Polarographic Evidence for the Structure of the so-called Phenylthiohydantoic Acid

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THE compound prepared by the reaction of monochloroacetic acid, ammonium thiocyanate, and aniline has been used under the name of "phenylthiohydantoic acid" (I) for the detection[1] and gravimetric determination[2] of cobalt and of other metals[3] for over fifty years; it appears under this name even in monographs.[3] At the turn of the century it was indicated[5,6] that the structure of this compound is not (I), but rather that of carbaminothioglycollic acid anilide (II). This information was nevertheless forgotten and in subsequent analytical publications[3] the compound was always considered to have structure (I).

During the study of the precipitation of cobalt from homogeneous solution with use of this reagent,[7] the polarographic behaviour of the reagent was studied and it was confirmed that the compound prepared by the usual synthetic method[3,4] has the structure (II) rather than (I). Indistinct anodic waves at pH 4—6·8 can be attributed to a thiocarbonic acid derivative (II) but not to a

$$\mathrm{PhN{=}C(NH_2)SCH_2{\cdot}CO_2H}\ (\mathrm{I}) \xrightarrow{\mathrm{H_2O}} \mathrm{PhNH{\cdot}CO{\cdot}NH_2} + \mathrm{HS{\cdot}CH_2{\cdot}CO_2H}\ (\mathrm{III})$$

$$\mathrm{PhNH{\cdot}CO{\cdot}CH_2{\cdot}S{\cdot}CO{\cdot}NH_2}\ (\mathrm{II}) \xrightarrow{\mathrm{H_2O}} \mathrm{PhNH{\cdot}CO{\cdot}CH_2{\cdot}SH}\ (\mathrm{IV}) + \mathrm{CO_2} + \mathrm{NH_3}$$

thioether (I) with a C–S–C grouping. At $pH > 7$ the compound undergoes hydrolysis and a well developed anodic wave (at $-0{\cdot}7$ v at pH 9·2 and $-0{\cdot}8$ v in 0·1N-sodium hydroxide) is formed. The anodic waves of the hydrolysis product when studied at pH 1 to 13 are identical in shape, in the type of adsorption pre-waves and in the half-wave potentials with the waves of thioglycollic acid anilide (IV), but differ completely from the anodic waves of thioglycollic acid (III). The formation of (IV) as the hydrolysis product is in agreement with the results of preparative work.[5,6] Hydrolysis at $pH > 7$ would be expected for the cleavage of the S–CO grouping, whereas the hydrolysis of an *S*-substituted thiourea would not be expected[8] at $pH < 10$. The course of hydrolysis is being studied[7] in more detail.

Elemental analysis does not distinguish between structures (I) and (II), but the fact that the compound could not be esterified with ethanol nor propylene oxide also indicates that structure (II) is correct, as does the absence of a CO_2H band in the 1700 cm.$^{-1}$ region. N.m.r. spectroscopy established the presence of a phenyl, a methylene, and an amino-group, but the singlet (one H) in the dimethyl sulphoxide solution at $\delta = -10{\cdot}5$ (against Me_4Si) could have been due either to the CO_2H of (I) or to the CONH of (II).

Thus, the compound used as an analytical reagent is not phenylthiohydantoic acid (I) but is carbaminothioglycollic acid anilide (II). The ease of hydrolysis of this compound partially accounts for the anomalous behaviour of the reagent when used for the gravimetric determination of cobalt.

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