The copolymers with butadiene were prepared according to the formula: butadiene 7.5 g., olefin 2.5 g., water 17.5 g., potassium persulfate 0.03 g., lauryl mercaptan 0.06 g. and soap 0.5 g. Sealed tubes containing this mixture were rotated in a water-bath at 40° until polymerization ceased as evidenced by the absence of further change in the height of the liquid meniscus in the tube. Satisfactory rubbers were obtained from 2-isopropenylfuran, 5-isopropyl-2-isopropenylfuran and 2-isopropenylbenzofuran. No rubbers were obtained with 4-methyl-5-vinylthiazole or 2-vinylbenzoxazole.

Summary

The preparation and polymerization of vinyl and isopropenyl derivatives of five-atom heterocyclic ring systems have been studied. The vinyl compounds investigated include: 2-isopropenylfuran, 5-isopropyl-2-isopropenylfuran, 2-vinylbenzoxazole and 4-methyl-5-vinylthiazole. Attempts to prepare 2-vinylbenzimidazole gave only the corresponding polymer. The polymerization characteristics of the above monomers have been briefly studied.

LAFAYETTE, INDIANA RECEIVED[17] FEBRUARY 17, 1949

[17] Original manuscript received August 25, 1948.

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

The Reaction between Hypochlorite and Bromides[1]

BY L. FARKAS, M. LEWIN AND R. BLOCH

The oxidation of bromide by hypochlorite has been studied by Job and Clarens[2a] and Meillère[2b] who showed that hypobromite was formed.

Experiments carried out in this Laboratory have shown that in the *p*H range of 10 to 14, the over-all reaction can be represented by the equation

$$OCl^- + Br^- = OBr^- + Cl^- \qquad (1)$$

while at lower *p*H values a series of further reactions takes place, in which the hypochlorite and hypobromite are oxidized to bromate and chlorate. The present paper is a report of studies on the rate and mechanism in the *p*H range 10–14, in which the simple equation (1) holds.

Experimental

Dark-colored, glass-stoppered flasks of 300-ml. volume served as reaction vessels. In a typical experiment, 100 ml. of 0.1 *N* sodium hypochlorite, 48 ml. of 0.5 *N* sodium hydroxide and 21 ml. of distilled water were mixed in the vessel and immersed in a thermostat at 25 ± 0.1°. To this mixture 81 ml. of a 1% potassium bromide solution, also at exactly 25°, was added. At certain intervals, samples were withdrawn for analysis. The reaction was brought to a standstill by the addition of alkali. In general, only the hypochlorite and the hypobromite were determined. In certain runs, however, bromide, bromate and chlorate concentrations were also estimated, according to an analytical method described in a previous communication.[3] A brief outline of the analytical procedure is the following: The sum of hypochlorite and hypobromite is estimated by adding to the sample an excess of arsenite which in the presence of bicarbonate reacts with both substances.[4] Then the excess of arsenite is titrated back with iodine solution. The estimation of the hypochlorite is carried out on a parallel sample. First phenol is added which, under suitable conditions, reacts only with hypobromite.[3] The unreacted hypochlorite is then estimated by addition of arsenite and back titration. The difference between the two titrations gives the amount of hypobromite present.

The *p*H values of the solutions were measured with a Cambridge Instrument Co. potentiometer with an accuracy of ±0.02 *p*H unit. As electrode an alki glass electrode was used. The instrument was standardized with borate buffer, the *p*H of which in turn was determined with a hydrogen electrode.

Results

The reaction between hypochlorite and bromide was investigated in the concentration range of 0.003–0.5 *M*. Table I gives the data of a typical experiment.

TABLE I

a = 0.003230 *M* sodium hypochlorite; b = 0.002508 *M* potassium bromide; temperature 25°; *p*H 11.28

Time in minutes	Mole/liter × 10²	k_{exp} liter/mole min.
0.0	0.0	0.0
3.65	.0560	23.42
7.65	.0953	23.30
15.05	.1420	23.52
26.00	.1800	23.90
47.60	.2117	23.80
90.60	.2367	23.80
600.00	.2501	...

The values of k_{exp} in the tables were calculated according to the equation

$$dx/dt = k_{exp}(a - x)(b - x) \qquad (2)$$

where $(a - x)$ is the total hypochlorite concentration $(OCl^-) + (HOCl)$ as found by the titration and $(b - x)$ the bromide concentration. The reaction is of second order and proportional to the concentration of bromide and hypochlorite.

A number of tests showed that the bromide is quantitatively oxidized to hypobromite and no bromate or chlorate is formed. The absence of chlorate was shown by the fact that the sum of hypobromite and hypochlorite remained constant during the course of the experiments. Furthermore, this sum as determined with thiosulfate and potassium iodide in acid solution was identical with that determined according to the arsenite method. No bromate and no chlorite could thus

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[1] This paper is part of a thesis submitted to the Senate of the Hebrew University by M. Lewin, in partial fulfilment of the requirements for the degree of Ph.D.

[2] (a) A. Job and J. Clarens, *J. Pharm. Chim.*, **30**, (VI), 100–101 (1909); (b) G. Meillère, *ibid.*, **30** (VI), 211 (1909).

[3] L. Farkas and M. Lewin, *Anal. Chem.*, **19**, 662 (1947).

[4] Chlorite is not reduced by arsenite under these conditions; *cf.* Chapin, THIS JOURNAL, **56**, 2211 (1934).

be present, since bromate and chlorite are included by the thiosulfate method, but are left out by the arsenite method. The absence of bromate was also proved directly. Bromite, according to Chapin,[4] does not react with phenol in an alkaline solution, and therefore by our method would have been determined together with the hypochlorite. In the presence of excess hypochlorite, the bromide completely disappeared from the solution at the end of the reaction. Therefore no bromite could have been formed, since any of it would have appeared as bromide which had not been oxidized.

TABLE II

DEPENDENCE OF THE RATE OF THE HYPOCHLORITE–BROMIDE REACTION ON THE *p*H

*p*H	$a \times 10^2$ mole/liter	$b \times 10^2$ mole/liter	μ	$k_{exp.}$ lit./mole min.	$k_{exp.}K_{HOCl}/(a_{H^+}) \times 10^{-5}$ lit./mole min.
13.32	3.32	2.81	1.049	0.086	0.56
12.98	3.800	2.690	0.488	0.35	1.09
12.55	3.340	2.710	.318	0.90	1.02
12.43	3.340	2.710	.282	1.15	1.00
12.26	0.910	0.820	.533	1.33	0.78
12.20	0.928	0.8312	.311	1.74	0.88
12.16	0.958	0.814	.511	1.76	0.82
12.09	3.340	2.700	.246	2.61	1.03
11.80	0.924	0.811	.069	6.75	1.36
11.39	0.914	0.817	.147	13.41	1.26
11.28	0.323	0.215	.030	23.62	1.44
10.81	2.210	1.815	.0654	59.04	1.22

Table II summarizes a series of experiments carried out at 25° with various concentrations of reactants and at different *p*H values.[5] Figure 1 shows the dependence of the second order rate constant on the *p*H. It is seen that log k_{exp} plotted against the *p*H gives approximately a straight line. The scattering of the points is not serious in view of the high and varying ionic strength (μ) of the solutions (*cf.* Table II, col. 4).[6]

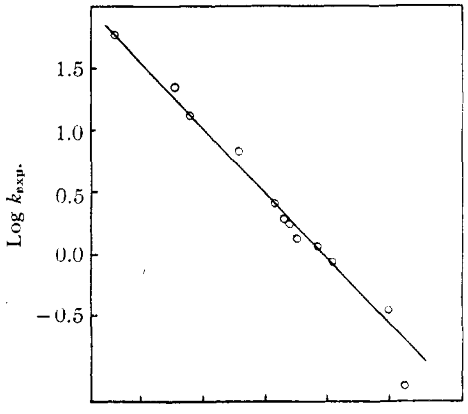

Fig. 1.—Dependence of the rate constant on the *p*H. The ionic strength is not constant.

The temperature dependence of the reaction was investigated at a *p*H which at 25° was 12.98. As shown in Fig. 2, the plots of log $b(a - x)/a(b - x)$ against time indicate a second order reaction over the whole temperature range. The corresponding values of log k_{exp} plotted against $1/T$ lie on a straight line as shown by Fig. 3. From the slope an over-all activation energy of 15 kcal. was calculated.

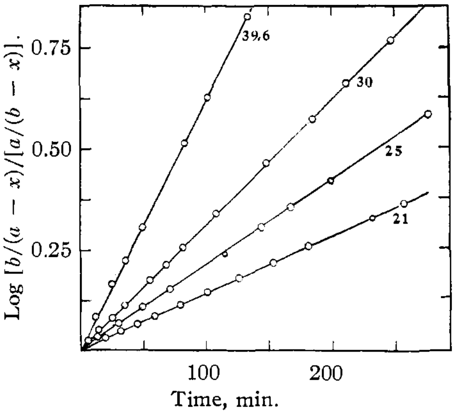

Fig. 2.—Plots of log $b(a - x)/a(b - x)$ against time at various temperatures.

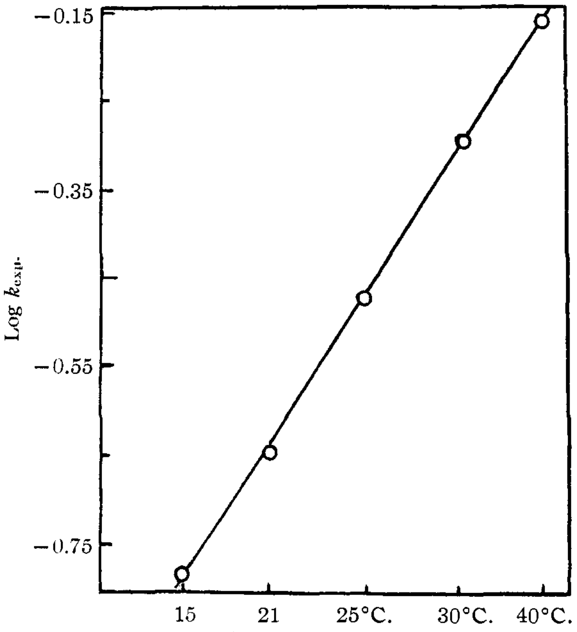

Fig. 3.—Dependence of the rate constant on temperature.

The temperature dependence of k_{exp} is due to two effects: (a) to the increase of the rate constant

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(5) The high rate of reaction at *p*H values below 12 is of importance for the estimation of bromides in a recently developed analytical method; *cf.* Farkas and Lewin, *Anal. Chem.*, **19**, 665 (1947).

(6) In calculating the ionic strength of the solutions, the amount of alkali added to obtain a given *p*H value, the concentration of the reactants and the sodium chloride present in the stock solution of hypochlorite or added to the reaction mixture, were taken into account.

itself with increasing temperature, and (b) to the change of the pH of the solution with the temperature. dpH/dT was determined by measuring the pH of the solution at 15, 25 and 35°. The apparatus was standardized at these temperatures with a borate buffer whose pH change with temperature was known from the literature. The pH readings obtained in the case of hypochlorite-bromide solutions were corrected for the presence of sodium ions according to the calibration curve of the alki glass electrode of the Cambridge Instruments Company. The mean value obtained from a series of measurements was $\mathrm{d}p\mathrm{H}/\mathrm{d}T = -0.033$. Thus the hydrogen ion concentration increases with increasing temperature and this effect accounts for the major part of the acceleration of the reaction with increase in temperature.

Discussion

The proportionality of the reaction rate to the hydrogen ion activity suggests that the rate-determining process in the formation of hypobromite is a reaction between HOCl and bromide ion.

We shall assume the mechanism

$$\mathrm{OCl^- + H_2O \rightleftharpoons HOCl + OH^-} \quad (3)$$

$$\mathrm{HOCl + Br^- \xrightarrow{k_2} HOBr + Cl^-} \quad (4)$$

$$\mathrm{HOBr + OH^- \rightleftharpoons Br^- + H_2O} \quad (5)$$

$$\mathrm{OCl^- + Br^- \xrightarrow{k_{exp.}} BrO^- + Cl^-}$$

The hydrolytic equilibria (3) and (5) are evidently rapid processes, so that reaction (4) is the rate-determining step. From the above set of reactions the decrease of the total hypochlorite $(a - x) = (\mathrm{OCl^-}) + (\mathrm{HOCl})$ is given by

$$-\frac{\mathrm{d}(a-x)}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t} = k_2(\mathrm{HOCl}) \times (\mathrm{Br^-}) \quad (6)$$

The concentration of HOCl is given by the expression

$$(\mathrm{HOCl}) = \frac{(a_{\mathrm{H^+}}) \times f_{\mathrm{ClO^-}}}{(a_{\mathrm{H^+}}) + K_{\mathrm{HOCl}}} \times (a - x) \quad (7)$$

where (a_{H^+}) is the activity of the hydrogen ion, $f_{\mathrm{ClO^-}}$ the activity coefficient of $\mathrm{OCl^-}$ and K_{HOCl} the thermodynamic dissociation constant of hypochlorous acid. (7) inserted into (6) gives

$$\mathrm{d}x/\mathrm{d}t = k_2\frac{(a_{\mathrm{H^+}})f_{\mathrm{OCl^-}}}{(a_{\mathrm{H^+}}) + K_{\mathrm{HOCl}}}(a - x)(b - x) \quad (8)$$

Since at 25° $K_{\mathrm{HOCl}} = 3.2 \times 10^{-8}$,[7–9] $(a_{\mathrm{H^+}})$ may be neglected against K_{HOCl} in the pH range 10–14. The comparison of equation (8) with equation (2) shows that

$$k_{\mathrm{exp.}} = k_2 f_{\mathrm{OCl^-}}(a_{\mathrm{H^+}})/K_{\mathrm{HOCl}} \quad (9)$$

Column 6 of Table II shows that the expression $k_{\mathrm{exp}}K_{\mathrm{HOCl}}/(a_{\mathrm{H^+}})$ varies within comparatively close limits.

In Fig. 4 log $(k_{\mathrm{exp}}K_{\mathrm{HOCl}}) - p\mathrm{H}$ has been plotted against $\sqrt{\mu}$. It is seen that most of the points are on a line which at zero ionic strength gives $k_2 = 1.77 \times 10^5$ liter/mole min. This extrapolation is of course arbitrary and probably the linear relationship between log $(k_{\mathrm{exp}}K_{\mathrm{HOCl}}) - p\mathrm{H}$ and $\sqrt{\mu}$ is fortuitous, since it cannot be justified theoretically.

The heat of activation of reaction (4) can be estimated from the over-all dependence of k_{exp} by taking into account the change of K_{HOCl}[7–9] with the temperature and the experimentally found value for dpH/dT. The calculation yields a temperature dependence of k_2 which corresponds to an activation energy of about 4.5 kcal. However, this value of the activation energy is uncertain, since the inaccuracy in dpH/dT and in dK_{HOCl}/dT introduces a large error into its evaluation.

For the entropy of activation of reaction (4) we obtain from the theoretical formula

$$k = \frac{\kappa T}{h}\, e\, e^{-\Delta H^{\ddagger}/RT} e^{-\Delta S^{\ddagger}/R} \quad (10)$$

$\Delta S^{\ddagger} = -14$ E.U. per mole.[10] This large negative value of the entropy of activation is unexpected, since bimolecular processes of the type of reaction (4), which take place between an ion and a polar molecule, generally have larger entropy factors than 10^{-3}. This, too, seems to indicate that the true value for the activation energy is somewhat higher than 4.5 kcal.

A mechanism similar to the above was assumed in the reaction between phenol and hypochlorite[11] in which the rate-determining step is a reaction between HOCl molecules and a phenoxide ion.

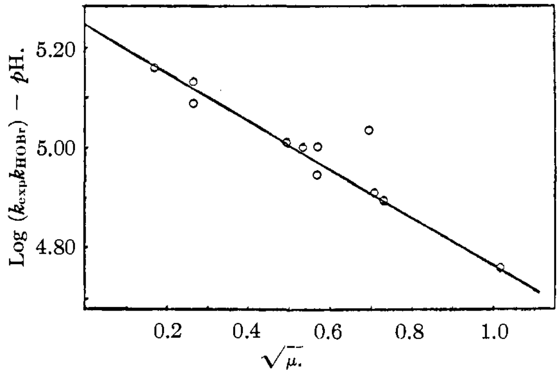

Fig. 4.—Extrapolation of the rate constant at zero ionic strength.

Acknowledgment.—One of the authors (M. L.) is indebted to Palestine Potash, Ltd., Jerusalem; Lodzia Textile Co., Ltd., Tel Aviv; and Ata Textile Co., Ltd., Haifa, for a grant which enabled him to carry out this investigation.

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(7) Ingham and Morrison, *J. Chem. Soc.*, 1200 (1933).

(8) Shilow and Gladtchikova, THIS JOURNAL, **60**, 490 (1938).

(9) Hagisawa, *Bull. Inst. Phys. Chem. Research* (*Tokio*), **19**, 1220 (1940).

(10) From thermochemical data it is found that $\Delta F°$ of reaction (4) is −7.52 kcal., and the heat of reaction approximately 8.2 kcal. These figures lead to a total change of entropy of reaction (4) of about −2.2 E. U. per mole.

(11) F. G. Soper and G. F. Smith, *J. Chem. Soc.*, 1582 (1926).

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.