Mikrochimica Acta [Wien] 1969, 62—77

Chemistry Department, Birmingham University, Birmingham 15,
Great Britain

The Properties of Dithiocarbamates

A Review

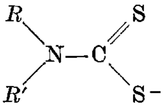
By

D. J. Halls*

With 1 Figure

(Received March 4, 1968)

In recent years, numerous papers have appeared on the use of dithiocarbamates as analytical reagents. As has been known for some time[1], these compounds possess the important property of being able to form complexes with many metal ions. These reactions, the basis of the analytical application of dithiocarbamates, have been the subject of a recent comprehensive review[2].



$R, R' =$ H, Alk, Ar

I

The purpose of the present review is to discuss recent contributions to our knowledge of the other important physical and chemical properties of dithiocarbamates (I). Nearly all the papers on these compounds have dealt solely with the properties of dialkyldithiocarbamates and little mention has been made of the properties of monoalkyldithiocarbamates. This is perhaps because of the general instability of monoalkyldithiocarbamates and their complexes, as a result of which they have found little use analytically. In this review, it is intended, wherever possible, to compare the properties of mono- and dialkyldithiocarbamates.

---

* Present Address: Analytical Chemistry Department, University of Chemical Industries, Veszprém, Hungary.

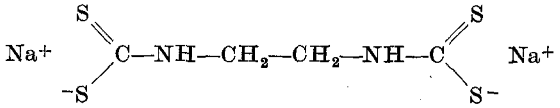
Synthesis

Dithiocarbamates are formed by the exothermic reaction between carbon disulphide and either ammonia or a primary or secondary amine in the presence of a base. The base may be an alkali such as sodium hydroxide or excess of the amine. The kinetics and mechanism of the formation of dithiocarbamates have been studied[3–5]. The rate of formation is inversely proportional to the p_H and it is believed to follow a mechanism that is the reverse of the decomposition in acid media[6,7] (Fig. 1).

Ammonium dithiocarbamate is produced[8] by the reaction of ammonia and carbon disulphide. The free dithiocarbamic acid can be obtained by treatment of the ammonium dithiocarbamate with cold acid. It is, however, unstable and decomposes to thiocyanic acid and hydrogen sulphide.

Monoalkyldithiocarbamates are formed from the exothermic reaction between carbon disulphide and a monoalkylamine; they decompose, however, on long standing in alkali. No such difficulty is experienced in the preparation of dialkyldithiocarbamates.

If a diamine such as ethylene diamine is used, a molecule with dithiocarbamate groups at either end can be obtained [e. g. disodium ethylenebisdithiocarbamate (IV)].



IV

The preparation of many dithiocarbamates from more complicated amino-compounds has been described; for these, special conditions are often necessary[8,9].

The sodium salts are extremely soluble in water and quite soluble in ethanol, but relatively insoluble in non-polar solvents such as ether and chloroform. Most of the sodium salts are hydrated.

Stability in acidic and alkaline solution

The free acids, which are formed from dithiocarbamates in acidic media, are generally unstable; diphenyldithiocarbamic acid is, however, said to be stable[10]. *Martin*[11] first showed the importance of the decomposition of diethyldithiocarbamic acid in the development of methods based on diethyldithiocarbamate as an analytical reagent; previously methods had been published which advocated the use of diethyldithiocarbamate at low p_H. However, *Bode*[12] was the first to examine quantitatively the acid decomposition of sodium diethyldithiocarbamate. He found that the decomposition at constant p_H was first order and that the rate

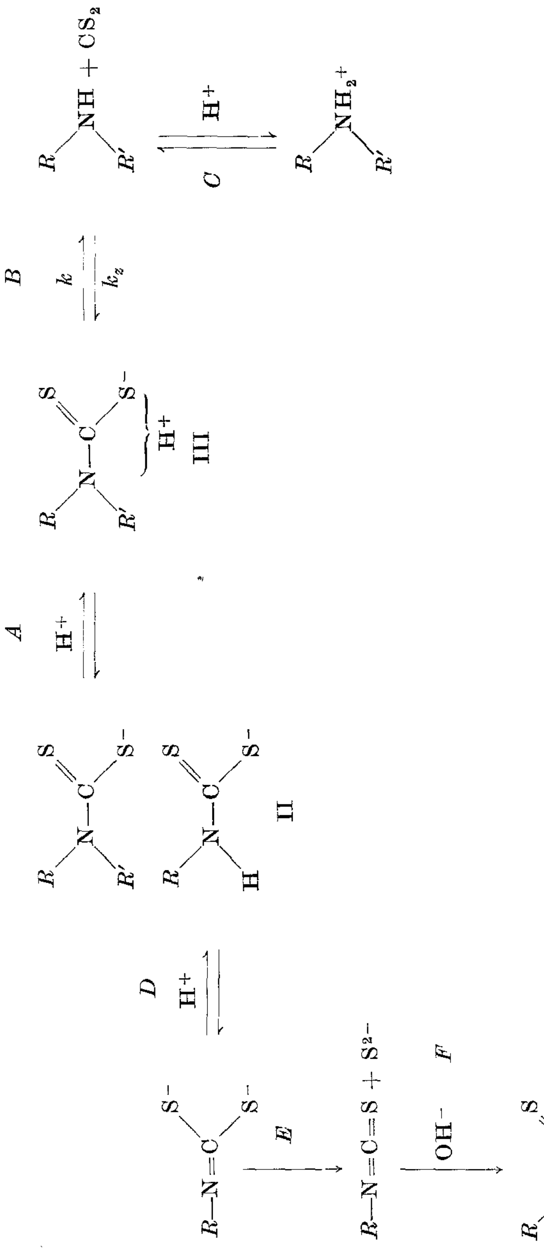


Fig. 1. The mechanism of synthesis and decomposition of dithiocarbamates

was proportional to the hydrogen ion concentration. The half-life of diethyldithiocarbamate at p_H 2 (0.3 seconds) illustrates the extreme instability of this compound at low p_H. Other dithiocarbamates, such as pyrrolidinedithiocarbamate and dibenzyldithiocarbamate, are far more stable at low p_H.

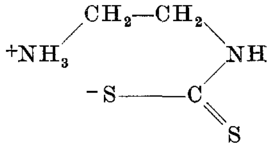
Zuman and *Zahradník*[6,7] studied polarographically the kinetics of decomposition of mono- and dialkyldithiocarbamates. They found that the measured rate constant when plotted against p_H took the form of a dissociation curve. This is explained by a protonation (Fig. 1, reaction *A*) preceding the decomposition (reaction *B*). The equilibrium *B* can not be measured because of the transfer of protons at *A* and *C*. The protonated form (III) is decomposed into the amine and carbon disulphide with reaction rate *k*. The equilibrium *C* is so shifted towards $RR'NH_2^+$ that the rate of the back reaction k_Z is insignificant. By this mechanism, they also explained the formation of dithiocarbamates in alkaline solutions from the amine and carbon disulphide.

Monoalkyldithiocarbamates were found to be more stable than dialkyldithiocarbamates in acid solutions. Indeed the limiting rate of decomposition of most dialkyldithiocarbamates at low p_H was so high that it could not be measured. This was explained by the steric influence of the second alkyl group causing a higher strain on the C–N bond. Moreover, the monoalkyldithiocarbamates showed a lower pK value than the corresponding dialkyldithiocarbamates. The inductive effect of the second alkyl group increases the electron density on the nitrogen which stabilises the ammonium form or influences the polarity of the S–H bond; the position of the hydrogen atom in the protonated form (III) was not known.

Zahradník[13] has studied the kinetics and mechanism of the decomposition of dithiocarbamylcarboxylic acids. These follow essentially the same mechanism as in Fig. 1 and do not form a thiazolidone ring as was observed for dithiocarbamates formed from the amides of amino-acids and from peptides.

The mechanism of decomposition in acid media has been studied further by *Miller* and *Latimer*[3]. By a comparison of the ultra-violet spectrum of the acid form of methyldithiocarbamic acid with that of the methyl ester, they concluded that $RR'NCSSH$ rather than a zwitterion was the acid form. They found further evidence in the high pK_a of β-aminoethyldithiocarbamic acid, the anion of which is stabilised in the form V; if the second proton were to attach itself to the nitrogen atom, the stability of V would have little influence on the pK_a. Because the proton attaches itself to the sulphur atom and because the disruption of the stable ring form is unfavourable, β-aminoethyldithiocarbamic acid has an anomalous pK_a.

The initial step in the synthesis and decomposition is therefore the transfer of a proton between the nitrogen and sulphur atoms.



V

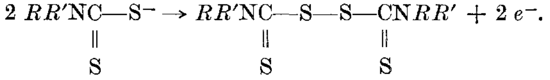
On the basis of conductimetric and potentiometric titrations of sodium diethyldithiocarbamate with acids, *Soni* and *Trivedi*[14] concluded that diethyldithiocarbamate is a diacidic base. However, the second inflection they observed in their experimental curves was probably due to the uptake of a proton by the amine liberated in the decomposition of the dithiocarbamate.

Dialkyldithiocarbamates are stable in alkaline solution, but monoalkyldithiocarbamates can undergo a reaction with hydroxide ions. *Wronski*[15] studied the kinetics of this reaction and found that, at constant concentration of hydroxide, it was first order. The rate was not proportional to the concentration of hydroxide but reached a limiting value with increasing hydroxide concentration. This was explained by the scheme shown in Fig. 1 (reactions *D* and *E*). The *pK* of equilibrium *D* appeared to be about 13. No evidence for the nature of the products was given. Isothiocyanates, if formed, would undergo a further reaction[16] to give monothiocarbamates (Fig. 1, reaction *F*).

Turner and *Cordon*[17] examined the decomposition of sodium methyldithiocarbamate in the presence of air at p_H 9.5 and found that methyl isothiocyanate and elemental sulphur were formed. No methyl isothiocyanate was formed in the absence of air.

Oxidation

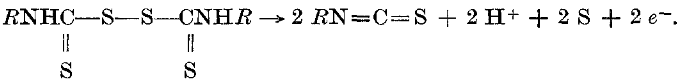
Dialkyldithiocarbamates form[18] thiuram disulphides on oxidation with iodine, bromine, potassium ferricyanide, iron(III) chloride or hydrogen peroxide:



$$2\,RR'N\underset{\underset{S}{\|}}{C}\text{—}S^- \rightarrow RR'N\underset{\underset{S}{\|}}{C}\text{—}S\text{—}S\text{—}\underset{\underset{S}{\|}}{C}NRR' + 2\,e^-.$$

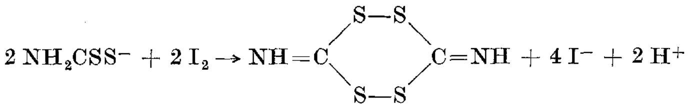
These thiuram disulphides are insoluble in aqueous solvents.

It is also reported[18] that the oxidation of monoalkyldithiocarbamates possibly goes further to form the isothiocyanate and elemental sulphur



$$RNH\underset{\underset{S}{\|}}{C}\text{—}S\text{—}S\text{—}\underset{\underset{S}{\|}}{C}NHR \rightarrow 2\,RN{=}C{=}S + 2\,H^+ + 2\,S + 2\,e^-.$$

Wronski[15] examined the iodine titration of dithiocarbamate and postulated two reactions which occurred under different conditions.

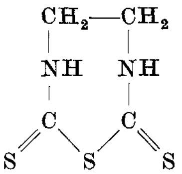


VI

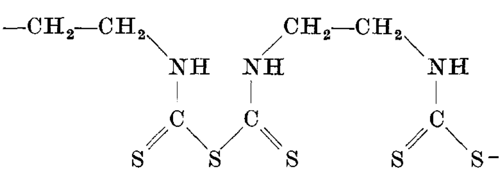
$$2\,NH_2CSS^- + I_2 \rightarrow NH_2CS{-}S{-}S{-}CSNH_2 + 2\,I^-.$$

No evidence for the nature of the product VI was given.

The aeration of disodium ethylenebisdithiocarbamate has been studied by *Thorn* and *Ludwig*[19], and has been found to give ethylenethiuram monosulphide (VII), polymeric 1,2-imidazolidinethione (VIII) and elemental sulphur.



VII



VIII

The Metal Complexes

The complexes of dithiocarbamates with heavy metals are prepared simply by adding a solution of the heavy metal to a solution of ammonium or alkali metal dithiocarbamate. These complexes are generally sparingly soluble in water but are more soluble in non-polar organic solvents such as chloroform, carbon tetrachloride and ether. The lead, zinc and mercury(II) salts are colourless, but the copper, nickel, cobalt and iron complexes are intensely coloured. These intense colours have been made the basis of numerous spectrophotometric analytical methods (see for example *Welcher*[20], *Reid*[9], *Thorn* and *Ludwig*[8], and *Sandell*[21]).

As previously mentioned, these reactions have already been covered in a review by *Hulanicki*[2], to which the reader is referred. The following references, not covered in that review, may also be of interest.

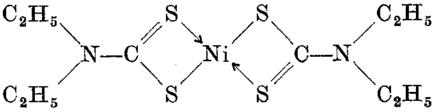
These dithiocarbamate complexes have the formula $(R_1R_2NCS_2)_2M$ where M is a bivalent metal. Dialkyldithiocarbamates form only this type of complex, but monoalkyldithiocarbamates can form at high p_H a further transient complex of the type $(R_1NCS_2)M$ which decomposes subsequently to the metal sulphide and isothiocyanate[22].

$$\begin{array}{l} (R_1NHCS_2)_2M + M^{2+} + 2\,OH^- \rightarrow 2\,R_1NCS_2M + 2\,H_2O \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\quad 2\,R_1{-}N{=}C{=}S + 2\,MS. \end{array}$$

The formation of this second unstable complex is dependent on the presence of a proton attached to the nitrogen atom in the dithiocarbamate molecule.

A number of important papers on the properties of dithiocarbamates of the heavy metals have been published by *Akerström*. Copper(I) dialkyldithiocarbamates have a trimeric or tetrameric structure in the solid state[23]. In inert organic solvents, they have a tetrameric structure, whereas silver(I) and gold(I) complexes have hexameric and dimeric structures respectively[24]. Thallium(I) dialkyldithiocarbamates, which are dimeric in organic solvents, react with thiuram disulphides to give thallium(III) dialkyldithiocarbamates[25,26]. Similarly the dialkyldithiocarbamates of the univalent coinage metals [Ag(I), Cu(I), Au(I)] readily react with thiuram disulphides to give the bivalent complexes[27]. Thus dithiocarbamates have a tendency to stabilise the higher oxidation state of the metal, as for example in the blue silver(II) complex, the existence of which was proved by ESR[28].

The crystal structures of some of the complexes have shown that the N–C bond in the complexes has a partial double-bond character. The nickel diethyldithiocarbamate molecule (IX) is approximately planar and the N–C bond order has been estimated[29] to be 1.30. In the copper[30,31] and zinc[32] diethyldithiocarbamate molecules, only the diethyldithiocarbamate radical is planar, but similarly the N–C bond order indicates a partial double bond.



IX

Thompson and *Moyer*[33] have described the preparation and properties of polymeric complexes of ethylenebisdithiocarbamate and hexamethylenebisdithiocarbamate. The polymers were practically insoluble in all organic solvents. In dilute solutions, where presumably polymers do not form, it has been shown that two types of complex can form at high pH[34]. The first, which has a 1 : 1 bivalent metal : ligand ratio, is partially soluble in aqueous solutions and gives rise to cathodic polarographic waves. The other, having a 2 : 1 metal : ligand ratio, is insoluble in water. It is unstable and decomposes to give the metal sulphide in the same way as the monoalkyldithiocarbamate complexes discussed previously.

Spectra

Ultraviolet spectra

Dithiocarbamates show three absorption maxima in the ultraviolet region of the spectrum.

A. A low intensity absorption ($\log \varepsilon \sim 1.8$) at a maximum between 330 and 360 nm.

B. A band ($\log \varepsilon \sim 4$) with maximum absorption between 275 and 296 nm.

C. A band ($\log \varepsilon \sim 4$) with maximum absorption between 240 and 260 nm.

Band A was found by *Janssen*[35] to have the characteristics of an $n \rightarrow \pi^*$ transition, i. e. the transition of an electron of the lone pair on a sulphur atom to an anti-bonding π-orbital.

Bands B and C were assigned originally by *Koch*[36] to the S—C=S group and N—C=S group respectively as a result of a comparison of the spectra of the dithiocarbamates with tetramethylthiourea. Later, *Janssen*[35] showed that this assignment ought to be reversed. A number of organic thiones was examined and the bands were classified according to their intensities and solvent effects. As band C was also found[37] in organic thiones not containing nitrogen, it was associated with the S—C=S group. Moreover, band C was the only absorption, besides band A, shown in the spectra of thioureas, and should be assigned to the N—C=S group. Further evidence for this assignment was provided by *Shankaranarayana* and *Patel*[38] from a comparison of the spectra of dithiocarbamates with those of xanthates and trithiocarbonates.

Band B was assigned by *Janssen* to an $n \rightarrow \sigma^*$ transition on the basis of his experimental evidence, but later[39] it appeared from LCAO MO calculations of the transition energies that band B was a $\pi \rightarrow \pi^*$ transition.

Band C has been assigned[37,38] to a $\pi \rightarrow \pi^*$ transition on the basis of the effect of polar solvents on its wavelength.

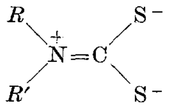
Zahradník[40] has reported the ultraviolet spectra of dithiocarbamoyl carboxylic acids. He compared their spectra with those of other sulphur compounds reported in the literature and assigned the bands in the same way as *Koch*[36]. He also studied the spectra of monothiocarbamates[41] which show only one peak at about 226 nm.

Infrared spectra

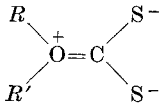
Dithiocarbamates show two strong absorption bands in the infrared which have received especial attention.

I. A band around 1500 cm^{-1}, known as the "thioureide" band.

II. A band in the region 1030–950 cm^{-1}.



X



XI

Canonical form X has been shown by *Chatt* et al.[42] to contribute to some considerable extent to the overall structure of dithiocarbamates. Band I, which is characteristic of the N—C=S system, appears in the double-bond region of the spectrum and was assigned to the stretching of the N—C partial double bond. Further evidence for the partial double bond was provided[43] by the high dipole moment of the dithiocarbamate esters and monoalkyldithiocarbamates. Xanthates, for which the corresponding canonical form XI contributes much less, show comparatively low dipole moments[43] and absorb between 1140 and 1260 cm^{-1}.[44] To account for the high dipole moments of the dithiocarbamates, the bond order must have been about 1.25–1.35[43].

The importance of the form X arises from the strong mesomeric electron-releasing property of the $-NR_2$ group and also the ability of the sulphur atom to accept electrons into its *d*-orbitals. The placing of a negative charge on the sulphur atoms would be expected to weaken the drift of electrons towards the sulphur atoms, thus lowering the C—N bond order and the frequency of band I. Such a lowering was indeed noted[43]. Furthermore, the metal complexes, which would be expected to show an increased drift of electrons towards the sulphur atoms, show the highest frequency. A slight decrease in bond order was observed with an increase in the size or number of alkyl groups. *Nakamoto* et al.[45] examined the spectra of a number of complexes and suggested that canonical form X contributes to an even greater extent than *Chatt* et al.[43] had proposed.

Shankaranarayana and *Patel*[44] who compared the infra-red spectra of xanthates, dithiocarbamates and trithiocarbonates, concluded that band II was due to the C=S group. With a greater contribution of the canonical forms X and XI, the frequency of absorption was lowered, and so band II appeared around 980 cm^{-1} in dithiocarbamates but around 1030 cm^{-1} in xanthates. On the formation of the dithiocarbamate anion, band II shifted to a lower frequency because of the lower C=S band order. Additional evidence for the assignment of band II to the C=S group was provided by *Jensen* et al.[46] who compared the spectra of dithiocarbamates with diselenocarbamates. The former showed a strong band around 1000 cm^{-1} whereas the latter showed a band near 900 cm^{-1}. Otherwise the spectra were more or less identical.

Mann[47] has recorded the infrared spectra of a number of dithiocarbamates used as accelerators and antioxidants and has used their spectra as a means of their identification in vulcanisates.

The Polarographic Behaviour

Although it was originally stated that the anodic waves of dithiocarbamates were due to the oxidation of the dithiocarbamate to the thiuram disulphide[48], it was later shown that they were in fact due to the formation of a mercury compound[49]. Thus the polarographic behaviour of dithiocarbamates is related to the reactions with heavy metals discussed earlier.

Most attention has been paid to the polarographic behaviour of dialkyldithiocarbamates[48–57]. Sodium diethyldithiocarbamate gives a single diffusion-controlled anodic wave (W_1) with an adsorption pre-wave (W_A)[48,52,54,57]. This adsorption pre-wave has been shown to correspond to the formation of a layer of mercuric diethyldithiocarbamate molecules adsorbed flat on the mercury surface[52]. At concentrations above $2 \cdot 10^{-4}$ M, the limiting current of the main wave becomes larger than expected, resulting in a non-linear concentration dependence[54] and the current oscillations at the limiting current become very irregular[57]. At higher concentrations, this current increase takes the form of a rounded maximum[53,54,57]. Similar irregularities are found in the polarographic behaviour of sodium dimethyldithiocarbamate[55]. These irregularities may be overcome by addition of gelatin or the use of ethanolic solutions[54,57].

Stricks and *Chakravarti*[54] explain this anomalous current increase as due to the formation of a secondary porous layer around the primary adsorption layer. This secondary layer is able to absorb relatively large amounts of dithiocarbamate from the solution. This accumulation of dithiocarbamate around the drop is said to explain the increase in current. However, it should be noted that any absorption of the electroactive species around the drop would still be governed by its rate of diffusion to the area of the drop and so the current must still necessarily be diffusion-controlled. *Zuman* et al.[57] suggest that the anomalous behaviour is due to the bursting of a further unstable adsorption layer formed on the mercury surface. The irregular bursting of this layer causes stirring in the vicinity of the drop which brings more dithiocarbamate to the surface, resulting in an increase in the current.

The waves of diethyldithiocarbamate correspond to an overall one-electron process to form mercury(I) diethyldithiocarbamate which subsequently is converted into mercury(II) diethyldithiocarbamate[54,57].

$$(C_2H_5)_2NCS_2^- + Hg \rightleftharpoons (C_2H_5)_2NCS_2Hg + e^-,$$

$$2\,(C_2H_5)_2NCS_2Hg \rightleftharpoons [(C_2H_5)_2NCS_2]_2Hg + Hg.$$

Monoalkyldithiocarbamates differ from dialkyldithiocarbamates in that they show, at more positive potentials than that of W_1, a further one-electron wave (W_2) which shifts to more negative potentials with increasing p_H[22]. At p_H 8, the two waves W_1 and W_2 coalesce to form a single wave W involving the over-all transfer of two electrons. This wave W shifts to more negative potentials with increasing p_H. This further one-electron process is believed to be due to the loss of a proton and to the formation of the second type of complex described earlier in the section on metal complexes.

Similar behaviour was observed by *Zahradník* and *Jensovsky*[58–60] for the monoalkyldithiocarbamates derived from amino-acids. However they concluded from a logarithmic plot that the over-all process involved one electron.

Disodium ethylenebisdithiocarbamate gives very complicated anodic waves[34] corresponding to an over-all four-electron electrode reaction. At low concentrations a similarity can be seen to the polarographic behaviour of the simple monoalkyldithiocarbamates.

Sodium diethyldithiocarbamate has proved to be a useful reagent for amperometric titrations, both at the rotating D. M. E.[54] and at the rotating platinum electrode[61–64]; other dithiocarbamates have also been used[65, 66]. Also the cathodic waves of some metal diethyldithiocarbamates in organic solvent mixtures have been examined and used for the determination of trace metals[67–70].

Uses of Dithiocarbamates

The most widespread use of dithiocarbamates is found in the rubber industry where they are used as vulcanisation accelerators. At the same time, they have good anti-oxidant properties which makes them even more valuable. These anti-oxidant properties are also put to good use in greases and oils.

Another use of dithiocarbamates which has become more important in recent years is as fungicides. The most important of these are disodium ethylenebisdithiocarbamate (known commercially as Nabam), its zinc and manganese complexes (Zineb and Maneb) and the zinc and iron complexes of dimethyldithiocarbamic acid (Ziram and Ferbam).

Analysis of dithiocarbamates

Methods for the analysis of dithiocarbamates can be divided into two groups. (*a*) Determination of the purity of dithiocarbamates for use in laboratory work, etc. (*b*) Determination of the amount of dithiocarbamates in fungicides and also in fungicide residues. Included also are methods for the determination and identification of accelerators in rubber. Surprisingly however, far more attention has been paid to the determination of fungicides than the determination of vulcanisation accelerators.

(*a*) Iodimetric methods for the determination of dithiocarbamates have been proposed[71, 72]. Although these were suggested as general methods for dithiocarbamates, only dialkyldithiocarbamates were given as examples. *Linch*[71] found that a gravimetric method, based on weighing the thiuram disulphide formed after oxidation, is even more accurate than the iodimetric method. A more sensitive reagent is chloramine-T[73], of which fourteen equivalents are consumed per mole of dithiocarbamate.

The amount of acid consumed in the decomposition of dithiocarbamates has been used as the basis of another method[74]. Two equivalents of acid are consumed per mole of dithiocarbamate - one to give the dithiocarbamic acid and the second to neutralise the liberated amine. Again only dialkyldithiocarbamates were examined.

(*b*) Most methods for the determination of fungicides are based on decomposing the dithiocarbamate in acidic conditions and determining the carbon disulphide evolved. The *Clarke* method[75] is the basis of most methods in use today. The dithiocarbamate is decomposed by heating with 1.1 *N* sulphuric acid and the liberated carbon disulphide is adsorbed in methanolic potassium hydroxide to give potassium methyl xanthate. After decomposition is complete, the xanthate is determined by an iodimetric titration. The conditions of acid digestion are quite critical, particularly for ethylenebisdithiocarbamates. *Bighi* and *Saglietto*[76] have studied chromatographically the decomposition of ethylenebisdithiocarbamates in the *Clarke* method[75]. *Roth* and *Beck*[77] used a mixture of pyridine and phosphoric acid to decompose the dithiocarbamate.

Stevenson[78] has reported the result of a collaborative study on methods of dithiocarbamate evaluation in which a modified *Clarke* method was proposed; this method was adopted by the Collaborative Pesticides Analytical Committee of Europe (CPAC). A similar method[79] was adopted in America.

For the determination of pesticide residues, the usual method[80, 81] is to decompose the dithiocarbamate to carbon disulphide and to determine the carbon disulphide spectrophotometrically by absorbing it in an ethanolic solution of copper acetate and an alkylamine and then measuring the absorbance of the resulting solution. Polarographic methods have also been suggested for the determination of residues of Zineb[82–84], Maneb[85], Ziram[86] and Ferbam[87]. *Rozaci*[88] used a polarographic method for the determination of the accelerators zinc diethyldithiocarbamate and zinc phenylethyldithiocarbamate in rubber.

Paper chromatography has been used to separate the dithiocarbamates[89], and infrared spectra[90] to identify the various pesticides. An infrared method has also been suggested[91] as a quantitative method for Maneb.

Conclusion

Although the early work[1] showed the properties of both mono- and dialkyldithiocarbamates, more recent systematic studies have shown very little interest in monoalkyldithiocarbamates. However, monoalkyldithiocarbamates have shown behaviour differing from dialkyldithiocarbamates in their stability in acid[6, 7], their stability in alkali[15], their reactions with metals[22] and with oxidising agents[18, 92], and their polarographic behaviour[22, 57]. Most of these differences are a result of the ability of monoalkyldithiocarbamates to lose a proton from the nitrogen atom in solutions of high p_H and to undergo further reactions. Dialkyldithiocarbamates have no proton to lose and so cannot undergo these reactions.

The author wishes to thank Prof. *R. Belcher*, Dr. *P. Zuman*, and Dr. *A. Townshend* of the University of Birmingham, England, and Prof. *E. Pungor* of the University of Chemical Industries, Veszprém, Hungary, for their advice and interest in this work.

Summary

The Properties of Dithiocarbamates

A review of the properties of dithiocarbamates is presented in which a comparison is made of the properties of mono- and dialkyldithiocarbamates. The various sections deal with the synthesis of dithiocarbamates, their stability in acidic and alkaline solution, their reaction with oxidising agents, their spectra, polarographic behaviour and uses, and with analytical methods for their determination.

Zusammenfassung

Eine Übersicht über die Eigenschaften der Dithiocarbamate wurde vorgelegt, wobei die Mono- und Dialkyldithiocarbamate miteinander verglichen wurden. Die einzelnen Abschnitte behandeln die Synthese der Dithiocarbamate, deren Stabilität in saurer und alkalischer Lösung, ihre Reaktionsweise mit Oxydationsmitteln, ihre Spektren, ihr polarographisches Verhalten, ihre Verwendung sowie die zu ihrer Bestimmung verwendeten analytischen Methoden.

References

[1] *M. Delépine*, Bull. soc. chim. France **1958**, 5.

[2] *A. Hulanicki*, Talanta **14**, 1371 (1967).

[3] *D. Miller* and *R. Latimer*, Can. J. Chem. **40**, 246 (1962).

[4] *R. Zahradník*, Coll. Czechoslov. Chemic. Commun. **23**, 1435 (1958).

[5] *R. Zahradník*, Coll. Czechoslov. Chemic. Commun. **21**, 447 (1956).

[6] *P. Zuman* and *R. Zahradník*, Z. physik. Chem. **208**, 135 (1957).

[7] *R. Zahradník* and *P. Zuman*, Chem. listy **52**, 231 (1958); Coll. Czechoslov. Chemic. Commun. **24**, 1132 (1959).

[8] *G. D. Thorn* and *R. A. Ludwig*, The Dithiocarbamates and Related Compounds. Amsterdam: Elsevier. 1962.

[9] *E. E. Reid*, The Organic Chemistry of Bivalent Sulfur, Vol. IV. New York: Chem. Publishing Co. 1962.

[10] *D. Craig*, *A. E. Juve*, *W. L. Davidson*, *W. L. Semon*, and *D. C. Hay*, J. Polymer Sci. **8**, 321 (1959).

[11] *A. E. Martin*, Analyt. Chemistry **25**, 1260 (1953).

[12] *H. Bode*, Z. analyt. Chem. **142**, 414 (1954).

[13] *R. Zahradník,* Chem. listy **50,** 808 (1956); Coll. Czechoslov. Chemic. Commun. **21,** 1111 (1956).

[14] *K. P. Soni* and *A. M. Trivedi,* J. Indian Chem. Soc. **37,** 349 (1960).

[15] *M. Wronski,* Zeszyty Nauk. Univ. Łódz, Nauki Mat.-Przyrod., Ser. II, No. 6, 121 (1959).

[16] *R. Zahradník,* Coll. Czechoslov. Chemic. Commun. **24,** 3407 (1959).

[17] *N. J. Turner* and *M. E. Cordon,* Phytopathology **53,** 1388 (1963).

[18] *R. Zahradník,* Chem. Tech. (Berlin) **11,** 546 (1959).

[19] *G. D. Thorn* and *R. A. Ludwig,* Can. J. Chem. **32,** 872 (1954).

[20] *F. J. Welcher,* Organic Analytical Reagents, Vol. 4. New York: Van Nostrand. 1948.

[21] *E. D. Sandell,* Colorimetric Determination of Traces of Metals, 3rd Ed. New York: Interscience. 1959.

[22] *D. J. Halls, A. Townshend,* and *P. Zuman,* Analyt. Chim. Acta **40,** 459 (1968).

[23] *S. Akerström,* Acta Chem. Scand. **10,** 699 (1956).

[24] *S. Akerström,* Arkiv Kemi **14,** 387 (1959).

[25] *S. Akerström,* Arkiv Kemi **24,** 495 (1965).

[26] *S. Akerström,* Acta Chem. Scand. **18,** 824 (1964).

[27] *S. Akerström,* Arkiv Kemi **14,** 403 (1959).

[28] *T. Vänngard* and *S. Akerström,* Nature **184,** 183 (1959).

[29] *M. Bonamico, G. Dessy, C. Mariani, A. Vaciago,* and *L. Zambonelli,* Acta Cryst. **19,** 619 (1965).

[30] *M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago,* and *L. Zambonelli,* Acta Cryst. **19,** 886 (1965).

[31] *R. Hesse,* Arkiv Kemi **20,** 481 (1963).

[32] *M. Bonamico, G. Mazzone, A. Vaciago,* and *L. Zambonelli,* Acta Cryst. **19,** 898 (1965).

[33] *L. C. A. Thompson* and *R. O. Moyer,* J. Inorg. Nucl. Chem. **27,** 2225 (1965).

[34] *D. J. Halls, A. Townshend,* and *P. Zuman,* Analyt. Chim. Acta **41,** 63 (1968).

[35] *M. J. Janssen,* Rec. trav. chim. Pays-Bas **79,** 454 (1960).

[36] *H. P. Koch,* J. Chem. Soc. London **1949,** 401.

[37] *M. J. Janssen,* Rec. trav. chim. Pays-Bas **79,** 464 (1960).

[38] *M. L. Shankaranarayana* and *C. C. Patel,* Acta Chem. Scand. **19,** 1113 (1965).

[39] *M. J. Janssen,* Rec. trav. chim. Pays-Bas **79,** 1066 (1960).

[40] *R. Zahradník,* Coll. Czechoslov. Chemic. Commun. **23,** 1443 (1958).

[41] *E. Svátek, R. Zahradník,* and *A. Kjaer,* Acta Chem. Scand. **13,** 442 (1959).

[42] *J. Chatt, L. A. Duncanson,* and *L. M. Venanzi,* Suomen Kemistilehti **29 B,** 75 (1956).

[43] *J. Chatt, L. A. Duncanson,* and *L. M. Venanzi,* Nature **177,** 1042 (1956).

[44] *M. L. Shankaranarayana* and *C. C. Patel,* Spectrochim. Acta **21,** 95 (1965).

[45] *K. Nakamoto, J. Fujita, R. A. Condrate,* and *Y. Morimoto,* J. Chem. Physics **39,** 423 (1963).

[46] *K. A. Jensen, J. B. Carlsen, A. Holm,* and *P. Nielsen,* Acta Chem. Scand. **17,** 550 (1963).

[47] *J. Mann,* Trans. Inst. Rubber Ind. **27,** 232 (1951).

[48] *E. C. Gregg* and *W. P. Tyler,* J. Amer. Chem. Soc. **72,** 4561 (1950).

[49] *P. Zuman, R. Zumanova,* and *B. Soucek,* Chem. listy **47**, 1522 (1953).

[50] *G. Sartori, A. Liberti,* and *C. Calzolari,* Comité Thermodynam. et Cinet. Electrochim., Compt. Rend. Reunion 1950, 301 (1951).

[51] *G. Sartori* and *C. Calzolari,* Ann. Triestini cura univ. Trieste, Sez. 2, **20**, 107 (1951); Chem. Abstr. **46**, 6968 (1952).

[52] *P. Zuman, R. Zumanova,* and *B. Soucek,* Coll. Czechoslov. Chemic. Commun. **18**, 632 (1953).

[53] *J. Davis, A. J. Easton,* and *J. Freezer,* Chem. Ind. (London) **1955**, 241.

[54] *W. Stricks* and *S. K. Chakravarti,* Analyt. Chemistry **34**, 508 (1962).

[55] *J. Pasciak,* Chem. analit. (Warsaw) **8**, 945 (1963).

[56] *J. Pasciak,* Chem. analit. (Warsaw) **9**, 39 (1964).

[57] *D. Halls, A. Townshend,* and *P. Zuman,* Analyt. Chim. Acta **41**, 51 (1968).

[58] *R. Zahradník* and *L. Jensovsky,* Chem. listy **48**, 11 (1954).

[59] *R. Zahradník,* Chem. listy **49**, 1002 (1955).

[60] *R. Zahradník,* Coll. Czechoslov. Chemic. Commun. **21**, 447 (1956).

[61] *Yu. I. Usatenko* and *F. M. Tulyupa,* Izv. Vysshykh. Ucheb. Zavedenii Khim i. Khim. Tekhnol. **1958**, No. 3, 56; Chem. Abstr. **53**, 1991d (1959).

[62] *Yu. I. Usatenko* and *F. M. Tulyupa,* Zh. Neorgan. Khim. **4**, 2495 (1959); Chem. Abstr. **54**, 16249a (1960).

[63] *Yu. I. Usatenko* and *F. M. Tulyupa,* Tr. Dnepropetr. Khim-Tekhnol Inst. **1959**, No. 12, Pt. I, 189; Chem. Abstr. **56**, 9403i (1962).

[64] *Yu. I. Usatenko* and *F. M. Tulyupa,* Zavodsk. Lab. **24**, 1327 (1958); Chem. Abstr. **54**, 13941b (1960).

[65] *Yu. I. Usatenko* and *K. A. Uvarova,* Ukr. Khim. Zh. **28**, 383 (1962); Chem. Abstr. **57**, 9200e (1962).

[66] *Yu. I. Usatenko* and *K. A. Uvarova,* Nauchn. Tr. Dnepropetr. Khim-Tekhnol. Inst. 1961, No. 12, Pt. 2, 177; Chem. Abstr. **57**, 15798a (1962).

[67] *T. Fujinaga, K. Izutsu,* and *K. Yamashita,* Rev. Polarog. (Kyoto) **13**, 52 (1965).

[68] *T. Fujinaga* and *K. Yamashita,* Bull. Chem. Soc. Japan **37**, 989 (1964).

[69] *T. Fujinaga, H. A. Brodowsky, T. Nagai,* and *K. Yamashita,* Rev. Polarog. (Kyoto) **11**, 217 (1963).

[70] *T. Fujinaga, T. Nagai,* and *K. Yamashita,* Nippon Kagaku Zasshi **84**, 506 (1963).

[71] *A. L. Linch,* Analyt. Chemistry **23**, 293 (1951).

[72] *M. L. Shankaranarayana* and *C. C. Patel,* Z. analyt. Chem. **179**, 263 (1961).

[73] *C. G. R. Nair, T. Joseph,* and *P. T. Joseph,* Chemist-Analyst **54**, 111 (1965).

[74] *M. L. Shankaranarayana* and *C. C. Patel,* Analyt. Chemistry **33**, 1398 (1961).

[75] *D. G. Clarke, H. Baum, E. L. Stanley,* and *W. F. Hester,* Analyt. Chemistry **23**, 1842 (1951).

[76] *C. Bighi* and *C. Saglietto,* J. Chromatography **17**, 13 (1965).

[77] *H. Roth* and *W. Beck,* Mikrochim. Acta [Wien] **6**, 845 (1957).

[78] *A. Stevenson,* J. Sci. Fd. Agric. **15**, 509 (1964).

[79] *W. Bontoyan,* J. Assoc. Off. Agric. Chem. **48**, 562 (1965).

[80] *T. E. Cullen,* Analyt. Chemistry **36**, 221 (1964).

[81] *R. F. Heuermann,* J. Assoc. Off. Agric. Chem. **40**, 264 (1957).

[82] *P. Nangniot,* Parasitica **16**, 85 (1960).

[83] *T. Zawadzka,* Roczniki Panstwowogo Zakladu Hig. **17**, 263 (1966).

[84] *P. Nangniot,* Bull. inst. agron. stns. rech. Gembloux **28**, 365 (1960).
[85] *D. J. Halls, A. Townshend,* and *P. Zuman,* Analyst **93**, 219 (1968).
[86] *P. Nangniot,* Bull. inst. agron. stns. rech. Gembloux **28**, 373 (1960).
[87] *P. Nangniot,* Bull. inst. agron. stns. rech. Gembloux **28**, 381 (1960).
[88] *O. Rozaci,* Plaste u. Kautschuk **6**, 386 (1959).
[89] *W. P. McKinley* and *S. A. Magarvy,* J. Assoc. Off. Agric. Chem. **40**, 264 (1957).
[90] *W. Fischer* and *U. Uhlich,* Z. analyt. Chem. **172**, 175 (1960).
[91] *H. Susi* and *H. Rector,* Analyt. Chemistry **30**, 1933 (1958).
[92] *D. J. Halls,* Ph. D. Thesis, University of Birmingham (1967).