Summary

The previous study of the ultraviolet absorption spectra of α-phenylcarbonyl compounds has been extended to include 1,1-diphenylbutanone-2, 1,3-diphenylpropanone-2, 1-mesitylpropanone-2, desoxybenzoin and 2-phenylcyclohexanone.

The spectra of these compounds are reported and a long wave length band around 295 mμ of extinction 150–300 has been shown to be common to all except 2-phenylcyclohexanone. The observations are discussed in terms of no-bond resonance, direct action through space and steric hindrance.

SAN FRANCISCO, CALIFORNIA
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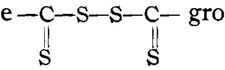
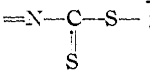
[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

Polarography of the Bis-(diethylthiocarbamyl) Disulfide–Diethyldithiocarbamate Ion Oxidation–Reduction System[1]

BY EARL C. GREGG AND WILLARD P. TYLER

Introduction

Bis-(diethylthiocarbamyl) disulfide is known to the medical profession as a treatment of alcoholism[2] and to the rubber industry as an accelerator of vulcanization. Polarographic reduction of compounds which contain the  $-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-$ group has been demonstrated by Proske[3,4,5] and by Kolthoff and Levitan.[6]

Proske made no systematic study of any one of the compounds he investigated, but confined his articles to reporting the feasibility of using the polarograph in the rubber laboratory for analysis for organic accelerators of vulcanization. Proske made one general statement which, prima facie, is not borne out by the evidence presented here, namely, that compounds containing the  $=N-\underset{\underset{S}{\|}}{C}-S-$ group are reducible at the d. m. e. at potentials in the vicinity of −0.4 volt *vs.* S.C.E. While this group is oxidizable in that potential region, actually, it does not reduce until the vicinity of −2.1 volts *vs.* S.C.E. is reached.

Experimental

A Sargent Model XX polarograph was used for recording all polarograms. The sensitivity dial settings were calibrated by means of a Shallcross Akra-ohm wire wound resistor of an accuracy ±1/4%. Errors up to 6% were found in the current as determined by the sensitivity setting and the equation for converting sensitivity settings to current per millimeter.

A water jacketed cell which was connected to a large area S.C.E. as external anode by means of an agar salt bridge constituted the electrolysis cell system. All polarograms were measured on solutions maintained at 25.00 ± 0.02° by continuously circulating thermostated water through the water jacket by means of a Precision Scientific Company circulating bath. The solutions were deaerated with oil-pumped nitrogen passed through a solvent composition which was the same as that of the solution to be analyzed. All potential settings were measured to the nearest millivolt with a calibrated Beckman laboratory model G *p*H meter used as a potentiometer. All half wave potentials were corrected for *iR* drop. The *p*H measurements were obtained with the glass electrode and the Beckman model G *p*H meter. All *p*H measurements of buffered solutions were taken directly on solutions which were 60% ethanol by volume and were corrected for the water activity.[7]

All solutions were 60% ethanol by volume. The maximum suppressor used was 0.01% gelatin in all cases.

Oxalic acid–sodium oxalate, citric acid–sodium dihydrogen phosphate and ammonia–ammonium chloride buffer systems were used. Neutral solutions were 0.1 *M* lithium chloride.

The capillary tip must be cleaned before recording each polarogram: it was immersed in concd. nitric acid and rinsed with distilled water, immersed in ethanol and wiped dry, immersed in concd. nitric acid, rinsed and wiped dry.

In order to produce consistent polarograms of diethyldithiocarbamate ion, hydrolysis and air oxidation must be avoided. Hydrolysis in the 0.01 *M* stock solution was suppressed by adding two pellets of KOH per 100 ml. of stock solution. When the stock solution was diluted with neutral solvents, no additional base was necessary. Air oxidation of dilute solutions, 3×10^{-4} *M* and less, was averted by deaerating the diluents with nitrogen before adding the requisite aliquot of stock solution.

The rate of decomposition of bis-(diethylthiocarbamyl) disulfide by base was measured with the automatic recording polarograph. Across a neutral unbuffered solution of 10^{-3} *M* disulfide, the potential was set at −0.8 volt *vs.* S.C.E. which is well into the limiting current region of the reduction wave of the disulfide. The current sensitivity vernier was adjusted so that the limiting current was represented by the full chart width. Fifty ml. of solution in the cell was deaerated with nitrogen as usual. The chart was allowed to run while the constant applied potential was maintained. Without stopping the chart an aliquot of lithium hydroxide stock solution was added to the cell and a short burst of nitrogen bubbles was blown through the cell at the same time to insure complete and rapid mixing. The instant base was added was taken as zero time. The chart speed was accurately determined so that the chart length represented the time axis and the chart width represented the current or concentration axis.

Materials.—Sodium diethyldithiocarbamate: Eastman Kodak Co. white label sodium diethyldithiocarbamate was crystallized once from ethyl acetate and once from 2-propanol. The composition of the crystals was 75.5% sodium

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(1) Presented in part at the Pittsburgh conference on analytical chemistry and applied spectroscopy, February, 1950.

(2) *J. Am. Med. Assoc.*, **139**, 918–922 (1949).

(3) G. Proske, *Angew. Chem.*, **53**, 550 (1940); *Rubber Chem. and Technol.*, **XIV**, 914 (1941).

(4) G. Proske, *Kautschuk*, **16**, no. 1, 1–5 (1940); **16**, no. 2, 13–17 (1940); *Rubber Chem. and Technol.*, **XIV**, 470 (1941).

(5) G. Proske, *Die Chemie*, **56**, 24–28 (1943).

(6) Kolthoff and Levitan, Univ. of Minn., to Office of Rubber Reserve, unpublished report, June 18, 1943.

(7) Dole, THIS JOURNAL, **54**, 3095 (1932).

diethyldithiocarbamate as analyzed by iodine titration and 24.7 ± 0.18% water of hydration as analyzed by the Karl Fischer method. This analysis corresponds to the calculated composition of the trihydrate.

Bis-(diethylthiocarbamyl) Disulfide.—A water solution of purified sodium diethyldithiocarbamate trihydrate was oxidized with ammonium persulfate solution to the insoluble disulfide. The disulfide was crystallized twice from methanol and once from diethyl ether, m. p. 71–72° (uncor.).

Results and Discussion

Bis-(diethylthiocarbamyl) Disulfide.—Figure 1 represents polarograms of varying concentrations of bis-(diethylthiocarbamyl) disulfide in neutral 60% ethanol solutions by volume. The cause of the double wave will be discussed later. The ratio of the first wave height to the second wave height decreases with decreasing concentration.

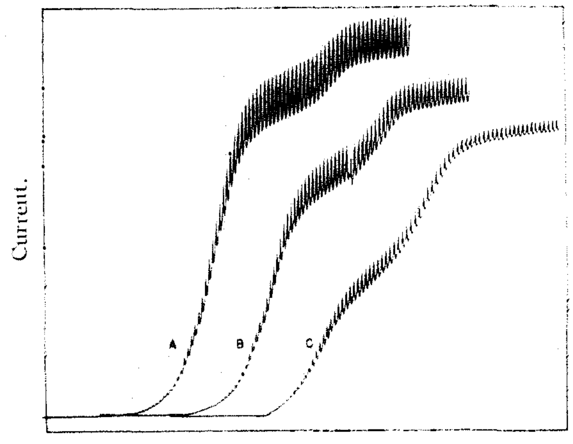


Fig. 1.—Polarograms of (A) 0.500, (B) 0.300, (C) 0.150 millimolar bis-(diethylthiocarbamyl) disulfide in 0.10 M LiCl in 60% ethanol by volume.

In order to obtain the diffusion current, the sum of the wave heights must be measured and the capillary tip must be cleaned meticulously before each polarogram is obtained. See experimental. When the capillary tip is insufficiently cleaned, high and erratic results invariably occur due to adsorption of the compound on the capillary tubing. The diffusion current constant in various supporting electrolytes appears in Table I. In strongly alkaline solution cleavage of the disulfide occurs to give one mole of diethyldithiocarbamate ion per mole of disulfide. Other products present were not identified. The decomposition rate of bis-(diethylthiocarbamyl) disulfide in several concentrations of lithium hydroxide is graphically illustrated in Fig. 2. For analytical purposes the recommended supporting electrolyte is 1 M NH_4OH + 0.1 M NH_4Cl. In supporting electrolyte solutions of pH greater than 11, decomposition occurs at an analytically significant rate.

Table I

Supporting electrolyte	pH	C, millimolar	i_d, microamp.	i_{ads}, microamp.	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
0.1 M LiCl	7.0	1.000	4.16	0.32	2.18
		0.600	2.31	.32	2.21
		.500	1.86	.31	2.16
		.400	1.50	.30	2.17
		.300	1.13	.27	2.17
		.200	0.765	.23	2.20
		.100	0.378	.21	2.19
		.0500	0.190	.19	2.19
1 M NH_4OH + 1 M NH_4Cl	9.4	1.000	4.30		2.16
		0.500	2.14		2.16
		0.300	1.282		2.16
1.5 M NH_4OH + 0.01 M citric acid + 0.1 M LiCl	10.9	1.000	4.40		2.15
		0.500	2.21		2.222
		0.300	1.322		2.15

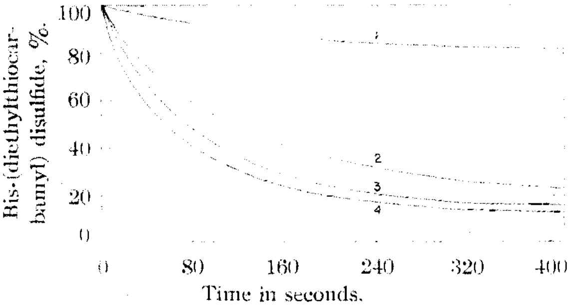
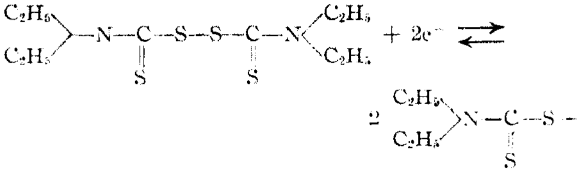


Fig. 2.—Decomposition rate of 1.00 millimolar bis-(diethylthiocarbamyl) disulfide in (1) 8, (2) 40, (3) 60, (4) 75 millimolar LiOH in 60% ethanol by volume.

At concentrations greater than 1.0×10^{-3} M, a maximum occurs at the top of the first wave which cannot be suppressed completely by gelatin concentrations as high as 0.11%. The presence of a maximum does not prevent a well defined limiting current from occurring so that solutions of concentration greater than 1.0×10^{-3} M may be analyzed readily. The diffusion current constant remains unchanged when a maximum is present.

The half wave potential is defined as that potential on a polarogram where $i = i_d/2$. In this case i_d refers to the *total* wave. The half wave potential changes with pH as graphed in Fig. 3. Since the reaction at the d. m. e. is



and since the diethyldithiocarbamate ion is the anion of a weak acid, the equation of the reduction wave of the free molecules in solution may be derived.[8,9]

$$\text{I.}\quad E_{d.e} = E^0 - 0.0296 \log \frac{k_{ox}}{(k_{red})^2} - 0.0591 \log \frac{K_a}{K_a + (H^+)} - 0.0296 \log \frac{i^2}{i_d - i}$$

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(8) J. Tomes, *Collection Czechoslov. Chem. Commun.*, **9**, 12, 81, 150 (1937).

(9) Kolthoff and Lingane, *Polarography*, 181 (1941).

k_{ox} = proportionality constant between the diffusion current and the concentration of the oxidized form, bis-(diethylthiocarbamyl) disulfide.

k_{red} = same proportionality constant for the reduced form, diethyldithiocarbamate ion.

K_a = dissociation constant of diethyldithiocarbamic acid.

II. $$E_{1/2} = E^0 - 0.0296 \log \frac{k_{ox}}{(k_{red})^2} - 0.0591 \log \frac{K_a}{K_a + (\mathrm{H})^+} - 0.0296 \log \frac{i_d}{2}$$

The value of E^0 may be obtained from these equations by two methods:

(1) in alkaline or neutral solution $(\mathrm{H}^+) << K_a$; $K_a + (\mathrm{H}^+) = K_a$

$i_{d\,ox} = k_{ox}C_{ox}$.

$k_{ox} = I_{ox}\, m^{2/3}t^{1/6}$, where I_{ox} = diffusion current constant of the oxidized form.

$k_{red} = I_{red}\, m^{2/3}t^{1/6}$, where I_{red} = diffusion current constant of the reduced form.

Substituting in II and combining terms obtain:

$$E_{1/2} = E^0 - 0.0591 \log \frac{I_{ox}}{I_{red}} - 0.0296 \log \frac{C_{ox}}{2}$$

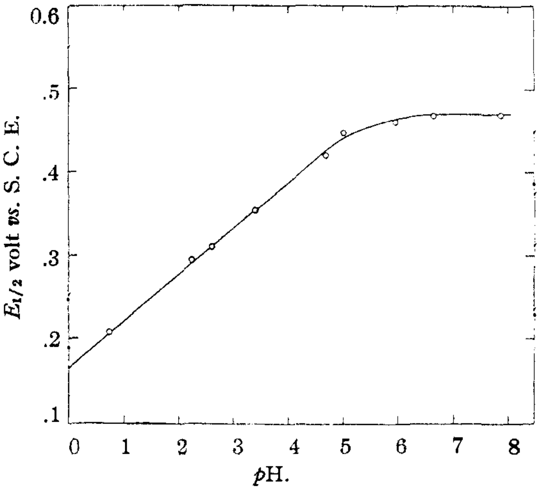

Fig. 3.—Effect of *p*H on the half wave potential of bis-(diethylthiocarbamyl) disulfide.

Table II shows the values of E^0 obtained by substituting the values for I_{ox} and I_{red} and measuring $E_{1/2}$ at several concentrations in neutral solution.

TABLE II

C molar	E^0 *vs.* S. C. E.
3×10^{-4}	−0.580
4×10^{-4}	− .577
5×10^{-4}	− .577
6×10^{-4}	− .579

(2) E^0 may be determined from equation I by plotting $E_{d.e.}$ *vs.* log $i^2/(i_d - i)$ for the free molecules in solution, Fig. 4. The data for the plot were obtained from a polarogram of bis-(diethylthiocarbamyl) disulfide in neutral solution, where $(\mathrm{H}^+) << K_a$.

The potential at the intercept of the plot with the abscissa, where log $i^2/(i_d - i) = 0$, is −0.576 volt *vs.* S.C.E. Substituting in equation I, obtain

$$-0.576 = E^0 - 0.0296\ k_{ox}/(k_{red})^2$$

Substituting $I_{ox}\, m^{2/3}t^{1/6} = k_{ox}$, obtain

$$-0.576 = E^0 - 0.0296 \log \frac{I_{ox}}{(I_{red})^2 m^{2/3}t^{1/6}}$$

$m^{2/3}t^{1/6}$ = 1.73 for the polarogram from which the data were taken. E^0 = −0.573 volt *vs.* S.C.E., in good agreement with −0.578 volt *vs.* S.C.E. obtained by the first method. This corresponds to E^0 − 0.33 volt *vs.* N.H.E.

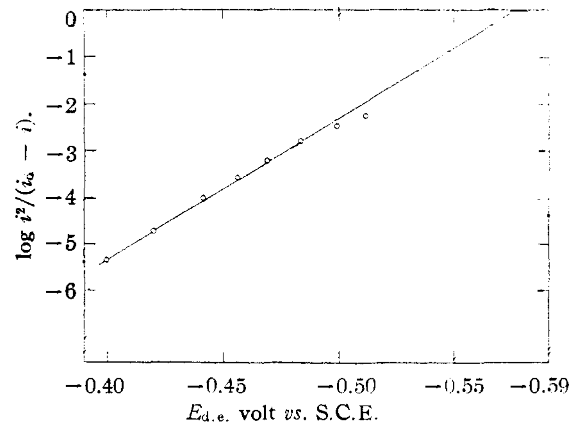

Fig. 4.—A log plot from a polarogram of 0.300 millimolar bis-(diethylthiocarbamyl) disulfide.

The K_a value for the unstable diethyldithiocarbamic acid may be measured from the intersection of the extrapolated straight sections of the plot in Fig. 3. At the intersection *p*H = *pKa*. $K_a = 2.9 \times 10^{-6}$ in 60% ethanol solution by volume at 25.0°.

The above arguments presume rapidly reversible reaction at the d.m.e. There are three criteria which confirm this: (1) The slope of the straight portion of the $E_{1/2}$ *vs.* *p*H curve, Fig. 3, on the acid side, λ = 0.055, agrees well with the slope, λ = 0.0596, predicted by the theoretical equation II at (H^+) values > > K_a which assumes reversibility in its derivation. (2) The slope of the plot $E_{d.e}$ *vs.* log $i^2/(i_d - i)$ in Fig. 4, λ = 0.033, agrees well with the theoretical value, λ = 0.0296, predicted by equation I which assumes reversibility in its derivation. (3) The polarogram obtained from a mixture of bis-(diethylthiocarbamyl) disulfide and diethyldithiocarbamate ion is shown in Fig. 5. There are no more inflection points than appear in a polarogram of either component alone.

Sodium Diethyldithiocarbamate.—The anodic wave for the diethyldithiocarbamate ion also consists of two waves, Fig. 5. The diffusion current constant data in Table III may be obtained under the fairly rigorous conditions outlined in experimental.

Again, the sum of the waves must be measured to obtain the diffusion current. For routine analysis 1 *M* NH_4OH + 0.1 *M* NH_4Cl is the recommended supporting electrolyte. The *p*H limit of the supporting electrolyte is 10. At lower *p*H's

TABLE III

Supporting electrolyte	pH	C, millimolar	i_d, microamp.	i_{ads}, microamp.	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
0.1 M LiCl + 0.001 M KOH	11	1.996	3.94	0.24	1.242
		0.998	1.99	.24	1.250
		.809	1.616	.24	1.252
		.599	1.190	.24	1.242
		.399	0.797	.24	1.248
		.3015	.605	.23	1.251
		.201	.402	.22	1.248
		.1505	.304	.19	1.244
		.1005	.205	.17	1.248
1 M NH_4OH + 1 NH_4Cl	9.4	Hydrolysis is too rapid			
1 M NH_4OH + 0.1 M NH_4Cl	10.4	Hydrolysis is 2% per hour			
		2.068	4.90		1.245
		1.034	3.46		1.250
		0.621	2.35		1.240

appreciable hydrolysis occurs which results in decomposition of the unstable diethyldithiocarbamic acid which is formed.

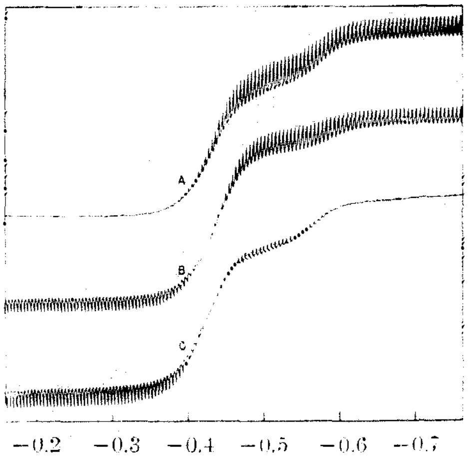

Fig. 5.—Polarograms of (A) 0.300 millimolar bis-(diethylthiocarbamyl) disulfide, (C) 0.500 millimolar sodium diethyldithiocarbamate (B) A + C in 0.1 M NH_4Cl + 1.0 M NH_4OH in 60% ethanol by volume.

For analyzing mixtures of bis-(diethylthiocarbamyl) disulfide and diethyldithiocarbamate ion the pH of the supporting electrolyte should lie between 10 and 11. This condition is fulfilled by 1 M NH_4OH + 0.1 M NH_4Cl.

At concentrations greater than 2×10^{-3} M a maximum occurs at the top of the first wave which cannot be suppressed by gelatin. Notwithstanding, a well defined limiting current forms which permits accurate analyses using the same diffusion current constant.

The Adsorption Wave.—The appearance of two waves in the polarograms of bis-(diethylthiocarbamyl) disulfide and diethyldithiocarbamate ion may be explained entirely on the basis of the adsorption of bis-(diethylthiocarbamyl) disulfide at the mercury-solution interface. For an excellent discussion of the adsorption wave see Brdicka.[10]

The complex process entailed in deciding the cause of the adsorption wave may be simplified. A convenient rule for this purpose is: on a polarogram, if the voltage direction of no reaction toward electrode reaction is followed, the adsorption wave will appear first when the reaction product is adsorbed; the adsorption wave will appear second when the reactant is adsorbed.

The criteria for establishing adsorption waves as expounded by Brdicka[10] have been fulfilled: (1) The marked effect of the compounds on the electrocapillary curve appears in Fig. 6. In the case of the bis-(diethylthiocarbamyl) disulfide electrocapillary curve at potentials more positive than −0.4 volt *vs.* S.C.E., a strongly capillary active substance is present as indicated by lowering of the drop time. As the potential becomes more negative, the electrocapillary curve of the solution rises to the electrocapillary curve of the supporting electrolyte. This indicates that the capillary active component is no longer active. On a polarogram of bis-(diethylthiocarbamyl) disulfide at potentials more positive than −0.4 volt *vs.* S.C.E., the disulfide is at the interface and lowers the interfacial tension. At more negative potentials the disulfide is reduced and is removed from the interface. Since the rise of the electrocapillary curve of the disulfide occurs at about the same potential range as the reduction occurs, the capillary active, *i. e.*, adsorbed, component is bis-(diethylthiocarbamyl) disulfide.

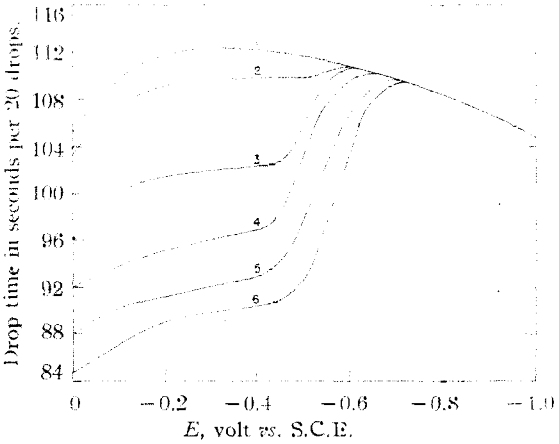

Fig. 6.—Electrocapillary curves of (1) supporting electrolyte, (2) 0.100, (3) 0.150, (4) 0.200, (5) 0.600 millimolar sodium diethyldithiocarbamate, (6) 0.500 millimolar bis-(diethylthiocarbamyl) disulfide in 0.10 M LiCl in 60% ethanol by volume.

A similar argument may be advanced to explain the electrocapillary curve of diethyldithiocarbamate ion. At potentials more positive than −0.4 volt *vs.* S.C.E. on the electrocapillary curve, a strongly capillary active substance is present. At

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[10] R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **12**, 522 (1947).

the same potentials on the polarogram of the diethyldithiocarbamate ion, bis-(diethylthiocarbamyl) disulfide is formed by oxidation at the interface. At potentials where the electrocapillary curve of the ion rises to the electrocapillary curve of the supporting electrolyte solution, the ion is no longer being oxidized to the disulfide. Again capillary activity, *i. e.*, adsorption, is manifested only in presence of the disulfide at the interface.

It may be seen from Fig. 6 that the change in unit interfacial tension, as indicated by drop time, decreases per unit change in concentration when the concentration increases. This indicates approaching saturation of the interface with adsorbed molecules. A similar effect is reflected in the current of the adsorption wave, Tables I and III. In his work with methylene blue, Brdicka observed that the adsorption wave was constant and independent of concentration.

(2) When the current, i_a, of the adsorption wave is equal to or greater than the current of the wave of the free molecules in solution, *i. e.*, $i_a > i_d - i_a$, only one wave is obtained and it appears at the potential of the adsorption wave, Table IV. When $i_a < i_d - i_a$, two waves appear. This effect was observed with methylene blue[10] also.

(3) Brdicka[10] showed that the adsorption current, i_a, is proportional to the time rate of change of surface of the mercury drop which in turn is proportional to the height of the mercury well. The mercury well height is inversely proportional to the drop time. Hence, the adsorption current should be inversely proportional to the drop time. This relation is realized as shown in Table IV.

TABLE IV

C, millimolar	i_{ads}, ampere	*t*, sec./drop	$i_{ads} \times t$, coulomb
0.300	0.372×10^{-6}	4.04	1.50×10^{-6}
	$.332 \times 10^{-6}$	4.48	1.49×10^{-6}
	$.286 \times 10^{-6}$	5.30	1.51×10^{-6}

The resolution of the polarographic reduction wave of bis-(diethylthiocarbamyl) disulfide into two separate waves, an adsorption wave and a reduction wave of the free molecules in solution, and the fact that the sum of the waves must be measured to obtain the diffusion current, suggest that the single reduction wave of some organic compounds includes an adsorption wave. The reduction potential of the adsorption wave would not be sufficiently different from the reduction potential of the free molecules in solution to be resolved, but would be sufficiently different from the reduction potential of the free molecules in solution to cause the wave to appear irreversible by the criterion of the log plot. This principle is supported by the appearance of maxima in the middle of some reduction waves which could be explained on the premise that adsorption waves are present and that the maxima are occurring at the top of the waves of the free molecules in solution as in the case of the disulfide.

Acknowledgment.—The authors wish to thank Donald W. Beesing of this Laboratory for his analysis of sodium diethyldithiocarbamate for water of hydration.

Summary

The polarographic properties of the bis-(diethylthiocarbamyl) disulfide–diethyldithiocarbamate ion oxidation–reduction system have been presented. The standard oxidation–reduction potential has been measured as −0.33 volt *vs.* N.H.E. The two-step reduction wave of bis-(diethylthiocarbamyl) disulfide and the two-step oxidation wave of diethyldithiocarbamate ion have been demonstrated to be caused by adsorption of the disulfide at the mercury-solution interface. The ionization constant of the unstable diethyldithiocarbamic acid has been measured: $K_a = 2.9 \times 10^{-6}$ in 60% ethanol by volume at 25.0°.

BRECKSVILLE, OHIO RECEIVED FEBRUARY 22, 1950

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Adsorption and Reduction of Tetrachloroplatinate(II) Ion at the Dropping Mercury Electrode

BY H. A. LAITINEN AND E. I. ONSTOTT[1]

Tetrachloroplatinate (II) ion is reduced at the dropping mercury electrode at small values of the applied e.m.f. At more negative potentials, a pronounced decrease in the current is observed. Under certain experimental conditions, an ordinary polarographic wave is observed just before the discharge of the supporting electrolyte.

The early reduction process does not proceed in the presence of camphor at potentials where camphor is adsorbed at the electrode. Since an adsorbed film of camphor has previously been observed to interfere with the adsorption and reduction of cystine[2] at the dropping mercury electrode, the early reduction process is best interpreted on the basis that adsorption is necessary for reduction and that desorption of the negatively charged complex ion is responsible for the decreasing current. The later reduction wave is interpreted as an irreversible reduction of the complex ion without adsorption.

Willis[3] unsuccessfully attempted to find a

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[1] Abstracted from the Doctorate Thesis of E. I. Onstott, 1950.

[2] Kolthoff and Barnum, THIS JOURNAL, **63**, 520 (1941).

[3] Willis, *ibid.*, **67**, 547 (1945).