Summary

The oxidation of bromide by hypochlorite in the *p*H range 10 to 13 and at various temperatures is a second-order reaction in which bromide is oxidized quantitatively to hypobromite. No measurable formation of chlorate, chlorite, bromate or bromite occurs under these conditions.

The rate constant for the reaction is approximately proportional to the concentration of hydrogen ions in the solution. Consequently the rate-determining step has been deduced to be the interaction

$$HOCl + Br^- \longrightarrow HOBr + Cl^-$$

At 25° the rate constant for this process is 1.77 $\times 10^5$ liter/mole minute.

JERUSALEM, ISRAEL RECEIVED[12] DECEMBER 28, 1948

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[12] Original manuscript received February 12, 1948.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HEBREW UNIVERSITY]

On the Rate of the Acid-Catalyzed *trans*-Esterification of Butyl Alcohol and Ethyl Acetate

BY L. FARKAS, O. SCHÄCHTER AND B. H. VROMEN

It is well known that mixture of an ester and an alcohol in the presence of hydrogen ions *trans*-esterification takes place. However, there are no quantitative data in the literature on the rate of this reaction in the case of simple aliphatic pairs. The following study deals with the rate of the reaction

$$C_4H_9OH + CH_3COOC_2H_5 \rightleftarrows C_2H_5OH + CH_3COOC_4H_9 \quad (1)$$

in the presence of sulfuric acid as catalyst.

Experimental

Materials.—Butyl alcohol, ethyl acetate and butyl acetate of an analytically pure quality served as starting materials. All were rectified in a column of twenty theoretical plates. The esters, after rectification, did not react with metallic sodium.

Ethyl alcohol of 99.8% (by weight) purity served mainly for the determination of the calibration curve of the analysis (see below) and the 0.2% water content did not interfere with the measurements.

Anhydrous sulfuric acid was made by mixing an acid of about "104%" sulfuric acid content with sulfuric acid p. a. The former was prepared by distilling sulfur trioxide from chemically pure oleum into sulfuric acid p. a.

Experimental Procedure.—Weighed quantities of the starting materials were introduced into a vessel with a ground-glass stopper together with an ampoule containing the sulfuric acid. The vessel was then immersed in a thermostat and after fifteen minutes, when the reaction mixture attained the temperature of the bath, the ampoule was broken with a glass rod, the vessel shaken and the time recorded. Samples were taken at various time intervals. The temperature of the thermostat was kept constant within ±0.1°.

The equilibrium concentration of the reactants was determined by starting from equimolar quantities of ethyl acetate and butyl alcohol in sealed ampoules, which were kept for several weeks in a thermostat in the presence of 0.1% sulfuric acid as catalyst.

Analytical Procedure.—Several methods are described in the literature for the analysis of mixtures of alcohols and esters. Fehlandt and Adkins[1] used fractionation, however, since in the present case the composition of the mixture would change during distillation, this method was not suitable for our purpose. Bogin[2] applied a method of titration with water for the analysis of binary mixtures, the appearance of turbidity serving as an indicator. This method and various modifications using different aqueous solutions, such as sodium chloride, calcium chloride, butanol and ethanol, were tried, but none of them gave sufficiently accurate results. The differences in the densities and refractive indices of the mixture in question are too small to allow an exact determination of the progress of the reaction.

Eventually it was found that the composition of various mixtures of the reactants could be determined by analyzing the quantity of ester in an aqueous extract under suitable conditions. The results are well reproducible and the method gives an accuracy of ±0.5%. The analysis is carried out in a test-tube of about 30 ml. capacity to which a side-tube closed with a cork is attached in the middle; 15 ml. of water and 10 ml. of the mixture to be analyzed are introduced into the test-tube, the vessel is closed, shaken and immersed in an ice–water-bath. When the contents have cooled to 0° the vessel is agitated again and this is repeated after a few minutes. As soon as the two layers have separated and the lower layer is completely clear, the test-tube is removed from the ice-bath and the upper layer is drained off completely through the open side-tube. Then 10 ml. of the aqueous layer is pipetted into an erlenmeyer flask and the saponification number is determined by adding 15 to 50 ml. of aqueous 0.2 *N* sodium hydroxide solution and heating the closed flask in a water bath for twenty minutes. The excess of alkali is back-titrated with 0.1 *N* acid. The introduction of any of the upper layer into the sample taken for the saponification impairs the accuracy of the analysis. To avoid it, the pipet is closed with a finger until it reaches the bottom of the test-tube and its lower end is wiped with a filter paper before the sample is poured into the erlenmeyer. Since the solubility of the esters in water decreases with increasing temperature, the sample in the pipet becomes turbid. This, however, has no effect on the accuracy of the analysis. The complete analysis takes less than an hour.

From the saponification number the composition of the reacting mixture is found by means of an empirical calibration curve, which is obtained by analyzing "synthetic" mixtures corresponding to various degrees of progress of the reaction. Some of the figures which served as a basis of the calibration curves for experiments started with butanol and ethyl acetate are given in Table I. The calibration curves drawn on the basis of these figures are almost linear.[3]

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(1) Fehlandt and Adkins, THIS JOURNAL, **57**, 193 (1935).

(2) Ch. D. Bogin, *Ind. Eng. Chem.*, **16**, 380 (1924).

(3) It was found that the present method of analysis cannot be employed for mixtures in which the ratio of butyl to ethyl groups is smaller than one. In the presence of sulfuric acid in a concentration higher than 0.2% by weight the accuracy of the analysis is greatly impaired. Nevertheless in a few cases the method was also used for the analysis of reacting mixtures with a sulfuric acid content up to 2% by weight.

Results

The position of the equilibrium was determined at 60 and 80°. The equilibrium constant is independent of the temperature in the range studied, the mean value of the constant being

$$K = \frac{(C_2H_5OH)(CH_3COOC_4H_9)}{(C_4H_9OH)(CH_3COOC_2H_5)} = 0.96$$

This value is in very good agreement with the measurement of Fehlandt and Adkins,[1] whose data give an equilibrium constant of 0.97 at 200°.

TABLE I

CALIBRATION VALUES

Mole fraction butyl acetate (= mole fraction ethanol)	Ratio Butyl groups/Ethyl groups 1:1, Added catalyst 0.1% H_2SO_4, ml. 0.1 *N* NaOH used	Ratio Butyl groups/Ethyl groups 1:1, Added catalyst 0.2% H_2SO_4, ml. 0.1 *N* NaOH used	Mole fraction butyl acetate (= mole fraction ethanol)	Ratio Butyl groups/Ethyl groups 1.55:1, Added catalyst 0.1% H_2SO_4, ml. 0.1 *N* NaOH used	Ratio Butyl groups/Ethyl groups 1.55:1, Added catalyst 0.2% H_2SO_4, ml. 0.1 *N* NaOH used
0.00	74.4	75.0	0.00	62.0	63.8
.10	60.6	61.4	.038	48.9	51.0
.20	46.1	47.8	.076	38.4	39.9
.30	33.2	34.4	.114	28.7	29.7
.40	20.5	..			
.50	8.3	..			

The main experiments were carried out at 60, 70 and 80° at catalyst concentrations of 0.1%[4] and 0.2% by weight and at butyl/ethyl group ratios of 1:1 and 1.55:1. Generally, the runs were made with butyl alcohol and ethyl acetate as starting materials, but in some experiments the rate of the reverse reaction was measured. A blank experiment carried out in the absence of catalyst showed that after ninety hours at 100° no reaction has taken place.

The results are given in Figs. 1, 2 and 3. Log $ab/(ab - x)$ is plotted against time, a and b denoting the mole fractions of the starting materials and x the mole fraction of one of the reaction products. The kinetics of the reaction discussed below show that this expression should be a linear function of the time.

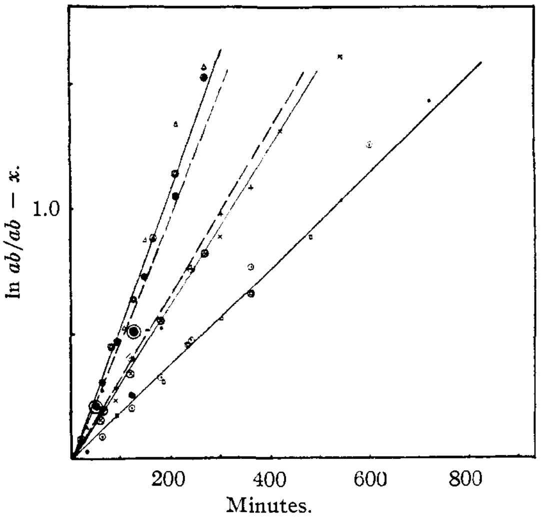

Fig. 1.—The rate of reaction at various temperatures. 0.1% sulfuric acid, butyl:ethyl ratio = 1:1.

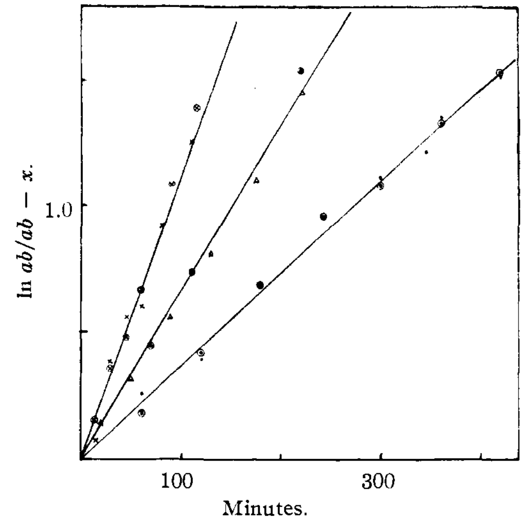

Fig. 2.—The rate of reaction at various temperatures: 0.2% sulfuric acid, butyl:ethyl ratio = 1:1.

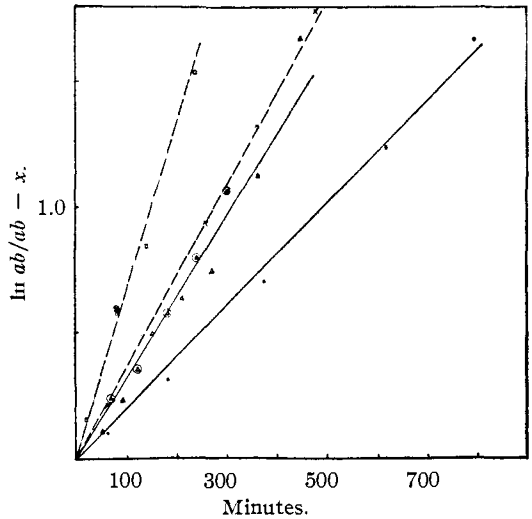

Fig. 3.—The rate of reaction at various temperatures: butyl:ethyl ratio = 1.55:1.

TABLE II

FIRST ORDER RATE CONSTANT 10^6 SEC.$^{-1}$

T, °C.	Catalyst concentration 0.1%, butyl/ethyl group ratio 1:1	Catalyst concentration 0.1%, butyl/ethyl group ratio 1.55:1	Catalyst concentration 0.2%, butyl/ethyl group ratio 1:1	Catalyst concentration 0.2%, butyl/ethyl group ratio 1.55:1
60	3.2 →	3.4 →	6.1 →	6.1 →
	3.2 ←			
70	5.2 →	5.5 →	11.0 →	11.2 →
	5.5 ←			
80	9.0 →	...	18.5 →	.. →
	8.3 ←			

→ forward reaction ← reverse reaction

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[4] The concentration of 0.1% sulfuric acid by weight corresponds at 60° to 0.0082 *M*, at 70° to 0.0081 *M* and, at 80° to 0.008 *M* solutions.

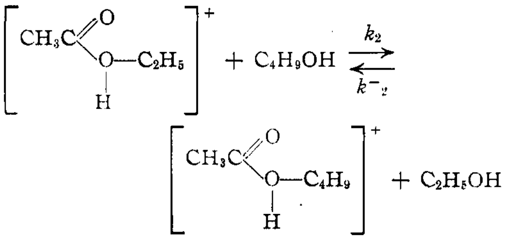
It is seen that the results of independent runs agree fairly well with each other. The first order rate constants calculated from the slopes of the various lines are summarized in Table II. The rate is proportional to the catalyst concentration. The rate constant of the forward reaction is practically equal to the rate constant of the reverse reaction, which confirms the results of the equilibrium measurements. The rate constants are independent of the ratio of butyl to ethyl groups.

In Fig. 4 log *k* of the forward reaction is plotted against 1/*T*. Data are included in the graph on the rate constants of a few experiments which were carried out at 25, 35 and 50° at catalyst concentrations of 1 and 2% sulfuric acid by weight. All values for the rate constant are reduced to 0.01 *M* concentration of the catalyst. Although the measurements below 60° are not accurate, it is seen that they check well with those carried out at lower catalyst concentrations and at higher temperatures. The activation energy of the reaction is 12.8 kcal./mole calculated from the slope of the line in Fig. 4.

Discussion

Recently Harfenist and Baltzly[5] proposed the following steps for the acid catalyzed alcoholysis of β-naphthyl esters in analogy to the mechanism of the acid hydrolysis of esters discussed by Day and Ingold:[6] (1) the ester and the proton of the catalyst form in a fast reversible reaction a positive ion; (2) this positive ion reacts with the alcohol and forms an addition complex; (3) the complex breaks up whereby an exchange of the alcohol groups takes place.

If steps (2) and (3) take place in a reversible bimolecular reaction according to



$$\left[CH_3C{\overset{\displaystyle O}{\underset{\displaystyle \underset{H}{O}-C_2H_5}{\lessgtr}}}\right]^+ + C_4H_9OH \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \left[CH_3C{\overset{\displaystyle O}{\underset{\displaystyle \underset{H}{O}-C_4H_9}{\lessgtr}}}\right]^+ + C_2H_5OH \quad (2)$$

This scheme is identical with Day and Ingold's mechanism (Reaction scheme A'2, *loc. cit.* p. 696).[7]

The kinetic equation describing the ester interchange is given by

$$dx/dt = [H^+]\ k_2K_{eth.ac.}\ (a - x)(b - x) - [H^+]\ k_{-2}\ K_{but.ac.} \quad (3)$$

where $K_{eth.ac.}$ and $K_{but.ac.}$ are the equilibrium constants of the formation of the ester oxonium (or carbonium), $(a - x)$ and $(b - x)$ the mole fractions (or concentrations) of ethyl acetate and butyl alcohol, and x that of ethyl alcohol and butyl acetate.[8] Introducing the equilibrium constant of reaction (1)

$$K = k_2K_{eth.ac.}/k_2K_{but.ac.} \quad (4)$$

and integrating, we obtain

$$k_2K_{eth.ac.}\ [H^+]t = \frac{1}{\{(a + b)^2 - 4ab(1 - 1/K)\}^{1/2}} \ln \frac{2ab - x\{(a + b) - ((a + b)^2 - 4ab(1 - 1/k))^{1/2}\}}{2ab - x\{(a + b) + ((a + b)^2 - 4ab(1 - 1/k)^{1/2}\}} \quad (5)$$

Since the equilibrium constant of (1) is nearly unity, and in case a and b denote mole fractions, also $a + b \cong 1$, equation (5) simplifies to

$$k_2 \cdot K_{eth.ac.}\ [H^+] \cdot t = 2.3 \log ab/(ab - x) \quad (6)$$

This relation is confirmed by the experimental results.[9] The activation energy of reaction (1) (12.8 kcal.) is the same as that observed by Harfenist and Baltzly for the alcoholysis of the β-naphthyl ester.

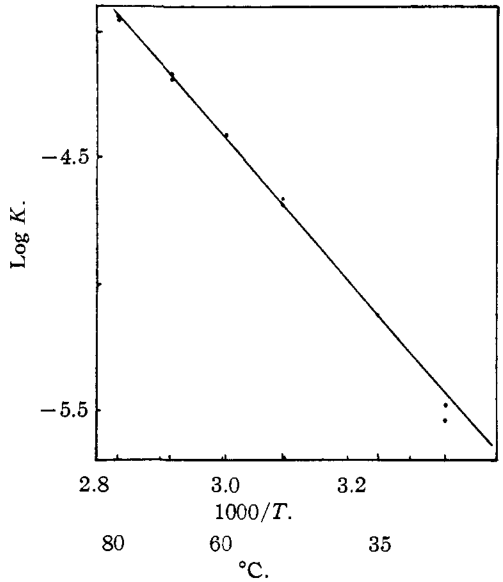


Fig. 4.—Dependence of the rate constant on the temperature.

Acknowledgment.—We are indebted to H. J. G. Hayman for valuable discussions.

Summary

1. The rate constants of the reaction between butyl alcohol and ethyl acetate at 60, 70 and 80° with 0.1 and 0.2% sulfuric acid catalyst concentrations are given.

2. The equilibrium constant is found to be in agreement with that given in the literature for 200°.

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[5] Harfenist and Baltzly, THIS JOURNAL, **69**, 362 (1947).

[6] Day and Ingold, *Trans. Faraday Soc.*, **38**, 686 (1941).

[7] In reaction (2) it is assumed that the ester forms with the hydrogen ion an oxonium complex. An alternative possibility is the formation of a carbonium ion as advocated also by Harfenist and Baltzly.[5]

[8] Strictly, during any given run $[H^+]$ is only constant if $K_{eth.ac.} = K_{but.ac.}$. These two equilibrium constants would be expected to be nearly equal, since the proton affinity of the two esters is probably similar. $[H^+]$ is a function of the total acid and ester concentration in different experiments.

[9] In equation (6), x reaches a maximal value equal to ab at equilibrium.

3. The activation energy calculated from the rate constant is 12.8 kcal./mole.
4. A simple method for analyzing the reaction mixtures is described.
5. The kinetics of the reaction agree with the generally proposed mechanism for acid-catalyzed *trans*-esterification.

JERUSALEM, ISRAEL RECEIVED DECEMBER 28, 1948

[CONTRIBUTION FROM THE PROPAEDEUTIC-CHEMICAL LABORATORY OF THE UNIVERSITY OF HELSINKI]

The Equilibria of Cupric Hydroxysalts in Mixed Aqueous Solutions of Cupric and Alkali Salts at 25°

BY REINO NÄSÄNEN AND VEIKKO TAMMINEN

In a previous paper[1] it was shown that the *p*H of a cupric salt solution changes on precipitating the cupric ion with alkali hydroxide in a manner as seen in Fig. 3. The titration curve is interpreted as follows. First the trihydroxy salt ($Cu(OH)_{1.5}Cl_{0.5}$) is precipitated and the course of the titration curve is determined by the solubility product equation

$$[Cu^{2+}][OH^-]^{1.5}[Cl^-]^{0.5} = S_{1.5} \qquad (1)$$

Near the end-point of the titration the product $[Cu^{2+}][OH^-]^2$ reaches the value of the solubility product of cupric oxide

$$[Cu^{2+}][OH^-]^2 = S_2 \qquad (2)$$

and henceforth equations (1) and (2) are both valid. By eliminating $[Cu^{2+}]$ between (1) and (2) we obtain

$$[OH^-] = (S_2/S_{1.5})^2[Cl^-] \qquad (3)$$

Thus the *p*H of the solution is nearly constant as long as two solid phases are present. When all the trihydroxy salt is turned into oxide an abrupt *p*H-change again occurs. The course of the curve is then determined by equation (2). The precipitation curve of trihydroxysulfate is similar as that of trihydroxychloride.

In the previous investigation $S_{1.5}$ and S_2 were measured at one ionic strength. These measurements have since been continued in dilute cupric chloride, sulfate, nitrate and perchlorate solutions. The influence of the corresponding alkali salts is especially investigated. In the following, the results of these studies are presented.

Experimental

Materials.—Cupric chloride and sulfate as well as potassium chloride, nitrate and sulfate were of the best qualities obtainable (Kahlbaum, for analysis) and were used without purification. Cupric nitrate and sodium perchlorate were of the quality "purissimum" and were used after a recrystallizing procedure. Cupric perchlorate was prepared from cupric oxide "for analysis" and perchloric acid. Nitrate and perchlorate solutions were standardized gravimetrically with nitron. Sulfate was determined as barium sulfate. Copper was titrated iodometrically. The solution of sodium hydroxide was obtained by dilution of strong carbonate-free solution with carbon dioxide-free water and standardized against potassium biphthalate or bi-iodate.

Procedure.—The experiments were made in conical Pyrex flasks with glass stoppers into which the cupric salt and corresponding alkali salt solutions as well as the required amount of water and alkali hydroxide solution were measured. Flasks were then kept at 25 ± 0.1° and occasionally stirred. The *p*H of the solutions became constant after four days at least. In all actual experiments, however, *p*H is measured at the earliest after one week.

The *p*H was determined with a "Radiometer, PHM 3" potentiometer using a glass electrode and saturated calomel electrode. The sensitivity of the potentiometer is better than 0.3 mv. The glass electrode was standardized against an acetic acid–acetate buffer[2] *p*H 4.65 and a phosphate buffer[3] *p*H 7.54. The temperature of the room where the measurements were made was maintained at 25° to within ±0.2°.

Analysis of Precipitate.—The composition of the precipitate can often be determined from the position of the inflection point of the titration curve and from the slope of the part of the curve which corresponds to the excess of cupric salt.[4] In some cases chemical analysis of the precipitate was required. It was performed as follows. The precipitate was filtered with a glass filter crucible, washed with a small amount of water, dissolved with sulfuric acid and analyzed as regards copper.

Calculation of Solubility Products

A cupric hydroxysalt can be represented by the formulas

$$nCu(OH)_2 \cdot Cu(A)_{2/z} \text{ or } Cu(OH)_k(A)_{(2-k)/z}$$

where z is the valence of the ion A^{z-}. The concentration of cupric ion in a solution in equilibrium with this compound can be calculated from

$$[Cu^{2+}] = {}^1/_2c_{Cu} - (c_B + [H^+])/k \qquad (4)$$

where c_{Cu} is the stoichiometric normality of cupric salt and c_B that of sodium hydroxide. The concentration of the anion A^{z-} is obtained respectively from

$$[A^{z-}] = c + c_{Cu}/z - (c_B + [H^+])(2 - k)/kz \qquad (5)$$

where c is the molarity of the added alkali salt. The ionic strength of the solution is obtained from

$$\mu = \mu_0 + c_{Cu}\,(1 + z/2) + 0.5c_B\left(1 - \frac{(2 - k)z + 4}{k}\right) \qquad (6)$$

where μ_0 comes from the added alkali salt. By deriving equations (4), (5) and (6) it is supposed that no complex formation occurs. This question

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[1] R. Näsänen, *Ann. Acad. Sci. Fennicae*, **A59**, 7 (1942).

[2] S. Kilpi and A. Meretoja, *Suomen Kemistilehti*, **B16**, 23 (1943).

[3] Y. Hentola, *Kemian Keskusliiton Julkaisuja*, **2**, 62 (1946).

[4] *Cf.* R. Näsänen, *Suomen Kemistilehti*, **B21**, 56 (1948).