reacted to give a white, amorphous precipitate of the nitronium salt.

$^{15}NO^+BF_4^-$. A similar procedure to that described for $^{15}NO_2{}^+BF_4$ was used by starting with $Na^{15}NO_2$ resulting in a clear solution of ^{15}N-enriched nitrosonium tetrafluoroborate.

Nuclear Magnetic Resonance Studies. **^{31}P NMR** studies were performed using a Varian XL-100 NMR spectrometer equipped with a heteronuclear decoupler, a variable-temperature probe, and a 620L computer with 32K memory capacity. The spectrometer was run in the Fourier transform pulse mode with proton decoupling. The total number of transients for suitable S/N for individual absorption varied from 200 to 500. The radio frequency was 39.80 MHz with the resonances referenced from external 85% phosphoric acid.

^{13}C NMR studies were performed using a Varian FT-80 NMR spectrometer equipped with a heteronuclear decoupler, variable-temperature probe, and 32K memory capacity computer. The spectrometer operated in the Fourier transform pulse mode with either proton decoupling or in the case of a proton-coupled experment with some nuclear Overhauser effect. The total number of transients for suitable S/N for individual absorption varied from 1000 to 3000. The radio frequency used was 20.00 MHz with the resonances referenced from external Me_4Si.

^{15}N NMR spectra were obtained using an FT-80 spectrometer operating at 8.059 MHz, using a broad-band variable-temperature probe. No heteronuclear decoupling was used during these experiments. Pyridine-^{15}N (150 mg) in 1 mL of methylene chloride contained in a 5-mm NMR tube served as external reference. The reference tube was centered in the 10-mm sample tube held by a Teflon plug. This reference resonance was found to be at $\delta^{15}N$ −65.2, i.e., 1.3 ppm downfield from that of an external solution of pyridine-^{15}N in methylene chloride, whose resonance was at $\delta^{15}N$ 63.9 (upfield from an external 2 M solution of $Na^{15}NO_3$ in H_2O). The reported chemical shifts are corrected with respect to the external 2 M $Na^{15}NO_3$ reference in H_2O (Table IV).

Acknowledgment. Support of our work by the U.S. Army Office of Research is gratefully acknowledged.

References and Notes

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(5) Probably this factor accounts for the low yields obtained in the case of dimethyl sulfide and dimethyl selenide. Also, we isolated small amounts of methanesulfonic acid during the oxidation of dimethyl sulfide, whose formation can be visualized through this mechanism.
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Structure and Stability of Radical Cations from Cyclic and Open-Chain Dithia Compounds in Aqueous Solutions

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Abstract: The formation of *intra-* and some *inter*molecular radical cation complexes has been observed during the oxidation of cyclic and open-chain organic dithia compounds (the two S atoms not adjacent) by hydroxyl radicals in aqueous solutions. These species are characterized by a new sulfur–sulfur bond established by interaction of the unpaired p electron from the oxidized sulfur atom with the free p-electron pair of a second sulfur atom. Two of these electrons form a σ bond while the third is promoted to an antibonding σ^* level. At low solute concentration (typically around 10^{-4} M) *intra*molecular complex formation predominates. The radical cation complexes show characteristic broad optical absorptions which are attributable to a $\sigma \rightarrow \sigma^*$ transition. The position of the absorption maximum (reflecting the σ/σ^* energy difference) and the extinction coefficients are related to the p-orbital overlap between the two interacting sulfur atoms. The extent of overlap depends on the internuclear distance, $r(S\therefore S)$, and particularly on the angular relationship between the interacting orbitals. Other structural parameters influencing λ_{max} are the flexibility of the species formed and possible interactions between the $\sigma(S,S)$ bond with $\sigma(C,C)$ bonds. λ_{max} is found to range from 400 to 650 nm, these particular values referring to the *intra*molecular radical cation complexes from 1,5-dithiacyclooctane and 1,4-dithiacyclohexane, respectively. ϵ values are found up to 7×10^3 M^{-1} cm^{-1}. The lifetimes of the radical cation complexes depend on the stability of the new sulfur–sulfur bond and may well extend into the millisecond range in aqueous solutions.

Introduction

The one-electron oxidation of organic sulfides formally leads to a molecular radical cation, $R_2S^+\cdot$, which shows a strong tendency to stabilize by coordination with a free electron pair from another sulfur atom[1-4] in an equilibrium (eq 1). Equilibrium constants of the order of 10^3–10^4 M^{-1} in favor of II for simple aliphatic thioethers indicate the relative stability of the complex radical cation.[4] Species II is characterized by a newly established sulfur–sulfur bond involving three electrons; two electrons form a σ bond and the third electron is located in an antibonding σ^* orbital.[2,3]

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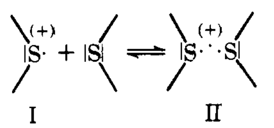


(1)

I II

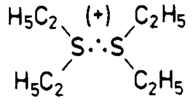
The two sulfur atoms in II are equivalent with respect to spin distribution and charge as can be deduced from ESR and optical measurements. The optical absorption spectrum of II, for example, typically reaches a maximum in the visible around 500 nm and is otherwise broad (half-width ≈ 1 eV) and structureless.[4]

Lifetimes of up to several milliseconds in aqueous solutions have been observed for II from simple aliphatic thioethers. In fact, the decay of II predominantly occurs through equilibration and decay of the molecular radical cation I, indicating the high degree of stabilization of the oxidized sulfur center in II.[4] Relative stabilization of I has been observed for a number of cases where the unpaired electron in $-\dot{\underline{S}}-^{+}$ was able to participate in a resonance structure as, for example, in the molecular radical cations from di-*tert*-butyl sulfide,[5] thioanisole,[6] thianthrene,[7] thiapolyenes,[8] etc.

A most interesting possibility besides *inter*molecular complexation (eq 1) is *intra*molecular coordination of the oxidized sulfur center with a second sulfur atom from the same molecule. Such *intra*molecular radical cation complexes have been observed from 1,4- and 1,3-dithiacyclohexane in aqueous solutions[9,10] and during conventional oxidation of some mesocyclic dithia compounds in acetonitrile and nitromethane solutions.[11,12] In the latter case the radical cation species were sufficiently stable to allow conventional ESR measurements.

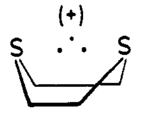
Stabilization of oxidized heteroatoms by a free electron pair from another heteroatom is not limited to sulfur. *Inter*molecular radical cation complexes similar to II have been observed for selenium[13] and phosphorus[14,15] compounds, and *intra*molecular complexing has been reported in the oxidation of nitrogen compounds[16,17] and has been suggested to take place in one particular case between two oxygen atoms.[18]

In the light of previous investigations of *inter*- and *intra*molecular radical cation complexes in aqueous[9,10] and hydrocarbon solutions[19] and by consideration of data published by Musker et al.[11,12] it becomes evident that the optical absorption spectra, and in particular the position of λ_{max}, provide information on the orbital overlap in the newly established sulfur-sulfur bond and the structure of the radical cation complex. For example, λ_{max} values of 480, 600, and 650 nm have been found for III, IV, and V, respectively, i.e., a red shift in the absorption seems to be associated with an increasing distance between the two interacting sulfur atoms.[4,9,10]



III

IV



V

The present investigation is mainly concerned with this particular aspect, i.e., the correlation of optical absorption data with the structure of *inter*- and, in particular, *intra*molecular radical cation complexes from cyclic and open-chain dithia compounds.

A suitable technique for the investigation of these generally transient radical cations is pulse radiolysis. It allows production of these species at concentrations up to 10^{-5} M within periods of much less than 1 µs and provides sensitive optical and conductometric detection techniques with time resolutions in the nanosecond range (optical <5 ns, conductometric 50–100 ns in aqueous solutions).

The present study has been carried out with aqueous solutions. In this solvent high yields of OH· radicals which readily oxidize organic sulfides[1,4] are formed during the radiolysis of H_2O. In addition, polar solvents are usually more convenient for the study of ionic species, produced by radiation chemical methods, since ions can much more readily escape the Coulombic field of their oppositely charged counterions (which are necessarily formed simultaneously during radiolysis) and diffuse homogeneously throughout the solution than in a less polar system. In principle, however, radical cations from organic sulfides are formed irrespective of the polarity of the solvent, as has been shown in studies with acetonitrile[11,12] and several hydrocarbon solutions.[19]

Experimental Section

The technique of pulse radiolysis and the interpretation and evaluation of optical and conductivity data obtained in pulse radiolysis experiments have already been described.[5,20,21] In this work short pulses of high-energy electrons of 5-ns and 1-µs duration (as a rule) from a 4- and 1.6-MeV v.d.Graaff accelerator, respectively, were applied to aqueous solutions of the organic thia compounds. Solutions were deoxygenated and saturated with N_2O. The latter converts hydrated electrons, produced in about equal yield to the OH· radicals in the radiolysis of H_2O, into hydroxyl radicals according to $N_2O + e^-_{aq} \rightarrow N_2 + OH^- + OH\cdot$. Irradiation of the aqueous solution thus yields around 5×10^{-6} to 10^{-5} M oxidizing OH· radicals which are homogeneously distributed in the solution within the duration of the electron pulse. The solute concentration was kept at least ten times higher than the OH· radical concentration (solubility permitting) to ensure as much scavenging of OH· as possible.

All data presented in this paper refer to room temperature.

Most of the sulfur compounds were obtained by synthesis except for 1,5-dithiacyclooctane, 1,4-dithiacycloheptane, and 1,6-dithiacyclodecane, which were kindly provided by W. K. Musker. Synthesis of the other compounds is described below.

The purity of the compounds was checked by NMR (Varian EM-390, 90 MHz, Me_4Si as internal standard), mass spectrometry (Varian MAT 44), and melting points (Mettler Fp 51); details are given below.

2-Methyl-1,3-dithiacyclopentane. A mixture of 5.1 mL of CH_3CHO and 15 mL of CH_2Cl_2 was added dropwise to a stirred solution of 6.6 mL of ethanedithiol and 16 mL of boron trifluoride etherate (45%) in 12 mL of CH_2Cl_2. After 30 min at room temperature the mixture was refluxed for 1 h and then poured over 20 g of ice. The organic layer was washed with dilute NaOH (twice) and H_2O (twice) and dried over $MgSO_4$. After removal of the solvent and distillation (twice) 3.55 g of the colorless compound was obtained, bp 76 °C (23 mm) (lit. bp 58 °C (12 mm)).[22]

NMR ($CDCl_3$): qu δ 4.65 (J = 6 Hz) (1 H), m 3.3 (4 H), d 1.6 (J = 6 Hz) (3 H). MS: *m/e* 120 (14%), 105 (20%), 92 (8%), 64 (33%), 61 (33%), 60 (59%), 59 (100%).

1,6-Dithiacyclododecane.[23] Two solutions of (a) 500 mL of C_2H_5OH, 0.92 g of Na, and 3 g of 1,6-hexanedithiol and (b) 2.54 g of 1,4-dichlorobutane and 500 mL of C_2H_5OH were added very slowly (over a period of 3.75 h) to 800 mL of refluxing C_2H_5OH under a stream of nitrogen. After another 1 h of refluxing and overnight settlement at room temperature the precipitate was filtered off. The solution was then concentrated down to 50 mL by evaporation of the solvent, 300 mL of H_2O was added, and the solution was warmed up for a short time. After filtration of the precipitate the filtrate was extracted with ether, dried over $MgSO_4$, and combined with the precipitate. Evaporation of the solvent and distillation yielded 0.16 g of the colorless 1,6-dithiacyclododecane, bp 120 °C (0.5 mm), mp 74 °C.

NMR ($CDCl_3$): t 2.6 (J = 7 Hz) and t 2.55 (J = 7 Hz) (8 H), m 1.8 (4 H), m 1.6 (8 H). MS: *m/e* 204 (36%), 120 (27%), 116 (43%), 115 (44%), 88 (46%), 87 (100%), 82 (48%), 67 (54%), 61 (52%), 55 (81%).

4-Methyl-3,5-dithiaheptane. This compound was prepared analogously to the 2-methyl-1,3-dithiacyclopentane using 2 equiv of ethyl mercaptan instead of 1 equiv of ethylenedithiol, bp 73–79 °C (19 mm) (lit. bp 73 °C (19 mm)).[22]

NMR ($CDCl_3$): qu 4 (J = 7 Hz) (1 H), m 2.7 (4 H), d 1.7 (J = 7 Hz) (3 H), t 1.3 (6 H).

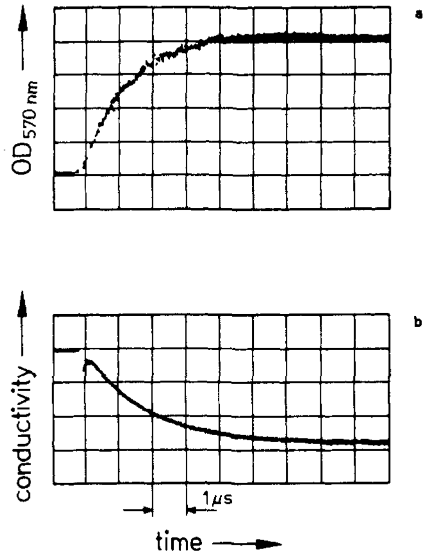


Figure 1. Traces of optical absorption at 570 nm (a) and conductivity (b) as function of time for pulse-irradiated, N_2O-saturated solutions of 5 × 10^{-5} M 4-methyl-3,5-dithiaheptane (pH 4.0); pulse length 5 ns; dose ca. 1 krad.

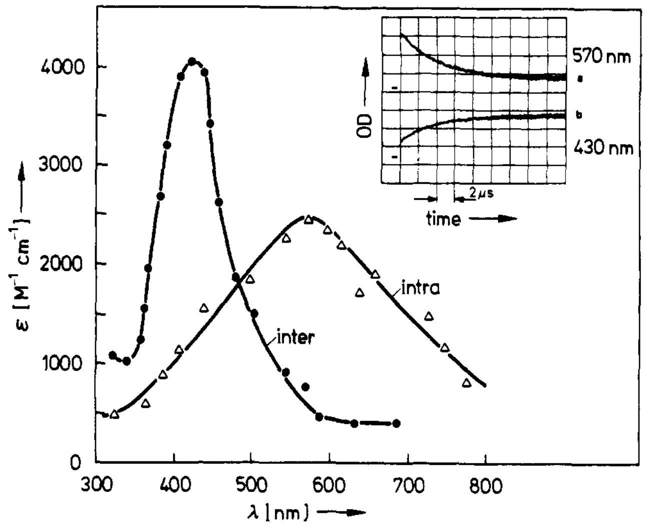


Figure 2. Optical absorption spectra of the *intra*- and *inter*molecular radical cation complexes from 4-methyl-3,5-dithiaheptane, and absorption–time curves at 570 (a) and 430 nm (b) for pulse-irradiated solutions of 10^{-3} M 4-methyl-3,5-dithiaheptane (N_2O saturated, pH 4); pulse width 5 ns; dose ca. 1 krad.

1,ω-Bismethylmercaptoalkanes. These compounds were obtained by methylation of the 1,ω-dimercaptoalkanes: 0.15 mol of dithiol was added to a solution of 0.35 g-atom of Na in 160 mL of C_2H_5OH under a stream of nitrogen, and 0.35 mol of CH_3I was added slowly to the stirred solution. The solvent was removed after 2 h of refluxing, 10% aqueous $Na_2S_2O_3$ solution was then added, and the solution was extracted with ether. The extracts were washed with H_2O and dried over $MgSO_4$. After evaporation of the solvent the residue was vacuum distilled.

2,5-Dithiahexane, bp 80 °C (21 mm) (lit. bp 80.1 °C (20.5 mm)).[22] NMR ($CDCl_3$): s 2.7 (4 H), s 2.15 (6 H). MS: *m/e* 122 (91%), 75 (46%), 61 (100%).

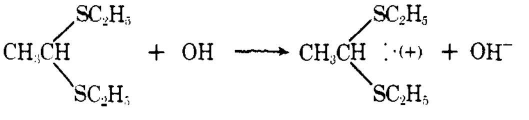
2,6-Dithiaheptane, bp 85 °C (12 mm) (lit. bp 92 °C (15 mm)).[22] NMR ($CDCl_3$): t 2.6 (J = 7 Hz) (4 H), s 2.1 (6 H), quintet (broad) 1.9 (J = 7 Hz) (4 H). MS: *m/e* 136 (81%), 121 (100%), 88 (17%), 73 (49%), 61 (31%), 58 (16%).

2,7-Dithiaoctane, bp 115 °C (22 mm) (lit. bp 121–123 °C (28 mm)).[22] NMR ($CDCl_3$): m 2.5 (4 H), s 2.1 (6 H), m 3.2 (4 H). MS: *m/e* 150 (52%), 135 (20%), 102 (12%), 87 (15%), 61 (100%).

2,9-Dithiadecane, bp 128–131 °C (12 mm) (lit. bp 142 °C (18 mm)).[22] NMR ($CDCl_3$): t 2.5 (J = 7 Hz) (4 H), s 2.1 (6 H), m 1.5 (8 H). MS: *m/e* 178 (11%), 131 (9%), 130 (8%), 115 (8%), 87 (11%), 83 (21%), 82 (42%), 67 (25%), 61 (100%).

Results

The formation of an *intra*molecular radical cation complex in the reaction of an organic dithia compound with hydroxyl radicals is typified in Figure 1 for 4-methyl-3,5-dithiaheptane (4-M-3,5-DTH). The optical absorption vs. time (traced at 570 nm) and conductivity vs. time curves which show identical kinetics reflect the formation of the radical cation formed in the reaction 2.



$$\mathrm{CH_3CH}\begin{matrix}\mathrm{SC_2H_5}\\ \mathrm{SC_2H_5}\end{matrix} + \mathrm{OH} \longrightarrow \mathrm{CH_3CH}\begin{matrix}\mathrm{SC_2H_5}\\ \mathrm{SC_2H_5}\end{matrix}\mathbin{:\!\cdot}(+) + \mathrm{OH^-} \qquad (2)$$

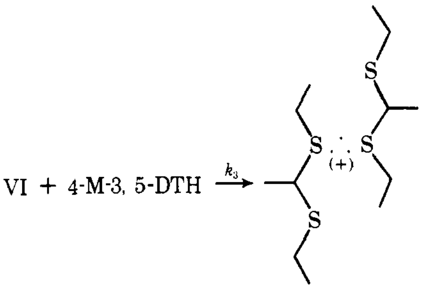
VI

The N_2O-saturated aqueous solution contained a low (5 × 10^{-5} M) concentration of the solute to avoid formation of *inter*molecular radical cations which occurs at higher solute concentration and which will be discussed in a later section of the present communication. Solutions were also acidified to pH 4 ($HClO_4$) to ensure immediate formation of the radical cation in reaction 2. Analogous to other sulfides and dithia compounds an OH· adduct may be formed as a short-lived precursor which is known, however, to undergo fast acid-catalyzed OH^- elimination.[4,10] Hence at low pH the rate-determining step for radical cation formation will be the initial reaction of OH· with the sulfur compound. This is further indicated by the fact that the change in optical absorption and conductivity as a function of time (Figures 1a,b) occurs exponentially with $t_{1/2}$ inversely proportional to the solute concentration ([OH·] ≪ [solute]). The bimolecular rate constant for reaction 2 derived from kinetic analysis of the curves in Figures 1a,b and analogous curves at other solute concentrations is determined as $(1.7 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1}, i.e., the reaction rate is practically diffusion controlled.

The observed decrease in conductivity in the irradiated solution (Figure 1b) reveals the formation of a positively charged species in reaction 2. In acid solution the OH^- ion formed in reaction 2 will of course immediately be neutralized by a proton, so that the net effect will be the replacement of a highly conducting H^+_{aq} (l = 315 Ω^{-1} cm^2) by a "normal" positive ion VI ($l = 40 \pm 20$ Ω^{-1} cm^2). The yield of positively charged species VI can be calculated from the maximum change in conductivity (signal voltage) after completion of reaction 2 which is proportional to the yield, $\Delta\Lambda = -l(H^+_{aq}) + l(VI)$. (Since l(VI) is small compared with $l(H^+_{aq})$ the uncertainty in the specific conductivity of the positive ion introduces only a relatively small overall uncertainty in ΔΛ and in the yield which is covered by the general error limit of ±10% for individual pulse radiolysis data.) The result shows that at this solute concentration 70% of the OH· radicals are scavenged and oxidize the sulfur compound via reaction 2.[24]

The optical absorption spectrum of the *intra*molecular radical cation VI has been determined from the maximum change in optical density after completion of reaction 2 at different wavelengths and is shown in Figure 2 (open triangles "*intra*"). It shows a maximum at 570 nm with an extinction coefficient calculated on the basis of the conductivity yields as ϵ_{570} 2500 ± 200 M^{-1} cm^{-1}. The spectrum is typically broad and structureless which has been found to be characteristic for complex three-electron radical cations from organic sulfides.[4,8,10,19]

The lifetime of the *intra*molecular radical cation VI is determined by its reaction with another solute molecule, and in this reaction VI is replaced by another absorbing radical cation. This is clear from Figures 2a,b, which show traces of the optical absorption at 570 and 430 nm, respectively, as a function of time (compressed time scale as compared with Figure 1) obtained from pulsed, N_2O-saturated solutions of 10^{-3} M 4-M-3,5-DTH. The fast rise in OD at both wavelengths owing to the formation of VI is followed by a decay and a secondary increase at 570 and 430 nm, respectively. The kinetics of the latter two processes are identical. Furthermore, the half-lives of the exponential changes in OD are inversely proportional to the solute concentration. By analogy with similar findings for radical cations derived from 1,4-dithiacyclohexane in aqueous[10] and 1,4- and 1,3-dithiacyclohexane in hydrocarbon[19] solutions these observations are attributed to the conversion of the *intra*molecular VI to the *inter*molecular radical cation VII (eq 3).



VII

(3)

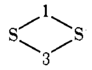
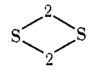
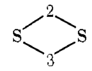
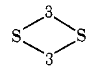
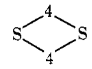
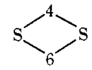
With $t_{1/2}$ values of 3.3 μs at 10^{-3} M and 30 μs at 10^{-4} M solute concentration, for example, the bimolecular rate constant k_3 can be derived as $(2.2 \pm 0.2) \times 10^8$ M^{-1} s^{-1}.

In VII the oxidized sulfur atom coordinates with a free electron pair from a sulfur atom of a second solute molecule. This configuration allows a much closer approach of the two interacting sulfur atoms and a more favorable orbital orientation, and thus the establishment of a much stronger bond. The optical absorption spectrum of VII (Figure 2, "*inter*") is of notably shorter wavelength (λ_{max} 430 nm) and much narrower (half-width ≈ 0.8 eV) as compared to the *intra*molecular radical cation VI. The extinction coefficient ϵ_{430} 4050 ± 500 M^{-1} cm^{-1} is about twice that of VI at 570 nm. The lifetime of VII is quite significant; it decays by mixed-order kinetics with a first half-life >4 ms. Conductivity experiments indicate that protons are eventually liberated during the decay of VII. The conversion of VI into VII is, however, not quantitative. Conductivity measurements extended into the submicrosecond time range show a considerably smaller yield (ca. 60%) of positively charged species at times when the absorption of VII is fully developed compared with the value immediately after the pulse when only VI is present. Partial decay of VI into nonionic species (accompanied by proton elimination) is therefore implied as a competitive route. The formation of a neutral species on decay of VI is further indicated by an optical absorption below 280 nm which, however, is too unspecific to allow definite conclusions.

The formation of *intra*molecular radical cation complexes could be followed for a large number of cyclic and open-chain dithia compounds. The pulse irradiated solutions were generally N_2O saturated, at pH 3-4, and contained 10^{-4} M or less (for compounds of lower solubility) of the solute. Under these conditions the formation of these species was usually complete within less than 1 μs, since the rate constants for the reaction of OH· radicals with the solute molecules were of the order of 10^{10} M^{-1} s^{-1} as found for reaction 2. On the other hand, a fast conversion of the *intra*- to an *inter*molecular complex was not found to take place, when this reaction occurred at all. The experimental results for the optical and conductivity experiments were similar to those shown in Figure 1 and described above for 4-M-3,5-DTH. The optical absorption spectra also had the same shape as shown in Figure 2, with the position of the absorption maximum varying markedly between 400 and 650 nm for the different compounds. The respective λ_{max} values are listed in Table I. The lowest λ_{max} values are observed for cyclic and for open-chain compounds with three methylene groups between the two sulfur atoms. Extinction coefficients listed in Table I were calculated as before on the basis of the conductivity results. They also vary with the nature of the compound and decrease with increasing λ_{max}. The maximum values of ϵ at $(5\text{-}7) \times 10^3$ M^{-1} cm^{-1}, found for radical cations with λ_{max} in the 400-500-nm range, are of the same magnitude as those determined for *inter*molecular radical cation complexes derived from simple aliphatic thioethers, $(R_2S)_2^{+\cdot}$.[4] Finally the width of the optical absorption spectra parallels the trends in λ_{max} and ϵ, with the bands narrowing with decreasing λ_{max}. For example, the half-widths are 0.73 and 1.15 eV for the radical cations from 1,5-dithiacyclooctane (λ_{max} 400 nm) and 1,4-dithiacyclohexane (λ_{max} 650 nm), respectively.

The first half-lives of the *intra*molecular radical cations are also listed in Table I. Not all of them are directly comparable since the decay kinetics are quite different for the various compounds. For example, the radical cation V from 1,4-dithiacyclohexane decays by a pure first-order proton elimination process,[9,10] while that from 1,5-dithiacyclooctane decays by an almost pure second-order process (disproportionation). Conversion of the *intra*- to the *inter*molecular radical cation as for 4-M-3,5-DTH leads to pseudo-first-order kinetics, and for most of the radical cations the decay kinetics are of mixed order (probably proton elimination and disproportionation). The values given in Table I refer, however, to conditions where the radical cation concentrations were roughly the same and thus some general conclusions may be drawn as to the stability of the radical cations. Generally, long lifetimes with respect to proton elimination appear to be associated with those

Table I[a]

compd	structure	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	$t_{1/2}$, μs
1,3-dithiacyclohexane		600	1650	300
1,4-dithiacyclohexane		650	1070	25
1,4-dithiacycloheptane		460	3500	650
1,5-dithiacyclooctane		400	5800	500
1,6-dithiacyclodecane		425	4900	500
1,6-dithiacyclododecane		440	4500	560
2,5-dithiahexane	1-S-2-S-1	525	3400	25
4-methyl-3,5-dithiaheptane	2-S-1-S-2	570	2500	30[b]
2,6-dithiaheptane	1-S-3-S-1	440	5800	750
2,7-dithiaoctane	1-S-4-S-1	450	5300	800
2,9-dithiadecane	1-S-6-S-1	485	6500	525

[a] Maxima of optical absorptions, extinction coefficients, and first half-lives of *intra*molecular radical cation complexes from cyclic and open-chain dithia compounds. Accuracy: λ_{max}, ±5 nm; ϵ and $t_{1/2}$, ±10%. The numbers in the "structure" column refer to the number of carbon atoms between the two sulfur atoms. [b] At 10^{-4} M solute concentration.

*intra*molecular radical cations which absorb at the shorter wavelengths.

An interesting result was obtained for the oxidation of 2-methyl-1,3-dithiacyclopentane, i.e., a compound in which the two sulfur atoms are at about the same distance as those in 1,3-dithiacyclohexane or 4-methyl-3,5-dithiaheptane (see above). The reaction of this compound with OH· radicals is also diffusion controlled with $k \approx 3 \times 10^{10}$ M^{-1} s^{-1}. However, no stabilized *intra*molecular radical cation complex could be detected. The only ionic species observable at a time where usually the full yield of *intra*molecular radical cations has been developed seems to be a very short lived ($t_{1/2} \approx 1$ μs) *inter*molecular complex, i.e., a radical cation involving two solute molecules. The yield of the latter is, moreover, very small at 10^{-4} M (accounting for only less than 20% of the OH· radicals) and increases then with increasing solute concentration similar to the yield-concentration dependence generally observed for the formation of *inter*molecular radical cation complexes.[4] After decay of this species a number of secondary reactions involving neutral species occur before another positively charged species is eventually formed at times >100 μs. This species does not show any characteristics of an *intra*molecular radical cation complex (only a narrow absorption band with λ_{max} 330 nm is observable). A more detailed study on the complex mechanism and the *inter*molecular radical cation complex formed during the early stages is currently underway.

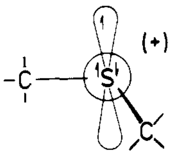
For most of the compounds investigated *inter*molecular radical cation complexes could not be observed. Exceptions are 1,4-dithiacyclohexane (λ_{max} 500 nm),[9] 2,9-dithiadecane, where the formation of an *inter*molecular complex with λ_{max} 450 nm is indicated in saturated solutions after ca. 1 ms, and the above-mentioned examples. Low solubility or slow rates for the reaction

$$\text{"}intra\text{"} + \text{solute} \rightarrow \text{"}inter\text{"} \qquad (4)$$

do not permit successful competition with other reactions which determine the natural lifetime of the *intra*molecular complexes.

Discussion

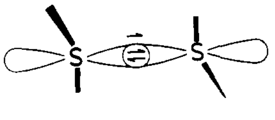
The one-electron oxidation of a sulfur center in an organic compound is expected to yield a π-type radical VIII with the



VIII

unpaired electron in the p orbital more or less perpendicular to the carbon-sulfur-carbon plane. This configuration affords a plausible explanation for resonance stabilization of the molecular radical cation by, e.g., a *tert*-butyl group or aromatic π systems.

Stabilization of the oxidized sulfur atom by coordination with another sulfur atom, on the other hand, most probably occurs through interaction of the unbound p-electron pair of the latter with the unpaired electron of the former (IX).



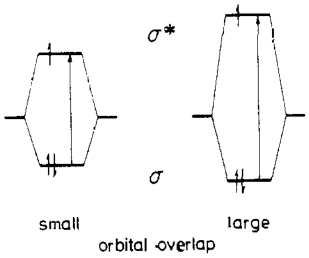
IX

This ensures sufficient orbital overlap to establish a new σ(p,p) sulfur-sulfur bond which is, however, weakened by the σ^* antibonded third electron. The participation of directed p orbitals rather than undirected s orbitals is further substantiated by ESR work[2,3] on some thioether radical cation complexes which indicates that the unpaired spin on the sulfur atoms is in an orbital perpendicular to the planes containing α-carbon and sulfur atoms.[2]

The same electronic configuration is also assumed for the radical cations presented here, although this is at variance with Musker et al.'s[11] interpretation of an ESR spectrum of the 1,5-dithiacyclooctane radical cation in terms of two nonequivalent sulfur atoms. The latter interpretation does not, however, appear completely unambiguous, since the probable structure of this cation (see XIII) is unlikely to give rise to only one set of equivalent protons at the carbon atoms adjacent to the sulfur atoms. In addition, some recent MNDO/2 calculations on our radical cations by Clark[33] clearly support the structure with a newly established σ(S,S) bond and an antibonding σ^* electron contributed to equally by both sulfur atoms.

In terms of this model the optical absorptions of the *intra*- and *inter*molecular radical cation complexes presented above are assigned to a $\sigma \rightarrow \sigma^*$ transition, and in the following the optical parameters (λ_{max}, ϵ, bandwidth) are discussed on this basis.

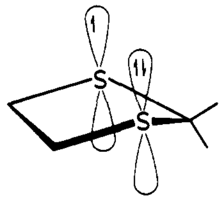
Comparison of the results obtained for *intra*molecular radical cation complexes derived from 1,4- and 1,3-dithiacyclohexane (IV and V) and *inter*molecular complexes (III), in our earlier experiments, indicates that the position of λ_{max} is related to the orbital overlap in the newly established sulfur-sulfur bond. Two obvious parameters controlling the latter are the internuclear separation, $r(\mathrm{S}\dot{-}\mathrm{S})$, of the two interacting S atoms[9,10,25] and a favorable angular orientation of the interacting p orbitals.



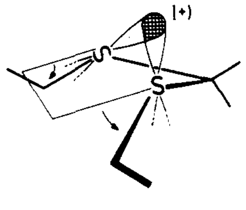
Generally the strength of the new σ bond will increase with decreasing bond length and increasing orbital overlap. As a result the σ,σ^* energy level separation shows a parallel increase explaining the red shift in λ_{max} with increasing r and decreasing orbital overlap.

The absolute stability of the three-electron bond is considered to depend on the degree of orbital overlap.[26] If the overlap integral is greater than zero ($S > 0$), the stabilization effect of the bonding level (σ) is smaller than the destabilization by the antibonding level (σ^*), i.e., the resulting σ and σ^* levels are not equidistant from the initial energy levels. At very high orbital overlap with $S \geq 1/3$ the destabilizing effect of the antibonding σ^* electron will eventually outweigh the stabilizing effect of the two bonding σ electrons. The experimental data on the radical cations discussed here do not allow a quantitative determination of the orbital overlap or the strength of the three-electron bond between the two sulfur atoms. Qualitatively, the optical absorptions do indicate an overall stabilization of the system. Since, however, dissociation of the three-electron bond to the simply oxidized sulfur center, $>\underline{S}^{+\cdot}$ (eq 1), readily takes place it would appear that the overall stability of the three-electron center cannot be very high. Recent MNDO/2 calculations by Clark[33] in fact indicate bond strengths for the sulfur-sulfur three-electron bonds in the range of ca. 40-120 kJ/mol.

The fact that favorable orbital direction is required to establish the new sulfur-sulfur bond explains the lack of *intra*molecular radical cation formation from 2-methyl-1,3-dithiacyclopentane. In this more or less planar (only slight envelope structure) and rigid molecule the possible degree of p-orbital overlap is much too slight to allow for the formation of a bond of significant strength (structure X).



X

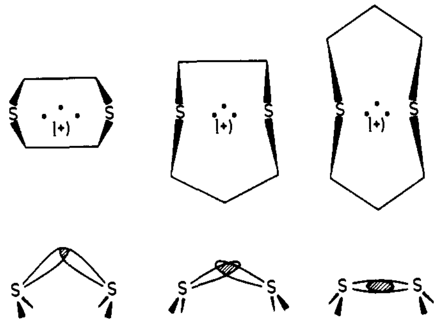


XI / VI

As, however, the cyclopentane-type molecule is opened between C-4 and C-5, the two S atoms can twist toward each other and the p orbitals can overlap as shown in structure XI. The resulting *intra*molecular radical cation complex, the stoichiometry of which is given by VI (eq 2), shows quite a significant absorption with λ_{max} 570 nm and an appreciable ϵ_{max} 2500 M^{-1} cm^{-1}, as mentioned above. By comparison the extent of p-orbital overlap is of the same order but slightly larger than that in the *intra*molecular radical cation complex from 1,3-dithiacyclohexane. This can probably be viewed in terms of a somewhat better angular orientation of the p orbitals in the less rigid open-chain system.

These examples together with the optical data presented and discussed above provide unambiguous support for the ESR conclusion on the σ character of the new sulfur-sulfur bond in the radical cation complexes.

The influence of orbital overlap on the position of λ_{max} is demonstrated, for example, in a series of *intra*molecular radical cation complexes from 1,4-dithiacyclohexane (V), 1,4-dithiacycloheptane (XII), and 1,5-dithiacyclooctane (XIII), respectively.



λ_{max} 650 nm 460 400

ϵ_{max} 1070 $M^{-1}cm^{-1}$ 3500 5800

V XII XIII

In the illustrations an attempt is made to give a pictorial representation of the most likely structures of these radical cation complexes, viewed from two different angles, including the overlapping regions of the interacting p orbitals. For 1,4-dithiacyclohexane direct orbital overlap is only possible in the boat configuration, and the relatively large r(S∴S) and unfavorable orbital orientation in this case suggest a low-energy band. Insertion of even a single CH_2 group permits a much more satisfactory configuration with respect to sulfur-sulfur interaction. Although the internuclear distance between the two sulfur atoms has not changed significantly (as may be seen from appropriate models), the establishment of a five-membered ring on one side of the new sulfur-sulfur bond results in a much more favorable angular orientation of the p orbitals. The significantly increased orbital overlap is reflected in a marked blue shift of λ_{max} to 460 nm. A still closer approach of the two interacting sulfur atoms seems possible in the oxidized 1,5-dithiacyclooctane where two structurally very favorable five-ring systems can be established. Further, a maximum degree of orbital overlap is now possible along the S···S coordinate, and the combined effect leads to an additional blue shift of λ_{max} to 400 nm.

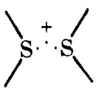
The increasing extinction coefficients at λ_{max} in going from V through XII to XIII also reflect the increasing extent of orbital overlap in the new sulfur-sulfur bond. More quantitatively, of course, the oscillator strengths or at least the product of (λ_{max} × half-width) should be compared instead of just ϵ_{max}, and indeed the same trend is observed with (ϵ_{max} × half-width) = 1230, 3000, and 4230 M^{-1} cm^{-1} eV for radical cations V, XII, and XIII, respectively.

For a more quantitative assessment, internuclear sulfur-sulfur distances and angular orientations of the orbitals in the radical cations would be required, i.e., parameters which may well differ from those for the unoxidized dithia compounds. MNDO/2 calculations for the radical cations V, XII, and XIII, kindly provided by Clark,[33] indicate maximum stabilization of these species at r(S∴S) of 2.298, 2.234, and 2.136 Å, respectively. Although these values are qualitatively in agreement with the general blue shift of λ_{max} in going from V to XIII, they certainly cannot account quantitatively for the changes in λ_{max}. The more important parameter appears to be the angular orientation of the interacting orbitals reflected in the C-S-S angles which according to the same MNDO/2 calculations are approximately 67° for V, 89 and 97° for XII (four- and five-membered ring, respectively), and 98° for XIII.[33] This would mean a most unfavorable orbital orientation for the *intra*molecular radical cation V from 1,4-dithiacyclohexane.

Looking at all the λ_{max} values listed in Table I, however, it would appear that r(S∴S) and angular orbital orientation are not the only parameters controlling the variations in λ_{max}. For example, the red shift in λ_{max} of V seems extremely large in comparison with XII, XIII, and the open-chain 2,5-dithiaheptane. Moreover, it is not immediately evident why the radical cation from 1,6-dithiacyclodecane should show a significant red shift compared to XIII in both of which r(S∴S) and p-orbital alignment are likely to be very similar. Further, the red shift of λ_{max} for the radical cations from the open-chain compounds relative to that from the cyclic compounds needs to be accounted for. A qualitatively satisfactory explanation can again be derived from the structural features of the radical cations. It can be seen, for example, that in V two carbon-carbon σ bonds are located parallel to the newly established sulfur-sulfur σ bond. The σ(C,C) and σ(S,S) are probably close enough for interaction the result of which would be raising of the σ(S,S) and lowering of the σ(C,C) energy level. Assuming that σ^*(S,S) is not affected in the same way—and this is indicated in Clark's calculations[33]—the σ/σ^* energy level separation will become smaller. As a result the σ(C,C)-σ(S,S) orbital interactions may account for part of the large red shift in λ_{max} of V. The corresponding effect is expected to be considerably smaller in XII and the radical cation from 2,5-dithiaheptane since only one C,C bond parallels the new σ(S,S) bond. C,C bonds parallel to the S,S bond at larger distance as in the cations of 1,6-dithiacyclodecane and 2,7-dithiaoctane will have a still smaller influence and lead to only a small raising of the σ(S,S) energy level. The latter may, however, still be enough to account, at least partially, for the slight red shift in λ_{max} of these radical cations compared to those from XIII and 2,6-dithiaheptane.

The comparison of cyclic with open-chain compounds also brings a number of interesting points to light. For example, the open-chain and thus much more flexible structures of 2,5-dithiahexane and 4-M-3,5-DTH (with two and one C atoms, respectively, between the S atoms) allow a better angular orientation of their p orbitals and therefore larger overlap than in the corresponding rigid cyclo compounds, 1,4- and 1,3-dithiacyclohexanes. This is also considered to account partially for the observed blue shift in λ_{max} and changes in extinction coefficients. For the other open-chain compounds with separation of the S atoms by more than two carbon atoms, λ_{max} for *intra*molecular radical cation complexes is generally slightly red shifted as compared to the cyclic compounds. We interpret this on the basis of the greater flexibility of the open-chain molecules. The radical cation complexes (*intra-* and *inter*-molecular) which are the visibly absorbing species and the molecular radical cations (see eq 1) are known to be in equilibrium. Thus neither the internuclear distance between the interacting S atoms, $r(\mathrm{S}\dot{-}\mathrm{S})$, nor the extent of p-orbital overlap can be regarded as constant in this dynamic system. λ_{max} is thus associated with the most probable values of these parameters and the broadness of the absorption band reflects the distribution of internuclear distances and p-orbital overlap. It seems reasonable to expect a greater degree of molecular mobility in the open-chain molecules as compared with the more rigid structures prevailing in the cyclic molecules. This model also affords a plausible explanation of the slight red shift in λ_{max} for the *intra*molecular radical cations from cyclic and open-chain dithia compounds in which the two interacting sulfur atoms are separated by a large number of carbon atoms as compared to those compounds with four or less C atoms between the two sulfur atoms. And it explains why *inter*molecular radical cation complexes are not as strong as and absorb at higher wavelengths (430–500 nm) than the strongest *intra*molecular complex (400 nm).

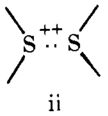
The relationship between λ_{max} and p-orbital overlap established above also neatly explains the—at first glance—intriguing result that λ_{max} for the *inter*molecular radical cation complex i



i

from methionine is blue shifted from ≈600 nm in single crystals at 77 K[27] to 480 nm in aqueous solutions at room temperature.[28] In the single crystal at 77 K the S–S internuclear distance and orbital alignment are defined within distinct limits, while in the liquid the interacting molecules can adopt a configuration with closer sulfur–sulfur distance and larger overlap.

Optical data also provide information on the character of the third, unpaired electron in the i bond which would not necessarily have to be antibonding. Further oxidation of the radical cation complex which can be effected chemically[12,29,30] or which results from disproportionation of this species yields a dication, ii:



ii

This species absorbs with λ_{max} in the 200–250-nm range indicating an increased separation between the σ and σ^* energy levels as compared with the radical cation. This, of course, implies an increase in S–S bond strength on removal of the third electron and demonstrates the antibonding character of the latter.

Finally, it is not surprising that the conclusions drawn from the optical parameters are consistent with the kinetic data. Thus, the rate constants for the conversion of *intra-* into *inter*molecular complexes decrease with increasing stability of the former. For example, $k = 5.8 \times 10^9$ and 2.2×10^8 M^{-1} s^{-1} were found for this reaction of the species derived from 1,4-dithiacyclohexane and 4-methyl-3,5-dithiaheptane, respectively. A still lower rate constant is expected for the "*intra*" → "*inter*" reaction for 1,5-dithiacyclooctane. In fact, within the solubility limits in aqueous solutions and even at relatively high concentrations in acetonitrile solutions[11] no evidence of an *inter*molecular radical cation complex from this compound has been found.

A correlation between the lifetimes of the *intra*molecular radical cations with respect to proton elimination and the stability of the three-electron sulfur–sulfur bond is not immediately apparent. It is known, however, that for simple aliphatic thioethers[4] proton elimination occurs via the molecular radical cation, $\mathrm{R_2S^{+}\cdot}$, rather than the complex i. Since the same kind of equilibrium between the simply oxidized sulfur center and its stabilized complex (eq 1) is also inferred for the *intra*molecular radical cations from dithia compounds, the above-mentioned lifetimes are also likely to reflect the stability of the three-electron bond. Consistent with this, the shortest lifetimes are found for those species with the weakest sulfur–sulfur interaction. Looking at the data in Table I it will be noticed that the $t_{1/2}$ values increase with increasing p-orbital overlap, but that maximum lifetimes do not absolutely correlate with minimum values of λ_{max}. Since a quantitative decay mechanism for the radical cations is yet to be established it is probably inopportune to draw any further conclusions from these findings. On the other hand, the results may be viewed in the light of the earlier suggestion that at high p-orbital overlap (S approaching $1/3$) the σ/σ^* energy splitting, i.e., λ_{max}, is no longer a direct criterion of the stability (strength) of a three-electron bond.[26] The fact that the values of the first half-lives of the *intra*molecular radical cations from 1,5-dithiacyclooctane and 2,6-dithiaheptane are slightly lower than those from 1,4-dithiacycloheptane and 2,7-dithiaoctane may indicate a slightly increased overall destabilization of the i bond in the former.

In summary, it has been demonstrated that the various optical parameters and the stability of radical cation complexes from organic thia compounds can be interpreted reasonably on the basis of structural considerations. This means conversely that structural features of the radical cation complexes may be inferred from the optical data. This aspect is of particular interest for multithia compounds (tri-, tetra-, etc.) and multicenter radical cation complexes where more than two sulfur atoms are involved in the stabilization of an oxidized sulfur atom.[19]

Acknowledgment. The authors would like to record their thanks to Mrs. E. Darnstädt for help in the synthesis of the sulfur organic compounds and Mr. J. Mönig for part-time assistance in the pulse radiolysis experiments. We would also like to thank Professor K. W. Musker from the University of California in Davis, Calif., for providing us with some of the cyclic dithia compounds. Our particular thanks are due to Dr. T. R. Clark of the University of Erlangen, who was stimulated by our experimental results to carry out MNDO/2 calculations on the radical cations reported, and kindly allowed us to use his not yet published results for interpretation of our data.

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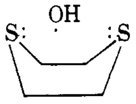
(34) One of the referees raised the question of sulfur orbital splitting by through-bond coupling (prior to oxidation) in 1,3- and 1,4-dithia compounds[31] and its possible implications on the interpretation of the optical data. Several results such as (a) the formation of an OH· radical adduct to 1,4-dithiacyclohexane involving both S atoms (iii)



iii

as a precursor of the corresponding *intra*molecular radical cation,[9,10] (b) the lack of *intra*molecular radical cation formation in the case of 2-methyl-1,3-dithiacyclopentane, and (c) the observed dependences of the extinction coefficients seem, however, intuitively more reasonable in terms of the proposed through-space interactions. Further, a direct relationship between the magnitude of the orbital splitting induced by through-bond coupling of ≤0.5 eV (e.g., 0.43 eV in 1,3-dithiacyclohexane)[32] and our optical transition energies is not apparent. We cannot, of course, exclude some contribution by through-bond coupling, but we find no compelling grounds for an interpretation of our data on this basis, i.e., to question the formation of a new sulfur-sulfur three-electron-bond in *all* of the radical cation complexes.

Disproportionation among Aryloxyphosphoranes

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Abstract: Methyltetraphenoxyphosphorane and methyltetra-*p*-nitrophenoxyphosphorane, on mixing, rapidly disproportionate to an equilibrium mixture of all of the intermediate phosphoranes and all the phosphonium salts that result from the loss of phenoxide or *p*-nitrophenoxide ion from the phosphoranes. The disproportionation equilibria can be measured by ^{31}P NMR spectroscopy and deviate remarkably little from the statistical distribution, although equilibrium constants for individual dissociations vary over a 10^{14}-fold range. Some understanding of these phenomena is advanced.

Introduction

The acid-catalyzed hydrolysis of phosphates presumably proceeds sequentially through protonated esters and hydroxyphosphoranes. For aryl triesters, the mechanism can be represented[1-3] schematically by the equations

$$(ArO)_3PO + H^+ \rightleftharpoons (ArO)_3P^+OH \tag{1}$$

$$(ArO)_3P^+OH + H_2O \rightleftharpoons (ArO)_3P(OH)_2 + H^+ \tag{2}$$

$$(ArO)_3P(OH)_2 \rightleftharpoons (ArO)_2P^+(OH)_2 + ArO^- \rightarrow (ArO)_2P({=}O)OH + ArOH \tag{3}$$

In some instances, pseudorotation[4,5] of the phosphorane intermediates intervenes as part of the hydrolytic process, or as a side reaction. In the present paper, the aryloxyphosphonium salts are offered as models for the protonated esters; the kinetics of their hydrolyses will presumably help in understanding those of the esters.

Mixtures of methyltetraphenoxyphosphorane and methyltetra-*p*-nitrophenoxyphosphorane in dry acetonitrile as solvent disproportionate at room temperature by way of the corresponding aryloxyphosphonium salts. The concentration of at least one of these salts is appreciable, and some of the reactions are fast on the NMR time scale, so that analysis of the equilibria is substantially more complicated than those for the slower equilibrations typical of many of the disproportionations previously analyzed.[6] By taking advantage of the rates and equilibrium constants previously determined for the dissociation of methyltetraphenoxyphosphorane in acetonitrile,[7,8] and a detailed analysis of the ^{31}P NMR spectra, all 16 of the rate constants and all of 8 of the equilibrium constants for this system can be found; they are presented in the accompanying paper.[9] We suggest that this is the most complex system that has so far been analyzed by NMR spectroscopy.

The definitions utilized in these papers are summarized in Scheme I, and the disproportionation constants are given by equations 4-6. The five phosphoranes in the system are designated by the symbols P(1), P(3), P(5), P(7), and P(9), and the four phosphonium salts are designated as P(2), P(4), P(6), and P(8), as shown in Scheme I.

$$L_1 = \frac{[P(1)][P(5)]}{[P(3)]^2} = \frac{K_{34}K_{32}}{K_{12}K_{54}} \tag{4}$$

$$L_2 = \frac{[P(3)][P(7)]}{[P(5)]^2} = \frac{K_{54}K_{56}}{K_{34}K_{76}} \tag{5}$$

0002-7863/79/1501-5329$01.00/0