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Isomorphous Relations Between Organic Compounds of Sulfur and Selenium. I. Thermal analysis of the systems: dibenzyl sulfide–dibenzyl selenide and *o*-nitrodiphenyl sulfide–*o*-nitrodiphenyl selenide

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The binary systems, dibenzyl sulfide–dibenzyl selenide and *o*-nitrodiphenyl sulfide–*o*-nitrodiphenyl selenide, were studied by the thaw-melting and the micro-thermal methods. It was found that each of these compounds is dimorphous and that the solid-liquid phase diagrams for each system indicate the presence of 'crossed isodimorphism'.[1]

A large number of binary systems have been subjected to thermal analysis by Fredga,[2,3] by Rheinboldt, *et al.*,[4,5] and by others, to identify the isomorphous replacement of sulfur by selenium in organic compounds. The study of analogous organic sulfur and selenium compounds was apparently begun in 1912 by Pascal.[6] He observed that a continuous series of mixed crystals was obtained for the binary system, diphenyl sulfide–diphenyl selenide. Later, continuous series were found for the sulfides and the analogous selenides of aliphatic, alicyclic, and other aromatic radicals.[2,4] Moreover, Fredga[3] has detected two series of mixed crystals, with a eutectic system composed of the racemates of α-methyl-α,α'-thiodiacetic acid and of the selenium analog. All of the foregoing investigators have apparently used only the classical thermal analysis or the thaw-melting technique.[7]

In this paper we report some studies of two binary systems, each composed of an organic sulfide and the analogous selenide. The experimental procedures employed were the thaw-melting method and the microthermal method described by Kofler.[8] In both cases solid-liquid phase diagrams of type V, [Roozeboom's classification[9]], were obtained, whereas type III had been reported by one of us,[5] for the system composed of the benzyl derivatives. The microthermal method showed that all the components of the systems are dimorphous and that the type V diagrams composed of the stable forms result from crossed isodimorphism[10] between the stable form of one component with the unstable form of the other. In many other systems Kofler[10] had already demonstrated analogous crossed isodimorphism in type V diagrams and, in many of these systems, had obtained qualitatively as well as quantitatively the whole series of mixed crystals composed of the corresponding polymorphic forms.

The studies of the systems containing analogous organic compounds of sulfur and selenium made until now have never revealed crossed isodimorphism. Only in exceptional cases do the macromethods of thermal analysis allow recognition of polymorphism and the preparation of systems with unstable forms.

In this paper an attempt was also made to verify whether the polymorphic forms occurred spontaneously in the substances. The results were negative, as Krc and French[11] had also observed in the case of dibenzyl sulfide.

METHODS AND APPARATUS

The solid-liquid phase diagrams of the binary systems composed of the polymorphic stable forms were obtained by means of the thaw-melting point method of Rheinboldt.[7] All the mixtures were prepared by complete and homogeneous melting of the two components. The thawing and melting points, measured to ±0.1° accuracy, were determined in the apparatus originally indicated by Rheinboldt, in samples contained in capillary tubes equipped with very thin agitating rods. All the percentages are by weight.

The phase diagrams were interpreted by the microthermal method following the technique of fusion preparations.[8] These preparations were obtained by successive melting of the components between a micro slide and a micro cover glass, in two different positions. The component with the highest melting temperature was melted first. Then the cold and completely solidified fusion preparation was sub-

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(1) Crossed isodimorphism occurs when the stable polymorphic forms of the components of the binary system give with unstable forms of the other components respectively, a complete series of mixed crystals. These two series cross themselves approximately in the middle.

(2) Fredga, *J. prakt. Chem.*, **150**, 124 (1938).

(3) Fredga, *Arkiv Kemi, Mineral. Geol.*, **17 A**, No. 17, 15 pp. (1944).

(4) Rheinboldt, *et al.*, *Univ. São Paulo, Faculdade Filosof. cienc. e letras, Bolet.* No. 129, Química No. **3** (1951); *Chem. Abstr.*, **46**, 7551 (1952).

(5) Rheinboldt and Giesbrecht, *J. Am. Chem. Soc.*, **68,** 2671 (1946).

(6) Pascal, *Bull. soc. chim.*, (4) **11,** 1030 (1912).

(7) Rheinboldt, Houben-Weyl, *Die Methoden der Organischen Chemie*, Stuttgart, 1953, Vol. II, p. 827.

(8) Kofler and Kofler, *Handbuch der Mikrochemischen Methoden*, Springer-Verlag, Wien, 1954, Vol. I, Part I, p. 159.

(9) Bakhuis Roozeboom, *Z. physik. Chem.*, **30,** 385 (1899).

(10) Kofler and Kofler, *Handbuch der Mikrochemischen Methoden*, Springer-Verlag, Wien, 1954, Vol. I, Part I, p. 166 and 189 to 196.

(11) Krc, Jr. and French, *Anal. Chem.*, **25,** 198 (1953).

mitted to microscopic and thermal examinations, which permitted one to recognize the general type of diagram furnished by the polymorphs of the components. The microthermal technique was also used to test the spontaneous polymorphism of the compounds. Small samples were melted between a micro slide and a cover glass and, after abrupt cooling of the liquid on a cold metal block, the solids obtained were examined microscopically and thermally. We used the complete apparatus developed by Kofler and manufactured by Reichert in Vienna. The calibrated thermometer permitted an accuracy of 1° for the temperatures determined on the micro hotstage.

SUBSTANCES

Dibenzyl sulfide and *dibenzyl selenide* were prepared by reaction between benzyl chloride and sodium sulfide or sodium selenide respectively, in boiling ethanol, by methods that are essentially those described by Shriner, Struck, and Jorison,[12] and Painter, Franke, and Gortner.[13] The sulfide was recrystallized from ethanol, forming prismatic, colorless and brilliant crystals which melted at 48.8° in the capillary tube and at 48.5° on the micro hotstage. The selenide, recrystallized from aqueous ethanol (50%), formed small brilliant and almost colorless needles. In the capillary it melted at 45.5° and on the hotstage at 45°. The melting points of both compounds agree with those reported in the literature.[5]

o-Nitrodiphenyl sulfide was prepared in accordance with the method described by Cullinane and Davies,[14] slightly modified. The ethanolic solution of benzenethiol and *o*-nitrochlorobenzene was boiled for one hour; yield, 82%. Recrystallized from ethanol, it formed prismatic, lemon-yellow crystals which melted at 81.8° in the capillary and at 81.5° on the hotstage. These temperatures agree with that reported by Cullinane and Davies.

o-Nitrodiphenyl selenide was prepared by the Behaghel and Hofmann method.[15] It was recrystallized from methanol, or a little ethanol, forming small orange-yellowish needles. In the capillary it melted at 91.0° and on the hotstage at 91°, in agreement with the melting point determined by Behaghel and Hofmann.

None of these four compounds showed spontaneous polymorphism. The liquids obtained by melting supercooled readily and only after some time were they crystallized in the stable forms.

It is well known that the crystals of the stable forms of dibenzyl and *o*-nitrodiphenyl sulfides belong to the orthorhombic[11] and to the monoclinic systems,[16] respectively.

STUDY OF THE SYSTEMS

In Figure 1 the solid lines represent the phase diagrams composed of the stable forms. Both refer to type V with very indistinct miscibility gaps. The dotted lines represent schematically the mixed crystals observed in the microthermal study, described below. These mixed crystals complete two continuous series for each diagram.

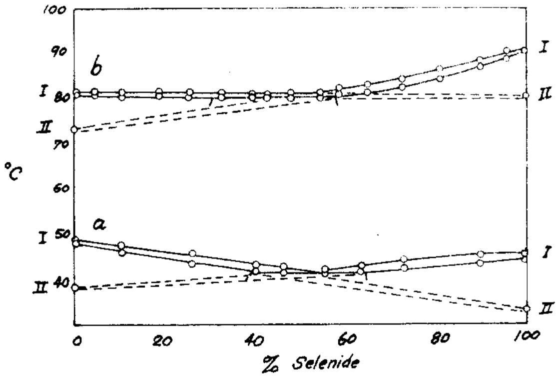

FIG. 1. PHASE DIAGRAMS SHOWING CROSSED ISODIMORPHISM: (a) System between dibenzyl sulfide and selenide; (b) System between *o*-nitrodiphenyl sulfide and selenide.

Microthermal study of the system: dibenzyl sulfide–dibenzyl selenide. The fusion preparation, immediately after having been obtained, contained solidified sulfide besides melted selenide. On cooling, the orthorhombic crystals of the stable form of the sulfide grew in the melted mass, without discontinuity, inducing the corresponding form of the selenide (Figure 2, a). In the subsequent thermal examination the latter melted at 33° (form II[17] of the selenide). The melting then proceeded through the contact zone in the direction of the sulfide which melted at 48.5°.

After being completely melted the fusion preparation was allowed to cool off and at the extremity which contained the selenide its solidification was initiated by seeding with little crystals of the stable form of the selenide. The crystals grew without discontinuity whatsoever, inducing the corresponding form II of the sulfide (Figure 2, b). In the thermal examination the following behavior was observed: the melting started with the sulfide at 38° and proceeded in the direction of the selenide, which melted at 44°.

Both behaviors characterize the formation of continuous series of mixed crystals, type I.

In the solidified preparations composed of the stable form of the sulfide and the unstable form of the selenide or the stable form of the selenide and the unstable form of the sulfide one could transform, by seeding, the unstable into stable forms of the components. In both cases the microscopic examination revealed two distinct zones of crystals. On heating, melting began always from the contact zone at 38.5°.

Microthermal study of the system: o-nitrodiphenyl sulfide–o-nitrodiphenyl selenide. All the results in this study were analogous to those obtained in the former system and could be repeated many times with the same fusion preparation. They are summarized in the following.

Formation of continuous series of mixed crystals, type I, occurred between the stable form of the sele-

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(12) Shriner, Struck, and Jorison, *J. Am. Chem. Soc.*, **52**, 2066 (1930).

(13) Painter, Franke, and Gortner, *J. Org. Chem.*, **5**, 587 (1940).

(14) Cullinane and Davies, *Rec. trav. chim.*, **55**, 881 (1936).

(15) Behaghel and Hofmann, *Ber.*, **72**, 587 (1939).

(16) Toussaint, *Bull. soc. roy. sci. Liège*, **12**, 533 (1943).

(17) The Roman number II is employed to characterize the unstable, low melting, polymorphic forms of the compounds whereas the number I is used for the stable, high melting, polymorphic forms.

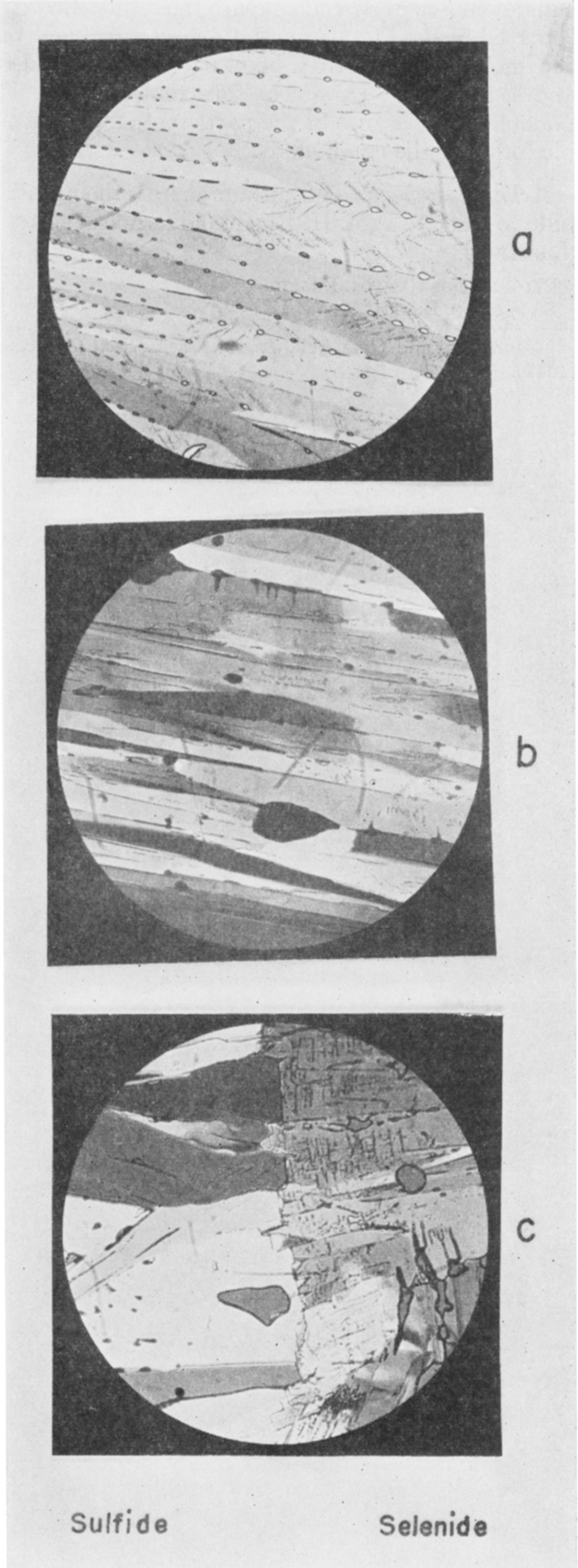

Figure 2. Microscopic Views of Fusion Preparations of the System: dibenzyl sulfide–dibenzyl selenide: (a) sulfide, form I–selenide, form II; (b) sulfide, form II–selenide, form I; (c) sulfide–selenide, forms I.

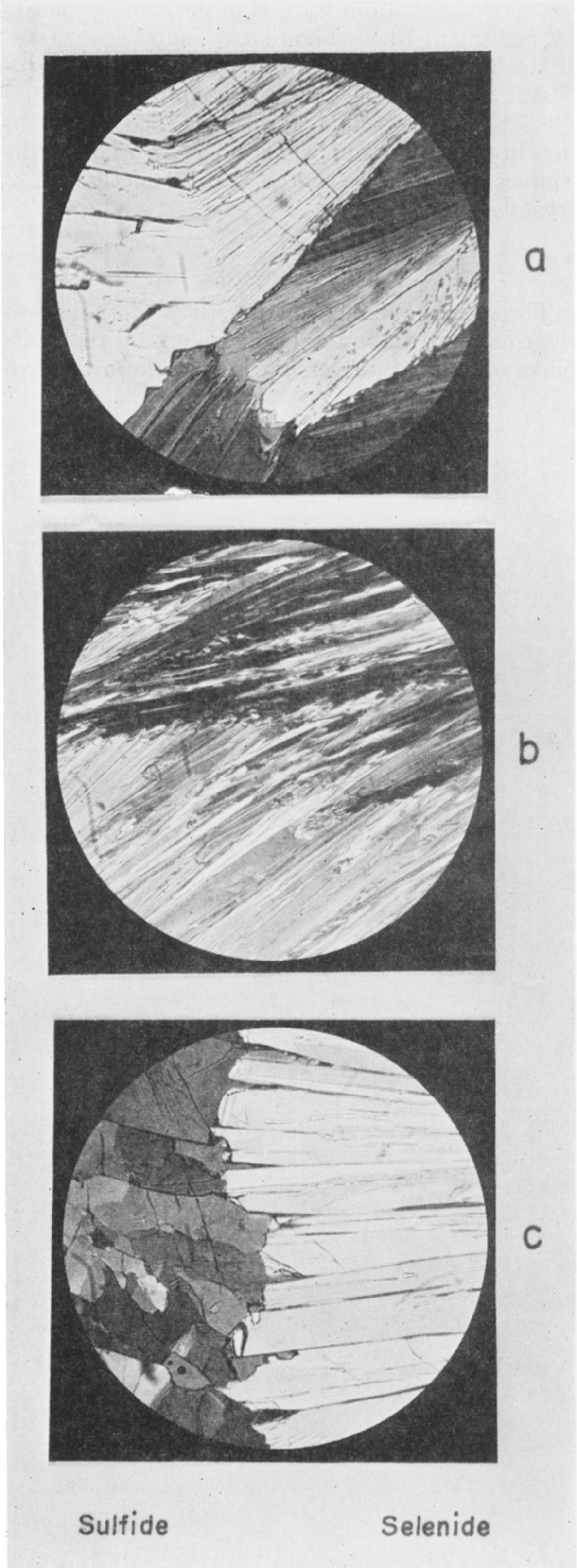

Figure 3. Microscopic Views of Fusion Preparations of the System: *o*-nitrodiphenyl sulfide–*o*-nitrodiphenyl selenide: (a) sulfide, form II–selenide, form I; (b) sulfide form I–selenide, form II; (c) sulfide–selenide, forms I.

nide and the unstable form II of the sulfide, the latter melting at 73.5° (Figure 3, a), and between the monoclinic stable form of the sulfide and the unstable form II of the selenide, melting point 80.5° (Figure 3, b). The two stable forms furnished a preparation in which melting began at 77° to 78.5° in the contact region between the two distinct zones of crystals (Figure 3, c).

DISCUSSION

The results obtained in the study of these two systems show that a total isomorphogenic replaceability of sulfur by selenium is possible in the two sulfides chosen in agreement with the results already reported in the literature, and expected in view of the molecular similarity between organic sulfides and selenides.[18] However, this replaceability is possible only because of the participation of unstable forms of the compounds.

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[18] Rogers and Campbell, *J. Am. Chem. Soc.*, 69, 2039 (1947).