

reciprocating type shaking apparatus and cooled by a strong stream of water through the external coil before addition of the W-4 Raney nickel catalyst¹³ (3-4 g.). While continuing the external cooling, hydrogen was admitted from a large low pressure hydrogen reservoir and shaking begun. Rapid circulation of water was necessary during the first 30-60 minutes of reduction to restrict the temperature to 35° but thereafter the optimum temperature of 25-35° could be maintained by slow or occasional water circulation. Absorption of hydrogen at 10-25 p.s.i. took place at a steady rate until approximately theoretical absorption had occurred (17.7 lb. in 14.5 hrs.; theoretical, 16.8 lb.). After filtration (filter-cel) and washing (ethanol) of the catalyst, the solvent was removed completely from the filtrate under reduced pressure on a steam-bath, ether (200 ml.) added to the viscous residue and the mixture triturated to induce crystallization. The first crop of 1-(1-hydroxycyclohexyl)-methylammonium acetate (acetic acid salt of V) (93.9 g., m.p. 115-118° (uncor.)) separated on standing in a refrigerator and a second crop (13.8 g., m.p. 108-113° (uncor.)); total yield 107.7 g., 91%) was obtained after removal of the dissolved nickel from an aqueous solution of the concentrated filtrate by saturation with hydrogen sulfide, concentration and treatment with ether. Comparable yields (86-87%) were obtained in larger runs (350 g.) or by hydrogenation in 15% acetic acid-85% ethanol solvent but rate decreased to about one-half in the diluted solvent. Recrystallization of a small portion of the salt from acetic acid-ether raised the melting point to 122-123°. Characterization of the product was accomplished by the preparation of derivatives from the free amine: picrate, large yellow plates from absolute ethanol, m.p. 168-170° (uncor.) (reported,²⁰ 164°); hydrochloride, colorless plates from ether-hydrogen chloride, m.p. 215-216° (uncor.) (reported,²⁰ 190°) (Calcd. for C₈H₁₆ONCl; Cl, 21.37. Found: Cl, 21.40).

Cycloheptanone (VI).—Ring enlargement of 1-(1-hydroxycyclohexyl)-methylammonium acetate by diazotization, essentially according to the procedures of Tchoubar²⁰ and of Ruzicka and co-workers,¹⁴ gave 59-65% yields on 0.5-1.5 mole runs; b.p. 68-74° (17 mm.), *n*_D²⁰ 1.4620; 2,4-dinitrophenylhydrazone, m.p. 146° (uncor.); semicarbazone, m.p. 160-161° (uncor.).

(13) A. A. Pavlic and H. Adkins, *THIS JOURNAL*, **68**, 1471 (1946).

(14) L. Ruzicka, Pl. A. Plattner and H. Wild, *Helv. Chim. Acta*, **26**, 1631 (1943).

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RECEIVED DECEMBER 15, 1950

Preparation of 1,1,1,3,3,3-Hexachloropropane

By H. W. DAVIS AND A. M. WHALEY

Recently the authors reported the synthesis of 1,1,3,3-tetrachloropropane,¹ leaving the 1,1,1,3,3,3-hexachloropropane as the only remaining chloropropane, out of twenty-nine, to be prepared. This work describes the preparation of the above hexachloride from the chlorination of 1,1,1,3,3-pentachloropropane, prepared in turn from both 1,1,1,3,3- and 1,1,3,3-tetrachloropropane.

The chlorination of the pentachloride can give only two possible hexachlorides, namely, the missing one and the 1,1,1,2,3,3-hexachloropropane. The latter is known² and has the properties: b.p. 216°, *d*₄²⁵ 1.6980, *n*_D²⁵ 1.5250. Therefore, the hexachloride boiling at 206° cannot be 1,1,1,2,3,3-hexachloropropane but must be 1,1,1,3,3,3-hexachloropropane.

Experimental

1,1,1,3,3-Pentachloropropane, b.p. 71-73° (16 mm.) was synthesized from 1,1,1,3- and 1,1,3,3-tetrachloropropane by chlorination of each at 80-100° with gaseous chlorine in the presence of ultraviolet light, followed by fractionation from the isomeric pentachlorides. This separation is comparatively easy as the possible pentachlorides boil at

(1) H. W. Davis and A. M. Whaley, *THIS JOURNAL*, **73**, 1382 (1951).

(2) H. J. Prins, *J. prakt. Chem.*, [2] **89**, 417-419 (1914).

180° (CHCl₂-CH₂-CCl₃), 199° (CHCl₂-CHCl-CHCl₂) and 192.4° (CH₂Cl-CHCl-CCl₃). The 1,1,1,3,3-pentachloride was then chlorinated similarly to yield a mixture of two hexachlorides from which was fractionated the 1,1,1,3,3,3-hexachloropropane, b.p. 206° (760 mm.), 89° (16 mm.), *n*_D²⁰ 1.5179, *d*₄²⁰ 1.6800, m.p. -27° ± 0.5. *Anal.* Calcd. for C₃H₂Cl₆: Cl, 84.83; molecular refraction, 45.22. Found: Cl, 84.61; mol. refr., 45.23.

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RECEIVED JANUARY 19, 1951

Addendum to "A Spectrophotometric Investigation of the Interaction between Antimony(III) and -(V) in Hydrochloric Acid Solutions"

By NORMAN DAVIDSON

Figure 3 of the above named article¹ exhibits values of the interaction constant, *k*_i(λ), for mixed solutions of antimony(III) and -(V) in concentrated hydrochloric acid. Figure 4 gives the extinction coefficients of antimony(III) and -(V) at several hydrochloric acid concentrations (11-3.5 *F*). To aid other workers who wish to use the numerical values of these constants, we have prepared a tabular presentation of the data.²

It is noteworthy that Edwards, Voigt and Diehl³ have presented data from which one can calculate values of *k*_i(λ). These results are in general agreement with ours but give a more detailed picture of the effect of acidity on the interaction constant.

(1) J. E. Whitney and N. Davidson, *THIS JOURNAL*, **71**, 3809 (1949).

(2) For detailed tables of data order Document 3039 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.00 for photocopies (6 × 8 inches) readable without optical aid.

(3) F. Edwards, A. Voigt and H. Diehl, *Proc. Iowa Acad. Sci.*, **55**, 247 (1948).

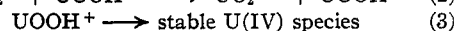
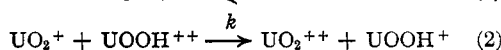
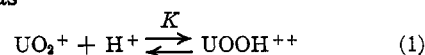
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RECEIVED NOVEMBER 10, 1950

Reactions Involving Like-Charged Ions. II. The Rate of Disproportionation of Uranium(V) in Deuterium Oxide¹

By FREDERICK R. DUKE AND RICHARD C. PINKERTON

The kinetics of the disproportionation of uranium (V) ion in perchloric acid solutions has been studied by Heal^{2a} and by Kern and Orleman.^{2b} The conclusion from both investigations is that the reaction is second order in uranium(V) ion and first order in hydrogen ion. The reactions are formulated as



The rate-determining step (2) is noteworthy because reaction apparently occurs between two

(1) Contribution No. 113 from the Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa. Work performed in the Ames Laboratory of the Atomic Energy Commission.

(2) (a) Heal, *Trans. Faraday Soc.*, **45**, 1 (1949); (b) Kern and Orleman, *THIS JOURNAL*, **71**, 2102 (1949).