nickel in agreement with our previously expressed viewpoint.

Summary

The x-ray absorption limits of various nickel compounds have been studied.

It is shown that a product claimed by us previously to be essentially $Ni_2O_3 \cdot 2H_2O$ contains nickel of a valence higher than two. It is most likely trivalent nickel. This gives further support to our previous conclusions.

BALTIMORE, MD. RECEIVED FEBRUARY 17, 1934

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE UNIVERSITY OF WISCONSIN]

Calculations of the Activation Energies of Some Reactions between the Halogens and the Ethylene Double Bond

BY ALBERT SHERMAN[1] AND C. E. SUN

Introduction.—In a series of papers[2] Eyring and his co-workers have set forth the general methods, with relevant details, which may be used in the calculation of activation energies of chemical reactions. Applications have been made to a variety of reactions, with considerable success. In this paper further applications of the method will be made. Attention will be primarily focused upon the chemical significance of the results, rather than upon their quantum mechanical aspects, already considered in detail in the previous papers. The calculations serve as a useful tool in considering hypothetical reaction mechanisms, and in suggesting significant experiments.

Arnold and Kistiakowsky[3] studied experimentally the thermal gaseous decomposition of ethylene iodide and found that two independent mechanisms are simultaneously operative in a given temperature interval, each giving approximately equal rates, and identical final products of ethylene and iodine. This means, of course, that the respective over-all activation energies for the two mechanisms are nearly the same. One mechanism is a unimolecular decomposition, found to have an activation energy of 36.6 ± 3 kg. cal.; the other is a reaction catalyzed by iodine atoms, with an over-all activation energy of 30.2 ± 3 kg. cal. It is of interest to calculate these energies and see if one is led to the prediction of the experimental facts, since it has been emphasized that the calculations are especially useful in deciding reaction mechanisms—*i. e.*, in finding *differences* in activation energies, rather than absolute values. The calculations have also been carried out for ethylene bromide and ethylene iodide, leading to predictions yet to be checked experimentally.

Bauer and Daniels[4] studied the photobromination of cinnamic acid in carbon tetrachloride. Two mechanisms had been proposed for the reaction. Berthoud and Beraneck[5] set forth the following scheme

$$Br_2 + h\nu \longrightarrow 2Br$$

$$Br + C_6H_5\text{—}C\text{=}C\text{—}COOH \longrightarrow C_6H_5CBr\text{—}\underset{|}{C}\text{—}COOH$$

$$Br_2 + C_6H_5CBr\text{—}\underset{|}{C}\text{—}COOH \longrightarrow C_6H_5CBr\text{—}CBr\text{—}COOH + Br$$

Purakayastha and Ghosh[6] suggested the following mechanism

$$Br_2 + h\nu \longrightarrow 2Br$$

$$Br + Br_2 \longrightarrow Br_3$$

$$Br_3 + C_6H_5C\text{=}C\text{—}COOH \longrightarrow C_6H_5CBr\text{—}CBrCOOH + Br$$

Bauer and Daniels discarded Berthoud and Beraneck's mechanism because it involves atom reactions having small activation energies while the reaction was found to have a large temperature coefficient. They were unable to say much about Purakayastha and Ghosh's mechanism, however, because of the difficulty of detecting Br_3 and distinguishing it from Br. It is in just such cases as this that the quantum-mechanical calculations are particularly useful and reliable. This latter mechanism is obviously only sensible if the activation energy for the reaction of Br_3 with the double bond is less than that for Br_2 with the double bond. The respective activation energies have been calculated and are given below, together with the results of similar calculations involving I_2 and I_3, and Cl_2 and Cl_3.

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[1] National Research Council Fellow, 1933–1934.

[2] Eyring, THIS JOURNAL, **53**, 2537 (1931); Sherman and Eyring, *ibid.*, **54**, 2661 (1932); Kimball and Eyring, *ibid.*, **54**, 3876 (1932); Eyring and Kimball, *J. Chem. Physics*, **1**, 239 (1933); Taylor, Eyring and Sherman, *ibid.*, **1**, 68 (1933); Eyring, Sherman and Kimball, *ibid.*, **1**, 586 (1933); Eyring, *Chem. Rev.*, **10**, 103 (1933).

[3] Arnold and Kistiakowsky, *J. Chem. Physics*, **1**, 166 (1933).

[4] Bauer and Daniels, THIS JOURNAL, **56**, 378 (1934).

[5] Berthoud and Beraneck, *J. chim. phys.*, **24**, 213 (1927); *Helv. Chim. Acta*, **10**, 289 (1927).

[6] Purakayastha and Ghosh, *Quart. J. Indian Chem. Soc.*, **2**, 26 (1926); **4**, 409 (1927); **4**, 553 (1927).

Calculations.—All calculations of activation energies were made along the lines given in earlier papers, and will therefore not be discussed in detail here. The various integrals involved were evaluated in the Eyring manner by constructing Morse potential energy curves for the bonds. The coulombic energy, for every bond, was taken as 14% of the total energy.[7] The constants used in constructing the Morse curves are given in Table I.

TABLE I

Bond	r_0	ω_0	D
C–C	1.46[a][8]	[b]	45.0[c] 61.0[d]
C–I	2.10[8]	497[11]	44.0[19]
C–Br	2.00[9]	560[10]	58.0[20]
C–Cl	1.85[10]	660[10]	78.6[15]
I–I	2.66[8]	213.67[12]	35.39[13]
Br–Br	2.28[8]	323.86[13]	45.23[13]
Cl–Cl	1.98[8]	565[14]	57.0[14]

[a] This value is equal to the mean of the distance between carbon atoms in a single and in a double bond.

[b] This value was not needed because no Morse curve was drawn for the C–C bond, its distance being taken as fixed.

[c] This value is the difference between the strength of the double and single carbon–carbon bond, and was used in calculating approximate heats of reaction (see Table II). The strength of a carbon–carbon single bond was taken as 77 kg. cal. [Kistiakowsky and Gershinowitz, *J. Chem. Physics*, **1**, 432 (1933)] and that of a carbon–carbon double bond as 122 kg. cal.

[d] This value is one-half the strength of the carbon–carbon double bond, and was used in all activation energy calculations.

The first column gives the bond in question, the second the equilibrium distance in Å. between the two atoms (when in the lowest state) forming the bond, the third column gives the vibrational frequency of the lowest state, in cm.$^{-1}$, and the last column gives the heat of dissociation of the bond, in kg. cal.

Considering, now, $C_2H_4I_2$, its unimolecular decomposition may be written

$$C_2H_4I_2 \longrightarrow C_2H_4 + I_2$$

The activation energy of the forward reaction differs from that of the reverse bimolecular reaction by the heat of the reaction. The activation energy for this reverse reaction was calculated, and the activation energy of the forward reaction was determined by adding the heat of the reaction. The bimolecular reaction was considered to involve the configuration of four electrons, one on each carbon atom and one on each iodine atom. The iodine molecule was assumed to approach the carbon–carbon double bond symmetrically and in the plane of the two atoms, as shown in Fig. 1.

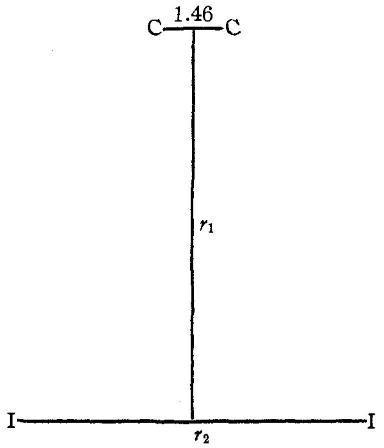

Fig. 1.—Addition of I_2 to C_2H_4.

At the beginning of the reaction r_1 is very large and r_2 is the normal distance between iodine atoms in I_2. As the reaction proceeds r_1 decreases and r_2 increases. By plotting r_1 against r_2 a potential energy surface may be constructed in the usual manner, and the position of the activated state and the activation energy determined. The result is given in Table II.

The reaction catalyzed by iodine atoms may be written as

$$I_2 \rightleftharpoons 2I \qquad (1)$$

$$I + C_2H_4I_2 \longrightarrow C_2H_4I + I_2 \qquad (2)$$

$$C_2H_4I \rightleftharpoons C_2H_4 + I \qquad (3)$$

Reaction (1) represents the ordinary thermal dissociation of I_2. If we assume with Schumacher[16] that reactions (1) and (3) are rapid compared to (2), *i. e.*, (2) is the rate determining reaction, then the over-all activation energy of the decomposition for this mechanism equals the activation energy of reaction (2) plus one-half the heat of dissociation of I_2.

The activation energy of reaction (2) was calculated (in the exothermic direction, the reverse of that as given above) by assuming it involves the configuration of three electrons, one on the

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(7) In Eyring's earlier work the value of 10% was used. This was changed to 14% in order to make the calculated activation energy agree with Geib and Harteck's (Bodenstein Festband, 1931) experimental value of 7.25 kg. cal. for the reaction $H + H_{2p} \longrightarrow H_{2o} + H$. The 14% value is found to give consistently better results. It is arbitrarily taken as fixed for all activation energy calculations, and so is not a parameter variable at our disposal.

(8) Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

(9) Dornte, *J. Chem. Physics*, **1**, 566 (1933).

(10) Mecke, *Z. physik. Chem.*, **16B**, 421 (1932).

(11) Kohlrausch, *ibid.*, **18B**, 65 (1932).

(12) Weizel, Handbuch der Exper. Physik, "Bandenspektrum."

(13) Brown, *Phys. Rev.*, **37**, 1007 (1931).

(14) Mulliken, *Rev. Mod. Phys.*, **4**, 1 (1932).

(15) Pauling, THIS JOURNAL, **54**, 3570 (1932).

(16) Schumacher, THIS JOURNAL, **52**, 3132 (1930).

free carbon atom, and one on each of the iodine atoms in I_2. The free carbon atom was considered to approach the I–I bond along the straight line joining the iodine nuclei, as shown in Fig. 2. Initially r_1 is very large and r_2 is the normal distance between iodine atoms in I_2. Finally r_1 is the normal C–I distance, and r_2 is very large. By plotting r_1 against r_2 a potential energy surface was constructed as usual, and the activation energy of the reaction determined, given in Table II below.

Fig. 2.—The reaction $C- + I_2 \longrightarrow C - I + I$.

Exactly similar calculations were made for the bromine and chlorine compounds, and are given below in Table II.

This latter value has already been calculated as an extension of the computations made in connection with Arnold and Kistiakowsky's work, described above, so that it is only necessary to make the calculation involving Br_3.

Before considering the reaction of Br_3 with the double bond it is first necessary to calculate its stability, *i. e.*, its heat of formation from Br_2 and Br. This will depend upon the percentage of coulombic binding assumed in Br_2. The stability of all the triatomic halogen molecules has already been calculated by Rollefson and Eyring,[17] it being plotted as a function of the coulombic percentage assumed in Br_2. Their results have been recalculated here for the particular value of 14%, and are given in Table II.

TABLE II

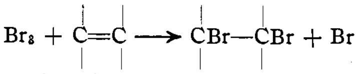
The negative sign in front of ΔH means that the reaction, as read from left to right, is exothermic

	Reaction	Calculated
1	$I + I_2 \longrightarrow I_3$	$\Delta H_1 = -4.95$ kg. cal.
2	$C_2H_4 + I_2 \underset{A_2'}{\overset{A_2}{\rightleftarrows}} C_2H_4I_2$	$\Delta H_2 = -7.6$ $A_2 = 22.4$ $A_2' = A_2 - \Delta H_2 = 30.0$
3	$C_2H_4I + I_2 \underset{A_3'}{\overset{A_3}{\rightleftarrows}} C_2H_4I_2 + I$	$\Delta H_3 = -8.6$ $A_3 = 1.8$ $A_3' = A_3 - \Delta H_3 = 10.4$
4	$I_3 + C_2H_4 \underset{A_4'}{\overset{A_4}{\rightleftarrows}} C_2H_4I_2 + I$	$\Delta H_4 = -2.7$ $A_4 = 29.7$ $A_4' = A_4 - \Delta H_4 = 32.4$
5	$Br + Br_2 \longrightarrow Br_3$	$\Delta H_5 = -6.05$
6	$C_2H_4 + Br_2 \underset{A_6'}{\overset{A_6}{\rightleftarrows}} C_2H_4Br_2$	$\Delta H_6 = -25.8$ $A_6 = 24.4^a$ $A_6' = A_6 - \Delta H_6 = 50.2$
7	$C_2H_4Br + Br_2 \underset{A_7'}{\overset{A_7}{\rightleftarrows}} C_2H_4Br_2 + Br$	$\Delta H_7 = -20.1$ $A_7 = 2.3$ $A_7' = A_7 - \Delta H_7 = 22.4$
8	$Br_3 + C_2H_4 \underset{A_8'}{\overset{A_8}{\rightleftarrows}} C_2H_4Br_2 + Br$	$\Delta H_8 = -19.7$ $A_8 = 35.6$ $A_8' = A_8 - \Delta H_8 = 55.3$
9	$Cl + Cl_2 \longrightarrow Cl_3$	$\Delta H_9 = -7.45$
10	$C_2H_4 + Cl_2 \underset{A_{10}'}{\overset{A_{10}}{\rightleftarrows}} C_2H_4Cl_2$	$\Delta H_{10} = -55.2$ $A_{10} = 25.2$ $A_{10}' = A_{10} - \Delta H_{10} = 80.4$
11	$C_2H_4Cl + Cl_2 \underset{A_{11}'}{\overset{A_{11}}{\rightleftarrows}} C_2H_4Cl_2 + Cl$	$\Delta H_{11} = -21.6$ $A_{11} = 3.0$ $A_{11} = A_{11} - \Delta H_{11} = 24.6$
12	$Cl_3 + C_2H_4 \underset{A_{12}'}{\overset{A_{12}}{\rightleftarrows}} C_2H_4Cl_2 + Cl$	$\Delta H_{12} = -47.7$ $A_{12} = 48.2$ $A_{12}' = A_{12} - \Delta H_{12} = 95.9$

[a] The activation energy of this reaction was also previously calculated by Eyring and Sherman at Princeton (unpublished).

Returning now to a consideration of Purakayastha and Ghosh's mechanism in connection with Bauer and Daniels' work, it is necessary to calculate the activation energy of the reaction of Br_3 with a double bond, and compare this value with that for the addition of Br_2 to a double bond.

The reaction



$Br_3 + \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} \longrightarrow \overset{|}{\underset{|}{C}}Br{-}\overset{|}{\underset{|}{C}}Br + Br$

was considered to involve the configuration of five electrons, one on each bromine atom, and one on each carbon atom. The Br_3 molecule was as-

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[17] Rollefson and Eyring, THIS JOURNAL, **54**, 170 (1932).

sumed linear, and approached the carbon–carbon bond in a plane, as shown in Fig. 3.

At the beginning of the reaction r_1 is very large and r_2 is practically the normal distance between bromine atoms in Br_2. As the reaction proceeds r_1 decreases and r_2 increases. A potential energy surface was constructed in the usual manner and the activation energy of the reaction found, and given in Table II.

Exactly similar calculations were carried out for iodine and chlorine compounds.

Results.—The results of all the calculations are given in Table II.

Discussion of Results.—The results, of course, depend upon the values given in Table I, particularly upon the bond strength, D. The heats of dissociation of iodine, bromine and chlorine are presumably known quite accurately, so that little choice was permitted for these values. But the values given in the literature for the strengths of the C–I, C–Br and C–Cl bonds are not in very close agreement, as is shown in Table III.

TABLE III

Bond	Heat of dissociation				
C–I	56.5[11]	64.0[18]	44[19]		
C–Br	65.3[11]	58[20]	60[21]	59[22]	91.0[11]
C–Cl	78.6[11]	71[20]	73[9]		

The value 44 kg. cal. for the strength of the C–I bond was chosen because it is in agreement with the value found by Ogg.[23] It also leads to a value of ΔH_2 and ΔH_3 in approximate agreement with the values of Polissar.[24]

The value of 78.6 kg. cal. for the strength of the C–Cl bond was chosen since it leads to a value of ΔH_{1C} in agreement with experiment (*cf.* Ref. 26 below).

The values of the heat of the various reactions given in Table II were calculated by taking the difference between the total strengths of the bonds broken and of the bonds formed in the reaction. These values are only approximate, of course, but are at least consistent with the choice of bond strengths given in Table I, and are in approximate agreement with the few known experimental values.

Let us now consider the decomposition of ethylene iodide. It is seen that A_2', the activation energy for the unimolecular decomposition, is calculated to be 30.0 kg. cal. This is to be compared with the value found by Arnold and Kistiakowsky of 36.6 ± 3 kg. cal. For the mechanism, involving catalysis by iodine atoms, the over-all activation energy, as discussed above, will be $A_3' + {}^1/_2\, D_{I_2} = 10.4 + 17.7 = 28.1$ kg. cal. This is to be compared with the experimental value of 30.2 ± 3 kg. cal. The agreement here is within the experimental error.

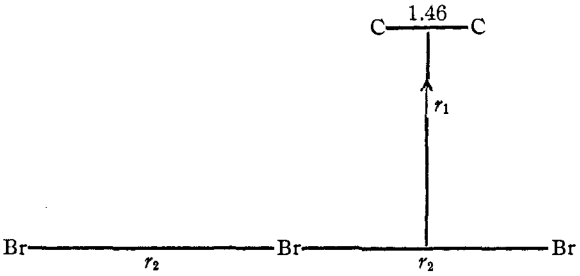

Fig. 3. The reaction $Br_3 + C{=}C \longrightarrow CBr{-}CBr + Br$.

The difference between the calculated over-all activation energies for the two modes of decomposition of $C_2H_4I_2$ is only 1.9 kg. cal. One would therefore predict, in agreement with experiment, that the two mechanisms would be simultaneously operative in approximately the same temperature region as found experimentally.

Similar considerations in the case of ethylene bromide give $A_6' = 50.2$ kg. cal. and $A_7' + {}^1/_2\, D_{Br_2} = 22.4 + 22.6 = 45$ kg. cal. for the unimolecular decomposition and atom-catalyzed decomposition respectively, a difference of 5.2 kg. cal. This difference is a little too great to predict definitely the simultaneous operation of two mechanisms in this case, but too small definitely to exclude it. On the basis of these calculations one would not be surprized at either the operation of the atom catalyzed mechanism or the simultaneous operation of this mechanism and the unimolecular decomposition.

Independent experimental evidence that $A_6 = 24.4$ kg. cal. is approximately correct, though probably a little too low, is furnished by Stewart and Edlund,[25] who found that the homogeneous gas-phase addition of Br_2 to C_2H_4 does not occur at appreciable rates at room temperatures, but does occur at 200°, signifying an activation energy

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(18) Iredale and Mills, *Nature*, **126**, 604 (1930).

(19) Eucken, "Handbuch der Exper. Physik," Energy and Heat Content, pp. 713–715.

(20) Grimm, "Handbuch Physik," **24**, 536 (1927).

(21) "Annual Reports" of the Chemical Society, Vol. XXVIII, pp. 401-402.

(22) K. W. F. Kohlrausch, "Der Smekal Raman Effekt," p. 167.

(23) Ogg, THIS JOURNAL, **56**, 526 (1934).

(24) Polissar, *ibid.*, **52**, 956 (1930).

(25) Stewart and Edlund, *ibid.*, **45**, 1014 (1923).

for the reaction somewhat greater than 23 kg. cal. It does occur rapidly in the gas phase at around 200°, showing that the activation energy is around 30 kg. cal. In general most reactions which proceed with appreciable velocities at room temperature have activation energies less than 25 kg. cal. and those proceeding around 200° have activation energies greater than 30 kg. cal.

In the case of the decomposition of ethylene chloride one sees from Table II that the activation energies for the unimolecular decomposition and for the atom catalyzed reaction are $A_{10}' = 80.4$ and $A_{11}' + {}^1/_2 D_{\mathrm{Cl}_2} = 24.6 + 28.5 = 53.2$ kg. cal., respectively, a difference of 27.2 kg. cal. This difference is much greater than in the former two cases, and one would expect the atom catalyzed reaction to be the mode of decomposition of $C_2H_4Cl_2$, and in a temperature range higher than for either ethylene bromide or ethylene iodide.

If one uses the value of 271 kg. cal. reported as the heat of combustion of $C_2H_4Cl_2(g)$,[26] one calculates ΔH_{10} to be -58.2 kg. cal., a value in close agreement with that given in Table II.

The results of the calculation for the ethylene halides are summarized in Table IV.

TABLE IV

Compound	Unimolecular decomposition activation energy, kg. cal.	Atom catalyzed decomposition activation energy, kg. cal.	Difference
$C_2H_4I_2$	30.0	28.1	1.9
$C_2H_4Br_2$	50.2	45	5.2
$C_2H_4Cl_2$	80.4	53.2	27.2

Considering, now, Purakayastha and Ghosh's mechanism in connection with Bauer and Daniels' paper, it is seen that A_8 is 11.2 kg. cal. *greater* than A_6. It is believed that this difference is quite significant. One is thus led to the conclusion that Purakayastha and Ghosh's mechanism is untenable.

Bauer and Daniels studied their reaction in carbon tetrachloride solution while the calculations really apply to the gas phase, but it is perhaps reasonable to assume that the solvent does not alter the activation energy of the reaction appreciably. Thus Arnold and Kistiakowsky[3] found their gas phase reaction had the same activation energy as Polissar[24] found for the same reaction in carbon tetrachloride solution (see Ref. 3, p. 169).

The calculated values of the activation energies for the reaction of Br_2 and Br_3 are for reaction with a carbon–carbon double bond in ethylene, while Bauer and Daniels studied the bromination of cinnamic acid, and the two are not strictly comparable—*i. e.*, the carbon–carbon double bond in cinnamic acid is part of a conjugated system, and there are resonance effects to be considered,[27] but this will increase both A_8 and A_6 somewhat, so that their difference will remain essentially unaltered.

It is seen from Table II that A_4 is greater than A_2, and A_{12} is greater than A_{10}, so that in all cases one would expect the diatomic halogen molecule to add to a carbon–carbon double bond more rapidly than a triatomic halogen molecule. The results are summarized in Table V.

TABLE V

Reaction	Activation energy, kg. cal.	Difference
$I_2 + C_2H_4 \longrightarrow C_2H_4I_2$	22.4	
$I_3 + C_2H_4 \longrightarrow C_2H_4I_2 + I$	29.7	7.3
$Br_2 + C_2H_4 \longrightarrow C_2H_4Br_2$	24.4	
$Br_3 + C_2H_4 \longrightarrow C_2H_4Br_2 + Br$	35.6	11.2
$Cl_2 + C_2H_4 \longrightarrow C_2H_4Cl_2$	25.2	
$Cl_3 + C_2H_4 \longrightarrow C_2H_4Cl_2 + Cl$	48.2	23.0

From Table V one is led to conclude that the homogeneous gas phase bimolecular iodination of ethylene is slightly more rapid than the bromination, in turn slightly more rapid than the chlorination. The difference in activation energies involved here are too small to be of significance. All one can say is that the calculations lead one to expect the rates of chlorination, bromination and iodination of ethylene to be approximately equal. This is in apparent contradiction to experiment, since, as carried out in the condensed phase under ordinary laboratory conditions, Br_2 adds to a double bond while I_2 does not. But it must be remembered that the calculations only apply to the reactions as carried out under special conditions, *i. e.*, when the only mechanism operative is a bimolecular one, and in the absence of effects of walls or certain solvents, etc.

Experimental proof that iodine will add to ethylene bimolecularly in the gas phase is furnished by Arnold and Kistiakowsky,[3] who found $C_2H_4I_2$ decomposed unimolecularly (in addition to an atom catalyzed reaction). By the principle of microscopic reversibility, therefore, iodine must add to ethylene bimolecularly.

Table V illustrates a general conclusion, drawn from experience in making such calculations. Of

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(26) Kharasch, *Bur. Standards J. Res.*, **2**, 359 (1929).

(27) See Pauling and Sherman, *J. Chem. Physics*, **1**, 606 (1933).

two possible mechanisms for a reaction, each involving the configurations of different numbers of electrons, the one involving the configuration of the smaller number of electrons will possess the smaller activation energy. In other words, a given reaction will occur in such a way as to make and break as few bonds as possible. Another example is given by Kimball and Eyring.[28]

Some of the predictions made in this communication are to be tested experimentally in this Laboratory.

We wish to thank Professor Daniels for many valuable discussions.

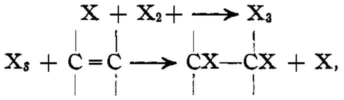
Summary

Activation energy calculations have been made for various reactions involved in the possible modes of decomposition of the ethylene halides. On the basis of these calculations one is led to expect:

1. Ethylene iodide will decompose homogeneously in the gas phase by the simultaneous operation of two mechanisms, a unimolecular decomposition, and an atom catalyzed reaction, but ethylene chloride will only decompose by the atom catalyzed reaction. Ethylene bromide is intermediate between ethylene iodide and ethylene chloride and one cannot safely predict whether it will behave like the iodide or like the chloride compound.

2. Ethylene iodide will decompose homogeneously in the gas phase at an appreciable rate at a lower temperature than ethylene bromide, which in turn will decompose at a lower temperature than ethylene chloride.

3. The type of chain proposed by Purakayastha and Ghosh is unsatisfactory. The diatomic halogen molecule will add to the double bond more rapidly than the triatomic molecule.



$$X + X_2 + \longrightarrow X_3$$

$$X_3 + \text{C}{=}\text{C} \longrightarrow \text{CX—CX} + X,$$

MADISON, WISCONSIN RECEIVED FEBRUARY 23, 1934

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(28) Kimball and Eyring, THIS JOURNAL, **54**, 3876 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

The Activity and Crystal Structures of Mixed Metal Catalysts[1]

BY J. H. LONG, J. C. W. FRAZER AND EMIL OTT

Introduction

It has been suggested that gaseous reactions which are catalyzed by solid surfaces should be sensitive to the arrangement of and the distance between the surface atoms.[2] Unfortunately, too little experimental evidence on the structure of crystalline catalysts has been advanced to support these views. However, it has been shown that the course of decomposition of methanol is influenced by the shift in the crystal structure of zinc oxide–copper catalysts.[3] It also has been shown that the energy of activation for the reaction between carbon monoxide and oxygen is influenced by the lattice dimensions of an alumina–ferric oxide catalyst.[4] Other work,[5,6] in which catalyst structure investigations were not carried out, indicates a dependence of catalytic activity on lattice type and lattice dimensions.

In view of the above, it was deemed advisable to continue this line of investigation. If a relationship does exist between the activity of a catalyst and the distance between and the arrangement of the surface atoms, such phenomena should become observable when the arrangement of the atoms of the underlying material is actually altered. By preparing the substitutional type of solid solution, the lattice constants and the lattice types of mixtures of iron, nickel, cobalt and copper can be varied in a systematic manner. Four series of mixed metal catalysts have been prepared under identical conditions. The structures of the catalysts have been determined by x-ray diffraction studies. The activities of the mixed metal and single metal catalysts have been determined by observing their relative effect in promoting the reaction between hydrogen and benzene to form cyclohexane.

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(1) From the thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy by J. H. Long. Presented in part at the 1933 Washington meeting of the American Chemical Society, by E. Ott.

(2) Langmuir, *Trans. Faraday Soc.*, **17**, 617 (1921); Balandin, *Z. physik. Chem.*, **B2**, 289 (1929).

(3) Frolich, Fenske and Davidson, *Ind. Eng. Chem.*, **21**, 109 (1929).

(4) Eckell, *Z. Elektrochem.*, **38**, 918 (1932).

(5) Kahlenberg and Ritter, *J. Phys. Chem.*, **25**, 89 (1921).

(6) Remy and Schaefer, *Z. anorg. allgem. Chem.*, **136**, 149 (1924).