Anal. Calcd. for $C_7H_{15}OBr$: C, 43.1; H, 7.8; Br, 41.0. Found: C, 43.0; H, 7.9; Br, 41.2.

Dehydrobromination of *n*-Butylethylene Methoxybromide.—Treatment of 50 g. (0.256 mole) of the methoxybromide obtained from *n*-butylethylene with sodium amide prepared from 6.9 g. (0.3 mole) of sodium essentially as described above for *t*-butylethylene methoxybromide gave on distillation, 11.2 g. (38%) of enol ether, b.p. 120–126° (760 mm.), and 14.1 g. (28%) of recovered methoxybromide, b.p. 75–80° (20 mm.). There was also obtained 4.9 g. (23%) of hexyne-1, b.p. 60–64°. The enol ether fraction was redistilled to obtain an analytical sample, b.p. 122° at 750 mm.

Anal. Calcd. for $C_7H_{14}O$: C, 73.6; H, 12.4. Found: C, 73.5; H, 12.4.

Structure of Enol Ether Obtained from *n*-Butylethylene Methoxybromide.—To the 2,4-dinitrophenylhydrazine reagent prepared from 1.7 g. of 2,4-dinitrophenylhydrazine, 3.5 ml. of concentrated hydrochloric acid and 40 ml. of 95% ethanol was added 1 g. of the enol ether fraction, b.p. 120–126°, obtained as described above. The precipitate was filtered to yield 2.1 g. (89%) of a mixture of methyl *n*-butyl ketone and *n*-hexaldehyde 2,4-dinitrophenylhydrazones, m.p. 80–102°. Recrystallization of a 1.33-g. portion from 60 ml. of 95% ethanol gave as first crop, 0.88 g. (66%) of short orange crystals, m.p. 103.5–107°. The mixed m.p. with authentic methyl *n*-butyl ketone 2,4-dinitrophenylhydrazone (m.p. 107.5–108.5°) was 106–108°. Partial evaporation and freezing of the filtrate yielded 0.4 g. of yellow-orange crystals, m.p. 82–95°. From the latter it was possible to separate by hand a few long yellow needles, m.p. 105.5–107.5°, mixed m.p. with authentic *n*-hexaldehyde 2,4-dinitrophenylhydrazone (m.p. 105.5–107.5°) 106.0–107.5°. However, attempts to further separate the second crop quantitatively by recrystallization and chromatography were unsuccessful.

The amount of terminal enol ether in the enol ether mixture, which was shown above to be less than 34%, was estimated by conversion to a mixture of aldehyde and ketone, oxidation of the mixture with silver oxide and titration of the acid formed from oxidation of the aldehyde, as described below.

A mixture of 8.5 g. of enol ether, 2 ml. of concentrated hydrochloric acid, 6 ml. of water and 10 ml. of ethanol was refluxed 5 minutes. The mixture was diluted with water, taken up in ether, dried and distilled to yield 5 g. (67%), b.p. 124–125°, of a mixture of methyl *n*-butyl ketone and *n*-hexaldehyde. To a silver oxide reagent prepared from 3.40 g. of silver nitrate in 10 ml. of water and 2.40 g. of sodium hydroxide in 10 ml. of water was added 2.50 g. of the ketone–aldehyde mixture. After stirring for 30 minutes, the mixture was filtered with suction and extracted with ether. The aqueous layer was then carefully acidified, salted out and extracted with four 20-ml. portions of ether. The ether extracts were washed with saturated sodium chloride solution and dried. Removal of the solvent left an acidic residue, which on titration with standard base was shown to contain 4.7 mmoles (19%) of acid calculated as caproic acid. The acid isolated from this titration was refluxed with excess aniline for 2 hr. One recrystallization of the crude anilide from 95% ethanol gave *n*-caproanilide, m.p. 95.0–95.5° (reported[16] m.p. 96°). A duplicate run gave an acid yield of 15%. A check on the method with a mixture of 0.02 mole of methyl ethyl ketone and 0.005 mole of *n*-heptaldehyde gave on titration 0.0049 mole (98% of theory) of acid formed.

The enol ether formed from dehydrobromination of the methoxybromide obtained from *n*-butylethylene was thus shown by these methods to consist of approximately 80–85% of 2-methoxyhexene-1 and 15–20% of 1-methoxyhexene-1.

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[16] A. Ludwig and S. Tache, *Bull. chim. soc. Romane chim.*, **39**, 87 (1937).

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[CONTRIBUTION FROM THE ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

aci-Nitroalkanes. IV. The Mechanism of the Hydrolysis of 1-Chloronitroethane

BY M. FREDERICK HAWTHORNE AND R. DONALD STRAHM

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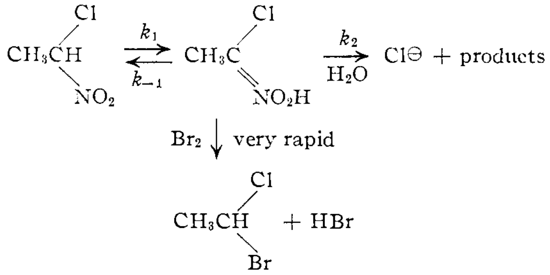
In water at 35.0° and in independent first-order rate determinations, 1-chloronitroethane has been found to release chloride ion approximately one-third as rapidly as it absorbs bromine. 1-Deutero-1-chloronitroethane when examined in an identical manner showed approximately a twofold diminution in both measured rate constants. These facts prove that the hydrolytic release of chloride ion from 1-chloronitroethane is preceded by a tautomerization to the reactive *aci*-isomer and that return of the *aci*-isomer to reactant is kinetically important relative to the hydrolysis of the *aci*-isomer. The products of hydrolysis of 1-chloronitroethane have been found to be equivalent amounts of hydrogen chloride, acetic acid and a colorless gas which is probably nitrous oxide. Conductometric examination of the rate of hydrolysis of 1-chloronitroethane affords an instance in which the approach of a reaction system to a steady state situation may be observed.

It was recently reported by Pearson and Dillon[1] that 1-chloronitroethane hydrolyzed in aqueous solution at 34.9° to yield chloride ion at a rate equal to approximately one-half the rate at which the same nitroalkane ionized (absorbed bromine) under the same conditions. In view of the recent finding that the displacement of chloride ion from 1-chloronitroethane by nitrite ion is preceded by the tautomerization of the nitro compound to its *aci*-nitroisomer, it was proposed[2] that the hydrolysis of 1-chloronitroethane and the kinetic observations of Pearson and Dillon[1] could be explained on a similar basis if the rate of return of *aci*-1-chloronitroethane to its hydrolytically stable isomer were comparable to the rate of displacement of chloride ion from the reactive *aci*-isomeride by solvent water ($k_{-1} \sim k_2$).



Therefore

$$\frac{d[Cl^{\ominus}]}{dt} = \frac{k_1k_2}{k_{-1}+k_2}[CH_3ClNO_2] \text{ and}$$

$$\frac{-d[Br_2]}{dt} = k_1[CH_3ClNO_2] \qquad (1)$$

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[1] R. G. Pearson and R. L. Dillon, THIS JOURNAL, **75**, 2439 (1953).

[2] M. F. Hawthorne, *ibid.*, **78**, 4980 (1956).

Since both the rate of chloride ion release and the rate of bromination depend, according to this rationalization, upon the magnitude of the ionization rate constant, k_1, both reactions should show a kinetic primary isotope effect of equal magnitude when deuterium is substituted for protium on the carbon atom alpha to the nitro group.[2] This prediction has been confirmed within possible experimental error and the products of hydrolysis determined.

Results

1-Chloronitroethane was purified carefully by regeneration from its anion followed by fractional distillation[2] and 1-deutero-1-chloronitroethane was prepared by regeneration in deuterium oxide and fractionally distilled.[2]

The initial rates of ionization of these two materials in water at 35.0° were determined under zero-order conditions by the conductometric bromination method of Pearson and Dillon.[1] Table I summarizes the ionization rate constants of both the protium (k_{iH}) and deuterium (k_{iD}) compounds.

TABLE I

THE RATES OF IONIZATION OF 1-CHLORO- AND 1-DEUTERO-1-CHLORONITROETHANE IN WATER AT 35.0°

Init. concentrations, mole/l.		
$(Br_2) \times 10^3$	(CH_3CHNO_2Cl)	k_i,[a] min.$^{-1}$ × 10^5
1.53	0.0509	11.7
1.45	.102	12.7
2.06	.974	12.0
0.66	.040[b]	6.00
.71	.0772[b]	6.37
.10	.0795[b]	6.00
		$k_{iH}/k_{iD} \sim 2.0$

[a] Pearson and Dillon (ref. 1) report $k_i = 1 \times 10^{-4}$ min.$^{-1}$ at 34.9° for protium compound. [b] 1-Deutero-1-chloronitroethane.

Table II reports the initial first-order rate constants obtained for the hydrolytic release of chloride ion from both 1-chloronitroethane (k_{sH}) and its 1-deutero analog (k_{sD}) in water at 35.0°. These first-order rate constants were obtained by direct titration of released chloride ion and the rate runs were carried to approximately 25% completion in every case.

TABLE II

THE RATE OF CHLORIDE ION RELEASE BY 1-CHLORO- AND 1-DEUTERO-1-CHLORONITROETHANE IN WATER AT 35.0°

$[CH_3CHNO_2Cl]$, mole/l. × 10^2	k_s,[a] min.$^{-1}$ × 10^5
0.97	3.50
1.99	3.49
3.48	3.56
3.56	3.45
0.88[b]	1.70
2.76[b]	1.75
	$k_{sH}/k_{sD} \sim 2.0$

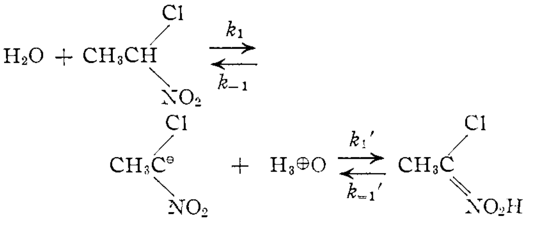
[a] Pearson and Dillon (ref. 1) report $k_s = 0.5 \times 10^{-4}$ for protium compound at 34.9°. [b] 1-Deutero-1-chloronitroethane.

The products of the hydrolysis of 1-chloronitroethane were accounted for in a quantitative fashion when the hydrolysis reaction was carried out in a sealed tube at 100°. These products consisted of one mole of hydrogen chloride and one mole of acetic acid per mole of 1-chloronitroethane consumed. The acetic acid was identified by conversion to its *p*-nitrobenzyl ester and by its characteristic potentiometric titration curve. Hydrogen chloride was determined by chloride ion analysis and by potentiometric titration of hydrogen ion. In addition to these products a considerable but undetermined amount of a colorless gas was produced which presumably was nitrous oxide. Nitrite ion was not present.

Discussion

Since the substitution of the 1-protium by deuterium produces an approximate twofold diminution in both rates of ionization and hydrolysis of 1-chloronitroethane at 35.0°, it may be concluded that the over-all hydrolysis reaction involves the breaking of a carbon–hydrogen bond prior to the expulsion of chloride ion. The near constant ratio of k_i to k_s which is equal to approximately 3.4 and which is obtained regardless of the isotopic nature of the reactant 1-chloronitroethane points up the fact that only a definite fraction of the molecules of 1-chloronitroethane which tautomerize to the *aci*-isomer react in such a manner as to produce chloride ion. All of these results are best rationalized in terms of the formulation (1) in which $k_{-1} \sim 2.4k_2$.

An additional piece of evidence also was obtained which indicates the correctness of this rationale. It was observed that freshly prepared aqueous solutions of 1-chloronitroethane initially gave only a very low rate of increase in conductance with time. However, this rate of increase of conductance increased as time progressed and finally became a linear function of time. Similarly, aqueous solutions of 1-chloronitroethane which had been employed in conductometric bromination rate determinations gave similar conductance *vs.* time curves following the consumption of the initially added bromine. These observations fit the proposed reaction scheme since the equilibria 2 are involved in the transformation of 1-chloronitroethane to its *aci*-isomer.



(2)

In these equilibria[3] k_1 and k_{-1} are small while k'_1 and k'_{-1} are large and k'_1/k'_{-1} may be of the order of 10^3. Thus, a solution which contains only very little *aci*-1-chloronitroethane will show a small initial conductance. However, as ionization (k_1 process) proceeds, the products of this ionization will be an equilibrium mixture of the solvolytically inert 1-chloronitroethane anion and the reactive *aci*-1-chloronitroethane. As a result of this situation, the first 1-chloronitroethane which ionizes will produce the electrolytes hydrogen ion and 1-chloronitroethane anion, but as these products accu-

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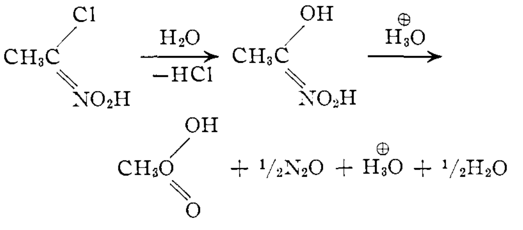
[3] See D. Turnbull and S. H. Maron, THIS JOURNAL, **65**, 212 (1943), for a discussion of similar equilibria.

mulate the concentration of *aci*-1-chloronitroethane will increase and the rate of appearance of the products of the hydrolysis of this material will also increase. Since these products are hydrogen ion, chloride ion and dissociated acetic acid, an enhancement in the rate of increase of conductance will occur until the concentrations of 1-chloronitroethane anion and *aci*-1-chloronitroethane reach the steady state concentrations of the reaction system. The length of time required to reach the steady state condition was roughly inversely proportional to the initial concentration of substrate. Figure 1 illustrates this point.

The products of the hydrolysis of 1-chloronitroethane may be explained on the basis of the reaction sequence 3 in which the proposed reaction



(3)

takes the course of the nucleophilic displacement of chloride ion by water followed by a Nef reaction[4] of the resulting *aci*-1-hydroxynitroethane.

Experimental

Materials.—The 1-chloronitroethane was a portion of material which had been purified previously for another study.[2] The 1-deutero-1-chloronitroethane was similarly a portion of previously prepared material.[2]

The solvent water employed in the conductometric experiments gave an infinite resistance reading in the apparatus employed and had been prepared by the passage of distilled water through a commercial Deeminizer ion exchange column.

Rates of Bromination.—The rates of bromination were determined using low concentrations of bromine (1×10^{-4} to 2×10^{-3} *M*) and much greater concentrations of 1-chloronitroethane or 1-deutero-1-chloronitroethane in conductivity water at 35.00 + 0.01°. Resistance readings were obtained in a low resistance conductivity cell using a Leeds and Northrup conductivity apparatus and a General Electric Type ST-2A oscilloscope as a null point indicator.

An accurately measured small volume of a standard aqueous bromine solution was added to a known volume of a 1-chloronitroethane solution prepared from a weighed amount of nitroalkane at zero time. Both solutions were thermostated previous to the time of mixing. Resistance readings were taken at various time intervals and conductance plotted *vs.* time. Linear plots were obtained up to the time at which all of the added bromine was consumed. Beyond this point the conductance remained constant for a few moments and then began to rise at a progressively greater rate until a new linear conductance *vs.* time curve was established. The curves of Fig. 1 are similar to those obtained under these conditions. The time, t, required for the consumption of the known added bromine $[Br_2]_0$, was used along with the initial nitroalkane concentration, $[RNO_2]_0$, to calculate the first-order ionization rate constant, k_1.

$$k_1 t = [Br_2]_0/[RNO_2]_0$$

The deuterated substrate was treated in an identical fashion as were the experiments which were carried out in the absence of bromine.

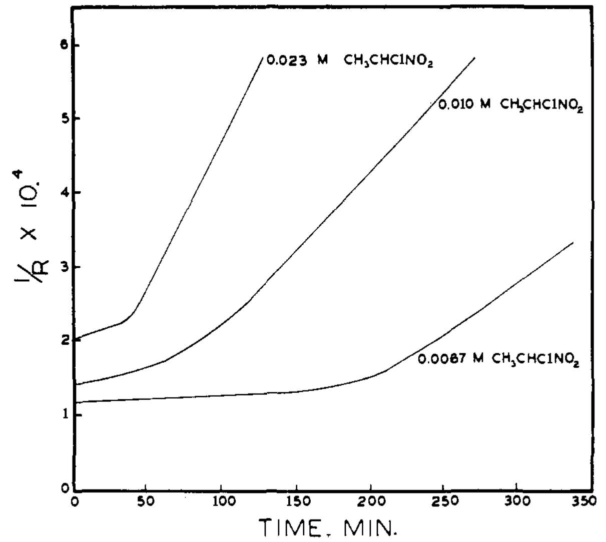


Fig. 1.—Conductivity *vs.* time curves for the hydrolysis of 1-chloronitroethane in water at 35.0°.

Rates of Hydrolysis.—Solutions of 1-chloronitroethane or 1-deutero-1-chloronitroethane were prepared in distilled water and thermostated at 35.00 ± 0.01°. Periodically, aliquots were withdrawn and chloride ion was titrated potentiometrically with 0.01 *N* standard silver nitrate solution using a Beckman model G *p*H meter with silver and calomel electrodes. The titration data were treated graphically and a correction was applied for the solubility of silver chloride. The reactions were carried to approximately 25% completion in every case and the first-order hydrolysis rate constants were obtained graphically from a plot of log [chloronitroethane] *vs.* time.

Product Analysis.—1-Chloronitroethane (1.180 g.) and 6 ml. of water were sealed in a glass tube and heated in a steam-bath for two weeks. The tube was then cooled to −80° and opened. A considerable quantity of colorless gas was released when the tube was opened. The contents were carefully washed into a 50-ml. volumetric flask and diluted to the mark with the distilled water.

A 10-ml. aliquot of the solution was titrated for chloride ion by the Mohr method after neutralizing with sodium hydroxide. The solution was found to be 0.215 *M* in chloride ion (99.7% of theoretical for complete hydrolysis). The concentration of hydrogen ion was found to be 0.427 *M* by the titration of another 10-ml. aliquot to a phenolphthalein end-point with standard sodium hydroxide.

A second acid titration was carried out on a 10-ml. aliquot using a Beckman *p*H meter. A break occurred at *p*H 3.1 indicating the solution to be 0.214 *M* in a strong acid. Another very sharp break occurred just beyond *p*H 7 giving a total hydrogen ion concentration of 0.427 *M*. A qualitative test for nitrite ion was negative.

The weak acid present in the reaction mixture was shown to be acetic acid by the partial neutralization of a 20-ml. portion of the reaction mixture with 10% sodium hydroxide solution followed by the addition of 0.5 g. of *p*-nitrobenzyl bromide and sufficient ethanol to give solution at reflux. The solution was refluxed several hours and cooled with ice. The material which crystallized melted at 72.5°[5] and gave an infrared spectrum identical with that of authentic *p*-nitrobenzyl acetate.

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[4] See M. F. Hawthorne, THIS JOURNAL, **79**, 2510 (1957), for a recent discussion of the mechanism of this reaction.

[5] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1947, report the melting point of *p*-nitrobenzyl acetate to be 78°.