

solution it gave mesitoic acid, m.p. 155°. *Trichloromethylmesitylene* was prepared according to the method of Hart and Fish⁴ by slowly adding 30 g. of mesitylene in 50 ml. of carbon tetrachloride to a mixture of 67 g. of aluminum chloride in 100 ml. of carbon tetrachloride. The reaction was carried out at room temperature over a total period of 5 hr. The mixture was poured onto 5% HCl-ice water and dried over CaCl₂. The CCl₄ solvent was removed under reduced pressure and the compound was distilled *in vacuo* (b.p. 115° at 2 mm.). *Anal.* Calcd.: C, 50.56; H, 4.67; Cl, 44.77. Found (Bernhardt, Max Planck Institut): C, 50.7; H, 4.70; Cl, 47.7.

Anhydrous hydrogen chloride was prepared by bubbling HCl from a cylinder through 98% sulfuric acid, then through a tower packed with glass wool, and finally through a cold trap. The results obtained for HCl dried in this way were the same as those obtained when HCl was dried by passing it through a long tube packed with magnesium perchlorate. The concentration of HCl in the conductometric experiments was determined by weighing the conductivity cell before and after HCl was slowly bubbled into the sulfuric acid contained in it. Freezing point depressions of HCl solutions were determined in a conventional cryoscope on solutions which were transferred from the conductivity cell.

The preparation of 100% sulfuric acid, the apparatus, and the method of carrying out the cryoscopic and conductometric measurements and the acid-base conductometric titrations have been described previously.^{11,14,15}

(14) R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2473 (1950).

Cryoscopic ν -factors were obtained as has been described previously¹⁶ from the equation

$$\nu = \theta(1 - 0.098ms)/(6.12m - m_a/m)$$

where m is the molal concentration of solute, θ is its freezing point depression calculated from the freezing point of hypothetical undissociated acid (10.625°), s is the number of moles of sulfuric acid used up in the ionization of 1 mole of solute, and $m_d = m_\alpha + m_\beta$, where m_α is the total concentration of autoprotolysis ions and m_β is the total concentration of ionic dehydration ions, resulting from incomplete repression of the self-dissociation of the solvent. The conductometric γ -factors were obtained by comparison of the concentrations of solute and potassium hydrogen sulfate or hydronium hydrogen sulfate which give equal specific conductivities.⁷

The ultraviolet-visible spectra were recorded on a Perkin-Elmer 250 spectrometer and a Bausch and Lomb 505 spectrometer. N.m.r. spectra were measured using a Varian Associates A-60 spectrometer.

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(15) R. J. Gillespie, J. V. Oubridge, and C. Solomons, *ibid.*, 1804 (1957).

(16) S. J. Bass, R. J. Gillespie, and E. A. Robinson, *ibid.*, 821 (1960)

The Effect of Pressure on the Hydrolysis of Chloroform, Chlorodifluoromethane, and 3-Chloro-3-methylbutyne. The Nature of the Intermediates¹

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The effects of hydrostatic pressure on the base-catalyzed hydrolysis of chloroform, chlorodifluoromethane, and 3-chloro-3-methylbutyne, as well as the neutral hydrolysis of the latter compound, have been measured over a range of 6-7 kbars. The activation volumes are +16, +8.5, +2, and -15 cm.³/mole, respectively. It is concluded that these values support the B1 mechanism, α -dehydrohalogenation, the B1 mechanism, and an S_N1 mechanism for these respective reactions; the positive, but rather small volume change accompanying the base-promoted reaction of 3-chloro-3-methylbutyne strongly suggests that the incipient intermediate carbene has a highly dipolar structure.

(1) For a preliminary account of this work, see W. le Noble and M. Duffy, *J. Am. Chem. Soc.*, 86, 4512 (1964).

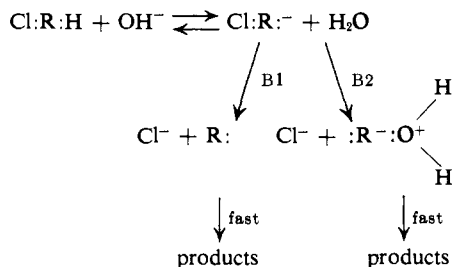
In the past few years increasing use has been made of liquid-phase, high-pressure reactions as a tool for learning details of reaction mechanisms otherwise not easily accessible.² Among such details, particularly important are the progress of bond formation and breakage and concomitant compression or decompression in the solvent surrounding the reacting molecules. One of the problems that can thus be solved is whether or not the transition state leading to an unstable intermediate involves a solvent molecule covalently bound. In essence, the technique works

(2) For recent reviews, see (a) S. D. Hamann, "Physico-Chemical Effects of Pressure," Academic Press Inc., New York, N. Y., 1957, Chapters 8 and 9; (b) E. Whalley, "Advances in Physical Organic Chemistry," Vol. 2, V. Gold, Ed., Academic Press Inc., New York, N. Y., 1964; (c) S. D. Hamann, *Ann. Rev. Phys. Chem.*, 15, 349 (1964).

about as follows. Experimental knowledge of the effect of pressure on the rate constant allows an estimate to be made of the quantity ΔV^* , which is the difference in molar volume between the transition state and the reactants; this activation volume is determined, with a precision of about 1 cm.³, by the relation $\Delta V^* = -RT(\partial \ln k/\partial p)$. A reasonable estimate is made of the volume change that would occur along the reaction coordinate if the transition state included covalently bound solvent, and what it would be if the solvent molecules remained at van der Waals distances. Both ΔV^* data from other reactions with well known, simple mechanisms, and density data of stable compounds are useful in making such estimates. Comparison of the experimental and theoretical values then permits a choice to be made. The principal alternative method for solving such problems is a study of the correlation of the rate constant with the appropriate acidity function³; however, this method has led to erroneous conclusions in a number of cases.^{2b,4} To date, measurements of the activation volume in this type of reaction have been applied only to acid-catalyzed hydrolysis, although in principle it should be useful in a wide variety of reactions. The present paper reports such a study of several reactions considered to proceed through carbene intermediates.

Discussion

The common aspects of the reactions discussed below are a preequilibrium with OH⁻ to give an intermediate anion, which then loses chloride with or without simultaneous bonding of the carbene to a solvent molecule (B1 or B2 mechanism).



A. Chloroform. Hine has studied⁵ this reaction in detail and reviewed⁶ the evidence, of which, however, very little has a bearing on the distinction between the B1 and B2 mechanisms. It has been shown⁷ that in the base-catalyzed methanolysis k_2 is proportional to h_- , suggesting that solvent molecules are not bound in the transition state, which therefore should be a carbene rather than an O-ylid.

The effect of pressure can be estimated in either of two ways: (1) from a direct comparison of the molar volumes of the various possible transition states with those of the original reactants, and (2) by tracing the volume changes during the reaction through the various intermediate stages to the most likely transition states. The former procedure has the advantage of directness; the latter method involves some extra steps and there-

fore extra errors, which cancel, however. If the latter procedure is followed, it is first of all necessary to consider the possibility of a change in the equilibrium concentration of CCl_3^- . Since in this equilibrium step neither the number of ionic charges nor the number of molecules changes, ΔV is likely to be very small. Experimental support for this view derives from two sources. Fanjung⁸ measured ΔV for the ionization of nine acids in water and found a $\Delta V_{\text{av}} = -11.4$ cm.³/mole. The difference between the several values is a measure of ΔV for the equilibrium step considered here; Fanjung's data show a spread of $\Delta\Delta V_{\text{av}} = 1.2$ cm.³/mole. Similarly, Hamann and Lim⁹ found that, for the ionization of seven amine bases in water, $\Delta V_{\text{av}} = -27.7$ cm.³/mole with a $\Delta\Delta V_{\text{av}} = 1.1$ cm.³/mole, and for six acids,¹⁰ $\Delta V_{\text{av}} = -13.5$ cm.³/mole with a $\Delta\Delta V_{\text{av}} = 2.2$ cm.³/mole. It is clear from these data that ΔV for the equilibrium is small and may be neglected, though it raises the uncertainty in the estimated values of ΔV^* to about 2–3 cm.³/mole.

The rate-determining step in the B1 mechanism has as its main features a stretched C–Cl bond, a negative charge in the process of being transferred from C to Cl and therefore probably somewhat more dispersed than before, and surrounding water molecules in the process of reorganization from the old center of charge to the new. All three of these changes would be expected to lead to a net increase in total volume. The first one should bring about an increase of about 10 cm.³/mole if the decomposition of di-*t*-butyl peroxide is used as a guide.¹¹ The other two contributions are more difficult to appraise. Drude and Nernst¹² first showed that charge dispersal should lead to volume expansion of the surrounding dielectric; Whalley^{2b} has interpreted data on the pressure induced changes in the hydrolysis constant of phenoxide ion⁹ as a consequence of charge dispersal in this ion, which in that case makes a contribution of about +5 cm.³/mole.¹³ An alternative way to make an estimate is to compare the reaction with the decomposition of benzenediazonium ion; all three contributions mentioned before are represented here. The activation volume for that reaction is about +10 cm.³/mole.¹⁴ In the present reaction

(8) I. Fanjung, *Z. physik. Chem.* (Leipzig), **14**, 673 (1894).

(9) S. D. Hamann and S. C. Lim, *Australian J. Chem.*, **7**, 329 (1954).

(10) Two acids listed by these authors were left out of this estimate: water, for which $\Delta V = -23.4$ cm.³/mole, and carbonic acid, for which $\Delta V = -29.0$ cm.³/mole. The former is expected to have a higher than normal value because the anion has a more concentrated charge than the other acids, a point further discussed in the text; the latter is expected to have a higher than normal value because ΔV in this case is a measure of two processes, the hydration of carbon dioxide and the ionization of the product carbonic acid. Indeed, judging by the equilibria involved and by the magnitude of ΔV , carbonic acid would be more properly classified with the amine bases studied by Hamann and Lim. A similar point has been made by Ellis in his studies of both carbonic acid and sulfurous acid: A. J. Ellis and D. W. Anderson, *J. Chem. Soc.*, 1765 (1961).

(11) C. Walling and A. Metzger, *J. Am. Chem. Soc.*, **81**, 5365 (1959).

(12) P. Drude and W. Nernst, *Z. physik. Chem.*, **15**, 79 (1894).

(13) Dr. H. Conroy, in a private discussion, pointed out that the charge in CCl_3^- may not be fully concentrated on carbon, but may in fact be distributed in the d-orbitals of the three chlorine atoms. If that is true, the charge would be more concentrated in the transition state. However, an equal but opposite error would also have been made in the estimate of ΔV for the equilibrium. It should be remembered that basically a comparison is being made here between the B1 transition state and hydroxide ion and chloroform, that charge dispersal occurs going from the latter to the former, and that charge dispersal in the intermediate anion is of no real consequence. These facts should serve to underline the remarks made in the text concerning the appraisal of ΔV^* .

(14) K. R. Brower, *J. Am. Chem. Soc.*, **82**, 4535 (1960).

(3) See, e.g., J. A. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **80**, 4162 (1958), and several references quoted in that paper.

(4) W. J. le Noble and M. Duffy, *J. Phys. Chem.*, **68**, 619 (1964).

(5) J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).

(6) J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, pp. 36–42.

(7) R. A. M. O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 5035 (1963).

Table I. The Effect of Pressure on the Rate Constants of Basic Hydrolysis of Chloroform, Chlorodifluoromethane, and 3-Chloro-3-methylbutyne, and on the Relative Densities of the Media Employed, at 25°

Pressure, kbars	$k_2 \times 10^6$ l./mole sec.			$k_1 \times 10^6$ sec. ⁻¹ ^d		Density ^a	
	CHCl ₃ ^a	CHF ₂ Cl ^b	C(CH ₃) ₂ - C≡CH ^c	C(CH ₃) ₂ - CC≡CH ^e	NaOH ^f	EtOH ^g	
0.00	7.39	93.8	45.2	0.23	1.039	0.850	
1.07	3.53	73.6	49.7	0.38	1.081	0.908	
2.13	2.15	51.4	39.5	0.74	1.113	0.941	
3.17	1.62	39.7	45.5	1.27	1.138	0.970	
4.21	1.08	32.0	40.4	2.04	1.162	0.994	
5.24	0.66	27.8	32.3	2.57	1.183	1.015	
6.45	0.70	24.4	42.1	3.09	1.205	1.036	
7.14	4.40	...	1.048	

^a Followed to about 70% completion; each value is the average of four measurements which agree to about 5%. ^b Followed to about 60% completion; each value is the average of five measurements which agree to about 5%. ^c Followed to about 70% completion; each value is the average of five measurements which agree to about 20%. ^d d is given in g./cm.³. ^e Followed to about 20% completion; each value is the average of four measurements which agree to about 15%. ^f Aqueous, 1.17 M. ^g Containing 20 vol. % water.

ΔV^* might be expected to be somewhat larger; it is undoubtedly more endothermic and according to the Hammond postulate should have proceeded further toward bond breakage when the free energy maximum is reached. Over-all, a positive value of about 15 ± 5 cm.³/mole seems a reasonable estimate. On the other hand, the incipient formation of an oxonium ylid, which is one way in which displacement of Cl⁻ by

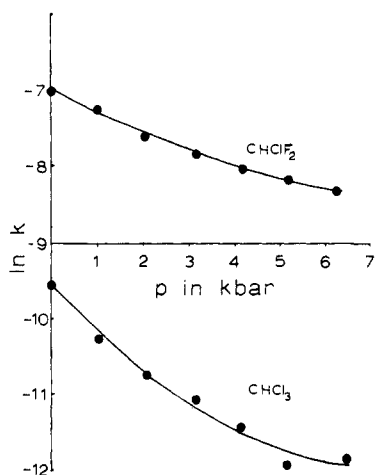


Figure 1. The effect of pressure on the rate constants of the hydrolyses of chloroform and chlorodifluoromethane, in water at 25°.

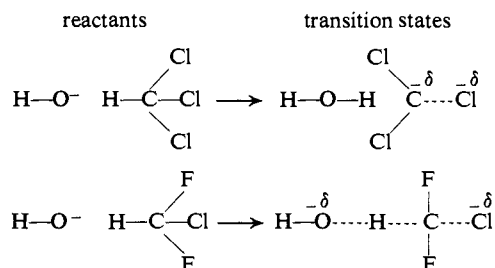
water might be visualized, is best compared with an ordinary S_N2 displacement. Such reactions have been studied in a number of high-pressure laboratories,¹⁵ and on the average are found to have an activation volume of -5 to -10 cm.³/mole.

In the present case, ΔV^*_0 was found to be $+16 \pm 1$ cm.³/mole. The hydrolysis of chloroform is therefore clearly an extreme case of a B1 mechanism, suggesting, in fact, that the transition state leads to free CCl₂. The details of the measurements are described below in the experimental part; it should be mentioned at this point that in the determination of the rate constants appropriate corrections were made for the heat of compression and for the compressibility of the solvent (see Table I). The graph from which ΔV^*_0 is de-

(15) (a) H. G. David and S. D. Hamann, *Trans. Faraday Soc.*, **50**, 1188 (1954); (b) J. Koskikallio and E. Whalley, *ibid.*, **55**, 815 (1959); (c) M. W. Perrin, *ibid.*, **34**, 144 (1938).

termined is shown in Figure 1. The curve obeys the least-squares expression $\ln kp/k_0 = -0.637p + 0.0413p^2$, where p is in kbars. The value for k_2 at 1 atm. and at 25°, $k_2 = 7.39 \times 10^{-5}$ l./mole sec., may be compared with the reported¹⁶ value at 1 atm. at 35°, $k_2 = 23.5 \times 10^{-5}$ l./mole sec.

B. Chlorodifluoromethane. In his extensive studies of the hydrolysis reactions of trihalomethanes, Hine found that in some cases the competition between reprotonation of the intermediate anion and the loss of a halide ion is markedly in favor of the latter; the reaction then amounts to an α -dehydrohalogenation. Chlorodifluoromethane is a good example of this mechanism, partly because fluorine is less effective than chlorine in stabilizing the anion, and partly because it is more effective in stabilizing the carbene.¹⁷ In order to estimate the pressure coefficient of this reaction, reference is made to the following schematic presentation of the difference between the chloroform and chlorodifluoromethane reactions.



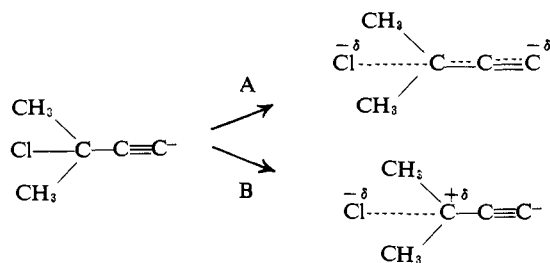
The fact that in the latter case OH⁻ is part of the transition state, whereas with chloroform this complex has already completely separated, suggests that in α -dehydrohalogenation the activated complex is more compact, and consequently that the activation volume is smaller than in the B1 reaction. The observed value, $\Delta V^*_0 = +8.4$ cm.³/mole, is entirely reasonable on these grounds, and it is concluded that knowledge of ΔV^*_0 permits a choice between the two. The result also rules out the possibility of rate-controlling carbanion formation. In that case, approach by OH⁻ is not accompanied by any lengthening of the C-Cl bond, and hence the activation volume would be still smaller and might even be negative. The curve

(16) J. Hine and A. M. Dowell, *J. Am. Chem. Soc.*, **76**, 2688 (1954).

(17) Which has in fact allowed the determination of its infrared spectrum: D. E. Milligan, D. E. Mann, M. E. Jacox, and R. A. Mitsch, *J. Chem. Phys.*, **41**, 1199 (1964).

shown in Figure 1 summarizes the experimental findings; it obeys the expression $\ln kp/k_0 = -0.339p + 0.0101p^2$, where p is in kbar units. The literature value¹⁸ for k_2 at 1 atm. at 25° is 8×10^{-4} l./mole sec.

C. *3-Chloro-3-methylbutyne*. The hydrolysis of this compound has attracted much attention; the conclusion that this reaction goes through a carbene intermediate is due to Hennion,¹⁹ Hartzler,²⁰ and Shiner,²¹ and is based primarily on studies of the kinetics and on product analysis. Measurement of the activation volume is somewhat complicated by the fact that simultaneous, slow solvolysis takes place. If this reaction goes through a carbonium ion, considerable rate enhancement by the application of pressure is expected because of the electrostriction of the solvent by the developing ions. If at the same time the carbene reaction is retarded as much as in the chloroform study, it is conceivable that the solvolysis, normally negligibly slow compared to the carbene reaction, might overtake and surpass the latter at high pressures. For this reason the hydrolysis rate was measured over the entire pressure range in both acidic and basic solutions. In acid solution, the activation volume was determined as -15.7 cm.³/mole, a value roughly expected for an S_N1 reaction. Thus, an average ΔV^*_0 of -15 cm.³/mole can be calculated from data obtained by Hamann for the solvolysis of several tertiary halides in aqueous alcohol.^{15a,22} The solvolysis reaction entered only as a small correction in the calculation of the rate constants of the base-promoted reaction at high pressures. The net effect of pressure on this reaction is remarkably small: $\Delta V^*_0 = +1.8$ cm.³/mole. Evidently there is a major difference between the rate-limiting steps of the 3-chloro-3-methylbutyne and chloroform reactions. The most reasonable interpretation is that when the chloride leaves the negative charge is not simply transferred from the acetylenic carbon to the chloride (path A), but that the departure of chloride is accompanied essentially by the creation of another pair of charges (path B). In the



earlier work quoted, the intermediate carbene had in fact been considered a hybrid of the structures $(\text{CH}_3)_2\text{C}=\text{C}=\text{:}$ and $(\text{CH}_3)_2\text{C}^+-\text{C}\equiv\text{C}^-$; the present result, however, is the first experimental evidence for either a highly dipolar or a highly polarizable intermediate. A rough estimate of the contributions of the two structures can be made on the basis of the result for chloroform ($+16$ cm.³/mole), that for ionization reactions (-15 cm.³/mole), and that for the reaction considered here ($+2$ cm.³/mole); they appear to be about equal.

(18) J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 5497 (1957).

(19) G. F. Hennion and D. E. Maloney, *ibid.*, **73**, 4735 (1951); G. F. Hennion and K. W. Nelson, *ibid.*, **79**, 2142 (1957).

(20) H. D. Hartzler, *ibid.*, **83**, 4990, 4997 (1961).

(21) V. J. Shiner, Jr., and J. W. Wilson, *ibid.*, **84**, 2402 (1962).

(22) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953).

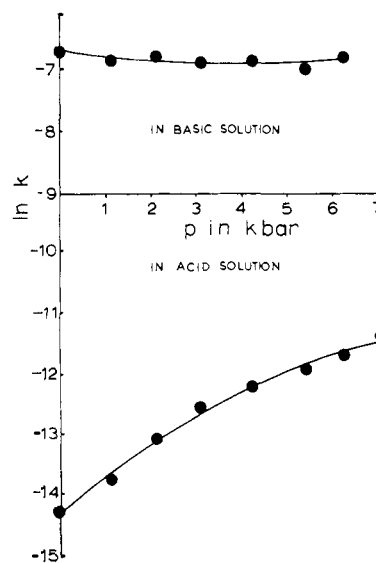


Figure 2. The effect of pressure on the rate constants of base-catalyzed and neutral solvolysis, in aqueous ethanol at 25°.

The result is also compatible with rate-controlling carbanion formation; that possibility is ruled out, however, by Shiner's demonstration of D exchange.²¹ Figure 2 shows the effect of pressure on the acid-catalyzed reaction ($\ln kp/k_0 = +0.634p - 0.0332p^2$) and that on the base-catalyzed hydrolysis ($\ln kp/k_0 = -0.0749p + 0.009p^2$); the literature¹⁰ value of k_1 at 1 atm. and 25° is 2.1×10^{-7} sec.⁻¹, and that¹⁰ of k_2 is 3.9×10^{-4} l./mole sec.

Experimental

The pressure equipment has been described.²³ The usual precautions were observed in the measurement of the rate constants; the pressure was generated at a rate of no more than 0.7 kbar/min. to avoid undue heating; the samples were precooled, and measurements of the progress of the reactions at 0.25 hr. (temperature equilibrium is reached in about 10 min.) permitted a correction to be made for the initial reaction. In all cases it was ascertained that the solutions to be compressed were far from saturated, so that complications arising from crystallization or separation of liquid phases were avoided. Compressibility measurements were made by means of the piezometer shown in Figure 3, which is much simpler to use than the commonly used instrument described by Richards²⁴; slow generation of pressure and a 15-min. period of temperature equilibration were used and corrections were made for the compressibility of glass²⁵ and mercury.^{24b}

A. *Chloroform*. A 7.00-ml. sample of methane containing 0.100 ml. of chloroform was diluted to 250 ml. with distilled water at 25°. This solution was cooled to 0°, as was a second 250-ml. volumetric flask which contained 30.00 ml. of 9.8 M aqueous sodium hydroxide. The first solution was then used to fill the second flask to the mark. A 25-ml. syringe (modified

(23) W. le Noble, *J. Am. Chem. Soc.*, **85**, 1470 (1963).

(24) (a) T. W. Richards and W. N. Stull, *Z. physik. Chem.*, **49**, 1 (1904); (b) P. W. Bridgman, "The Physics of High Pressure," G. W. Bell and Sons, Ltd., London, 1952, Chapter V.

(25) M. Diaz Peña and M. L. McGlashan, *Trans. Faraday Soc.*, **55**, 2018 (1959).

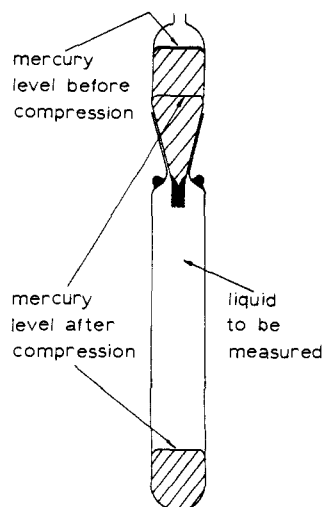


Figure 3. Piezometer used for the measurement of isothermal compressibilities of liquids.

as described previously²³) was filled and submerged in the high-pressure vessel. When the desired time had elapsed at the desired pressure, 20.0 ml. of the solution was added to a mixture of 1.4 ml. of concentrated sulfuric acid and 15 g. of ice. The resulting solution was extracted twice with 1.9 ml. of carbon disulfide; the extracts were combined in a 4-ml. volumetric flask, which was then filled to the mark. The optical density at 13.1μ of this solution was used to determine the concentration. In earlier experiments it had been ascertained that the recovery of chloroform exceeded 99%, and that the concentration could be determined with an accuracy of at least 3%.

B. Chlorodifluoromethane. This gas, obtained from K & K Laboratories, was purified by several fractional condensations in a vacuum line. A 1 *M* stock solution in methanol was stored at -80° in a bulb which permitted the withdrawal of samples by means of a precooled syringe through a serum bottle cap and a wide-bore stopcock. Each run was conducted as follows. A 0.06 *N* aqueous sodium hydroxide solution, a 150-ml. beaker, a magnetic stirring bar, a 5-ml. syringe and needle, and four 20-ml. syringes with caps were cooled to 0° . Three of the four 20-ml. syringes contained 10 ml. of 2 *N* aqueous sodium

hydroxide and several glass beads; air bubbles had been removed. The small syringe was used to transfer about 1 ml. of the stock solution of chlorodifluoromethane to 100 ml. of the cold 0.06 *N* base solution in the 150-ml. beaker; after momentary stirring, the four 20-ml. syringes were filled to the 20-ml. mark. The syringe originally empty was used in the rate experiment; the other three were shaken (the glass beads rapidly caused the formation of a homogeneous mixture) and stored for at least 4 hr. at room temperature; this was sufficient for complete hydrolysis. These solutions thus allowed appraisal of the strength of the solution used in the rate run; this was necessary since the volatility of the substrate did not allow the assumption that the starting solutions were always equally concentrated. For analysis, titrations with 0.005 *N* silver nitrate by means of a silver-silver chloride electrode, a mercuric sulfate reference electrode, and a Beckman Zeromatic instrument were used. The mixtures to be determined were neutralized to methyl red with nitric acid and diluted to 100 ml. before titration. Blank experiments allowed a small correction to be made for an effect that potassium nitrate appeared to have on the end point. The three completely hydrolyzed samples generally agreed to 1%. From the fact that virtually no gas formation was observed and from the known solubility of carbon monoxide in water it was deduced that the substrate decomposed at least 90% to formate ion; in the calculations it was therefore assumed that 4 equiv. of base were consumed per mole of substrate. For the compressibility corrections, Bridgman's data for pure water^{24b} were employed.

C. 3-Chloro-3-methylbutyne. This material was prepared as described by Hennion.¹⁹ In the solvolysis experiments, 100 ml. of the substrate was pipetted into a 100-ml. volumetric flask filled to the mark with a mixture of ethanol, water, and sulfuric acid in a volume ratio of 1600:400:1. The extent of solvolysis could be followed by chloride liberation as described in part B. In the base-catalyzed experiments, the aqueous ethanol was approximately 0.1 *M* in sodium hydroxide; in that case also, after neutralization, use was made of chloride titration for analysis.

Acknowledgment. Generous financial support from the National Science Foundation is gratefully acknowledged.