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¹ Mikkelsen, D. S., and Toth, S. J., *J. Amer. Soc. Agron.*, **39**, 165 (1947).

² Bradfield, E. G., *Analyst*, **85**, 666 (1960).

³ Bradfield, E. G., *Anal. Chim. Acta*, **27**, 262 (1962).

⁴ Schachtschabel, P., *Z. Pflanzenernähr. Düng. Bodenk.*, **67**, 9 (1954).

Charge Transfer Properties of *dl*-Thioctic Acid and Other Disulphides

THE ability of organic sulphur compounds to act as donors with electron acceptor molecules is well established. As far as disulphides are concerned, previous studies have been limited to simple aliphatic compounds with iodine as the acceptor¹. In these systems, the charge transfer (CT) band appears between the disulphide absorption and the blue-shifted iodine absorption, and its position appears to be little affected by changing the alkyl groups. We wish to report that alkyl aryl and cyclic disulphides form 1 : 1 complexes in solution with tetracyanoethylene (TCNE), which show well-separated CT bands in the visible region. Further, the position of these bands clearly reflects steric and electronic factors in the disulphide molecule.

The complexes are readily generated by mixing rigorously purified solutions of the donor and acceptor. Special care must be taken to remove thiols, which are the major impurities in disulphides, since these react with TCNE. Table 1 lists some representative spectral data; several sulphides are included for comparison. It is apparent that (1) simple alkyl disulphides show a progressive decrease in CT transition energy with increasing chain length; (2) branched chain complexes absorb at longer wave-lengths than the corresponding straight chain complexes; (3) for disulphides, ring closure has a larger effect on the CT transition than elongation of the alkyl chain, while the opposite is the case for sulphides. The complexes have low formation constants (K_c , l./mole) and molar extinction coefficients (ϵ). In dichloromethane at 25° typical values are: methyl disulphide $K_c=0.16$, $\epsilon=2,100$; *tert.*-butyl disulphide $K_c=0.36$, $\epsilon=4,500$; *dl*-thioctic acid $K_c=1.22$, $\epsilon=6,500$. The corresponding enthalpies of formation are -0.4 , -1.5 , and -7.2 kcal/mole. Based on the photoionization value of 8.46 eV for methyl disulphide², we estimate the ionization potentials of *tert.*-butyl disulphide and *dl*-thioctic acid to be 7.78 and 7.53 eV, respectively. The general trend of these data may be rationalized in terms of the increased inductive (electron-releasing)-effect of the larger alkyl groups, and the decrease in the dihedral angle between the adjacent sulphur 3- $p\pi$ orbitals which accompanies an increase in the size of the group or ring closure³. Both factors would be expected to enhance the stability of the complex.

Apart from the CT band, the complexes show absorption arising from the complexed components. Resolution of the spectrum of a TCNE-*dl*-thioctic acid solution (Fig. 1) reveals that the band associated with the —S—S— group

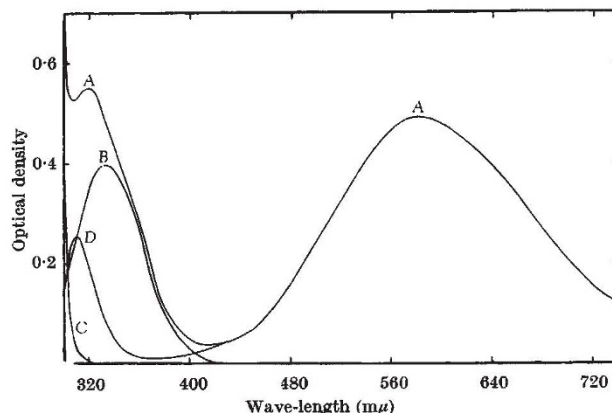


Fig. 1. Resolution of spectrum of dichloromethane solution, 2.786×10^{-2} M in *dl*-thioctic acid and 4.726×10^{-2} M in TCNE. A, Total absorption; B, free —S—S—; C, free TCNE; D, complexed —S—S—

of the complexed acid (curve D) is shifted to shorter wave-lengths by about 23 mμ, relative to that of the free acid (curve B). With TCNE-ethyl disulphide the component absorptions overlap, and the complexed —S—S— band cannot be clearly separated from the complexed TCNE band. The shift is estimated to be 0.6 mμ to longer wave-lengths. For ethyl disulphide, complexation can be envisaged to increase the dihedral angle¹ with consequent lowering of the transition energy. No such structural adaptation occurs with the rigid cyclic disulphide. Consideration of the orientation of the donor orbitals indicates that the two complexes would differ in geometry, particularly with respect to symmetry in the donor-acceptor bond region, and that consequently the perturbation of these orbitals would be different. A forthcoming publication will elaborate this concept.

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¹ McGlynn, S. P., Nag-Chaudhuri, J., and Good, M., *J. Amer. Chem. Soc.*, **84**, 9 (1962) (earlier references are cited).

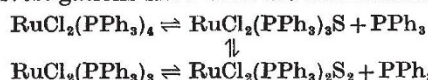
² Watanabe, K., Nakayama, T., and Motil, J., *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

³ Bergson, G., *Arkiv Kemi*, **12**, 233 (1957).

Homogeneous Hydrogenation and Hydroformylation using Ruthenium Complexes

WE have shown¹ that the rhodium (I) complex, $\text{RhCl}(\text{PPh}_3)_3$, is an extremely efficient catalyst for the homogeneous hydrogenation of olefines and acetylenes at 25° C and at < 1 atmosphere pressure in benzene solutions. This activity is due, in part, to the dissociation of the complex in solution to give a solvated species $\text{RhCl}(\text{PPh}_3)_2\text{S}$, which has a vacant co-ordination site additional to the solvent-occupied axial positions.

We now find that the ruthenium (II) complexes, $\text{RuCl}_2(\text{PPh}_3)_4$ and $\text{RuCl}_2(\text{PPh}_3)_3$, prepared respectively by the interaction of cold and refluxing methanol solutions of hydrated ruthenium trichloride with excess triphenylphosphine, dissociate in benzene solutions². Molecular-weight investigations show that the dissociation is:



Since the solutions are sensitive to air, the colour changes reported³ for solutions of $\text{RuCl}_2(\text{PPh}_3)_3$ are probably attributable to oxidation.

Table 1. CHARGE TRANSFER MAXIMA OF TCNE-SULPHUR COMPLEXES IN DICHLOROMETHANE SOLUTION

Donor	λ_{max} (mμ)	Donor	λ_{max} (mμ)
Alkyl, aryl disulphides:		Cyclic disulphides:	
Methyl	425	Tetramethylene	535
Ethyl	450	Trimethylene	575
<i>n</i> -Propyl	453	<i>dl</i> -Thioctic acid	583
<i>n</i> -Butyl	460	Sulphides:	
<i>iso</i> -Propyl	465	Ethyl	505
<i>tert.</i> -Butyl	530	<i>n</i> -Butyl	530
Cyclohexyl	525	Phenyl	590
Phenyl	515	Pentamethylene	495
Mesityl	430	Tetramethylene	515