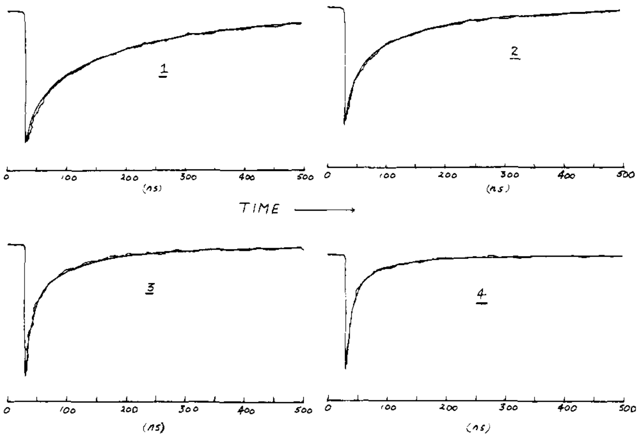

Figure 5. Rate of decay of pyrene fluorescence in CPC–P-μE in the presence of nitrobenzene; [pyrene] = 10^{-5} M; [nitrobenzene]: (1) 10^{-3} M; (2) 2.5×10^{-3} M; (3) 5×10^{-3} M; and (4) 10^{-2} M. Coarse curve, experimental data; smooth curve, calculated curve according to eq 2.

Table IV. Kinetic Parameters for Quenching the Fluorescence of 1.0×10^{-6} M P in 0.01 M CPC–P-μE by Nitrobenzene, NB

$[Q] \times 10^3$	A^a	$k_1 \times 10^{-6}$ s^{-1}	$E\nu \times 10^{-10}$ s^{-1}
0	0	2.52	0
1.0	0.002	2.52	1.0
2.5	0.0035	2.52	1.0
5.0	0.005	2.52	1.0
7.5	0.0062	2.52	1.0

[a] $A = {}^4/_3\pi a^3N_Q$.

pyridinium head groups as effective quenchers of P*, it can be safely presumed that this fluorescence is exclusively emanating from P* intercalated in the polymerized matrix of pμE. However, in the presence of NB at a quencher occupancy level greater than one hundred, where the statistical distribution of quenchers among the p-μE particles becomes unimportant, the decay of the fluorescence of P* is distinctly nonexponential, and attempts to fit it with a double exponential function proved unsuccessful. The apparent dynamic quenching of P* cannot be explained by a diffusional encounter mechanism between P* and Q within the sphere of the polymerized latex particle, since it has already been established that movement of entrapped species is greatly restricted if not absent within the time of the experiment.

On the other hand, excellent fits to the fluorescence decay curves (Figure 5) were obtained with the tunneling equation (2) by maintaining the parameters ($F\nu$) and k_1 fixed and varying (${}^4/_3\pi a^3N_Q$). Optimal values of these parameters are displayed in Table IV. Attention should be given to the fact that the parameter (${}^4/_3\pi a^3N_p$) was found to increase with quencher concentration, but a linear relationship was not found according to the theoretical prediction. This could be a consequence of a nonuniform and complex distribution of quencher between the polymerized phase, the surfactant layer, and the aqueous phase. Nonetheless, the goodness of fit between the experimental decay curves at different concentrations of quencher and the computer-generated curves using eq 2 lend credence to the electron tunneling kinetic model presented above.

Conclusion

Polymerized microemulsion systems add yet another attractive parameter to the use of micelles and microemulsions in photochemistry, namely the possibility of arranging reactants into two well-defined regions of space in the same molecular assembly. Reactants may be in the surfactant coating, where the dominant kinetic event is diffusion, or the reactants may be on the polymerized core, where the dominant kinetic events are Förster type energy transfer and tunneling type electron transfer.

Registry No. CTAB, 57-09-0; CPC, 123-03-5; P, 129-00-0; Pe, 198-55-0; NB, 98-95-3; divinylbenzene–styrene copolymer, 9003-70-7.

Variable-Temperature Photoelectron Spectral Study of 1,3-Dithiol-2-one and 4,5-Disubstituted 1,3-Dithiol-2-ones. Thermal Generation of 1,2-Dithiete, 3,4-Disubstituted 1,2-Dithietes, and Dialkyl Tetrathiooxalates[1]

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Abstract: The thermal fragmentation of 1,3-dithiol-2-one, its 4,5-dimethyl, dicyano, monocyclic 4,5-dialkylthio ($R^4 = R^5 = SCH_3$, SC_2H_5, $SCH(CH_3)_2$), and bicyclic alkylthio derivatives ($R^{4,5} = SCH_2S$, $S(CH_2)_2S$, $S(CH_2)_3S$) was investigated by variable-temperature photoelectron spectroscopy and in part by the matrix-isolation technique and infrared spectroscopy. The photoelectron spectra of the reactive intermediates 1,2-dithiete, 3,4-dimethyl-1,2-dithiete, and diethyl tetrathiooxalate are presented and interpreted. The new reactive species are unambiguously identified by photoelectron spectral and quantum chemical means. In addition, the photoelectron spectra of the stable (i.e., isolable at room temperature) compounds 3,4-bis(trifluoromethyl)-1,2-dithiete and dimethyl tetrathiooxalate are discussed. The influence of substituents on the relative stabilities of the 1,2-dithiete vs. the 1,2-dithione structures is studied using the MNDO method. The theoretical as well as the experimental results show that 1,2-dithiete and 3,4-dimethyl-1,2-dithiete are thermodynamically favored above their 1,2-dithione counterparts.

Variable-temperature photoelectron spectroscopy (VTPES) is a valuable tool for generating and observing reactive species in thermal reactions.[3,4] Our present experimental setup allows for the detection of reactive intermediates having a lifetime of ca.

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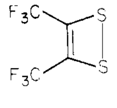
0.1 s[5] at a pressure of ca. 0.05 torr.

Below we report a VTPES investigation of 1,3-dithiol-2-one and several 4,5-disubstituted derivatives leading to 1,2-dithiete and 3,4-disubstituted dithietes or dialkyl tetrathiooxalates depending on the type of substituent. A preliminary account of the detection of 1,2-benzodithiete using the aforementioned technique and type of reaction has been given elsewhere.[6]

Over the years 1,2-dithiete and its derivatives have been attractive systems (i) as potential reactive intermediates in chemical reactions,[7-9] particularly because of their involvement in photochemical reactions,[8,9] or (ii) from a theoretical point of view, as potential 6π aromatic systems.[10,11] Only a few 1,2-dithietes could be isolated, namely, polyfluoroalkyldithietes as, e.g., 3,4-bis(trifluoromethyl)-1,2-dithiete (**1**)[12] and the sterically (kinetically) stabilized 1,2-dithietes **2**[13] and **3**.[14] Spectroscopic evidence as well as an electron diffraction study of **1**[15] and an X-ray diffraction study of **3**[16] established the four-ring geometry.



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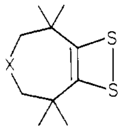

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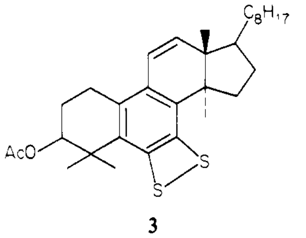


3

X = S, SO$_2$

According to the Woodward–Hoffmann rules the interconversion between the dithiete and dithione forms is photochemically allowed, but thermally forbidden.[11,17] Nevertheless, the activation energy of the ring-opening reaction **4** → **5** is only 17.5 kcal/mol, and 22.4 kcal/mol for the reverse reaction.[8] 1,2-Dithiete and 3-*tert*-butyl-1,2-dithiete were photochemically generated in a matrix at 77 K and identified by their UV/vis absorptions.[9] Photochemical transformations between these systems and their dithione valence isomers were performed. However, these experiments offered no evidence for the relative stabilities of the isomers since photostationary states were being generated. At 77 K no dark reactions were observed.

4 5

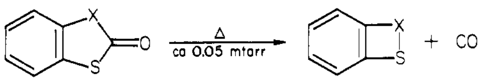
Ar = p-(CH$_3$)$_2$N-C$_6$H$_4$

Early HMO calculations indicated that electron-withdrawing substituents favor the dithiete form whereas electron-donating groups stabilize the dithione.[10] Based on these results 3,4-dicyano-1,2-dithiete was postulated as a reactive intermediate.[18] Previous experience appears to confirm the HMO results. For electron-releasing substituents such as dialkylamino or alkylthio groups, only the dithione form is known, while for trifluoromethyl groups the dithione form is unknown. However, the question of the relative stabilities of 1,2-dithiete and dithioglyoxal as well as simple alkyl-substituted analogues is totally open. EH and CNDO/2 calculations were contradictory in their results.[11]

A distinct advantage of VTPES experiments is that they lead (in contrast to photochemical experiments at low temperature) to the thermodynamically most stable product. Thus our present investigations will make, for the first time, a decision about the relative stabilities of the dithiete and dithione forms in cases where such decisions have not been possible until now. In addition, some insight into the unimolecular decay reaction of these compounds will be gained. Finally, it will turn out that thermal fragmentation of dithiolones offers a new route to dialkyl tetrathiooxalates.[19]

Results and Discussion

Preceding VTPES investigations of molecules of the general type of structure **6** have shown that they decompose into molecules of type **7** meaning that exclusively CO is split off and not COS.[6,20]



6 7

X = CH$_2$, CO, S

Therefore, there was good reason to expect that 1,3-dithiol-2-one and its derivatives will thermally react in the same way.

In order to describe our investigations on this reaction in a logical way, we first discuss the photoelectron spectra of 1,3-dithiol-2-one and two selected examples of 4,5-disubstituted 1,3-dithiol-2-ones which are some of our precursor molecules. In the subsequent section we report the VTPES studies of 1,3-dithiol-2-one and derivatives having substituents which are anticipated to stabilize the dithiete form. We present the photoelectron spectra of 1,2-dithiete, 3,4-dimethyl-1,2-dithiete, and 3,4-bis(trifluoromethyl)-1,2-dithiete and a hint at the existence of 3,4-dicyano-1,2-dithiete. In the third section we briefly discuss the photoelectron spectrum of dimethyl tetrathiooxalate needed for the identification of this compound in the new thermal pathway described in the subsequent section. The next section deals with the VTPES investigation of alkylthio-substituted 1,3-dithiol-2-one compounds which are expected to lead to the dithione forms known as dialkyl tetrathiooxalates. Some supplementary infrared data obtained by isolating the reaction products of the thermolysis of 1,3-dithiol-2-one and some of its derivatives in an argon matrix at 10 K will be given in the fifth section. The sixth and final section summarizes some considerations about the reactions studied.

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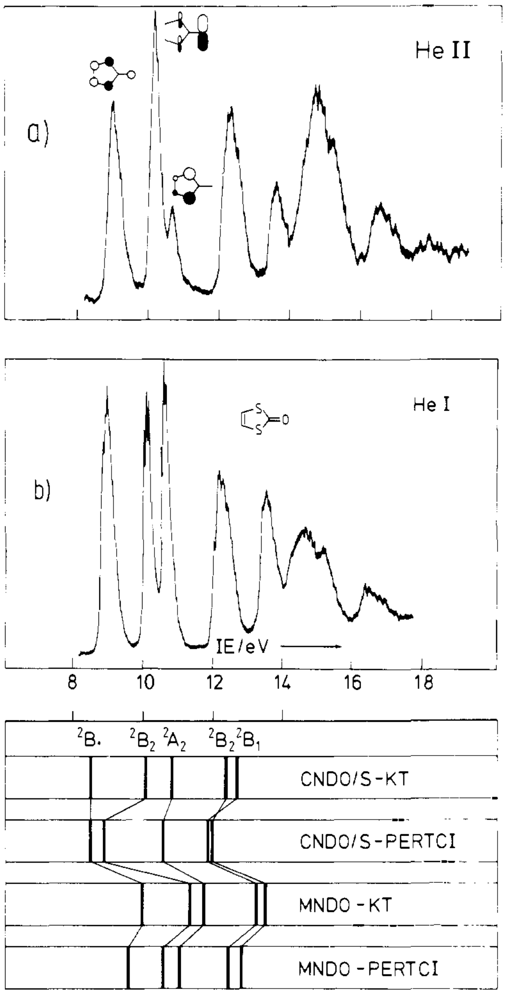
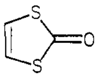


Figure 1. He I (b) and He II (a) photoelectron spectra and calculated CNDO/S-KT (Koopmans' theorem), CNDO/S-PERTCI, MNDO-KT, and MNDO-PERTCI ionization spectra of 1,3-dithiol-2-one (**8**). The assignments of ionizations are: $^2B_1$, $^2B_2$, $^2A_2$, $^2B_2$, $^2B_1$.

I. Photoelectron Spectra of 1,3-Dithiol-2-one, 4,5-Dimethyl-1,3-dithiol-2-one, and 4,5-Dicyano-1,3-dithiol-2-one

Figure 1 shows the He I and He II photoelectron spectra of 1,3-dithiol-2-one (**8**) along with the calculated CNDO/S[21]-KT



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(Koopmans' theorem), CNDO/S-PERTCI,[22] MNDO[23]-KT, and MNDO-PERTCI ionization spectra. PERTCI is a large-scale configuration interaction method and thus the PERTCI spectra incorporate effects of electron correlation and reorganization. It is worth mentioning that it is our experience that the MNDO method generally overestimates the ionization energies of molecules containing several sulfur atoms by ca. 1 eV.[24] This discrepancy is reduced to ca. 0.6 eV if the MNDO-PERTCI approach is used. We have further found that the CNDO/S-PERTCI approach tends to underestimate carbonyl n(O) ionization energies as well as the first σ ionization energies of π systems in general.[20,25] Taking these effects into account the agreement between the experimental and the calculated spectra is satisfactory.

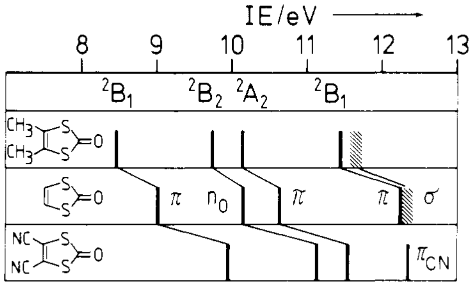
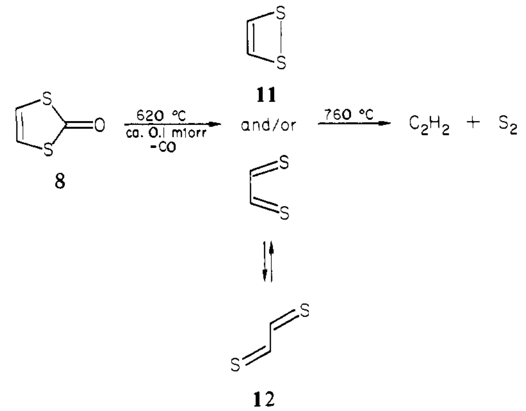


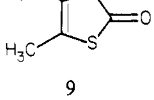
Figure 2. Measured vertical ionization energies and assignments of 1,3-dithiol-2-one (**8**), 4,5-dimethyl-1,3-dithiol-2-one (**9**), and 4,5-dicyano-1,3-dithiol-2-one (**10**).

Scheme I



The calculations yield the assignments $^2B_1(\pi)$, $^2B_2(n_O)$, and $^2A_2(\pi)$ for the first three ion states. The $b_1(\pi)$, $b_2(n_O)$, and $a_2(\pi)$ orbitals, from which an electron is ejected in the Koopmans ionization processes, are shown with the first three ionization bands of the He II spectrum in Figure 1. The $a_2(\pi)$ orbital is predominantly localized on the sulfur atoms. Thus we expect that the intensity of the corresponding ionization is strongly reduced when going from He I to He II excitation energy.[26] It was further shown that the intensity of oxygen lone pair (n_O) ionization is enhanced in the He II spectrum as compared to the He I spectrum.[26] Figure 1 shows that both expectations are fulfilled, thus supporting the quantum chemical assignments.

The same arguments apply to the photoelectron spectra of 4,5-dimethyl-1,3-dithiol-2-one (**9**) and 4,5-dicyano-1,3-dithiol-2-one (**10**). The correlation diagram of the measured ionization



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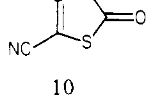

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energies of **8**, **9**, and **10** is presented in Figure 2. As can be seen, the methyl group uniformly lowers the ionization energies by ca. 0.5 eV, whereas the cyano substituents increase the ionization energies by ca. 1 eV.

II. VTPES Studies of 1,3-Dithiol-2-one, 4,5-Dimethyl-1,3-dithiol-2-one, and 4,5-Dicyano-1,3-dithiol-2-one. Photoelectron Spectra of 1,2-Dithiete, 3,4-Dimethyl-1,2-dithiete, and 3,4-Bis(trifluoromethyl)-1,2-dithiete

On heating the thermal reactor of the photoelectron spectrometer above 600 °C, and simultaneously recording the pho-

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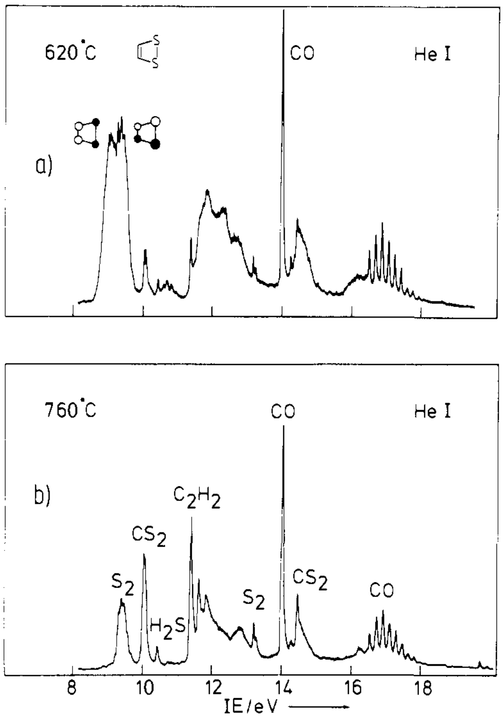

Figure 3. He I VTPE (variable-temperature photoelectron) spectra of 1,3-dithiol-2-one (**8**) at 620 °C (a) and 760 °C (b). The VTPE spectrum at 620 °C is essentially composed of the photoelectron spectra of 1,2-dithiete (**11**) and carbon monoxide. The VTPE spectrum at 760 °C exhibits bands belonging to carbon monoxide, decomposition products of **11**, as well as secondary products as carbondisulfide and hydrogen sulfide.

toelectron spectrum of gaseous 1,3-dithiol-2-one (**8**) flowing through the reactor, one notices that the spectrum of **8** (cf. Figure 1) has completely disappeared at this temperature and a new, clearcut spectrum is obtained. The vertical ionization energies of the new compound occur at 9.05, 9.36, 11.83, 12.31, 12.61, 14.54, and 16.17 eV. In addition, the intense bands of carbon monoxide appear at 14.01 eV ($^2\Sigma_g{}^+$ ion state) and around 15.7 eV ($^2\Pi_u$ state). Not a trace of COS can be seen. Less intense sharp bands at 11.40 and 13.19 eV indicate the simultaneous formation of acetylene ($^2\Pi_u$ ion state) and sulfur (S_2, $^4\Sigma_g{}^-$ state). Finally, small amounts of CS_2 (band at 10.1 eV) and traces of H_2S (band at 10.51 eV) which are common byproducts of thermal decomposition reactions of many organic sulfur compounds are observed.[27] When the temperature of the reactor is further raised to ca. 760 °C, the bands of the newly formed compound have completely disappeared and the photoelectron spectrum consists only of the bands of S_2, CO, C_2H_2, CS_2, and H_2S. Figure 3 displays the photoelectron spectra at 620 and 760 °C.

A logical explanation of all the observations described above is offered with the reactions in Scheme I. Accordingly, 1,3-dithiol-2-one decomposes at 620 °C into 1,2-dithiete (**11**) and/or dithioglyoxal (**12**) and CO and, in a consecutive reaction at the higher temperature of 760 °C, **11** decays into acetylene and sulfur.

The important question of whether 1,2-dithiete (**11**) or dithioglyoxal (**12**) is formed in the first step (i.e., whether the spectrum a of Figure 3 belongs to **11** or **12**) can be decided on the basis of purely photoelectron spectroscopic arguments.

We have to show that the new bands contained in the photoelectron spectrum of Figure 3a are due either to 1,2-dithiete (**11**) or to dithioglyoxal (**12**). If we are successful, this will prove the first step of Scheme I and, at the same time, decide the question asked in the Introduction about the relative stabilities of **11** and **12**.

To this end, we calculated the CNDO/S-KT, CNDO/S-PERTCI, MNDO-KT, MNDO-PERTCI, and 4-31G[28]-KT ionization spectra of **11** and **12** using MNDO optimized molecular geometries. For the dithiete, the results are displayed in Figure 4. All methods agree (recall the aforementioned defect of the MNDO method with regard to molecules containing several sulfur atoms) that the photoelectron spectrum of 1,2-dithiete consists of two closely spaced bands at 9 eV (due to transitions of the molecule to the $^2B_1(\pi)$ and $^2A_2(\pi)$ ion states) followed by the onset of σ bands at >11.5 eV. Comparison of these results with the photoelectron spectrum of Figure 3a shows that the calculated ionization spectrum of **11** perfectly matches the measured spectrum. For **12** the aforementioned methods also predict two bands around 9 eV (the two n_S ionizations), but then a band at 10.5 eV (first π ionization). It is to be added that these predictions are equally valid for the cis and trans forms of **12**. The photoelectron spectrum of Figure 3a exhibits no band at 10.5 eV. Thus we conclude from our calculations that the photoelectron spectrum of Figure 3a most probably is the spectrum of 1,2-dithiete and, furthermore, that 1,2-dithiete is thermodynamically more stable than its isomer dithioglyoxal.

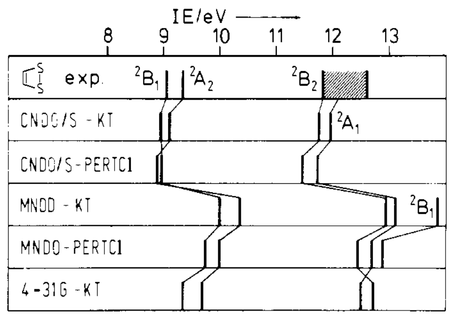

Figure 4. Calculated ionization spectra of 1,2-dithiete (**11**) using the CNDO/S-KT, CNDO/S-PERTCI, MNDO-KT, MNDO-PERTCI, and 4-31G-KT procedures.

Because the weight of these conclusions rests on a quantum chemical (calculational) identification procedure, the results will now be buttressed by presenting spectroscopic (experimental) reference data.

3,4-Bis(trifluoromethyl)-1,2-dithiete (**1**) is known to possess the dithiete structure **1** and not the dithione structure **13**.[12,15]

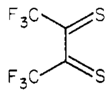

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Figure 5 exhibits the He I and He II photoelectron spectra and calculated CNDO/S-KT, CNDO/S-PERTCI, MNDO-KT, and MNDO-PERTCI ionization spectra of **1**. The low intensity of the first four bands in the He II spectrum (assigned to the ion states $^2B_1(\pi)$, $^2A_2(\pi)$ at 10.2 eV; $^2B_2(\sigma)$ at 12.95 eV; and $^2A_1(\sigma)$ at 13.45 eV) reflects the sizable sulfur 3p contributions to the corresponding orbitals involved in the Koopmans' ionizations.[26] The bands above 15 eV, however, are strongly intensified in the He II spectrum. This is due to the fluorine 2p contributions to the ionized orbitals in the Koopmans ionization processes.[29] What is of basic interest, however, is that both the He I photoelectron spectrum and the calculated ionization spectra of **1** (cf. Figure 5b and 5c) are very similar to the photoelectron spectra of the compound formed in the thermolysis of 1,3-dithiol-2-one at 620 °C and the calculated ionization spectra of 1,2-dithiete (**11**) (cf. Figures 3a and 4, respectively). Indeed if we take into account the effect of the CF_3 substituents (ca. 0.55 to 0.65 eV per CF_3 group[30]), the photoelectron spectra of Figure 3a and Figure 5a

---

[27] H_2S and CS_2 are thermodynamically stable products of C, H, S compounds in the gas phase at higher temperatures.

[28] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. Hehre, W. J.; Lathan, W. A. *Ibid.* **1972**, *56*, 5255. Hehre, W. J.; Pople, J. A. *Ibid.* **1972**, *56*, 4233. Hehre, W. J. *Acc. Chem. Res.* **1976**, *9*, 399. The calculations were performed using Gaussian 76 (*QCPE*, **1978**) with parts integrated from Gaussian 80 (*QCPE*, **1981**).

[29] Schweig, A.; Thiel, W. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 199

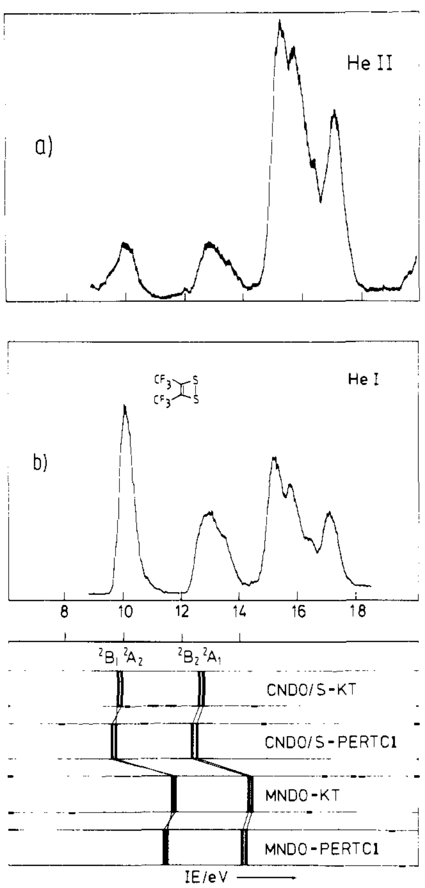
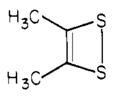


Figure 5. He I (b) and He II (a) photoelectron spectra and calculated CNDO/S-KT, CNDO/S-PERTCI, MNDO-KT, and MNDO-PERTCI ionization spectra of 3,4-bis(trifluoromethyl)-1,2-dithiete (**1**). The assignments of the first ionizations are: $^2B_1$, $^2A_2$, $^2B_2$, $^2A_1$.

perfectly match in the lower ionization energy region. This result as well as the fact that bis(trifluoromethyl)dithiolglyoxal (**13**) is expected to exhibit an ionization at ca. 11 eV (according to calculation results) clearly confirms that 1,2-dithiete (**11**) has been formed in the thermal reaction of 1,3-dithiol-2-one (**8**). Hence it is confirmed that 1,2-dithiete exists in the gas phase at low pressure at 620 °C and that 1,2-dithiete is more stable than dithioglyoxal.

After having established that the thermolysis of 1,3-dithiol-2-one leads to 1,2-dithiete in the VTPES experiment, the route is free now for producing other, hitherto unknown, nonisolable derivatives of 1,2-dithiete. This will be demonstrated for the example of 3,4-dimethyl-1,2-dithiete (**14**).



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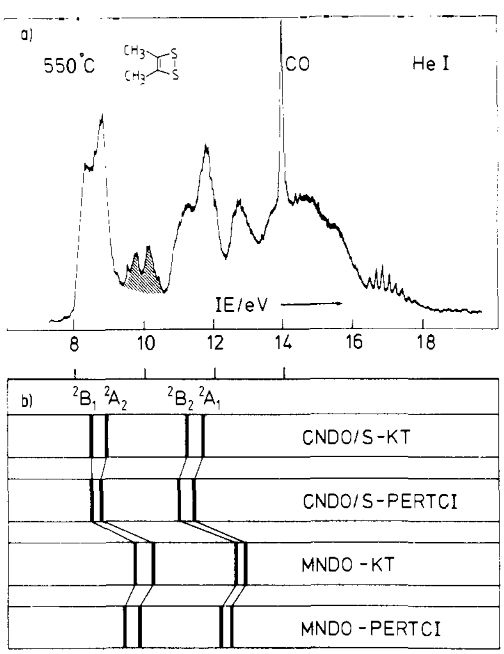
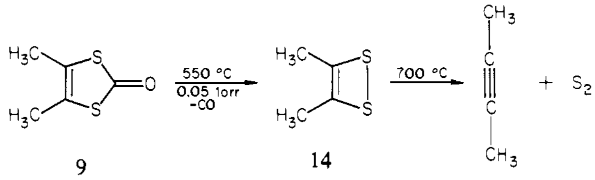
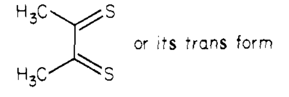


Figure 6. He I VTPE spectrum of 4,5-dimethyl-1,3-dithiol-2-one (**9**) at 550 °C and calculated CNDO/S-KT, CNDO/S-PERTCI, MNDO-KT, and MNDO-PERTCI ionization spectra of 3,4-dimethyl-1,2-dithiete (**14**). The VTPE spectrum is essentially composed of the photoelectron spectra of **14**, carbon monoxide, and **9** (hatched area).

Scheme II



The results of the VTPES experiment using 4,5-dimethyl-1,3-dithiol-2-one (**9**) as the precursor material are summarized in Scheme II. In the first step of the reaction 3,4-dimethyl-1,2-dithiete (**14**) is generated. The photoelectron spectrum of the new dithiete is shown in Figure 6a (vertical ionization energies: 8.36, 8.77, 11.32, 11.83 eV). Figure 6b displays the CNDO/S-KT, CNDO/S-PERTCI, MNDO-KT, and MNDO-PERTCI ionization spectra. The agreement between the measured spectrum and the calculated ionization spectra (note the aforementioned MNDO defect), the absence of an ionization in the range of 9 to 11 eV (this ionization is expected for the dithione **15**), the similarity of both the measured and calculated spectra to the corresponding spectra of 1,2-dithiete (**11**), and the uniform shift of ca. 0.5 eV to lower ionization energies of the first few ionizations as compared to the same ionizations of **11** (in analogy to the cases of 4,5-dimethyl-1,3-dithiol-2-one (**9**) and 1,3-dithiol-2-one (**8**); cf. Figure 2) give proof of the structure of **14** and thus of the first step of Scheme II.



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At 700 °C 3,4-dimethyl-1,2-dithiete (**14**) fragments into 2-butyne and S_2 which is clearly seen from the VTPE spectrum at that temperature.

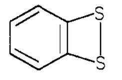

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Figure 7 shows the correlation diagram for the ionization energies of *cis*-butadiene,[31] 1,2-benzodithiete (**16**),[6] 1,2-dithiete (**11**), 3,4-bis(trifluoromethyl)-1,2-dithiete (**1**), and 3,4-dimethyl-1,2-

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(30) Methylenimine, 10.52 (n_π), 12.43 eV (π) (cf. Peel, J. B.; Willett, G. D. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1799); hexafluoropropan-2-imine, 11.8 (n_π), 13.7 eV (π) (cf. Vocelle, D.; Darglos, A.: Pottier, R.; Sandorfy, C. *J. Chem. Phys.* **1977**, *66*, 2860); benzene, 9.25 eV (π), and 1,2-bis(trifluoromethyl)benzene, 10.4 eV (π) (cf. Rosmus, P.; Bock, H.; Solouki, B.; Maier, G.; Mihm, G. *Angew. Chem.* **1981**, *93*, 616; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 598) (note that the scale in the abscissa of Figure 1 of this paper is in error by 1 eV); acetylene, 11.40 eV (π), and hexafluoro-2-butyne, 12.74 eV (π) (cf. Bieri, G.; Heilbronner, E.; Stadelmann, J. P.; Vogt, J.; v.Niessen, W. *J. Am. Chem. Soc.* **1977**, *99*, 6832).

(31) Heilbronner, E.; Gleiter, E.; Hopf, H.; Hornung, V.; de Meijere, A. *Helv. Chim. Acta* **1971**, *54*, 783.

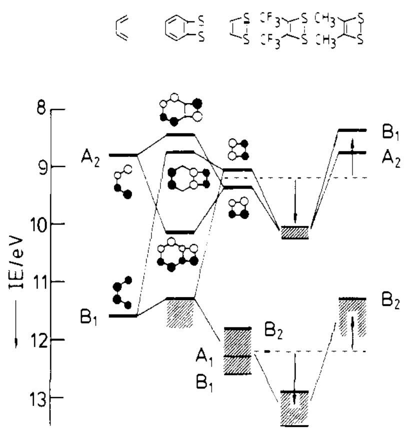


Figure 7. Measured vertical ionization energies of *cis*-butadiene, 1,2-benzodithiete (**16**), 1,2-dithiete (**11**), 3,4-bis(trifluoromethyl)-1,2-dithiete (**1**), and 3,4-dimethyl-1,2-dithiete (**14**). The molecular orbitals shown are those from which an electron is ejected according to Koopmans' theorem. Such a diagram, known as a correlation diagram, allows one to visualize subunit interaction effects as, e.g., the substituent effects of the trifluoromethyl groups (dnr) or the methyl group (upr) on the ionization enegies of **11**.

dithiete (**14**). The diagram makes visible the effects on the ionizations occurring when the *cis*-butadiene and 1,2-dithiete systems are coupled together to **16** or when the hydrogen atoms of **11** are substituted by the CF_3 (**1**) or by the CH_3 (**14**) groups. The effect of two CF_3 groups amounts to −1.1 eV, in excellent agreement with literature data,[30] and the influence of the CH_3 groupings to 0.5 eV. Notably, the effect of a CF_3 substituent on a π system is rather independent of the nature of the latter system.

Let us now turn to the VTPE spectra of 4,5-dicyano-1,3-dithiol-2-one (**10**). Applying a temperature of 800 °C and a pressure of 3 torr, the thermolysis of **10** is used as an efficient source of dicyanoacetylene for preparative purposes;[32] the mechanism of this decomposition reaction is unknown. Furthermore, it is reported that **10** decomposes completely at 500 °C and 3 torr without any dicyanoacetylene being generated.[32,33] The results of our aforementioned investigations suggest a similar two-step decay mechanism as described above for 1,3-dithiol-2-one (**8**) and 4,5-dimethyl-1,3-dithiol-2-one (**9**) to be valid for 4,5-dicyano-1,3-dithiol-2-one (**10**). The VTPE spectra show that even at a temperature of 400 °C and a pressure of 0.05 torr dicyanoacetylene is produced (besides CO and S_2); this reaction is complete at 550 °C. Carbon oxysulfide is not formed under our conditions; carbon disulfide, however, occurs and is likely formed by the reaction of S_2 with carbon deposited on the surface of the reactor.

We expect the first ionization bands in the photoelectron spectrum of **17** at ca. 10 eV. Indeed, when the temperature of the reactor is raised slowly from 400 to 550 °C, a new band system at 9.5 to 10.5 eV appears in the VTPE spectrum at 500 °C, which, however, partially overlaps with bands from the precursor material **10** and from the byproduct CS_2. In spite of carefully optimizing the temperature, it was not possible to get a spectrum of the pure intermediate **17**. Because of this result which is due to the fact that both steps of the reaction depicted in Scheme III occur at similarly low temperatures, our results can be considered only to give some hint to the possible existence of 3,4-dicyano-1,2-dithiete (**17**) and not to constitute a proof of the system.

To summarize, the results described above have shown (i) that 1,3-dithiol-2-one and some of its derivatives thermally react to form the corresponding 1,2-dithietes under the conditions of the VTPES technique, (ii) that the structures of 1,2-dithiete and 1,2-dithione and of corresponding derivatives can be distinguished by photoelectron spectroscopy, and (iii) that 1,2-dithiete, 3,4-dimethyl-1,2-dithiete, and 1,2-benzodithiete are the thermodynamically favored products in equilibrium with their 1,2-dithione counterparts.

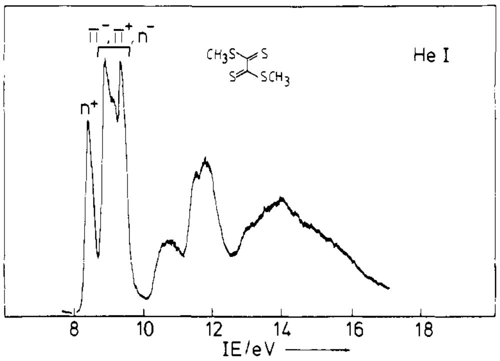
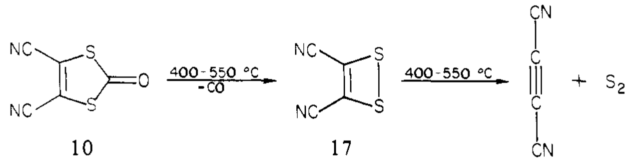


Figure 8. He I photoelectron spectrum of dimethyl tetrathiooxalate (**18**). The tentative assignments are n^+ and (π^+, π^-, n^-). For the notation used, see ref 35.

Scheme III



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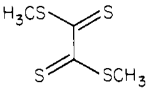
III. Photoelectron Spectrum of Dimethyl Tetrathiooxalate

Figure 8 displays the He I photoelectron spectrum of dimethyl tetrathiooxalate (**18**).[19] Unfortunately, no experimental information about the conformation of **18** is available. MNDO test calculations on similar compounds have shown that the results are not reliable. We therefore presume, in accord with considerations made for comparable compounds,[18,34-36] that **18** exists in the planar trans conformation. For this conformation MNDO and CNDO/S calculations lead to the assignments: n^+ and π^-, π^+, n^- (for these designations, see ref 35) for the first band at 8.38 eV and the region of ionizations between 8.90 and 9.35 eV, respectively.



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IV. VTPES Studies of 4,5-Bis(methylthio)-1,3-dithiol-2-one, 4,5-Bis(ethylthio)-1,3-dithiol-2-one, 4,5-Bis(isopropylthio)-1,3-dithiol-2-one, 2,4,6,8-Tetrathiabicyclo[3.3.0]oct-1(5)-en-7-one, 2,5,7,9-Tetrathiabicyclo[4.3.0]non-1(6)-en-8-one, and 2,6,8,10-Tetrathiabicyclo[5.3.0]dec-1(7)-en-9-one. Photoelectron Spectrum of Diethyl Tetrathiooxalate

All spectroscopic results known so far for the dialkyl dithiooxalates,[36] dialkyl trithiooxalates,[36] dialkyl tetrathiooxalates,[19] and dithiooxamides[35] are in accord with the dithione structure for these systems. Thus it is anticipated that thermal reactions of 4,5-diamino-, 4,5-bis(dialkylamino)-, or 4,5-bis(alkylthio)substituted 1,3-dithiol-2-ones will yield disubstitued 1,2-dithiones and no 1,2-dithietes.

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(32) Ciganek, E.; Krespan, C. G. *J. Org. Chem.* **1968**, *33*, 541.

(33) Cf. Brown, R. F. C. "Pyrolytic Methods in Organic Chemistry"; Academic Press: New York, 1980; p 208, and references quoted therein.

(34) Persson, B.; Sandström, J. *Acta Chem. Scand.* **1964**, *18*, 1059. Carter, R. E.; Sandström, J. *J. Phys. Chem.* **1972**, *76*, 642. de Lachevrotière, J. C.; Sandström, J.; Lumbroso, H. *C. R. Acad. Sci., Ser. C* **1973**, *276*, 1134. Larsson, D. B.; Arnett, J. F.; McGlynn, S. P. *Chem. Phys. Lett.* **1973**, *23*, 322.

(35) Henriksen, L.; Isaksson, R.; Liljefors, T.; Sandström, J. *Acta Chem. Scand. Ser., B* **1981**, *35*, 489.

(36) (a) Hartke, K.; Hoppe, H. *Chem. Ber.* **1974**, *107*, 3121. (b) Niemer, U.; Mennemann, K.; Mattes, R. *Ibid.* **1978**, *111*, 2113. (c) Cf. also: Hoppe, H.; Hartke, K. *Arch. Pharm.* (*Weinheim, Ger.*) **1975**, *308*, 526.

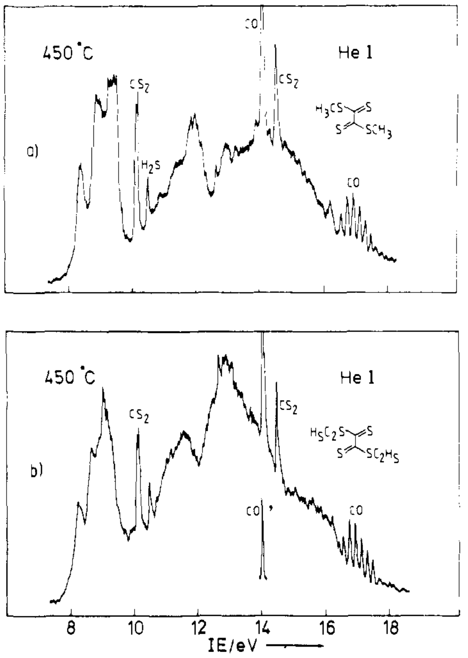
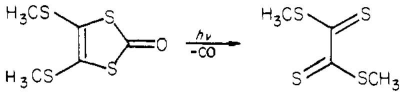


Figure 9. He I VTPE spectra of 4,5-bis(methylthio)-1,3-dithiol-2-one (**19**) at 450 °C (a) and 4,5-bis(ethylthio)-1,3-dithiol-2-one (**20**) at 450 °C (b). Spectrum a is essentially composed of the photoelectron spectra of dimethyl tetrathiooxalate (**18**), carbon monoxide, carbon disulfide, and hydrogen disulfide, and spectrum b of the photoelectron spectra of diethyl tetrathiooxalate (**25**) and the aforementioned byproducts.

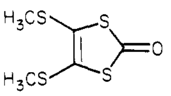
At the beginning of the present investigations only one tetrathiooxalate, namely, dimethyl tetrathiooxalate (**18**), was known.



18

This compound was obtained photochemically.[19] Surprisingly, this reaction did not work for other alkylthio (as, e.g., ethylthio) substituents.

VTPES experiments were carried out for the following series of 4,5-*S*-alkyl-1,3-dithiol-2-ones: 4,5-bis(methylthio)-1,3-dithiol-2-one (**19**), 4,5-bis(ethylthio)-1,3-dithiol-2-one (**20**), 4,5-bis(isopropylthio)-1,3-dithiol-2-one (**21**), 2,4,6,8-tetrathiabicyclo[3.3.0]oct-1(5)-en-7-one (**22**), 2,5,7,9-tetrathiabicyclo[4.3.0]non-1(6)-en-8-one (**23**), and 2,6,8,10-tetrathiabicyclo[5.3.0]dec-1(7)-en-9-one (**24**). The results are as follows: **19** and **20** decompose to the desired dimethyl and diethyl tetrathiooxalates **18** and **25** and CO (in addition some CS_2 and H_2S is observed) at 450 °C and 0.05 torr. The structural proof of the products is based on the similarity of the obtained VTPE spectra at 450 °C (Figure 9) and the photoelectron spectrum of the authentic sample of **18** shown in Figure 8. The measured vertical ionization potentials of **25** are 8.26 and 8.65–9.3 eV. Only propene, CS_2, CO, and H_2S could be detected in the thermolysis of **21**.



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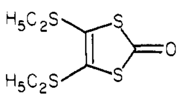

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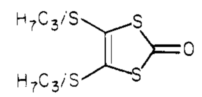

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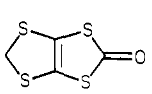

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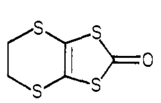

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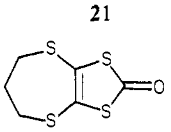

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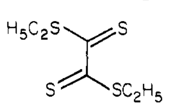

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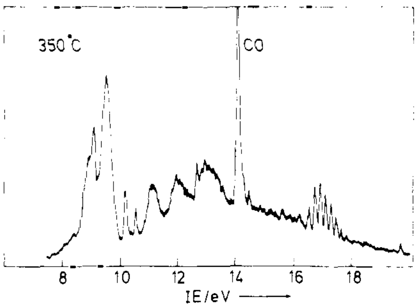
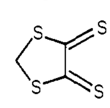


Figure 10. He I VTPE spectrum of 2,4,6,8-tetrathiabicyclo[3.3.0]oct-1(5)-en-7-one (**22**) at 350 °C. This spectrum is believed to be essentially composed of the photoelectron spectra of 1,3-dithiol-4,5-dithione (**26**) and carbon monoxide.

From the bicyclic compounds **22** to **24** only **22** is converted at 350 °C and 0.05 torr in a smooth reaction into a new product possessing vertical ionization energies of 8.88, 9.07, 9.49, 11.10, and 11.96 eV, carbon monoxide, and only very little CS_2 and H_2S (Figure 10). We believe that the new compound is 1,3-dithiol-4,5-dithione (**26**) although the final structural proof must await comparison of the spectrum obtained here with the spectrum of an authentic sample or a suitable reference compound. Calculations show that the photoelectron spectrum of the new compound is in agreement with the calculated ionization spectrum of **25** but not with that of 2,4,6,7-tetrathiabicyclo[3.2.0]hept-1-(5)-ene (**27**). It is to be added that materials **23** and **24** decompose into small fragments without any evidence for definite intermediate compounds.



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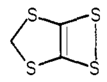

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V. Infrared Spectroscopy Studies of the Reaction Products of the Thermolysis of 1,3-Dithiol-2-one, 4,5-Dimethyl-1,3-dithiol-2-one, 4,5-Bis(methylthio)-1,3-dithiol-2-one, 4,5-Bis(ethylthio)-1,3-dithiol-2-one, and 2,4,6,8-Tetrathiabicyclo[3.3.0]oct-1(5)-en-7-one in an Argon Matrix at 10 K

The products of the gas-phase pyrolysis of 1,3-dithiol-2-one (**8**), 4,5-dimethyl-1,3-dithiol-2-one (**9**), 4,5-bis(methylthio)-1,3-dithiol-2-one (**19**), 4,5-bis(ethylthio)-1,3-dithiol-2-one (**20**), and 2,4,6,8-tetrathiabicyclo[3.3.0]oct-1(5)-en-7-one (**22**) were isolated in an argon matrix at 10 K and investigated by infrared spectroscopy.

The infrared spectrum of the products of 1,3-dithiol-2-one (**8**) shows that carbon monoxide and acetylene but no carbon oxysulfide was formed in the thermal decomposition reactions. The spectrum indicates formation of another compound with an intense absorption at 735 cm^{-1} which disappeared at 35 K when the matrix was softened. This band could be due to the CH δ_{OOP} vibration of 1,2-dithiete (**11**); the excitation energy of this vibration decreases with decreasing number of atoms in the ring, and it occurs at 820 cm^{-1} in 1,3-dithiol-2-one and at 563 cm^{-1} in thiirene.[37]

The infrared spectrum of the products of 4,5-dimethyl-1,3-dithiol-2-one (**9**) as well as that of 2,4,6,8-tetrathiabicyclo[3.3.0]oct-1(5)-en-7-one (**22**) did not show bands that could be

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(37) Krantz, A.; Laureni, J. *J. Org. Chem.* **1979**, *44*, 2730.

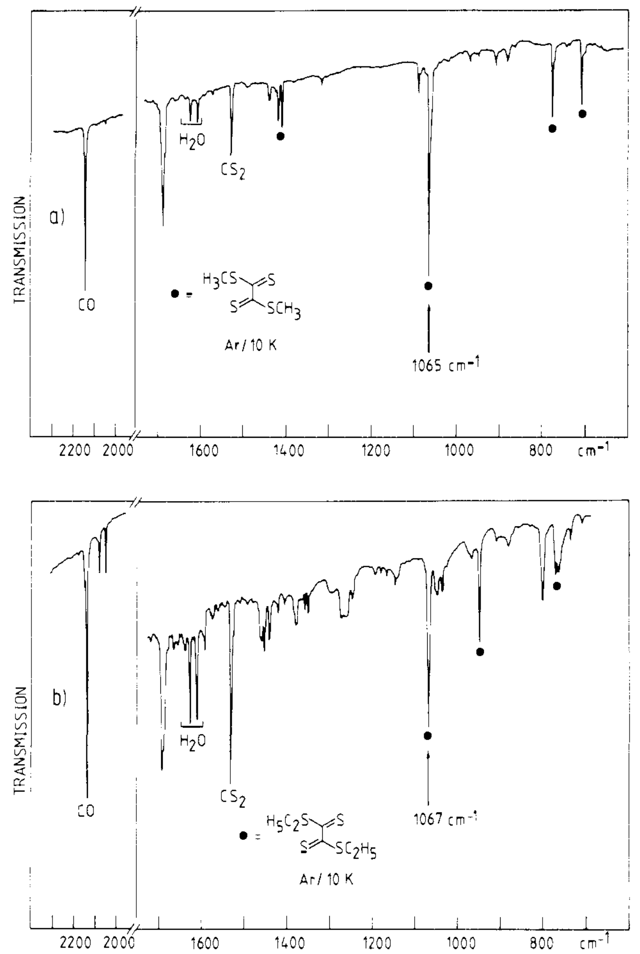

Figure 11. Infrared spectra of the reaction products of the decomposition of (a) 4,5-bis(methylthio)-1,3-dithiol-2-one (**19**) and (b) 4,5-bis(ethylthio)-1,3-dithiol-2-one (**20**) in an argon matrix at 10 K. Bands due to dimethyl and diethyl tetrathiooxalate **18** and **25** are marked ●. Note especially the band at 1065 or 1067 cm^{-1}, respectively.

considered characteristic for vibrations of 3,4-dimethyl-1,2-dithiete (**14**) or 1,3-dithiol-4,5-dithione (**26**), owing to lack of suitable reference data.

Absorption bands at 1180–1245 cm^{-1} have been assigned to the C=S vibration of dithioesters.[38] In dimethyl trithiooxalate and dimethyl tetrathiooxalate (**18**) the characteristic bands appear at 1138[36b] and 1045 cm^{-1},[39] respectively. The infrared spectrum of the reaction products of 4,5-bis(methylthio)-1,3-dithiol-2-one (**19**) (Figure 11) shows the characteristic bands of CO, CS$_2$, as well as the characteristic C=S band of **18** at 1065 cm^{-1}. The infrared spectrum of the products of 4,5-bis(ethylthio)-1,3-dithiol-2-one (**20**) exhibits the same intense band at 1067 cm^{-1} (Figure 11) which confirms the formation of diethyl tetrathiooxalate (**25**) in the thermolysis of **20**. It is to be added that this absorption of **20** starts disappearing at a temperature of 150 K.

In accordance with these findings, the gas-phase pyrolysis of 4,5-bis(methylthio)-1,3-dithiol-2-one (**19**) can be easily carried out on a preparative scale leading to the same yield of dimethyl tetrathiooxalate (**18**) as obtained via the photochemical route.[19]

To summarize, the results of the aforementioned photoelectron and infrared spectroscopic investigations have shown (i) that gas-phase pyrolysis of 4,5-bis(methylthio)-1,3-dithiol-2-one (**19**) and 4,5-bis(ethylthio)-1,3-dithiol-2-one (**20**) yields dimethyl tetrathiooxalate (**18**) and diethyl tetrathiooxalate (**25**), respectively, and (ii) that **25** starts disappearing at 150 K (probably because of reaction with itself) so that isolation at room temperature is not possible, in contrast to **19**.

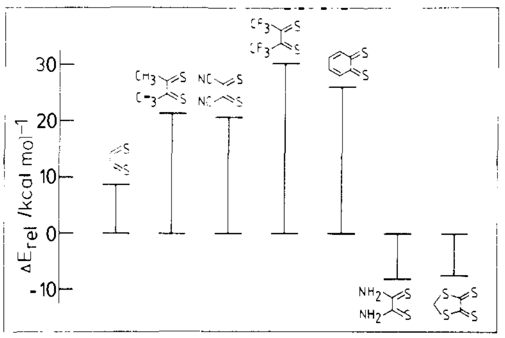

Figure 12. Energies of the *cis*-1,2-dithiones relative to the energies of their 1,2-dithiete isomers (or standard reaction enthalpies of the isomerization reaction 1,2-dithiete → *cis*-1,2-dithione) using the MNDO method.

VI. MNDO Study of the Relative Stabilities of 1,2-Dithione and 1,2-Dithiete and Their Derivatives. High Reactivities of 3,4-Dicyano-1,2-dithiete and Diethyl Tetrathiooxalate in Secondary Thermal Reactions

Figure 12 summarizes the energies of some *cis*-1,2-dithione systems relative to the energies of their 1,2-dithiete counterparts obtained using the MNDO method. Dithiooxamide is included as a second example of a system with electron-donating substituents (besides the alkylthio groups considered in the present work), and 1,3-dithiol-4,5-dithione (**26**) is selected as a representative example of the alkylthio-substituted materials. The results of the MNDO method are in full accord with our experimental findings; particularly the MNDO approach is correct in predicting 1,2-dithiete (**11**) to be more stable than dithioglyoxal (**12**) as well as 3,4-dimethyl-1,2-dithiete (**14**) to be more stable than dimethyldithioglyoxal (**15**). The energy difference between both isomeric forms is largest in the case of the CF$_3$ grouping. Conversely, the 1,2-dithione structure is favored for NH$_2$ and alkylthio substituents.

In the preceding sections it was shown that 1,2-dithiete (**11**), 3,4-dimethyl-1,2-dithiete (**14**), and 3,4-dicyano-1,2-dithiete (**17**) thermally decay to acetylene or disubstituted acetylenes and S$_2$. The decay of **17** occurs at lower temperatures (ca. 200 to 300 °C, i.e., practically in the same range of temperatures where the decay of the precursor material 4,5-dicyano-1,3-dithiol-2-one (**10**) is observed) than for all other dithietes studied. This conflicts with the clear VTPE observation of **17** as described in a preceding section. On the other hand, it was previously found that 1,2-benzodithiete (**16**) does not decompose into benzyne and S$_2$.[6] In order to find some explanation for these observations we calculated the standard reaction enthalpies of the aforementioned dithiete decay reactions using the MNDO procedure. Assuming the Bell–Evans–Polanyi principle[40] to be applicable to the present reactions, the nonfragmentation of **16** to benzyne and S$_2$ is clearly borne out by the calculated data (standard reaction enthalpy ca. 135 kcal/mol as compared to 50 to 60 kcal/mol in the other cases). The relatively easy fragmentation of **17** to dicyanoacetylene and S$_2$, however, is not explicable on the basis of the calculated reaction enthalpies (e.g., 53 kcal/mol for the fragmentation of **14** and 54 kcal/mol for the fragmentation of **17**). Obviously, the transition state of the thermolysis of **17** is over-proportionally (i.e., more than presumed from the calculated value of the reaction enthalpy) stabilized within the series of reactions considered.

Finally, attention should be drawn to the particularly puzzling observation described in the preceding sections that dimethyl tetrathiooxalate (**18**) can be isolated at room temperature whereas

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diethyl tetrathiooxalate (**25**) definitely cannot be isolated; investigations at low temperatures with subsequent warming up have established that **25** starts disappearing (probably because of dimerization and polymerization reactions) even at −120 °C. Presently we are unable to offer a conclusive explanation for this unexpected dramatic substituent effect.

VII. Conclusion

The question about the relative stabilities of 1,2-dithiete and 3,4-dimethyl-1,2-dithiete and their dithione valence isomers has been unambiguously answered in the present work. The systems exist as 1,2-dithietes. This result was achieved by photoelectron spectroscopic arguments. It was hardly imagined before that 1,2-dithiete and simply alkyl-substituted dithietes would exist as stable molecules at ca. 600 °C. 3,4-Dimethyl-1,2-dithiete has not been previously made, and from 1,2-dithiete it was known only that it can be generated in a matrix at 77 K and that it exhibits UV absorptions at 355 nm and below 240 nm.[9] 1,2-Dithiete (**11**) and 3,4-dimethyl-1,2-dithiete (**14**) are smoothly formed from 1,3-dithiol-2-one (**8**) and 4,5-dimethyl-1,3-dithiol-2-one (**9**) by thermal extrusion of CO. At higher temperatures **11** and **14** fragment into acetylenes and S_2.

We observed that 4,5-bis(methylthio)- and 4,5-bis(ethylthio)-1,3-dithiol-2-ones thermally react to the dithione forms, dimethyl and diethyl tetrathiooxalates. The diethyl compound has not been observed before. Most puzzling, however, is that the diethyl compound reacts (probably with itself) at −120 °C whereas the dimethyl compound had been isolated at room temperature. This powerful and unexpected substituent effect as well as questions about the characterization and structural proof of 3,4-dicyano-1,2-dithiete and 1,3-dithiol-4,5-dithione will be the subject of future investigations.

VIII. Experimental Section

Apparatus and Procedure. The UV photoelectron spectra were obtained using a Perkin-Elmer PS-16 photoelectron spectrometer equipped with a Helectros He I/He II light source and electrically heated temperature-controlled inlet system (thermal reactor).[3] The thermal reactor consisted of a 20 × 0.5 cm stainless steel tube. The temperature was measured using a chromel–alumel thermocouple and could be varied from room temperature to ca. 800 °C. The pressure inside the reactor was ca. 0.05 to 0.1 torr. The spectra were calibrated using acetylene ($^2\Pi_u$ at 11.40 eV) and nitrogen ($^2\Sigma_g{}^+$ at 15.57 eV and $^2\Pi_u$ at 16.69 eV).

The infrared spectra of the reaction products were recorded at 10 K in an argon matrix using a Beckman IR 4250 infrared spectrometer. The thermal reactor consisted of an electrically heated 5 × 0.4 cm quartz tube. Heat radiation was shielded by a tantalum foil. The temperature of the reactor was measured using a chromel–alumel thermocouple. The reactor was directly connected to the vacuum shroud of an Air Products CS 202E Displex System. Simultaneously with the reaction products argon was condensed in excess on a cold (10 K) KBr window or a polished copper block mounted at the cold end of the refrigeration system. A pressure of ca. 4×10^{-6} torr was maintained in the vacuum system during the deposition process by additional pumping with a turbomolecular pump.

Materials. 1,3-Dithiol-2-one (**8**),[41] 4,5-dicyano-1,3-dithiol-2-one (**10**),[42] 4,5-bis(methylthio)-1,3-dithiol-2-one (**19**),[19] 2,5,7,9-tetrathiabicyclo[4.3.0]non-1(6)-en-8-one (**23**),[19] 2,6,8,10-tetrathiabicyclo[5.3.0]dec-1(7)-en-9-one (**24**),[19] 4,5-bis(trifluoromethyl)-1,2-dithiete (**1**),[12] and dimethyl tetrathiooxalate (**18**)[19] were prepared according to literature.[12,19,41,42]

4,5-Dimethyl-1,3-dithiol-2-one (9). A solution of 9.8 g (60 mmol) of 4,5-dimethyl-1,3-dithiol-2-thione[43] in 80 mL of $CHCl_3$ was added dropwise to a solution of 38 g (120 mmol) of $Hg(OAc)_2$ in 500 mL of HOAc. The mixture was heated at reflux on a water bath for 1 h. After the reaction mixture was cooled to room temperature and filtered, it was poured into 2 L of water and extracted with 4 × 150 mL of $CHCl_3$. The organic phase was washed with a saturated aqueous $NaHCO_3$ solution and dried with $MgSO_4$; the solvent was removed in vacuo. Sublimation (50 °C, 15 torr) of the residue gave pure **9** (7 g, 80%), mp 45.5 °C: IR (film, crystn) $\tilde{\nu}_{max}$ 2945 cm^{-1}, 2920, 2855, 1755, 1657, 1635, 1600, 1440, 1095, 887, 755, 415; UV (C_2H_5OH) λ_{max} 216 nm (ϵ 3400 L mol^{-1} cm^{-1}), 237 (3100), 273 (2800); ^{1}H NMR ($CDCl_3$) δ 2.16. Anal. Calcd for $C_5H_6OS_2$: C, 41.07; H, 4.14; O, 10.94; S, 43.85. Found: C, 41.20; H, 4.19; O, 10.97; S, 43.98.

Lit.[44]: mp 45–46 °C; UV (C_2H_5OH) λ_{max} 218 (ϵ 3710 L mol^{-1} cm^{-1}), 238 nm (2990), 276 (2730); ^{1}H NMR ($CDCl_3$) δ 2.14.

4,5-Bis(ethylthio)-1,3-dithiol-2-thione. A solution of 5.4 g (100 mmol) of $NaOCH_3$ in 50 mL of CH_3OH was added to 20.3 g (50 mmol) of 4,5-bis(benzoylthio)-1,3-dithiol-2-thione.[45] After the mixture was stirred for 20 min under nitrogen, a solution of 15.6 g (100 mmol) of C_2H_5I in 30 mL of CH_3OH was added dropwise to the deeply red solution. Stirring was continued for some hours until the solution became colorless. The solvent was removed in vacuo and 100 mL of CCl_4 was added to the residue. The mixture was washed with water (2 × 100 mL) and dried with Na_2SO_4. Fractional distillation yielded 12.0 g (95%) of 4,5-bis(ethylthio)-1,3-dithiol-2-thione, bp (0.07 torr) 154–156 °C: MS *m/e* 254 (M^+); IR (neat) $\tilde{\nu}_{max}$ 2980 cm^{-1}, 2930, 2880, 1450, 1380, 1260, 1070, 1035, 970, 890, 850, 760, 715; ^{1}H NMR ($CDCl_3$) δ 2.92, 1.36; ^{13}C NMR ($CDCl_3$) δ 210.9, 136.0 ($^3J_{^{13}CH}$ = 5.0 Hz), 30.8 ($^1J_{^{13}CH}$ = 144.0 Hz), 14.8 ($^1J_{^{13}CH}$ = 131.0 Hz).

Anal. Calcd for $C_7H_{10}S_5$: C, 33.04; H, 3.96; S, 63.00. Found: C, 33.33; H, 3.52; S, 62.82.

4,5-Bis(isopropylthio)-1,3-dithiol-2-thione (84% yield) was analogously prepared from 4,5-bis(benzoylthio)-1,3-dithol-2-thione[45] and isopropyl iodide: bp (0.05 torr) 145 °C; MS *m/e* 282 (M^+); IR (neat) $\tilde{\nu}_{max}$ 2970 cm^{-1}, 2935, 2875, 1455, 1385, 1370, 1240, 1155, 1070, 1050, 885; ^{1}H NMR ($CDCl_3$) δ 3.41, 1.36; ^{13}C NMR ($CDCl_3$) δ 211.8, 137.4 ($^3J_{^{13}CH}$ = 3.0 Hz), 41.6 ($^1J_{^{13}CH}$ = 142.5 Hz), 23.2 ($^1J_{^{13}CH}$ = 127.0 Hz).

Anal. Calcd for $C_9H_{14}S_5$: C, 38.26; H, 4.99; S, 56.74. Found: C, 38.16; H, 4.85; S, 56.66.

2,4,6,8-Tetrathiabicyclo[3.3.0]oct-1(5)-ene-7-thione. $NaOCH_3$ (5.4 g, 100 mmol) was added to a solution of 20.3 g (50 mmol) of 4,5-bis(benzoylthio)-1,3-dithiol-2-thione[45] in 300 mL of tetrahydrofuran. After the solution was stirred under nitrogen for 45 min a mixture of 13.4 g (50 mmol) of CH_2I_2 and 30 mL of tetrahydrofuran was added. Stirring was continued for 24 h under nitrogen. The solvent was evaporated in vacuo, $CHCl_3$ (250 mL) and powdered charcoal were added, and the stirred mixture was heated at reflux for 1 h. The solution was filtered, dried with Na_2SO_4 and concentrated in vacuo until red crystals appeared which were purified by sublimation (70–80 °C, ca. 0.1 torr) to yield 6.9 g (66%) of 2,4,6,8-tetrathiabicyclo[3.3.0]oct-1(5)-ene-7-thione, mp 158 °C: MS *m/e* 210 (M^+); IR (KBr) $\tilde{\nu}_{max}$ 1465 cm^{-1}, 1050, 1035, 1010, 950; ^{1}H NMR ($CDCl_3$) δ 4.96; ^{13}C NMR ($CDCl_3$) δ 212.9, 125.5 ($^3J_{^{13}CH}$ = 2.0 Hz), 43.0 ($^1J_{^{13}CH}$ = 155.5 Hz).

Anal. Calcd for $C_4H_2S_5$: C, 22.84; H, 0.96; S, 76.20. Found: C, 22.92; H, 0.99; S, 76.12.

4,5-Bis(ethylthio)-1,3-dithiol-2-one (20). A solution of 12.7 g (40 mmol) of $Hg(OAc)_2$ in 125 mL of glacial acetic acid was added to a solution of 10.2 g (40 mmol) of 4,5-bis(ethylthio)-1,3-dithiol-2-thione in 125 mL of $CHCl_3$ with rigorous stirring. The mixture was heated at reflux for 5 h and filtered through a funnel covered with Na_2SO_4. The Na_2SO_4 was washed with $CHCl_3$ (several times), and the total filtrate was stirred in an open flask while adding an equal amount of water and Na_2CO_3 in small portions to remove the glacial acetic acid from the organic phase. The $CHCl_3$ solution was washed twice with water, dried with Na_2SO_4, and concentrated in vacuo. The yellow residue was purified by distillation under reduced pressure to yield 9.2 g (97%) of pure **20**, bp (0.1 torr) 124–125 °C: MS *m/e* 238 (M^+); IR (neat) $\tilde{\nu}_{max}$ 2980 cm^{-1}, 2935, 2880, 1670, 1615, 1450, 1380, 1260, 1070, 1055, 970, 885, 765; ^{1}H NMR ($CDCl_3$) δ 2.87, 1.35; ^{13}C NMR ($CDCl_3$) δ 189.7, 127.1 ($^3J_{^{13}CH}$ = 5.0 Hz), 30.7 ($^1J_{^{13}CH}$ = 141.0 Hz), 14.8 ($^1J_{^{13}CH}$ = 128.0 Hz).

Anal. Calcd for $C_7H_{10}OS_4$: C, 35.27; H, 4.23; S, 53.80. Found: C, 35.50; H, 4.12; S, 53.65.

4,5-Bis(isopropylthio)-1,3-dithiol-2-one (21) (96% yield, bp (0.1 torr) 118–120 °C) and **2,4,6,8-tetrathiabicyclo[3.3.3]oct-1(5)-en-7-one (2)** (82% yield, mp 101 °C) were analogously prepared (except for the purification of **22** by sublimation at 60–70 °C and ca. 0.1 torr) from 4,5-bis(isopropylthio)-1,3-dithiol-2-thione and 2,4,6,8-tetrathiabicyclo[3.3.0]oct-1(5)-ene-7-thione.

Spectral data of **21**: MS *m/e* 266 (M^+); IR (neat) $\tilde{\nu}_{max}$ 2970 cm^{-1}, 2935, 2875, 1675, 1610, 1450, 1385, 1365, 1240, 1155, 1050, 885, 740; ^{1}H NMR ($CDCl_3$) δ 3.38, 1.35; ^{13}C NMR ($CDCl_3$) δ 190.1, 128.3 ($^3J_{^{13}CH}$ = 2.5), 41.3 ($^1J_{^{13}CH}$ = 143.0 Hz), 23.1 ($^1J_{^{13}CH}$ = 128.5 Hz).

Anal. Calcd for $C_9H_{14}OS_4$ (**21**): C, 40.57; H, 5.30; S, 48.13. Found: C, 40.60; H, 5.26; S, 48.38.

Spectral data of **22**: MS *m/e* 194 (M^+); IR (neat) $\tilde{\nu}_{max}$ 1660 cm^{-1}, 1600, 960, 875, 850, 740, 710, 685; ^{1}H NMR ($CDCl_3$) δ 4.73; ^{13}C NMR ($CDCl_3$) δ 192.8, 113.8 ($^3J_{^{13}CH}$ = 2.0 Hz), 38.3 ($^1J_{^{13}CH}$ = 155.5 Hz).

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Anal. Calcd for $C_4H_2OS_4$ (**22**): C, 24.72; H, 1.04; S, 66.00. Found: C, 24.70; H, 1.12; S, 66.07.

Preparation of Dimethyl Tetrathiooxalate (18) by Gas-Phase Pyrolysis. 4,5-Bis(methylthio)-1,3-dithiol-2-one (0.3 g, 1.4 mmol) was sublimed (150 °C) into a hot quartz tube (25 × 1.6 cm, 450 °C) and the pyrolysate collected in a liquid N_2 trap (pressure behind the trap ca. 5 × 10^{-3} torr). The pyrolysate was dissolved in acetone, filtered, and purified by column chromatography (2.5 × 10 cm, silica gel, 0.063–0.200 mm thick, CCl_4). The dark solution was concentrated and cooled to yield 0.14 g (54%) of pure **18**, mp 66 °C; MS *m/e* 182 (M^+); IR (KBr) $\tilde{\nu}_{max}$ 2990 cm^{-1}, 2910, 1410, 1395, 1310, 1080, 1050, 945, 770, 700; ^1H NMR ($CDCl_3$) δ 2.64.

Lit.[19]: mp 66 °C; IR (KBr) $\tilde{\nu}_{max}$ 2980 cm^{-1}, 2900, 1415, 1400, 1310, 1045, 945, 770, 700.

Note Added in Proof. Professor Heilbrohher has kindly provided us with a preprint of a paper[46] reporting the He I photoelectron spectra of some stable 1,2-olithietes, including the recently synthesized 3,4-di-*tert*-butyl-1,2-dithiete.[47]

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The calculations were carried out on the TR 440 computer at the University of Marburg. We thank Dr. G. Schaden for performing preparative pyrolysis experiments.

Registry No. 1, 360-91-8; **8**, 2314-40-1; **9**, 49675-88-9; **10**, 934-31-6; **11**, 7092-01-5; **12**, 23783-27-9; **14**, 74378-81-7; **18**, 61485-47-0; **19**, 61485-46-9; **20**, 85720-61-2; **21**, 77102-71-7; **22**, 85720-62-3; **23**, 74962-29-1; **24**, 74962-30-4; **25**, 85720-63-4; **26**, 85720-64-5; 4,5-dimethyl-1,3-dithiol-2-thione, 17534-27-9; 4,5-bis(ethylthio)-1,3-dithiol-2-thione, 59065-21-3; 4,5-bis(isopropylthio)-1,3-dithiol-2-thione, 77102-72-8; 2,4,6,8-tetrathiabicyclo[3.3.0]oct-1(5)-ene-7-thione, 70800-59-8.

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Variable Pressure and Temperature Nuclear Magnetic Resonance and Visible Spectrophotometric Studies of Lanthanide Ions in Dimethylformamide: Solvation and Solvent Exchange Dynamics[1]

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Contribution from the Institut de chimie minérale et analytique, University of Lausanne, 3, Place du Château, 1005 Lausanne, Switzerland. *Received December 13, 1982*

Abstract: The equilibrium $[Ln(DMF)_8]^{3+} + DMF \rightleftharpoons [Ln(DMF)_9]^{3+}$ has been studied in solutions of lanthanide perchlorates. For Nd the following thermodynamic parameters were obtained from spectrophotometric studies: $\Delta H = -14.9 \pm 1.3$ kJ mol^{-1}, $\Delta S = -69.1 \pm 4.2$ J K^{-1} mol^{-1} and $\Delta V = -9.8 \pm 1.1$ cm^3 mol^{-1}. The NMR study of Ln = Ce–Nd and Tb–Yb shows that the coordination equilibria also take place for the other light lanthanides. At room temperature the major species is $[Ln(DMF)_8]^{3+}$ when Ln = Ce–Nd, and this becomes the only stable species when Ln = Tb–Lu. Characteristic ^{17}O, ^{13}C, and ^1H NMR shifts for $[Ln(DMF)_8]^{3+}$ are also reported. Kinetic parameters for the exchange of DMF on $[Ln(DMF)_8]^{3+}$ (Ln = Ty–Yb) have been determined by variable temperature and pressure ^1H NMR in neat DMF. For Tb, ΔH^* (kJ mol^{-1}), ΔS^* (J mol^{-1} K^{-1}) and ΔV^* (cm^3 mol^{-1}) are respectively 14.1 ± 0.4, −58 ± 2, and +5.2 ± 0.2 while for Yb the corresponding values are 39.3 ± 0.6, +40 ± 3, and +11.8 ± 0.4. The observed systematic variations in activation parameters from Tb to Yb are interpreted in terms of a mechanistic crossover at Er. Kinetic rate law determinations in CD_3NO_2 diluent indicate than an interchange mechanism operates for Tb ($K_{os} = 0.5$ mol^{-1} kg at 231 K) whereas a D mechanism is operative for Yb.

Introduction

The tripositive lanthanides constitute the longest series of chemically similar metal ions and exhibit a steady decrease in ionic radius of from lanthanum to lutecium. In view of the insignificance of effects attributable to ligand fields (e.g., preference for certain coordination polyhedra) or ligand π orbital back-bonding, a study of these ions in solution provides an opportunity to closely assess any observed variations in solvation and solvent exchange kinetics in simple electrostatic and steric terms.

While considerable effort has gone into attempts at understanding lanthanide hydration and the kinetics of water exchange, it appears that the inherently great labilities of these ions are largely responsible for the paucity of accurate data. Indeed, Marcus[3] has recently discussed lanthanide aquo ions from various standpoints and has highlighted a large number of uncertainties. For example, controversy[4,5] still exists as to whether there is a change in coordination number (nine to eight) across the series. From a kinetic viewpoint, extension of the research dealing with aqueous solutions to include nonaqueous solvents has been informative and has yielded accurate DMF (*N*,*N*-dimethylformamide) exchange parameters for $[Tm(DMF)_8]^{3+}$ by ^{13}C and ^1H NMR.[6] The present work seeks to establish the kinetics and mechanisms of DMF exchange for other members of the lanthanide series by variable temperature and pressure studies.

Experimental Section

A. Materials and Preparation of Solutions. Lanthanide oxides (Research Chemicals, 99.9%) and hydrated cerium(III) perchlorate (Ventron) were used as received. DMF (Fluka, puriss) was purified by fractional distillation at reduced pressure. Benzene (Merck, p.a.), dichloromethane, and nitromethane (Fluka, puriss) were redistilled before

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[1] This paper is to be considered part 19 of the series, "High Pressure NMR Kinetics". For part 18, see ref 2.

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