

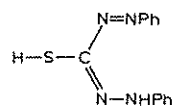
STUDIES WITH DITHIZONE. PART XIV. A NEW OXIDATION  
PRODUCT OF DITHIZONE

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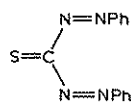
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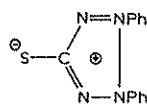
The deterioration of solutions of the reagent dithizone (1,5-diphenyl-3-mercaptoformazan; (I),  $H_2Dz$ ) is a matter of some consequence in analytical practice and it has commonly been attributed to oxidation. Deliberate attempts to oxidise dithizone with amyl nitrite led BAMBERGER *et al.*<sup>1</sup> to isolate a reddish orange compound which he formulated as the thiocarbodiazone (II). The same compound can be obtained with a variety of oxidising agents (*e.g.* hydrogen peroxide, iodine, manganese dioxide, potassium permanganate) and one of us<sup>2</sup> has shown the product to be identical with that isolated by OGILVIE AND CORWIN<sup>3</sup> by oxidising dithizone with alkaline hexacyanoferrate (III), and formulated by him as the sydnone (III). Another isomeric oxidation product of dithizone is the purple compound first reported by OGILVIE AND CORWIN<sup>3</sup> and investigated in greater detail by MAHNOT<sup>4</sup>. It appears from its chemical reactions and X-ray crystallography<sup>5</sup> to possess the unexpected structure (IV).



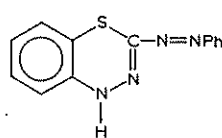
(I)



(II)



(III)



(IV)

If the oxidation of dithizone is carried out by treating its solution in chloroform with a weakly alkaline solution of hydrogen peroxide, the sydnone (III) is the main product. If, however, the oxidation is carried out with 30% hydrogen peroxide in a strongly alkaline medium, the main product is a violet-purple compound  $C_{13}H_{12}O_3N_4S$  that is not identical with (IV) and which proves to be 1,5-diphenylformazan-3-sulphonic acid (V). The presence of a sulphonic group is indicated by two strong absorption bands in the infrared spectra (KBr disc) at 13.28 and 13.50  $\mu$  indicative of an  $-SO_3H$  group<sup>6</sup>. The intense absorption band at 9.66  $\mu$  is characteristic of an  $S=O$  stretching vibration<sup>7</sup>. The new compound formed a characteristic derivative with benzylthiuronium hydrochloride, *viz.* the crystalline red benzylthiuronium-1,5-diphenylformazan-3-sulphonate.

1,5-Diphenylformazan-3-sulphonic acid dissolves readily in most organic sol-

vents to give solutions whose characteristics are shown in Table I. The differences in colour are quite striking, and when the spectra are compared (Fig. 1), it is obvious that the two absorption bands in acetone (curve 2) correspond closely with the separate long-wave peaks in chloroform (curve 1) and ethanol (curve 3) and that the three curves intersect at a common point (460 nm). This resemblance to an isosbestic point suggested that an acid-base equilibrium might be involved. This was confirmed by the spectra in chloroform saturated with hydrogen chloride (curve 4) and ammonia gas (curve 5) respectively. The acidic solutions of the sulphonic acid are reddish-violet in colour and absorb at  $\lambda_{\max}$  523 nm ( $\epsilon_{\max}$   $3.62 \cdot 10^4$ ); whereas the basic solution contain-

TABLE I

ABSORPTION SPECTRA OF 1,5-DIPHENYLFORMAZAN-3-SULPHONIC ACID  
(Molecular extinction coefficients in parentheses given as  $10^3 \epsilon$ )

Chloroform	Acetone	Ethanol
$\lambda_{\max}$ 523 (31.17) (shoulder at 548 nm)	512 (18.52) (shoulder at 542 nm)	—
$\lambda_{\min}$ 448 (12.43)	470 (14.19)	423 (15.47)
$\lambda_{\max}$ 289 (10.08) (shoulder at 335 nm)	—	350 (4.96)
$\lambda_{\min}$ 270 (9.35)	—	(broad shoulder ~ 300 nm)
$\lambda_{\max}$ 265 (10.01)	—	250 (14.30)

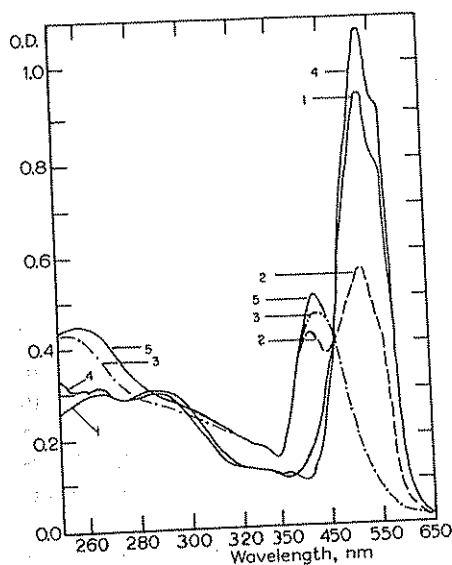
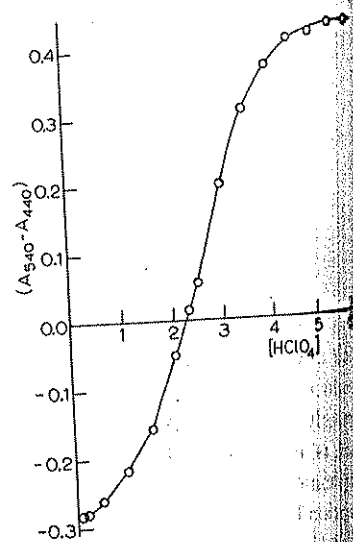


Fig. 1. The absorption spectra of  $3.0 \cdot 10^{-5}$  M solutions of 1,5-diphenylformazan-3-sulphonic acid in chloroform (curve 1), acetone (curve 2), ethanol (curve 3), chloroform saturated with HCl (curve 4), chloroform saturated with ammonia gas (curve 5).

Fig. 2. The optical density of  $1.850 \cdot 10^{-5}$  M solutions of 1,5-diphenylformazan-3-sulphonic acid in perchloric acid at 540 nm minus the optical density at 440 nm.

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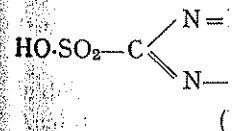


TABLE II

THE ABSORPTION SPEC  
DETERMINATION OF pK

[HClO <sub>4</sub> ]	H <sub>0</sub>
0.1	—
0.2	—
0.5	—
1.0	—
1.5	—
2.0	—
2.5	—
3.0	—
3.5	—
4.0	—
4.5	—
5.0	—
5.5	—
6.0	—

\* Measurements in 4-cl

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$$H_0 = \log [B]/$$

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ing the sulphonate ion absorbs at  $\lambda_{\max}$  425 nm ( $\epsilon_{\max}$   $2.34 \cdot 10^4$ ). In aqueous solution the sulphonate ion absorbs at 540 nm ( $\epsilon_{\max}$  28,540) and the sulphonate ion at 440 nm ( $\epsilon_{\max}$  18,780). By measurements (Table II) on a  $1.850 \cdot 10^{-5}$  M solution in perchloric acid of concentrations ranging from 0.1 to 6 M, it was possible to determine spectrophotometrically the position of equilibrium in the dissociation  $V \rightleftharpoons VI$ :

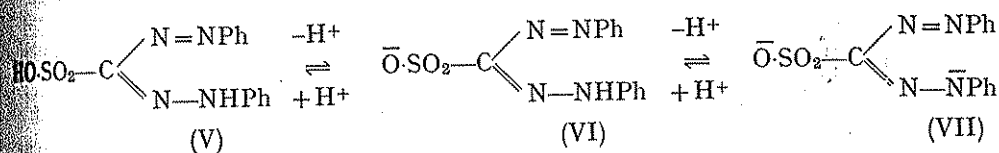


TABLE II

THE ABSORPTION SPECTRUM OF 1,5-DIPHENYLFORMAZAN-3-SULPHONIC ACID IN PERCHLORIC ACID. DETERMINATION OF  $pK_1$

[HClO <sub>4</sub> ]	$H_0$ value	Absorbancy (1-cm cell) at	
		440 nm	540 nm
0.1		0.347	0.265 <sup>a</sup>
0.2		0.350	0.283 <sup>a</sup>
0.5		0.341	0.323 <sup>a</sup>
1.0	-0.22	0.326	0.430 <sup>a</sup>
1.5	-0.53	0.312	0.152
2.0	-0.78	0.278	0.227
2.5	-1.01	0.236	0.291
3.0	-1.23	0.192	0.393
3.5	-1.47	0.152	0.462
4.0	-1.72	0.134	0.508
4.5	-1.97	0.121	0.517
5.0	-2.23	0.105	0.520
5.5	-2.52	0.100	0.531
6.0	-2.84	0.099	0.530

<sup>a</sup> Measurements in 4-cm cell.

The isobestic point at 475 nm is clearly defined and from the position of the point of inflection in the plot of the difference in absorbancy at 540 and 440 nm against the concentration of perchloric acid (Fig. 2), the acid dissociation constant  $pK_1$  defined by the equation

$$H_0 = \log [B]/[BH^+] + pK_1$$

was calculated, as described by DAVIS AND GEISSMAN<sup>8</sup>, as  $-0.92 \pm 0.1$ .

When aqueous solutions of 1,5-diphenylformazan-3-sulphonic acid are made alkaline, the yellow colour changes to reddish violet as the equilibrium  $VI \rightleftharpoons VII$  is displaced to the right. The absorption spectra (Fig. 3) show a well defined isobestic point at 472 nm and by plotting the difference between the optical densities at 520 and 440 nm against the pH the value  $pK_2 = 12.9$  ( $\mu = 1$  M sodium nitrate) was derived by the method previously used<sup>8</sup>.

Whereas the sydnone (III) is the main product when the oxidation of dithizone (I) is carried out in neutral or slightly alkaline solution, the proportion of the sydnone

diminishes and that of the sulphonic acid (V) increases as the alkalinity is raised. It would appear that kinetic factors favour the formation of (V) from the anion derived by loss of a proton from the acidic thiol group in (I) for which the value  $pK = 4.5$  has been reported<sup>9</sup>. It is noteworthy that conditions that favour the formation of the purple isomer (IV) of the sydnone (III), viz. heating under reflux with glacial acetic acid<sup>9</sup> or

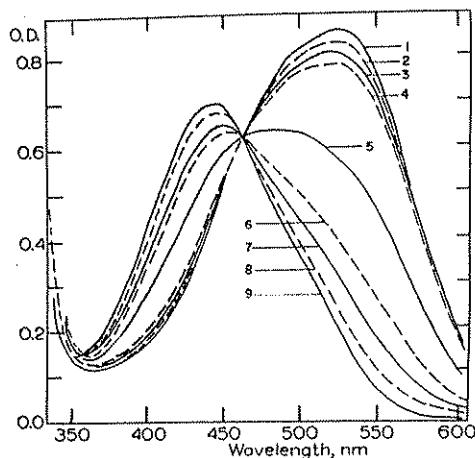


Fig. 3. The absorption spectra of  $1.85 \cdot 10^{-5} M$  solutions of 1,5-diphenylformazan-3-sulphonic acid in aqueous sodium hydroxide containing sodium nitrate ( $\mu = 1 M$ ). Curves 1-9 for pH 13.73, 13.63, 13.54, 13.42, 13.12, 12.73; 12.12, 11.42, and 7.73 respectively.

prolonged contact with concentrated solutions of mineral acids in aqueous dioxan<sup>4,10</sup> are those in which the thiol function of (I) is suppressed and the dithizone reacts predominantly in the tautomeric thione form  $\text{Ph.N}=\text{N.CS.NH.NH.Ph}$  or even as its conjugate acid.

#### EXPERIMENTAL

##### Preparation of 1,5-diphenylformazan-3-sulphonic acid

Dithizone (B.D.H. laboratory grade) was first purified by taking up in isopiastically distilled dilute ammonia solution, filtering and reprecipitation by hydrochloric acid. The purified dithizone (2.0 g) was dissolved in sodium hydroxide solution (250 ml of 0.5 M) and treated dropwise with 30% hydrogen peroxide (40 ml; excess) in a 500-ml flask fitted with a mechanical stirrer (20 min). Stirring was continued for a further 40 min and the reaction mixture was filtered through a sintered glass funnel. The filtrate was cooled to 0° and acidified with the minimum amount of sulphuric acid (10 M) when 1,5-diphenylformazan-3-sulphonic acid separated as a brownish-black precipitate. It was taken up in the minimum amount of 0.1 M sodium hydroxide and after cooling to 0°, the sulphonic acid was reprecipitated with hydrochloric acid, dried, and finally recrystallized from chloroform as very fine brown-black needles (m.p. 181° decomp.; yield, 56%). (Found: C, 51.10, 51.15; H, 3.95, 3.85; N, 18.45, 18.25; S, 10.87, 10.45%.  $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_3\text{S}$  requires, C, 51.28; H, 3.97; N, 18.41; S, 10.54%).

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TABLE III

THE ABSORPTION  
AT  $\mu = 1.0$  (NaNO

[NaOH]

1.0 · 10 <sup>-6</sup>
1.0 · 10 <sup>-5</sup>
1.0 · 10 <sup>-4</sup>
1.0 · 10 <sup>-3</sup>
2.5 · 10 <sup>-3</sup>
5.0 · 10 <sup>-3</sup>
1.0 · 10 <sup>-2</sup>
2.5 · 10 <sup>-2</sup>
5 · 10 <sup>-2</sup>
1.0 · 10 <sup>-1</sup>
1.5 · 10 <sup>-1</sup>
2.5 · 10 <sup>-1</sup>
3.5 · 10 <sup>-1</sup>
5.0 · 10 <sup>-1</sup>
6.5 · 10 <sup>-1</sup>
7.5 · 10 <sup>-1</sup>
8.0 · 10 <sup>-1</sup>
8.5 · 10 <sup>-1</sup>
9.5 · 10 <sup>-1</sup>
10.0 · 10 <sup>-1</sup>

ity is raised. Its anion derived  $pK = 4.5$  has n of the purple acetic acid<sup>3</sup> or

#### Preparation of thiuronium derivative

When cold aqueous solutions of 1,5-diphenylformazan-3-sulphonic acid (0.2 g) and S-benzylisothiuronium chloride (0.2 g) were mixed, S-benzylthiuronium-1,5-diphenylformazan-3-sulphonate separated in quantitative yield and formed bright orange needles (m.p. 179°) on crystallization from 50% aqueous ethanol. (Found: C, 53.58, 53.51; H, 4.80, 4.79%.  $C_{21}H_{22}N_6O_3S_2$  requires C, 53.65; H, 4.71%).

#### Determination of $pK_1$

Aliquot portions (2 ml) of a stock solution of  $2.3125 \cdot 10^{-4}$  M sulphonic acid (V) in deionised water were mixed in various proportions with a concentrated solution of AnalaR perchloric acid and made up to 25 ml. The optical density of each sample was measured at 540 and 440 nm with a Unicam S.P. 500 spectrophotometer instrument in matched silica cells. All measurements were controlled thermostatically at 25°. The results are given in Table II and shown graphically in Fig. 2.

The absorption spectra of all the samples were recorded with a Unicam S.P. 700 spectrophotometer. All the curves intersected at an isosbestic point at 475 nm.

#### Determination of $pK_2$

Aliquot portions (2 ml) of  $2.3125 \cdot 10^{-4}$  M sulphonic acid (V) in deionised water were mixed with  $x$  ml of standard carbonate-free 2.5 M sodium hydroxide and  $(10-x)$  ml of 2.5 M sodium nitrate and made up to 25 ml. All solutions were made up in  $CO_2$ -free water and transferred by nitrogen pressure into vessels flushed with nitrogen. Spectra were recorded in cells thermostatted at 25° immediately after the solutions

TABLE III

THE ABSORPTION SPECTRA OF 1,5-DIPHENYLFORMAZAN-3-SULPHONIC ACID IN SODIUM HYDROXIDE AT  $\mu = 1.0$  ( $NaNO_3$ ) AND 25°

[NaOH]	pH	Absorbancy (2-cm cell) at	
		440 nm	520 nm
$1.0 \cdot 10^{-6}$	7.725	0.688	0.238
$1.0 \cdot 10^{-5}$	8.725	0.690	0.240
$1.0 \cdot 10^{-4}$	9.725	0.687	0.245
$1.0 \cdot 10^{-3}$	10.725	0.687	0.250
$2.5 \cdot 10^{-3}$	11.123	0.687	0.260
$5.0 \cdot 10^{-3}$	11.424	0.678	0.270
$1.0 \cdot 10^{-2}$	11.725	0.667	0.300
$2.5 \cdot 10^{-2}$	12.123	0.638	0.333
$5 \cdot 10^{-2}$	12.424	0.615	0.410
$1.0 \cdot 10^{-1}$	12.725	0.580	0.520
$1.5 \cdot 10^{-1}$	12.901	0.550	0.586
$2.5 \cdot 10^{-1}$	13.123	0.515	0.672
$3.5 \cdot 10^{-1}$	13.269	0.487	0.727
$5.0 \cdot 10^{-1}$	13.424	0.471	0.780
$6.5 \cdot 10^{-1}$	13.538	0.455	0.803
$7.5 \cdot 10^{-1}$	13.601	0.448	0.818
$8.0 \cdot 10^{-1}$	13.628	0.443	0.826
$8.5 \cdot 10^{-1}$	13.654	0.440	0.842
$9.5 \cdot 10^{-1}$	13.703	0.440	0.845
$10.0 \cdot 10^{-1}$	13.725	0.440	0.850

had been made up. The various spectra intersected at a well-defined isosbestic point at 472 nm (Fig. 3), confirming the acid-base equilibrium  $\text{VI} \rightleftharpoons \text{VII}$ . The optical densities at 440 nm (yellow ion; VI) and 520 nm (reddish-violet anion; VII) were measured with a Unicam S.P. 500 spectrophotometer and are given in Table III.

In calculating the pH corresponding to calculated  $[\text{OH}^-]$ , the value  $K_w = 1.884 \cdot 10^{-14}$  for  $25^\circ$  and  $\mu = 1.0$  was used<sup>11</sup>. The optical density at 520 nm minus the optical density at 440 nm was plotted against pH to give a sigmoid curve (not reproduced, but resembling Fig. 2), from which the value  $\text{p}K_2 = 12.90$  was calculated as previously described<sup>8</sup>.

## SUMMARY

The oxidation of dithizone with hydrogen peroxide in strongly alkaline solutions yields 1,5-diphenylformazan-3-sulphonic acid as a violet compound which loses a proton to give yellow solutions of the corresponding sulphonate ion and reddish-violet solutions on removal of a second proton from an imino-group. The acid dissociation constants  $\text{p}K_1 = -0.92$  and  $\text{p}K_2 = 12.9$  ( $\mu = 1 \text{ M NaNO}_3$ ) were determined spectrophotometrically.

## RÉSUMÉ

L'oxydation de la dithizone par le peroxyde d'hydrogène en solutions fortement alcalines conduit à la formation de l'acide 1,5-diphénylformazane-3-sulfonique violet qui par perte d'un proton donne des solutions jaunes de l'ion sulfonate correspondant et des solutions violet rouge par départ d'un second proton du groupe imino. Les constantes de dissociation acides  $\text{p}K_1 = -0.92$  et  $\text{p}K_2 = 12.9$  ( $\mu = 1 \text{ M NaNO}_3$ ) ont été déterminées par spectrophotométrie.

## ZUSAMMENFASSUNG

Die Oxydation von Dithizon mit Wasserstoffperoxyd in stark alkalischer Lösung führt zu 1,5-Diphenylformazan-3-sulfonsäure. Diese violette Verbindung führt bei Angabe eines Protons zu gelben Lösungen des korrespondierenden Sulfonats und zu rötlich-violetten Lösungen bei Angabe eines zweiten Protons von der Imino-Gruppe. Die Säuredissoziationskonstanten  $\text{p}K_1 = -0.92$  und  $\text{p}K_2 = 12.9$  ( $\mu = 1 \text{ M NaNO}_3$ ) wurden spektralphotometrisch bestimmt.

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STUDIES WITH  
ORGANOMERCU

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Department of In

(Received Janua

Dithizone is widely used spectrographically for detection and *et al.*<sup>2</sup> reported with solutions which can be to be similar to and that of o-

IRVING of other organo-plexes of the  $\text{C}_6\text{H}_5$ , *p*- $\text{CH}_3$ -mercury(II) acid to form  $\text{Hg}(\text{H}$  error<sup>6</sup>. The im-mercury dithizone and alkaline a paper<sup>8</sup> but the year could be organomercur-

With the complex stable to yield strong into carbon tetrachloride (cf. Table I). established, the method of two-phase system shown in Fig. numbered 16, each component

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A<sub>1</sub> =  $\alpha$