Summary

Infrared methods have been used in determining 1,2- and *trans*-1,4-addition in polybutadiene polymerized in the temperature range −19 to 97° and butadiene–styrene copolymers prepared at −18, 5 and 50°. *trans*-1,4-Addition increases and 1,2-addition decreases with decreasing temperature of polymerization. At −19°, substantially all of the 1,4-addition product is present in the *trans*-1,4-form. Approximately 20% 1,2-addition occurs at this temperature and is concluded to account for the major part of the non-crystallizable portion of polymers made at low temperatures. The influence of styrene on 1,2- and *trans*-1,4-addition in butadiene–styrene copolymers is also discussed. Free energy, heat and entropy of activation are calculated for 1,4- *vs.* 1,2-addition and *trans*-1,4- *vs.* *cis*-1,4-addition in the polymerization process.

PASSAIC, NEW JERSEY RECEIVED SEPTEMBER 23, 1948

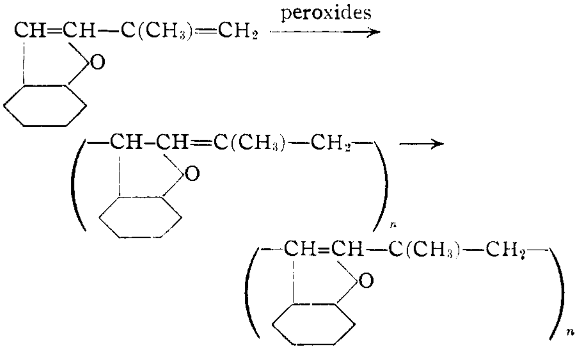
[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Monomers and Polymers. VI. The Preparation of Vinyl Derivatives of Five-atom Heterocyclic Rings[1,2]

BY G. BRYANT BACHMAN AND LOWELL V. HEISEY[3]

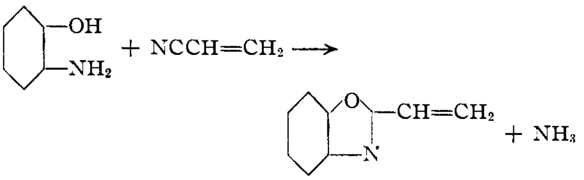
The preparation and polymerization of vinyl heterocyclic compounds of the thiophene[2c] and pyridine[2d] series have already been reported from this Laboratory. The present paper extends these studies to vinyl derivatives of other five-atom heterocyclic rings particularly in the furan and azole series.

2-Isopropenylfuran,[4] 2-isopropenyl-5-isopropylfuran and 2-isopropenylbenzofuran were prepared by dehydrating the tertiary alcohols obtained from the corresponding carboxylic acid esters and methylmagnesium halides. The dehydrations in the first two cases were very unsatisfactory with most dehydrating catalysts because of ring cleavages, but proceeded well (50–55% yields) on refluxing with sodium acetate and acetic anhydride. The dehydration of 2-(2′-hydroxy-2′-propyl)-benzofuran proceeded spontaneously on vacuum distillation to give the desired 2-isopropenylbenzofuran. The last compound is interesting because of its ability to polymerize alone with peroxide catalysts. It was pointed out previously[2b] that isopropenylbenzenes do not polymerize alone with peroxide catalysts, and in keeping with this 2-isopropenylfuran and 2-isopropenyl-5-isopropylfuran also do not polymerize alone with peroxide catalysts. 2-Isopropenylbenzofuran, however, is structurally related to coumarone which polymerizes by virtue of the active double bond of the furan ring. The isopropenyl compound probably behaves like a typical diene which accounts for its unusual ease of polymerization in the absence of comonomers.



All three of these vinylfurans copolymerized with butadiene to give rubbers.

A number of attempts were made to prepare vinyl derivatives of heterocyclic systems by condensing *o*-difunctional benzenes with vinyl compounds. 2-Vinylbenzoxazole was prepared in this manner from *o*-aminophenol and acrylonitrile or acrylic acid.



The yields were poor (14%); and other combinations were totally unsuccessful. Crotonic acid and *o*-aminophenol gave 2-methylbenzoxazole, a curious reaction first observed by Doeller.[5] Acrylic acid and *o*-phenylenediamine apparently gave a seven-atom ring compound (2-oxo-2,3,4,5-tetrahydro-1,5-benzodiazepine) instead of the desired 2-vinylbenzimidazole.

Preparations of 2-vinylbenzimidazole by other methods invariably led to polymers of this substance indicating its great readiness to polymerize. A group of substituted 2-ethylbenzimidazoles

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[1] From the Ph.D. thesis of L. V. Heisey, Purdue University, June, 1947. Read before the Organic Division at the St. Louis meeting of the American Chemical Society, September, 1948.

[2] For previous papers in this series see Bachman, *et al.*, THIS JOURNAL, (a) **69**, 2022 (1947); (b) **70**, 622 (1948); (c) **70**, 1772 (1948); (d) **70**, 2378 (1948); (e) **70**, 2381 (1948).

[3] Present address: McPherson College, McPherson, Kansas.

[4] Reichstein, Zschokke, Gehrig and Rona, *Helv. Chim. Acta*, **15**, 1118 (1932).

[5] Doeller, *Ber.*, **72B**, 2148 (1939).

(including 1′-chloro-, 1′-acetoxy-, 2′-ethoxy-, 2′-chloro-, 2′-bromo- and 2′-hydroxy-) was prepared and treated in such a way as to yield the corresponding vinyl compound. Only polymers could be isolated although inhibitors were employed. Similar results were obtained from attempts made to prepare 2-isopropenylbenzimidazole.

A series of interesting intermediates was obtained from α-acetylbutyrolactone which is now commercially available. The previously reported[6] synthesis of 4-methyl-5-vinylthiazole was simplified and a large quantity of the vinyl compound was prepared. Its polymerization behavior was very disappointing. On long standing a viscous oil was obtained, but no hard homopolymer nor satisfactory copolymers (except with maleic anhydride) could be prepared. Other syntheses from α-acetobutyrolactone led to new heterocyclic compounds, but these could not be converted to the corresponding vinyl compounds. Decarboxylation followed by reaction with nitrous acid gave the 3-oxime of 5-hydroxy-2,3-pentanedione. This was treated with phenylhydrazine and then acetic anhydride to obtain the 2-phenylhydrazone-3-O-acetoxime of the diketone. Conversion of this product to 5-β-hydroxyethyl-4-methyl-2-phenyl-1,2,3-triazole by the method of Pechmann[14] was unsuccessful. α-Acetobutyrolactone reacted with hydrazine to give 3-methyl-4-(2′-hydroxyethyl)-5-pyrazolone. All attempts to dehydrate this compound to 3-methyl-4-vinyl-5-pyrazolone gave tars. α-Acetobutyrolactone was converted to 3-chloro-4-hydroxy-2-pentanone by the method of Buchman.[12] Treatment of this product with formamide gave tars but no 4-methyl-5-(2′-hydroxyethyl)-oxazole, although this type of synthesis has been applied successfully to the preparation of other oxazoles.

The new compounds 3-ethyl-1,2,4-triazole and 3-(2′-ethoxyethyl)-5-amino-1,2,4-triazole were obtained as intermediates in the synthesis of a vinyltriazole which was not completed.

Acknowledgment.—The authors are indebted to the General Tire and Rubber Company for financial support in the form of a fellowship.

Experimental

2-Isopropenylfuran.[4]—2-(2′-Hydroxy-2′-propyl)-furan[4] b. p. 161–163° (atm. press.), 71–72° (15 mm.), m. p. 10–11°, $n^{25}\mathrm{D}$ 1.4700, d^{25}_{25} 1.037, was dehydrated by refluxing with molar amounts of acetic anhydride and half-molar amounts of sodium acetate for half an hour; yield 56%, b. p. 125–126° (atm. press.), 56–57° (75 mm.), $n^{25}\mathrm{D}$ 1.4966, d^{25}_{25} 0.9445.

2-Isopropenyl-5-isopropylfuran.—Methyl 5-isopropyl-2-furoate[7] was treated with two molar quantities of methylmagnesium bromide to obtain a 90% yield of 2-(2′-hydroxy-2′-propyl)-5-isopropylfuran, b. p. 84–86° (2 mm.), $n^{25}\mathrm{D}$ 1.4669, d^{25}_{25} 0.9395. Dehydration as above gave a 53% yield of 2-isopropenyl-5-isopropylfuran, b. p. 66–68° (10 mm.), $n^{25}\mathrm{D}$ 1.4890, d^{25}_{25} 0.9020.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.98; H, 9.39. Found: C, 79.93, 80.05; H, 9.22, 9.32.

2-Isopropenylbenzofuran.—Ethyl 2-benzofurancarboxylate[8] reacted with methylmagnesium bromide to give a 54% yield of 2-isopropenylbenzofuran, b. p. 76–77° (2 mm.), m. p. 24°, $n^{25}\mathrm{D}$ 1.5998, d^{25}_{25} 1.0550.

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.25, 83.40; H, 6.10, 6.15.

2-Vinylbenzoxazole.—Equimolar quantities of *o*-aminophenol and acrylonitrile were refluxed with a little trinitrobenzene (inhibitor) for several hours and then distilled. The fraction boiling at 125–236° was extracted with hexane, the hexane was washed with dilute alkali, dried and distilled. A 14% yield of 2-vinylbenzoxazole was obtained, b. p. 60–61° (1 mm.), m. p. −16°, $n^{25}\mathrm{D}$ 1.5581, d^{25}_{25} 1.116.

Anal. Calcd. for C_9H_7NO: N, 9.65. Found: N, 10.02. 10.09.

Acrylic acid in place of the nitrile gave an 11% yield. Crotonic acid gave 2-methylbenzoxazole.[5]

2-Vinylbenzimidazole Preparations

2-Oxo-2,3,4,5-tetrahydro-1,5-benzodiazepine.—A mixture of 53 g. (0.5 mole) of *o*-phenylenediamine, 90 g. (0.75 mole) of 60% aqueous acrylic acid, and 40 ml. of concd. hydrochloric acid was heated three hours on a steam cone, cooled, basified with concd. ammonium hydroxide, and filtered. The tan crystals were recrystallized from carbon tetrachloride; yield 67% of white needles, m. p. 140.5–141.5°, soluble in water, dioxane, chloroform and ethanol, less soluble in benzene and carbon tetrachloride, insoluble in ether and hexane. They showed no tendency to polymerize.

Anal. Calcd. for $C_9H_{10}N_2O$: C, 66.65; H, 6.21; N, 17.28. Found: C, 66.70, 66.92; H, 6.20, 6.30; N, 17.31.

2-(1′-Chloroethyl)-benzimidazole.[9]—2-(1′-Hydroxyethyl)-benzimidazole[9] with 4 mole equivalents of thionyl chloride gave an 83% yield of the desired product, m. p. 133°. Attempted dehydrohalogenation with 5% aqueous sodium hydroxide or 20% methanolic potassium hydroxide gave only water-insoluble polymer.

2-(1′-Acetoxy)-benzimidazole.—2-(1′-Hydroxyethyl)-benzimidazole[9] was acetylated in quantitative yield by treatment with sodium acetate and acetic anhydride; m. p. 152–153° from water.

Anal. Calcd. for $C_9H_{12}O_2N_2$: C, 64.69; H, 5.92. Found: C, 64.72, 64.79; H, 5.90, 5.96.

Refluxing this acetate or the corresponding alcohol with phosphorus pentoxide in benzene for eight hours gave no change, and both also distilled unchanged at atmospheric pressure. No definite compounds could be isolated after passage through a hot tube at 500°, or through a tube packed with activated alumina at 300°.

2-(2′-Ethoxyethyl)-benzimidazole.—A mixture of *o*-phenylenediamine, 54 g., ethyl 3-ethoxypropionate, 76 g., and 4 *N* hydrochloric acid, 185 ml., was refluxed for four hours, cooled, neutralized, filtered and the precipitated product recrystallized from water (Norite); yield 74 g. (82%) of colorless plates, m. p. 156.5–157.0°.

Anal. Calcd. for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.41. Found: C, 69.31, 69.45; H, 7.31, 7.42.

2-(2′-Chloroethyl)-benzimidazole.—The above ether, 4 g., was heated with 34 ml. of concd. hydrochloric acid at 150° in a sealed tube for five hours. Neutralization of the cooled reaction mixture with ammonium hydroxide and recrystallization of the precipitate from water gave 1 g. (26%) of white needles. m. p. 88.5–89.0°.

Anal. Calcd. for $C_9H_9N_2Cl$: N, 15.51. Found: N, 15.80, 15.88.

This 2′-chloroethyl derivative spontaneously dehydrohalogenated on standing at room temperature longer than twenty-four hours, or on being boiled in water or dilute sodium hydroxide, giving mainly insoluble polymeric material.

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(6) Buchman and Richardson, THIS JOURNAL, **67**, 395 (1945).

(7) Gilman and Calloway, *ibid.*, **55**, 4198 (1933).

(8) Fuson, Kneisley and Kaiser, "Organic Syntheses," Vol. 24, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 33.

(9) Skolnik, Miller and Day, THIS JOURNAL, **65**, 1854 (1943).

2-(2′-Bromoethyl)-benzimidazole.—Repetition of the above procedure using 50 ml. of 48% hydrobromic acid instead of hydrochloric acid gave 2.7 g. (57%) of white powder, m. p. 227–229° (dec.).

Anal. Calcd. for $C_9H_9N_2Br$: N, 12.45. Found: N, 12.42, 12.60.

This 2′-bromoethyl derivative dehydrohalogenates more readily than the corresponding chloro-derivative, giving polymeric material.

2-(2′-Hydroxyethyl)-benzimidazole.—*o*-Phenylenediamine, 21 g. (0.2 mole), and 18 g. (0.25 mole) of 3-hydroxypropionitrile dissolved in 48 ml. of water containing 48 ml. (0.2 mole) of concd. hydrochloric acid were refluxed for five hours. Neutralization with ammonia at ice-bath temperatures gave a brown powder which upon recrystallization from water (Norite) gave 19 g. (59% yield) of shining platelets, m. p. 153.5–154.5°.

Anal. Calcd. for $C_9H_{10}N_2O$: N, 17.27. Found: N, 17.18, 17.41.

This alcohol dehydrates when heated above its m. p. and forms a clear, brittle, amber-colored plastic.

Poly-2-vinylbenzimidazole.[10]—The polymeric materials from the spontaneous dehydrohalogenations of the (A) 2′-chloroethyl- and (B) 2′-bromoethylbenzimidazoles were boiled in 5% sodium hydroxide to remove the acids, then repeatedly boiled in water to remove low molecular weight materials. The insoluble material formed a brittle plastic upon drying.

Anal. Calcd. for $C_9H_8N_2$: N, 19.44. Found: N, (A) 19.19, (B) 18.96.

2-(2′-Hydroxy-2′-propyl)-benzimidazole.[9]—This compound was prepared in greatly improved yields by a different method from that previously reported.[9] *o*-Phenylenediamine (5.4 g.) and ethyl α-hydroxyisobutyrate (6 g.) were mixed with 6.6 ml. of concd. hydrochloric acid and 12 ml. of water and refluxed for nine hours. After neutralization of the reaction mixture with concd. ammonium hydroxide, the precipitated product was isolated by filtration. Charcoal decolorization and recrystallization from dilute alcohol gave 8.2 g. (93.3% yield) of 2-(2′-hydroxyisopropyl)-benzimidazole, m. p. 226–227.5°, as white shining crystal platelets.

Distillation of this alcohol at atmospheric pressure gave a 57% yield of benzimidazole but none of the corresponding isopropenylbenzimidazole. Dehydration by heating with potassium bisulfate gave only polymeric material. Treatment of the alcohol with thionyl chloride gave 2-(2′-chloro-2′-propyl)-benzimidazole.[9] This compound reacted with bases to regenerate the original alcohol or to form tars.

Attempts to Prepare 2-Isopropenylbenzimidazole.—In addition to the experiments described above, an unsuccessful attempt was made to prepare this olefin by direct condensation of *o*-aminophenol with methyl and ethyl methacrylates. No reaction occurred at reflux temperatures.

Compounds from α-Acetylbutyrolactone. 4-Methyl-5-vinylthiazole.[6]—4-Methyl-5-(2′-hydroxyethyl)-thiazole was distilled slowly from 25% by weight of potassium hydroxide at 30 mm. pressure and 155°. The product on rectification was a colorless liquid, b. p. 66° (10 mm.), m. p. −15°, $n^{25}\text{D}$ 1.5621, d^{25}_{25} 1.093, yield 41%.

Attempted Preparation of 4-Methyl-5-(2′-hydroxyethyl)-oxazole.—The oxazole synthesis of Lewy[11] was employed. α-Acetylbutyrolactone was converted by chlorination, hydrolysis, and decarboxylation to 3-chloro-5-hydroxy-2-pentanone following the directions of Buchman.[12] This compound (0.5 mole) was heated with formamide (0.75 mole) and calcium carbonate (0.25) at 125° for five hours. Starting materials and tar only were recovered.

3-Methyl-4-(2′-hydroxyethyl)-5-pyrazolone.—Slow addition of 46 g. (0.4 mole) of 42% aqueous hydrazine hydrate to 50 g. (0.4 mole) of α-acetylbutyrolactone followed by cooling gave colorless rhombic crystals of the desired pyrazolone, m. p. 182.5–183° (from water); yield 38 g. (66%).

Anal. Calcd. for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09. Found: C, 50.49, 50.63; H, 7.09, 7.13.

Dehydration attempts on this pyrazolone alcohol made by distilling with solid potassium hydroxide or with solid disodium hydrogen phosphate led to complete decomposition. The compound distilled with some decomposition alone or in the presence of alumina.

4-Phenylhydrazo-3-oximinopentanol Acetate.—3-Oximinopentanol[13] was prepared from 185 g. (1.8 moles) of 5-hydroxy-2-pentanone, 145 g. of butyl nitrite and 4 ml. of concd. hydrochloric acid. The solution was made basic with 100 ml. of 40% sodium hydroxide in an equal weight of ice, and the impurities were extracted with ether. The solution was adjusted to *p*H 6.5 and extracted continuously with ether for five hours. The vacuum-concentrated, partly crystalline, ethereal extract of the oxime (93 g. 0.71 mole) was mixed with 100.5 g. (0.74 mole) of phenylhydrazine, causing the crystals to dissolve. In one-half hour 450 ml. of acetic anhydride was added with stirring, keeping the temperature below 80°. In one-half hour the resulting solution was poured into 2 liters of ice-water, giving 182 g. (97% yield based upon the oxime) of tan crystals of the acetate of 4-phenylhydrazo-3-oximinopentanol. Recrystallization from dilute ethanol (Norite) gave the pure compound as light yellow needle-shaped crystals, m. p. 144.5–145°.

Anal. Calcd. for $C_{13}H_{17}N_3O_3$: N, 15.96. Found: N, 15.70.

Attempted deacetylation of the pyrazolone acetate by the procedure of Pechmann[14] gave none of the desired triazole.

3-Ethyl-1,2,4-triazole.—3-Ethyl-5-amino-1,2,4-triazole,[15] 5 g. (0.045 mole), was diazotized in sulfuric acid, 130 ml., and acetic acid, 200 ml., and treated with 78 ml. (0.75 mole) of cold 50% hypophosphorus acid. The mixture was maintained for twenty-four hours at ice temperatures, adjusted to *p*H 8 with alkali, filtered, and extracted continuously with ether. The ether solution yielded 2.0 g. (45%) of the white hygroscopic triazole, m. p. 61–62°.

Anal. Calcd. for $C_4H_7N_3$: N, 43.27. Found: N, 43.50, 43.65.

When the above experiment was repeated using hydrochloric acid, 160 ml., in place of sulfuric and acetic acids, reduction of the diazonium salt did not occur and the product was 5-chloro-3-ethyl-1,2,4-triazole.[16]

3-(2′-Ethoxyethyl)-5-amino-1,2,4-triazole.—A mixture of 14 g. (0.1 mole) of ethyl 3-ethoxypropionate, 15 g. (0.11 mole) of aminoguanidine bicarbonate, and 18 g. (0.11 mole) of 48% hydrobromic acid was heated and refluxed for fourteen hours, cooled, adjusted to *p*H 7 with alkali, evaporated to dryness under vacuum, and the residue extracted with acetone. The extract yielded 11 g. (70%) of hygroscopic white crystals, m. p. 132–133°. Analytical samples were purified by sublimation at 2 mm.

Anal. Calcd. for $C_6H_{12}N_4O$: N, 35.88. Found: N, 35.72, 35.80.

Polymerization Experiments.—Small samples of the vinyl compounds described were heated to 70° alone and with styrene, methyl methacrylate, vinyl acetate or maleic anhydride in 3-inch test-tubes and in the presence of about 0.5% benzoyl peroxide. Solid homopolymers were obtained from 2-isopropenylbenzofuran only. Good, hard copolymers were obtained with 2-vinylbenzoxazole and methyl methacrylate or styrene and with 2-isopropenyl-5-isopropylfuran and methyl methacrylate. Maleic anhydride gave hard copolymers with each of the vinyl compounds prepared. Other copolymers either did not form or were sticky and oily.

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(10) Ahmed, *et al.*, *J. Indian Chem. Soc.*, **15**, 152 (1938); *C. A.*, **32**, 7040 (1938).

(11) Lewy, *Ber.*, **20**, 2576 (1887).

(12) Buchman, THIS JOURNAL, **58**, 1803 (1936).

(13) Fox, Sargent and Buchman, *ibid.*, **67**, 496 (1945).

(14) Pechmann, *Ann.*, **262**, 265 (1891).

(15) Reilly and Madden, *J. Chem. Soc.*, 816 (1929).

(16) Bachman and Heisey, THIS JOURNAL, **68**, 2496, footnote 13 (1946).

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

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[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).