small sorptions to which data at these temperatures are limited.[8] It does not appear possible to decide definitely whether this type of analysis is applicable to the lower temperatures without extensions of the data to larger sorptions. For the higher-temperature region, however, there seems little doubt that the model yields a satisfactory interpretation of the experimental data. It does not follow that the underlying assumptions are entirely correct. As has already been suggested, the correction factor $(1 + R\alpha)^{-1}$ is introduced in an arbitrary way.

A precise treatment of the diffusion factor would necessitate a consideration of the geometry of the model. Such an analysis might conceivably result in a decision as to whether the phenomenon of slow sorption on chromic oxide gel corresponds more closely to a surface diffusion from active centers,[9] to surface adsorption followed by diffusion to the interior,[10] or to diffusion into Smekal cracks.[11] The assumption that there is no direct sorption on the secondary centers can represent at best merely an approximation to the case where the amount of such sorption is small. The sorptive regions of a real catalyst may not be amenable to a classification as simple as that which we have used, and although the introduction of more types of centers would probably lead to equations of the same form as we have found, the experimental constants would be less simply related to the fundamental rate constants. The model makes no assumption with regard to the physical nature of the sorption centers, and its success therefore contributes nothing to the solution of this problem.

Summary

An analysis of Burwell and Taylor's data on the activated sorption of hydrogen by chromium oxide has led to the derivation of a rate equation that fits the data for moderate amounts of sorption very well. The derivation is based on a simple model of the sorption process, involving primary adsorption followed by diffusion to secondary centers. This model also accounts, qualitatively at least, for the failure of the equation at extreme conditions.

PITTSBURGH, PA. RECEIVED DECEMBER 30, 1936

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(9) H. S. Taylor, *Z. Elektrochem.*, **35**, 542–549 (1929).

(10) A. F. H. Ward, *Proc. Roy. Soc.* (London), **A133**, 506–535 (1931).

(11) Adolf Smekal, *Z. Elektrochem.*, **35**, 567–573 (1929).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHERN MONTANA COLLEGE]

Acylselenoureas

BY IRWIN B. DOUGLASS

The investigation of the acyl isothiocyanates and certain acylthiourea derivatives by the author[1] and a review of certain organic selenium derivatives by Bradt[2] suggested the possibility that acid chlorides might react with metallic selenocyanates in a manner analogous to their reaction with the thiocyanates.

The work thus far accomplished indicates that there is a vigorous reaction when acid chlorides and KSeCN are brought together in acetone solution. In no case has the product (I) been

$$\mathrm{RCOCl} + \mathrm{KSeCN} \longrightarrow \mathrm{RCOCSeN}\ (\mathrm{I}) + \mathrm{KCl} \qquad (1)$$

isolated and the evidence thus far accumulated does not definitely establish it as a selenocyanate, an isoselenocyanate, or an equilibrium mixture of the two. The fact, however, that (I) in acetone solution when treated with amines forms selenoureas according to reaction (2) indicates

$$\mathrm{RCOCSeN} + \mathrm{R'NH_2} \longrightarrow \mathrm{RCONHCSeNHR'} \qquad (2)$$

that (I) must have the structure RCONCSe or at least must consist of an equilibrium mixture containing a large proportion in that form. On the basis of this evidence, the acyl derivatives resulting from the reactions between acid chlorides and potassium selenocyanate will be referred to as acyl isoselenocyanates or acylselenocarbimides.

This paper describes the properties of a few acylselenoureas prepared by reactions (1) and (2). The grouping RCO– was varied to include acetyl, carbethoxy, pyromucyl and benzoyl so as to gain some idea of the behavior of various acyl isoselenocyanates when treated with aniline, and the group R′ was varied to determine the behavior of benzoyl isoselenocyanate when treated with different amines.

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(1) Douglass and Dains, THIS JOURNAL, **56**, 719, 1408 (1934); Douglass and Forman, *ibid.*, **56**, 1609 (1934).

(2) Bradt, *J. Chem. Ed.*, **12**, 363 (1935).

Experimental

Acyl isoselenocyanate solutions were prepared by dissolving slightly more than 0.1 mole of potassium selenocyanate in 200 ml. of acetone and adding to the solution exactly 0.1 mole of acid chloride. In each case an immediate exothermic reaction took place with the separation of potassium chloride and the formation of a colored solution. The solutions were used immediately to react with amines to form selenoureas. No attempts have been made as yet to isolate the acyl isoselenocyanates.

With the addition of the last acid chloride to the selenocyanate solution, 0.1 mole of amine, in acetone solution, was added as rapidly as the vigorous boiling of the reaction mixture would permit. Lower yields of selenourea seemed to be obtained when the addition of amine was delayed. When the reaction had subsided, the mixture was poured slowly with stirring into 600–800 ml. of cold water. The solid selenourea which separated was removed by filtration and crystallized from a suitable solvent.

Potassium selenocyanate was prepared by fusing together potassium cyanide and slightly more than an equivalent amount of black powdered selenium.[3] The black melt was dissolved in water, and the solution boiled to coagulate the undissolved selenium. The solution was then filtered and evaporated with stirring until the temperature of the melted residue had reached 190°. The product was broken up as it cooled, pulverized, and used without further purification.

Constitution of the Selenoureas.—An alcoholic solution of the product resulting from benzoyl chloride, potassium selenocyanate, and aniline was boiled with alcoholic silver nitrate solution. After removing the precipitated silver selenide white needles having a melting point of 209° (corr.) separated from the alcoholic solution. Similar treatment of α-benzoyl-β-phenylthiourea yielded an identical product. A mixed melting point of the two was not lowered. The highest melting point recorded for α-benzoyl-β-phenylurea is 210°.[4]

Anal. Calcd. for $C_{14}H_{12}O_2N_2$: N, 11.67. Found (deselenized product): N, 11.49.

Bitter Taste of Benzoylselenourea.—While working with benzoylselenourea it was noticed that when the crystals were disturbed a very bitter dust arose. Since certain of the thioureas are very bitter to some individuals but have no taste to others,[5] it seemed of interest to determine whether there would be individuals taste-blind to benzoylselenourea. Strips of filter paper, dipped into a dilute alcoholic solution of benzoylselenourea, were cut into small pieces and given to Northern Montana College students to taste. Of 175 cases 131 reported the papers as having a decidedly bitter taste whereas 44 reported either no taste or some taste other than bitter.

Yields.—The percentage yields of the selenoureas varied somewhat with the acid chloride used and also with the amine used. The data in regard to yields can be considered as only of a qualitative nature, however, for there was considerable variation in yield with successive preparations of the same selenourea. It would seem that there are factors affecting yield not yet fully understood. Low yields were usually accompanied by the production of colored by-products.

Acetyl Isoselenocyanate and Aniline.—The reaction of acetyl isoselenocyanate with aniline seems to follow the same two courses as acetyl isothiocyanate and aniline.[6] In the preparation of α-acetyl-β-phenylselenourea a yield of only 12% was obtained. From the water into which the reaction mixture was poured a 27% yield of acetanilide, based on the original quantity of aniline was obtained as a first crop.

Selenoureas

Benzoyl-.—White prisms from alcohol, m. p. 194–195° (corr.), yield 27%. Spontaneously oxidized in alcoholic solutions to selenium and benzoylurea. *Anal.* Calcd. for $C_8H_8ON_2Se$: N, 12.34. Found: N, 12.25.

α-Benzoyl-β-phenyl-.—Long yellow needles from alcohol, m. p. 144–145° (corr.), yield, 72%. A mixed melting point of this compound with the corresponding thiourea was not lowered appreciably. *Anal.* Calcd. for $C_{14}H_{12}ON_2Se$: N, 9.24. Found: N, 9.09.

α-Benzoyl-β-*o*-tolyl-.—Long yellow prisms from alcohol, m. p. 124–125° (corr.), yield 70%. *Anal.* Calcd. for $C_{15}H_{14}ON_2Se$: N, 8.83. Found: N, 8.99.

α-Benzoyl-β-*p*-tolyl.—Yellow needles from a mixture of dioxane and alcohol, m. p. 154–155° (corr.), yield 56%. *Anal.* Calcd. for $C_{15}H_{14}ON_2Se$: N, 8.83. Found: N, 8.90.

α-Benzoyl-β,β-naphthyl-.—Yellow prisms from dioxane, m. p. 171–172° (corr.), yield 58%. *Anal.* Calcd. for $C_{18}H_{14}ON_2Se$: N, 7.93. Found: N, 7.86.

α-Benzoyl-β-benzyl-.—Long orange prisms from alcohol, m. p. 115–116° (corr.), yield 19%. *Anal.* Calcd. for $C_{15}H_{14}ON_2Se$: N, 8.83. Found: N, 8.93.

α-Benzoyl-β,β-diethyl-.—Yellow needles and yellow prisms, m. p. 110° (corr.), yield 49%. *Anal.* Calcd. for $C_{12}H_{16}ON_2Se$: N, 9.93. Found: N, 9.76.

α-Acetyl-β-phenyl-.—Pink plates from alcohol, m. p. 184–185° (corr.), yield 12%. *Anal.* Calcd. for $C_9H_{10}ON_2Se$: N, 11.62. Found: N, 11.43.

α-Phenyl-β-pyromucyl-.—Yellow needles from alcohol, m. p. 106–107° (corr.), yield 24%. *Anal.* Calcd. for $C_{12}H_{10}O_2N_2Se$: N, 9.56. Found: N, 9.52.

An attempt was made to prepare α-carbethoxy-β-phenylselenourea, but no solid product was isolated. The reaction between ethyl chlorocarbonate and potassium selenocyanate was smooth and resulted in the formation of practically no colored by-products. Likewise the reaction of the supposed carbethoxy isoselenocyanate with aniline appeared to be normal. The colorless oil which separated when the mixture was poured into water would not solidify, however, and on standing for several days acquired such an offensive odor that it was discarded.

Summary

1. The action of acid chlorides on acetone solutions of potassium selenocyanate yields compounds which react with amines to form selenoureas.

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(3) Obtained through the courtesy of the Anaconda Copper Mining Company.

(4) Billeter *Ber.*, **36**, 3220 (1903).

(5) Fox, *Proc. Nat. Acad. Sci. U. S.*, **18**, 115 (1932).

(6) Dixon and Hawthorne, *J. Chem. Soc.*, **87**, 468 (1905).

2. The compounds formed by the action of acid chlorides on potassium selenocyanate, although not yet isolated, appear to be very similar in their reactivity to the acyl isothiocyanates and are believed to be acyl isoselenocyanates.

3. Benzoylselenourea possesses a very bitter taste to most individuals, but is tasteless to others, thus emphasizing the similarity of the selenoureas to the thioureas.

HAVRE, MONTANA RECEIVED FEBRUARY 18, 1937

[CONTRIBUTION FROM LAND-WHEELWRIGHT LABORATORIES]

Optical Properties and Polymorphism of Paraffins

BY C. D. WEST

When a molten paraffin or similar long chain compound is allowed to solidify in a film on a flat glass surface, the film, in spite of being turbid to the naked eye, and showing many randomly oriented small crystals under the microscope, still has sufficient homogeneity to show a peculiar effect when examined with a total reflection refractometer. Instead of one boundary between total and ordinarily reflected light, two such boundaries of a somewhat diffuse character are observed, separated by an interval of up to 0.05 unit in the refractive index scale. The state of polarization of the light at these boundaries proves that the film is optically equivalent to the basal section of a uniaxial positive crystal.

This effect was first described in a paper by Camerer,[1] then by Gaubert,[2] and by Walter.[3] Vorländer and Selke[4] showed that the effect is to be observed with a great variety of pure long chain compounds (paraffins, unsaturated fatty acids, esters of fatty acids, alcohols and ketones, etc.) which solidify in soft solid crystals.

In the past year Page[5] published measurements on five natural paraffins with melting points in the range 49.4–60.6°. Page assigned an incorrect optical character to his films; he arbitrarily called the ordinary refractive index the extraordinary, and *vice versa*. His calculations based on this error are accordingly incorrect. He carried his measurements for each specimen through a considerable temperature range. The irregularity of these curves at temperatures near the melting points suggests that at least some of his materials (for example, that melting at 60.6°) underwent polymorphic transitions in the course of the measurements, as they would be expected to do according to the X-ray structure work that has been published on this point.

More recently Seyer and Fordyce[6] gave refractive index data for the pure paraffin dicetyl (dotriacontane, $C_{32}H_{66}$) in the solid state from 30° up to the melting point, 70°. These writers failed to note the double edge of total reflection, nor did they take into consideration the fact that this material has a sharp reversible inversion at 5° below its melting point. Rather they concluded from their refractive index curve, together with the solubility curves in propane and butane, that dicetyl has a transition at 55°.

The prior work of Piper and co-workers[7] showed clearly that dicetyl has a sharp reversible transition at about 65°. This was observed macroscopically, microscopically and by means of X-rays. Other straight chain paraffins near to dicetyl all exhibit the same transition about 5° below the melting point.[8]

In the following is described a repetition of the work of Seyer and Fordyce with dicetyl, rather for the purpose of illustration than to give the precise numerical constants of this material in a state of known purity.

Experimental

An Abbe refractometer with front opening for the front or refracting prism (Bausch and Lomb) was used. The dicetyl was obtained from Eastman Kodak Company; it melts sharply at 69.5–69.7°, and solidifies at 68.8–67.7°. For some of the measurements the molten material was poured onto the refracting prism and allowed to solidify without closing the back prism; for others the back prism was closed after melting the material on the front prism. The character and position of the edges is the same in the

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[1] R. Camerer, *Ann. Physik*, **54**, 84–103 (1895).

[2] P. Gaubert, *Bull. soc. franç. mineral.*, **33**, 326 (1910).

[3] R. Walter, *Ber.*, **59**, 971–972 (1926).

[4] D. Vorländer and W. Selke, *Z. physik. Chem.*, **129**, 435–474 (1927).

[5] J. M. Page, Jr., *Ind. Eng. Chem.*, **28**, 856–859 (1936).

[6] W. F. Seyer and R. Fordyce, THIS JOURNAL, **58**, 2029 (1936).

[7] S. H. Piper and others, *Biochem. J.*, **25**, 2027 (1931).

[8] L. Deffet, *Bull. soc. chim. Belg.*, **44**, 97 (1935), reported the melting point 70.0° and the transition point 64.3° for dicetyl at atmospheric pressure.