

nitrogen until the gas evolution ceased and a clear solution resulted (0.75 h). The solution was cooled, made alkaline with potassium carbonate and extracted with ether. The combined ethereal abstracts were dried over solid potassium carbonate, filtered through a short alumina column (neutral alumina, activity IV) and evaporated. The resulting crude, crystalline tri-piperidine was crystallized once from acetone yielding 1.84 g of isotripiperidine, III, m.p. 96–98°, identical with isotripiperidine prepared according to Schöpf¹ (TLC, IR, and mixed m.p.).

This work was supported by a grant from the Svenska Tobaks AB.

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Received December 6, 1966.

Complex Formation in Concentrated Sulfuric Acid between Selenium(IV) and 1,2'-Dianthrimide

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The present paper describes the complex formation in concentrated (96.0 %) sulfuric acid between selenium(IV) and 1,2'-dianthrimide.

Instruments and equipment. A Zeiss spectrophotometer PMQ II, a Beckman DB recording spectrophotometer and 1 cm cells were employed.

All solutions were prepared and heated in 50 ml bottles (Jena Gerätglas) with ground-glass stoppers. The solutions were heated in an ordinary, thermostatically controlled drying oven.

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Reagents. 1,2'-Dianthrimide was synthesized according to the procedure given in DRP 174 699. An infrared spectrum and elemental analysis showed that the product was pure.

In all experiments selenium dioxide (Light and Co, Ltd., Great Britain) and 96.0 % sulfuric acid, both of reagent-grade quality, were used.

Standard solutions. The different standard solutions were prepared by dissolving the proper amounts of the reagents in sulfuric acid (to dissolve all of the selenium dioxide, the acid had to be heated slightly), transferring the solutions to volumetric flasks and diluting to volume with acid.

Heating time, heating temperature and concentration of sulfuric acid. On the basis of preliminary experiments, a heating time of 5 h, a heating temperature of 70°C and an acid concentration of 96.0 % were chosen.

Absorption curves. Fig. 1 shows the absorption curves recorded. The curves of

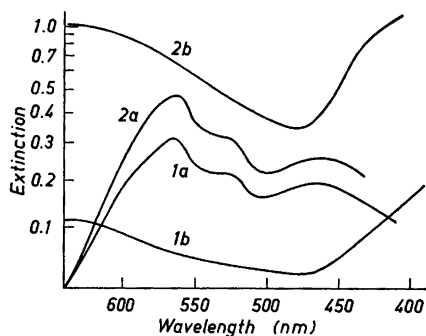


Fig. 1. Absorption curves of solutions of 1,2'-dianthrimide and of the selenium(IV) 1,2'-dianthrimide complex. The concentration of the standard solutions of the reactants was 2.00×10^{-4} M. Curve 1a: Absorption curve of a mixture of 18 ml of selenium and 2 ml of 1,2'-dianthrimide standard solutions measured against a blank solution of 2 ml of 1,2'-dianthrimide standard solution and 18 ml of sulfuric acid. Curve 1b: Absorption curve of the above blank solution measured against sulfuric acid. Curve 2a: Absorption curve of a solution containing 2 ml of selenium and 18 ml of 1,2'-dianthrimide standard solutions measured against a blank solution of 18 ml of 1,2'-dianthrimide standard solution and 2 ml of sulfuric acid. Curve 2b: Absorption curve of the latter blank solution measured against sulfuric acid.

the solutions of the complex exhibit the same form, irrespective of the concentration ratio between the reactants, this indicating the presence of only one complex.

The method of continuous variation. Curves of continuous variation showed a rounded maximum at the mole fraction 0.5, the curve branches had no inversion and the gradient at the end point was different from zero, these features pointing to the presence of only one complex with the composition SeDi. Detailed curves of continuous variation recorded in the low mole fraction range of selenium confirmed the above conclusions.

The straight-line method. Presupposing the presence of a complex of the form Se_mDi_n , the straight-line method of Asmus¹ with the modification introduced by Klausen and Langmyhr² gave the coefficients $m = 1$ and $n = 1$, this confirming the composition SeDi.

Stability constant. With the experimental data from the method of continuous variation and from the straight-line method the stability constant for the complex SeDi was calculated to be 2.8×10^4 and 2.5×10^4 , respectively.

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Received November 22, 1966.

Effect of Crystal Dimensions on the Yield of Radiation Induced Radicals in Organic Substances

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It is generally assumed that the chemical alterations observed when organic substances are exposed to ionizing radiation to a large extent are mediated by free radicals. Information about the formation and properties of radiation-induced free radicals

can be obtained by electron spin resonance (ESR) spectroscopy. The radical yield, expressed by the G -value (number of radicals observed per 100 eV absorbed radiation energy), has been determined for a large number of organic substances. The results presented in the literature usually refer to conditions such as high vacuum, a fixed temperature like, for example, room temperature, and extrapolation to zero dose or to doses below 1 megarad where linear "dose-effect" curves are obtained. It appears that even under well-defined conditions the radical yield for a substance may vary considerably from one laboratory to another.¹ These discrepancies may in part be attributed to factors involved in the ESR technique such as the reference system and the quantitative procedure used. However, the observed radical yield may also be influenced by the chemical and physical form of the organic compound. Thus, the hydrochloride of a substance very often exhibits a larger radical yield than the pure compound.² Some recent experiments carried out in this laboratory (to be published) demonstrate that the radical yield for a freeze-dried substance may vary with the pH of the solution prior to lyophilization.

In the present communication experimental data will be presented which indicate that the physical dimensions of the crystals in a sample may be of importance with regard to the observable yield of radiation induced radicals.

The amino acid glycine, the dipeptide glycylglycine, and the two enzymes trypsin and lysozyme were studied. Single crystals of glycine and glycyl-glycine, grown by slow evaporation from aqueous solutions, were compared with freeze-dried samples. The two enzymes were dissolved in water and recrystallized by slow evaporation at 0°C. In this way relatively large particles were obtained which probably consist of microcrystals held together by more amorphous regions. These enzyme particles were ground in a mortar and particles, more or less spherical in shape, were obtained. Particles with a diameter within a certain range were selected by a series of sieves with well-defined openings. In the present experiments the diameter varied from approximately 20 μ up to about 500 μ . For all substances the yield data were compared to those for freeze-dried samples which presumably consist of the smallest particles.

The samples were evacuated to a vacuum of about 10^{-4} mm Hg, which is sufficient to