trast to simple acids and bases, act independently of other catalytic species in the solution, and hence *via* a bimolecular rather than a termolecular transition state species. In the table, it is attempted to show as much comparability as possible between different catalysts and different solvents; but, it should be realized that usually only k or kK, not both, can be determined with certainty, and rather rough estimates of equilibrium constants must be used in calculating the other. It is difficult to say with certainty which constant, k or kK, represents the more fundamental measure of catalytic activity.

A typical kinetic run is given in Table VIII.

TABLE VIII

RUN 28. MUTAROTATION OF 0.0929 M TETRAMETHYLGLUCOSE WITH 0.0496 M 2-HYDROXYPYRIDINE IN BENZENE AT 25°

Time, min.	Rotation, deg.	$k_1 \times 10^6$, sec.$^{-1}$
0.00	6.20	..
3.33	5.65	2160
3.93	5.57	2180
4.43	5.51	2190
4.98	5.47	2100
5.60	5.40	2130
6.32	5.34	2110
7.00	5.28	2110
7.72	5.22	2130
8.40	5.17	2130
9.07	5.13	2120
9.67	5.10	2100
10.47	5.04	2150
11.30	5.00	2150
11.98	4.97	2150
12.75	4.945	2120
13.87	4.90	2130
136	4.635	..

Average: 2130 ± 25 × 10^{-6} sec.$^{-1}$

CAMBRIDGE, MASS. RECEIVED JULY 27, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. IV. Some Properties of the Polymers[1]

BY GEORGE B. BUTLER, ROBERT L. BUNCH AND FRANCIS L. INGLEY

It has been shown by titration that the polymers obtained by polymerization of unsaturated quaternary ammonium salts function as strongly basic ion exchange resins. Titration curves resemble a typical strong base–strong acid titration curve. Under certain polymerization conditions, the polymers showed a small amine capacity as the result of thermal decomposition of the quaternary ammonium salt. The hydroxide form of the polymers decomposes by a Hofmann degradation when heated. Polymers prepared by polymerization at low temperatures show decreased swelling coefficients and correspondingly decreased capacities, probably as the result of screening. Polymers prepared by suspension polymerization show an increase in capacity with decreasing swelling coefficient. A comparison of the rate of exchange of the chloride ion by the hydroxyl ion and the reverse exchange was made, showing that hydroxyl ions were replaced more rapidly than chloride ions under the conditions of the experiment.

Previous work[2-4] has shown that certain unsaturated quaternary ammonium salts will undergo polymerization in presence of peroxide catalysts to produce water-insoluble polymers suitable for strongly basic ion exchange resins. The ion exchange reactions of these polymers were demonstrated as indicated

$$n\mathrm{R_4NBr} \xrightarrow[\text{hydroperoxide}]{t\text{-butyl}} (\mathrm{R_4NBr})_n$$

R groups may be equal or different. At least two groups are unsaturated.	Cross-linked, water insoluble polymer washed free of soluble bromides.

$$(\mathrm{R_4NBr})_n + n\mathrm{KOH} \longrightarrow (\mathrm{R_4NOH})_n + n\mathrm{KBr}$$

Continued until no halogen present in filtrate. Resin washed until neutral filtrate obtained.

$$(\mathrm{R_4NOH})_n + n\mathrm{KCl} \longrightarrow (\mathrm{R_4NCl})_n + n\mathrm{KOH}$$

Filtrate was very strongly basic.

Since polymers have been prepared from a number of compounds and under a variety of conditions, the properties of these polymers have varied considerably. This paper summarizes the more pertinent results obtained in our exploratory study of these polymers, and compares the properties of polymers obtained under the different conditions.

Experimental

Preparation of Materials.—The polymers studied in this work were prepared by the procedures previously described,[2-4] or as outlined in detail in this section.

Determination of Ion Exchange Capacities.—The method employed for determination of capacities of resins studied in this work involved titration of a known quantity of the hydroxyl form of the resin with standard acid.[5] The resin as prepared in the halide form was washed free of soluble material and dried. It was then ground to uniform particle size, usually in the range of 40-mesh. A known weight of the resin was placed in a 2 × 40 cm. column with a 50-mesh metal screen sealed 4 cm. from the bottom. An overflow tube was passed up from the bottom of the column in an elongated "S" curve so that the exit end was always above the top of the resin bed. This overflow tube was used in order to keep the liquid level above the resin at all times, since the hydroxyl form of the resin is unstable when dry. Normal sodium hydroxide was added through a one-liter addition funnel securely stoppered in the top of the column. Passage of the sodium hydroxide solution was continued until the effluent contained less than ten parts per million of halide ion. The value of ten parts per million was selected arbitrarily since the concentration of halide ion in the effluent approaches zero asymptotically.

After conversion was complete, the resin was washed free of excess base by passing distilled water through the column until the effluent no longer gave a color change with phenolphthalein. The wet resin was then removed from the column and stored under water until used.

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[1] This paper was presented before the Symposium on Preparation of Ion Exchange Materials at the Diamond Jubilee Meeting of the American Chemical Society, New York, September, 1951. Most of this work was done under the sponsorship of the Office of Naval Research under Contract No. N7-onr-346.

[2] G. B. Butler and R. L. Bunch, THIS JOURNAL, **71**, 3120 (1949).

[3] G. B. Butler and F. L. Ingley, *ibid.*, **73**, 895 (1951).

[4] G. B. Butler and R. L. Goette, *ibid.*, **73**, 1939 (1951).

[5] Private communication from the National Aluminate Corporation, Chicago, Illinois.

The converted resin was allowed to settle until no further volume change occurred, and a standard volume was then removed. All titration curves are based on use of a standard volume of 22 ml. of wet resin in the hydroxide form. The sample was placed in a 400-ml. beaker equipped with a mechanical stirrer, a Beckman 4990 glass electrode and a Beckman 4970 calomel electrode. Potassium chloride solution of known concentration was added so that an initial chloride ion concentration of 0.01 *N* was obtained, unless otherwise specified. The resin was titrated with 1 *N* hydrochloric acid, using a Beckman Model H-2 *p*H meter. The acid was added in increments of one ml. at 3-minute intervals. The *p*H of the solution was determined just prior to each addition of acid. The capacity of the resin in milliequivalents per ml. was computed by dividing the number of millimoles of acid required to give the titration break by the volume of wet resin used. The capacity was also computed in milliequivalents per gram of the dry halide form in some cases. The amine capacities of the resins were determined from the volume of standard acid required to give the second break in the *p*H curve as shown in curves A and B of Fig. 1. Such a break did not appear in some of the titrations. The capacities of a number of polymers and copolymers are shown in Table I.

TABLE I

CAPACITIES OF RESINS

Polymer or copolymer, bromide	Amine capacity meq./ml.	Quaternary cap. meq./ml.
Tetraallylammonium[a]	0.12	0.32
Tetraallylammonium[b]	.084	.40
Triallylbutylammonium	...	.15
Hexaallylethylenediammonium[c]	.11	.25
Hexaallylethylenediammonium[d]	...	.29
Triallylbutylammonium and tetraallylammonium	...	.25
Diallylmorpholinium and tetrallylammonium	...	.27
Diallylpiperidinium and tetraallylammonium	...	.26

[a] Polymerized in formamide at 70°. [b] Polymerized in water at 70°. [c] Polymerized at 75°. [d] Polymerized at 70°.

Effect of Coefficient of Swelling on Ion Exchange Capacity.—The resins on which this study was based were prepared by polymerization of the monomers by the procedure which has been previously described.[3] Poly-2-vinyloxyethyl-triallylammonium bromide was prepared at 60° while the other polymers were prepared at 30°. The coefficient of swelling, defined as the ratio of the settled wet volume of the resin to the dry volume, was determined by measuring the volume of a known quantity of the dry resin, then adding distilled water sufficient to cover the resin, and measuring the volume of the wet resin after no further change in volume occurred. Capacities of these resins were determined as previously described. The results of this study are recorded in Table II.

TABLE II

EFFECT OF COEFFICIENT OF SWELLING ON ION EXCHANGE CAPACITY

Monomer, ammonium bromide	Swelling coefficient	Yield, %	Wt. resin per ml., wet	Capacity meq./ml.	Capacity meq./g.	% of theor. capacity
2-Vinyloxyethyltriallyl-	5.08	53.8	0.10	0.308	3.08	88.8
Triallyl-2-chloroallyl-	1.83	43.0	.195	.405	2.08	61.0
Tetraallyl-	1.17	65.5	.289	.450	1.56	40.2

Effect of Temperature of Polymerization on Capacity of Polymer.—The resins on which this study was based were prepared by the previously described method[3] at 65° for 24 hours, at 40° for 36 hours, at 30° for 7 days, and at 23° for 14 days. Capacities, yields and swelling coefficients were determined by the methods previously described. Theoretical capacities were based upon the assumption that the resin had the same percentage composition as the monomer in those cases in which the titration showed no amine capacity as the result of decomposition. This assumption was substantiated by analysis in several instances. A few typical nitrogen determinations by the Kjeldahl method are recorded in Table III. The results of this study are recorded in Figs. 1, 2 and 3, and Table IV.

TABLE III

NITROGEN CONTENT OF TYPICAL POLYMERS BY KJELDAHL METHOD

Polymer	Temp. of polym.	Nitrogen, % Theor.	Nitrogen, % Found
Polytetraallylammonium bromide	30	5.44	5.33
Polytetraallylammonium chloride	65	6.55	6.48
Polytetraallylammonium bromide	65	5.44	5.45
Polytetraallylammonium bromide	65	5.44	5.46

Suspension Polymerization.—Ten grams of tetraallylammonium bromide, 5 g. of water and 50 ml. of ethylben-

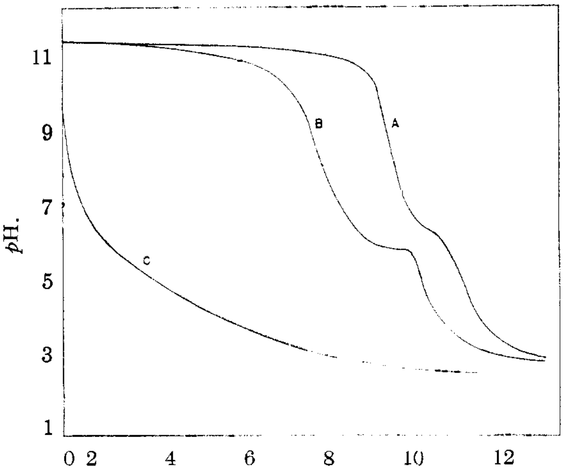

Fig. 1.—Effect of solvent on capacity of polymer, and effect of heat on hydroxide form: A, tetraallylammonium bromide polymerized in water at 70°; B, tetraallylammonium bromide polymerized in formamide at 70°; C, polymer A dried in hydroxide form before titration.

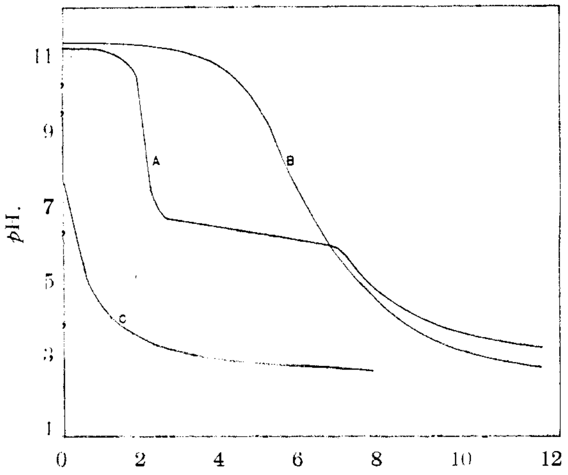

Fig. 2.—Effect of temperature of polymerization on capacity of polymer, and effect of heat on hydroxide form: A, hexaallylyethylene diammonium dibromide polymerized at 75°; B, same monomer polymerized at 70°; C, polymer A dried in hydroxide form at 103° before titration.

TABLE IV

EFFECT OF TEMPERATURE OF BULK POLYMERIZATION ON CAPACITIES OF POLYMERS

Monomer, bromide	Temp., °C.	Swelling coefficient	Yield, %	Wt. resin per ml. wet	Capacity meq./ml.	Capacity meq./g.	% of theor capacity
Tetraallylammonium	65	1.91	65.5	0.284 g.	0.640	2.24	57
Tetraallylammonium	40	1.26	77.0	.3777	.523	1.39	36
Tetraallylammonium	30	1.17	65.5	.289	.450	1.56	40
Tetraallylammonium	23	1.13	77.0	.430	.432	1.01	26

TABLE V

EFFECT OF TEMPERATURE OF SUSPENSION POLYMERIZATION ON CAPACITIES OF POLYMERS

Monomer, bromide	Temp., °C.	Swelling coefficient	Yield, %	Wt. resin per ml., wet	Capacity meq./ml.	Capacity meq./g.	% of theor. capacity
Tetraallylammonium	70	1.77	87.0	0.378	0.664	1.76	45.3
Tetraallylammonium	40	1.53	86.0	.312	.773	2.48	64.0

zene were heated to the desired temperature while stirring at a uniform rate so regulated that the monomer solution was broken up into small globules. This rate of stirring was uninterrupted throughout the experiment. After the selected temperature was reached, 0.17 g. of 60% *t*-butylhydroperoxide was added. Heating and stirring were continued for 24 hours at 70°, and for 48 hours at 40°. A large proportion of the polymers were in the form of pearls or beads. These were washed and dried, and capacities determined as previously described. Results of this study are recorded in Table V and Fig. 4.

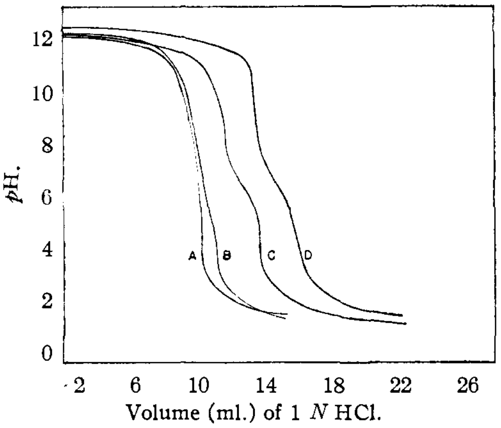

Fig. 3.—Effect of temperature of polymerization on capacity of tetraallylammonium bromide polymer: A, 23°; B, 30°; C, 40°; D, 65°.

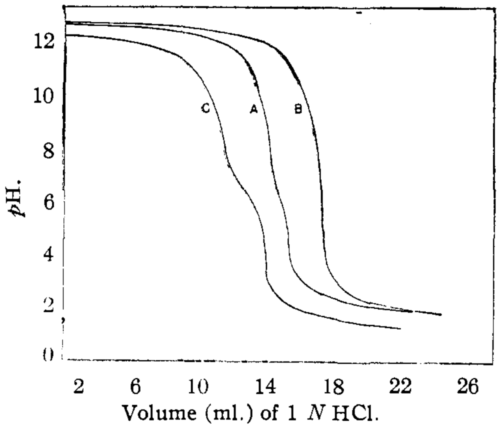

Fig. 4.—Effect of temperature of suspension polymerization on capacity of polymer and comparison of capacities of suspension and bulk polymers prepared at 40°: A, polymer prepared by suspension polymerization at 70°; B, polymer prepared by suspension polymerization at 40°; C, polymer prepared by bulk polymerization at 40°.

Effect of Initial Concentration of Chloride Ion on Capacities of Polymers.—For this study, four equal quantities of a typical polymer were converted to the hydroxide form, and titrated by the method previously described except the initial concentrations of the anion varied as indicated. The concentrations used were zero, 0.001, 0.01 and 0.1 *N*. Titration curves are shown in Fig. 5.

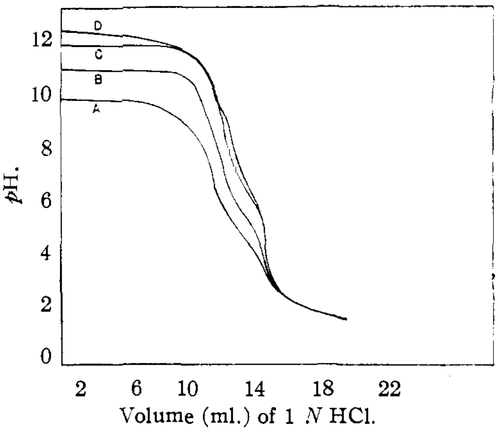

Fig. 5.—Effect of initial concentration of chloride ion on capacity of tetraallylammonium polymer: A, 0.000 mole/l.; B, 0.001 mole/l.; C, 0.010 mole/l.; D, 0.100 mole/l.

Rates of Ion Exchange.—A sample of resin produced by bulk polymerization of tetraallylammonium bromide at 65° was used for this study. Three 22-ml. samples of the hydroxide form of the resin were mixed with water in 250-ml. volumetric flasks and the solutions adjusted to 0.01 molar in KCl and 0.20 molar in HCl. These concentrations were selected to represent the ultimate concentrations found in the titrations of the resins. The mixtures of resin and solution were stirred mechanically in three 500-ml. flasks. The reactions were stopped at the end of 2 minutes, 3 hours and 48 hours, respectively, by rapid filtration of the resin. Aliquots were withdrawn from the filtrates, and the excess acid titrated with standard sodium hydroxide, using phenolphthalein as indicator. Based upon the known weight of dry bromide form of the resin, it was known that 24.4 millimoles of quaternary ammonium groups were present in each sample. From this information, the percentage conversion of each sample to the halide form was calculated. Results of these experiments are recorded in Table VI.

TABLE VI

RATE OF ION EXCHANGE REACTION

Sample number	Time of exposure	Conversion, %
1	2 minutes	71.5
2	3 hours	71.0
3	48 hours	70.3

For the experiment conducted to compare rates of exchange of hydroxyl and chloride ions a sample of tetraallylammonium bromide polymerized in suspension with ethylbenzene at 70° was used. This sample (8.7 g. in the bromide form, 233 ml. wet) was first converted to the hydroxyl form by means of the usual method in the column already described. The resin formed a column about 14 cm. in height. After washing, the resin was drained, but not dried. Potassium chloride solution (1.00 normal) was then allowed to flow through the resin, maintaining a constant rate of 13.5 ml. per minute. A total of twenty consecutive samples of the effluent were collected, the first eighteen, of 25 ml. each, and the last two, of 100-ml. volume. Ten-ml. aliquots of each sample were titrated in duplicate for free hydroxyl ion, using standard hydrochloric acid. Methyl red was used as the indicator.

The corresponding conversion from the chloride form to the hydroxyl form of the resin was conducted, using the same sample, *in situ*. Complete conversion to the chloride form was assured by washing the resin with 6 *N* HCl, and then with water. After all free chloride ions had been washed out, the resin was air dried, using an aspirator. To effect the conversion, normal sodium hydroxide solution was passed through the resin at a constant rate of 5.0 ml. per minute. Eighteen consecutive 25-ml. samples of the effluent were collected, followed by one sample of 125 ml., two of 100 ml. each, one of 225 ml., and the final, 25 ml. A total volume of 1025 ml. of effluent was collected in these twenty-three samples. Aliquots of these samples were neutralized with nitric acid and analyzed gravimetrically for the chloride ion. The results of this experiment are recorded in Fig. 6.

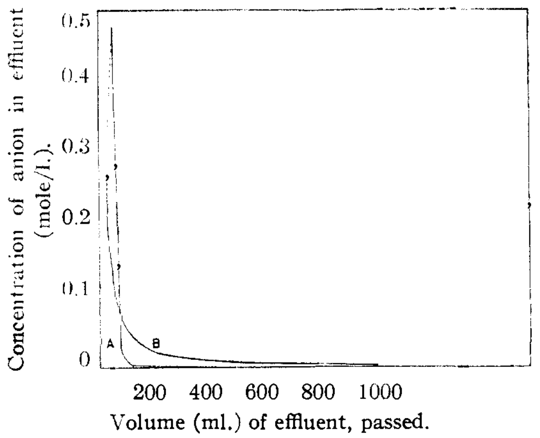

Fig. 6.—Relationship between concentration of chloride ion in effluent and volume of effluent passed: A, concentration of hydroxyl ion replaced; B, concentration of chloride ion replaced.

Discussion of Results

Effect of Coefficient of Swelling on Ion Exchange Capacity.—Those polymers prepared by bulk polymerization show a definite relationship between the coefficient of swelling and the ion exchange capacity. The theoretical capacity of the resin is approached only when the coefficient of swelling is high. Table II shows a typical series of polymers in which this study was made.

These results strongly indicate that in the highly cross linked polymers, *i.e.*, those having a low coefficient of swelling, a certain fraction of the halide ions incorporated into the polymer in the polymerization process are not available for exchange. These halide ions are not removed on long treatment with sodium hydroxide, indicating that hydroxyl ions are not capable of penetrating the polymer network, or the bromide ions are not capable of escaping. As shown in Table II, when the coefficient of swelling is high, the polymer network is no doubt extended to such a degree that exchange is more nearly complete.

Effect of Temperature of Polymerization on Capacity of Polymer.—Initial experiments in attempts to polymerize these salts employed temperatures in the range of 90–100°. Ion exchange capacity determinations indicated that the polymers possessed considerable amine capacity and relatively little quaternary ammonium capacity. This was especially true when polymerization occurred exothermally resulting in the polymer being subjected to considerably higher temperatures, depending upon the rate of heat transfer. Later experiments in which the temperature of polymerization was lowered considerably, the amine capacity became negligible. The amine capacity apparently arises by thermal decomposition of the quaternary ammonium salt. Many examples of this type of reaction have been observed.

In addition to the pronounced temperature effect, there appears to be a solvent effect also, the polymerization apparently proceeding at a more rapid rate in one solvent than another. Since the polymerization proceeds exothermally, the polymer prepared at the higher rate would be subjected to a higher temperature. Figure 1 compares the titration curves of polytetraallylammonium bromide prepared using water and formamide as solvents at 70°, all other conditions being identical with those previously described.[3] The amine capacity of the polymer prepared in formamide is somewhat greater. This figure also compares the titration curve of a polymer which was dried at 101° in the hydroxide form before titration with that of the original polymer. This indicates that the polyquaternary ammonium hydroxide is decomposed completely by a Hofmann degradation to the polytertiary amine.

Figure 2 shows the pronounced effect of temperature of polymerization on the capacity of the polymer. The polymer prepared at 70° shows little or no amine capacity, while in the polymer prepared at 75°, all other conditions being identical, about half of the total capacity of the polymer is amine capacity. Curve C shows the effect of drying the hydroxide form of the polymer at 103° before titration. The Hofmann degradation appears to be complete in this case also.

Later experiments showed that catalyzed polymerization of these salts occurred, even at temperatures below room temperature, however at a much slower rate. In order to study the effect of temperature of polymerization on the properties of the polymer, experiments were run in which polymers were prepared at 65, 40, 30 and 23°. It was hoped that polymerizations conducted at lower temperatures would increase the degree of linear polymerization thereby improving the physical properties, such as hardness, coefficient of swelling, etc., and as a result, capacities per unit volume would be improved. Figure 3 shows the titration curves of these polymers and Table IV includes some additional data.

These results substantiate the evidence obtained above for a decrease in capacity with decreasing coefficient of swelling, apparently due to screening.

Suspension Polymers.—Suspension polymerization of these quaternary ammonium salts was accomplished by suspending a concentrated aqueous solution of the salt, with catalyst added, in a hydrocarbon solvent, and heating at the desired temperature. In contrast to the bulk polymers, these suspension polymers showed an increase in capacity with decreasing swelling coefficient. The titration curves for two polymers prepared at different temperatures and having different swelling coefficients are shown in Fig. 4. Some additional physical characteristics of the polymers are shown in Table V.

For comparison, the titration curve for a typical polymer of tetraallylammonium bromide prepared by bulk polymerization at 40° is included. The swelling coefficient of this polymer is 1.26, and 36% of the theoretical capacity was available.

Effect of Initial Concentration of Chloride Ion on Capacities on Polymers.—As stated above, determination of capacities of the polymers was carried out by suspending the hydroxide form of the polymer in 0.01 *N* sodium chloride solution, and titrating with 1 *N* hydrochloric acid. In order to determine whether or not this initial anion concentration affected the ultimate capacity of the sample, a number of determinations were made in which varying initial concentrations of chloride ion were used. The titration curves for these determinations are shown in Fig. 5. These results indicate that the ultimate capacity of the resin is not affected, although the initial *p*H is higher. Previous work of this type has been done, using a different ion exchange resin.[6]

Rates of Ion Exchange.—The rapidity with which ion exchange reactions take place in the quaternary ammonium polymers makes rate determination rather difficult. Since the method employed for determination of capacities involved adding a known volume of hydrochloric acid, usually one milliliter, waiting for a three-minute interval, then reading the *p*H value, we considered it rather important to determine whether or not this three-minute interval was sufficient to allow the reaction to procede to completion. In order to check this, three samples of equal weight of a polymer were converted to the hydroxyl form and subjected to 0.01 molar potassium chloride and equivalent volumes of a known excess of standard hydrochloric acid for varying times. The results of this determination as recorded in Table VI appear to vary only within the limits of experimental error, and indicate that the reaction reached equilibrium in two minutes or less.

Throughout this work, it was obvious that the rate of exchange of hydroxyl for halide was much slower than the reverse reaction. As may be observed from a study of Fig. 6, the exchange reaction proceeded very rapidly during the passage of the first 150 ml. of potassium chloride solution, reaching a hydroxyl ion content of 0.0026 mole per liter. The conversion thereafter was much slower since the last sample collected (after 650 ml. had passed) showed a concentration of approximately 0.001 mole per liter. The dotted portion of the graph represents the effect of the dilution of the first sample of effluent by the small amount of water which did not drain from the resin.

As observed from curve B of Fig. 6, the rate of exchange of hydroxyl ion for chloride ion was slower than the reverse reaction. Approximately 500 ml. of alkali was necessary to bring the chloride ion concentration in the effluent to a reasonably constant value. The concentration of chloride ion in the effluent after 650 ml. had passed was about 0.006 mole per liter. After 1025 ml. had passed, the concentration was reduced to about 0.004 mole per liter.

GAINESVILLE, FLORIDA

RECEIVED AUGUST 13, 1951

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(6) R. Kunin and F. X. McGarvey, *Ind. Eng. Chem.*, **41**, 1265 (1949).

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[1]]

The Hydrolysis Rate of Betaine Amide and Ester Chlorides

BY H. G. WALKER, JR., AND H. S. OWENS

RECEIVED OCTOBER 23, 1951

The acidic and alkaline hydrolysis rates of a typical betaine ester and betaine amide have been studied. These derivatives are hydrolyzed faster in alkali and slower in acid than similar uncharged compounds.

Betaine hydrochloride (carboxymethyltrimethylammonium chloride) can be readily obtained from sugar-beet processing liquors but, up to the present, large-scale recovery of this non-toxic compound for chemical purposes has not been considered worthwhile. Since betaine hydrochloride is both a quaternary salt and a carboxylic acid, its use for the preparation of stable, water-soluble derivatives of a large number of otherwise insoluble amines and alcohols appears attractive.[2] Hence, we have investigated the rate of hydrolysis of a typical betaine ester and an amide in acid and alkaline media. For this study betaine cyclohexyl ester chloride and betaine anilide chloride were chosen, because both can be purified satisfactorily and neither is excessively hygroscopic.

The hydrolysis of cationic esters or amides has not been investigated thoroughly. It is apparent that the presence of the positive center due to the quaternary nitrogen should facilitate the approach

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(1) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Report of a study made under the Research and Marketing Act of 1946. Article not copyrighted.

(2) A. L. Linch, U. S Patents 2,359,862, 2,359,863, and 2,359,864 (1944).