

Theoretical Considerations Concerning the Reactions Between Ethylene and the Halogens and Their Products

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Theoretical Considerations Concerning the Reactions Between Ethylene and the Halogens and Their Products

ALBERT SHERMAN, OSCAR T. QUIMBY AND RICHARD O. SUTHERLAND, *University of Wisconsin, Madison, Wisconsin*

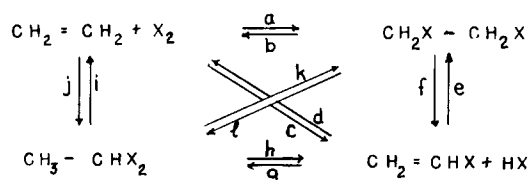
(Received July 27, 1936)

Ethylene may react with a halogen by a substitution reaction to give a vinyl halide and hydrogen halide, or the halogen may add to the double bond to give 1,2-dihaloethane or rearrange and give ethylidene halide. It is found that the symmetrical addition is favored in the case of each halogen. 1,2-dihaloethane, or the corresponding ethylidene compound may decompose to give ethylene and the halogen, or the vinyl halide and hydrogen halide. It is

found that ethylene formation is favored in the bromine and iodine derivatives, whereas, in agreement with experiment, vinyl chloride and HCl would be produced from either 1,2-dichloroethane or ethylidene chloride. In most of the reactions considered mechanisms involving free radicals are slightly more probable than the corresponding unimolecular or bimolecular reactions.

INTRODUCTION

A CONVENIENT and useful scheme for representing the various possible reactions between ethylene and the halogens is as follows:



X denotes any one of the halogens Cl, Br, or I. The twelve reactions given in the above scheme are labeled *a*, *b*, *c*, \dots *l*. In this paper we shall calculate, theoretically, the activation energies of the various reactions and then predict the behavior of the different compounds given in the scheme. From each corner of the above rectangle arrows go out in three directions, and which of the three courses is taken will depend upon the rate or activation energy of the reaction concerned.

Sherman and Sun¹ were primarily interested in the addition of the halogens to ethylene, and the decomposition of the products formed—i.e., reactions *a* and *b*—and calculated the relevant activation energies by the so-called semi-empirical method of Eyring. We shall incorporate their results in the present paper and extend the calculations to other reactions, using the same method.

Sun² has calculated the activation energies involved in the addition of the hydrogen halides to a

double bond by Eyring's method, but we have repeated his work because he did not use Morse constants consistent with our choice of values. Our results differ only slightly from his.

CALCULATIONS

The method of calculating activation energies by the semi-empirical method of Eyring has frequently been described elsewhere,³ and will not be repeated here. We shall merely give in Table I the constants used for constructing the various Morse curves in question.

The constants used for the bonds C—C, C—Cl, C—Br, C—I, Cl₂, Br₂, and I₂ are as given in Table I of the paper of Sherman and Sun. (See reference 1.)

RESULTS

The activation energies and heats of reaction, calculated from our Morse constants, are given in Table II.

Based on considerable experience it should be pointed out that the calculated values of activation energies are not very sensitive to the particular bond constants chosen. For example, in the reaction $\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$ increasing the strength of the H—H bond by 5 kcal. increases *A* by less than 2 kcal. This is particularly true for the difference between two calculated activation energies and since almost all our reasoning is based upon a knowledge of such differences it is highly probable that none of our conclusions

¹ Sherman and Sun, *J. Am. Chem. Soc.* **56**, 1096 (1934).

² Sun, *J. Chinese Chem. Soc.* **41**, 98 (1936).

³ See, for example, Van Vleck and Sherman, *Rev. Mod. Phys.* **7**, 167 (1935).

TABLE I.

Bond	$r_0(\text{\AA})$	$\omega_0(\text{cm}^{-1})$	$D(\text{kcal.})$
H—Cl	1.28 ^a	2841	101.0 ^b
H—Br	1.42 ^a	2603	86.2 ^b
H—I	1.62 ^a	2233 ^c	70.8 ^b
C—H	1.12 ^d	2930 ^d	99.6 ^c

^a Weizel, *Bandenspektrum* (Leipzig, 1931).^b Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).^c Kohlrausch, *Der Smekal-Raman Effekt* (J. Springer, Berlin, 1931).^d Mulliken, Rev. Mod. Phys. **4**, 1 (1932).^e Pauling and J. Sherman, J. Chem. Phys. **1**, 606 (1933).

would be changed by slightly altering our Morse constants.

In Table II the A 's are activation energies, ordinarily defined by the Arrhenius equation $d\ln k/dT = A/RT^2$.⁴ ΔH is the change in heat content of the reaction, calculated by taking the difference between the strengths of the bonds formed and broken. A minus sign means that the reaction, as read from left to right, is exothermic.

The activation energies of the various reactions in the scheme given in the introduction may now be determined. These will, of course, depend

TABLE II.

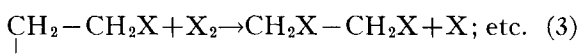
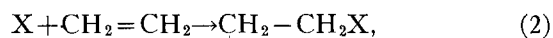
Reaction	Halogen	A	A'	ΔH
1. $\text{CH}_2=\text{CH}_2 + \text{X}_2 \xrightleftharpoons[A_{1'}]{A_1} \text{CH}_2\text{X}-\text{CH}_2\text{X}$	Cl Br I	25.2 24.4 22.4	80.4 50.2 30.0	-55.2 -25.8 -7.6
2. $\text{CH}_2=\text{CH}_2 + \text{X}_2 \xrightleftharpoons[A_{2'}]{A_2} \text{CH}_2=\text{CHX} + \text{HX}$	Cl Br I	45.0 47.0 54.0	68.0 46.4 33.8	-23.0 +0.6 +20.2
3. $\text{CH}_2=\text{CHX} + \text{HX} \xrightleftharpoons[A_{3'}]{A_3} \text{CH}_2\text{X}-\text{CH}_2\text{X}$	Cl Br I	43.5 41.9 36.4	75.7 68.3 64.2	-32.2 -26.4 -27.8
4. $\text{CH}_2=\text{CH}_2 + \text{X} \xrightleftharpoons[A_{4'}]{A_4} \text{CH}_2-\text{CH}_2\text{X}$	Cl Br I	0 0 2.2	33.6 13.0 1.2	-33.6 -13.0 +1.0
5. $\text{CH}_2-\text{CH}_2\text{X} + \text{X}_2 \xrightleftharpoons[A_{5'}]{A_5} \text{CH}_2\text{X}-\text{CH}_2\text{X} + \text{X}$	Cl Br I	3.0 2.3 1.8	24.6 15.1 10.4	-21.6 -12.8 -8.6
6. $\text{CH}_2=\text{CH}_2 + \text{X} \xrightleftharpoons[A_{6'}]{A_6} \text{CH}=\text{CHX} + \text{HX}$	Cl Br I	14.9 23.4 33.5	16.3 10.0 4.7	-1.4 +13.4 +28.8
7. $\text{CH}=\text{CH}_2 + \text{X}_2 \xrightleftharpoons[A_{7'}]{A_7} \text{CH}=\text{CHX} + \text{X}$	Cl Br I	3.0 2.3 1.8	24.6 15.1 10.4	-21.6 -12.8 -8.6
8. $\text{CH}_2\text{X}-\text{CHX} + \text{HX} \xrightleftharpoons[A_{8'}]{A_8} \text{CH}_2\text{X}-\text{CH}_2\text{X} + \text{X}$	Cl Br I	16.3 10.0 4.7	14.9 23.4 33.5	+1.4 -13.4 -28.8

⁴ For a more exact definition see Eyring, J. Chem. Phys. **3**, 107 (1934).

upon the particular mechanism assumed. We proceed as follows:



If the mechanism of this reaction is considered to be bimolecular the activation energies are as given in Table II for reaction 1. The reaction may, however, proceed by the following chain mechanism for chlorine and bromine:



The above reactions constitute a chain since the halogen atom which is used up in (2) is formed in reaction (3), and so may react with another ethylene molecule, etc.

By the usual methods it may be shown that for this mechanism the over-all activation energy of reaction a is equal to the activation energy of reaction (2) plus one-half the heat of dissociation of the halogen, i.e., $A = A_{(2)} + \frac{1}{2}D_{\text{X}_2}$.⁵ This equals $0 + 28.5 = 28.5$ kcal. for chlorine and $0 + 22.6 = 22.6$ kcal. for bromine.

⁵ We shall illustrate the method by deriving the given relation in this particular case. Let the k 's be the specific reaction rate constants of the reactions concerned, and let E denote $\text{CH}_2=\text{CH}_2$; EX , $\text{CH}_2-\text{CH}_2\text{X}$; and K the equilibrium constant of reaction (1). Then, assuming that the rate of a reaction is proportional to the concentration of reacting substances, and the concentration of the free radicals do not change after the initial instant, we have

$$\begin{aligned} -\frac{d(E)}{dt} &= k_2(X)(E); \\ -\frac{d(X_2)}{dt} &= k_1(X_2) - k_1'(X)^2 + k_3(X_2)(EX), \\ \frac{d(X)}{dt} &= 2k_1(X_2) - k_1'(X)^2 - k_2(X)(E) + k_3(X_2)(EX) = 0, \\ \frac{d(EX)}{dt} &= k_2(X)(E) - k_3(X_2)(EX) = 0. \end{aligned}$$

Therefore $2k_1(X_2) = k_1'(X)^2$, or

$$\begin{aligned} (X) &= \sqrt{\frac{2k_1}{k_1'}}(X_2)^{\frac{1}{2}} = \sqrt{2K^{\frac{1}{2}}}(X_2)^{\frac{1}{2}}, \\ (EX) &= \frac{k_2}{k_3} \sqrt{\frac{2k_1}{k_1'}} \frac{(X_2)^{\frac{1}{2}}}{(X_2)} (E), \\ -\frac{d(E)}{dt} &= -\frac{d(X_2)}{dt} = \sqrt{2K^{\frac{1}{2}}}(X_2)^{\frac{1}{2}}(E). \end{aligned}$$

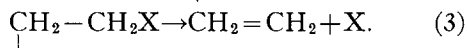
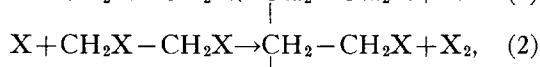
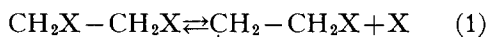
But, neglecting entropy, and remembering $k = \text{constant} \cdot e^{-A/RT}$, $\text{constant} \cdot e^{-A/RT} = \text{constant} \cdot e^{-A_{(2)}/RT} \cdot e^{-\Delta H/2RT} = \text{const} \cdot e^{-A_{(2)}/2RT + \Delta H/RT}$ or $A = A_{(2)} + \frac{1}{2}D_{\text{X}_2}$.

For iodine it is clear from Table II that the chain mechanism just given must be modified by including the reverse of reaction (2), since the activation energies of the forward and reverse reaction only differ by one kilogram calorie. We then have $A = A_{(2)} + A_{(3)} + \frac{1}{2}D_{I_2} - A'_{(2)}$, where $A'_{(2)}$ stands for the activation energy of the reaction which is the reverse of (2). Hence, $A = 2.2 + 1.8 + 17.7 - 1.2 = 20.5$ kcal.

Reaction b: $\text{CH}_2\text{X}-\text{CH}_2\text{X} \rightarrow \text{CH}_2=\text{CH}_2 + \text{X}_2$.

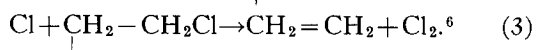
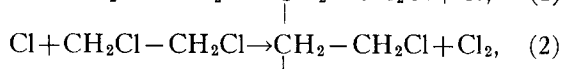
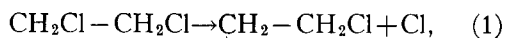
This reaction may occur as a unimolecular decomposition, in which case the activation energies are as given in Table II for reaction 1 (the A' 's).

In the case of the bromine and iodine compounds the following chain mechanism is possible:



The activation energy of the decomposition reaction then becomes $A = \frac{1}{2}(D_{\text{C-X}} + A_{(2)} + A_{(3)})$. This is $\frac{1}{2}(58.0 + 15.1 + 13.0) = 43.1$ kcal. for the bromine derivative and $\frac{1}{2}(44 + 10.4 + 1.2) = 27.8$ kcal. for the iodine compound.

In the case of $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ the above mechanism does not appear reasonable because the reaction $\text{CH}_2-\text{CH}_2\text{Cl} \rightarrow \text{CH}_2=\text{CH}_2 + \text{Cl}$ is endothermic 33.6 kcal., i.e., the decomposition of $\text{CH}_2-\text{CH}_2\text{Cl}$ is improbable compared to its reaction, since the activation energy of a reaction involving a free radical (provided the reaction is not endothermic) is much less than this. The following scheme is suggested:

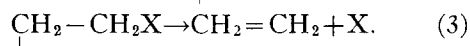
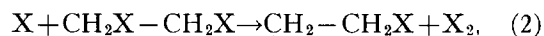


It is seen that the above reactions do not constitute a chain but rather a series of reactions in

⁶ It is of course more probable that the monochloroethylene free radical collide with the dichlor derivative than a chlorine atom, but the most likely chemical reaction would not be detectable in this case, i.e., $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl} + \text{CH}_2-\text{CH}_2\text{Cl} \rightarrow \text{CH}_2\text{Cl}-\text{CH}_2+\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$.

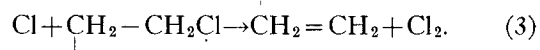
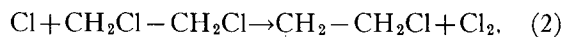
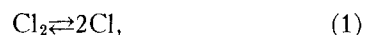
which the first one is taken to be the slow step, i.e., is rate determining. Although (3) involves two free radicals, the concentrations of which are small, its rate is considered to be greater than that of reaction (1) because of the approximately zero value for the activation energy of this reaction and the large value for (1). The activation energy for the decomposition of $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ thus becomes equal to that of the first reaction,—assumed to equal or exceed its endothermicity. Hence $A = D_{\text{C-Cl}} = 78.6$ kcal.

Reaction *b* is really auto-catalytic since X_2 , a product of the reaction, may act as a catalyst for the decomposition of the dihalide. The following mechanism is suggested in the case of the bromine and iodine derivatives:



In this case $A = A_{(2)} + \frac{1}{2}D_{\text{X}_2} = 15.1 + 22.6 = 37.7$ kcal. for the bromine compound⁷ and $10.4 + 17.7 = 28.1$ kcal. for the iodine derivative.

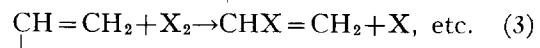
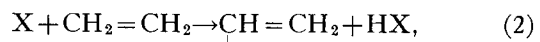
For the dichloride the following mechanism is considered:



Here the dissociation of Cl_2 is the slow step and hence $A = D_{\text{Cl}_2} = 57.0$ kcal.⁸

Reaction c: $\text{CH}_2=\text{CH}_2 + \text{X}_2 \rightarrow \text{CH}_2=\text{CHX} + \text{HX}$.

If this reaction has a bimolecular mechanism as written the activation energies are as given in Table II. The following chain mechanism is however possible:



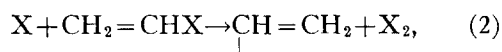
⁷ This value differs from the value given in reference 1 because in that paper ΔH_f of Table II was incorrectly calculated.

⁸ This value differs from that given in reference 1 because there the same mechanism was assumed for the decomposition of the dichloride as for the other dihalide derivatives.

The over-all activation energy is $A = A_{(2)} + \frac{1}{2}D_{X_2}$. For the chlorine, bromine, and iodine compound the reverse of reaction (2) should be considered but this does not affect the value of A since this reverse reaction is slow compared to reaction (3). Hence $A = 14.9 + 28.5 = 43.4$ kcal. for chlorine, $23.4 + 22.6 = 46.0$ kcal. for bromine, and $33.5 + 17.7 = 51.2$ kcal. for the iodine compound.

Reaction d: $CH_2 = CHX + HX \rightarrow CH_2 = CH_2 + X_2$

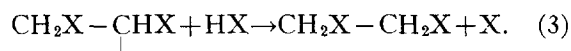
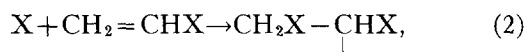
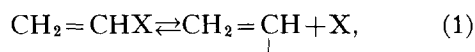
In addition to the bimolecular mechanism, for which activation energies are given in Table II, the following chain is suggested:



Here $A = \frac{1}{2}(D_{C-X} + A_{(2)} + A_{(3)})$
 $= \frac{1}{2}(78.6 + 24.6 + 16.3) = 59.8$ kcal. for Cl,
 and $\frac{1}{2}(58.0 + 15.1 + 10.0) = 41.6$ kcal. for Br,
 and $\frac{1}{2}(44.0 + 10.4 + 4.7) = 29.6$ kcal. for I.

Reaction e: $CH_2 = CHX + HX \rightarrow CH_2X - CH_2X$

The activation energies of this reaction, for a bimolecular mechanism, are given in Table II. The following chain mechanism is suggested:



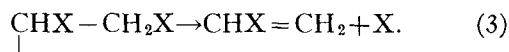
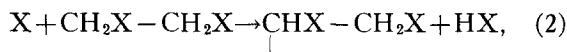
For chlorine and bromine compounds the reverse of (2) is slow compared to (3) and hence $A = A_{(2)} + \frac{1}{2}D_{C-X} = 0 + 39.3 = 39.3$ kcal. for Cl, and $0 + 29.0 = 29.0$ kcal. for Br. For the iodine compound the reverse of (2) is faster than (3) and therefore

$$A = A_{(2)} + A_{(3)} - A'_{(2)} + \frac{1}{2}D_{C-X} = 2.2 + 4.7 - 1.2 + 22.0 = 27.7 \text{ kcal.}$$

Reaction f: $CH_2X - CH_2X \rightarrow CH_2 = CHX + HX$

The activation energies for the unimolecular decompositions are given in Table II. No plausible mechanism involving free radicals for the decomposition of $CH_2X - CH_2X$ into the desired products suggests itself. However, as for reaction

b, the halogen catalyzed decomposition may be considered. For bromine and iodine it is assumed that the following mechanism is operative:

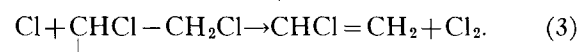


Here

$$A = A_{(2)} + \frac{1}{2}D_{X_2} = 35.5 + 17.7 = 51.2 \text{ kcal. for I,}$$

and $23.4 + 22.6 = 46.0$ kcal. for Br.

For Cl we have the following:

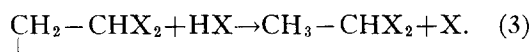
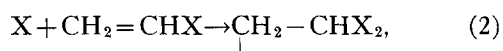
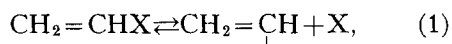


In this case $A = D_{Cl_2} = 57.0$ kcal.

Reaction g: $CH_2 = CHX + HX \rightarrow CH_3 - CHX_2$

According to Markownikoff's rule in organic chemistry the hydrogen atom in this reaction will go to the carbon atom having the greatest number of hydrogen atoms. Hence this reaction should predominate over reaction *e*. However, to the degree of approximation used in these calculations, the activation energy of reactions *e* and *g* are the same. That they are approximately equal is evidenced by the fact that both the symmetrical and the unsymmetrical dihalides are usually found experimentally in any given reaction.

The chain mechanism suggested is similar to that given for *e*:

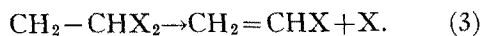
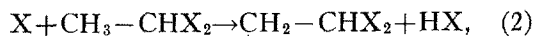


The activation energies are equal to those given under reaction *e*.

Reaction h: $CH_3 - CHX_2 \rightarrow CH_2 = CHX + HX$

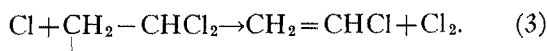
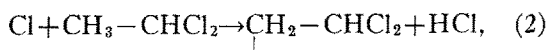
From what has been said about reaction *g* it follows that this decomposition will be of the same nature as that of $CH_2X - CH_2X$. Here also

no satisfactory free radical mechanism suggests itself. However, a halogen catalyzed decomposition mechanism for bromine and iodine is as follows:

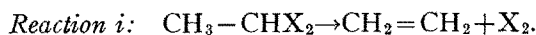


The activation energies are the same as given for the free radical mechanism of reaction *f*.

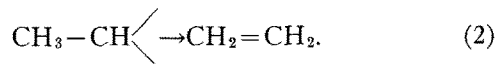
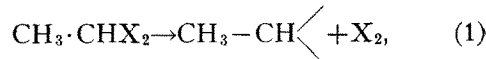
For Cl the following chain is proposed:



Here $A = 57.0$ kcal.



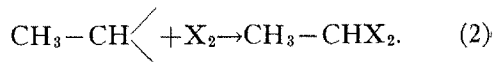
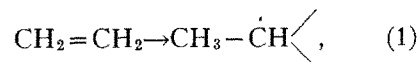
A reasonable mechanism for this decomposition involves a preliminary splitting out of the halogen, followed by a rearrangement of the ethylidene radical. The formation of X_2 could be imagined to take place when the two halogen atoms come close together as a result of a deformation vibration. The two reactions are as follows:



Reaction (2) probably involves a small activation energy and is quite rapid.⁹ Reaction (1) is endothermic 100.2, 70.8, and 52.6 kcal. for Cl, Br, and I, respectively. Hence, according to the above mechanism, the activation energy of reaction *k* is at least 100.2, 70.8 and 52.6 kcal. for Cl, Br, and I, respectively.



The mechanism suggested for this case is the reverse of that for reaction *i*:



Reaction (2) undoubtedly involves a small activation energy and (1) is accordingly considered the rate determining step. This reaction

⁹F. O. Rice and O. K. Rice, *Aliphatic Free Radicals* (Johns Hopkins Press, 1935), pp. 70, 71, 184.

TABLE III.

Reaction	Cl			Br			I		
	Activation Energy		ΔH kcal.	Activation Energy		ΔH kcal.	Activation Energy		ΔH kcal.
	Molecular Mechanism	Free Radical Mechanism		Molecular Mechanism	Free Radical Mechanism		Molecular Mechanism	Free Radical Mechanism	
<i>a</i>	25.2	28.5	-55.2	24.4	22.6	-25.8	22.4	20.5	-7.6
<i>b</i>	80.4	78.6 57.0 (Cl ₂ catalyz.)	55.2	50.2	43.1 37.7 (Br ₂ catalyz.)	25.8	30.0	27.8 28.1 (I ₂ catalyz.)	7.6
<i>c</i>	45.0	43.4	-23.0	47.0	46.0	0.6	54.0	51.2	20.2
<i>d</i>	68.0	59.8	23.0	46.4	41.6	-0.6	33.8	29.6	-20.2
<i>e</i>	43.5	39.3	-32.2	41.9	29.0	-26.4	36.4	27.7	-27.8
<i>f</i>	75.7	57.0 (Cl ₂ catalyz.)	32.2	68.3	46.0 (Br ₂ catalyz.)	26.4	64.2	51.2 (I ₂ catalyz.)	27.8
<i>g</i>	43.5	39.3	-32.2	41.9	29.0	-26.4	36.4	27.7	-27.8
<i>h</i>	75.7	57.0 (Cl ₂ catalyz.)	32.2	68.3	46.0 (Br ₂ catalyz.)	26.4	64.2	51.2 (I ₂ catalyz.)	27.8
<i>i</i>		100.2	55.2		70.8	25.8		52.6	7.6
<i>j</i>		50.0	-55.2		50.0	-25.8		50.0	-7.6
<i>k</i>			0			0			0
<i>l</i>			0			0			0

is endothermic 45.0 kcal., and if we consider the reverse reaction to have an activation energy of 5 kcal.⁹ the value for (1) becomes 50 kcal. Therefore, with the mechanism assumed, the activation energy of reaction *j* is 50 kcal. in the case of each of the halogens.

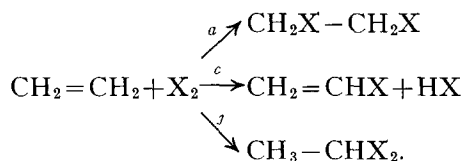
Reactions k and l: The activation energies of these reactions have not been calculated, the main reason being that we are primarily interested in this paper in the decomposition of the dihalides rather than in their rearrangements.

The preceding results are summarized in Table III.

DISCUSSION

Several interesting conclusions may be drawn from Table III, but this must be done cautiously. It must be remembered that the calculations apply to rather unusual experimental conditions, namely, the reaction must be carried out in the gas phase (or in solution if the solvent is "inert" and doesn't affect the rate) and in the absence of possible catalysts or inhibitors such as oxygen, water vapor, wall effects, and light. Not many experiments are carried out with all of these conditions controlled, and so it is not always possible to directly compare the calculations with laboratory results. It is also to be realized that many of the conclusions which we shall draw will naturally depend upon the particular mechanisms considered. These mechanisms are of course not necessarily unique, and other schemes may possibly be thought of which give rise to lower activation energies. Kassel¹⁰ has emphasized this point. Also, in the case of chain mechanisms efficient chain breaking reactions may be present under some experimental conditions.

From the scheme given in the introduction it is seen that the halogens may react with ethylene in three different ways, i.e., reactions *a*, *c*, and *j*. From Table III it is clear that reaction *a* is favored in the case of chlorine, bromine, and iodine. This is brought out in Table IV.



¹⁰ L. S. Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Company, 1932), p. 118.

TABLE IV. *Activation energies.*

Reaction	Cl	Br	I
<i>a</i>	25.2	22.6	20.5
<i>c</i>	43.4	46.0	51.2
<i>j</i>	50.0	50.0	50.0

In Table IV the lowest value of the activation energy (molecular or free radical mechanism) is given in each case. The table may not only be used to determine the relative probability of the various possible reactions but also, for any given reaction, the relative reactivity of the three halogens. It is seen that the symmetrical addition of a halogen to ethylene is much more likely than substitution. Also, the bimolecular mechanism is slightly to be preferred in the case of chlorine, whereas the proposed radical mechanism is predominant for bromine and iodine. However, the differences in activation energies are so small that it may well be that both mechanisms are simultaneously operative in each case. Additional remarks concerning the addition of the halogens to ethylene are given in the paper by Sherman and Sun. It was pointed out there that the low activation energy for the addition of iodine to ethylene is in apparent disagreement with the commonly accepted ideas of organic chemistry concerning the reaction. One further piece of experimental evidence qualitatively confirming our calculations is furnished by Cuthbertson and Kistiakowsky¹¹ who studied the thermal gas phase equilibrium between ethylene iodide, ethylene, and iodine in the temperature range 50–125°C. They found that the equilibrium is established in the course of several hours, and the activation energy required for the addition must be low enough for the reaction to occur in this time and temperature interval.

There have been several experimental studies of the reaction between ethylene and bromine^{12–17}

¹¹ Cuthbertson and Kistiakowsky, *J. Chem. Phys.* **3**, 631 (1935).

¹² Stewart and Edlund, *J. Am. Chem. Soc.* **45**, 1014 (1923).

¹³ Norrish, *J. Chem. Soc.* **123**, 3006 (1923).

¹⁴ Davis, *J. Am. Chem. Soc.* **50**, 2769 (1928).

¹⁵ G. Williams, *J. Chem. Soc.* 1747, 1758 (1932).

¹⁶ D. M. Williams, *ibid.* 2911 (1932).

¹⁷ Mitsukuri, Kinumaki and Asaoda, *J. Chem. Soc. Japan* **54**, 1061 (1933).

TABLE V. Activation energies.

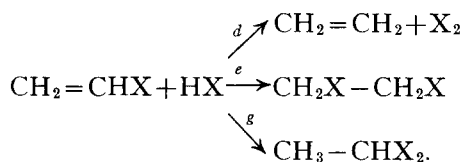
Reaction	Cl	Br	I
<i>d</i>	59.8	41.6	29.6
<i>e</i>	39.3	29.0	27.7
<i>g</i>	39.3	29.0	27.7

but the results are complicated. In a glass vessel the reaction apparently occurs on the walls. G. Williams reports that the order of the reaction may be 2, 1, or 0, depending upon the reaction vessel employed. Davis, G. Williams, and D. M. Williams report a negative temperature coefficient for the reaction, the explanation of which can only be furnished by a more detailed treatment than we have presented. G. Williams reports that the substitution reaction was not detected since all attempts to prove the formation of HBr by freezing out the reaction product failed.

Bahr and Zieler¹⁸ and Stewart and Smith¹⁹ report that substitution takes place between ethylene and chlorine but not between ethylene and bromine.

Kinumaki²⁰ studied the reaction between ethylene and chlorine and reports that a negative temperature coefficient is observed.

The vinyl halides and corresponding hydrogen halides may react in three ways, i.e., reactions *d*, *e*, and *g*. From Table III it is seen that reactions *e* and *g* are favored. This is brought out in Table V.



One thus predicts that the vinyl halides and hydrogen halides will react, by *e* and *g*, to give mixtures of the corresponding ethylidene halides and symmetrical dihalide ethane derivatives, in each case preferably by a free radical mechanism. In the case of the iodine compounds one would also expect some ethylene to be formed since the activation energy for the reaction concerned is only slightly higher.

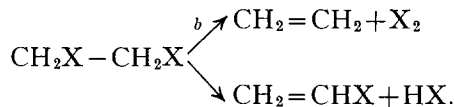
TABLE VI. Activation energies.

Reaction	Cl	Br	I
<i>b</i>	57.0	37.7	28.1
<i>f</i>	57.0	46.0	51.2

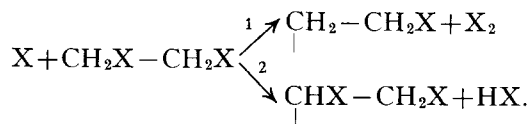
Kharasch, McNab and Mayo²¹ studied the reaction between HBr and liquid vinyl bromide and found an addition reaction took place, but the nature of the products depends upon the presence or absence of peroxides, and the reaction is probably heterogeneous.

Kharasch and Hannum²² report that HCl won't add appreciably to vinyl chloride in the presence or absence of peroxides or under strong illumination, but will do so rapidly in the presence of a catalyst such as FeCl₃. This is to be expected, since from Table V it is seen that the activation energy concerned is 39.3 kcal.

Considering, now, the halogen catalyzed decomposition of the CH₂X-CH₂X compounds, we note that the reaction may proceed via *b* to give ethylene and X₂, or via *f* to give vinyl halide and the corresponding hydrogen halide. The results are summarized in Table VI.



We see that CH₂Br-CH₂Br and CH₂I-CH₂I would be expected to decompose more rapidly into ethylene and bromine or iodine. The decomposition of CH₂Cl-CH₂Cl must be considered in more detail. Considering the mechanisms proposed it is evident that the slow step in the decomposition via *b* or *f* is the formation of Cl atoms. These atoms now have a choice of picking off a hydrogen atom or a chlorine atom from CH₂Cl-CH₂Cl. From Table II it is seen that the former possibility is to be expected, whereas for the bromine or iodine atoms halogen formation would be predicted. This is brought out in Table VII.



¹⁸ Bahr and Zieler, *Zeits. f. angew. Chem.* **43**, 233 (1930).

¹⁹ Stewart and Smith, *J. Am. Chem. Soc.* **51**, 3082 (1929).

²⁰ Kinumaki, *J. Chem. Soc. Japan* **54**, 142 (1933).

²¹ Kharasch, McNab and Mayo, *J. Am. Chem. Soc.* **55**, 2521 (1933).

²² Kharasch and Hannum, *J. Am. Chem. Soc.* **56**, 712 (1934).

TABLE VII. *Activation energies.*

Reaction	Cl	Br	I
1	24.6	15.1	10.4
2	14.9	23.4	33.5

Hence one concludes that $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ will give $\text{CH}_2=\text{CHCl}+\text{HCl}$, whereas $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$ and $\text{CH}_2\text{I}-\text{CH}_2\text{I}$ will give $\text{CH}_2=\text{CH}_2+\text{Br}_2$ and $\text{CH}_2=\text{CH}_2+\text{I}_2$, respectively. Experimental confirmation of the former conclusion is afforded by the experiments of Boeseken and Bastet.²³

Arnold and Kistiakowsky²⁴ studied experimentally the decomposition of $\text{C}_2\text{H}_4\text{I}_2$ and found it to decompose into C_2H_4 and I_2 , in agreement with our calculations. They reported that the unimolecular and free radical mechanism are both operative. Ogg²⁵ later showed that the observed rate expression could be derived by assuming only the radical chain, but this does not mean that some $\text{C}_2\text{H}_4\text{I}_2$ may not be decomposing unimolecularly.

Turning now to the ethylidene halides we have two possible decomposition products, ethylene or vinyl halides. We considered the halogen catalyzed decomposition to give the vinyl compounds but no plausible catalyzed reaction for ethylene formation readily suggests itself. With the schemes considered we see that in the case of each halogen reaction h can occur more readily than i . However, in the case of the bromine and iodine compounds reactions e and b have lower activation energies than h . Therefore the products of the decomposition of $\text{CH}_3-\text{CHBr}_2$ will be C_2H_4 and Br_2 , and of CH_3-CHI_2 they will be C_2H_4 and I_2 , and it is immaterial whether or not reaction h or i is more rapid as far as the nature of the decomposition products of these ethylidene halides is concerned.

It is apparent, however, that $\text{CH}_3-\text{CHCl}_2$ will give $\text{CH}_2=\text{CHCl}$ and HCl as decomposition

products. With the mechanism assumed reaction i is altogether improbable for this compound. There is some experimental evidence that this conclusion is correct.²⁶

Although the activation energies of reactions k and l have not been calculated it turns out that a knowledge of them is not necessary as far as predicting the products of the decomposition of the symmetrical and unsymmetrical dihalide ethane derivatives is concerned. Thus, whether we start out with CH_3-CHX_2 or $\text{CH}_2\text{X}-\text{CH}_2\text{X}$, and whether there is a preliminary rearrangement or not, the final products are ethylene and halogen in the case of bromine and iodine, and in the case of chlorine $\text{CH}_2=\text{CHCl}$ and HCl .

The scheme given in the introduction, and the preceding discussion, indicate a number of possible mechanisms for the rearrangement of CH_3-CHX_2 into $\text{CH}_2\text{X}-\text{CH}_2\text{X}$. Thus, the formation of $\text{CH}_2\text{X}-\text{CH}_2\text{X}$ may occur directly via reaction k , or indirectly via reactions h followed by e , or i followed by a , or i followed by c and then e , or h followed by d and a . As far as our calculations are concerned we would expect the rearrangement through reactions h and e to be the most likely, although, of course, the direct reaction k may be preferred. It is interesting to note in this connection that in the rearrangement of $\text{CH}_3\text{CHBr}-\text{CH}_2\text{Br}$ to give $\text{CH}_3-\text{CBr}_2-\text{CH}_3$ or $\text{CH}_3\text{CH}_2\text{CHBr}_2$ a mechanism involving the splitting out of HBr and its subsequent addition has been postulated.²⁷

A few general remarks are now, perhaps, not out of order. It is rather surprising that in so many cases a radical mechanism can be put forth which gives rise to an over-all activation energy which is usually about the same or somewhat lower than the value found for the straight unimolecular or bimolecular reaction. In only one case (reaction a , chlorine) is the activation energy for the radical mechanism greater than for the bimolecular reaction, and here by only 3.3 kcal.

It was formerly common for chemical kineticists to regard most reactions as unimolecular or bimolecular. Present day fashion is apparently

²³ Boeseken and Bastet, *Rec. trav. chim.* **32**, 187 (1914). See also reference 9, p. 138, and C. D. Hurd, *Pyrolysis of Carbon Compounds* (Chemical Catalog Company, 1929), p. 131.

²⁴ Arnold and Kistiakowsky, *J. Chem. Phys.* **1**, 166 (1933).

²⁵ Ogg, *J. Am. Chem. Soc.* **58**, 607 (1936).

²⁶ See C. D. Hurd, reference 23, p. 131.

²⁷ Reference 23.

tending more and more toward free radical mechanisms. However, Table III suggests that, insofar as the reactions there considered are concerned, in many cases both a molecular and a free radical mechanism may be operative. This is brought out in reactions *a* for Cl, Br, and I, *b* for I, *c* for Cl, Br, and I, *d* for Br and I, and *e* for Cl, where the activation energies for the two mechanisms differ by less than 5 kcal.

CONCLUSIONS

In the present paper all the arguments concerning the probable course of a reaction, where the reactants may give several different products, are based upon the assumption that the speed of the various reactions determine which products will be formed. This has the advantage of allowing for the possibility of a mixture of products in any proportions (see, for example, reactions *e* and *g*). It was further assumed that the relative rates of several reactions could be predicted from a knowledge of their relative activation energies. This is of course not always safe since the speed of a reaction also depends upon a constant term (the expression for the specific reaction rate constant is taken as $k = \text{constant} \cdot e^{-A/RT}$)²⁸ and upon the concentration of reacting substances. However since *A* enters the rate expression exponentially it is usually the most important term, unless it happens to be nearly equal to zero. Particularly if, for example, two reactions differ in activation energy by 6 or more kcal. their relative rates are predictable with considerable probability unless the concentration of some of the reacting substances is exceedingly small. One exception concerning the reliability of relative activation energies must be noted. This is the

²⁸ For an evaluation of this constant see Eyring, *J. Chem. Phys.* **3**, 107 (1935). It is also possible that the rate determining step for a reaction involving a proton, may involve a leakage through a potential energy barrier.

case where different mechanisms are involved, and different bonds are being broken, such as reactions *a* and *j*, but not, for example, reactions *a* and *b*. In the case of mechanisms involving free radicals it is seen that we have the interesting case that although two reactions have the same over-all activation energy one is much more probable than the other (reaction *b* and *f* for $\text{C}_2\text{H}_4\text{Cl}_2$).

It has been pointed out many times that relative activation energies can be calculated with more assurance than absolute values.²⁹ In this paper these relative values constitute the basis of all of our conclusions.

It must also be remembered that, strictly speaking, our conclusions only apply at the beginning of a process, when the reaction is far removed from the stage of equilibrium.

In spite of the above difficulties it seems fairly safe to draw the following conclusions:

1. Chlorine, bromine, and iodine will add to ethylene to form 1,2-dihaloethane rather than the vinyl or ethylidene derivatives.
2. The hydrogen halides of chlorine and bromine will add to the corresponding vinyl compounds rather than react to form ethylene and halogen, whereas the iodine compounds will probably undergo both types of reaction.
3. The symmetrical dihalo derivatives and also the ethylidene compounds of bromine and iodine will decompose to give ethylene and the corresponding halogen, whereas 1,2-dichloroethane and ethylidene chloride will give vinyl chloride and HCl upon decomposition.
4. In most of the reactions considered mechanisms involving free radicals are slightly more probable than the corresponding unimolecular or bimolecular reactions.

We wish to express our appreciation to Professor Farrington Daniels for his constant interest and help in this problem. One of us (A. S.) wishes gratefully to acknowledge financial assistance from the Wisconsin Alumni Research Foundation.

²⁹ See, for example, reference 3.

Errata: The Absolute Rate of Reactions in Condensed Phases

W. F. K. WYNNE-JONES AND HENRY EYRING, *Frick Chemical Laboratory, Princeton University*
(*J. Chem. Phys.* **3**, 492 (1935))

ON p. 497, line 12, first column and again in line 14 should read $(\alpha^*)^{-1}$. The values of α for nitromethane and carbon tetrachloride are 0.00233 and 0.00213, respectively. We wish to thank Mr. Frank Brescia for calling this to our attention.