acetate exceeds a certain limit, *i.e.*, *ca.* 0.250 *M* chromic acetate containing 0.083 *M* chromium trioxide. The quenching effect exhibited by chromic acetate seems to be explicable by this decrease of the acidity which is assumptively expressed as $\{b - x - (y/h)\}$ in equation (1). Since the acidity of chromic acid is very large,[10] it may be reasonable to assume that chromium trioxide gives one mole of proton per mole of the trioxide and the proton is then neutralized by chromic acetate. The values of h vary from 2 to 10 according to the nature of substituents probably owing to the different range of the acidity in which the oxidation is possible; *i.e.*, the larger is h, the lower is the limit of the acidity. The addition of a solution of prepared chromic acetate also produces a retarding effect to the same extent that equation (1) requires, provided a relatively small amount of the acetate is added (last line of no substituent in Table I).

Within this limited range of the initial concentration of chromium trioxide b (0.2945–0.2535 mole/l.), the rate constant κ diminishes with increasing initial concentration of toluenes.

Acknowledgments.—The authors wish to thank Drs. W. A. Waters, R. Slack, R. Oda, Prof. T. Nishi, Mr. M. Okano and Mr. Y. Kitamura for assistance and advice and also to referees of THIS JOURNAL for important suggestions.

KYOTO, JAPAN RECEIVED APRIL 9, 1951

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[10] For the first ionization constant (0.18 at 25°) see J. D. Neuss and W. Rieman, THIS JOURNAL, **56**, 2238 (1934).

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL CHEMISTRY, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION]

The Mechanism of the Reaction between Glycerol and Hydriodic Acid

BY R. B. BRADBURY

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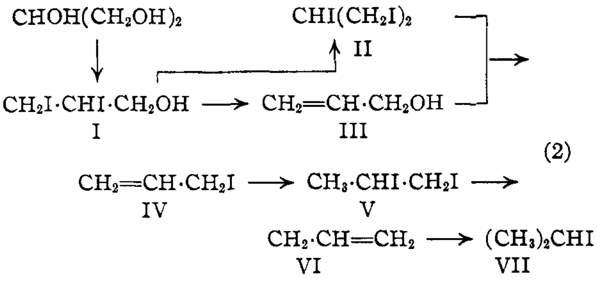
The reaction between glycerol and hydriodic acid to give isopropyl iodide as the final product has been studied kinetically by determining the rates of formation of iodine. Comparison of the reaction velocities of glycerol and of 1-iodo-2,3-propanediol with hydriodic acid, indicates that the substitution of one of the primary hydroxyl groups by iodine is probably the slowest step in the transformation. When the reaction between glycerol and hydriodic acid takes place in the presence of an organic acid, there is a marked increase in the reaction rate, and higher yields of isopropyl iodide are obtained. This catalytic effect of the organic acid is considered to result from esterification by it of the primary hydroxyl groups of glycerol, the acyloxy groups being subsequently replaced by iodine through the rupture of an alkyl–oxygen bond.

Introduction

The over-all reaction between glycerol and hydriodic acid to give isopropyl iodide

$$C_3H_8O_3 + 5HI = C_3H_7I + 3H_2O + 2I_2 \qquad (1)$$

has often been represented as occurring in the steps[1]



When hydriodic acid is used in excess, isopropyl iodide (VII) is the main product, when glycerol is in excess allyl iodide (IV) and propylene (VI) are formed. Allyl alcohol (III) has also been isolated but not triiodopropane (II) or 1,2-diiodopropane (V). Malbot[1] has suggested that 1,2-diiodopropane could be converted directly to isopropyl iodide, propylene becoming the product of a side reaction. The likely intermediates 1-iodo-2,3-propanediol and 2-iodo-1,3-propanediol have been prepared[2] from the corresponding chlorohydrins, but not from glycerol. An alternative scheme has been proposed by Sattler[3] who, without experimental support suggested the formation of cyclopropanol from 1,3-diiodo 2-propanol.

This paper is concerned more with the mechanism of substitution of the hydroxyl groups of glycerol by iodine, than the subsequent elimination and addition reactions which lead finally to isopropyl iodide.

Experimental

Purification of Materials.—Hydriodic acid of analytical grade (sp. gr. 1.7) purified by refluxing with red phosphorus and distilling in a stream of nitrogen gave a colorless product, b.p. 127°, which when stored in ampoules in the dark showed no liberation of iodine after 3–4 weeks.

Glycerol (B.D.H. reagent) was twice distilled at 15 mm. in a stream of dry nitrogen, the middle fraction collected and kept in a desiccator over phosphorus pentoxide. Its purity was checked by its density, and by determination after dilution according to the dichromate procedure.

Allyl alcohol (B.D.H. reagent) dried over anhydrous potassium carbonate and fractionated had b.p. 98°.

Allyl propionate prepared from allyl alcohol and propionic anhydride, washed with 25% aqueous sodium carbonate and dried over calcium chloride had b.p. 124°. The saponification equivalent showed it to be 99.7% pure.

Allyl iodide prepared by the method of McCullough and Cortese,[4] washed with dilute aqueous sodium hydroxide, dried over calcium chloride and fractionated in a stream of dry nitrogen had b.p. 101°. Its iodine content corresponded to 99.0% purity. Propionic acid (B.D.H. reagent) purified by conversion to the ethyl ester, fractionation and hydrolysis had b.p. 140–143°.

1-Iodo-2,3-propanediol prepared by the method of Glatt-

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(1) C. A. Wurtz, *Ann. Chim.*, [3] **43**, 495 (1854); M. Berthelot and S. de Luca, *ibid.*, [3] **43**, 258 (1854); **44**, 350 (1855); E. Erlenmeyer, *Ann.*, **139**, 211 (1866); L. Henry, *Ber.*, **14**, 403 (1881); H. Malbot, *Ann. Chim.*, [6] **19**, 347 (1890).

(2) J. W. E. Glattfeld and R. Klass, THIS JOURNAL, **55**, 1114 (1933).

(3) L. Sattler, *ibid.*, **54**, 830 (1932).

(4) R. McCullough and F. Cortese, *ibid.*, **51**, 225 (1929).

Table I

Reaction of Glycerol and 1-Iodo-2,3-propanediol with Hydriodic Acid

Expt. No.	Glycerol g. mole per l.	Hydrogen iodide, g. mole per l.	Temp., °C.	Time, hr.	Equivalents iodine liberated per mole reactant	$b - x$	k_1, hr.$^{-1}$	k_2, liter mole^{-1} hr.$^{-1}$	Period of half reaction, hr.
1	0.195	7.32	100	1.0	0.88	0.152	0.25	0.035	3.2
2	.195	7.32	100	2.0	1.49	.123	.23	.033	
3	.195	7.32	110	1.0	1.82	.107	.60	.085	1.2
4	.195	7.32	110	2.0	2.64	.066	.54	.078	
5	.195	7.32	120	0.5	2.14	.091	1.52	.217	0.45
6	.195	7.32	120	1.0	3.10	.044	1.49	.219	
7	.195	7.32	120	2.0	3.68	.016	1.25	.187	
8	.279	7.22	100	2.0	1.44	.179	0.22	.032	3.4
9	.279	7.22	100	4.0	2.18	.127	.20	.029	
10	.519	7.14	100	4.0	1.70	.299	.14	.021	6.0
11	.519	7.14	100	7.13	2.15	.240	.11	.017	
12	.444	7.61	100	0.53	0.47	.392	.23	.032	2.7
13	.444	7.61	100	1.0	0.84	.350	.24	.033	
14	.444	7.61	100	2.01	1.50	.277	.23	.033	
15	.444	7.61	100	2.50	1.86	.237	.25	.036	
16	.444	7.61	100	4.18	3.01	.111	.33	.051	
17	.325	6.67^b	60	0.25	1.44	.208	1.79	.282	0.5
18	.325	6.67^b	60	.58	2.17	.149	1.34	.219	
19	.325	6.67^b	70	.25	2.18	.148	3.14	.512	0.2
20	.325	6.67^b	70	.50	2.85	.093	2.50	.419	
21	.389	7.08^c	60	.25	0.65	.326	0.72	.130	1.5
22	.389	7.08^c	60	1.0	1.69	.164	.55	.085	
23	.389	7.08^c	60	2.0	2.32	.164	.43	.067	
24	.417^a	7.17	60	0.083	0.82	.332	2.76	.339	0.5
25	.417	7.17	60	.25	1.39	.272	1.71	.250	
26	.417	7.17	60	.45	1.91	.218	1.44	.214	
27	.417	7.17	60	1.0	2.63	.143	1.07	.164	
28	.417	7.17	70	0.17	1.93	.216	3.94	.578	
29	.417	7.17	70	.20	2.10	.198	3.73	.557	
30	.417	7.17	100	.083	3.89	.011	43	7.4	

[a] 1-Iodo-2,3-propanediol, g. mol. per l. [b] Propionic acid at a concentration of 1.08 g. mol. per l. was present. [c] Propionic acid at a concentration of 0.382 g. mol. per l. was present.

feld and Klass[2] and recrystallized from chloroform had m.p. 47.5° (uncor.). Glattfeld and Klass obtained m.p. 47–47.5°.

Anal. Calcd. for $C_3H_7O_2I$: C, 17.8; H, 3.5. Found: C, 18.0; H, 3.4.

Methods.—The kinetic measurements were obtained by using an electrically heated, stirred thermostat controlled to within ± 0.1° of the temperature required. The Pyrex tubing used for the ampoules was thoroughly cleaned with hot chromic acid and distilled water. During the introduction of 1.00 ml. of the reaction mixture into each ampoule particular care was taken that the pipet did not contact that portion of the tube which was to be subjected to heat during sealing. The air was displaced by nitrogen, the ampoule sealed, and kept at 0° until required. The measurements wêre made by completely immersing the ampoules in the thermostat at the required temperature, and shaking for 5 seconds to obtain temperature equilibrium, then allowing them to remain in the thermostat for the period desired. On withdrawal they were cooled rapidly to 0° and iodine analyses carried out by withdrawing 10–15 mg. of the solution with a capillary pipet and weighing in small stoppered weighing bottles on a microbalance. The weighing bottles were transferred to 5–10 ml. of distilled water in an "iodine flask" and the iodine determined by titration with 0.01 or 0.005 *N* sodium thiosulfate solution to the starch end-point.

One set of determinations (Table I, Expts. 12–16) was obtained by the use of a flask containing the reaction mixture, through which a slow stream of nitrogen was passed. Samples for analysis were withdrawn at intervals and treated in the manner described above.

Tests were made to estimate quantitatively the conversion of glycerol, allyl alcohol, allyl propionate and allyl iodide to isopropyl iodide. Details of the apparatus and the determination which was carried out according to the procedure of Vieböck and Brecher,[5] are given elsewhere.[6]

The 50% aqueous glycerol used for these experiments was weighed in small stoppered weighing bottles, the allyl alcohol, allyl propionate and allyl iodide in small ampoules. The latter were crushed by a glass rod of such a length that it could be left in the reaction flask of the apparatus. Pure isopropyl iodide treated in similar manner gave almost 100% recovery and propionic acid gave negligible blank values.

Results and Calculations

The kinetic results obtained for the reaction of glycerol and of 1-iodo-2,3-propanediol with hydriodic acid are shown in Table I. Experiments 1–16 show the reaction between glycerol and hydriodic acid, in which the molecular excess of the latter was varied from 2.75 to 7.5. Experiments 1–11 were carried out in sealed tubes, others 12–16 in a flask through which a slow stream of nitrogen could be passed. At 100° the period of half reaction[7] was reduced from six to three hours when the molecular excess of hydriodic acid was increased from 2.75 to 5.17. Where volatile products could escape from the reaction mixture (Expt. 12–16) the time of half reaction at 100° was reduced to 2.7 hr., although hydriodic acid was present in 3.43 molecular excess.

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(5) F. Vieböck and C. Brecher, *Ber.*, **63**, 3207 (1930).

(6) R. B. Bradbury, *Mikrochemie.*, **38**, 114 (1951).

(7) The periods of half reaction were obtained graphically by plotting equivalents of iodine liberated per mole of reactant, against time.

The marked catalytic effect of propionic acid on the reaction between glycerol and hydriodic acid is shown in Expts. 17–23. When the molecular concentrations of glycerol to propionic acid were 1:1 (Expts. 21–23) and 1:3 (Expts. 17–20) the times of half reaction at 60° were 1.5 and 0.5 hr., respectively. A correspondingly increased reaction velocity was observed with 1-iodo-2,3-propanediol and hydriodic acid (Expts. 24–30), the time of half reaction at 60° also being 0.5 hr.

The experimental data (Table I) have been used to calculate the velocity constants, making the assumption that the first step of the reaction is rate controlling and all subsequent steps immeasurably fast. Correction for variation of the volume with temperature is omitted, since error from this source is less than experimental variation. The reverse reaction, namely, the solvolysis of the alkyl halide has not been considered since equilibrium is unlikely to be attained in the initial rate determining steps. First order constants for equation (1) were calculated from the expression

$$K_1 = \frac{1}{t} \ln \frac{b}{b - x} \qquad (3)$$

where b is the initial concentration of glycerol (g. mole per l.) and x the amount reacting in time t (hr.). Second order constants were calculated from the expression

$$K_2 = \frac{1}{t(a - 5b)} \ln \frac{b(a - 5x)}{a(b - x)} \qquad (4)$$

where b, x and t have the same significance and a is the initial concentration of hydriodic acid (g. mole per l.). For the reaction between 1-iodo-2,3-propanediol and hydriodic acid the expression employed for the unimolecular constant was (3) and for the bimolecular

$$K_2 = \frac{1}{t(a - 4b)} \ln \frac{b(a - 4x)}{a(b - x)} \qquad (5)$$

where b and x now refer to 1-iodo-2,3-propanediol.

Quantitative experiments by the writer had shown that in the reaction between glycerol and hydriodic acid the ratio of iodine liberated to isopropyl iodide formed, approximated that required by equation (1). By a modified Zeisel procedure it was found in agreement with Marchi[8] that even when a large excess of hydriodic acid was present glycerol could be converted to isopropyl iodide in only 93.9 ± 0.5% (7 determinations) yield. Marchi found that in the presence of an organic acid almost quantitative conversion was obtained. This has been confirmed in the present work, the yield of isopropyl iodide being raised to 99.4 ± 0.3% (3 determinations) when propionic acid was present in a molecular ratio to glycerol of at least 3:1. Allyl alcohol, allyl propionate and allyl iodide gave 95.3 ± 0.4% (6 determinations), 95.2 ± 0.1% (2 determinations) and 98.2 ± 1.9% (5 determinations) of isopropyl iodide, respectively, with hydriodic acid alone. The larger variation between determinations with allyl iodide was attributed to its instability.

Discussion

From the scheme (2) given, it is clear that a kinetic study of the reaction between glycerol and hydriodic acid requires a consideration of substitution, elimination and addition reactions. The fact that the reaction velocity of 1-iodo-2,3-propanediol with hydriodic acid (Expts. 24–30) is much greater than that of glycerol (Expts. 1–16) indicates that the main rate-controlling step in the reaction between glycerol and hydriodic acid is one of substitution in which 2-iodo-1,3-propanediol is converted to 2,3-diiodopropanol. The rate-controlling step involving substitution in the 1-position was not unexpected since Bennett and Reynolds[9] had shown that the reactivity of alcohols with halogen acids increases in the order: primary, secondary, tertiary. Therefore in the reaction between glycerol and hydriodic acid 2-iodo-1,3-propanediol should be formed first, followed by its slower conversion to 2,3-diiodopropanol. Bennett and Reynolds point out that chlorohydrins have a lower reactivity than their corresponding glycols. Iodohydrins can be expected to behave similarly, and the conversion of 2-iodo-1,3-propanediol to 2,3-diiodopropanol for this reason should be relatively so much slower than the initial step. However in the reaction of 1-iodo-2,3-propanediol with hydriodic acid the decreased reactivity in the 2-position caused by the iodine atom already present is considerably outweighed by the ease of substitution of the secondary hydroxyl group.

In the reaction of both glycerol and 1-iodo-2,3-propanediol with hydriodic acid (Table I) both uni- and bimolecular constants diminish with time, thus making a distinction between the two mechanisms impossible and activation energies derived therefrom of doubtful value.[10] Decrease of the velocity constant as the reaction proceeds appears to be a characteristic feature of the reaction between monohydric alcohols and halogen acids and has been attributed to the water formed during the reaction.[11] This is substantiated in the present work for when the reaction between glycerol and hydriodic acid was conducted in a flask through which a slow stream of nitrogen was passed (Expts. 12–16), the reaction appeared to be first order with respect to glycerol. These constants are also in agreement with those obtained in sealed tubes (Expts. 1 and 2), where a relatively large excess of hydriodic acid (7.5 molecular excess) was present, and the reaction had not proceeded too far. The amount of water produced according to equation (1), together with that corresponding in the constant boiling acid to the hydrogen iodide used, is approximately 30 molecules of water from each molecule of glycerol reacting. Consequently in experiments 12–16 in which 4.439×10^{-4} mole glycerol and 76.1×10^{-4} mole hydriodic acid were used,

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[8] C. Marchi, *Staz. sper. agrar. ital.*, **56**, 231 (1923).

[9] G. M. Bennett and F. M. Reynolds, *J. Chem. Soc.*, **138**, 131 (1935).

[10] Calculations based on half completion of the reaction gave the following approximate values: glycerol and hydriodic acid $E_{\text{act.}}$, 29 kcal./mole (Bennett and Reynolds[9] obtained similar values for the reaction between alcohols and halogen acids); 1-iodo-2,3-propanediol and hydriodic acid $E_{\text{act.}}$, 23 kcal./mole; glycerol, hydriodic acid, propionic acids $E_{\text{act.}}$, 18 kcal./mole.

[11] J. F. Norris, *Rec. trav. chim.*, **48**, 885 (1929); P. A. Levene and A. Rothen, *J. Biol. Chem.*, **81**, 359 (1929); G. M. Bennett and F. M. Reynolds[9]; E. Grunwald and S. Winstein, THIS JOURNAL, **69**, 2051 (1947).

the amount of water produced at completion of the reaction would be 1.32×10^{-2} mole (0.238 g.). Removal of half this quantity of water in the nitrogen stream over a period of 2.5 hr. at 100° appears quite possible, and is considered to account for the agreement in the first order constants to half completion of the reaction.

The catalytic effect of propionic acid in increasing the rate of reaction between glycerol and hydriodic acid (Expts. 17–23) shows that the reaction follows a different course in its presence. Marchi[8] considered the effect of the organic acid in increasing the yield of isopropyl iodide from glycerol, to be due to the formation of unstable 2-iodo-1,3-diacyloxy-esters of glycerol. It is apparent that there is first esterification, followed by substitution of the acyloxy groups by iodine. The work of de la Acena[12] makes it probable that halogenation by this mechanism occurs first at the primary hydroxyl groups. He found that the reaction of triacetin with hydrobromic acid gave 1-bromo-2,3-diacetoxypropane at 0°, and 1,3-dibromo-2-acetoxy-propane at 100°. This explanation receives further support from the work of Bennett and Reynolds[9] who found that in the esterification of alcohols by organic acids the order of increasing reactivity is: tertiary, secondary, primary alcohols—the reverse of that found with halogen acids. These authors explain this reversal by the fact that in esterification it is a hydrogen–oxygen bond that is broken, but in halogenation a carbon–oxygen bond. In the presence of propionic acid therefore the primary hydroxyl groups of glycerol are rapidly esterified, and the esters readily converted to the corresponding halides by the rupture of an alkyl–oxygen bond. The rate-controlling step is probably substitution in the 2-position, since the period of half completion (Expts. 17, 18) agrees with that obtained for 1-iodo-2,3-propanediol and hydriodic acid (Expts. 24–27). Although the marked catalytic effect of propionic acid is fully apparent where its molecular ratio to glycerol is 3:1 (Expts. 17–20) this is confirmed also where the ratio is only 1:1 (Expts. 21–23).

The course of the reaction is summarized in the set of equations (6). A series of esterifications and halogen substitutions lead to triiodopropane, and thence loss of iodine to allyl iodide, from which isopropyl iodide is formed according to the scheme given in equation (2).

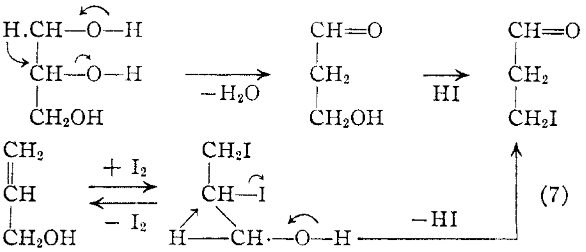
$$CH_2OH\cdot CHOH\cdot CH_2OH \longrightarrow CH_2OH\cdot CHOH\cdot CH_2O\cdot COR \longrightarrow$$

$$CH_2OH\cdot CHOH\cdot CH_2I \longrightarrow CH_2\cdot(OCOR)\cdot CHOH\cdot CH_2I \longrightarrow$$

$$CHOH\cdot(CH_2I)_2 \longrightarrow CHI(CH_2I)_2 \longrightarrow CH_2{=}CH\cdot CH_2I \quad (6)$$

It is of interest to recall that Perkin and Simonsen[13] found that symmetrical tribromopropane was produced when triacetin was heated to 150° with acetic acid and hydrobromic acid.

Comparison of the mechanisms proposed for the formation of isopropyl iodide from glycerol and hydriodic acid shows that in the absence of an organic acid allyl alcohol is formed, but in its presence the formation of triiodopropane is postulated. Since lower yields of isopropyl iodide have been obtained from glycerol, allyl alcohol and allyl propionate than from allyl iodide, and glycerol in the presence of propionic acid, it is concluded that side reactions not leading to isopropyl iodide occur in the former instances. Charon and Paix-Seailles[14] found that on heating 2,3-diiodopropanol, 3-iodopropanol was formed. It is suggested that formation of this aldehyde, which would not be reducible to isopropyl iodide, could occur by rearrangement of glycerol or of diiodopropanol according to equations (7).



(7)

An observation of Caughley and Robertson[15] that a satisfactory rate constant for the addition of iodine to allyl alcohol, could be obtained at 25° but that at 50° it decreased with time, indicates the possibility of side reactions becoming increasingly important at the higher temperatures required in the conversion of glycerol to isopropyl iodide.

Acknowledgments.—Thanks are due to Drs. H. H. Hatt and R. J. L. Martin for helpful criticism in the preparation of this paper.

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[12] R. de la Acena, *Compt. rend.*, **139**, 867 (1904).

[13] W. H. Perkin and J. L. Simonsen, *J. Chem. Soc.*, **87**, 855 (1905).

[14] E. Charon and C. Paix-Seailles, *Compt. rend.*, **130**, 1631 (1900).

[15] F. G. Caughley and P. W. Robertson, *J. Chem. Soc.*, **136**, 1323 (1933).