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The Ionic Telomerization of Styrene

BY DONALD D. COFFMAN AND EDWARD L. JENNER

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The ionic telomerization of styrene with acetic acid has yielded the acetates of alcohols containing from one to several styrene units, $H(CH_2CHPh)_nOAc$. Esters containing 1, 2 and 3 units have been isolated. From styrene and acetonitrile, acyl derivatives of primary amines having a number of styrene units have been obtained, and amines from the first two members have been identified. Similarly, styrene and formaldehyde in acetic acid have given the acetates of glycols containing one methylene group and a variable number of styrene units.

The telomerization of an ethylenically unsaturated monomer, M, yields a family of products of the type $A\text{-}M_n\text{-}B$ in which n is a small integer and A and B are derived from reactants other than the monomer. The literature records such telomerization brought about by free radicals[1] and by ionic[2] catalysts.

The present investigation is concerned with acid-catalyzed telomerization in which the intermediates are cationic as represented schematically in the following steps

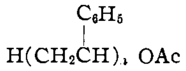
$$A^+ + M \longrightarrow A\text{-}M^+ \quad \text{Initiation}$$
$$A\text{-}M^+ + M \longrightarrow A\text{-}M\text{-}M^+ \quad \text{Propagation}$$
$$A\text{-}M_n^+ + B^\ominus \longrightarrow A\text{-}M_n\text{-}B \quad \text{Termination}$$

The compound A-B may serve as the source of A^+ and $B^\ominus$, although this is not necessary. B may be a neutral molecule and thus require, as an additional step, the loss of a cation (for example, a proton) or the addition of an anion. In this work, styrene was employed as monomer, and A and B were

	A	B
1.	$H^\oplus$	$OAc^\ominus$
2.	$H^\oplus$	CH_3CN (followed by $OAc^\ominus$ or $HSO_4^\ominus$)
3.	$HOCH_2^\oplus$	$OAc^\ominus$

These combinations lead, respectively, to the acetyl derivatives of alcohols, amines and glycols each containing from one to several styrene units.

Telomerization of Styrene with Acetic Acid.—From a family of telomers, one (n = 2) was selected for determination of structure.



$$H(CH_2\overset{\overset{\displaystyle C_6H_5}{|}}{C}H)_2\ OAc$$

This telomer was demonstrated to be the acetate of 1,3-diphenylbutanol by hydrolysis to the alcohol which in turn was oxidized to β-phenylbutyrophenone identified by its melting point and those of its oxime and phenylhydrazone. The formation of 1,3-diphenylbutyl acetate can be accounted for by (1) the addition of a proton to the β-carbon of a styrene molecule followed by (2) the attack of the resulting carbonium ion on the β-carbon of a second styrene molecule, and (3) termination by the addition of an acetate ion to the carbonium ion. This reaction is analogous to the previously described telomerization of butadiene with acetic acid.[2]

The telomerizations were conducted at 25° by adding styrene to an acetic acid solution of the catalyst. Among the catalysts investigated, perchloric acid was the most active. Sulfuric acid was approximately as active as the boron fluoride–acetic acid complex (Table I).

TABLE I

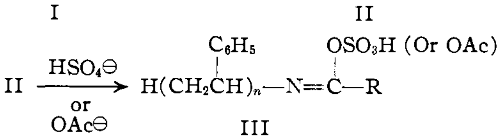
COMPARISON OF CATALYSTS FOR THE IONIC TELOMERIZATION OF STYRENE WITH ACETIC ACID

Molar concn. of catalyst in acetic acid	Reaction time, hr.	Total conversion,[a] %	Yield of telomer, n = 2, %
0.1 $HClO_4$	5	87	25
0.3 H_2SO_4	65	84	28
0.27 $BF_3 \cdot CH_3COOH$	65	72	18

[a] Total conversion was calculated as the weight of the total product divided by the weight of the styrene charged.

The boron fluoride–acetic acid complex was generally chosen for use to avoid the hazards accompanying the use of perchloric acid and to avoid the possibility of sulfonation which might occur with sulfuric acid. In a telomerization at 25° with a 20-hour reaction time and 0.5 *M* boron fluoride–acetic acid complex as catalyst, the product had the following molecular weight distribution: n = 1, 11%; n = 2, 38%; n = 3, 20%; and $n > 3$, 31%. These fractions contained low proportions of hydrocarbon impurities. The fraction containing two styrene units was selected for detailed investigation. This fraction was composed of the telomeric ester (90%) and styrene dimer (10%). The hydrocarbon was separated by distillation; its concentration in the product was estimated from the refractive index.

Telomerization of Styrene with Acetonitrile.—The telomerization of styrene with acetonitrile offers a route to aliphatic primary amines having phenyl groups attached to alternate carbon atoms in the chain. By analogy with the products obtained from styrene and acetic acid and also from consideration of the established synthesis of amides from the reaction of olefins with nitriles,[3] the telomerization probably proceeded through an intermediate enol sulfate or acetate III which was hydrolyzed to the amide.



$$\underset{\text{I}}{H(CH_2\overset{\overset{\displaystyle C_6H_5}{|}}{C}H)_n^\oplus} \xrightarrow{RCN} \underset{\text{II}}{H(CH_2\overset{\overset{\displaystyle C_6H_5}{|}}{C}H)_n\text{—}N{=}\overset{\oplus}{C}\text{—}R}$$

$$\text{II} \xrightarrow[\text{or } OAc^\ominus]{HSO_4^\ominus} \underset{\text{III}}{H(CH_2\overset{\overset{\displaystyle C_6H_5}{|}}{C}H)_n\text{—}N{=}\overset{\overset{\displaystyle OSO_3H\ (\text{Or } OAc)}{|}}{C}\text{—}R}$$

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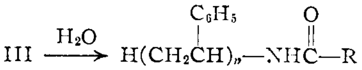
[1] T. A. Ford, W. E. Hanford, J. Harmon and R. D. Lipscomb, THIS JOURNAL, **74**, 4323 (1952); J. Harmon, T. A. Ford, W. E. Hanford and R. M. Joyce, *ibid.*, **72**, 2213 (1950); R. M. Joyce, W. E. Hanford and J. Harmon, *ibid.*, **70**, 2529 (1948); M. S. Kharasch, E. V. Jensen and W. H. Urry, *ibid.*, **69**, 1100 (1947).

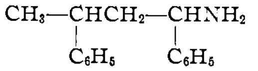
[2] E. L. Jenner and R. S. Schreiber, *ibid.*, **73**, 4348 (1951).

[3] J. J. Ritter and P. P. Minieri, *ibid.*, **70**, 4045 (1948), and H. Wieland and E. Dorrer, *Ber.*, **63**, 404 (1930).



$$\mathrm{III} \xrightarrow{H_2O} H(CH_2\underset{}{\overset{C_6H_5}{\overset{|}{C}}}H)_n{-}NH\overset{\overset{O}{\|}}{C}{-}R$$

The structure indicated for the telomer is supported by the identification of the amine



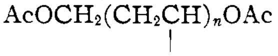
$$CH_3{-}\underset{\underset{C_6H_5}{|}}{C}HCH_2{-}\underset{\underset{C_6H_5}{|}}{C}HNH_2$$

This formulation was substantiated by the preparation of the amine picrate which had a melting point identical with that reported for the picrate of 1,3-diphenylbutylamine.[4]

The telomerization of styrene with acetonitrile was conducted with sulfuric acid catalyst in either acetic acid or nitrobenzene. Nitrobenzene solvent was preferable to acetic acid, which competed as a telogen and led to small amounts of esters in addition to the desired amides. In some cases the telomers were isolated as the amides, but more frequently the crude product was hydrolyzed, and the resulting amines were isolated.

In a telomerization conducted in nitrobenzene solution at 25° with 1:2:1 mole ratios of styrene: acetonitrile:sulfuric acid, a 68% conversion was obtained in 24 hours. The hydrolyzed product comprised 21% amine, $n = 1$; 18% amine, $n = 2$; and 61% amines, $n > 2$. Here, as with the telomeric ester, the fractions contained hydrocarbon contaminants. The $n = 2$ fraction contained approximately 2% hydrocarbon and 98% diphenylbutylamine. It was found that a lower ratio of acetonitrile to styrene increased the formation of the by-product styrene dimer. In an experiment similar to the one described above but having mole ratios of styrene:acetonitrile:sulfuric acid of 2:2:1, a 51% yield of total product was obtained in three hours. Of this, 11% was $n = 1$, 17% was $n = 2$, and 72% was $n > 2$. The $n = 2$ fraction from this experiment contained 15% hydrocarbon.

Telomerization of Styrene with Formaldehyde in Acetic Acid.—In the Prins reaction, an olefin reacts with formaldehyde in the presence of an acid catalyst to form a 1,3-glycol.[5] By the telomerization of an olefin with formaldehyde, α,ω-glycols have been prepared which contain a plurality of hydrocarbon units in the chain. The products have been isolated as the diacetates, which are believed to have the structure $AcOCH_2(CH_2\underset{\underset{C_6H_5}{|}}{C}H)_nOAc$ when styrene is employed as the olefin. The product containing two styrene units was presumed to be the diacetate of 1,3-diphenyl-1,5-pentanediol. That it was the diacetate of a C_{17} glycol was supported by its boiling point, saponification equivalent and elemental analysis.



The telomerizations were conducted by adding styrene to a solution of formaldehyde and an acid catalyst in acetic acid. The formation of esters containing a plurality of monomer units was achieved by using a high ratio of styrene to formaldehyde. In a representative experiment conducted at 25° with the boron fluoride–acetic acid complex as catalyst, a 114% conversion (weight of product divided by weight of styrene) was obtained in 72 hours. The approximate molecular weight distribution of this product as determined by fractional distillation was: $n = 1$, 35%; $n = 2$, 17%; and $n > 2$, 48%. These fractions were chiefly glycol acetates but contained simple styrene–acetic acid telomers as contaminants.

Experimental

Telomerization of Styrene with Acetic Acid.—A solution of the catalyst, boron fluoride–acetic acid complex, was prepared by absorbing 500 g. of boron fluoride in 1 l. of acetic acid cooled in an ice-bath. The resulting solution was diluted with glacial acetic acid as required before reacting with styrene. The telomerization was brought about by adding 720 g. of styrene to 4 l. of solution which was 0.5 *M* boron fluoride–acetic acid complex in acetic acid. After the homogeneous solution had been held at 25° for 20 hours, it was drowned in 25 l. of ice-cold sodium hydroxide. The resulting mixture was extracted with toluene, and the organic extract was washed with water and dried over calcium chloride. The toluene and unreacted styrene were removed by distillation under reduced pressure, and the telomers were fractionally distilled (Table II).

TABLE II

DISTILLATION OF STYRENE–ACETIC ACID TELOMERS

No. of fraction	Wt. of fraction, g.	B.p., °C.	Pressure, mm. of mercury	$n^{25}D$
1	86.3	73	3	1.4930
2	12.3	79–140	1	1.5445
3	52.3	138–143	1	1.5480
4	54.0	143	1	1.5441
5	67.8	143–144	1	1.5419
6	55.1	144–145	1	1.5381
7	33.0	145	1	1.5378
8	10.4	132–160	0.2	1.5399
9	26.0	160–200	0.2	1.5420
10	86.7	200–205	0.3	1.5622
11	47.4	205–210	0.3	1.5620
R	174.0	.....	...	....
Total	681.9			

Fraction 1 was α-phenylethyl acetate. Its boiling point and refractive index confirm its identification as α- rather than β-phenylethyl acetate (Table III). The corresponding fraction from a similar experiment was characterized by elemental analysis and determination of its saponification equivalent.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37; sapn. equiv., 164. Found: C, 72.88; H, 7.52; sapn. equiv., 161.

TABLE III

IDENTIFICATION OF TELOMERIC ACETATE, $n = 1$

	B.p., °C.	Refractive index
Fraction 1	73 (3 mm.)	$n^{25}D$ 1.4930
α-Phenylethyl acetate	72–75 (3 mm.) (extrapolated from 105–108 (15 mm.)[6])	$n^{18}D$ 1.5003[8]
β-Phenylethyl acetate	90–92 (3 mm.) (extrapolated from 118–120 (13 mm.)[7])	$n^{22.5}D$ 1.5108[9]

1,3-Diphenylbutyl Acetate.[10]—Fractions 3 through 9 comprised principally the telomer containing two styrene units and one acetic acid, namely, 1,3-diphenylbutyl acetate. They were contaminated with varying proportions

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(4) F. Henrich, *Ann.*, **351**, 176 (1907).

(5) E. Arundale and L. A. Mikeska, *Chem. Revs.*, **51**, 505 (1952).

(6) J. Marshall, *J. Chem. Soc.*, **107**, 523 (1915).

(7) A. Skita, *Ber.*, **48**, 1694 (1915).

(8) H. Olsson, *Z. physik. Chem.*, **133**, 234 (1928).

(9) J. H. Gladstone, *J. Chem. Soc.*, **45**, 246 (1884).

(10) E. L. Jenner, U. S. Patent 2,533,939 (1950).

of the hydrocarbon dimer 1,3-diphenyl-1-butene. This impurity possesses a high refractive index ($n^{25}\text{D}$ 1.5900), and the approximate composition of the various fractions was estimated from their refractive indices. Fraction 3, the least pure fraction, contained about 25% of the hydrocarbon. The analysis of fraction 7 identified it as the acetate of an alcohol containing two styrene units.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51; sapn. equiv., 268. Found: C, 81.07; H, 7.71; sapn. equiv., 256.

The structure of this ester was established by converting it to 1,3-diphenylbutanol which was oxidized to β-phenylbutyrophenone.

1,3-Diphenylbutanol.—To a solution of 1 g. of sodium in 200 ml. of absolute methanol was added 29.4 g. of the styrene–acetic acid telomer, $n = 2$. The mixture was allowed to stand for three days at room temperature, and the sodium methoxide was then neutralized by the addition of acetic acid. The methanol and methyl acetate were distilled, and the residue was taken up in ether and washed with water. The ether solution was dried over magnesium sulfate and then distilled. 1,3-Diphenylbutanol was obtained as a 13.6-g. fraction (55% yield), b.p. 136° (0.8 mm.), $n^{25}\text{D}$ 1.5631. Mastagli reported[11] the boiling point as 202° (15 mm.) and $n^{25}\text{D}$ 1.5652.

β-Phenylbutyrophenone.—A solution was prepared by dissolving 2.5 g. of chromic acid in 2.4 ml. of water and adding 10 ml. of acetic acid. This solution was added to a solution of 8 g. of diphenylbutanol, prepared as above, in 25 ml. of acetic acid. The addition was made slowly with ice cooling to maintain a temperature of 15°. At the end of the addition, the mixture was warmed to 70° to decolorize the last trace of chromic acid. The acetic acid was then neutralized with an excess of aqueous sodium hydroxide, and the emulsion which resulted was filtered. The aqueous solution was extracted with toluene and ether, and the combined extracts were dried over magnesium sulfate. Distillation of the extract yielded 5.46 (68%) of β-phenylbutyrophenone, b.p. 158° (3 mm.), which crystallized to a yellow solid in the receiver. Upon recrystallization from ethanol, the ketone was obtained as stout white needles, m.p. 72–73°. Kohler[12] reported a melting point of 74° for β-phenylbutyrophenone.

The oxime of β-phenylbutyrophenone was prepared by heating a mixture of the ketone from the oxidation, hydroxylamine hydrochloride and potassium acetate in aqueous alcohol for three hours. Upon cooling the mixture, the oxime crystallized from solution. It was recrystallized from ethanol–water to yield tufts of fine needles, m.p. 92–93°. Kohler[12] reported a melting point of 93°.

The phenylhydrazone of β-phenylbutyrophenone was prepared by heating the ketone from the oxidation in an alcohol solution with phenylhydrazine containing a trace of acetic acid. The phenylhydrazone melted at 79–80° (Kohler[12] reported 79°). After standing for three days at room temperature, the phenylhydrazone turned brown and partially liquefied. The same behavior for this phenylhydrazone was reported by Harries.[13]

1,3,5-Triphenylhexyl Acetate.—Fractions 10 and 11 were presumably acetates of alcohols containing three styrene units. The analyses indicated that the ester contained 10–15% of a hydrocarbon contaminant, probably styrene trimer.

Anal. Calcd. for $C_{26}H_{28}O_2$: C, 83.83; H, 7.58; sapn. equiv., 372. Found: C, 85.34; H, 7.65; sapn. equiv., 398.

The residue comprised a mixture of telomers which in composition averaged quite close to $n = 4$.

Anal. Calcd. for $C_{34}H_{36}O_2$: C, 85.60; H, 7.61; sapn. equiv., 477. Found: C, 86.17; H, 7.99; sapn. equiv., 493.

Telomerization of Styrene with Acetonitrile in Acetic Acid as Solvent.—A solution was prepared by dissolving 448 ml. (4 moles) of styrene and 421 ml. (8 moles) of acetonitrile in 500 ml. of acetic acid. To this solution was added a solution of 222 ml. (4 moles) of sulfuric acid in 300 ml. of acetic acid. The mixture was held at 25° during the hour required for this addition. The clear solution which was obtained was allowed to stand at 25° for 26 hours and then 500 ml. of water was added. The mixture was steam distilled whereupon a viscous, white material separated in the distillation flask. This material, comprising a mixture of telomeric amides, was hydrolyzed by boiling in a mixture of 1 l. of butyl alcohol and 1 l. of concentrated aqueous hydrochloric acid for 72 hours. The mixture was again subjected to steam distillation to remove butyl alcohol and hydrochloric acid, and the residue was cautiously made alkaline by the addition of solid potassium hydroxide. When the mixture reached *p*H 8, 500 ml. of 20 *M* sodium hydroxide was added. The resulting mixture was extracted with toluene, and the toluene extracts were dried over magnesium sulfate. The toluene was distilled, and the telomeric amines were separated by fractional distillation under reduced pressure (Table IV).

TABLE IV

DISTILLATION OF AMINES FROM THE TELOMERIZATION OF STYRENE WITH ACETONITRILE

No. of fraction	Wt. of fraction, g.	B.p., °C.	Pressure, mm.	$n^{25}\text{D}$
1	17.5	71	12	1.5211
2	21.0	71–74	12	1.5218
3	17.4	75	12	1.5221
4	16.4	76	13	1.5228
5	8.2	76	13	1.5221
6	1.0	44	2	1.5181
7	18.9	133	1.1	1.5575
8	19.1	133–135	1.2	1.5566
9	18.7	135–137	1.2	1.5565
10	6.7	137–139	1.6	1.5571
Residue	154.0	.....	..	....
Total	298.9			

The yield of total product (298.9 g.) corresponds to a 72% conversion on a weight basis. Fractions 1 through 6 which comprised 27% of the hydrolyzed product were α-phenylethylamine. Fractions 7 through 10 which made up 21% of the hydrolyzed product were the telomer corresponding to an n value of 2, namely, 1,3-diphenylbutylamine. The residue, which comprised 52% of the product, was a mixture of telomeric amines with n values above 2.

The identity of fraction 4, typical of the fractions corresponding to n values of 1, was supported by analysis.

Anal. Calcd. for $C_8H_{11}N$: N, 11.56; neut. equiv., 121. Found: N, 11.27; neut. equiv., 126.

This compound was indicated to be α- rather than β-phenylethylamine by its boiling point, 76° (13 mm.). R. Paul[14] reports a boiling point of 75–76° (13 mm.) for α-phenylethylamine, whereas Robinson and Snyder[15] report a boiling point of 90–93° (15 mm.) for the β-isomer.

Fraction 8, typical of the $n = 2$ cuts, was characterized as an amine containing two styrene units by the determination of its elemental analysis and neutral equivalent.

Anal. Calcd. for $C_{16}H_{10}N$: C, 85.28; H, 8.51; neut. equiv., 225. Found: C, 85.60; H, 8.90; neut. equiv., 248.

The diphenylbutylamine fraction from a similar experiment was treated with the calculated amount of picric acid in ethanol. The picrate melted at 187–188° after recrystallization from alcohol. Henrich[4] reported a melting point of 187° for the picrate of 1,3-diphenylbutylamine.

Telomerization of Styrene with Acetonitrile in Nitrobenzene as Solvent.—A solution was prepared from 448 ml. (4 moles) of styrene, 421 ml. (8 moles) of acetonitrile and 404 ml. of nitrobenzene. To this solution was added a solution of 222 ml. (4 moles) of sulfuric acid in 404 ml. of nitrobenzene. The addition, which required one hour, was carried out at 25°. The first half of the addition, in particular, was accompanied by an exothermic reaction. At the end of 24 hours, 500 ml. of water was added, and the nitrobenzene was steam distilled. One liter each of n-butanol and of concentrated hydrochloric acid were added, and the mixture was hydrolyzed and the product was isolated as in the

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[11] Pierre Mastagli, *Ann. chim.*, **10**, 362 (1938); *C. A.*, **45**, 1293 (1939).

[12] E. P. Kohler, *Am. Chem. J.*, **31**, 655 (1904).

[13] C. Harries, *Ann.*, **330**, 233 (1904).

[14] R. Paul, *Bull. soc. chim.*, [5] **4**, 1125 (1937).

[15] J. C. Robinson, Jr., and H. R. Snyder, *Org. Syntheses*, **23**, 71 (1943).

previous example. The total conversion to telomer was 68% on a weight basis. The composition of the product was approximately 21%, $n = 1$; 18%, $n = 2$; and 61% $n > 2$. A representative fraction of the telomer $n = 2$ had a neutral equivalent of 229 (calcd. 225 for diphenylbutylamine), demonstrating that it was substantially pure amine free from hydrocarbon contamination (contrast with the neutral equivalent of 248 for the amine obtained in the previous example which used acetic acid as solvent).

Telomerization of Styrene with Formaldehyde in Acetic Acid.—To a solution of 60 g. (2 moles) of formaldehyde introduced as paraformaldehyde and 68 g. (1 mole) of boron fluoride in 700 ml. of acetic acid was added 560 ml. (5 moles) of styrene. A clear solution was obtained. The exothermic reaction which occurred increased the temperature from 25° to 40° in spite of ice-bath cooling. The reaction mixture was held at 25° for 72 hours, and the reaction was terminated by adding ice, water and 200 ml. of 20 *M* sodium hydroxide. The organic layer was separated, washed with water, and dried over calcium sulfate. After distillation of the solvent, the product was fractionally distilled under reduced pressure. The telomer $n = 1$ (208 g., 35% of the product) had b.p. 117° (2.8 mm.)–140° (0.6 mm.) and $n^{25}D$ 1.4971–1.5189. The telomer $n = 2$ (98 g., 17% of the product) had b.p. 141° (0.6 mm.)–196° (0.8 mm.) and $n^{25}D$ 1.5189–1.5349. The residue (285 g., 48% of the product) consisted of telomers containing an average of five styrene units (*Anal.* Found: C, 81.35; H, 7.45; sapn. equiv., 313; mol. wt., 606). The glycol diacetates obtained in this synthesis were contaminated with varying quantities of the simple styrene–acetic acid telomers. In addition, there may have been some unsaturated products corresponding in structure to the loss of an acetic acid molecule from a glycol diacetate. The presence of these unsaturated compounds was indicated by the high refractive indices of certain of the fractions.

Diphenylpentanediol.[16]—One of the fractions (b.p. 183–188° (0.6 mm.) $n^{25}D$ 1.5341) representative of the telomers $n = 2$ was selected for hydrolysis to the glycol. Its analysis confirmed its identity as the diacetate of a C_{17} glycol.

Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11; sapn. equiv., 170.2. Found: C, 75.15; H, 7.19; sapn. equiv., 194.8.

An 18.3-g. sample of this glycol diacetate was saponified by heating for nine hours with 50 ml. of 20 *M* sodium hydroxide and 200 ml. of ethanol. The ethanol was distilled, and toluene was added to facilitate the separation of the glycol from the aqueous alkali. After distillation of the toluene, the glycol was distilled, b.p. 200° (0.5 mm.). The diphenylpentanediol (11 g.) was a clear, very viscous liquid.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.87; hydroxyl equiv., 128. Found: C, 79.74; H, 8.06; hydroxyl equiv., 145.

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[16] D. D. Coffman and E. L. Jenner, U. S. Patent 2,555,918 (1951).

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

Carbon Dihalides as Intermediates in the Basic Hydrolysis of Haloforms. III. Combination of Carbon Dichloride with Halide Ions[1]

BY JACK HINE AND ARTHUR M. DOWELL, JR.

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Additional evidence has been found in support of the proposal that carbon dichloride is an intermediate in the basic hydrolysis of chloroform. Since sodium fluoride, nitrate and perchlorate, at concentrations up to 0.16 *N* have an identical effect on the reaction rate, within experimental error, this effect is believed to be due to the concentration and not the identity of the anions present. At the same concentrations, however, sodium chloride, bromide and iodide all decrease the reaction rate. In the case of sodium chloride this is due to a "mass-law effect" produced by the recombination of carbon dichloride with chloride ions. Bromide and iodide ions combine with carbon dichloride to form carbanions which are changed to dichlorobromomethane and dichloroiodomethane, the latter compound having been isolated. The rate "constants" obtained in the presence of bromide and iodide ions climb as the reaction proceeds, in agreement with expectation since the new haloforms arising in these reactions are more reactive than chloroform. Excellent agreement is found between the magnitude of the decrease in the rate of chloroform hydrolysis produced by the various halide ions (NaI > NaBr > NaCl) and the *nucleophilic constants* of the halide ions given by Swain and Scott. These data rule out all of the alternative mechanisms which have been suggested.

Introduction

Considerable evidence has been presented to show that the alkaline hydrolysis of chloroform consists of a relatively rapid reversible formation of the trichloromethyl anion, followed by the rate-controlling loss of a chloride ion to give the reactive intermediate carbon dichloride, which is then rapidly transformed into the final products, carbon monoxide and formate ion (mechanism I).[2]

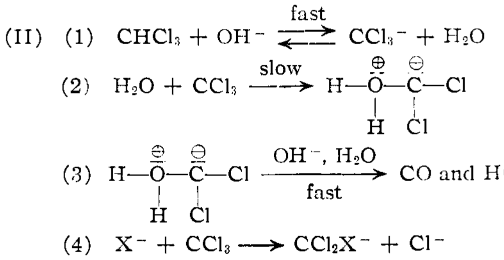
$$\text{(I)}\quad (1)\quad CHCl_3 + OH^- \overset{\text{fast}}{\rightleftharpoons} CCl_3^- + H_2O$$

$$(2)\quad CCl_3^- \xrightarrow{\text{slow}} Cl^- + CCl_2$$

$$(3)\quad CCl_2 \xrightarrow[\text{fast}]{OH^-,\ H_2O} CO \text{ and } HCO_2^-$$

$$(4)\quad CCl_2 + X^- \longrightarrow CCl_2X^-$$

While it could not be ruled out unequivocally, a number of arguments were advanced to show the improbability of an alternate mechanism (II) in which the trichloromethyl anion is decomposed by a nucleophilic attack by water.



$$\text{(II)}\quad (1)\quad CHCl_3 + OH^- \overset{\text{fast}}{\rightleftharpoons} CCl_3^- + H_2O$$

$$(2)\quad H_2O + CCl_3 \xrightarrow{\text{slow}} H\!-\!\overset{\oplus}{\underset{|}{\underset{H}{O}}}\!-\!\overset{\ominus}{\underset{|}{\underset{Cl}{C}}}\!-\!Cl$$

$$(3)\quad H\!-\!\overset{\ominus}{\underset{|}{\underset{H}{O}}}\!-\!\overset{\ominus}{\underset{|}{\underset{Cl}{C}}}\!-\!Cl \xrightarrow[\text{fast}]{OH^-,\ H_2O} CO \text{ and } HCO_2$$

$$(4)\quad X^- + CCl_3 \longrightarrow CCl_2X^- + Cl^-$$

The possibility that the reaction involves a rate-controlling S_N2 attack[3] by the hydroxide ions on chloroform (mechanism III) has been shown to be

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[1] From a Ph.D. thesis submitted by Arthur M. Dowell, Jr., to the Graduate School of the Georgia Institute of Technology. For Part II see J. Hine, R. C. Peek, Jr., and B. D. Oakes, THIS JOURNAL, **76**, 827 (1954).

[2] J. Hine, *ibid.*, **72**, 2438 (1950).

[3] For the significance of the terms S_N1 and S_N2 see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. VII.