Radical Cation Complexes in the Oxidation of Organic Di-, Tri-, and Tetrathia Compounds in Hydrocarbon Solutions

K.-D. Asmus,*

Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Bereich Strahlenchemie, D-1000 Berlin 39, West Germany

H. A. Gillis, and G. G. Teather

National Research Council of Canada, Division of Physics, Ottawa, Canada K1A 0R6 (Received August 2, 1977; Revised Manuscript Received September 18, 1978)

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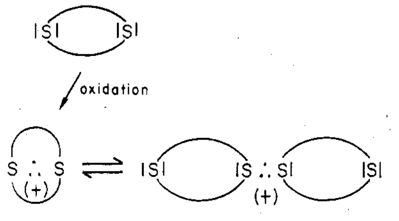
The formation of intermolecular radical cation complexes has been observed in the oxidation of a number of cyclic and open chain di-, tri-, and tetrathia compounds (1,4- and 1,3-dithiacyclohexane, 1,3,5-trithiacyclohexane, 1,4,7,10-tetrathiacyclododecane, 1,5,8,12-tetrathiacyclotetradecane; 4-methyl-3,5-dithiaheptane) in neohexane, 3-methylpentane, and squalane. At high solute concentrations (>10^{-3} M) two types of intermolecular complexes are formed. One of them which absorbs at 500 nm and which is known also from corresponding work in aqueous solutions is characterized by a newly established three-electron bond between two sulfur atoms of two neighboring molecules. The other complex which is formed only in hydrocarbons absorbs at $\simeq$750 nm and results from stabilization of an oxidized sulfur atom in a multicenter interaction complex involving more than two sulfur atoms. The probablity of its formation requires favorable configuration for p-orbital overlap from participating sulfur atoms and is highest for complexes involving sulfur atoms from two separate molecules.

Introduction

The formation of radical cation complexes in the oxidation of organic compounds containing two or more sulfur atoms not adjacent to each other has been demonstrated in a number of recent publications.[1-4] Depending on the solute concentration intra- (I) or intermolecular (II) complexes are formed from cyclic dithia compounds. Similarly intra- and intermolecular stabilization of an oxidized sulfur atom has been observed in open chain organic dithia compounds.[4]



I II

The common characteristic of both is a newly formed three-electron bond between two sulfur atoms of the same (I) or two different molecules (II). Two of the electrons establish a σ bond; the third electron is located in an antibonding σ^* orbital.[3-6] Type II intermolecular complexes typically absorb around 500 nm[3,7,8] while the position of the absorption maximum of the type I intramolecular complexes varies much more with the nature of the sulfur organic compound. For example, a $\lambda_{\max}$ of 650, 530, 600, and 475 nm has been observed for the intramolecular radical cations from 1,4-dithiacyclohexane, 2,5-dithiahexane, 1,3-dithiacyclohexane, and 1,4-dithiacycloheptane, respectively,[4] and the position of the absorption maximum reflects the distance between the two sulfur atoms which establish the new bond. Intramolecular radical cations (I) from some cyclic dithia compounds have also been observed by ESR during conventional chemical oxidation of several mesocyclic thioethers in acetonitrile and nitromethane.[2] Type II intermolecular radicals are well known from the oxidation of thioethers in aqueous and single crystal studies using optical and ESR techniques.[3-8]

In a previous publication we have reported the formation and properties of the intramolecular complexes from 1,4- and 1,3-dithiacyclohexane and 1,3,5-trithiacyclohexane in aqueous solutions.[3] In general, the intra- and intermolecular complexes exist in equilibrium

$$\mathrm{I} + \overset{\frown}{\mathrm{S}\;\mathrm{S}} \rightleftharpoons \mathrm{II} \tag{1}$$

i.e., intermolecular complex II predominates at high solute concentration. Both forms have been identified for 1,4-dithiacyclohexane and the open chain 4-methyl-3,5-dithiaheptane, whereas II could not be verified for the cyclic 1,3-di- and 1,3,5-trithia compound because of insufficient solubility of these latter compounds in water.

It is known that positive ions which are strong oxidizing species are formed in the radiolysis of hydrocarbons:[9]

$$\mathrm{RH} \rightarrow \mathrm{RH}^{+}\cdot + e^{-} \tag{2}$$

It therefore seemed appropriate to look at intermolecular complexation during the oxidation of various organic compounds containing more than one sulfur atom per molecule by $\mathrm{RH}^{+}\cdot$ in hydrocarbon solutions where the solubility of these solutes is much greater than in H_2O. Two problems have to be taken into consideration, however, in going from a polar to a nonpolar solvent: (1) Radiation chemical yields of freely diffusing $\mathrm{RH}^{+}\cdot$ in hydrocarbons are generally much lower than that of the freely diffusing oxidizing species in water, $\mathrm{OH}\cdot$. (2) The lifetime of the radical cations formed in an irradiated hydrocarbon solution does not reflect its chemical stability and is generally smaller than in the nonpolar solvent. Both effects result from a fast recombination process due to the strong Coulombic attraction between the ionic species produced initially in the irradiation or between their products (geminate recombination). The investigation of intra- and intermolecular complexation of an oxidized sulfur center in a hydrocarbon therefore requires a sensitive optical detection technique with submicrosecond time resolution.

Experimental Section

Experiments were carried out with high-energy electron pulses of 40-ns duration from the 35-MeV linear accelerator of the National Research Council of Canada and in

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part with a 4-MeV Van de Graaff accelerator of the Hahn-Meitner-Institut Berlin. The optical detection system for the transient species produced in the pulse radiolysis experiments is based on a silicon photodiode (425–1050 nm) and an InAs photodiode (>1000 nm).[10] For measurements of spectra, the analyzing light was split after passing through the cell so that optical absorption at a given wavelength could be related to that taken simultaneously at a reference wavelength (either 500 or 650 nm), in order to take account of pulse-to-pulse variations. Further details have been described previously.[11]

The 3-methylpentane and neohexane were Phillips Research and Phillips Pure Grade, respectively, the squalane was from Chemical Samples. All solutes were further purified by passing them through columns of activated silica gel and molecular sieve 4A.

The commercially available sulfur compounds (1,4-di-, 1,3-di-, and 1,3,5-trithiacyclohexane) were purified by recrystallization. The open chain 4-methyl-3,5-dithiaheptane was synthesized from C_2H_5SH and CH_3CHO in the presence of $BF_3 \cdot C_2H_5OC_2H_5$ in dichloromethane solutions. The 1,4,7,10-tetrathiacyclododecane ($C_8H_{16}S_4$), i.e., a cyclic compound where the four sulfur atoms are separated from each other by two methylene groups, respectively, was prepared by condensation of $NaS(CH_2)_2SNa$ with $Cl(CH_2)_2OH$ to form $HO(CH_2)_2S(CH_2)_2OH$ (reflux in ethanolic solution). After conversion of OH into SH and SNa[17] condensation of this tetrathia intermediate with 1,2-dibromoethane by refluxing in ethanolic solution yielded the cyclic tetrathia compound.[17] The 1,4,8,11-tetrathiacyclotetradecane ($C_{10}H_{20}S_4$) was synthesized in the same way by using $NaS(CH_2)_2SNa$ and $Br(CH_2)_3Br$ instead of the ethane derivatives in the initial and final step of the synthesis, respectively.[17] All synthesized compounds have been identified and checked for purity through NMR (Varian EM 390) and mass spectrometry (Varian MAT 44). Furthermore, the melting points of the two tetrathia compounds were practically identical with those found by Ochrymowycz who had synthesized these compounds in a different way.[20]

Solutions were prepared according to standard radiation chemical methods. Oxygen was removed from solutions by bubbling them with N_2O (Union Carbide), so that the highly mobile electrons from reaction 2 would be converted to less mobile secondary ions, such as O^-. This should have increased the observable yield of the sulfur-containing radical cations. The N_2O generally was passed through the solvent in a prebubbler flask before being bubbled through the sample in the irradiation cell, in an effort to remove impurities. However, small absorptions resulted from the irradiation of N_2O-bubbled solutions without sulfur compounds as a solute; the spectra presented in this paper have been corrected for these blank absorptions which may be due to products of reactions of O^-.

The experiments were carried out at room temperature.

Results and Discussion

(1) *Oxidations in Neohexane.* (a) *1,4-Dithiacyclohexane.* Figure 1a shows a trace of the optical absorption as a function of time at 750 nm in a pulsed, N_2O saturated solution of 10^{-2} M 1,4-dithiacyclohexane in neohexane. An immediate increase in absorption is noticed after the pulse. It then decays with a first half-life of ca. 250 ns.

The spectrum of this transient species is presented in Figure 2a. It shows a maximum at 500 nm and a long red tail extending to >1000 nm. The maximum of the absorption at 500 nm and the wavelength on the low-energy side at which the height is half-maximum are identical with that of the intermolecular radical cation formed in aqueous solutions.[3] The main absorption band is therefore attributed to the complex (V) formed in the reaction sequence

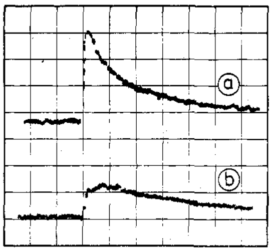


Figure 1. Oscilloscope traces in N_2O-bubbled solutions of neohexane: (a) 10^{-2} M 1,4-dithiacyclohexane; (b) saturated solution ($<10^{-2}$ M) of 1,3,5-trithiacyclohexane. For both traces, λ was 750 nm; a horizontal division represents 200 ns. The pulse length was 40 ns.

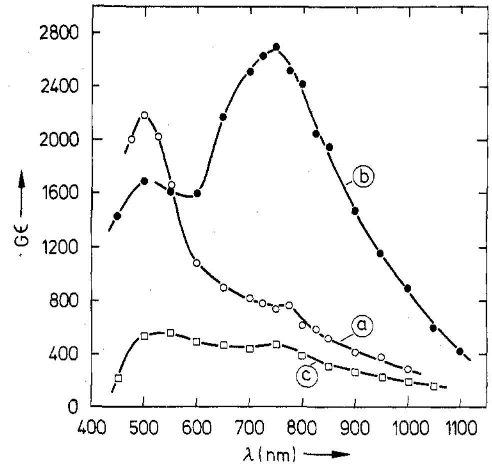
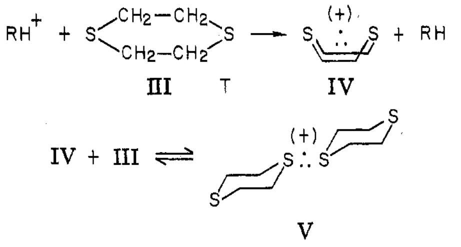


Figure 2. Spectra of radical cations from (a) 1,4-dithiacyclohexane (10^{-1} M), (b) 1,3-dithiacyclohexane (10^{-2} M), and (c) 1,3,5-trithiacyclohexane (saturated solution) in pulsed, N_2O bubbled neohexane solutions.



(3)

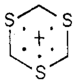
(4)

A small shoulder around 750 nm is indicated in Figure 2a. This part of the spectrum was scanned repeatedly to confirm the presence of the shoulder, and its significance is increased by the appearance at about the same wavelength of a shoulder in the spectrum of 1,3,5-trithiacyclohexane solutions and a peak in the spectrum of 1,3-dithiacyclohexane solutions (see below). Also the low-energy tail of the spectrum in Figure 2a is more prominent than that for the spectrum of the intermolecular radical cation complex in aqueous solutions; the ratio $G\epsilon_{1000}/(G\epsilon_{500})$ is 0.13 and 0.026 for 1,4-dithiacyclohexane in neohexane and aqueous solutions, respectively. This increased infrared absorption must be part of the band which gives the shoulder around 750 nm in Figure 2a. We assign this band to a second type of intermolecular complex; a possible structure for this species will be presented in a later section of this paper.

Absorption in an irradiated 10^{-4} M solution was qualitatively similar to, and only slightly greater than, that in a blank. This result was expected because the extinction coefficient of IV is expected to be only one-sixth that of V, by analogy with results in aqueous solution,[3] and the solute concentration was not high enough to result in a significant concentration of intermolecular complex V if the equilibrium constant for reaction 4 is similar in neohexane to its value in aqueous solutions.[3]

(b) *1,3-Dithiacyclohexane.* Figure 2b shows the spectrum of the transient absorption obtained immediately after the pulse in an N_2O saturated solution of 10^{-2} M 1,3-dithiacyclohexane. The spectrum shows two maxima, one at 500 nm and another stronger one at 750 nm. At low solute concentration these absorptions are not present and only the comparatively weak absorption of the type I intramolecular radical cation seems to be present. The 500-nm peak clearly indicates that an intermolecular complex is formed also from 1,3-dithiacyclohexane, if a high enough concentration of the solute is provided.

(c) *1,3,5-Trithiacyclohexane.* The spectrum of the transient cationic radical formed in the oxidation of a saturated solution of 1,3,5-trithiacyclohexane in neohexane taken 200 ns after the pulse is shown in Figure 2c. Again the spectrum shows two broad maxima of practically equal intensity at about 500 and 750 nm, respectively, which indicates the formation of intermolecular radical cation complexes from this compound also. The yields (expressed in terms of $G\epsilon$) were found to be smaller than those for the dithiacyclohexanes. However, this may be due simply to the fact that the solubility of 1,3,5-trithiacyclohexane in neohexane is not very high (considerably less than 10^{-2} M). Formation of the intermolecular complex which requires a second molecule and usually is achieved only at high solute concentrations may well be less complete than in the solutions of dithiacyclohexanes. In addition, kinetic considerations would explain the relatively lower yields. Thus, Figure 1b shows a trace of the optical absorption at 750 nm as a function of time in a pulsed solution (N_2O-bubbled) saturated with 1,3,5-trithiacyclohexane. Immediately after the pulse a fast increase is observed which is followed by a second slower step and finally the absorption decays. The spectrum of the species formed in the initial fast process, although not well characterized because the absorptions are so small, seems to be that of the intramolecular radical cation (λ_{max} 610 nm),[3] i.e., it is attributed to the "low concentration" oxidation product VI. The slower second increase in absorption is probably caused by the reaction of VI with a second 1,3,5-trithiacyclohexane molecule to form an intermolecular complex, the spectrum of which is shown in Figure 2c. For the half-life of this complexation reaction only an estimate of $t_{1/2} \approx 100$ ns can be given, which yields a bimolecular rate constant of $k \approx 10^9$ M^{-1} s^{-1} for the process



VI

$$\text{VI} + \text{1,3,5-trithiacyclohexane} \rightarrow \text{intermolecular radical cation VII} \quad (5)$$

It may be noted that a rate constant of 5.8×10^9 M^{-1} s^{-1} has been found for the corresponding complexation process of the 1,4-dithiacyclohexane radical cation in aqueous solution. The lifetime of the intermolecular complex is rather short ($t_{1/2}$ = 500 ns). Therefore, since the rate of decay is almost as high as the rate of formation the observable maximum yield (measured at 200 ns after the pulse) is considerably smaller than the total yield of species VII formed.

(d) *4-Methyl-3,5-dithiaheptane.* Two transient absorption bands of about equal intensity with maxima at 530 and 760 nm are also observed during the oxidation of a high concentration (10^{-2} M) of an open chain dithia compound, namely, 4-methyl-3,5-dithiaheptane, in neohexane. Since these absorptions are not present at low solute concentrations, this result also indicates intermolecular stabilization of the oxidized sulfur center by other sulfur atoms.

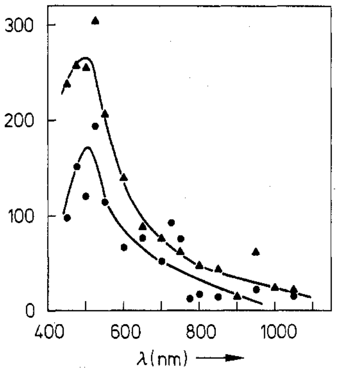


Figure 3. Spectra of radical cations from 1,4,7,10-tetrathiacyclododecane in neohexane (N_2O saturated) taken at 75 ns after a 40-ns pulse (corrected for the absorption produced in the N_2O saturated solution containing no sulfur compound): (●) 10^{-4} M $C_8H_{16}S_4$; (▲) $<10^{-3}$ M $C_8H_{16}S_4$ (saturated solution).

(e) *Cyclic Tetrathia Compounds.* Figure 3 shows the absorption spectra observed at 75 ns after the start of a 40-ns pulse in N_2O saturated solutions of 10^{-4} M and a saturated ($\leq 10^{-3}$ M) 1,4,7,10-tetrathiacyclododecane in neohexane. Though there is considerable scatter of the experimental points owing to the low yields of oxidized species significant differences are noticed by comparison with the other sulfur compounds discussed so far. (a) Essentially the same spectrum is obtained at both solute concentrations with an absorption maximum at around 500 nm. The ca. 50% difference in yield is easily explained by the scavenging efficiency for the solute parent radical cation, $RH^{+}\cdot$, at the higher solute concentration. Both spectra show a long tail extending into the IR without, however, any distinct peak around 750 nm. Since the molecule provides four sulfur atoms, it can be assumed that the absorption is due to an intramolecularly stabilized sulfur radical cation complex.

The same result is obtained, in principle, for another cyclic tetrathia compound, namely, 1,5,8,12-tetrathiacyclotetradecane. Again only one pronounced absorption maximum at 460 nm is observed, and a small shoulder is indicated between 550 and 600 nm at the red tail of the absorption in pulse irradiated neohexane solutions of up to 2×10^{-3} M solute concentration.

(2) *Oxidations of Cyclic Dithia Compounds in 3-Methylpentane and Squalane.* The results obtained in 3-methylpentane and squalane as solvents show no significant differences. In addition to a 500-nm band, a new absorption at 750 nm is generally observed for all dithia compounds at high solute concentrations. The yield of the latter is a factor of 1.5 that at 500 nm for the 1,3-dithiacyclohexane, irrespective of the solvent. For 1,4-dithiacyclohexane only a shoulder at the red tail of the 500-mm absorption is observed (see Figure 2a).

No intramolecular radical complexes could be observed from 1,3,5-trithiacyclohexane in squalane. The reasons are probably an insufficient solubility of this compound in squalane and a lower rate constant for the complexation reaction of the intramolecular radical cation (eq 5) due to the high viscosity of the solvent.

(3) *Yields and Decay Kinetics.* The yield of scavengable primary radical cations $RH^{+}\cdot$ in the radiolysis of a hydrocarbon depends very much on the total scavenger

TABLE I: Spectroscopic Data and Yields of Intermolecular Radical Cation Complexes from Cyclic Dithia Compounds[a]

solvent	solute	concn, M	λ, nm	$G\epsilon$	G(II)	$G_{\text{free ion}}$
neohexane	1,4-dithiacyclohexane	10^{-2}	500	2180	0.40	0.35
			750	760		
	1,3-dithiacyclohexane	10^{-2}	500	1700		
			750	2670		
	1,3,5-trithiacyclohexane	$<10^{-2}$	500	540		
		(satd)	750	470		
3-methyl-pentane	1,4-dithiacyclohexane	$\leqslant 10^{-2}$	500	1820	0.34	0.15
		(satd)	750	545		
	1,3-dithiacyclohexane	10^{-2}	500	1255		
			750	1870		
	1,3,5-trithiacyclohexane	$<10^{-2}$	500	210		
		(satd)	750	220		
squalane	1,4-dithiacyclohexane	10^{-1}	500	3370	0.62	0.12
			750	1060		
	1,3-dithiacyclohexane	10^{-2}	500	4820		
			750	7120		

[a] G(II) is the yield of complex II calculated by using an ϵ of 5400 M^{-1} cm^{-1}.

(sulfur compound) concentration.[12] A comparatively small yield, the so-called "free" ion yield (see Table I), diffuses freely into the bulk of the solution. The majority of $RH^{+}\cdot$ does not escape the Coulombic field of mutual attraction with its negative counterion (either e^{-} or a negative ion), and even if reaction of $RH^{+}\cdot$ with a sulfur compound occurs the resulting sulfur organic radical cation will be neutralized with high probability within a very short time of <50 ns (geminate recombination). The yield of species observable at a time scale accessibly by our experiments is therefore expected to be only slightly larger than the "free" ion yield.

The $G\epsilon$ values for the absorption maxima of the intermolecular radical cations of the three cyclic dithia compounds in the three different solvents are also listed in Table I. (G represents the species formed per 100-eV absorbed energy.) For 1,4-dithiacyclohexane which gave principally the 500-nm absorption band estimates of the yield can be evaluated by assuming identical extinction coefficients of the intermolecular complexes in aqueous and the hydrocarbon solutions with an ϵ of 5600 M^{-1} cm^{-1}. The values of $G = 0.40$ and 0.34 obtained for neohexane and 3-methylpentane, respectively, are much less than the yields for "geminate" ions ($G = 4$)[12,13] and only slightly larger than the "free" ion yields[13] (0.35 and 0.15, respectively). In squalane a G of 0.62 is observed which is somewhat higher than the "free" ion yield of 0.12. There are too likely reasons for this: (1) The concentration of solute used was higher (10^{-1} M) than that for the neohexane and 3-methylpentane solutions, so that the fraction of $RH^{+}\cdot$ undergoing reaction with solute rather than geminate recombination with an electron should have been higher. (2) All reactions including geminate recombination processes are slowed down in this highly viscous solvent, and a considerable number of radical cations, which would be neutralized during the pulse in neohexane or 3-methylpentane, survive in squalane until the first observation time.

Radical cation yields cannot be calculated for the other dithia compounds because the extinction coefficients for the two species with peaks at 500 and 750 nm are unknown. The relative yield of the 500- and 750-nm absorption did not change significantly with solute concentration.

For the radical cation of 1,4,7,10-tetrathiacyclohexane an estimate for the extinction coefficient may be derived. Assuming that at 10^{-4} M only the free ion yield of $G = 0.35$ is observable and with $G\epsilon = 170$ at 500 nm an ϵ of ≈500 M^{-1} cm^{-1} is calculated.

Kinetic analysis of the decay of both the 500- and 750-nm band show that the decay at early times follows the typical pattern observed for geminate recombination processes, i.e., mixed order without dose rate dependence.[14] At later times the decay kinetics are probably determined by a proton elimination process[7] from the radical cations.

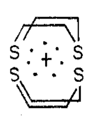
A noticeable difference in lifetime is found for the two absorption bands observed in the oxidation of the open chain 4-methyl-3,5-dithiaheptane. While the 530-nm band decays with a first half-life of ca. 500 ns, the 760-nm band decays faster with $t_{1/2} \approx 200$ ns. This result would indicate that these bands have to be attributed to two different species. For all the other radical cations, the decay kinetics of the two bands are very similar and preclude any decision on how many individual species are responsible for the absorptions.

(4) *Structure of the Radical Cations.* The characteristic feature of the radical cation complexes is the stabilization of an oxidized sulfur center through free electron pairs of other sulfur atoms. Intermolecular complexation usually occurs between two sulfur atoms of two different molecules involving three electrons in the formation of a new sulfur-sulfur bond (2 σ and 1σ^* electron). The intermolecular complexes typically absorb around 500 nm irrespective of the solvent as has been found in aqueous[3,4] and Me_2SO[16] solutions. The presence of this band in hydrocarbon solutions at high solute concentrations of the di- and trithia compounds therefore clearly shows the formation of intermolecular complexes, and thereby substantiates the general reaction mechanisms derived from the aqueous system and outlined in the introductory section.

Spectroscopic data obtained for intramolecular radical cations in aqueous solution indicate that the position of the absorption maxima depends on the distance between the two interacting sulfur atoms.[1,3,4] The strength of the newly formed sulfur–sulfur σ bond (intra and/or intermolecular) will reflect the extent of p orbital overlap along the interaction coordinate. Accordingly the energy difference between the σ and σ^* levels and therefore the position of the absorption maximum for the $\sigma \rightarrow \sigma^*$ transition is expected to depend on the distance between the two interacting atoms.[16,18] On the other hand, the independence of the position of the 500-nm band in the various solvents would indicate that the structure of the intermolecular complex (II) is affected very little by the polarity of the solution.

The other absorption band peaking around 750 nm is also only observed at high solute concentrations which strongly suggests that it arises from an intermolecular radical complex. In addition, this band appears only in hydrocarbons. For example, for the open chain 4-methyl-3,5-dithiaheptane where solubility allowed high concentration experiments in aqueous as well as in the hydrocarbon solution the IR band showed up only in the latter solvent. No such absorption bands around 750 nm could also be detected in solutions of, e.g., the cyclic dithia compounds in dimethyl sulfoxide.[15] The formation of the species responsible for this absorption band therefore seems to depend on the polarity of the solvent.

On the basis of our results we suggest the formation of multicenter radical cation complexes in the nonpolar hydrocarbon solutions, i.e., intermolecular complexes, where the stabilization may involve more than two and possibly even all of the sulfur atoms from two molecules. Considering that the establishment of the multi-sulfur atom complex requires a favorable orbital direction with the p orbitals perpendicular to the carbon–sulfur–carbon plane, a tetrahedral arrangement of four sulfur atoms from two molecules appears to be most likely for the dithia compounds. Structures may then be assigned to the multicenter radical cations from 1,4-dithiacyclohexane (VIII), 1,3-dithiacyclohexane (IX), and 4-methyl-3,5-dithiaheptane (X), with the four sulfur atoms arranged in a tetrahedron (XI).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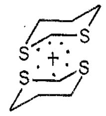
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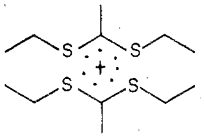
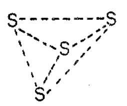

X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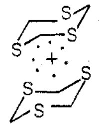
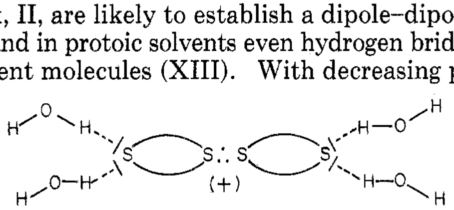

XII

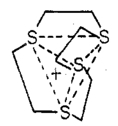
For 1,3,5-trithiacyclohexane a multicenter radical cation involving three sulfur atoms is formed intramolecularly, independent of the nature of the solvent. The IR band at high solute concentration in a hydrocarbon is attributed to a complex involving all six sulfur atoms of two molecules (XII).

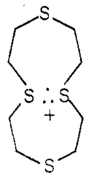
The formation of intermolecular multicenter radical cation complexes in hydrocarbons and their absence in water can be rationalized on the basis of the polarity of the solvent. In a polar solvent all sulfurs except the two forming the three-electron bond of the intermolecular complex, II, are likely to establish a dipole–dipole interaction, and in protoic solvents even hydrogen bridges with the solvent molecules (XIII). With decreasing polarity, interaction of these sulfur atoms with solvent molecules becomes less and less, however, interaction with the oxidized sulfur atom becomes increasingly important.


XIII

The proposed structures of the multicenter complexes VIII–XII also explain the relative yields of these species. High yields may be expected for the 4-methyl-3,5-dithiaheptane and also for the cyclic 1,3-dithiacyclohexane, since the latter can remain in the thermodynamically more stable chair configuration. The radical cation XII involves two 1,3,5-trithiacyclohexane molecules which would have to arrange in a sandwich type structure but also could remain in the chair configuration. A relatively low yield is expected and found for the multicenter complex VIII of 1,4-dithiacyclohexane because both molecules have to be present in the unfavorable boat configuration. In addition, the relatively greater distance between the sulfur atoms in the 1,4 compound will probably not allow very sufficient p-orbital overlap from all four sulfur atoms of the two molecules.

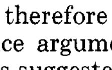
Another parameter which influences the probability of multicenter complexation, seems to be the flexibility (or rigidity) of the molecule. At first thought it might be surprising that no pronounced IR band is observed for the one-electron oxidation product from the cyclic tetrathia compounds where the four sulfur atoms could well coordinate intramolecularly to a four-center radical cation, XIV.


XIV

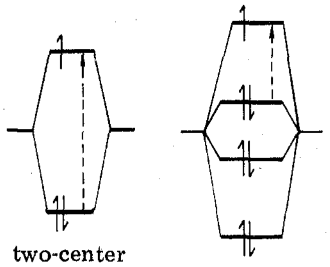

XV

This tetrahedral structure, however, seems to be rather labile and the overlap of the p orbitals pointing toward the center of the tetrahedron also is not large enough to stabilize the multicenter radical cation. A considerably higher degree of stabilization, however, is achieved if the oxidized sulfur atom pulls in the free electron pair from just one other sulfur atom to establish a new three-electron bond as, for example, in XV between the sulfur atoms in positions 1 and 7. This intramolecular arrangement leads to a much closer approach of two sulfur atoms than in the tetrahedron and the larger orbital overlap will lead to a relatively stronger new sulfur bond. Consequently, the energy required for a $\sigma \rightarrow \sigma^*$ transition will be higher and thus the absorption maximum will be shifted toward the blue. In view of this consideration it is not surprising that optical absorption spectra of the intramolecular radical cations from these cyclic tetrathia compounds peak at almost the same wavelengths, e.g., between 430 and 460 nm in aqueous solutions.[4]

It has been pointed out[1,4,18] that an increasing distance between the two sulfur atoms forming the new three-electron (σ, σ^*) bond results in a red shift of the optical absorption of the radical cation complex. One might therefore be tempted to associate the IR band observed at about 750 nm in the hydrocarbon solutions to a distance between interacting sulfur atoms even larger than, for example, in the intramolecular radical cation from 1,4-dithiacyclohexane which absorbs at 650 nm. However, it has been demonstrated in a series of two-center radical cations of cyclic dithia compounds in aqueous solutions[4] that a decrease in extinction coefficient parallels the decrease in orbital overlap with increasing sulfur–sulfur distance. The IR absorption which in most cases was about equal or even greater than the 500-nm absorption of configuration XVI may therefore not be rationalized on the basis of the distance argument. The multicenter radical cation complexes suggested above would require more than two energy levels to accomodate all participating electrons since only a maximum of two electrons can be on the same energy level. Generally the complex radical cations involving n sulfur atoms have to accomodate $2n$


XVI

– 1 electrons on n energy levels as shown for two- and four-center complexes.



Transitions will predominantly occur between the two upper energy levels and this can satisfactorily explain the low energy IR band as well as the relatively high extinction coefficients of species VIII–XI. Also the large IR contribution to the very broad absorption band (half-width = 1.45 eV) of the intramolecular radical cation from 1,3,5-trithiacyclohexane[3] found in aqueous solutions is in accord with a three-center energy level picture, while the absorption of species XII is to be described by a six-center scheme.

From our experiments no information may, of course, be derived on the spacing of the multicenter energy levels which may well be not equidistant. A similar effect on energy level splitting by resonance interaction of, e.g., Π^* orbitals of a carbonyl group with symmetric benzene orbitals has recently been suggested by Christophorou[19] to explain negative ion resonance spectra.

The odd number of participating electrons ensures an overall binding effect, the magnitude of which, however, may be expected to decrease with increasing number of participating electrons. The latter could possibly explain the reduced lifetime of the 760-nm absorption band of the four-center species X relative to the 530-nm absorption band which is assigned to a two-center complex.

In summary our experiments have shown that stabilization of an oxidized sulfur center may occur by interaction with not only just one other sulfur atom but in a multicenter coordination complex as well. While intramolecular multicenter complexation seems to depend only on structural parameters and little on the nature of the solvent, intermolecular multicenter complexation appears to be facilitated by a low polarity environment.

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Structural Aspects of Solid Solutions of Enantiomers. The 3-Hydroxymethyl- and 3-Carboxy-2,2,5,5-tetramethylpyrrolidinyl 1-Oxyl Systems as Examples

Bernadette Chion, Janine Lajzerowicz,* Denise Bordeaux,

Laboratoire de Spectrométrie Physique, B.P. 53, 38041 Grenoble Cedex, France

André Collet, and Jean Jacques

Laboratoire de Chimie Organique des Hormones, Groupe de Recherche du CNRS No. 20, Collège de France, 75231 Paris Cedex 05, France *(Received July 26, 1978)*

Enantiomer mixtures of the title compounds 3 and 4 crystallize as solid solutions: a series of continuous solid solutions for 4 and limited solid solutions for 3. The synthesis of enantiomers, the melting point (phase) diagram of 3, solubility diagram of 4 in chloroform, and the crystal structure determination of the racemic solid solution of 4 and of the 40% R–60% S mixture of 3 are reported. These solid solutions are of static disorder type; cell parameters are close to those of enantiomers; space groups are either identical (3) or supergroup (4) of the enantiomer space groups. General criteria for the formation of solid solutions and special features for compounds 3 and 4, particularly the influence of hydrogen bonding networks, are discussed.

Most equimolecular mixtures of enantiomers, i.e., racemates, crystallize as racemic compounds, while relatively few (there are ca. 250 inventoried cases[1]) are conglomerates, i.e., cases which permit spontaneous resolution.

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