The Non-existence of Selenium Dithizonate

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Summary The yellow substance produced by the action of a solution of selenium dioxide in concentrated hydrochloric acid on a solution of dithizone (I;H_2Dz) in carbon tetrachloride is not selenium dithizonate, $Se(HDz)_4$, as alleged, but a disulphide (II) formed by oxidation of (I).

ALTHOUGH polonium and tellurium(II) show some metallic character, selenium behaves only as a non-metal and it is surprising that the reported preparation[1] of a selenium(IV) dithizonate of formula $Se(HDz)_4$ has not hitherto been questioned, especially since the known extractable complexes of dithizone (I;H_2Dz) are confined to a small group of typical metals in the centre of the Periodic Table and to alkyl or aryl derivatives of tin(IV), lead(IV), thallium(III), and mercury(II).[2]

The yellow organic phase ($\lambda_{\text{max.}}$ *ca.* 410 nm.) obtained when a solution of dithizone (I) in CCl_4 is treated with one of selenium dioxide in 6M-HCl or 11N-H_2SO_4 has been suggested for the spectrophotometric determination of trace amounts of the element.[3,4] The yellow colour was assumed to be due to selenium dithizonate.

More recently[1] Starý and Růžička deduced the formula $Se(HDz)_4$ from the observations (a) that 4·0 μmole of selenium(IV) consumed 16·2 and 16·8 μmole of dithizone (excess of which was stripped from the organic phase by treatment with dilute ammonia), and (b) that the amount of dithizone "liberated in a reversion reaction" by adding an excess of diethyldithiocarbamic acid (HDDC) was 15·6 and 17·0 μmole per 4·0 μmole of selenium. This last reaction was represented as

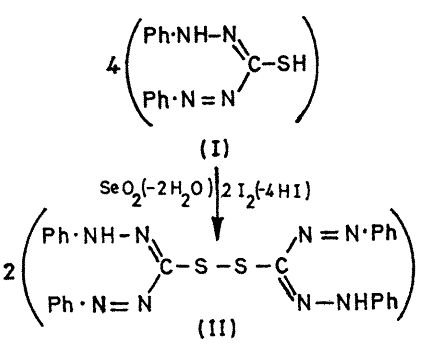
$$\mathrm{Se(HDz)_4 + 4HDDC = Se(DDC)_4 + 4H_2Dz} \qquad (1)$$

and although attempts to measure its equilibrium constant directly "did not give reproducible results" the value $10^{6\cdot27}$ was calculated from measurements of the exchange constant ($10^{-0\cdot78\pm0\cdot10}$) for the reaction

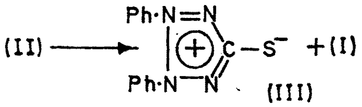
$$\mathrm{Se(HDz)_4 + 2Cd(DDC)_2 = Se(DDC)_4 + 2Cd(HDz)_2} \qquad (2)$$

and that ($10^{3\cdot53}$) for the exchange reaction between $Cd(HDz)_2$ and HDDC. From the measured equilibrium constants of the exchange reactions between $Se(HDz)_4$ and $As(DDC)_3$ ($10^{-9\cdot2\pm0\cdot2}$) and between $As(DDC)_3$ and H_2Dz ($10^{-7\cdot93}$) the equilibrium constant for reaction (1) was determined independently as $10^{6\cdot67}$, in excellent agreement with the previous value.

Unfortunately for the significance of these measurements the species $Se(HDz)_4$ does not exist, for we find that the yellow organic phase produced by contacting a solution of dithizone in carbon tetrachloride with one of selenium(IV) in concentrated hydrochloric acid does not contain selenium combined as a cation. Even when the dithizone is in large excess the selenium is found in the aqueous phase in the reduced elemental state as a red colloid. Small amounts do dissolve in the organic solvent and this may have misled the Japanese workers[3] who carried out some measurements with ^{75}Se. That selenium is not essential to the formation of the yellow organic-soluble product is shown by the formation of a substance with an identical spectrum and properties (q.v.) when dithizone is oxidised with iodine in the presence of some water.[5] The stoicheiometry of this reaction is consistent with the formation of the disulphide (II) and Starý and Růžička's quantitative data confirm that selenium(IV) acts purely as an oxidant for the thiol groups of (I).



Whether prepared by oxidation of (I) with selenium(IV) or with iodine, the disulphide (II) is characterised by a striking property in that on standing at room temperature the spectrum of dithizone gradually reappears. This is due to the disproportionation reaction



leading to equimolecular proportions of the sydnone (III) and dithizone (I). We have not yet succeeded in isolating solid (II) in an analytically pure state.

Treatment of the yellow solution of the disulphide (II) with an excess of HDDC certainly regenerates dithizone, and while the yield is at least 85% the reaction is far from instantaneous. Moreover, the process is one of reduction and the diethyldithiocarbamic acid can be replaced by hypophosphorous acid and similar reductants. Equation (1) ought therefore to be written as

$$\mathrm{(II) + 2HDDC = 2(I) + oxidation\ products\ of\ HDDC.}$$

It is not reversible, and it is not obvious how Starý and Růžička could have measured equilibrium constants for reactions (1) and (2) and for other reactions involving the non-existent species $Se(HDz)_4$.

(*Received, September 8th,* 1969; *Com.* 1355.)

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