reciprocating type shaking apparatus and cooled by a strong stream of water through the external coil before addition of the W-4 Raney nickel catalyst[13] (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,[2c] 164°); hydrochloride, colorless plates from ether–hydrogen chloride, m.p. 215–216° (uncor.) (reported,[2c] 190°) (Calcd. for $C_7H_{16}ONCl$; 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 Tchoubar[2c] and of Ruzicka and co-workers,[14] gave 59–65% yields on 0.5–1.5 mole runs; b.p. 68–74° (17 mm.), $n^{20}{}_D$ 1.4620; 2,4-dinitrophenylhydrazone, m.p. 146° (uncor.); semicarbazone, m.p. 160–161° (uncor.).

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[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).

SEATTLE 5, WASH. 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- 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 known[2] and has the properties: b.p. 216°, $d^{34}{}_4$ 1.6980, $n^{17}{}_D$ 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 180° ($CHCl_2$–CH_2–CCl_3), 199° ($CHCl_2$–$CHCl$–$CHCl_2$) and 192.4° (CH_2Cl–$CHCl$–CCl_3). 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.), $n^{20}{}_D$ 1.5179, $d^{20}{}_4$ 1.6800, m.p. −27° ±0.5. *Anal.* Calcd. for $C_3H_2Cl_6$: Cl, 84.83; molecular refraction, 45.22. Found: Cl, 84.61; mol. refr., 45.23.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, S. C. RECEIVED JANUARY 19, 1951

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[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).

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 article[1] exhibits values of the interaction constant, $k_i(\lambda)$, 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 Diehl[3] have presented data from which one can calculate values of $k_i(\lambda)$. These results are in general agreement with ours but give a more detailed picture of the effect of acidity on the interaction constant.

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[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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Reactions Involving Like-Charged Ions. II. The Rate of Disproportionation of Uranium(V) in Deuterium Oxide[1]

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

$$UO_2^+ + H^+ \overset{K}{\rightleftarrows} UOOH^{++} \qquad (1)$$

$$UO_2^+ + UOOH^{++} \xrightarrow{k} UO_2^{++} + UOOH^+ \qquad (2)$$

$$UOOH^+ \longrightarrow \text{stable U(IV) species} \qquad (3)$$

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

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[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).

positively charged species, and the prior equilibrium involving the proton results in an increase in charge of the one participant. It would seem that a simple electron transfer between the two ions would not be facilitated by the increase in repulsive forces, and there is no obvious role for the proton in a simple electron transfer mechanism. Two mechanisms which do take into account the presence of the proton are

$$OUO^{+}-HOUO^{++}\longrightarrow OUOH^{+}-OUO^{++}$$

which symbolizes the removal of hydrogen atom from $UOOH^{++}$ by UO_2^+ and:

$$OUOH^{++}-UO_2^{+}\longrightarrow OU^{++}-HOUO_2^{+}$$

which means oxidation of UO_2^+ by the removal of neutral OH from $UOOH^{++}$.

In view of the success attained by the use of deuterium in the investigation of mechanisms, it was decided to determine the relative rates of this disproportionation in deuterium oxide and water.

Experimental

Materials.—A perchloric acid solution of $UO_2(ClO_4)_2$ was prepared by boiling down $UO_2(NO_3)_2$ several times with 70% $HClO_4$. The uranium solution was standardized gravimetrically as U_3O_8. Stock solutions of 0.5 *M* $NaClO_4$ were prepared by dissolving a weighed quantity of the anhydrous salt in light or heavy water.

Apparatus.—The polarographic method of Kern and Orleman[2b] was used. A simple manual instrument was constructed and provided with a switching arrangement so that the circuit could also be used as a potentiometer for the measurements of *p*H. A combined electrolysis and polarograph cell was employed, similar to the model of Kern and Orleman[2b] except that it was of reduced dimensions and provided with a water jacket to maintain a temperature of 25.0 ± 0.2°.

Procedure.—A preliminary examination was made in which it was found that the polarographic wave for the couple $UO_2^{++} = UO_2^{+} + e^-$ was almost identical in heavy water to that ordinarily obtained. Hence the same potentials were employed for electrolysis and analysis in D_2O as in H_2O. The values of the diffusion coefficients of UO_2^+ were assumed to be the same, and the value of Kern and Orleman was used.

In a typical run, 20 ml. of salt solution (light or heavy water) and 1 ml. of stock $UO_2(ClO_4)_2$ solution (light water) were electrolyzed for 20–30 min. at a current of about 3 ma. With the smaller cathode area used this was sufficient to maintain a potential suitable for the reduction. The mercury cathode was stirred rapidly and nitrogen was bubbled through both the main cell and anode compartment throughout the electrolysis. Then 1 ml. of dilute $HClO_4$ (in ordinary water) was added and the polarograph was used to follow the diffusion current for 40 min.

The hydrogen ion activity was determined with the quinhydrone electrode against a satd. calomel cell. In the case of the heavy water solutions (mole fraction D_2O, 0.91) the reference potential used was 0.4865. This value was obtained by interpolation from the data of Rule and LaMer,[3] and is here referred to the satd. calomel cell.

Interpretation of Results

The values of k''/a_{H^+} reported here are somewhat higher than those obtained by Kern and Orleman.[2b] The greatest source of error involved is in the determination of $a_{H^+} + a_{D^+}$, due to an uncertain liquid junction potential between the calomel cell and solution. However, if we may assume that the same liquid junction exists for the heavy water solution as the ordinary, the error involved will cancel out in the ratio of the two rates k_D/k_H.

It is seen that the rate in D_2O is about 1.7 times as fast as in water. This may be the result of two effects, which are inseparable in these experiments. The value of the equilibrium constant of reaction (1) may be changed, and the magnitude of the specific rate constant of reaction (2) may be affected. The ratio of equilibrium constants of (1) in D_2O and H_2O should be somewhat less than 3, since we may reckon $UOOH^{++}$ to be a strong acid.[2b] This effect alone can explain the increased rate in D_2O. As for the effect on reaction (2), if any is present, it would be expected from previous experimental results in which it is possible to isolate the isotope effect that the specific rate constant observed in heavy water should be lower than that in light water. The transfer of a deuteron from carbon to oxygen is said to be 3.5 to 10 times as slow as that of a proton.[4]

TABLE I

Mole fraction D_2O	k''[a]	*E* quinhydrone *vs.* S.C.E.	$a_{H^+} + a_{D^+}$	$k''/(a_{H^+} + a_{D^+})$
(ionic strength = 0.5)				
0	1.17	0.3281	7.60×10^{-3}	154
0	1.24	.3288	7.80×10^{-3}	159
0	2.17	.3238	1.41×10^{-2}	154
Av. $k''/a_{H^+} = 156 = k_H$				
0.91	1.56	.3547	5.90×10^{-3}	264
0.91	3.89	.3791	1.53×10^{-2}	255
Av. $k''/a_{H^+} = 260 = k_D$				
$k_D/k_H = 1.7$				

[a] The symbols used here are chosen to agree with those adopted by Kern and Orleman.

Another effect which cannot be ignored is that resulting from the change in solvent. Ionic mobilities are lower in deuterium oxide. A few experiments are listed which have some bearing on the question.[5] The general conclusion is that, except for acid–base equilibria, the solvent effect of a change to deuterium oxide is to lower slightly the rate of reaction.

From the results, a mechanism involving proton transfer appears to be highly improbable. An electron exchange mechanism which depends in some unknown manner on the presence of a proton may apply; or the proton may be required so that a neutral OH can be transferred rather than an O^-.

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(3) Rule and LaMer, THIS JOURNAL, **60**, 1974 (1938).

(4) Bonhoefer, *Trans. Faraday Soc.*, **34**, 252 (1938).

(5) (a) Hughes, Yudken, Kemp and Rideal, *J. Chem. Soc.*, 1105 (1934); (b) Champetier, *Compt. rend.*, **201**, 1118 (1934); (c) Yamasaki, *Bull. Chem. Soc. Japan*, **11**, 431 (1936).

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The Path of Oxygen in Photosynthesis[1]

BY G. D. DOROUGH[2] AND M. CALVIN

It now appears established[3] that the source of oxygen evolved in photosynthesis is the water

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(1) The work described in this paper was sponsored by the Atomic Energy Commission.

(2) While on leave from the Department of Chemistry, Washington University, St. Louis, Missouri.

(3) Ruben, Randall, Kamen and Hyde, THIS JOURNAL, **63**, 877 (1941). Holt and French, "Photosynthesis in Plants," Iowa State College Press, Ames, Iowa, 1949, Chap. 14.