

INVESTIGATIONS ON THE REDOX CHARACTER OF DITHIZONE BY
VOLTAMMETRIC METHODS
PART II. THE ELUCIDATION OF THE DETERIORATION OF DITHIZONE
SOLUTIONS

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SUMMARY

The electrochemical redox behaviour of dithizone and its oxidation products have been examined in detail and the mechanisms of the electrochemical and aerial oxidation of dithizone are considered. All the oxidation products (tetrazolium and disulphide compounds) can be followed by voltammetric methods. The results of the electrochemical investigation of dithizone are useful for practical analytical and electroanalytical applications of dithizone.

The preparation and storage of dithizone solutions has been a well known problem since the introduction of the reagent for trace analysis. Various methods have been suggested to decrease the decomposition of dithizone solutions, but the mechanism of the cleavage of dithizone has been studied only recently [1], by e.s.r., i.r. and electronic spectroscopic methods. It has been suggested that a disulphide is formed under oxidative conditions, which may disproportionate to dithizone and mesoinic tatrazolium compounds.

Electrochemical methods seem promising for mechanistic studies of this oxidation, for the expected oxidation products can be characterized by polarographic and voltammetric techniques. Moreover, possible oxidation pathways can be evaluated on the basis of a knowledge of the oxidation-reduction properties.

EXPERIMENTAL

The conditions for the polarographic and voltammetric measurements have already been described [2]. During controlled potential electrolysis on a macro scale, the spectra of the solutions were measured with a Pye-Unicam spectrophotometer with a thermostatted flow-through cell. A peristaltic pump circulated the solution during the experiments.

Microphotographs were taken with a MBS II binocular microscope and an Exacta Warex camera with Agfacolor CN17 film. This equipment was installed on the stand of the Radiometer E69 hanging mercury drop electrode.

The impregnated graphite (IGE) and carbon paste (CPE) electrodes were

prepared as described previously [3, 4]; the glassy carbon electrode (GCE) was obtained from Tokay Company, Japan.

3-Mercapto-1,5-diphenyltetrazolium was prepared as described by Irving et al. [1] by oxidation of dithizone with permanganate in basic solution.

All measurements were made at 25 °C. The chemicals used were analytical grade.

Experiments were generally performed in test solutions containing $5 \cdot 10^{-4}$ M dithizone, with 1 M sodium hydroxide—0.2 M sodium sulphate—20 % ethanol as supporting electrolyte (pH 13.0).

RESULTS AND DISCUSSION

Among the products of chemical oxidation of dithizone, tetrazolium and disulphide species have been recognized [1]. The waves attributed to these two species in solutions of dithizone oxidized by atmospheric oxygen are discussed here in some detail. In addition, the electro-oxidation of dithizone was studied at mercury and carbon electrodes.

Electrochemical behaviour of the tetrazolium derivative

In dithizone, the azo group undergoes a 2-electron reduction to a hydrazo group [2]. When dithizone undergoes autoxidation, this wave is preceded by another wave at more positive potentials. The height of this wave, which is about 0.1 V more positive than the original wave, increases with the time of oxidation, and finally reaches the same height as the original wave. This result, in conjunction with controlled potential coulometry, indicates that the autoxidation product is reduced in a 2-electron step. The linear dependence of the height of this wave on the square root of the mercury column height, and the fact that the temperature coefficient varies between 1.4 and 1.8 %/°C, indicate that the wave is diffusion-controlled, and its height is therefore a linear function of the concentration of the oxidized form. The same behaviour was observed for the oxidation product formed by reaction of dithizone with permanganate.

The oxidation product can be converted to the parent dithizone by electroreduction. This was proved both by controlled potential electrolysis and by cyclic voltammetry. Electroreduction at the potential of the more positive wave, gave a reduction product which showed the single polarographic wave of dithizone (Fig. 1) and an absorbance spectrum (Fig. 2) identical with that obtained from an equimolar solution of dithizone.

In the cyclic voltammetric studies at the HMDE (Fig. 3), the red reaction product of the electrode process was observed and photographed at an electrode potential more negative than that of the peak potential of the first wave.

Hence the autoxidation product is easily reduced to dithizone which can then be further reduced at the N=N bond. Because of the previous identification of the tetrazolium species [1], and because the half-wave potential of

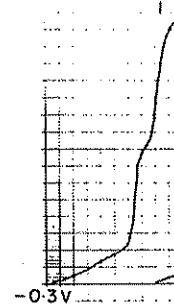
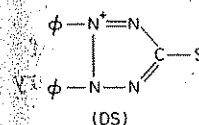


Fig. 1. Polarogram of oxidized dithizone.

Fig. 2. Absorbance spectrum of oxidized dithizone (1-cm cells).

the more positive wave is about 0.1 V more positive than the original wave, with a slope characteristic of a 2-electron electrode reaction, the following scheme can be proposed:



This proposed scheme shows the difference in the reduction potential of the oxidized form and the parent dithizone.

Attempts to reduce the tetrazolium compound to dithizone were unsuccessful.

The present study shows that the tetrazolium oxidation product of dithizone is a macroscopic species.

Polarographic studies

In the cyclic voltammetric studies the reduction wave was observed at a more negative potential than that of the oxidized solution. The reduction product was identified as a disulphide intermediate.

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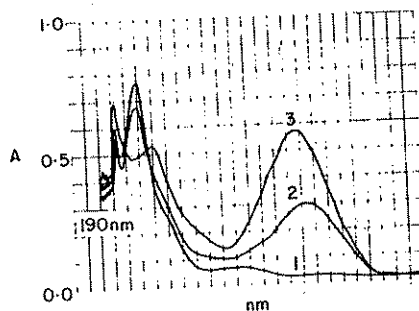
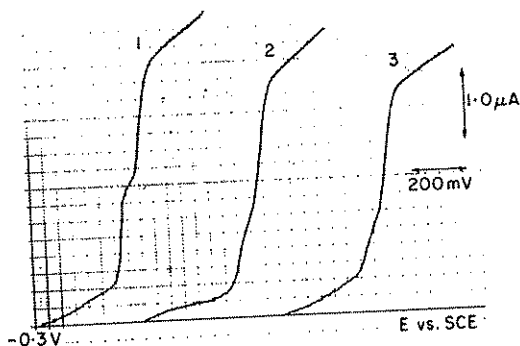
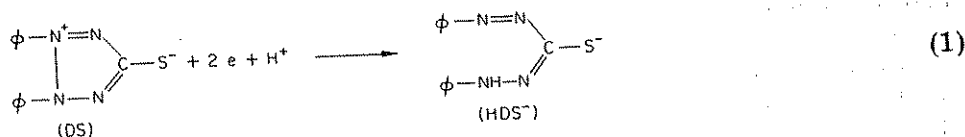


Fig. 1. Polarographic waves recorded during a controlled potential electrolysis when the oxidized dithizone was reduced, $t_3 > t_2 > t_1$.

Fig. 2. Spectra recorded for the same solutions as for the polarographic waves in Fig. 1 (1-cm cells).

the more positive wave of the oxidation product is a linear function of pH with a slope of 29 mV/pH over the pH range 9–14 (corresponding to an electrode reaction involving 2 electrons and one proton exchange), the following scheme can be proposed for the reduction of the autoxidized product:



This proposed scheme is supported by comparison with the waves of triphenyl-tetrazolium chloride, which occur in a similar potential region. The small difference in the half-wave potentials can be attributed to the effect of replacement of the mercapto group by a phenyl group.

Attempts to oxidize dithizone electrochemically at the HMDE to the tetrazolium compound failed.

The present study indicates that dithizone solutions free from the tetrazolium oxidation product can be prepared by controlled potential electrolysis on a macro scale.

Polarographic reduction of an autoxidation intermediate

In the course of autoxidation of alkaline dithizone solutions, a new reduction wave was observed at -1.25 V vs. SCE; this disappears in completely oxidized solutions (Fig. 4). The wave corresponds to a reduction of a disulphide intermediate in the autoxidation process



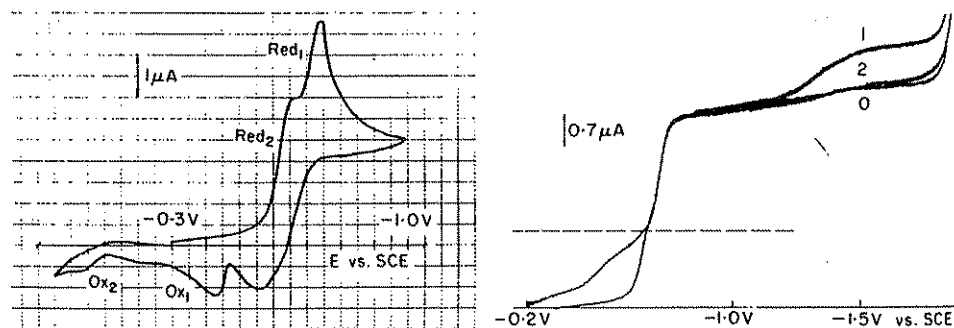


Fig. 3. Cyclic voltammogram of oxidized dithizone solution at the HMDE. Red₁: azo-hydrazo reduction. Red₂: tetrazolium-azo reduction.

Fig. 4. Polarographic waves recorded for dithizone solutions before (0), during (1) and after (2) an aerial oxidation.

Anodic waves of dithizone at mercury electrodes

The one-electron anodic wave of dithizone [2] corresponds to mercury salt formation



This scheme is supported by the results of cyclic voltammetry, which indicates that the product of the anodic reaction is solid and can be stripped (Fig. 5). The solid violet product was observed by microphotography; the spectrum of a carbon tetrachloride solution of the product was the same as that of mercury dithizonate. The dependence of i_p on $v^{1/2}$ indicates that the mercury(I) dithizonate formed can undergo disproportionation.

The anodic wave is therefore a measure of the concentration of the thiol form of dithizone, and can be used for the determination of this reduced form. Accordingly, the height of this anodic wave decreases in the course of chemical oxidation.

Electro-oxidation of dithizone at carbon electrodes

Attempts to carry out electrooxidation on platinum or impregnated graphite electrodes [5] led to the formation of insoluble layers at the electrode surface. Useful current-voltage curves were obtained with glassy carbon and carbon paste electrodes (Fig. 6). Nevertheless, even with the carbon paste electrode, the initial oxidation process involved the formation of a solid layer at the electrode surface. Thus it is impossible to draw proper conclusions about the mechanisms, although, as in the case of autoxidation, it appears that the primary electro-oxidation product is a sparingly soluble disulphide compound which disproportionates and can be oxidized in the second electrochemical step. From the analytical point of view, the peak current, or limiting current at a rotating carbon paste electrode is proportional to the concentration of dithizone.

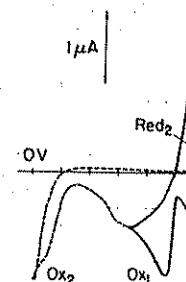
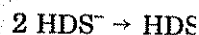


Fig. 5. Cyclic volt electrolysis (dash)

Fig. 6. Oxidation

Conclusions

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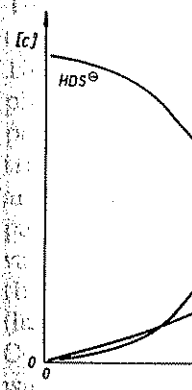
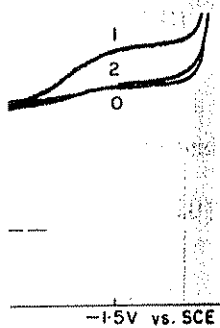


Fig. 7. Changes of



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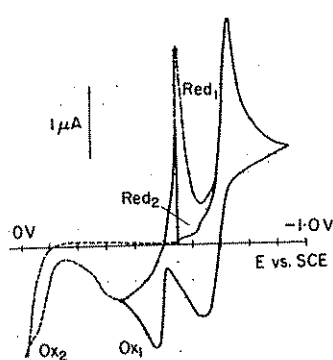


Fig. 5. Cyclic voltammogram of dithizone solution at the HMDE recorded after a pre-electrolysis (dashed line).

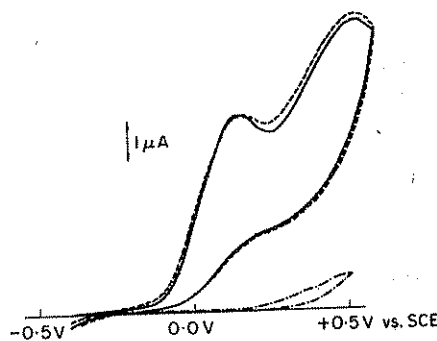


Fig. 6. Oxidation of dithizone at the CPE. The dashed line shows the background current.

Conclusions

The application of the electrochemical methods allows the concentration changes of dithizone (HDS^-), its disulphide (HDSSDH) and the tetrazolium species (DS^+) to be followed during an aerial oxidation process (see Fig. 7 and Table 1). This is consistent with the overall scheme



The aerial oxidation of dithizonate to the disulphide compound takes place at a larger reaction rate than the disproportionation of the disulphide compound (Fig. 7); hence the concentration curve of the disulphide species shows a maximum. Consequently, the rate of oxidation reaction is controlled by the disproportionation of disulphide in aqueous basic dithizone solutions.

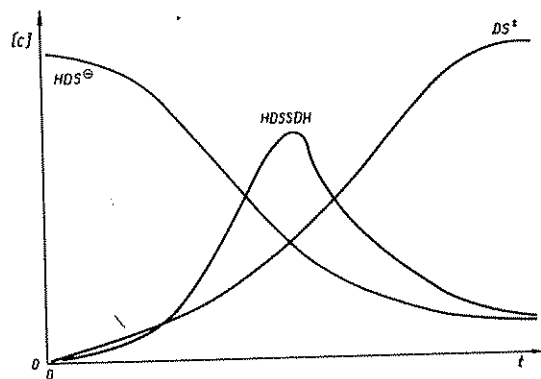


Fig. 7. Changes of concentration of dithizone and its intermediates during an aerial oxidation.

TABLE 1

Limiting currents and absorbance of dithizone and its intermediates during an aerial oxidation in aqueous basic solution

Time	i_{ox} (μA)	i_{red_1} (μA)	i_{red_2} (μA)	i_{red_3} (μA)	A_{250}	A_{472}	A_{473}
0 min	0.70	2.38	—	—	—	—	—
5 min	—	—	—	—	0.50	0.81	1.00
30 min	0.61	2.30	—	0.31	—	—	—
40 min	—	—	—	—	0.56	0.79	0.93
60 min	0.54	2.24	—	0.36	0.57	0.77	0.88
90 min	0.48	2.19	0.34	0.42	0.63	0.75	0.83
2 h	0.42	2.24	0.45	0.53	0.69	0.72	0.76
3 h	0.36	2.24	0.50	0.70	0.77	0.69	0.66
5 h	0.22	2.24	0.98	1.01	0.92	0.60	0.40
7 h	0.17	2.24	1.18	1.26	1.04	0.54	0.16
9 h	—	2.24	1.62	1.93	—	—	—
21 h	—	2.24	1.57	2.10	1.03	0.40	0.05
28 h	—	2.24	0.90	2.10	—	—	—

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