

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 isoöctane 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 $(8.08 \pm 0.45) \times 10^{-5}$ sec.⁻¹ was obtained and with the same buffer ratio but only half the concentration a value of $(7.30 \pm 0.40) \times 10^{-5}$ sec.⁻¹ was found. From the data of Everett and Wynne-Jones on the ionization of ammonia²² values of

3.5 ± 0.4 l. mole⁻¹ sec.⁻¹ and $(4.6 \pm 2) \times 10^{-3}$ l. mole⁻¹ 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-trifluoroethanes¹

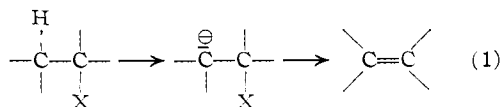
By JACK HINE, ROBERT WIESBOECK AND O. BERTRAND RAMSAY

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-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.^{2,3} Another reaction mechanism that would fit the same bimolecular reaction kinetics has been called the carbanion mechanism² or the E1cB mechanism.⁴ In this mechanism the basic reagent removes from the β -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.⁵ 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.⁶ Observations of varying amounts of deuterium exchange of unreacted starting material have also been used to support the carbanion mechanism for various dihaloethylenes,⁷ β -benzene hexachloride,⁸ malic acid⁹ and fluorobenzene.¹⁰ The carbanion mechanism has also been inferred from the magnitude of the deuterium kinetic isotope effect in the reaction of chlorobenzene with potassium amide¹⁰ and a kinetic argument has been presented that the decomposition of 1,1,1,3-tetra-nitro-2-phenylpropane to nitroform and β -nitrostyrene in methanol solution also proceeds by the carbanion mechanism.¹¹

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).

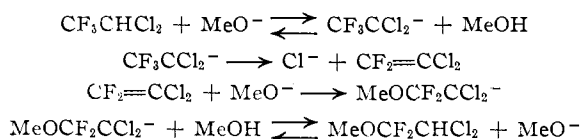
(11) J. Hine and L. A. Kaplan, *ibid.*, **82**, 2915 (1960).

formation, it also seems clear that others do not. Lack of deuterium exchange of the reactant¹² seems to be necessary but not sufficient evidence for the concerted E2 mechanism, since it leaves the possibility that a carbanion is formed but practically never protonated to regenerate the starting material. Probably stronger evidence is the fact that many dehydrohalogenations proceed much more rapidly than carbanions would be expected to be formed under the conditions. For example, the carbanion mechanism does not explain the preferential *trans* character of the reaction since *cis* hydrogens would be expected to be removed to form carbanions about as fast as the corresponding *trans* hydrogens in at least some of the cases that have been studied. Other examples could be given but in general we feel that the effective use of the reactivity criterion to delineate the areas of applicability of the E2 and carbanion mechanisms demands more data on the effect of substituents (particularly β -halo substituents) on reactivity in carbanion formation. For this reason and also because the carbanion mechanism has not yet been shown to operate for any saturated aliphatic halide, we have studied the deuterium exchange of some 2,2-dihalo-1,1,1-trifluoroethanes,¹³ and are now studying the reactions in which these halides consume base.

Results and Discussion

Evidence for Elimination.—When the four 2,2-dihalo-1,1,1-trifluoroethanes studied were treated with sodium methoxide under conditions considerably more severe than those required for deuterium exchange,¹³ methoxide ions were consumed. In all cases fluoride ions were formed. At 70.5° about 11% of the methoxide consumed liberated iodide ions from the diiodo compound but not more than 4% of bromide and/or chloride was formed from the dibromo, bromochloro or dichloro compounds. Within the experimental error the total concentration of halide ions formed was equal to the concentration of methoxide ions that reacted.

Although no product studies have been made, the only plausible course for the liberation of the fluoride ions is the dehydrofluorination of the reactant. The olefinic product of one of the reactions, 1,1-dichloro-2,2-difluoroethylene, is known to add alcohol readily in the presence of a basic catalyst.¹⁴



In fact, we made measurements showing that while this dichlorodifluoroethylene is stable in neutral methanol for hours, in the presence of 0.00945 *M* sodium methoxide it undergoes a first-order reaction (rate followed by infrared measurements) with a rate constant of $(2.9 \pm 0.4) \times 10^{-4} \text{ sec}^{-1}$ at 0° to give 2,2-dichloro-1,1-difluoro-1-methoxy-

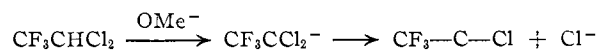
(12) Cf. P. S. Skell and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 1861 (1945).

(13) J. Hine, R. Wiesboeck and R. G. Ghirardelli, *ibid.*, **83**, 1219 (1961).

(14) W. T. Miller, Jr., E. W. Fager and P. H. Griswold, *ibid.*, **70**, 431 (1948).

ethane. Assuming that the reaction is second order the second-order rate constant is 3×10^{-2} . Since this value is more than 10^8 times as large as the second-order rate constant for the reaction of 2,2-dichloro-1,1,1-trifluoroethane with sodium methoxide (extrapolated from data at higher temperatures; see Table I), we would not expect it to be possible to isolate significant amounts of the dichlorodifluoroethylene as a reaction product under the conditions we employed.

In view of the fact that product-isolation experiments could therefore not be useful in establishing the nature of the initial fluoride-producing reaction, the arguments against all reaction paths other than dehydrofluorination should be given in some detail. While such reactions as methylene formation¹⁵ and nucleophilic displacement of halo-



gens other than fluoride might seem probable, our experimental observations show that at 70.5° such reactions occur to the extent of no more than 11% (and probably to an extent of less than 5.5% when it is considered that the replacement of one iodine, bromine or chlorine by methoxy would probably so activate the remaining one as to bring about its almost immediate replacement^{16,17}). The dependence of the reaction rate on the methoxide ion concentration rules out any first-order reactions of the halide. Therefore the only plausible possibilities that remain are dehydrofluorination and the S_N2 displacement of fluorine by methoxide ions. However, our compounds liberate fluoride at a rate that appears to be unreasonably fast for the S_N2 mechanism. They are from 100 to 1000 times as reactive toward sodium methoxide in methanol as typical primary fluorides are toward sodium ethoxide in ethanol.¹⁸ Since α - and β -halogen substituents have been found to decrease S_N2 reactivity in the cases that have been studied^{17,19,20} these dihalotrifluorides should be *less* reactive than unsubstituted primary fluorides. The change in reagent and solvent seems unlikely to increase the reactivity greatly in view of the fact that ethyl bromide is about twice as reactive toward ethoxide in ethanol²¹ as toward methoxide in methanol.¹⁷ We have therefore concluded that the reaction consists very largely of an initial dehydrofluorination.

The rapid subsequent addition of methanol to the difluorodihaloethylene will have no effect on our kinetic studies, in which the reaction was followed by measurements of methoxide and fluoride ion concentrations, but the difluorodihaloethyl methyl ether produced does undergo dehydrohalogenation, giving decreased reliability to our rate

(15) Cf. J. Hine and S. J. Ehrenson, *ibid.*, **80**, 824 (1958), and references cited therein.

(16) Cf. P. Ballinger, P. B. D. de la Mare, G. Kohnstam and B. M. Prestt, *J. Chem. Soc.*, 3641 (1955).

(17) J. Hine, C. H. Thomas and S. J. Ehrenson, *J. Am. Chem. Soc.*, **77**, 3886 (1955).

(18) N. B. Chapman and J. L. Levy, *J. Chem. Soc.*, 1673 (1952).

(19) J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *J. Am. Chem. Soc.*, **78**, 2282 (1956).

(20) J. Hine and W. H. Brader, Jr., *ibid.*, **75**, 3964 (1953).

(21) E. D. Hughes, C. K. Ingold, S. Masterman and B. J. McNulty, *J. Chem. Soc.*, 899 (1940).

TABLE I
KINETICS OF DEHYDROFLUORINATION OF 2,2-DIHALO-1,1,1-TRIFLUOROETHANES BY METHANOLIC SODIUM METHOXIDE

	—10% ^k —		ΔH^\ddagger , kcal./ mole ^a	ΔS^\ddagger , e.u. ^a
	55.0°	70.5°		
CF ₃ CHCl ₂	1.5 ± 0.2	19 ± 2 ^b	37.2	28
CF ₃ CHBrCl	2.9 ± 0.3	33 ± 4	34.5	21
CF ₃ CHBr ₂	5.5 ± 1	56 ± 5	32.9	17
CF ₃ CHI ₂	51 ± 10	490 ± 50	32.0	19
CH ₂ OCF ₂ CHCl ₂	3.0 ± 0.2	27 ± 2	31.1	11

^a The uncertainties in ΔH^\ddagger and ΔS^\ddagger are estimated at 3 kcal./mole and 9 e.u., respectively. ^b At 70.0°.

constants for the reactions of the 2,2-dihalo-1,1,1-trifluoroethanes listed in Table I. We have attempted to take this and other relevant factors into account in arriving at the listed uncertainties, which are considerably larger than the average deviations obtained.

The Carbanion Elimination Mechanism.—The occurrence of deuterium exchange, rapid compared to the rate of elimination, as in the present case,¹³ has generally been accepted as proof of the carbanion mechanism for elimination. One might object that the deuterium exchange does not prove that carbanions were being formed since the exchange could have occurred by a concerted mechanism. However, since no base-catalyzed exchange reaction of carbon-bound hydrogen has yet been shown to be a one-step process, while there is strong evidence that many such reactions proceed *via* carbanions, we shall assume that there was carbanion formation in the present case. A second possible objection is that the carbanion formation is simply an irrelevant side reaction, having nothing to do with the elimination reaction. However even in a concerted E2 reaction, the function of the removal by base of β -hydrogen without its bonding electron pair must be to liberate this electron pair so that it can be used as the second electron pair of the double bond that is being produced. In the concerted reaction the partial removal of the β -hydrogen and the concomitant partial freeing of the bonding electron pair is sufficient to cause the beginning of the formation of the double bond and the ejection of the halide ion (or other group) with its bonding electron pair. If this partial freeing of a β -electron pair is enough to bring about the ejection of the halide ion, it is difficult to understand why the complete freeing of the electron pair, as in carbanion formation, should not bring about the ejection of a halide ion even more effectively, unless the carbanion is being formed from a rotational conformer that is inactive toward the concerted E2 reaction or unless the freeing of the β -electron pair must be synchronized with certain vibrations of the group being ejected with its bonding electron pair and/or the four groups attached to the double bond of the olefin that is being formed. The dehydrohalogenation of the 2,2-dihalo-1,1,1-trifluoroethanes cannot be complicated by conformational isomerism since all three conformers are identical.²² Furthermore,

(22) The deuterium exchange observed with β -benzene hexachloride,⁸ however, may involve the formation, from the predominant all-equatorial conformer, of carbanions, some of which are reprotonated before they are transformed to a conformer from which a chloride ion is more rapidly ejected.

if the carbanions are true intermediates (corresponding to energy minima in a potential energy *versus* molecular geometry plot) then they must be more abundant (having a lower energy content) than the species in which the hydrogen has been almost removed and the carbanion almost formed. This being the case, it is in the carbanions that the presence of a large excess of electrons on the β -carbon atom is by far the most likely to become synchronized with the proper vibrations of the other parts of the molecule so as to result in transformation to the olefin. It therefore seems unlikely that any major part of the elimination reaction proceeds by a concerted E2 mechanism.

All of the existing reports⁵⁻¹¹ seem to be in agreement with the generalization that the carbanion mechanism for base-catalyzed elimination reactions can be made more important relative to the E2 mechanism by (1) changing X (in eq. 1) so as to decrease its ease of departure with its bonding electron pair,²³ (2) introducing structural features so as to stabilize the possible intermediate carbanion,²⁴ (3) decreasing the stability of the unsaturated compound being formed by the elimination (the stability of acetylenes relative to the corresponding olefins is usually less than that of olefins relative to the corresponding saturated compounds) and (4) inhibiting the E2 reaction by preventing H and X from being oriented *trans* to each other.²⁵ The first three of these factors seem to be important in the present case. It is well known to be difficult to displace fluorine from organic molecules, especially when there are several other fluorine atoms attached to the same carbon atom.^{12,26} The intermediate carbanion is fairly well stabilized by two α -halogens and three β -fluorines.¹³ It has been suggested earlier that fluorine substituents destabilize olefins relative to related saturated compounds because of a decrease in that part of the C-F bond energy due to the difference in electronegativity of the two atoms.²⁷ More direct evidence for this suggestion may be found in the studies of Lacher, Park and co-workers on the heats of reaction of certain fluoroolefins.²⁸

Relative Reactivities.—The *relative* rates of dehydrofluorination of the dichloro, bromochloro and dibromo compounds are about the same as their *relative* rates of carbanion formation.¹³ This suggests that the transition state for olefin formation still has a large amount of carbanion character and that the difference in the behavior of the three compounds can be attributed largely to the differing abilities of the two α -halogen atoms to stabilize carbanions. The diiodo compound is dehydrofluorinated significantly more rapidly, how-

(23) J. Weinstock, R. G. Pearson and F. G. Bordwell, *J. Am. Chem. Soc.*, **78**, 3173 (1956).

(24) Cf. ref. 4, footnote 12.

(25) S. J. Cristol, N. L. Hause and J. S. Meek, *J. Am. Chem. Soc.*, **73**, 674 (1951).

(26) Cf. ref. 2, p. 167, and A. L. Henne in "Organic Chemistry," 2nd ed., ed. by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 959-961.

(27) J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **78**, 5002 (1956).

(28) J. R. Lacher, A. Kianpour and J. D. Park, *J. Phys. Chem.*, **61**, 584 (1957); J. R. Lacher, L. Casali and J. D. Park, *ibid.*, **60**, 608 (1956); J. R. Lacher, A. Kianpour, P. Montgomery, H. Knedler and J. D. Park, *ibid.*, **61**, 1125 (1957).

ever, although its carbanion formation rate is no faster than that of some of the other compounds studied. This tendency of the 1,1-diiodo-2,2,2-trifluoroethyl anion to decompose to olefin a considerably higher percentage of the times that it is formed must, from the principle of microscopic reversibility, be partly due to steric interference in protonation of the carbanion if our suggestion of the importance of steric effects in carbanion formation from these pentahaloethanes¹³ is correct. Decreased stability of the saturated reactant relative to the olefinic product in the case of the diiodo compound, perhaps resulting from greater crowding of the bulky iodine atoms in the sp^3 hybridized pentahaloethane than in the sp^2 hybridized olefin, may also be important.

The 1,1-dichloro-2,2-difluoro-2-methoxyethyl anion would also be expected to decompose to olefin a relatively higher percentage of the time that it is formed in view of the fact that the olefin produced would have only one destabilizing fluorine substituent. Comparison of rates of deuterium exchange¹³ and sodium methoxide consumption suggests that this does occur but, as the α -methoxy substituent is known to increase SN_2 reactivity,^{16,17} there is some possibility that the reaction with sodium methoxide is largely a substitution rather than elimination process.

Experimental

The reagents used have been described previously.¹⁸

Kinetics of the Addition of Methanol to 2,2-Dichloro-1,1-difluoroethylene.—To 100 ml. of 0.00945 *M* sodium methoxide in methanol at 0° was added 0.080 ml. of the dichlorodifluoroethylene. As soon as possible after shaking, a 10-ml. sample was taken, added to 10 ml. of 0.07 *M* aqueous perchloric acid and extracted with 2 ml. of carbon tetrachloride. The extract was dried with a little silica gel and analyzed for 2,2-dichloro-1,1-difluoro-1-methoxyethane by measurements at 9.345 μ where the olefin reactant absorbs only negligibly. Treating the first point taken as a "zero point" the data on five other points between 900 and 3300 seconds (23 and 62% reaction) gave first-order rate constants between 2.06 and 3.40×10^{-4} sec.⁻¹ with no noticeable trend.

Kinetics of the Reactions of 2,2-Dihalo-1,1,1-trifluoroethanes with Sodium Methoxide in Methanol.—In a typical run 1.1238 g. (4.65 mmoles) of 2,2-dibromo-1,1,1-trifluoroethane was diluted to 100 ml. with methanolic sodium methoxide at 0°. Each of nine Pyrex tubes was filled with 10 ml. of this material and sealed. Eight were placed in a 70.5° bath and one was used as a "zero point." It was titrated with standard acid and then with thorium nitrate solution to determine the fluoride ion concentration.²⁹ After 12 days, when 1.08 moles of fluoride ion had been formed per mole of organic halide originally present, only 4% more methoxide had been used up than fluoride had been formed.³⁰

Calculation of Rate Constants.—Rate constants calculated from the simple second-order rate equation showed a marked tendency to climb during the individual kinetic runs. This is very probably due to the subsequent reaction of the 2,2-dihalo-1,1-difluoro-1-methoxyethane formed by the addition of methanol to the initial reaction product. This explanation is supported by the observation that for several of the compounds well over one mole of fluoride ion could be liberated per mole of reactant. Separate studies on 2,2-dichloro-1,1-difluoro-1-methoxyethane (Table I) show that in the case of 2,2-dichloro-1,1,1-trifluoroethane this subsequent reaction is somewhat faster than the initial reaction. Since

the rigorous calculation of rate constants for consecutive bimolecular reactions with comparable rate constants is not a simple matter³¹ and since highly accurate rate constants are not required in any of the arguments presented in this paper, we have devised an approximate method of calculation.

The transformation of the reactant halide to an intermediate of equal reactivity has the same effect on the rate of consumption of base as maintaining the organic halide concentration constant. Since the reactivity of the intermediate is comparable to that of the reactant in the only case on which we have direct observations, we have assumed it will also be in all of the other cases. The usual second-order rate equation may then be reduced to a first-order equation

$$k_1 = \frac{2.303}{t} \log \left(\frac{[\text{MeO}^-]_0}{[\text{MeO}^-]_t} \right)$$

where the first-order rate constant k_1 is equal to the total second-order rate constant k_2 multiplied by the organic halide concentration.

The data obtained in one run are shown in Table II. The average first-order rate constant obtained was divided by the organic halide concentration to give the total second-order rate constant, which was transformed to the second-order rate constant for dehydrofluorination (2.69×10^{-8} l. mole⁻¹ sec.⁻¹) by multiplication by 0.955 since 4.5% of the methoxide ions were found to have been used up by a side reaction to give bromide and/or chloride ions. Titrations showed that at 70.5° about 11% iodide ion was formed in the reaction of the diiodide but that none of the other reactants gave more than 4% bromide and/or chloride ions. At 55° this side reaction consumed rather more of the base, reaching a maximum of 20% with the diiodide. Our method of correcting for the side reaction involves the implicit assumption that it yields only chloride, bromide and/or iodide ions (probably by an SN_2 mechanism). If this assumption is incorrect and fluoride ions are produced, by a dehalogenation reaction for example,³² there will be a corresponding error in our rate constants listed in Table I. This error should be a maximum for the diiodo compound, for which it will amount to 25 and 12% at 55 and 70.5°, respectively.

TABLE II

REACTION OF CF_3CHBrCl WITH MeONa IN MeOH AT 55.0°^a

Time, sec.	$[\text{MeO}^-]$	$10^7 k_1$, sec. ⁻¹
351,000	0.03385	1.90
780,000	.03144	1.80
1,270,800	.02937	1.64
1,870,200	.02564	1.84
2,563,200	.02375	1.64
3,175,200	.02095	1.71
3,943,800	.01730	1.87
5,165,100	.01397	1.84
6,726,200 ^b	.01188	1.79

Av. 1.78 ± 0.08

^a Initial concentrations of base and organic halide were 0.03618 and 0.06321 *M*, respectively. ^b At this point the total concentration of bromide and chloride ions was found to be 0.0011 *M*.

In order to ensure that the organic halide being studied (rather than an intermediate derived from it) was the principal reacting species, we used only data taken before two-thirds of it had reacted. In some cases where a relatively large amount of base was used up in a short time at the beginning of the reaction this was assumed to be due to the

(29) I. M. Kolthoff and E. B. Sandell, "Quantitative Inorganic Analysis," 3rd ed., The Macmillan Co., New York, N. Y., 1952, p. 721.

(30) In other runs direct titration with silver nitrate showed that about 4% bromide ion was formed.

(31) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 165.

(32) Cf. V. V. Korshak, K. K. Samplavskaya and N. M. Dovol'skaya, *J. Gen. Chem. U. S. S. R. (Eng. trans.)*, 20, 2153 (1950).

presence of a relative impurity and the first point taken was used as the "zero point."

Almost every one of the rate constants in Table I is the result of at least two runs of at least five points each. The concentration of at least one of the reagents was usually different, by a factor of about two, in the two runs.

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

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE 5, WASH.]

Cyclopropene. IV. The Infrared, Ultraviolet and N.m.r. Spectra of Cyclopropene and Some Related Compounds¹

BY KENNETH B. WIBERG AND BERNARD J. NIST

RECEIVED JUNE 22, 1960

The infrared, ultraviolet and n.m.r. spectra of cyclopropene and a number of related compounds have been examined. The results are discussed in terms of the structures of the compounds.

Our interest in the effects of bond angle deformation on the properties of organic compounds has led us to investigate the infrared, ultraviolet and n.m.r. spectra of cyclopropene, and to compare these data with those for other cyclic compounds. The results obtained with each type of spectral transition will be discussed separately.

Infrared Spectra.—Before considering the infrared spectral data for the cycloalkenes and cycloalkanones given in Table II, it would seem appropriate to summarize the available data for the cycloalkanes. Table I gives the type A vibrational fre-

TABLE I

VIBRATIONAL FREQUENCIES FOR CYCLOALKANES ^a				
Vibration	Cyclopropane ²	Cyclobutane ³	Cyclopentane ⁴	Cyclohexane ⁵
A ₁ ' or A _{1g} C-H str.	3009	2870	2868	2853
A ₂ '' or A _{2u} C-H str.	3103	2896	2965	2960
A ₁ ' or A _{1g} ring breathing	1188	1003	886	802
K C-C stretching ^b	4.27	4.21	...	4.00
K C-H stretching ^c	5.1	4.5	4.6	4.6

^a Values are given in cm.⁻¹; A₁ frequencies are from liquid phase Raman spectra, and A₂ frequencies are from gas phase spectra. ^b Values were taken from ref. 3; it was assumed that the interaction constant for cyclopropane is zero as with cyclobutane. ^c The values for this force constant are not available from a normal coordinate analysis, and therefore they were roughly approximated from the average of the A₁ and A₂ frequencies.

quencies for carbon-hydrogen stretching and for ring breathing. The A₁' and A_{1g} vibrations are totally symmetric and are observed only in the Raman spectrum, whereas the A₂'' and A_{2u} frequencies are infrared active. The carbon-hydrogen vibrational modes which corresponds to these designa-

(1) This work was supported by the Office of Ordnance Research and in part by a Sloan Foundation grant. Part III: P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959).

(2) A. W. Baker and R. C. Lord, *ibid.*, **23**, 1636 (1955).

(3) G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5634 (1953).

(4) F. A. Miller and R. G. Inskeep, *J. Chem. Phys.*, **18**, 1519 (1950).

(5) C. W. Beckett, K. S. Pitzer and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2488 (1947); R. S. Rasmussen, *J. Chem. Phys.*, **11**, 249 (1943). The A_{1g} C-H frequency was taken as that of the most intense polarized Raman line in the 3000 cm.⁻¹ region, and the A_{2u} C-H frequency was taken as that of the strongest infrared active band in this region, in analogy with cyclopentane.

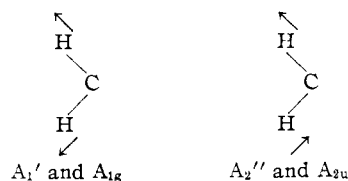
TABLE II

VIBRATIONAL FREQUENCIES FOR SOME CYCLIC COMPOUNDS^a

Ring size	Cycloalkene =CH		>C=C<	Cycloalkanone >C=O	Methylene-cycloalkene >C=CH ₂
	A	B			
3	3076	..	1641	1815 ^f	1730 ^g
4	3048	3126	1566 ^e	1788	1678
5	3061	..	1611	1746	1657 ^d
6	3024	3067	1649	1715	1651 ^d
7	3020	3059	1650	1703	...
8	3016	3053	1648	1702	...
Straight chain ^b	3023	..	1658	1720	1654

^a Values in cm.⁻¹ for CCl₄ solutions (10%) using an instrument with a calcium fluoride prism, except for the data to which reference is given below. Estimated error in frequency is ±5 cm.⁻¹ at 3000 cm.⁻¹ and ±2 cm.⁻¹ at 1600 cm.⁻¹. The frequencies for a number of these compounds have been reported elsewhere. All the values given here, with the exceptions noted, were determined with the same instrument in order to make them more comparable. ^b The compounds are *cis*-2-butene, diethyl ketone and isobutene. ^c Raman frequency, ref. 10. ^d Raman frequencies: P. A. Akishin and V. M. Tatevskii, *Vestnik Moskov Univ.*, 6, No. 2 Ser. Fiz. Mat. i Estestven Nauk, No. 1, 103 (1951). ^e This datum was kindly supplied by Dr. B. E. Anderson, E. I. du Pont de Nemours and Co. ^f W. B. De More, H. D. Pritchard and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5878 (1959), gas phase spectrum. This datum does not refer to material which has been isolated and identified as cyclopropanone, but rather to the product of the reaction of methylene with ketene in a solid matrix. Its properties makes it appear likely that it is cyclopropanone.

tions are approximately as noted



As has been noted previously,⁶ the frequencies of the symmetrical carbon-hydrogen vibration show a general increase as the bond angle deformation is increased. Unfortunately, the more fundamental quantity, the carbon-hydrogen stretching force constant, has not been determined for these compounds. It has been roughly approxima-

(6) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5030 (1951).