of this compound in carbon tetrachloride showed a strong Si–H absorption band at 2125 cm.$^{-1}$. The identity of this substance was confirmed by a mixed melting point determination and also by a comparison of the infrared spectrum with an authentic sample of tri-*o*-tolylsilane.[9]

Tri-*o*-tolylsilylcesium.—Tetrahydrofuran (75 ml.) was added during 1 hr. to a mixture of 3.4 g. (0.01 mole) of chlorotri-*o*-tolylsilane and 3.31 g. (0.03 g. atom) of cesium. The mixture became light red-brown within 5 min. and the reaction was exothermic. The flask was cooled in an ice-bath and stirred for 2 hr. The deep red-brown solution obtained gave a psoitive Color Test I. Subsequent to acid hydrolysis, work-up as in the previous experiment gave 0.9 g. (21.4%) of tri-*o*-tolylsilane, m.p. 87–88° (mixed m.p.).

Reaction of Chlorotriphenylsilane with Magnesium.—To 14.7 g. (0.05 mole) of chlorotriphenylsilane and an excess of magnesium turnings was added 50 ml. of tetrahydrofuran. Stirring was started, 2 drops of ethyl iodide was added, and the reaction mixture was warmed to reflux temperature. A yellow color and hexaphenyldisilane were observed within 15 minutes indicating initiation of the reaction. After stirring for 24 hr. the mixture was hydrolyzed by filtering through glass wool into dilute hydrochloric acid. Filtration and purification yielded 7.8 g. (60.5%) of hexaphenyldisilane, m.p. 356–359°.

Reaction of Chlorotriphenylsilane with Sodium.—A mixture of 1.15 g. (0.05 g. atom) of finely cut sodium metal was fused slowly with 7.35 g. (0.025 mole) of chlorotriphenylsilane. Subsequently, 40 ml. of tetrahydrofuran was slowly added. After stirring for 24 hr. the solution was yellow and gave a positive Color Test I, indicating the presence of triphenylsilylsodium. However, the color test faded on prolonged stirring. Work-up of the reaction mixture after one week of stirring yielded 2.9 g. (44.8%) of hexaphenyldisilane.

Triphenylgermyllithium.—To a stirred mixture of 3.84 g. (0.01 mole) of bromotriphenylgermane and 0.69 g. (0.1 g. atom) of lithium, 50 ml. of tetrahydrofuran was added during a 1-hr. period. A white precipitate was formed inside the flask after about 15 min. of stirring and the solution turned light yellow at the end of 4 min. Stirring was continued for 3 hr. at room temperature and the deep red-brown solution was filtered through glass wool. The solution gave a positive Color Test I and was treated with 1.5 g. (0.01 mole) of chlorotriethylsilane. The mixture was hydrolyzed and extracted with ether. Removal of the solvent gave 2.2 g. (52.5%) of triphenyl-(triethylsilyl)-germane, which melted at 95–96° after crystallization from ethanol. The identity of this product was established by a mixed melting point determination and comparison of the infrared spectrum of an authentic sample.[13]

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AMES, IOWA

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES OF HARVARD UNIVERSITY AND FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Chromic Acid Oxidation of Diisopropyl Ether[1,2]

BY ROBERT BROWNELL, ALBERT LEO, Y. W. CHANG AND F. H. WESTHEIMER

RECEIVED JUNE 26, 1959

Chromic acid in aqueous sulfuric acid solution oxidizes diisopropyl ether to acetone in good yield without prior hydrolysis to isopropyl alcohol. The reaction proceeds about five times as fast as does the corresponding reaction of $(CH_3)_2CDOCD(CH_3)_2$, but only about $^1/_{1500}$ as rapidly (per secondary hydrogen atom) as does that for isopropyl alcohol under the same experimental conditions. The mechanisms of chromic acid oxidations are discussed.

The kinetics of the chromic acid oxidations of alcohols[3,4] and of aldehydes[5,6] has been extensively investigated. Two mechanisms for the reactions have been advanced. One requires the preliminary formation of an ester[7] of chromic acid which then undergoes decomposition to products; the other[3a,8] mechanism involves the direct removal of a hydride ion (or hydrogen atom) from the secondary carbon atom of the alcohol. In order to help elucidate the mechanisms of oxidation–reduction processes, the reaction of chromic acid with isopropyl ether has been investigated.

$$3(CH_3)_2CHOCH(CH_3)_2 + 4HCrO_4^- + 16H^+ \longrightarrow 6CH_3COCH_3 + 4Cr^{+++} + 13H_2O \quad (1)$$

Experimental

Materials.—Eastman Kodak Co. white label diisopropyl ether was freed from peroxides with acidified ferrous sulfate solution, washed, dried and distilled. Ether of half-degree boiling range, with an index of refraction,[9] $n^{20}D$ 1.3679, was stored in a brown bottle over sodium wire. The ether, stored in this way, gave no peroxide test with acidified potassium iodide for several months; when the test became positive, the compound was discarded, and a fresh lot prepared.

The sulfuric acid solutions were prepared from distilled water and J. T. Baker "Sulfuric Acid, Special. Low in N and As. Subs. Oxid. by $KMnO_4$ (as SO_2): 0.0005%." Ordinary C.P. sulfuric acid contains impurities which react with chromic acid, and even the special reagent reacted slowly; a 0.0002 *M* solution of chromic acid in 5.47 *M* sulfuric acid decreased in optical density 4.2% in 30 hours. Other materials were of reagent grade, or were prepared as described in earlier publications.

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[1] Taken in part from the thesis of Robert Brownell (University of Chicago, 1949) and the thesis of Albert Leo (University of Chicago, 1952).

[2] Presented at the Symposium on the Oxidation of Organic Compounds, Queen Mary College, London, April 13–14, 1959.

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[8] J. Roček and J. Krupička, *Coll. Czech. Chem. Comm.*, **23**, 2068 (1958); *Chemistry & Industry*, 1668 (1957).

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Diisopropyl Ether-α,α-d_2.—Isopropyl alcohol-2-*d* was prepared[3d] by the reduction of acetone with lithium aluminum deuteride. The alcohol (9.1 g.) reacted under reflux with 2.9 g. of red phosphorus and 25 g. of iodine. The organic layer was distilled, washed, and redistilled to yield 19.6 g. of CH_3CDICH_3. The iodide was converted to the corresponding ether with silver oxide by Erlenmeyer's method[10] and finally yielded 1.11 g. of diisopropyl ether boiling at 66.5° (748 mm.), $n^{20}\text{D}$ 1.3675. The deuterium content of the compound was determined by burning it to water, converting the water to a mixture of hydrogen and deuterium, and then analyzing the mixture mass-spectrometrically.[11] The mole per cent. deuterium in the hydrogen of the diisopropyl ether was 13.8% (calcd. 14.3%).

Kinetic Method.—The reagents were mixed at 25°, in a volumetric flask, and samples pipetted at intervals from the thermostated container. The samples were diluted with sufficient water to reduce the concentration of acid to 3.23 *M* (if the spectrophotometric analysis was to be conducted at 447 mμ) or to 2.27 *M* (if the analysis was to be conducted at 349.5 mμ). The samples were then analyzed spectrophotometrically, using a Beckman DU spectrophotometer, with the aid of previously constructed calibration curves. At 447 mμ, corrections were made for the absorption of the Cr^{+++} ion, but at the lower wave length these corrections were unnecessary.

Products.—Thirty ml. of 0.1 *M* chromic acid in 45% by weight sulfuric acid was allowed to react for two hours at room temperature with 100 mg. of diisopropyl ether. The solution was diluted with 150 ml. of water, and the excess chromic acid carefully destroyed with sodium bisulfite. The solution was mixed with 0.9 g. of 2,4-dinitrophenylhydrazine in 300 ml. of 2 *M* sulfuric acid. The average yield from three such experiments was 93% of acetone 2,4-dinitrophenylhydrazone[12] melting at about 124.5–125.5°. Control experiments were slightly less than quantitative; when the results from the oxidation reaction were corrected for the losses found in the controls, the calculated yield approached 97%. The rate of oxidation of acetone, by chromic acid, under the experimental conditions employed was about $^1/_{50}$ that for diisopropyl ether; the destruction of acetone, then, accounts for part of the small deviation from stoichiometry.

Hydrolysis.—Three ml. of ether was dissolved in 250 ml. of 5.47 *M* sulfuric acid at 25°. From time to time, samples were withdrawn, diluted with water to a sulfuric acid concentration of 3.33 *M*, and a solution of chromic acid added. At this sulfuric acid concentration, the oxidation of isopropyl alcohol is almost instantaneous, but that of the ether is slow. Such tests showed that less than 1% of the ether had hydrolyzed in 60 hours.

Effect of Air.—A few experiments were conducted in 5.47 *M* sulfuric acid with degassed reagents and high-vacuum technique. The rate of the reaction was found to be about 12% less than that of the reactions conducted in air. Although this difference is real, presumably it is not large enough to affect the validity of the conclusions here drawn.

Solubility of Diisopropyl Ether in Sulfuric Acid Solutions.—Diisopropyl ether is soluble in aqueous sulfuric acid to the following extent: 23% acid, 0.04 *M;* 31% acid, 0.08 *M;* 41% acid, 0.14 *M;* 52% acid, 0.52 *M;* 58% acid, 2.9 *M;* 65% acid, 6.3 *M*.

Kinetics in D_2O.—The rates of the oxidation of isopropyl alcohol in D_2O were measured spectrophotometrically. The 99.7% D_2O was obtained from the Atomic Energy Commission. Eastman Kodak Co. white label *p*-toluenesulfonic acid was recrystallized from water, and dried in a vacuum desiccator. The corresponding deuterioacid was prepared by dissolving the compound in D_2O and lyophilizing; the process was repeated three times. The acids were standardized by titration.

Results

Kinetics.—Since the acidity of any particular sulfuric acid solution remained essentially constant during a single experiment, second-order rate constants were computed for each "run." These constants, determined at various concentrations of chromic acid, diisopropyl ether and sulfuric acid, are reported in Tables I, II and III.

TABLE I

RATE OF OXIDATION OF DIISOPROPYL ETHER IN 5.47 *M* (40.90%) SULFURIC ACID

Diisopropyl ether, 0.0848 *M;* *T* 25.00 ± 0.01°

Init. concn. of CrO_3, m./l.	*k*, l./mole min.	Init. concn. of CrO_3, m./l.	*k*, l./mole min.
0.0000999	0.246	0.01000	0.173
.0001181	.240	.01040	.180
.000346	.233	.03014	.154
.001039	.246	.03014	.155
.000993	.234	.1131	.153
.00315	.200	.1131	.153
.00315	.200	.3160	.167
.00329	.194	.3160	.174

TABLE II

RATE OF OXIDATION OF DIISOPROPYL ETHER IN 5.47 *M* (40.90%) SULFURIC ACID

Chromic acid, 0.00329 *M;* *T* 25.00 ± 0.01°

Init. concn. of ether, m./l.	*k*, l./mole min.
0.0848	0.197
.0396	.179
.0184	.156
.0184	.160
.00848	.150
.00848	.149

TABLE III

RATE OF OXIDATION OF 0.0565 *M* DIISOPROPYL ETHER WITH 0.00329 *M* CHROMIC ACID AT 25.00 ± 0.01°

H_2SO_4			
M	%	H_0	*k*, l./mole min.[a]
2.768	23.30	−1.11	0.00317
3.861	30.89	−1.60	.0169
5.47	40.90	−2.36	.187
6.315	45.72	−2.79	.578
6.315	45.72	−2.79	.575
7.42	51.59	−3.41	2.89
7.42	51.59	−3.41	2.84

[a] A few of these constants are interpolated from experiments with somewhat different ether concentrations; the corrections involved are small (see Table II).

The chromic acid oxidation of isopropyl alcohol[3] and of pinacol[2,13] in aqueous solution, and the chromic acid oxidation of aromatic aldehydes in aqueous acetic acid[5] solution proceed by way of the acid chromate ion, $HCrO_4^-$. In both of these solvents[5,14] the equilibrium constant for reaction 2

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^- + H_2O \qquad (2)$$

is known, and in both solvents at high concentrations of chromic acid an appreciable fraction of the total hexavalent chromium is present as the dichromate ion. The observed first-order rate constants calculated on the basis of the total hexavalent chromium fall with increasing concentration of chromic acid, but the constants calculated on the basis of the $HCrO_4^-$ present in solution is constant. These facts provide the basis for the statement that $HCrO_4^-$ is the effective oxidant in these reactions. In the oxidation of diisopropyl ether in aqueous sulfuric acid solution, the chromic acid

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(10) E. Erlenmeyer, *Ann.*, **126**, 305 (1863).

(11) R. B. Alfin-Slater, S. M. Rock and M. Swislocki, *Anal. Chem.*, **22**, 421 (1950).

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(13) Y. W. Chang and F. H. Westheimer, in press.

(14) J. Tong and E. King, THIS JOURNAL, **75**, 6180 (1953).

is presumably complexed with sulfuric acid, and the equilibrium constant for the formation of dichromate ion (or of dichromic acid) is unknown. Therefore the small diminution of the rate constant for the oxidation of diisopropyl ether with increasing chromic acid concentration (calculated for total hexavalent chromium as oxidant) cannot yet be interpreted.

The data in Table II show that the rate constant increases about 30% with a tenfold increase in the concentration of diisopropyl ether. A similar small increase in rate constant with increasing concentration of reducing agent was noted in the chromic acid oxidation of isopropyl alcohol.

A plot of the logarithm of the rate constant, from Table III, against H_0[15] does not yield a straight line. An accurate determination of the equilibrium constants for the formation of sulfuric acid–chromic acid complex, and for the formation of dichromate in the sulfuric acid media, are prerequisites to an interpretation of the dependence of the rate on the sulfuric acid concentration.

Isotope Effects.—The effect of deuterium substitution on the rate of the oxidation of diisopropyl ether, and the effect of D_2O as solvent on the rate of oxidation of isopropyl alcohol, are shown in Tables IV and V.

TABLE IV

RATE OF OXIDATION OF DIDEUTERIODIISOPROPYL ETHER BY 0.00214 M CHROMIC ACID AT 25.2°

Isotope	Concn. of ether	k, l./mole min.	k_H/k_D
H	0.0768	0.184	
D	.0967	.0346	5.3
D	.0599	.0354	

TABLE V

THE OXIDATION OF 0.2 M ISOPROPYL ALCOHOL IN H_2O AND IN D_2O SOLUTIONS AT 30°; $\mu^b = 0.20$

Concn. acid[a]	Concn. Cr^6	$k_2^{H_2O}$, l./mole min.	$k_2^{D_2O}$, l./mole min.
0.200	0.0006	0.0362	0.201
.200	.0006	.0378	.212
.0050	.0006	.000193	.000545
.0050	.0006	.000186	.000523

[a] Toluenesulfonic acid. [b] Maintained with sodium p-toluenesulfonate.

The kinetics for the chromic acid oxidation of isopropyl alcohol contains two terms, one with the first and one with the second power of the hydrogen ion concentration.

$$v = [k_3(H^+) + k_4(H^+)^2]\,(HCrO_4^-)(\text{isopropyl alcohol}) \quad (3)$$

When the data in H_2O and D_2O are analyzed according to equation 3, the individual rate constants, and the ratios of the rate constants in D_2O to those in H_2O are

$$k_3^{H_2O} = 0.0342\ \text{l.}^2/\text{m.}^2\ \text{min.};\quad k_4^{H_2O} = 0.755\ \text{l.}^3/\text{m.}^3\ \text{min.};$$

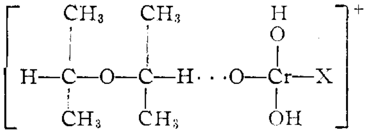
$$k_3^{D_2O} = 0.0832\ \text{l.}^2/\text{m.}^2\ \text{min.};\quad k_4^{D_2O} = 4.73\ \text{l.}^3/\text{m.}^3\ \text{min.}$$

From these data, one calculates that

$$k_3^{D_2O}/k_3^{H_2O} = 2.44 \text{ and } k_4^{D_2O}/k_4^{H_2O} = 6.26$$

Discussion

Diisopropyl ether is directly oxidized by chromic acid to acetone in aqueous sulfuric acid solution, without prior hydrolysis. The kinetics and the isotope effect shown in Table IV show that, in the rate-controlling step of the reaction, a hydrogen nucleus (with or without accompanying electrons) is removed from a complex formed from one molecule of chromic acid and one of the ether. Presumably, the activated complex is represented by the formula



$$\left[\begin{array}{c} CH_3CH_3H \\ H-C-O-C-H\cdots O-\overset{\displaystyle O}{Cr}-X \\ CH_3CH_3OH \end{array}\right]^+$$

here X may either be OH, or an acid sulfate residue. The number of protons attached to the complex is uncertain.

Although a direct attack by chromic acid on the ether is the most probable route to the oxidation products, the nature of the reaction has not been further elucidated. The reduction of a molecule of chromic acid to a chromic ion requires three electrons; the oxidation of each half of the diisopropyl ether molecule contributes two electrons. Since the kinetics show that one molecule of chromic acid reacts, in the rate-controlling step, with one of ether, a three-electron change to chromic ion is not likely; chromic acid must be reduced first to pentavalent chromium or to tetravalent chromium. If pentavalent chromium is formed, then a hydrogen atom must be removed from the ether to produce a free radical, $(CH_3)_2CHO\underset{\cdot}{C}(CH_3)_2$, which would then quickly react further. If tetravalent chromium is formed, then a hydride ion must be removed to produce the ion $(CH_3)_2CH\text{-}\underset{+}{O}{=}C(CH_3)_2$; this ion would then be hydrolyzed to acetone and isopropyl alcohol. In either event, the chromium compounds of intermediate valance state would react rapidly, either with more diisopropyl ether or by disproportionation.[3b]

Whatever the detailed mechanism for the reaction may be, the rate of oxidation of diisopropyl ether in 3.86 M sulfuric acid is only about 1/750 that of isopropyl alcohol under the same experimental conditions; when the statistical factor is taken into account (diisopropyl ether has two oxidizable sites, whereas isopropyl alcohol has only one), the difference in rates of oxidation per secondary hydrogen atom is a factor of about 1500. It is now necessary to account for this difference in rate.

Perhaps the most obvious and simplest explanation for the facts is the suggestion (a) that isopropyl alcohol is oxidized by an ester mechanism,[7] whereas diisopropyl ether cannot react in this fashion. Other possibilities must, however, be considered. Previous work[3b,16] has made it probable that the first step in the oxidation of isopropyl alcohol is a two-electron change, in which chromic acid is reduced to a derivative of tetravalent chromium, and the additional mechanistic possibilities (b) and (c) are discussed below on the assumption of a two-electron change.

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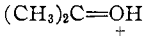
[15] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., nc., New York, N. Y., 1940, Chapter **IX**.

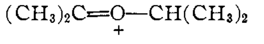
[16] E. Pungor and J. Trompler, *J. Inorg. Nuclear Chem.*, **5**, 123 (1957).

(b) An alternative mechanism for the oxidation of isopropyl alcohol assumes chromic acid removes a hydride ion from it to produce the ion I; the oxidation of diisopropyl ether might then yield II.



$(CH_3)_2C{=}\underset{+}{O}H$

I

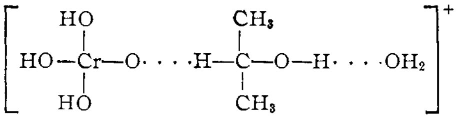


$(CH_3)_2C{=}\underset{+}{O}{-}CH(CH_3)_2$

II

The difference in rates could be explained if the ion I is very much more stable than II. The usual effect of substituents should act rather strongly in the opposite direction, since alkyl groups are electron-donating relative to hydrogen. However, phenol is brominated more rapidly than is anisole, and, in order to explain this phenomenon, Robertson, de la Mare and Swedlund[17] suggested that an ion similar to I would be stabilized by hyperconjugation relative to one similar to II. Their explanation, however, is not unique; the results of bromination could also be accounted for if a proton is removed from the phenol in the rate-controlling step; this possibility is made more probable by Cannell's observation[18] that the brominative desulfonation of 2,6-dibromophenol-4-sulfonic acid proceeds by way of a cyclohexadieneone. A similar example is considered in the paragraphs below.

(c) A modification of mechanism b requires that chromic acid remove a hydride ion from the secondary carbon atom of the alcohol, accompanied by the concerted loss of a proton from the alcoholic hydroxyl group. The transition state for this process would be the ion III. This type of transition state is unavailable for the oxidation of the ether. However, the results of the solvent isotope effect, recorded in Table V and in the paragraph following that table, make this explanation relatively improbable. This statement requires some amplification.



III

The ionization constants of most acids in H_2O exceed those in D_2O by a factor of about 2.5–3, and the stronger acids generally exhibit the lower factor.[19] Therefore, a particular solution of chromic acid in aqueous perchloric or *p*-toluenesulfonic acid will contain about 2.5 times as much D_2CrO_4 in D_2O as H_2CrO_4 in H_2O. The rate of a reaction which proceeds by way of undissociated chromic acid should then be about 2.5 times as fast in D_2O as in H_2O, provided that an OH bond (or OD bond) is not broken in the rate-controlling step. The chromic acid oxidation of isopropyl alcohol proceeds both by a reaction first order in hydrogen ion, and one second order in hydrogen ion (see eq. 3); the reaction which requires an additional proton (or deuteron) would be expected to take place about $(2.5)^2$ or 6.25 times as fast in D_2O as in H_2O, again assuming that an OH bond (or OD bond) is not broken in the rate-controlling step. These predictions compare well with the factors of 2.4 and 6.3, found for $k_3^{D_2O}/k_3^{H_2O}$, and for $k_4^{D_2O}/k_4^{H_2O}$, respectively. If an O–H were broken in the rate-controlling step of the reaction (as postulated in complex III), then this bond would probably be cleaved more rapidly in H_2O than in D_2O, with the result that the effect of D_2O on the rate could scarcely be so large as that observed in fact the reaction might actually be faster in H_2O than in D_2O.

These considerations from theory are reinforced by a survey of the literature.[20] A specific example is offered by the dehydration of acetaldehyde hydrate,[21] which proceeds considerably faster than the hydrolysis of diethyl acetal.[22] But the former reaction is general acid catalyzed, and therefore involves the breaking of an O–H bond as part of the rate-controlling step, whereas the latter is specifically hydrogen ion catalyzed. The effect of changing the solvent from H_2O to D_2O in the dehydration of acetaldehyde is in accord with expectations for reactions where an O–H bond and an O–D bond, respectively, are broken in the transition state.[23] A similar example concerns the oxidation of isopropyl alcohol by bromine, where a C–H and an O–H isotope effect have been observed.[24] Although both k_H/k_D ratios here are small, effects of comparable magnitude, if they were present, would be observed in the chromic acid oxidation.

The solvent isotope effect suggests that explanation (c) is probably faulty. Explanation (b) cannot be eliminated with certainty, and a decision between it and (a) must await further experimentation.

Finally, it must be noted that the oxidation of methylarylcarbinols is accelerated by electron releasing and decelerated by electron-withdrawing substituents[4]; the value of Hammett's[25] "ρ" is negative. The substituent effects in the oxidation of purely aliphatic alcohols are probable similar. A possible explanation for these facts has been offered by Kwart and Francis.[4] It should in addition be noted that the effect of substituents in the oxidation of aromatic aldehydes by permanganate[26] at *p*H 6.5 exhibits a negative "ρ." But under these experimental conditions, Wiberg and Stewart[26] have established that the rate-controlling step in the reaction is the removal of a proton from an ester-anion, formed from one molecule of aldehyde and one permanganate ion.[27] In other

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[17] P. W. Robertson, P. B. D. de la Mare and B. E. Swedlund, *J. Chem. Soc.*, 782 (1953).

[18] L. G. Cannell, THIS JOURNAL, **79**, 2927, 2932 (1957).

[19] G. Schwarzenbach, *Z. Elektrochem.*, **44**, 46 (1938).

[20] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[21] R. P. Bell and J. C. Clunie, *Proc. Roy. Soc. (London)*, **A212**, 33 (1952); R. P. Bell and M. H. Rand, *Bull. soc. chim. France*, **22**, 115 (1955).

[22] J. N. Brönsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929); J. N. Brönsted and C. Grove, THIS JOURNAL, **52**, 1394 (1930).

[23] Y. Pocker, private communication; *cf.* Y. Pocker, *Chemistry & Industry*, 599 (1959).

[24] C. G. Swain and R. A. Wiles, private communication.

[25] L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

[26] K. B. Wiberg and R. Stewart, THIS JOURNAL, **77**, 1786 (1955).

[27] For the argument given here, the effect of substituents on the "esterification" reaction (from an aldehyde plus MnO_4^-) should also be taken into account. A little consideration will show that the true "ρ" value for the step in which a proton is removed from the ester-anion will be even more negative than the value of −0.25 reported by Wiberg and Stewart.

words, for the permanganate oxidation of aldehydes, substituents have a greater effect upon the withdrawal of two electrons, by the oxidant, than upon the removal of the proton which also accompanies the reaction. From this work, one must infer that the acceleration of an oxidation–reduction by electron-releasing substituents is not a valid argument against an ester mechanism.

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CAMBRIDGE 38, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE UNIVERSITY AND THE DIVISION OF PHYSICAL SCIENCES, UNIVERSITY OF CALIFORNIA AT RIVERSIDE]

Specific Rotations of Pure 2-Bromobutanes. Stereochemistry of the 2-Butanol to 2-Bromobutane Conversion

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There is no satisfactory method for demonstrating the optical purity or for resolving alkyl halides with halogen at the asymmetric center. The purest 2-bromobutane reported in the literature ($[\alpha]^{25}\mathrm{D}$ 28.6°) is now demonstrated to be 28% racemized. Introduction of one deuterium in the 3-position creates a second asymmetric center which serves as an internal standard of configuration, enabling one to define the stereochemical course of reactions without resorting to resolutions. *erythro*- and *threo*-3-deuterio-2-butanols are converted to the bromides with phosphorus tribromide. Comparison of these products with pure *erythro*- and *threo*-3-deuterio-2-bromobutanes indicates the alcohol to bromide conversion occurs without skeletal rearrangement and produces a product which is 85–90% inverted at the carbinol carbon corresponding to 20–30% racemization, the remainder having the same configuration as the alcohol. Thus it becomes possible to estimate $[\alpha]^{25}\mathrm{D}$ for optically pure 2-bromobutane (39.4°), *erythro*-3-deuterio-2-bromobutane (38.9°) and *threo*-3-deuterio-2-bromobutane (39.9°). Racemization is minimized by low reaction temperatures, 2-bromobutane with $[\alpha]^{25}\mathrm{D}$ +32.09° being produced at −15°.

Introduction

Although the specific rotations of the completely resolved haloalkanes are necessary for interpretations of mechanism studies employing these enantiomorphs, there are probably no satisfactory values recorded in the literature. The 2-bromobutanes have been prepared from the resolved 2-butanols by reaction with phosphorus tribromide or hydrogen bromide, and by brominating 2-butylmercuric bromide in pyridine yielding preparations with $[\alpha]^{25}\mathrm{D}$ 28.6°,[4] 26.1°,[5] 28.45°,[6] 28.6°,[7] etc., these being the highest values which appear in the literature. Unpublished experimental results,[8] which will be presented in detail elsewhere, suggested that the pure enantiomers probably have a value of $[\alpha]^{25}\mathrm{D}$ 36°.

Since further resolution of 2-bromobutane is not feasible at present, an alternative means of gaining information about optical purity was conceived. Substitution of a deuterium atom for one of the hydrogens of the $-CH_2-$ introduces a second asymmetric center which serves as an internal standard of configuration. Thus it becomes possible to determine the extent of isomerization during conversion of 3-deuterio-2-butanol to 3-deuterio-2-bromobutane without resorting to resolutions. For example, if *erythro*-3-deuterio-2-butanol is converted to the bromide, the major product might be *threo*-3-deuterio-2-bromobutane, and the extent of isomerization during the conversion would be indicated by the *erythro*-3-deuterio-2-bromobutane content of the product. Since these substances are diastereomerically related, the full array of available physical properties may be used to distinguish these isomers.

Pure samples of *d,l-erythro*- and *d,l-threo*-3-deuterio-2-bromobutanes are available by radical chain additions of deuterium bromide to *trans*- and *cis*-2-butenes, respectively.[9] These bromides can also be prepared from the corresponding *threo*- and *erythro*-3-deuterio-2-butanols, which are available by lithium aluminum deuteride reduction of *meso*- and *d,l*-2,3-epoxybutanes.[6]

Analysis for Diastereomers.—Unfortunately the non-congruous infrared absorption bands (up to 15 μ) of *erythro*- and *threo*-3-deuterio-2-bromobutanes are not sufficiently resolved for convenient determination of extent of intercontamination. However, since alkaline dehydrohalogenations of these substances to the butenes are stereospecific *trans* processes,[9] this reaction was used for two independent methods of analysis.

A. Dehydrohalogenation of the *erythro* isomer yields *trans*-2-butene and 2-deuterio-*cis*-2-butene, and the *threo* isomer yields *cis*-2-butene and 2-deuterio-*trans*-2-butene. A mixture of *erythro* and *threo* yields the four 2-butenes. The *cis*- and *trans*-olefins were separated by vapor phase chromatography. The percentage C_4H_8 in each of them was determined by quantitative infrared analysis and the C_4H_7D content by difference.

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