ and 2.0171, respectively. These parameters

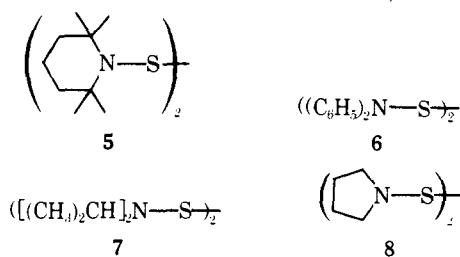
compare with $a^N = 15.6$ G and 14.5 G and $g = 2.0061$ for the corresponding nitroxides. The higher g factor for the thionitroxide radical is expected since the spin-orbit coupling constant for sulfur is larger than that of oxygen. The smaller nitrogen hyperfine splittings observed for the thionitroxides suggest that there is less unpaired spin density on nitrogen in these radicals as compared to the corresponding nitroxides.

Bis(dialkylamino) disulfides have been investigated as potential insecticides,⁹ fungicides,^{10,11} polymerization catalysts,¹² corrosion inhibitors in lubricating oils,¹¹ and as stabilizers for polyurethane fibers.¹³ In addition, much effort has gone into evaluating the usefulness of such disulfides for the vulcanization of rubber.¹⁴⁻¹⁷ There is a high probability that thionitroxide radicals mediate in many of these processes.

We have sought to further elucidate the thermal dissociation of this class of compounds. The rate of thermal dissociation of bis(pyrrolidyl-1) disulfide was measured by radical scavenging techniques at several temperatures allowing a value for the enthalpy and entropy of activation to be obtained. Electron spin resonance spectra of several thionitroxides produced by both thermal and photochemical dissociation of the corresponding disulfides were recorded, and the relative reactivities of a member of this class of compounds and two dialkyl disulfides toward homolytic substitution by phenyl radicals were determined.

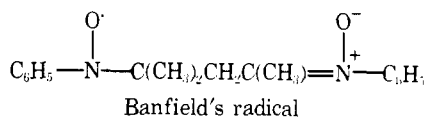
Results and Discussion

Preparation. The bis(disubstituted amino) disulfides **5-8**

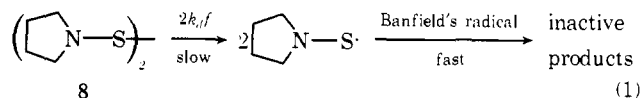


were prepared by reacting the appropriate amine with S_2Cl_2 as described in the Experimental Section.

Kinetics of Thermal Decomposition of 8. The rate of thermal decomposition of bis(pyrrolidyl-1) disulfide (**8**) was determined at several temperatures. The compound was allowed to decompose, and the radical fragments were scavenged by Banfield's radical,¹⁸ a stable, colored radical uti-



lized in studying the thermal decomposition of dimethyl tetrasulfide¹⁹ and other radical precursors.^{20,21} Equation 1 was used in analyzing the data.¹⁹ Equation 2 can be derived



$$(B)_t = (B)_0 - 2k_d f(Z)t \quad (2)$$

in which $(B)_t$ and $(B)_0$ are the Banfield radical concentrations at time t and 0, respectively, f is 1 - the fraction of cage return, k_d is the specific rate constant for decomposition of **8**, and Z is the concentration of this compound. The rate of disappearance of Banfield's radical was monitored by measuring the optical density at 473 nm. The observed rate constants are presented in Table I. These were derived from a least-squares analysis of the data and are the average of at least three runs at a given temperature. The rela-

Table I. Rate Constants and Activation Parameters for the Decomposition of **8** at Various Temperatures in Toluene

$2k_d f$ ($\times 10^6 \text{ sec}^{-1}$)	Temp, °C
0.122 ± 0.003	45.0
0.277 ± 0.066	50.0
1.08 ± 0.09	60.0
3.65 ± 0.02	68.0

$\Delta H^\ddagger = 30.8 \text{ kcal/mol}; \Delta S^\ddagger = 6.5 \text{ eu}$

Table II. S-S and O-O Bond Dissociation Energies of Selected Classes of Organic Compounds

Compound	$D(\text{S-S})$, kcal/mol	Compound	$D(\text{O-O})$, kcal/mol
RS-SR	60-70 ^a	RO-OR	36-37 ^d
RSS-SSR	36.6 ^b	ROO-OOR	~8-10 ^e
R ₂ NS-SNR ₂	30.8 ^c	R ₂ NO-ONR ₂	~0 ^f

^a S. Sunner, *Acta Chem. Scand.*, 9, 837 (1955); H. Makle, *Tetrahedron*, 19, 1159 (1963). ^b Reference 19. ^c This work. ^d J. A. Kerr, *Chem. Rev.*, 66, 465 (1966). ^e K. Adamic, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, 47, 3803 (1969); J. E. Bennett, D. M. Brown, and B. Mile, *Trans. Faraday Soc.*, 66, 397 (1970). ^f Although certain nitroxides have been shown to dimerize, all evidence suggests that the dimerization occurs via a four-center bond involving two N-O groups and not via O-O coupling.⁵⁻⁷

tively high concentration of Banfield's radical precluded any recombination process involving two thionitroxide radicals. By analogy, to work with dimethyl tetrasulfide¹⁹ and dimethyl trisulfide²⁰ as well as the fact that the decomposition was first order over a fourfold decrease of Banfield's radical in a given kinetic run, it was concluded that a second-order reaction between Banfield's radical and **8** was unimportant.

The rate of decomposition of **8** is given by

$$2k_d f = 4.825 \times 10^{14} \exp(-31500/RT) \quad (3)$$

Since most free radical recombination reactions occur with little or no activation energy, ΔH^\ddagger of the first step in eq 1 may be equated to the S-S bond dissociation energy of the central bond in **8**. We observe $\Delta H^\ddagger = 30.8$ kcal/mol. Since the carbon moiety in bis(dialkylamino) disulfides is not expected to influence significantly the strength of the central S-S bond, this value may be considered representative of the S-S bond formed by the dimerization of two nonsterically hindered dialkyl thionitroxide radicals.

On the basis of arguments similar to those advanced by Kende et al.,¹⁹ we are quite confident in assuming that the value of 30.8 kcal/mol indeed represents the energy for dissociation of the S-S bond in **8**. Homolysis of a S-N bond of a bis(dialkylamino) disulfide to produce $\text{R}_2\text{NSS}\cdot$ and $\text{R}_2\text{N}\cdot$ would appear prohibitively energy demanding on the basis of recently revised heats of formation of amino radicals.²²

It is interesting to compare this value with $D(\text{S-S})$ for other sulfur compounds. From the data in Table II, it is seen that the central S-S bond in **8** is 30-40 kcal/mol weaker than that observed for most dialkyl disulfides. This large difference is most logically attributed to the stabilization of thionitroxide radicals by the lone pair of electrons on the attached nitrogen atom, as represented by **2b**.

The $D(\text{S-S})$ for bis(dialkylamino) disulfides is also somewhat lower than $D(\text{S-S}) = 36.6$ kcal/mol for the central S-S bond of dialkyl tetrasulfides (Table II); this latter value is very similar to the S-S bond energy in the S_8 ring and polymeric sulfur system.¹⁹

Several interesting correlations between S-S and O-O bonds in analogous compounds may be noted from the data in Table II. The $D(\text{S-S})$ for tetrasulfides is 25-35 kcal/mol lower than $D(\text{S-S})$ for simple disulfides; a similar differ-

ence of ~ 27 – 29 kcal/mol exists between the $D(O-O)$ of peroxides and tetroxides. Likewise, the S-S bond in thionitroxide dimers is ~ 6 kcal/mol weaker than the central bond in tetrasulfides as compared to an 8–10-kcal/mol difference between the O-O bonds in the analogous oxygen compounds. It is apparent that for all three types of compounds listed in Table II the S-S bond is consistently stronger than the analogous O-O bond by ~ 30 kcal/mol. A nitrogen atom attached to the sulfur of a thiyl radical (i.e., a thionitroxide) obviously leads to considerable stabilization. Direct comparison with nitroxides is not possible, however, since $D(O-O) = 0$ for (nonexistent) nitroxide dimers is only an upper limit and does not reflect the true stability of nitroxides. The differences in ESR a^N values ($a^N \sim 11$ and 15 G for thionitroxides and nitroxides, respectively) would indicate a somewhat smaller interaction of the unpaired electron with nitrogen in thionitroxides, but it is difficult to relate a_N to the actual spin density on nitrogen because of electronic and configurational differences in these two types of radicals.

The entropy of activation of 6.5 eu observed for the thermal decomposition of **8** appears somewhat small for a reaction producing two product radicals. The ΔS^\ddagger values for dissociation of $CH_3S_4CH_3$, $ArSO_2-SO_2Ar$, $ArSO-SO_2Ar$, and $PhSO-SPh$ were 22.4,¹⁹ 16.6,²³ 11.2,²⁴ and 12.1 eu,²⁵ respectively. Benson²⁶ has noted an average $\Delta S^\ddagger \sim 11.5 \pm 5$ eu for the simple fission of various molecules into two radicals, although production of a conformationally dependent resonance stabilized radical such as benzyl occurs with a relatively low ΔS^\ddagger . It is plausible that several degrees of freedom are sacrificed by **8** in attaining the transition state in order to properly align the nitrogen lone pair with the developing sulfur p orbital possessing the unpaired electron.

Upon submission of our studies for publication we learned of a related study by Maillard and Ingold⁴² in which the equilibria between thionitroxide and dimer for **5** and **7** were measured by an ESR technique. The two studies appear to complement each other. They obtained "best" values of $\Delta H^\ddagger = 27 \pm 2$ kcal/mol and $\Delta S^\ddagger = 23 \pm 4$ eu for decomposition of **5** and **7**. The lower ΔH^\ddagger value suggests a slightly weaker S-S bond which might reflect steric encumbrances in these more bulky compounds. The large ΔS^\ddagger value likewise may indicate relief of restrictive crowding in **5** and **7**.

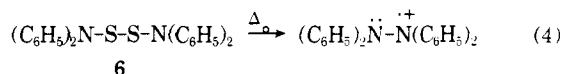
ESR Results. The low value of 30.8 kcal/mol observed for $D(S-S)$ in bis(dialkylamino) disulfides is attributed to the stabilization of the product thionitroxide radicals by the lone pair of electrons on the neighboring nitrogen atom. This stabilization of the thionitroxide might allow the concentration of such radicals to build up to a level detectable by ESR. To test for this, the bis(disubstituted amino) disulfides **5**–**8** were decomposed both thermally and photolytically in the cavity of an ESR spectrometer equipped with a variable-temperature controller.

When heated from 80 to 160°, a solution of **5** in diphenyl ether gave a spectrum consisting of three lines of equal intensity due to the interaction of the unpaired electron with a single nitrogen nucleus. The ESR parameters, $a^N = 11.6$ G and $g = 2.0171$, were identical with those reported by Bennett et al.⁸ and arise from homolytic cleavage of the S-S bond to produce the thionitroxide **3**. The signal increased in intensity upon heating over the temperature range noted and disappeared upon cooling to room temperature. The spectrum of a second radical was also observed: a single line, $g = 2.0072$. Although the paramagnetic species giving rise to this signal was not identified, the low g value would seem to rule out a sulfur centered radical such as $R_2N-S-S\cdot$ or $\cdot S-S_n-S\cdot$ with $n \geq 1$.²⁷

Photolysis of **6** in *tert*-butylbenzene yielded an ESR

spectrum of three rather broad lines, $a^N = 8.0 \pm 0.2$ G, $g = 2.017$, attributable to the diphenyl thionitroxide radical. Hyperfine interactions with the ring protons were not resolved. These parameters compare with $a^N = 9.66$ G, $g = 2.0055$ ⁴⁰ for diphenyl nitroxide, again illustrating somewhat more localization of the spin on sulfur in the thionitroxide than on oxygen in the corresponding nitroxide.

When solutions of **6** in *o*-dichlorobenzene were heated to 100°, an ESR spectrum arose which could be interpreted as arising from interaction of the unpaired electron with two nitrogen atoms ($a^N = 5.7$ G) and six hydrogens ($a^H = 0.9$ G). Such couplings and the low g value of 2.0028 were very similar to the parameters reported for the tetraphenylhydrazine radical cation (eq 4).²⁸ Indeed, heating a solution of



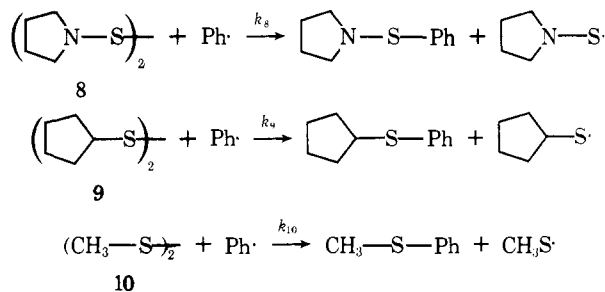
tetraphenylhydrazine to 100°C yielded a spectrum identical with that observed from **6**. This suggests that **6** can also decompose via N-S cleavage to produce diphenylamino radicals which dimerize to form tetraphenylhydrazine which may be oxidized to produce the highly delocalized radical cation. However, the ESR signal intensity for this radical varied inexplicably among experiments suggestive perhaps of a trace impurity or possible sample handling artifact.

Photolysis of **7** in toluene or *tert*-butylbenzene at -60 to -80° gave an ESR spectrum consisting of a triplet of triplets, $a^N = 10.9 \pm 0.1$, $a^H = 2.5 \pm 0.1$ G, $g = 2.015$. This compares with $a^N = 14.7$ G, $a^H = 4.5$ G, for diisopropyl nitroxide.⁴¹ The same radical could be also be observed in lower concentrations by heating a sample of **7** to 80°. Heating to 150° in *o*-dichlorobenzene produced an ESR spectrum of 13 observable lines split by ~ 2 G with $g = 2.0071$. No attempts were made to elucidate the radical species giving rise to the observed spectrum.

Solutions of **8** in decane, *o*-dichlorobenzene, or diphenyl ether yielded no detectable ESR signals when heated to 140 or 150°. The solutions darkened, however, indicating that reaction had taken place. Photolysis of solutions of **8** in toluene or *tert*-butylbenzene produced only very weak, uninterpretable spectra.

In summary, the ESR results indicate that detectable concentrations of both dialkyl and diaryl thionitroxides can usually be generated from the corresponding dimers. Photolysis at reduced temperatures generally produced higher concentrations of radicals than thermolysis. Bulky substituents such as in **5** and **7** also appeared effective in yielding more intense ESR signals. Finally, radicals other than thionitroxides were detected in several instances, but the identities of these species were not ascertained.

Homolytic Substitution on 8. To further probe the stability of thionitroxide radicals, homolytic substitution (SH2) reactions by the phenyl radical on **8**–**10** were investigated.



Pryor et al.²⁹ have studied the reactions of phenyl radicals with a variety of dialkyl disulfides and have shown that the bulk of the groups attached to sulfur plays a predominant role in the rate of the SH2 reaction. We have determined the relative reactivity of both **8** and **9** vs. **10** to phenyl radi-

cals generated from phenylazotriphenylmethane (PAT) at 60°. If a thionitroxide is stabilized significantly by the nitrogen atom as compared to a simple thiyl radical, and if significant S-S bond homolysis occurs in the transition state of these displacement reactions, the relative rate k_8/k_{10} should be larger than k_9/k_{10} . Cyclopentyl disulfide (**9**) was chosen to minimize steric differences with **8**. Values of $k_8/k_{10} = 0.23 \pm 0.04$ and $k_9/k_{10} = 0.11 \pm 0.01$ were obtained yielding $k_8/k_9 \sim 2.0$. The effect observed is obviously in the right direction, but the difference in reactivity between **8** and **9** is not pronounced and might not even reflect the stabilities of the radicals being formed. It may be noted that **10** is ca. nine times as reactive as **9** even though the thiyl radicals produced should exhibit similar stabilities. The difference in reactivity in this case must result from the different steric restraints imposed on the attacking phenyl radical. The smaller difference in reactivity between **8** and **9** could plausibly reflect subtle steric and/or electronic differences between these two compounds. However, as was shown above, the S-S bond dissociation energy of **8** is 30–40 kcal/mol less than that of **9**. The small ratio of k_8/k_9 indicates that there is little or no breaking of the S-S bond in the transition states of these SH₂ reactions. The low value may also be interpreted as further evidence for a stepwise, addition-elimination, displacement process in which the rate-determining step is attack of the phenyl radical on the disulfide bond with the formation of a metastable species having nine electrons around the sulfur atom.^{29c}

Experimental Section

General. All ESR spectra were obtained on a Varian Model 4502 X-band spectrometer equipped with a dual cavity and standard variable-temperature apparatus. Sample preparation, photolytic apparatus, and methods for the determination of hyperfine splitting constants and *g* values of the observed radicals have been previously described.³⁰

A Hewlett-Packard F&M Model 700 Chromatograph equipped with a flame ionization detector was used in gas-liquid chromatographic analysis.

Measurements of optical density were obtained from a Model 240 Gilford photospectrometer equipped with micro cells for the analysis of small volumes of solutions.

Analyses were performed by Chemalytics, Inc.

Compound Preparation. Bis(pyrrolidyl-1) Disulfide (8). The bis-(dialkylamino) disulfides were prepared from the corresponding dialkylamine and S₂Cl₂. To synthesize **8**, a solution of 0.84 mol of pyrrolidine dissolved in 400 ml of dry ether was cooled in an ice bath. To this solution was slowly added 0.20 mol of S₂Cl₂ dissolved in 90 ml of dry ether. After stirring for several hours, the hydrochloride salt of pyrrolidine was filtered off. The resulting solution was washed with water and then dried over Na₂SO₄.

After solvent removal, the solid was recrystallized from 30% methanol–70% ethyl ether to give *N,N'*-dithiobispyrrolidine in 25% yield, mp 50.3–51.3° (lit.¹⁰ 50.0–50.5°).

Anal. Calcd for C₈H₁₆N₂S₂: C, 47.02, H, 7.89; N, 13.71. Found: C, 47.31; H, 7.96; N, 13.45.

Bis(diisopropylamino) Disulfide (7). The same method was used for the preparation of **7**, except with pentane as solvent. Upon removal of the solvent, a light brownish yellow oil was obtained which could be recrystallized from pentane at reduced temperatures to yield white crystals which melted just below ambient. At room temperature **7** is a clear oil.

Anal. Calcd for C₁₂H₂₈N₂S₂: C, 54.49; H, 10.67; N, 10.59. Found: C, 54.48; H, 10.54; N, 10.60.

Bis(2,2,6,6-tetramethylpiperidyl-1) Disulfide (5). In a similar manner, **5** was prepared from 2,2,6,6-tetramethylpiperidine and S₂Cl₂ in ether. Recrystallization from methanol and diethyl ether gave an apparent mixture of the desired compound and *N,N'*-trithiobis(2,2,6,6-tetramethylpiperidine) melting at ~80°. These compounds could not be separated by recrystallization.⁸

Bis(diphenylamino) Disulfide (6). To a solution of 0.101 mol of diphenylamine in cyclohexane was slowly added 0.101 mol of butyllithium dissolved in cyclohexane. After the addition was com-

plete, the system was stirred 1 hr, and to this solution was slowly added a solution of 0.05 mol of S₂Cl₂ dissolved in dry ether. The solution was stirred for 30 min, was washed with water until neutral, and dried with MgSO₄. When the solvent was removed, a brownish yellow solid was obtained. Repeated recrystallization from a solution of methanol and diethyl ether gave 1.4 g, 7% yield, of light-yellow crystals, mp 96.8–98.3°.

Anal. Calcd for C₂₄H₂₀N₂S₂: C, 71.96; H, 5.03; N, 7.00. Found: C, 71.75; H, 5.32; N, 6.81.

Cyclopentanethiol. The general method of Urquhart, Gates, and Connor was followed.³¹ A mixture of 0.28 mol of cyclopentyl bromide and 0.28 mol of thiourea was added to 150 ml of water and refluxed 8½ hr. To this was added 0.5 mol of sodium hydroxide in 100 ml of water and a few milliliters of benzene to protect against oxidation. The solution was refluxed 3 hr and neutralized; the organic material was extracted with diethyl ether and dried with MgSO₄. Removal of solvent and distillation gave cyclopentanethiol in 13% yield, bp 129–131° (lit.³² 129.5–130.5°).

Dicyclopentyl Disulfide. Cyclopentanethiol (4 g) was dissolved in 100 ml of benzene, and a mixture of iodine crystals in 100 ml of water was added. The mixture was shaken until the iodine color disappeared. More iodine was added, and the process was repeated until the iodine color would no longer fade.³³ Distillation gave the pure product, bp 89–90° (0.40 mm) (lit.³⁴ 110.5° (2 mm)).

Cyclopentyl Phenyl Sulfide. Reaction of the sodium salt of thiophenol with cyclopentyl bromide gave cyclopentyl phenyl sulfide,³⁵ bp 77–79° (0.3 mm) (lit.³⁶ 139.5° (13 mm)).

Phenyl Pyrrolidyl Sulfide. An equimolar amount of chlorine gas dissolved in CCl₄ was slowly added with cooling to a CCl₄ solution of thiophenol. The solvent was removed, and the resulting red oil was dissolved in dry diethyl ether and added to a 4 molar excess of pyrrolidine dissolved in CCl₄.³⁷ Distillation gave phenyl pyrrolidyl sulfide; bp 82° (1.0 mm).

Methyl Phenyl Sulfide. Methyl iodide was allowed to react with the potassium salt of thiophenol to give methyl phenyl sulfide, bp 74° (10.5 mm) (lit.³⁸ 74.2° (12 mm)).

Banfield's Free Radical. This stable free radical was prepared by the method of Banfield¹⁸ and Tudos.³⁹ A concentrated acetone solution of phenylhydroxylamine was stirred 3 days. After this time crystals could be observed. The solution was cooled and filtered and the product isolated in 15% crude yield. A pentane solution of this condensation product was then oxidized with silver oxide. Recrystallization from pentane gave Banfield's radical, a red powder, in 10% yield, mp 86.5–88.3° (lit.¹⁸ 88–90°).

Kinetics. Reaction of 8 and 10 with Phenyl Radicals. The above two compounds plus 1',1',1'-triphenylbenzeneazomethane (PAT) were mixed in the molar ratios of 10:10:1 in a small glass tube. The resulting heterogeneous mixture was degassed by five freeze-pump-thaw cycles; the tube was sealed and placed in a constant-temperature bath at 60.0 ± 0.1° for 4 hr. At this temperature a homogeneous solution existed. At the end of the kinetic run, the reaction was quenched by immersion in a dry ice-acetone trap, the tube opened, a known quantity of dichlorobenzene added as an internal standard, and the resulting mixture dissolved in benzene.

The above solution was analyzed by GLC, and the amounts of methyl phenyl sulfide and phenyl pyrrolidyl sulfide were determined by comparison with known mixtures of these compounds. The amount of methyl phenyl sulfide relative to dichlorobenzene was determined with a 6 ft × ¼ in. 5% SE-30 column while the amount of phenyl pyrrolidyl sulfide relative to dichlorobenzene was determined with a 12 ft × ⅛ in. Carbowax-20M column attached to a 6 ft × ⅛ in. 10% SE-30 column.

Reaction of 9 and 10 with Phenyl Radicals. The two above compounds plus PAT were mixed in the molar ratio 10:10:1. The same procedures as outlined above were then followed. A 6 ft × ¼ in. 5% SE-30 column was used for GLC analysis.

Kinetics of Thermal Decomposition of 8. Method I. Bis(pyrrolidyl-1) disulfide and Banfield's radical, in the molar ratio of 100:1, were dissolved in 7 ml of reagent grade toluene and placed in eight constricted ampules. The ampules were degassed, sealed, wrapped in aluminum foil to protect from light, and placed in an oil bath with temperature control to ±0.04°. Ampules were removed at intervals with reaction being quenched by immersion into liquid nitrogen, warmed to room temperature, and opened; the optical density at 473 nm was immediately measured on a Gilford spectrophotometer.

Runs at 60.0° with no 8 showed that Banfield's radical was stable under the kinetic conditions.

Method II. Bis(pyrrolidyl-1) disulfide and Banfield's radical, in the molar ratio of 100:1, were dissolved in 7 ml of reagent grade toluene. This solution was placed in a container with a septum covering one opening and a stopcock closing a second opening. The solution was frozen and degassed as above by pulling a vacuum through the open stopcock. A positive nitrogen pressure was left in the system when the degassing was complete. The whole container was wrapped in aluminum foil and placed in an oil bath as above. Samples were removed with a syringe through the septum, frozen in liquid nitrogen, and analyzed as above.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XXII. Dialkylaminothiyl Radicals¹

B. Maillard² and K. U. Ingold*

Contribution from the Division of Chemistry,
National Research Council of Canada, Ottawa, Canada K1A 0R9.
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Abstract: The equilibria between 2,2,6,6-tetramethylpiperidyl-1-thiyl and diisopropylaminothiyl and the corresponding bis-(dialkylamino) disulfides have been examined by EPR spectroscopy: $R_2NSSNR_2 \rightleftharpoons 2R_2NS$ (k_1, k_{-1}). Within experimental error, the equilibrium constants are the same for both radicals ($\Delta S = 23 \pm 4$ gibbs/mol, $\Delta H = 27 \pm 2$ kcal/mol), as are the rate constants for disulfide decomposition and radical combination which can be represented, respectively, by $\log(k_1/\text{sec}^{-1}) = 16.8 - 31/\theta$ and $\log(k_{-1}/M^{-1}\text{sec}^{-1}) = 11.8 - 4.0/\theta$, where $\theta = 2.3RT$ kcal/mol. These radicals were generated in solution both thermally and photochemically, but photolysis in solid matrices at low temperatures gives some N-S bond scission. Dialkylaminothiyl radicals are unreactive toward a variety of molecular substrates. The first sulfur analogue of an iminoxy radical, diphenyliminothiyl, has been generated by photolysis of the corresponding disulfide. Its EPR parameters are $g = 2.0152$, $a^N = 18.16$ G.

Dialkylaminothiyl radicals, $R_2NS\cdot$, the sulfur analogues of the well-known dialkyl nitroxides, have received no attention since Bennett, Sieper, and Tavs reported on two of these radicals in 1967.³ These workers detected 2,2,6,6-tetramethylpiperidyl-1-thiyl (1) and 2,2,6,6-tetramethyl-4-oxopiperidyl-1-thiyl (2) radicals by EPR spectroscopy dur-

ing the thermolysis of the corresponding disulfides in iodobenzene at temperatures in the range 90 to 200°. The intensity of the EPR signals increased and decreased reversibly as the temperature was raised and lowered, which suggested that the radicals were formed reversibly. The possibility that the equilibrium was an artifact and that the radicals