

Alkali Solubility of Alcoholized Cellulose.—Hydrolyzed cellulose is known to undergo extensive degradation by hot aqueous alkalis. Data given in Table I show that methanolized cotton cellulose does not undergo such an effect. This finding provides support for the view expressed by others that the loss of weight suffered by hydrocellulose in hot, dilute alkali is a function of reactivity, and not of solubility.¹² Alkaline solutions heated with hydrocellulose become discolored, whereas when heated with alcoholized cellulose they show no discoloration.

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Dehydrogenation of 1,4-Pentanediol

BY L. P. KYRIDES AND F. B. ZIENTY

The availability of 1,4-pentanediol (I) prompted the study of the dehydrogenation¹ of this glycol. Using a typical copper chromite hydrogenation catalyst,² and operating in the liquid phase under reflux, two moles of hydrogen were evolved and γ -valerolactone (II) was produced in 80% yield (an unexpected result). When the reaction mixture was slightly acidified with an organic acid and a downward condenser was used, as much as 30% of γ -acetopropanol³ (III) was produced together with some (II).

Anal. Calcd. for $C_5H_8O_2$: mol. wt., 100.1; *MR*, 24.7. Found: mol. wt., 100.0; *MR*, 24.6.

Addition of a small amount of potassium hydroxide, monobasic sodium phosphate, alundum or decolorizing charcoal (Darco) to the reaction mixture produced an 87–90% yield of (II).

(b) **In Presence of Organic Acids.**—Under slightly acid conditions, such as could be attained by the addition of 0.003–0.005 mole per cent. of a non-volatile fatty acid like stearic acid,¹ to the reaction mixture, water and a low-boiling organic material could be distilled off and condensed in appreciable amounts. The mechanism in this reaction probably involves dehydrogenation of the secondary alcohol group in (I) to form (III), which, in its cyclic form,⁵ dissociates into water and 2-methyl-4,5-dihydrofuran⁶ (IV) which distill over and subsequently recombine to form (III).⁷ The reaction of (IV) with water is slow (24–48 hours) and may be accelerated by stirring, but will proceed instantly, and even with violence, in the presence of a small amount of mineral acid, such as hydrochloric acid.

In order to separate the (III) from the (II) formed in the reaction, the crude reaction products were distilled slowly at atmospheric pressure using a short column. The volatile dissociation products of (III) distilled over, leaving the (II) behind in the still. (II) and (III) have similar boiling points under atmospheric pressure.

Reaction in an atmosphere of hydrogen was without benefit in producing (III). Activated copper made by decomposition of cupric carbonate in (I) caused some dehydrogenation to (II), but no (III) was obtained. A nickel

TABLE I

Derivative	Recrystn. solvent	M ₀ p., ^a °C.	Formula	% Nitrogen ^b Calcd.	Found
(I) Bis- <i>p</i> -nitrobenzoate	Me ₂ CO-EtOH	150–151	C ₁₉ H ₁₈ N ₂ O ₈	7.0	6.8
(III) Semicarbazone	EtOH	154–155 ^c	C ₆ H ₁₃ N ₃ O ₂	26.4	26.5
(III) Thiosemicarbazone	H ₂ O	102–103	C ₆ H ₁₃ N ₃ OS	24.0	23.9
(III) Acetate semicarbazone ^d	H ₂ O	125–126	C ₈ H ₁₆ N ₃ O ₃	20.9	21.0
(III) Acetate thiosemicarbazone ^d	MeOH	117–118	C ₈ H ₁₆ N ₃ O ₂ S	19.3	19.3

^a All melting points are corrected. ^b The analyses were performed by Mrs. J. D. Nevins of the Monsanto Analytical Laboratory. ^c Paul, *Bull. soc. chim.*, **53**, 426 (1933), reported 155–157°. ^d Prepared from (III) acetate, b. p. 88–89° (7 mm.). Slobodin, Zigel and Yanishevskaya, *C. A.*, **39**, 702 (1945), reported b. p. 100–115° (22 mm.). Palomaa, *Chem. Zentr.*, **84**, II, 1959 (1913), reported 211–213°. Bergel, U. S. Patent 2,358,618 (September 19, 1944), reported b. p. 96–99° (12 mm.), 103–104° (14 mm.) and 110–112° (17 mm.).

Several derivatives of (III) were prepared (Table I).

Experimental

Dehydrogenation of (I). (a) **In Absence of Organic Acids.**—A mixture of 104 g. (1 mole) of (I), 4 g. of copper chromite catalyst² and 0.15 g. of powdered reagent sodium hydroxide was stirred vigorously and heated under reflux. At 200° a lively evolution of hydrogen occurred and the temperature soon dropped to 190–192° where the dehydrogenation proceeded smoothly. The evolution of gas (39 liters or two moles on the (I) reacted) ceased in about three hours. The reaction mixture was cooled to about 30°, filtered from the catalyst and distilled under reduced pressure, producing 79 g. (87%) of (II), b. p. 90–92° (16 mm.), n_D^{20} 1.4290, d_4^{25} 1.0474, and 12 g. of unreacted (I), b. p. 124–126° (16 mm.) or 120–121° (14 mm.). The (II) was analyzed by titration with alkali.

(1) Kyrides and Zienty, U. S. Patent 2,382,071 (August 14, 1945); *C. A.*, **40**, 90 (1946).

(2) Calingaert and Edgar, *Ind. Eng. Chem.*, **26**, 878 (1934).

(3) Several other examples of the formation of keto alcohols by dehydrogenation of glycols are described in the literature: McNamee and Blair, U. S. Patent 2,143,383 (January 10, 1939), *Chem. Zentr.*, **110**, I, 4842 (1939); Hilger, U. S. Patent 1,955,882 (April 24, 1934), see *Chem. Zentr.*, **104**, I, 2172 (1933); Neish, *Can. J. Research*, **23B**, 67 (1945); Holmes, U. S. Patent 2,036,940 (April 7, 1936), *Chem. Zentr.*, **107**, II, 402 (1936).

(4) Schuette and Sah, *THIS JOURNAL*, **48**, 3165 (1926), reported n_D^{20} 1.4301 and d_4^{25} 1.04608.

hydrogenation catalyst caused extensive dehydration of (I), and produced only about 15% of (III).

(5) Buchman, *THIS JOURNAL*, **58**, 1804 (1936).

(6) Lipp, *Ber.*, **22**, 1199 (1889).

(7) Marshall and Perkin, *J. Chem. Soc.*, **59**, 882 (1891). Paul, *Bull. soc. chim.*, **53**, 419 (1933), produced γ -acetopropanol by addition of water to 2-methylene-tetrahydrofuran in the presence of sulfuric acid. Knunyantz, Chelintzev, and Osetrova, *C. A.*, **28**, 4382 (1934), reported b. p. 115–116° (30 mm.) for γ -acetopropanol, while we found b. p. 85–86° (10 mm.).

RESEARCH LABORATORIES

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Solubility Product of Silver Selenocyanate at 25°

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Subsequent to studies dealing with selenocyanic acid and the gravimetric analysis of $SeCN^-$ as silver selenocyanate ($AgSeCN$)¹ it became of interest to determine the solubility of this silver salt.

A solubility product of 6.9×10^{-16} (K_{sp} average of four determinations) was found for silver selenocyanate at $25 \pm 0.1^\circ$ using the cell: $Ag/$

(1) Waitkins, M. S. Thesis, Syracuse University, 1934.

AgSeCN, KSeCN/KNO₃/AgNO₃/Ag. The cell was permitted to attain equilibrium in the dark in ten to fifteen hours with the salt-bridge removed. Upon insertion of the salt-bridge, the immediate potentiometer reading was taken as the final equilibrium point owing to the rapid deposition of selenium on the silver electrode and the resultant lowering in e.m.f. Table I lists e.m.f. values observed for this cell at several concentrations of potassium selenocyanate near 0.1 *M* and the *K*_{sp} values that were obtained by solving the Nernst equation. The activity coefficients of potassium selenocyanate required for these calculations were taken as the mean of values for the activity coefficients of potassium bromide and iodide.^{2,3} The *K*_{sp} values appear to be in fair agreement considering the difficulty of measurement arising from the drift in potentiometer readings as noted above.

TABLE I

*K*_{sp} VALUES FOR SILVER SELENOCYANATE AT 25 ± 0.1°

Expt.	<i>M</i> _{KSeCN}	<i>M</i> _{AgNO₃}	E.m.f., volt	<i>K</i> _{sp} × 10 ⁻¹⁸
1	0.0894	0.1363	0.7081	7.1
2	.0935	.0856	.7008	6.5
3	.0958	.3183	.7288	6.6
4	.0644	.1340	.6988	7.4

A comparison of the *K*_{sp} values for silver halides and halogenoids (thiocyanate and selenocyanate) as shown in Table II reveals the interesting fact that these values decrease progressively with increase in ionic weight of the anion attached to the silver ion. Points obtained by plotting ionic weights against the log of the reciprocal of *K*_{sp} values will be found to lie very nearly along a straight line. This would seem to be further evidence for the assumption that halide and halogenoid ions are structurally similar. The fluoride and cyanide ion which form complexes with silver ion fall outside this classification. The *K*_{sp} value for silver cyanate (AgOCN) is not known but might be predicted to lie between that of silver chloride and silver thiocyanate.

TABLE II

COMPARISON OF *K*_{sp} VALUES FOR SILVER HALIDES AND HALOGENOIDS

Anion combined with Ag ⁺	Ionic weight	<i>K</i> _{sp} value at 25°
Cl ⁻	35.46	1.95 × 10 ⁻¹⁰ 4
OCN ⁻	42.02
SCN ⁻	58.08	1.34 × 10 ⁻¹² 5
Br ⁻	79.92	6.3 × 10 ⁻¹³ 4
SeCN ⁻	104.98	6.9 × 10 ⁻¹⁵
I ⁻	126.92	9.7 × 10 ⁻¹⁷ 4

Experimental.—The concentration cell, held in a constant-temperature bath and away from

(2) Harned, *THIS JOURNAL*, **51**, 416 (1929).

(3) Robinson, *ibid.*, **57**, 1161 (1935).

(4) Hess and Jelinek, *Z. physik. Chem.*, **A162**, 153 (1932).

(5) (Average of four determinations) Vol. 11, p. 1182, Landolt-Börnstein "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1923.

light in a dark-room, was connected with a Type K potentiometer (Leeds and Northrup), a standard cell, a 2-volt battery, and a galvanometer. One arm of the concentration cell consisted of a standard silver nitrate solution (50 ml.) in a 100-ml. glass weighing bottle. The other side of the cell was formed in a similar fashion by dissolving a weighed sample of pure potassium selenocyanate (thrice recrystallized from absolute ethanol and dried at 100-105°) in 50 ml. of water. Silver nitrate (one drop of 0.1 *M*) was then added to the potassium selenocyanate solution and the mixture was allowed to reach equilibrium after ten to fifteen hours in the dark with occasional stirring by hand for a few minutes after every two to three hours. A thin layer of silver was flashed over the surface of the silver electrodes⁶ prior to immersion in the two arms of the cell and the electrical circuit was completed by immediately setting the salt-bridge in place (saturated potassium nitrate in agar). Potentiometer readings were made within ten to fifteen seconds thereafter since the selenocyanate polarized the silver electrode in a few minutes by electrochemical deposition of an observable layer of red selenium, with the probable formation of cyanide ion and possibly some free cyanogen. In any case it is not believed that these side reactions could have seriously affected the final e.m.f. values during the short interval required for taking the readings. In the last determination (Table I) the procedure was varied by adding silver nitrate (10 ml. of 0.001 *M*) to the potassium selenocyanate solution. In this case the solubility was increased somewhat possibly owing to the colloidal nature of the precipitated silver selenocyanate.

The solubility product of silver chloride determined by the use of the above apparatus under the same experimental conditions was found to be 1.93 × 10⁻¹⁰ which compares favorably with the value of 1.95 × 10⁻¹⁰ determined by Hess and Jelinek.

(6) Hoyt, *J. Chem. Ed.*, **14**, 185 (1937).

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Synthesis of Methyl Ketones from Diethyl Acylmalonates

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A convenient method for preparing certain methyl ketones consists in the acylation of the sodium or, preferably, the magnesiummethoxy derivative of diethyl malonate with the appropriate acid chloride, followed by hydrolysis and decarboxylation of the two ester groups of the resulting diethyl acylmalonate in the presence of acid, thus

