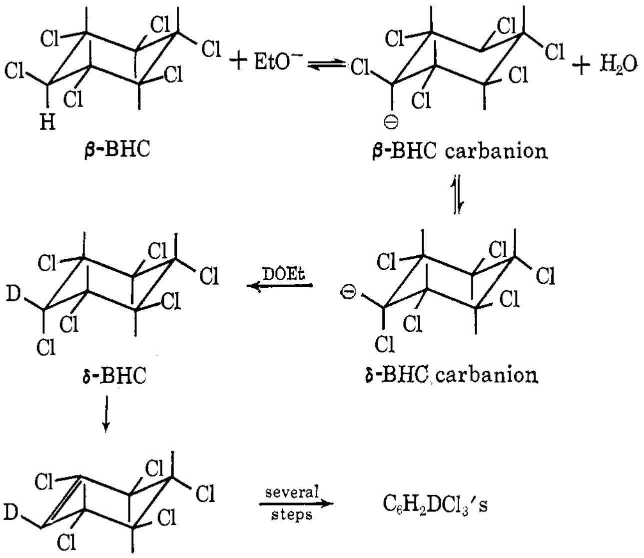
The Mechanism of the Dehydrochlorination of β-Benzene Hexachloride[1]

Jack Hine,[2] Richard D. Weimar, Jr., Paul B. Langford, and O. Bertrand Ramsay

Contribution from the School of Chemistry of the Georgia Institute of Technology, Atlanta, Georgia, and the Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received August 25, 1966*

Abstract: The dehydrochlorination of β-benzene hexachloride by sodium methoxide in methanol-O-*d* yields a trichlorobenzene mixture (containing about 87% 1,2,4 isomer) that contains 0.02–0.05 deuterium atom/molecule when the dehydrochlorination is stopped at 70% completion. This amount of deuterium is no more than would have been expected to arise by deuterium exchange of the trichlorobenzene after its formation. It is therefore concluded that the dehydrochlorination does not involve an initial isomerization of β-benzene hexachloride to the δ isomer. An estimate of the rate constant to be expected for carbanion formation from β-benzene hexachloride under the dehydrochlorination conditions gives a value fairly near the observed rate constant for dehydrochlorination. It is therefore plausible that elimination proceeds *via* intermediate carbanion formation. However, it is also plausible that the reaction consists largely of a concerted *cis* elimination from a boat conformer.

The kinetics of the basic dehydrochlorination of five of the eight isomers of benzene hexachloride have been studied by Cristol, *et al.*,[3,4] and by Hughes, *et al.*,[5] among others. The α, γ, δ, and ε isomers were all found to react at the same rate, within a factor of about 15, but β-benzene hexachloride was less reactive by about 10,000-fold. The relative unreactivity of the β isomer was attributed to the fact that it is the only isomer for which no initial *trans* dehydrochlorination is possible. In order to learn whether the much slower *cis* dehydrochlorination of the β isomer proceeds *via* an intermediate carbanion, Cristol and Fix studied the reaction in ethanol containing about 75% ethanol-O-*d*.[6] The unreacted β-benzene hexachloride isolated after the reaction had proceeded about 50% to completion was found to contain about 0.08% excess deuterium; apparently an intermediate carbanion had been formed and had abstracted a deuteron or proton from the solvent.[7] The intermediate carbanion might also lose a β chloride to complete the initial dehydrochlorination, but there is still another possibility. The intermediate carbanion may be protonated with inversion of configuration to give δ-benzene hexachloride, which would then be dehydrochlorinated relatively rapidly under the reaction conditions. If this is the case, then, as Cram has pointed out,[8] the reaction in a deuterated solvent will lead to the deuterio-δ-benzene hexachloride shown in the following reaction scheme. Subsequent *trans* dehydrochlorination would lead to the deuteriopentachlorocyclohexane shown, since the only other *trans* dehydrochlorination possible would have to proceed through a conformer with five axial chlorine atoms. Subsequent dehydrochlorination of the pentachlorocyclohexene, which would be *cis* but activated by the double bond(s) already present in the molecule, would not be likely to remove the deuterium. Therefore the trichlorobenzenes formed would be expected to be partly deuterated.



As an extension of previous investigations of *cis*[9] and carbanion-type[10–12] elimination reactions, and after learning that neither Professor Cristol nor Professor Cram planned such a study, we investigated the deuterium content of the trichlorobenzene formed in the dehydrochlorination of β-benzene hexachloride in a deuterated solvent.

Experimental Section

Materials. The β-benzene hexachloride used melted at 304–305°; the reported melting points cover the range 297–312°.[13] The

---

[1] (a) Part VI in the series "The Carbanion Mechanism for β-Elimination Reactions." For part V see J. Hine, R. D. Weimar, Jr., P. B. Langford, and O. B. Ramsay, *J. Am. Chem. Soc.*, 85, 3894 (1963). (b) Abstracted in part from the Ph.D. Thesis of P. B. Langford, Georgia Institute of Technology, 1962.

[2] Address correspondence to The Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210.

[3] S. J. Cristol, *J. Am. Chem. Soc.*, 69, 338 (1947); 71, 1894 (1949).

[4] S. J. Cristol, N. L. Hause, and J. S. Meek, *ibid.*, 73, 674 (1951).

[5] E. D. Hughes, C. K. Ingold, and R. Pasternak, *J. Chem. Soc.*, 3832 (1953).

[6] S. J. Cristol and D. D. Fix, *J. Am. Chem. Soc.*, 75, 2647 (1953).

[7] The 0.08% excess deuterium reported is too large to be accounted for in terms of concentration (by a kinetic isotope effect—even an infinite one) of the deuterium present in the benzene hexachloride used as starting material.

[8] D. J. Cram, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 319–321.

[9] J. Hine and O. B. Ramsay, *J. Am. Chem. Soc.*, 84, 973 (1962).

[10] J. Hine and L. A. Kaplan, *ibid.*, 82, 2915 (1960).

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

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

[13] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p 505.

δ isomer melted at 138°, as reported by Hughes, Ingold, and Pasternak.[5]

In early experiments methanol-O-*d* obtained from Merck Sharp and Dohme of Canada, found by nmr measurements to contain about 95% CH_3OD and 5% CH_3OH, was used. For all the experiments described in detail here, methanol-O-*d* was prepared from trimethyl borate, deuterium oxide, and sodium carbonate, using a method based on that of Bunnett and Reinheimer.[14] The crude product obtained by the method of these workers, containing small amounts of water and trimethyl borate, was purified by adding sodium to it before the next distillation. The final product contained 97 ± 2% methanol-O-*d*.

Kinetics of the Reaction of β-Benzene Hexachloride with Sodium Methoxide. In a typical experiment, 5.00 ml of 0.01989 *M* β-benzene hexachloride and 0.500 ml of 0.9895 *M* sodium methoxide, both in methanol, were added to each of several 12-ml vials. Each vial was sealed and placed in a constant-temperature bath for a measured period of time, then removed and cooled. The cooled vial was opened; its contents plus two aqueous rinses were poured into a flask and, in the runs at 70°, titrated with standard hydrochloric acid to the phenolphthalein end point. In the runs at 100° the flask already contained excess acid, which was back-titrated with standard base. The various operations were carried out promptly so that only a negligible amount of reaction took place when the vials were not in the constant-temperature bath.

Data obtained at 70° are summarized in Table I. The rate constants were calculated from the following equation which takes into account the fact that 3 moles of base is used up per mole of organic halide

Table I. Kinetics of the Reaction of β-Benzene Hexachloride with Sodium Methoxide in Methanol at 70° [a]

Time, sec	0.0758 *M* HCl,[a] ml	[β-BHC]	$10^4 k$, M^{-1} sec^{-1}
0	6.52	0.01808	
6,930	5.82	0.01484	3.34
14,220	5.22	0.01208	3.53
22,080	4.77	0.01002	3.51
28,260	4.50	0.00878	3.48
36,420	4.23	0.00754	3.39
46,470	3.99	0.00643	3.26
		Av	3.42 ± 0.09

[a] Per 5.50 ml of reaction solution.

$$k = \frac{2.303}{t(b - 3a)} \log \frac{3a(b - 3x)}{b(3a - 3x)}$$

where *a* is the initial concentration of β-benzene hexachloride, *x* is the change in that concentration that has occurred at time *t*, and *b* is the initial concentration of sodium methoxide. At 100° the second-order rate constant, 236 ± 5 × 10^{-4} M^{-1} sec^{-1}, was obtained. These rate constants are based on concentrations at room temperature and have not been corrected for solvent expansion.

Products of the Dehydrochlorination of β- and δ-Benzene Hexachloride. To a solution of 0.08773 g (0.302 mmole) of β-benzene hexachloride in 33.50 ml of methanol, 1.50 ml of 1.170 *M* sodium methoxide in methanol was added. The resulting solution was placed in a sealed tube in a 99° bath for 30 min and cooled, and 7.00 ml of 0.2576 *M* aqueous perchloric acid in 70 ml of water was added. Titration of the excess acid required 7.37 ml of 0.1044 *M* aqueous sodium hydroxide, showing that 80% of the benzene hexachloride had reacted. The titrated solution was extracted with three 15-ml portions of carbon tetrachloride, which were then combined and concentrated to a volume of about 2 ml by distillation from a water bath through a 3-in. Vigreux column. Gas–liquid partition chromatography of the residue through a 6-ft column packed with Apiezon L showed the peaks characteristic of 1,3,5-trichlorobenzene, 1,2,4-trichlorobenzene, and 1,2,3-trichlorobenzene, in that order. Comparison of the results with those obtained using synthetic mixtures of the three isomeric trichlorobenzenes having about the same composition showed that 87 ± 1% 1,2,4-trichlorobenzene, 9 ± 1% 1,3,5-trichlorobenzene, and 4 ± 1% 1,2,3-trichlorobenzene were present.

When δ-benzene hexachloride was exposed to very similar conditions, it was found to have reacted essentially completely. Although the basic solution was permitted to stand at room temperature for less than a minute before it was sealed and placed in the 99° bath, it is probable that significant amounts of dehydrohalogenation occurred at temperature lower than 99°. Analysis of the trichlorobenzenes formed showed that 87 ± 1% 1,2,4 isomer, 8 ± 1% 1,3,5 isomer, and 5 ± 1% 1,2,3 isomer were formed.

Dehydrochlorination of β-Benzene Hexachloride in Methanol-O-*d*. A 0.637-g (2.19 mmoles) sample of β-benzene hexachloride was dissolved in 100 ml of refluxing methanol-O-*d*, and 1.55 ml of 4.45 *M* sodium methoxide in methanol-O-*d* was rinsed down the condenser with 2 ml of methanol-O-*d*. After 15 hr at 67° the solution was distilled until 65 ml of distillate had been collected. The residue was cooled and found to require 20.80 ml of 0.1128 *M* aqueous perchloric acid for titration to the brom thymol blue end point. Hence 4.55 mmoles of base, or 1.52 mmoles of benzene hexachloride (70% of that originally present), had reacted. The titrated solution was extracted with two 5-ml portions of carbon tetrachloride, which were then placed in a distilling flask that was slowly heated to 150° by an oil bath. The remaining material consisted of about 0.38 ml of almost colorless liquid and a little solid β-benzene hexachloride. The supernatant liquid was removed from the solid and its nmr spectrum was found to be essentially identical with that of the product obtained when the procedure described above was carried out (on a somewhat different scale) using ordinary methanol instead of methanol-O-*d*. Each nmr spectrum was essentially identical with that of synthetic mixtures of trichlorobenzenes containing 87 ± 2% 1,2,4 isomer, 8 ± 1% 1,3,5 isomer, and 5 ± 1% 1,2,3 isomer. Blank experiments using 1,2,4-trichlorobenzene-3-*d* prepared as described previously[15] showed that if 10% of the 1,2,4-trichlorobenzene present had contained deuterium in the 3 position it would have been detected, but that less than ~5% would have escaped detection.

Analysis of the trichlorobenzene mixture produced in the dehydrochlorination reaction carried out in methanol-O-*d* at the 8.430-μ band characteristic of 1,2,4-trichlorobenzene-3-*d* and the 9.135-μ band characteristic of 1,2,4-trichlorobenzene was in agreement with a 1,2,4-trichlorobenzene-3-*d* content of 3.6 ± 1%.

Results and Discussion

In an early run in which the dehydrochlorination of β-benzene hexachloride in methanol-O-*d* was allowed to proceed past 99.9% completion, the trichlorobenzene mixture produced was found to be largely deuterated. When it was found that 1,2,4-trichlorobenzene, the principal product, undergoes deuterium exchange to a significant extent under the reaction conditions, however, it was seen that this result was meaningless. As a guide to further work, the kinetics of the base-catalyzed deuterium exchange of 1,2,4-trichlorobenzene and the dehydrochlorination of β-benzene hexachloride were studied, both in methanol. In the former study, which has already been published,[15] the second-order rate constant for the dedeuteration of 1,2,4-trichlorobenzene-3-*d* was found to be 4.8 × 10^{-6} M^{-1} sec^{-1} at 70°. In the present study the second-order rate constant for the dehydrochlorination of β-benzene hexachloride under the same conditions was found to be 342 × 10^{-6} M^{-1} sec^{-1}. Thus even if there is a sevenfold deuterium kinetic isotope effect in the dedeuteration reaction, the rate constant for the formation of the trichlorobenzene is ten times as large as the rate constant for its subsequent exchange.

If, in the following four-reaction scheme

$$C_6H_6Cl_6 + MeO^- \xrightarrow{k_1} C_6H_5Cl_5 + MeOH + Cl^-$$

$$C_6H_5Cl_5 + 2MeO^- \xrightarrow{\text{fast}} C_6H_3Cl_3 + 2MeOH + 2Cl^-$$

---

(14) J. F. Bunnett and J. D. Reinheimer, *J. Am. Chem. Soc.*, **84**, 3284 (1962).

(15) J. Hine and P. B. Langford, *J. Org. Chem.*, 27, 4149 (1962).

Hine, et al. / Dehydrochlorination of β-Benzene Hexachloride

$$C_6H_3Cl_3 + MeO^- \xrightarrow{k_2} C_6H_2Cl_3^- + MeOH$$

$$C_6H_2Cl_3 + MeOD \xrightarrow{\text{fast}} C_6H_2DCl_3 + MeO^-$$

k_1 is ten times as large as k_2 then when the dehydrohalogenation of benzene hexachloride is 70% complete only about 4.9%[16] of the trichlorobenzene formed will have undergone deuterium exchange. If the kinetic isotope effect is less than sevenfold, the trichlorobenzene will have exchanged even less. This small an amount of exchange should not interfere with our learning whether any major part of the trichlorobenzene produced contains deuterium when it is first formed.

Therefore β-benzene hexachloride was dehydrochlorinated by sodium methoxide in methanol-O-*d* at about 67° until the reaction was 70% complete. Proton magnetic resonance measurements showed no deuterium in the trichlorobenzene mixture (about 87% 1,2,4-trichlorobenzene) produced although 0.1 deuterium atom/molecule would certainly have been detected. The infrared spectrum of the reaction mixture was essentially identical with that of trichlorobenzene mixtures containing 3.6 ± 1% 1,2,4-trichlorobenzene-3-*d*. We therefore concluded that very little, if any, deuterium was present in the trichlorobenzene as formed, and that the dehydrochlorination of β-benzene hexachloride does not proceed *via* the δ isomer.

In relation to Cristol's suggestion that the dehydrochlorination of β-benzene hexachloride proceeds by a carbanion mechanism, it is of interest to estimate whether the dehydrochlorination proceeds at a rate that is plausible for carbanion formation. We do not have data on sufficiently closely related model compounds to permit a very reliable estimate, but even a crude estimate may be useful. Let us consider the second-order rate constants for the formation of carbanions from species of the type XYCHCl. The Taft σ^* constant for long straight-chain alkyl groups is around -0.13.[17] We will assume that the reactivity of the hydrogen on the same carbon atom as the chlorine atom in cyclohexyl chloride is the same as that of a hydrogen atom on the same carbon atom as chlorine in a long-chain secondary chloride, *i.e.*, that the α-hydrogen atom in cyclohexyl chloride is as reactive as in any other compound of the type XYCHCl where $\sigma^*_X + \sigma^*_Y$ is equal to -0.26. Each α-chlorine substituent increases the value of σ^* for an alkyl group by about 1.05,[18] and each β chlorine increases it by about 0.48.[19] We shall assume that the effect of γ chlorine is $(1/2.8)(0.48)$, that of δ chlorine is $(1/2.8)^2 \cdot (0.48)$, and that of ε chlorine $(1/2.8)^3(0.48)$. This leads to the expectation that benzene hexachloride would form carbanions at the same rate as an XYCHCl compound for which $\sigma^*_X + \sigma^*_Y$ is equal to 3.56. The rate of carbanion formation should be somewhat faster than that of CF_3CH_2Cl, an XYCHCl compound for which $\sigma^*_X + \sigma^*_Y$ is equal to $\sim$3.3.[20] The fact that the rate constant for formation of carbanions from methoxide ions and CF_3CDCl_2 is essentially the same as from methoxide ions and $CDCl_3$[11] suggests that the α-CF_3 substituent has about the same effect on carbanion formation rates that α-Cl does. If this is true then CH_2Cl_2 should form carbanions at a rate characteristic of XYCHCl compounds for which $\sigma^*_X + \sigma^*_Y$ is about 3.3. Duke has found that, in the presence of potassium *t*-butoxide in *t*-butyl alcohol, at 36°, both methylene iodide and methylene bromide undergo deuterium exchange 530 times faster than in the presence of methanolic sodium methoxide.[21] If this factor is also applicable to methylene chloride, whose second-order rate constant for carbanion formation in *t*-butyl alcohol at 36° is $1.07 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$, then its rate constant for carbanion formation in methanol at 36° is about $2 \times 10^{-7}\ M^{-1}\ \text{sec}^{-1}$. If this rate constant is characteristic of a case in which $\sigma^*_X + \sigma^*_Y$ is about 3.3, benzene hexachloride, for which $\sigma^*_X + \sigma^*_Y$ was estimated to be 3.56, should react somewhat faster. The rate constant for the dehydrochlorination of β-benzene hexachloride by sodium methoxide in methanol at 36°, extrapolated from our measurements at 70 and 100° (which yield an Arrhenius activation energy of 36 kcal/mole), is $1.0 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$. In view of the estimate that we have made this seems to be a perfectly plausible rate constant for the formation of carbanions from β-benzene hexachloride under the given conditions. In view of the uncertainties in the estimate, however, the preceding cannot be considered a significant positive argument for the carbanion mechanism; it merely shows that the carbanion mechanism cannot be ruled out at present on the basis of a reactivity argument.

It also seems that one cannot at present rule out the possibility that the carbanion formation established[22] by Cristol and Fix's observation of deuterium exchange occurs for only a very small percentage of the reacting molecules, most of which are dehydrochlorinated by a concerted *cis* elimination, perhaps proceeding through a boat conformer. Reaction *via* a boat conformer would add to the activation energy the energy (perhaps around 5 kcal/mole[23]) required for isomerization to the boat form, but the Arrhenius activation energy for the dehydrochlorination of β-benzene hexachloride is 10–14 kcal/mole higher than that for the α, γ, δ, or ε isomer.[3–5] (The free energy of activation for the β isomer is only 5.5–7.0 kcal/mole higher than that of the other isomers.) Perhaps part or most of the higher activation energy for the β isomer is due to the intermediacy of a boat form. *cis* elimination *via* a boat form would permit a concerted elimination with a dihedral angle between the reacting C–H and C–Cl bonds of 0° or very near it. As DePuy, Thurn, and Morris have pointed out[24] such eliminations, like those in which the dihedral angle is near 180°, appear to be favored relative to those in which the dihedral angle is of an intermediate size. In the accompanying paper[25]

---

(16) Because of the well-known difficulties associated with the exact treatment of consecutive bimolecular reactions, this number was calculated by a graphical integration.

(17) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 97.

(18) Compare $\sigma^*_{CH_3}$ and $\sigma^*_{CH_2Cl}$.[17]

(19) Compare $\sigma^*_{C_2H_5}$ and $\sigma^*_{CH_2CH_2Cl}$.[17]

(20) $\sigma^*_{CF_3}$ is estimated to be 2.80, larger by 0.15 than $\sigma^*_{CCl_3}$, since $\sigma^*_{CH_2F}$ is 0.05 larger than $\sigma^*_{CH_2Cl}$ and $\sigma^*_{CHF_2}$ is 0.11 larger than $\sigma^*_{CHCl_2}$.

(21) R. B. Duke, unpublished observations from the Georgia Institute of Technology.

(22) We are making here the usual assumption that there is no concerted base-catalyzed (SE2) exchange of deuterium on carbon, since no such mechanism appears yet to have been established for any deuterium exchange at saturated carbon.

(23) *Cf.* W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Am. Chem. Soc.*, 82, 1255 (1960).

(24) C. H. DePuy, R. D. Thurn, and G. F. Morris, *ibid.*, 84, 1314 (1962).

(25) J. Hine, *ibid.*, 88, 5525 (1966).

the basis for this relationship between dihedral angles and rates of elimination reactions is discussed in terms of the principle of least motion.[26,27]

Acknowledgment. We wish to acknowledge our indebtedness to the National Science Foundation for Grant GP-2002 in partial support of this investigation and for a grant that permitted the purchase of the nmr spectrometer used, and to Dr. Rayner Johnson of E. I. du Pont de Nemours and Company for the gift of some of the β-benzene hexachloride used.

---

(26) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939).

(27) J. Hine, *J. Org. Chem.*, **31**, 1326 (1966).

Application of the Principle of Least Motion to the Stereochemistry of Elimination Reactions[1]

Jack Hine[2]

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia, and the Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received August 25, 1966*

Abstract: For the transformation of ethyl chloride to ethylene, calculations are made to determine the distances the two carbon and four hydrogen atoms must move during the reaction. The geometry of the ethylene formed (relative to that of the reactant) that minimizes the sums of the squares of the distances these six atoms must move is calculated for elimination reactions with dihedral angles between the eliminated C–H and C–Cl bonds of 0 (pure *cis* elimination), 60, 120, and 180° (pure *trans* elimination). The calculated least-squares distances are 0.421, 1.326, 1.130, and 0.185 A^2, respectively. Thus, according to the principle of least motion, there should be a tendency for pure *trans* eliminations to be faster than pure *cis* eliminations, which should in turn be faster than eliminations in which the dihedral angle is near the range 60–120°.

In the accompanying paper, the possibility was considered that the dehydrochlorination of β-benzene hexachloride involves a concerted *cis* elimination from a boat conformer.[3] DePuy, Thurn, and Morris have described evidence that when the dihedral angle is near 0° such eliminations proceed more rapidly than when the dihedral angle is nearer 90°, although not as rapidly as pure *trans* eliminations, where the dihedral angle is 180°.[4] In the present paper it will be shown that according to the principle of least motion[1b,5] there should be a tendency for elimination reactions to be fastest when the dihedral angle is near 180°, slower when it is near 0°, and still slower when it is near the range 60–120°.

According to the principle of least motion, those elementary reactions will be favored that involve the least change in atomic position and electronic configuration.[1b,5] In the present discussion, as in the previous application of the principle to the reactions of resonance-stabilized species, only the magnitude of changes in atomic position will be considered. It will be assumed that all the changes in atomic position take place simultaneously, and when any atomic position has undergone a certain fraction of the over-all change that it will undergo in the reaction, all the other atomic positions have also undergone the same fraction of their final over-all change.

It is postulated that the reaction will occur in such a fashion as to involve the least expenditure of energy in changing the relative positions of atoms. The energy required to stretch or bend a bond is proportional, to the degree to which Hooke's law is applicable, to the square of the distance that the bond is bent or stretched. Therefore we shall assume that the reaction takes place so as to minimize the sums of the squares of the atomic displacements. This approach would demand that all the force constants for the displacements of various atoms be identical if it were to be completely applicable. In the present case, however, where we shall consider only the displacements, in various directions, of the various atoms in a given molecule, it amounts largely to the approximation that the various atoms move in isotropic force fields.

Calculations

For simplicity all calculations will be made for the case of the E2 transformation of ethyl chloride to ethylene. In ethyl chloride the carbon atoms are assumed to have 109° 28′ bond angles and the carbon–carbon and carbon–hydrogen bond distances have been set equal to the averages of the values (1.538 and 1.104 A, respectively) quoted by Stoicheff for such distances in saturated compounds.[6] For ethylene, the carbon–carbon bond length, 1.337 A, the carbon–hydrogen bond length, 1.086 A, and the H–C–H bond angle, 117° 22′, given by Allen and Plyler have been used.[7]

---

(1) (a) Part XI in the series "Polar Effects on Rates and Equilibria." (b) For part X see J. Hine, *J. Org. Chem.*, **31**, 1326 (1966).

(2) Address correspondence to The Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210.

(3) J. Hine, R. D. Weimar, Jr., P. B. Langford, and O. B. Ramsay, *J. Am. Chem. Soc.*, **88**, 5522 (1966).

(4) C. H. DePuy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1314 (1962).

(5) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939).

(6) B. P. Stoicheff, *Tetrahedron*, **17**, 135 (1962).

(7) H. C. Allen, Jr., and E. K. Plyler, *J. Am. Chem. Soc.*, **80**, 2673 (1958).