ELECTRONIC SPECTRA OF SALTS OF DITHIOCARBAMIC ACIDS

Drahomír OKTAVEC[a], Jozef ŠTEFANEC[a], Bohumil SÍLEŠ[a], Václav KONEČNÝ[b]
and Ján GARAJ[a]

[a] *Analytical Chemistry Department,*
Slovak Institute of Technology, 880 37 Bratislava and
[b] *Research Institute of Agrochemical Technology, 810 04 Bratislava*

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The report gives synthesis and UV spectra of a series of alkali and ammonium salts of the dithiocarbamic acids derived from dimethyl-, diethyl-, dipropyl-, dibutyl-, dipentyl-, dihexyl-, diheptyl-, dioctyl-, diisopropyl-, diisobutyl-, methylisopropylamine, piperidine, morpholine, piperazine and pyrrolidine. The absorption bands due to transitions localized in the groups CSS (λ_{max} ~260 nm) and NCS (λ_{max} ~280 nm) show a red shift with increasing length of the alkyl chain. Increasing polarity of solvent causes, with some of the compounds, a small red shift of λ_{max} of the band due to CSS group, but it causes a considerable blue shift of λ_{max} of the band due to NCS group in all the studied compounds. The absorption band near 207 nm is ascribed to the carbon disulphide produced by decomposition of the dithiocarbamates.

Determination of metals in the form of DTC* chelates in UV spectral region necessitates to know absorption spectra of the free DTC ligands, because absorption of the latter strongly interferes with and often prevents the analyses.

This communication deals with absorption spectra of DTC ligands with the aim of elucidation of effects of substituents at nitrogen atom and those of solvent polarity on position of the absorption bands assigned to transitions inside the groups CSS and NCS and with the aim of interpretation of the band near 207 nm.

Electronic spectra of alkali salts of DTC involve absorption bands with λ_{max} in the following wavelength ranges[1]: A – little intensive band ($\log \varepsilon \sim 1{\cdot}8$) with λ_{max} near 330–360 nm, B – intensive band ($\log \varepsilon \sim 4$) with λ_{max} near 275–295 nm, C – intensive band ($\log \varepsilon \sim 4$) with λ_{max} in the region 240–260 nm.

The first detailed description of the band A was given by Janssen[2] who assigned it to the $n-\pi^*$ transition localized in the group S—C=S. Shankaranarayana and Patel[3-10] and other authors[4-7] assigned the band C to $\pi-\pi^*$ transition in the group CSS.

The band B was, for a long time, non-assigned to any certain type of electronic transition[8,9]. Janssen[2,11] and other authors[4-6] assigned this band to $n-\pi^*$ transition,

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* DTC denotes dithiocarbamates (*i.e.* salts and chelates of dithicarbamic acids) and dithiocarbamate ligands.

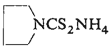
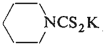
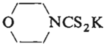
but application of the LCAO–MO method shows that the band is due to $\pi-\pi^*$ transition[12,13]. Nikolov and coworkers[14] confirmed this assignement with the use of LCAO–MO–SCF–CI method.

EXPERIMENTAL

Reagents. Alkali and ammonium salts of the DTC acids were used (Table I) which were prepared as follows: Sodium or potassium hydroxide (1 mol) was dissolved in 500 ml water, and 1 mol of the corresponding amine was added carefully with stirring. Then at 12—16°C 1 mol

TABLE I

Alkali and Ammonium Salts of Dithiocarbamic Acids

No	Compound	Denotation	Content %
I	$(CH_3)_2NCS_2Na$	Na(Me$_2$DTC)	95
II	$(C_2H_5)_2NCS_2Na$	Na(Et$_2$DTC)	99
III	$(C_3H_7)_2NCS_2K$	K(Pr$_2$DTC)	96
IV	$(CgH_9)_2NCS_2Na$	Na(Bu$_2$DTC)	27[a]
V	$(C_5H_{11})_2NCS_2K$	K(Pe$_2$DTC)	30[a]
VI	$(C_6H_{13})_2NCS_2K$	K(He$_2$DTC)	20[a]
VII	$(C_7H_{15})_2NCS_2K$	K(Hp$_2$DTC)	22[a]
VIII	$(C_8H_{17})_2NCS_2K$	K(Ok$_2$DTC)	18[a]
IX	$(iC_3H_7)_2NCS_2Na$	Na(i-Pr$_2$DTC)	97
X	$(iC_4H_9)_2NCS_2Na$	Na(i-Bu$_2$DTC)	98
XI	$(CH_3, iC_3H_7)NCS_2K$	K(Mei-PrDTC)	97
XII		NH$_4$(PlDTC)	99·8
XIII		K(PpDTC)	99
XIV		K(MoDTC)	98
XV		K$_2$(Pz(DTC)$_2$)	97

[a] Aqueous solution.

carbon disulphide was added drop by drop from a dropping funnel. The stirring was continued at room temperature. Excess carbon disulphide was removed with a stream of nitrogen. Water was removed from the aqueous salt solution by azeotropic distillation with toluene. The separated solid salt was filtered off, washed with toluene and light petroleum. It was dried under reduced pressure at 80°C. The compounds *I—III*, *IX—XI*, *XIII—XV* (Table I) prepared in this way contained 95—99% sodium or potassium salt of dithiocarbamic acid and water.

The alkali salts of the DTC acids *IV—VIII* (Table I) were prepared in the same way and used direct as aqueous solutions (after removing carbon disulphide with stream of nitrogen).

Ammonium salt of 1-pyrrolidinecarbodithioic acid (*XII*, Table I) was prepared by dissolving 0·5 mol pyrrolidine in 250 ml ethanol (99·5%), addition of 0·5 mol aqueous ammonia (25·5%) and, with continuous stirring at 15—18°C, 0·55 mol carbon disulphide, whereafter the reaction mixture was stirred 3 h. The precipitated white solid was separated by filtration, washed with ethanol and dried. The salt prepared in this way contained 99·8% ammonium 1-pyrrolidinecarbodithioate.

The prepared alkali and ammonium salts of the dithiocarbamic acids were submitted to elementar analysis (C, H, N, S), iodometric titration and spectrophotometric titration with standard solution of copper(II) sulphate.

Electronic Spectra in UV Region

For the measurements of absorption spectra of the salts of dithiocarbamic acids we used their aqueous solutions of pH 6·5 to 7·0, methanolic and ethanolic solutions of concentrations $\sim 10^{-3}$M, as well as aqueous carbon disulphide solutions ($\sim 10^{-5}$M) and the solutions of piperidine and diethylamine ($\sim 10^{-3}$M) prepared in usual way. The spectra were recorded with a Specord UV VIS spectrophotometer (Zeiss, Jena) in 0·2, 0·5, 1·0 and 3·0 cm quartz cells. The λ_{max} values of important absorption bands were verified with a VSU-1 apparatus (Zeiss, Jena) with the accuracy of ±1 nm.

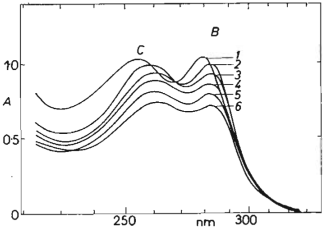


FIG. 1

Absorption Spectra of Aqueous DTC Solutions

1 Na(Me_2DTC); *2* Na(Et_2DTC); *3* K(Pr_2DTC); *4* Na(Bu_2DTC); *5* K(Pe_2DTC); *6* K(He_2DTC).

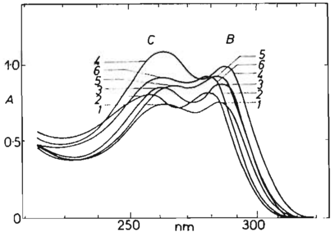


FIG. 2

Absorption Spectra of Aqueous DTC Solutions

1 Na(i-Bu_2DTC); *2* K(Me i-PrDTC); *3* K(MoDTC); *4* Na(i-Pr_2DTC); *5* K_2(Pz.(DTC)$_2$); *6* K(PpDTC).

RESULTS AND DISCUSSION

The spectra of the studied salts of dithiocarbamic acids are given in Figs 1 and 2. Time changes of the absorption spectra of alcoholic and aqueous solutions of DTC are given in Figs 3 and 4.

From Figs 1 to 4 it is seen that absorption spectra of the studied compounds do not contain any band in the range 330 to 360 nm, which can be explained by low intensity of the band: it was imperceptible at the used concentrations but could be recorded at higher concentrations.

Besides the described absorption bands[2-7] the spectra of aqueous, methanolic and ethanolic solutions of all the compounds also contained a very intensive band D at λ_{max} 207–208 nm ($\log \varepsilon \sim 5$), its absorption maximum being increased with time. The absorption curves intersect in an isosbestic point near 215 nm, and the absorption bands B and C show proportional decrease with time. This fact can be explained by decomposition of the compounds in aqueous and alcoholic DTC solutions[15,16]:

$$(R_1R_2)N{-}CSS^- \xrightleftharpoons{H^+} (R_1R_2)\overset{+}{N}H{-}CSS^- \rightleftharpoons (R_1R_2)NH + CS_2\,,$$

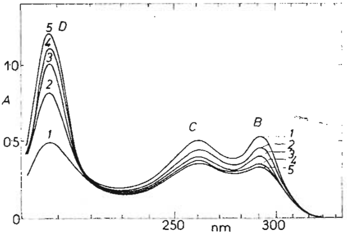


FIG. 3

Change of Absorption Spectrum of Aqueous Na(Et$_2$DTC) Solution with Time

1 Immediately after preparation of the solution; *2* 20 min; *3* 40 min; *4* 60 min; *5* 80 min after preparation of the solution.

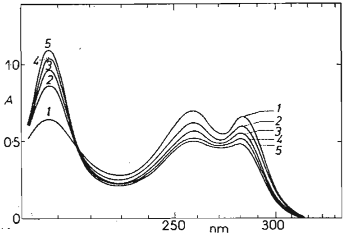


FIG. 4

Change of Absorption Spectrum of Ethanolic Na(Et$_2$DTC) Solution with Time

1 Immediately after preparation of the solution; *2* 20 min; *3* 40 min; *4* 60 min; *5* 80 min after preparation of the solution.

$$(R_1R_2)NH \xrightleftharpoons{H^+} (R_1R_2)\overset{+}{N}H_2\,,$$

the decomposition rate decreases with time, as it can be seen from intensity decrease of the bands B and C in Figs 3 and 4, and this fact agrees with increasing concentration of the products on the system corresponding to the absorption band D. Comparison of absorption spectra of aqueous solutions of carbon disulphide, diethylamine, piperidine, and sodium diethyldithiocarbamate (Fig. 5) indicates that the mentioned absorption band is due to carbon disulphide and not $n-\pi^*$ transition of DTC (ref.[17]), because the bands of the amines are far less intensive and are not shifted to the region 200–210 nm until in alkaline medium. Absorption spectrum of diethyldithiocarbamoyl disulphide does not have any corresponding absorption band in the given region, the values λ_{max} of Na(Et$_2$DTC) and CS$_2$ being almost identical.

From analysis of absorption spectra of DTC (Table II) effects of the alkyl substituent and of the solvent polarity on the absorption maxima of the bands B, C and D can be judged.

The absorption maximum of the band D does not show any shift of λ_{max} with increasing length of the alkyl chain in the whole studied series and with change of solvent, which confirms that the band is not due to the dithiocarbamates.

The λ_{max} values of the bands B and C of the n-substituted derivatives show a red shift with increasing length of the alkyl chain as compared with the derivative containing $(CH_3)_2N$—, the order being: $(CH_3)_2N— < (C_2H_5)_2N— < (C_3H_7)_2N— \approx \approx (C_4H_9)_2N— \approx (C_5H_{11})_2TN— \approx (C_6H_{13})_2N—$, the bands B and C are shifted by 4–8 and 2–3 nm, respectively. The derivatives containing (i-$C_3H_7)_2N$— and (i-$C_4H_9)_2N$— groups showed the λ_{max} shift by 9 and 10 nm (B band) and by 8 and 5 nm (C band), respectively. The described effect can be explained by the inductive influence of the alkyl groups causing more probable participation of electrons at

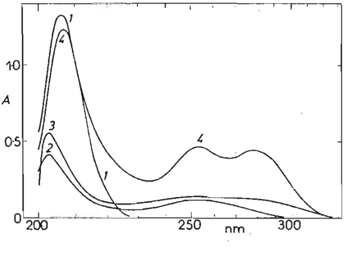


FIG. 5

Absorption Spectra of Aqueous Solutions

1 Carbon disulphide; *2* diethylamine (pH 9·4); *3* piperidine (pH 9·4); *4* sodium diethyldithiocarbamate.

nitrogen in conjugation, *i.e.* their delocalization towards the S—C=S group and resulting lengthening of the absorbing system. This presumption is supported by strong red shift of the $(i\text{-}C_3H_7)_2N$— derivative where hyperconjugation effect of C—H bonds can make itself felt. Thus from the results given in Figs 1 and 2 and in Table II it is obvious that the alkyl substituent at nitrogen affects position of the absorption bands B and C on the wavelength axis, and the λ_{max} shift of these bands is connected with electronic effects of the alkyl groups, which does not agree with conclusions of Tulyupa and coworkers[4] concerning this problem.

The results given in Table II show that the solvent polarity increase causes a small red shift of λ_{max} of the band C with higher n-alkyl, isopropyl and isobutyl derivatives. The other substances show either no shift or an opposite one, which agrees with conclusions of other authors[17]. The largest influence of the solvent polarity change from ethanol to water is observed with λ_{max} of the B band due probably to $\pi-\pi^*$ transition in N—C=S group[14]. This solvent polarity change results in a blue shift of λ_{max} by $6-10$ nm for all the studied substances, the greatest shift being observed with the derivatives containing $(i\text{-}C_4H_9)_2N$— and $(C_5H_{10}N)_2$— groups. The smallest shift is observed with the DTC containing $(CH_3)_2N$— and $(CH_3, i\text{-}C_3H_7)N$— groups. Shift of λ_{max} of the B band of the n-alkyl derivatives of DTC containing the groups $(C_3H_7)_2N$—, $(C_4H_9)_2N$—, $(C_5H_{11})_2N$— and $(C_6H_{13})_2N$— is the same (9 nm). It is likely that the existence of the blue shift observed in the whole series of the investigated DTC is connected with $n-\pi^*$ transitions of the group N—C=S.

TABLE II

Influence of Solvent on λ_{max} Values of the Absorption Bands B, C and D of Alkali Salts of DTC

Compound	H_2O			MeOH			EtOH		
	D	C	B	D	C	B	D	C	B
$Na(Me_2DTC)$	207	254	280	207	253	286	208	254	287
$Na(Et_2DTC)$	207	258	282	207	257	289	208	258	291
$K(Pr_2DTC)$	208	260	282	207	258	290	207	260	291
$Na(Bu_2DTC)$	207	260	282	208	260	290	207	258	291
$K(Pe_2DTC)$	208	260	282	207	260	290	207	259	291
$K(He_2DTC)$	208	261	283	208	260	291	207	260	292
$Na(i\text{-}Pr_2DTC)$	208	263	288	207	262	297	208	262	297
$Na(i\text{-}Bu_2DTC)$	207	264	285	208	261	293	207	261	295
K(Mei-PrDTC)	207	257	280	207	256	287	208	257	288
K(PpDTC)	207	263	280	207	262	287	208	262	290
K(MoDTC)	207	262	286	208	262	291	207	264	294
$K_2(Pz(DTC)_2)$	208	265	284	207	263	291	207	266	291

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