

most of the termination reaction involves a very small fraction of the total  $\text{RO}_2$  bound in the form of a complex. We agree that this is a puzzling fact and can only point to the fact that the rate constants for termination by interaction between two  $\text{RO}_2$  are small enough<sup>12</sup> to permit entertainment of the view that some bimolecular reactions, such as reaction 3, may be faster by several orders of magnitude. Finally, we should like to mention that our confidence in the molecular-complex hypothesis has been considerably fortified by the elegant demonstrations by Russell<sup>13</sup> and by Walling and Mayahi<sup>14</sup> that chlorine atoms are extensively complexed in aromatic solvents with consequent modification of their chemical reactivity. Russell has observed similar but smaller effects on the reactivity of *t*-butoxy radicals.<sup>15</sup> Since both the polarizability and electron affinity of peroxy radicals must be higher than those of alkoxy radicals, we would expect peroxy radicals to be intermediate between alkoxy radicals and chlorine atoms in their aptitude for formation of charge-transfer complexes with electron-rich aromatic systems. Since the radical-complex mechanism is only established for aromatic

solvents it is possible that variations in the inhibition mechanism may occur in other solvents.<sup>16</sup>

**Acknowledgment.**—We gratefully acknowledge support of this work by a grant from the Petroleum Research Fund of the American Chemical Society.

### Experimental

**Materials.**—Cumene (Matheson Coleman and Bell, reagent grade) was washed with concentrated sulfuric acid until the acid layer showed no more coloration and then washed with distilled water, dried over anhydrous sodium sulfate, and distilled, b.p. 152–153°. Chlorobenzene (Matheson Coleman and Bell white label, reagent grade) was dried over Drierite and distilled, b.p. 130–131°.  $\alpha, \alpha'$ -Azoisobutyronitrile (ABN) (Westville Laboratories, recrystallized grade) was recrystallized twice from methanol, m.p. 101–102°. Phenol (Baker and Adamson, reagent grade) was used. *N,N'*-Diphenyl-*p*-phenylenediamine (B. F. Goodrich Co.) was recrystallized from a chlorobenzene-nigroin mixture; m.p. 148–149°. 4-Methoxyphenol (Universal Oil Products Co.) was recrystallized twice from benzene; m.p. 52–53°. Cumyl hydroperoxide was used as supplied by Matheson Coleman and Bell Division.

**Inhibition Period and Oxidation Rates.**—The apparatus and procedure were the same as<sup>9</sup> described in our previous publication.<sup>17</sup> The total volume of reaction mixture was 6 ml. in all cases.

(16) C. E. Boozer, G. S. Hammond, C. E. Hamilton and C. Peterson, *J. Am. Chem. Soc.*, **77**, 3380 (1955).

(17) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3233 (1955).

(12) C. Walling, ref. 11, p. 422.

(13) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).

(14) C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959).

(15) G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA 13, GA.]

## The Kinetics of the Base-catalyzed Deuterium Exchange of 2,2-Dihalo-1,1,1-trifluoroethanes<sup>1</sup>

BY JACK HINE, ROBERT WIESBOECK AND ROBERT G. GHIRARDELLI

RECEIVED JULY 22, 1960

The base-catalyzed deuterium exchange of  $\text{CF}_3\text{CDCl}_2$ ,  $\text{CF}_3\text{CDBrCl}$ ,  $\text{CF}_3\text{CDBr}_2$  and  $\text{CF}_3\text{CDI}_2$  was found to proceed with negligible interference from base-consuming side reactions. Kinetics of the exchange were studied in water and methanol and the following reactivity sequence noted:  $\text{CF}_3\text{CDBr}_2 > \text{CF}_3\text{CDI}_2 \sim \text{CF}_3\text{CDBrCl} > \text{CF}_3\text{CDCl}_2$ . By studies on  $\text{CF}_3\text{-CHCl}_2$  and  $\text{CF}_3\text{CHBrCl}$  in heavy water the deuterium kinetic isotope effects were estimated to be 1.26 and 1.41, respectively. The trifluoromethyl substituent appears to be equal to or superior to the fluoro substituent at facilitating carbanion formation.

### Introduction

Previous articles on the kinetics of the base-catalyzed deuterium exchange of haloforms have shown that  $\alpha$ -halogen substituents facilitate carbanion formation in the order  $\text{I} \sim \text{Br} > \text{Cl} > \text{F}$ .<sup>2</sup> This order, being almost exactly the reverse of the relative electronegativities of the halogens, did not agree with some of the existing explanations of the activity of the hydrogen atoms of haloforms. A knowledge of the effect of more distantly situated halogen substituents on ease of carbanion formation would be useful in several ways. For example, one of the strongest points of evidence that the dehydrohalogenations of most saturated organic halides (and many other elimination reactions) are concerted E2 reactions that do not involve intermediate carbanions is the fact that many such reactions are much faster than seems plausible for

carbanion formation.<sup>3</sup> The most obvious loophole in this argument is our ignorance of the effect of  $\beta$ -halogen substituents on ease of carbanion formation.

Fluorobenzene has been found to form carbanions at its *ortho* position quite rapidly in the presence of potassium amide in liquid ammonia but the rate at which the other monohalobenzenes do so is unknown and may also be quite fast.<sup>4</sup> The interpretation of the semi-quantitative experiments of Miller and Lee on the deuterium exchange of the dihaloethylenes<sup>5</sup> is complicated by the simultaneous changing of both an  $\alpha$ - and a  $\beta$ -substituent. However, if it is assumed that the  $\alpha$ -halogen substituents on these unsaturated compounds have the same relative effect that has been observed with the haloforms, then it follows that

(1) Part X in the series "The Effect of Halogen Atoms on the Reactivity of Other Halogen Atoms in the Same Molecule"; for part IX see J. Hine and R. J. Rosscup, *J. Am. Chem. Soc.*, **82**, 6115 (1960).

(2) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957).

(3) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 169.

(4) G. A. Hall, R. Piccolini and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 4540 (1955); J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *ibid.*, **78**, 601 (1956).

(5) S. I. Miller and W. G. Lee, *ibid.*, **81**, 6313 (1959).

TABLE I  
 RATE CONSTANTS FOR DEUTERIUM EXCHANGE OF 1,1-DIHALO-2,2,2-TRIFLUOROETHANES<sup>a</sup>

Reactant	10 <sup>4</sup> k, l. mole <sup>-1</sup> sec. <sup>-1</sup>				Activation parameters in methanol	
	In D <sub>2</sub> O <sup>b</sup>	In H <sub>2</sub> O	0°	In methanol 20°	ΔH <sup>‡</sup> , kcal./mole	ΔS <sup>‡</sup> , e.u.
CF <sub>3</sub> CDCl <sub>2</sub>	6.18 ± 0.24	3.53 ± 0.12	0.649 ± 0.007	10.2 ± 0.2	21.4	5.2
CF <sub>3</sub> CDBrCl	21.8 ± 1	11.1 ± .3	1.66 ± .06	22.0 ± .6	20.0	2.1
CF <sub>3</sub> CDBr <sub>2</sub>		21.6 ± .4 <sup>c</sup>	4.19 ± .15	.74 ± 3	22.3	12.3
CF <sub>3</sub> CDI <sub>2</sub>		18.3 ± 1	1.40 ± .06	29.0 ± 0.7	23.6	14.8
CH <sub>2</sub> OCF <sub>2</sub> CDCl <sub>2</sub>				~0.07		

<sup>a</sup> The ± figures listed are the average deviations; the experimental uncertainty is probably somewhat greater. The activation energies are believed reliable within 1 kcal. and the activation entropies within 3 e.u. <sup>b</sup> The reactant in these runs is not the deuterium derivative listed but the corresponding hydrogen compound. <sup>c</sup>  $k = 3.5 \pm 0.4$  l. mole<sup>-1</sup> sec.<sup>-1</sup> at 40°.

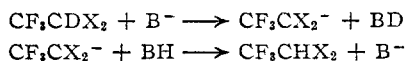
the β-halogen substituents facilitate carbanion formation in the order Cl > Br > I.

The rates of formation of β-halo carbanions cannot be studied in the cases of most saturated organic halides because of the incursion of a much faster concerted elimination reaction or because the competing olefin formation makes it impossible to capture and hence prove the intermediacy of the carbanion. However, it seemed to us that a carbanion that was stabilized by α-halogen substituent and that could form an olefin only by loss of a fluoride ion might have a long enough life to be reprotonated. We have therefore studied some 2,2-dihalo-1,1,1-trifluoroethanes.

### Results and Discussion

All of the 2,2-dihalo-1,1,1-trifluoroethanes studied were found to undergo base-catalyzed deuterium exchange at a rate rapid compared to the rate at which they consumed alkali. Upon treatment with alkaline heavy water their infrared spectra were found to change in a manner that was plausible for a deuteration process. When the deuteriated materials were treated with alkaline protium oxide, the infrared spectral changes were found to be completely reversed, ruling out all other reasonable explanations for the original changes in spectra.

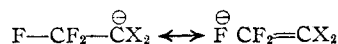
The kinetics of the exchange of the deuteriated halides were studied, with some runs being made in aqueous and others in methanolic solution. In no case was there any appreciable exchange with the solvent alone under the conditions used. With all of the compounds except 2,2-diiodo-1,1,1-trifluoroethane the deuterium exchange was so rapid compared to processes in which base was consumed that the reaction was cleanly first order in any given run. The second-order character of the reaction was, however, established in several cases by the observation that the first-order rate constants obtained in various runs on a given compound were proportional to the concentration of base used in these runs. Thus there seems little doubt that the reaction mechanism is



with the first step rate-controlling and essentially irreversible because of the large excess of the protiated solvent. The first-order rate constants for the diiodide were found to fall slightly during the individual runs. Acidimetric titrations showed that this was due to a decrease in the base concentration resulting from some minor side reaction. When second-order rate constants were calculated

by dividing the first-order rate constant obtained at a given point by the average base concentration present during the point, the values obtained showed no significant drift. The second-order rate constants obtained are listed in Table I with those obtained for the other compounds and the value determined roughly for 2,2-dichloro-1,1-difluoro-1-methoxyethane.

The effect of the various α-halogen substituents on the rate of carbanion formation is qualitatively much like that observed in the case of the haloforms,<sup>2</sup> I ~ Br > Cl, although the difference in reactivities is smaller and in the present case the diiodide is clearly less reactive than the dibromide, in methanol at least. The trifluoromethyl substituent probably stabilizes the carbanion by the contribution of no-bond resonance structures of the type suggested by Roberts, Clement and Drysdale.<sup>6</sup> Its ability to facilitate carbanion formation



relative to that of the halogen substituents is somewhat variable. For example CF<sub>3</sub>CDCl<sub>2</sub> is 40 times as reactive as FCDCl<sub>2</sub> while CF<sub>3</sub>CDI<sub>2</sub> is only 0.36 times as reactive as FCDI<sub>2</sub>.<sup>7</sup> Some of these irregularities can be explained by the hypothesis that with the trifluoromethyl substituent steric hindrance to the attack of the base has become of considerable importance. Thus we may assume that, disregarding steric effects, the α-halogen substituents facilitate carbanion formation in the order I > Br > Cl > F. In the case CDI<sub>2</sub>F > CDBr<sub>2</sub>F,<sup>7</sup> the polar factors predominate over steric hindrance; with somewhat bulkier molecules it is found that CDI<sub>3</sub> and CDBr<sub>3</sub> are of comparable reactivity<sup>2</sup> and when the considerably larger trifluoromethyl group is present steric hindrance reduces the activity of CF<sub>3</sub>CDI<sub>2</sub> below that of CF<sub>3</sub>CDBr<sub>2</sub>.

Unlike the results obtained with the haloforms, where the relative rates of carbanion formation seem to have been controlled by enthalpy factors, the present results seem to spring from a mixture of entropy and enthalpy effects. We have no convincing explanation for this result and it may simply come from experimental uncertainties.

The kinetic isotope effect may be estimated from the data obtained in heavy water solution by assuming as before<sup>8</sup> that deuterioxide ion in heavy

(6) J. D. Roberts, R. A. Clement and J. J. Drysdale, *J. Am. Chem. Soc.*, **73**, 2181 (1951).

(7) J. Hine, R. Butterworth and P. B. Langford, **80**, 819 (1958).

(8) J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956).

water forms carbanions 39% faster than hydroxide ions in light water. The resultant values of  $k_H/k_D$  of 1.26 and 1.41 for  $\text{CF}_3\text{CHCl}_2$  and  $\text{CF}_3\text{CHBrCl}$  are somewhat smaller than those obtained for the haloforms (1.48 to 1.76 for carbanion formation<sup>2,8</sup> and 2.02 for concerted dehydrohalogenation<sup>9</sup>), but much smaller than that obtained in the reaction of  $\text{CH}_3\text{OCHCl}_2$  with potassium isopropoxide ( $5.4 \pm 2.2$ ).<sup>10</sup> With the  $k_H/k_D$  values in these simple carbanion formation reactions being so much smaller than the values (*ca.* 6) obtained in other carbanion formations<sup>11</sup> and those obtained in other proton removals that appear to be concerted eliminations,<sup>9,10</sup> it seems difficult to rule out the possibility that other hydrogen-transfer reactions proceeding at moderate rates will be found that have still smaller deuterium kinetic isotope effects. For this reason it would be well to view with skepticism the generalization that the absence of a marked deuterium kinetic isotope effect proves that a hydrogen is not being transferred in the rate-controlling step of a reaction.<sup>12</sup>

The reactivities toward sodium methoxide in methanol are only about one-fifth as large as toward sodium hydroxide in water. A measurement on deuteriochloroform in methanol gave a second-rate constant of  $8.9 \times 10^{-3}$  l. mole<sup>-1</sup> sec.<sup>-1</sup> at 20.2°, about one-eleventh of the value found in water.<sup>13</sup> Part of this decrease in rate is no doubt due to the fact that methoxide ions are weaker bases than hydroxide ions.<sup>14</sup>

The observed deuterium exchange provides evidence that the dehydrohalogenation of these compounds proceeds by the carbanion mechanism,<sup>3</sup> a point that will be discussed in connection with a study of the alkali-consuming reactions of these halides.<sup>15</sup>

### Experimental

**Reagents.**—A modification of the method of Gilman and Jones<sup>16</sup> was used in the preparation of 2,2-diiodo-1,1,1-trifluoroethane,  $n_D^{20}$  1.5375,  $d_4^{20}$  2.600; reported<sup>16</sup>  $d_4^{20}$  2.595. Methanol was purified as described by Fieser<sup>17</sup>; 2-bromo-2-chloro-1,1,1-trifluoroethane (Ayerst Laboratories) was fractionally distilled to give material of b.p. 49.8° (739 mm.); 2,2-dichloro-1,1,1-trifluoroethane (du Pont) was purified by several bulb-to-bulb low pressure distillations; and 2,2-dichloro-1,1-difluoro-1-methoxyethane ( $n_D^{20}$  1.4238,  $d_4^{20}$  1.3862; reported  $n_D^{20}$  1.4262,  $d_4^{20}$  1.3861) was prepared from 2,2-dichloro-1,1-difluoroethylene by the method of Miller, Fager and Griswold.<sup>18</sup>

**2,2-Dibromo-1,1,1-trifluoroethane.**—The method of preparation of 2,2-dibromo-1,1,1-trifluoroethane was analogous to that used for the corresponding diiodide. Trifluoroacetamide was reduced to trifluoroethylamine with lithium aluminum hydride.<sup>19</sup> On two occasions, EXPLOSIONS OCCURRED DURING THE ADDITION OF WATER

UNDER NITROGEN IN WORKING UP THIS REACTION MIXTURE. A solution of alcohol in ether should be used to decompose the initially-formed complex, which should not be allowed to form any dry deposits on the inside of the flask.<sup>20</sup> To 45 g. (0.32 mole) of trifluoroethylamine hydrochloride in 150 ml. of water was added 300 ml. of methylene chloride and then at 0°, 21 g. (0.3 mole) of sodium nitrite over the period of an hour. After an additional half-hour, the organic layer was separated and the aqueous layer stirred for 30 minutes with 150 ml. of methylene chloride. The combined methylene chloride solutions were "titrated" with 0.5 M bromine in methylene chloride until about 350 ml. (0.175 mole bromine) had been added, at which time the red color of the bromine was no longer discharged. The solution was filtered and fractionally distilled to give 21 g. (27% based on amine hydrochloride) of 2,2-dibromo-1,1,1-trifluoroethane, b.p. 71–72° (745 mm.),  $n_D^{20}$  1.4041,  $d_4^{20}$  2.219; reported<sup>21</sup> values are b.p. 73°,  $n_D^{20}$  1.4029,  $d_4^{20}$  2.224.

**Preparation and Analysis of 2-Deuterio-2,2-dihalo-1,1,1-trifluoroethanes.**—In a typical experiment 4 g. of 2,2-dichloro-1,1,1-trifluoroethane was shaken with 5.5 ml. of 0.4 M NaOD in  $\text{D}_2\text{O}$  for 24 hours, separated, and the process repeated. In the reaction product the 11.995  $\mu$  absorption band of the protium compound had decreased in intensity to less than 1% of its original value, showing that more than 99% deuteration had occurred. Extinction coefficients were determined for both the deuterated and protiated materials at the 8.190 and 10.675  $\mu$  bands characteristic of the deuterated material and the 8.460 and 11.995  $\mu$  bands of the protium compound.

In the case of 2,2-dibromo-1,1,1-trifluoroethane the 8.948 and 13.170  $\mu$  bands of the deuterium compound and the 10.450 and 11.350  $\mu$  bands of the protium compound were used. The deuterated material was at least 97% isotopically pure.

For 2,2-diiodo-1,1,1-trifluoroethane, 2-bromo-2-chloro-1,1,1-trifluoroethane and 2,2-dichloro-1,1-difluoro-1-methoxyethane, respectively, the 8.340, 11.025 and 10.620  $\mu$  absorption bands of the deuterium compounds and the 9.145, 8.875 and 9.345  $\mu$  bands of their protium analogs were used in the isotopic analysis. The compounds used were at least 98, 97 and 97% isotopically pure, respectively.

For those compounds whose isotopic analysis was carried out by measurements at four wave lengths two independent sets of results could be calculated, permitting an internal check on the analytical method. Since the rate of consumption of base was very small compared to the rate of deuterium exchange it is not necessary to know the isotopic content of the deuterium starting material, only the *ratio* of this content to the content at the times when points are taken during the runs.<sup>2</sup>

**Kinetic Runs.**—In a typical run, 343 mg. of deuterated 2,2-dibromo-1,1,1-trifluoroethane was dissolved in 50 ml.

TABLE II

KINETICS OF BASE-CATALYZED EXCHANGE OF  $\text{CF}_3\text{CDBr}_2$  IN METHANOL AT 0°<sup>a</sup>

Time, sec.	% $\text{CF}_3\text{CDBr}_2$ <sup>b</sup>	$10^4 k_1$ , <sup>b</sup> sec. <sup>-1</sup>	% $\text{CF}_3\text{CDBr}_2$ <sup>c</sup>	$10^4 k_1$ , <sup>c</sup> sec. <sup>-1</sup>
0	97.89		98.88	
1835	88.80	5.32	89.10	5.57
4151	79.20	5.16	78.67	5.51
5820	72.39	5.19	71.42	5.59
7100	67.40	5.26	66.75	5.52
9600	59.08	5.11	58.04	5.54
12800	50.22	5.29	49.14	5.55
14580	45.82	5.21	44.58	5.47
16200	41.56	5.29	41.16	5.42

Average  $k_1 = 5.37 \pm 0.15 \times 10^{-5}$  sec.<sup>-1</sup>

<sup>a</sup> In the presence of 0.01259 M sodium methoxide.

<sup>b</sup> From measurements at 8.948 and 10.450  $\mu$ . <sup>c</sup> From measurements at 11.348 and 13.170  $\mu$ .

(20) Cf. T. S. Reid and G. H. Smith, *Chem. Eng. News*, **29**, 3042 (1951).

(21) B. T. McBee, H. B. Hass, W. G. Toland, Jr., and A. Truchan, *Ind. Eng. Chem.*, **39**, 420 (1947).

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

(10) J. Hine, R. J. Roscup and D. C. Duffey, *ibid.*, **82**, 6120 (1960).

(11) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(12) Cf. L. Melander, *Acta Chem. Scand.*, **3**, 95 (1949).

(13) J. Hine, R. C. Peek, Jr., and B. D. Oakes, *J. Am. Chem. Soc.*, **76**, 827 (1954).

(14) J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952).

(15) J. Hine, R. Wiesboeck and O. B. Ramsay, *ibid.*, **83**, 1222 (1961).

(16) H. Gilman and R. Jones, *ibid.*, **65**, 1458 (1943).

(17) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Inc., Boston, Mass., 1941, p. 359.

(18) W. T. Miller, Jr., E. W. Fager and P. H. Griswold, *J. Am. Chem. Soc.*, **70**, 431 (1948).

(19) E. J. Bourne, S. H. Henry, C. E. M. Tatlow and J. C. Tatlow, *J. Chem. Soc.*, 4014 (1952).

of 0.00040 *M* methanolic perchloric acid. When this solution had cooled to 0°, 5-ml. samples were added to 5-ml. samples of 0.02559 *M* sodium methoxide in methanol in 25-ml. volumetric flasks also at 0°. At various times 8-ml. portions of 0.0343 *M* aqueous perchloric acid were added to these flasks to stop the reaction. The resultant solutions were extracted with 2-ml. portions of iso-octane which were then dried with a small amount of silica gel and analyzed by infrared measurements. The results obtained are shown in Table II.

In runs on dibromotrifluoroethane in aqueous solution at 40° in the presence of 0.03417 *M* ammonia-0.05019 *M* ammonium perchlorate a rate constant of  $(8.08 \pm 0.45) \times 10^{-3} \text{ sec.}^{-1}$  was obtained and with the same buffer ratio but only half the concentration a value of  $(7.30 \pm 0.40) \times 10^{-3} \text{ sec.}^{-1}$  was found. From the data of Everett and Wynne-Jones on the ionization of ammonia<sup>22</sup> values of

$3.5 \pm 0.4 \text{ l. mole}^{-1} \text{ sec.}^{-1}$  and  $(4.6 \pm 2) \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$  may be obtained as rate constants for carbanion formation due to the bases hydroxide ion and ammonia, respectively.

Each of the rate constants listed in Table II is the result of at least two runs, each containing at least five points. In most cases the concentration of base in the two runs differed by about a factor of two.

**Acknowledgments.**—We should like to acknowledge our indebtedness to the U. S. Atomic Energy Commission for partial support of this investigation and to E. I. du Pont de Nemours and Co., Inc., and Ayerst Laboratories, Inc., for gifts of chemicals.

(22) D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc. (London)*, **A169**, 190 (1938).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA 13, GA.]

## The Carbanion Mechanism for the Dehydrohalogenation of 2,2-Dihalo-1,1,1-trifluoroethanes<sup>1</sup>

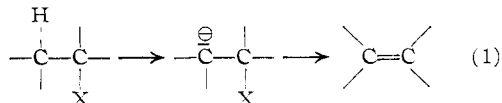
By JACK HINE, ROBERT WIESBOECK AND O. BERTRAND RAMSAY

RECEIVED JULY 22, 1960

Kinetic studies are reported for the reactions of 2,2-dichloro-1,1,1-trifluoroethane, 2-bromo-2-chloro-1,1,1-trifluoroethane, 2,2-dibromo-1,1,1-trifluoroethane, 2,2-diiodo-1,1,1-trifluoroethane and 2,2-dichloro-1,1,1-difluoro-1-methoxyethane with sodium methoxide in methanol and for the sodium methoxide-catalyzed addition of methanol to 1,1-dichloro-2,2-difluoroethylene. Arguments are presented to show that the pentahaloethanes studied undergo dehydrofluorination *via* an intermediate carbanion to give a tetrahaloethylene that rapidly adds methanol to give a methyl tetrahaloethyl ether, which then reacts with sodium methoxide at a rate comparable to that of the reactant pentahaloethane. The factors that favor the carbanion mechanism (relative to the concerted E2 mechanism) for elimination are discussed. The relative reactivities,  $\text{CF}_3\text{CHI}_2 > \text{CF}_3\text{CHBr}_2 > \text{CF}_3\text{CHBrCl} > \text{CF}_3\text{CHCl}_2$ , are rationalized in terms of the carbanion elimination reaction.

### Introduction

It seems rather generally accepted that the base-catalyzed dehydrohalogenation of most saturated aliphatic halides brought about by such bases as potassium hydroxide and sodium ethoxide is a concerted one-step process called the E2 mechanism.<sup>2,3</sup> Another reaction mechanism that would fit the same bimolecular reaction kinetics has been called the carbanion mechanism<sup>2</sup> or the E1cB mechanism.<sup>4</sup> In this mechanism the basic reagent removes from the  $\beta$ -carbon atom a hydrogen atom without its bonding electron pair, leaving a carbanion that rapidly loses a halide ion to give the olefin. Hughes, Ingold and Patel suggested



that the decomposition of the 2-(*p*-nitrophenyl)-ethyltrimethylammonium ion to *p*-nitrostyrene, which proceeds much faster in neutral solution than in 0.5 *M* hydrochloric acid probably follows the carbanion mechanism.<sup>5</sup> While it is possible

that acid slows the reaction by protonating intermediate carbanions that would otherwise have lost trimethylamine to give olefin, it may be that the decomposition in neutral solution is a concerted elimination involving hydroxide ion, whose concentration is much smaller in acid solution, of course. The carbanion mechanism seems first to have been established by the observation that trichloroethylene undergoes base-catalyzed deuterium exchange considerably faster than it undergoes dehydrohalogenation.<sup>6</sup> Observations of varying amounts of deuterium exchange of unreacted starting material have also been used to support the carbanion mechanism for various dihaloethylenes,<sup>7</sup>  $\beta$ -benzene hexachloride,<sup>8</sup> malic acid<sup>9</sup> and fluorobenzene.<sup>10</sup> The carbanion mechanism has also been inferred from the magnitude of the deuterium kinetic isotope effect in the reaction of chlorobenzene with potassium amide<sup>10</sup> and a kinetic argument has been presented that the decomposition of 1,1,1,3-tetra-nitro-2-phenylpropane to nitroform and  $\beta$ -nitrostyrene in methanol solution also proceeds by the carbanion mechanism.<sup>11</sup>

While it thus seems clear that some basic elimination reactions involve intermediate carbanion

(1) Part XI in the series "The Effect of Halogen Atoms on the Reactivity of Other Halogen Atoms in the Same Molecule"; part X, ref. 13, accompanying paper.

(2) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, sec. 7-1a.

(3) The term "E2" seems to be used by some to include both the concerted and stepwise mechanisms and by others to refer only to the concerted process. We shall use the latter terminology here, with the frequent addition of "concerted" for clarity.

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, sec. 30a.

(5) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 523 (1933); E. D. Hughes, C. K. Ingold and C. S. Patel, *ibid.*, 526 (1933).

(6) L. C. Leitch and H. J. Bernstein, *Can. J. Research*, **28B**, 35 (1950); T. J. Houser, R. B. Bernstein, R. G. Miekka and J. C. Angus, *J. Am. Chem. Soc.*, **77**, 6201 (1955).

(7) S. I. Miller and W. G. Lee, *ibid.*, **81**, 6313 (1959).

(8) S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953).

(9) L. E. Erickson and R. A. Alberty, *J. Phys. Chem.*, **63**, 705 (1959).

(10) G. A. Hall, R. Piccolini and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 4540 (1955); J. D. Roberts, D. A. Semenov, H. E. Simmons, Jr., and L. A. Carlsmith, *ibid.*, **78**, 601 (1956).

(11) J. Hine and L. A. Kaplan, *ibid.*, **82**, 2915 (1960).