and any methyl iodide formed may react with HI[18]

$$CH_3I + HI \longrightarrow CH_4 + I_2$$

so that the resulting HI is below the sensitivity of the mass spectrometer.

The evidence from the reaction in the presence of propylene sheds some light on the question of whether the propylene reacts with CH_3 or with CH_3COCH_2 to inhibit the decomposition. Since the CD_3H/CD_4 ratio is elevated in the presence of propylene, the CD_3 prefers to react with propylene rather than with acetone. The residual allyl radical apparently is unreactive and reacts only with another allyl radical. This picture appears to explain propylene inhibition if it is noted that acetonyl radicals and methyl radicals act to propagate the chains. If the methyl radicals preferentially abstract hydrogen from propylene, some chains are broken and the average chain length is shortened.

The percentage of CO_2 is not appreciably changed when as much as 33% CO is present during pyrolysis. CO_2 is thus probably formed from the decomposition of ketene.[19]

Acknowledgment.—The authors wish to thank Dr. S. R. Smith for development of mass spectrometer techniques employed in this research, and Professor Milton Burton for many stimulating discussions. The authors also wish to thank Mr. E. A. Fay for his assistance in the statistical analysis of the data.

[19] W. D. Walters, private communication.

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

The Kinetics of the Base-catalyzed Deuterium Exchange of Chloroform in Aqueous Solution[1,2]

BY JACK HINE, ROY C. PEEK, JR., AND BILLY D. OAKES

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The kinetics of the reaction of deuterochloroform with sodium hydroxide in homogeneous aqueous solution has been studied by infrared measurements of the isotopic content of the haloform. Rate constants at 0, 20.1 and 35° and values of the heat and entropy of activation have been determined. The reaction appears to be only slightly subject to general base catalysis and has been found to proceed very nearly half as fast as the analogous reaction of chloroform with sodium deuteroxide in deuterium oxide solution.

As part of a study of the relative importance of inductive and resonance effects on acidity, and also in relation to the mechanism of the basic hydrolysis of chloroform,[3] we became interested in studying the rate of the base-catalyzed deuterium exchange of chloroform. By use of a heterogeneous mixture of chloroform and alkaline heavy water, Horiuti and Sakamoto have shown that the reaction is rapid compared to the basic hydrolysis.[4] However, we were interested in learning the rate constants and heat and entropy of activation in homogeneous solutions, and something about the kinetic isotope effect and existence of general base catalysis. For economy we have in most cases used deuterochloroform as the reactant and "ordinary" water as the solvent.

Experimental

Reagents.—Deuterochloroform was prepared from chloral and 99.8% deuterium oxide (obtained from the D. A. Stuart Oxygen Co. on allocation from the Atomic Energy Commission) by a modification of the method of Boyer, Bernstein, Brown and Dibeler,[5] fractionated through a 30-in. column packed with glass helices and stored in a number of small sealed glass tubes under nitrogen until used. The material used had a boiling point range of less than 0.2° and an isotopic purity of 98.5% as determined by the spectroscopic method described in the next section.

Carbonate-free sodium hydroxide solutions and "isoöctane" (2,2,4-trimethylpentane) of greater than 99 mole per cent. purity were used. The methylamine was freshly distilled from a 25% aqueous solution of the C.P. material into distilled water.

Analysis.—The chloroform–deuterochloroform mixtures were analyzed by infrared measurements using a Perkin-Elmer Model 21 instrument. The deuterochloroform was analyzed for chloroform by measurements on the 8.233 μ band in carbon disulfide solution and on the 13.085 μ band in isoöctane solution. If it is assumed that pure deuterochloroform has no absorption at either of these wave lengths, these analyses show the presence of 1.6 ± 0.1% and 1.4 ± 0.1% chloroform, respectively, and the material was therefore taken to be 98.5% isotopically pure.[6]

The analyses for kinetic runs were made on isoöctane solutions at two absorption maxima for deuterochloroform and one for chloroform. The Beer–Lambert law was shown to hold in all cases, and the following molecular extinction coefficients (and average deviations), determined with the resolution control set at 960 (corresponding to slit schedule 3 for earlier machines), were used[7]

$$\epsilon^{CDCl_3}_{11.005} = 376 \pm 2 \quad \epsilon^{CDCl_3}_{13.085} = -0.006 \pm 0.002 \quad \epsilon^{CDCl_3}_{13.536} = 731 \pm 4$$

$$\epsilon^{CHCl_3}_{11.005} = -0.010 \pm 0.003 \quad \epsilon^{CHCl_3}_{13.085} = 915 \pm 8 \quad \epsilon^{CHCl_3}_{13.536} = 25.3 \pm 0.4$$

The deuterochloroform concentration was the average of that determined at its two maxima, the average deviation being about 1%. All measurements were made in the same cell, the solutions being diluted if necessary to bring the optical density in the range 0.2–0.6.

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[1] This study was carried out as part of a project sponsored by the Atomic Energy Commission.

[2] Paper II in the series "The Mechanism of the Base Catalyzed Decomposition of Haloforms." For Paper I see ref. (3).

[3] J. Hine, THIS JOURNAL, **72**, 2438 (1950).

[4] Y. Sakamoto, *J. Chem. Soc. Japan*, **57**, 1169 (1936); J. Horiuti and Y. Sakamoto, *Bull. Chem. Soc. Japan*, **11**, 627 (1936).

[5] W. M. Boyer, R. B. Bernstein, T. L. Brown and V. H. Dibeler, THIS JOURNAL, **73**, 770 (1951).

[6] If the assumption is incorrect the isotopic purity is even higher.

[7] The extinction coefficients listed for deuterochloroform are for the isotopically pure material. All extinction coefficients were determined from the optical density of a standard solution compared with pure solvent in the same cell and are therefore "apparent" extinction coefficients, the negative values corresponding to wave lengths at which the solvent absorbs more strongly than the haloform.

Kinetic Runs.—The kinetic runs were made by a procedure of which the following point is an example. By use of a 0.25-ml. "tuberculin" syringe graduated in 0.01 ml., 0.10 ml. of the 98.5% deuterochloroform was dissolved in 90 ml. of boiled distilled water under nitrogen in a 100-ml. volumetric flask. When the material had reached thermal equilibrium in a 35.0 ± 0.1° bath, 5 ml. of 0.06056 *N* sodium hydroxide solution also at 35° was added and the flask shaken vigorously. At a recorded time the reaction was stopped by the addition of 3 ml. of 0.114 *N* hydrochloric acid and the resultant solution was extracted with about 20 ml. of isoöctane. The isoöctane solution was dried over indicating silica gel[8] and analyzed as described. Blank experiments showed that the procedure used did not interfere with this analysis.

For the runs in deuterium oxide solution, only 9 ml. of solvent, 0.02 ml. of chloroform and 4 ml. of isoöctane were used.

Results

The reaction mechanism is almost undoubtedly the following

$$CDCl_3 + OH^- \xrightarrow{\text{slow}} CCl_3^- + HOD$$

$$CCl_3^- + H_2O \xrightarrow{\text{fast}} CHCl_3 + OH^-$$

the first step being rate-controlling. Neglecting reversibility (the molar ratio of water to haloform being about 4000:1 in most runs) the rate equation should therefore be

$$v = k[OH^-][CDCl_3]$$

Since the rate constant for the basic hydrolysis of chloroform under the conditions here employed is never as much as 0.05% of that for the deuterium exchange,[9] the change in the hydroxide concentration is almost negligible during the main course of the deuterium exchange. Therefore, since the reaction will be pseudounimolecular

$$k[OH^-] = \frac{2.303}{t} \log \frac{[CDCl_3]_0}{[CDCl_3]_t} \qquad (1)$$

If p is the isotopic purity of the haloform used, it may be shown that

$$[CDCl_3]_t = \frac{[CDCl_3]_0}{p([CHCl_3]_t/[CDCl_3]_t + 1)} \qquad (2)$$

Substituting 2 in 1

$$k[OH^-] = \frac{2.303}{t} \log \left(p + p\,\frac{[CHCl_3]_t}{[CDCl_3]_t}\right) \qquad (3)$$

From this equation it is seen to be unnecessary to know the absolute concentration of either reactant or product, but only the ratio $[CHCl_3]_t/[CDCl_3]_t$ at a given time. Thus, although the isoöctane extraction of the haloform is not absolutely quantitative, the only error produced thereby will be a very minor one due to isotopic fractionation. It may be shown that to the extent to which the reaction is actually first order, an error in the determination of the isotopic purity of the haloform used will have no effect on the evaluation of the rate constant by equation 3.

The data obtained justified the use of equation 3, since the average deviation of rate constants within a run was in all cases less than 3% (for a typical run see Table I) and since a thirteen-fold increase in the hydroxide ion concentration changed the rate constant by less than 8% (see Table II, no. 4 and 5). In all cases the rate constants showed a slight tendency to fall as the reaction proceeded. This was probably due to (1) a small amount of hydrolysis of chloroform and perhaps also phosgene present as an impurity, (2) the small amount of haloform in the vapor space of the reaction vessel, and at 0° (3) the small increase in temperature which occurs when the reaction vessel is briefly removed from the bath for shaking at the beginning of the reaction.

TABLE I

DEUTERIUM EXCHANGE OF $CDCl_3$ IN WATER AT 35.0°

$[CDCl_3] \sim 0.0130$, $[OH^-] = 0.003136$

Time, sec.	$[CHCl_3]_t/[CDCl_3]_t$	100 k, l. sec.$^{-1}$ mole^{-1}
125	0.358	74.3
325	1.172	74.6
495	2.152	73.0
690	3.833	72.1
	Av.	73.5 ± 1.0

TABLE II

RATE CONSTANTS FOR DEUTERIUM EXCHANGE OF $CDCl_3$ IN WATER[a]

No.	Temp., °C.	No. of points	100 k, l. sec.$^{-1}$ mole^{-1}
1	0.0	8	0.470 ± 0.010
2	20.1	9	10.2 ± 0.2
3	35.0	4	73.5 ± 1.0
4[b]	0.0	4	0.462 ± 0.006
5[c]	0.0	5	0.498 ± .008
6[d]	20.0	3	20.7 ± .2

[a] $[CDCl_3]_0 \sim 0.013$ $[OH^-] \sim 0.0031$, except where otherwise stated. [b] $[OH^-] = 0.003136$, $[NaClO_4] = 0.0380$. [c] $[OH^-] = 0.04100$. [d] D_2O solvent, $[CHCl_3] \sim 0.026$.

From the tabulation of Bonhoeffer, Geib and Reitz[10] of rate constants for the removal of carbon-bound hydrogen by deuteroxide ions in deuterium oxide solution at 25°, it may be seen that the hydrogen atom in chloroform is about as reactive as those in acetaldehyde or acetone.

The heat and entropy of activation were calculated from the absolute rate equation[11]

$$k = \frac{\mathrm{k}T}{h}\, e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

yielding the values $\Delta H^{\ddagger} = 23.8$ kcal./mole and $\Delta S^{\ddagger} = 18.2$ e.u./mole for the 0–20.1° temperature interval and $\Delta H^{\ddagger} = 23.2$ kcal./mole and $\Delta S^{\ddagger} = 16.1$ e.u./mole for the 20.1–35° interval.

The possibility of general base catalysis was investigated by the use of a methylamine buffer. In this case the kinetic equation should take the form

$$k[OH^-] + k'[CH_3NH_2] = \frac{2.303}{t} \log \left(p + p\,\frac{[CHCl_3]_t}{[CDCl_3]_t}\right) \qquad (4)$$

In the presence of 0.1105 *N* methylamine and 0.0812 *N* methylamine hydrochloride at 35.0°

$$k[OH^-] + k'[CH_3NH_2] = (7.49 \pm 0.08) \times 10^{-4} \qquad (5)$$

while with the same buffer ratio at a concentration

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[8] Very little silica gel is needed and no more should be used since it adsorbs the haloform. Even much larger amounts of silica gel gave no isotopic fractionation, within experimental error, however.

[9] J. Hine and A. M. Dowell, Jr., unpublished data.

[10] K. F. Bonhoeffer, K. H. Geib and O. Reitz, *J. Chem. Phys.*, **7**, 664 (1939).

[11] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

15% as large (the ionic strength being kept constant with 0.0690 N sodium perchlorate)

$$k[\mathrm{OH}^-]' + k'[\mathrm{CH_3NH_2}]' = (6.48 \pm 0.08) \times 10^{-4} \quad (6)$$

From the known strengths of the methylamine buffer solutions used and the value of k from Table II, No. 3 (no. 1 and 4 show that the ionic strength effect is not large), equations 5 and 6 can be solved simultaneously with two ionization constant expressions for methylamine to yield the results

$$[\mathrm{OH}^-] = 9.7 \times 10^{-4} \qquad [\mathrm{OH}^-]' = 8.7 \times 10^{-4}$$
$$k' = 3 \times 10^{-4} \qquad K_i^{\mathrm{CH_3NH_2}} = 7.27 \times 10^{-4}$$

The value for the ionization constant of methylamine is in surprisingly good agreement with a value 7.24×10^{-4} interpolated from the data of Everett and Wynne-Jones.[12] While we believe that we have demonstrated general base catalysis for the reaction, the value of k', having been obtained from a small difference between two large numbers, may be considerably in error.

In relation to the kinetic isotope effect, the rate of exchange of chloroform in alkaline 99.8% deuterium oxide solution was studied. Although reversibility is greater in this case, it is still minor compared to the experimental error and a kinetic equation analogous to 3 was used to calculate the rate constant shown in Table II, No. 6. Although this rate constant is more than twice that for deuterochloroform in protium oxide solution, part of the increased reactivity may be due to the generally increased reactivity of the deuteroxide ion in deuterium oxide solution over the hydroxide ion in aqueous solution.[13]

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[12] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc. (London)*, **A177**, 499 (1941).

[13] S. H. Maron and V. K. La Mer [THIS JOURNAL, **60**, 2588 (1938)] point out increases of 39–42, 36, 33, 22 and 20% for five different reactions.

ATLANTA, GEORGIA

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

Mechanism of the Homogeneous Alkaline Decomposition of Cyclotrimethylenetrinitramine: Kinetics of Consecutive Second- and First-order Reactions. A Polarographic Analysis for Cyclotrimethylenetrinitramine[1]

BY WALTER H. JONES

RECEIVED APRIL 27, 1953

The mechanism and kinetics of the reaction of methoxide ion with cyclotrimethylenetrinitramine in absolute methanol have been studied, both with and without added neutral salt, in the temperature range 19.00–44.93°. The stoichiometry and kinetics were interpreted in terms of the mechanism given in steps 1–4 where the base C^- is of intermediate strength, titratable at neutral but not at alkaline pH. From knowledge of k_1 and the total rate of production of nitrite, it was possible by mathematical analysis to evaluate k_2. The experimental rate of production of nitrite could then be fitted satisfactorily by means of k_1 and k_2 for at least 85% of the reaction. Added neutral salt depressed k_1 slightly, but had a larger positive effect on k_2. Enthalpies and entropies of activation are reported, and the results interpreted in terms of possible structures for the intermediates. A polarographic analysis for cyclotrimethylenetrinitramine has been developed, valid to ±2.5%. This compound gave at least three polarographic waves in absolute methanol at pH 7.4 (borate buffer) and 30.1°. The first, $E_{1/2} = -0.811 \pm 0.001$ v. (*vs.* S.C.E.) was used for analytical purposes; the concentration was, in the range employed, linear with diffusion current.

Somlo[2] has identified a number of products of the heterogeneous decomposition by hot concentrated aqueous alkali of the high explosive cyclotrimethylenetrinitramine (hereinafter called RDX). While the present study was in progress, Epstein and Winkler[3] reported briefly on the homogeneous decomposition in aqueous acetone but did not determine products or undertake a detailed kinetic study. The present paper describes an investigation of the stoichiometry and kinetics of the homogeneous reaction in methanol solution.

Since the initial reaction of secondary nitramines with alkali has been reported to be the elimination of nitrous acid,[4–6] we have studied the production of nitrite ion, destruction of RDX, and disappearance of alkali during the course of the reaction. Methanolic solutions of potassium hydroxide and both sodium and lithium methoxides were employed as bases; for purposes of illustration, methoxide ion will be used in subsequent formulations.

All of the kinetic and stoichiometric results could be rationalized in terms of the mechanism

$$\mathrm{RDX} + (\mathrm{OCH_3}^-) \xrightarrow{k_1} \mathrm{A} + \mathrm{CH_3OH} + (\mathrm{NO_2}^-) \quad (1)$$

$$\mathrm{A} + (\mathrm{OCH_3}^-) \xrightarrow{\text{fast}} (\mathrm{B}^-) + \mathrm{CH_3OH} \quad (2)$$

$$\mathrm{B}^- + (\mathrm{OCH_3}^-) \xrightarrow{\text{fast}} (\mathrm{C}^=) + \mathrm{CH_3OH} \quad (3)$$

$$(\mathrm{C}^=) \xrightarrow{k_2} \mathrm{D}^- + (\mathrm{NO_2}^-) \quad (4)$$

Here $C^=$ is a base of intermediate strength, quantitatively titratable at neutral (brom thymol blue) but not at alkaline (phenolphthalein) pH. B^- and D^- are weaker bases which build up late in the reaction at the expense of $(\mathrm{OCH_3}^-)$ and lead to a

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[1] Material supplementary to this article has been deposited as Document number 4104 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[2] F. Somlo, *Z. ges. Schiess-u. Sprengstoffw.*, **35**, 175 (1940); *C. A.*, **35**, 319¹ (1941).

[3] S. Epstein and C. A. Winkler, *Can. J. Chem.*, **29**, 731 (1951).

[4] A. P. N. Franchimont and H. van Erp, *Rec. trav. chim.*, **14**, 224 (1895).

[5] H. van Erp, *ibid.*, **14**, 48, 242, 327 (1895); **15**, 166 (1896); *Ber.*, **30**, 1251 (1897).

[6] A. H. Lamberton, *Quart. Rev.*, **5**, 75 (1951).