

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

TRIATOMIC HALOGEN MOLECULES IN PHOTOCHEMICAL REACTIONS

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In recent years it has become generally accepted that the primary action of the light in photochemical reactions involving the halogens is a dissociation of the molecule into two atoms.¹ In building up mechanisms for such reactions the possibility of the existence of X_3 molecules has been raised; as for example, Göhring² in discussing the reaction between H_2 and Cl_2 introduced Cl_3 as an intermediate and Lenher and Rollefson³ assumed what amounts to that in postulating a specific action of Cl_2 in the formation of $COCl$ as an intermediate in the phosgene synthesis. Recent developments in quantum mechanics have made it possible to investigate the stability of X_3 molecules from theoretical considerations.⁴ While there may be some question concerning the exactness of such calculations, nevertheless we feel that limiting values and probable values which are of significance can be obtained.

In this paper we shall apply these methods to the halogens and discuss the significance of the results in a few special cases.

Three monovalent atoms form the most stable configuration when they are in a straight line. For three atoms in a straight line the formula for the binding energy

$$E_3 = A + B + C + \sqrt{\frac{1}{2}((\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2)} \quad (1)$$

may be expected to apply for p electrons.

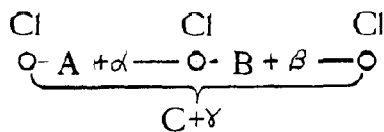


Fig. 1.

Figure 1 represents three chlorine atoms. The energy written between pairs is that which would be required to separate them if the other atom were absent. The quantities, $A + \alpha$, $B + \beta$, $C + \gamma$, can be determined from the

Morse curve for chlorine and will depend only on the distance between the atoms.⁵

The Morse curve is

$$E_2 = D(2e^{-a(r-r_0)} - e^{-2a(r-r_0)}) \quad (2)$$

¹ This occurs directly if the absorption is in the continuum and probably occurs as a second step if the band absorption is used.

² Göhring, *Z. Elektrochem.*, **27**, 511 (1921).

³ Lenher and Rollefson, *THIS JOURNAL*, **52**, 500 (1930).

⁴ Eyring and Polanyi, *Z. physik. Chem.*, **12B**, 279 (1931).

⁵ Morse, *Phys. Rev.*, **34**, 57 (1929).

$A + \alpha$, $B + \beta$, $C + \gamma$ are functions of r , the distance in Ångströms between the chlorine atoms, and are the values E_2 takes for the corresponding distances. D' is the heat of dissociation, D , of the molecule plus a half quantum of vibrational energy; r_0 is the distance between the atoms corresponding to the lowest potential energy; a is determined by the equation

$$a = 0.1227 W_0(M/D') \quad (3)$$

W_0 is the vibration frequency of the molecule in its lowest quantum state expressed in wave numbers. D' has been defined and must be expressed in wave numbers. M , the reduced mass, is defined by the equation $M = M_1M_2/(M_1 + M_2)$ where M and M_2 are the two atomic weights.

TABLE I
CONSTANTS USED IN CONSTRUCTING THE MORSE CURVES

Gas	D	D'	r_0	a	W_0
F ₂	72	73.5	1.4	2.52	1071.5
Cl ₂	58	58.8	1.74	2.22	570
Br ₂	45.7	46.2	2.26	2.00	326.6
I ₂	34.5	34.8	2.66	1.50	213.9

To determine E_3 it is necessary to know the ratio of the coulombic binding, A , B , C , to the corresponding interchange binding α , β and γ .

Curves are drawn for chlorine with E_3 as ordinate and the distance between the central chlorine atom and an outside one as abscissa, keeping the distance between the central Cl atom and the other outside atom equal to 1.74×10^{-8} Å., the normal distance for Cl₂.

If the calculations are carried out for all possible separations of the atoms, it is found that the real energy minimum occurs for a configuration in which the chlorine molecule has expanded 0.02 Å. and the minimum is 0.1 k. cal. deeper than we have plotted it. This expansion is negligible, however, and is ignored throughout.

For Curve 1 in Fig. 2 it is assumed that $A = B = C = 0$; *i. e.*, that the entire binding is valence or interchange binding. For Curve 2 it is assumed that

$$\frac{\alpha}{A + \alpha} = \frac{\beta}{B + \beta} = \frac{\gamma}{C + \gamma} = 90\%$$

for all distances, r , used in the calculation. This is the theoretical value of the ratio for H₂. For Curve 3 it is assumed that $\alpha = \beta = \gamma = 0$, *i. e.*, that there is no valence binding, the whole being the so-called coulombic binding. The actual curve must lie between 1 and 3.

Curves similar to 1, 2 and 3 of Fig. 2 were drawn for F₂, Br₂ and I₂. They are just the same in their general form as those given here for Cl₂.

In Table II, Curves 1, 2 and 3 have the same meaning as in Fig. 2. r of the last column refers to the distance between the approaching atom and the near atom of the diatomic molecule at which the potential energy is a

TABLE II
VALUES OF THE ACTIVATION ENERGIES FOR THE FOUR GASES

Gas	Curve	Activation energies		ΔH $x_1 + x_2 = x_3$	r Ångströms, maximum
		$x_1 + x_2 = x_3$	$x_1 = x_2 + x_3$		
F ₂	1	12.2	8.2	+ 4.0	1.87
	2	6.2	10.2	- 4.0	1.95
	3	0	77.7	-77.7	..
Cl ₂	1	8.6	6.3	+ 2.3	2.24
	2	4.5	8.6	- 4.1	2.39
	3	0	61.1	-61.1	..
Br ₂	1	6.3	5.4	+ 0.9	2.88
	2	3.5	7.3	- 3.8	3.02
	3	0	47.3	-47.3	..
I ₂	1	5.1	3.8	+ 1.3	3.45
	2	2.6	5	- 2.4	3.58
	3	0	36.3	-36.3	..

maximum. After this distance r has been passed, the X₃ atom will not dissociate for a time corresponding to a great number of vibrations even though it is not stabilized by collision with another molecule.

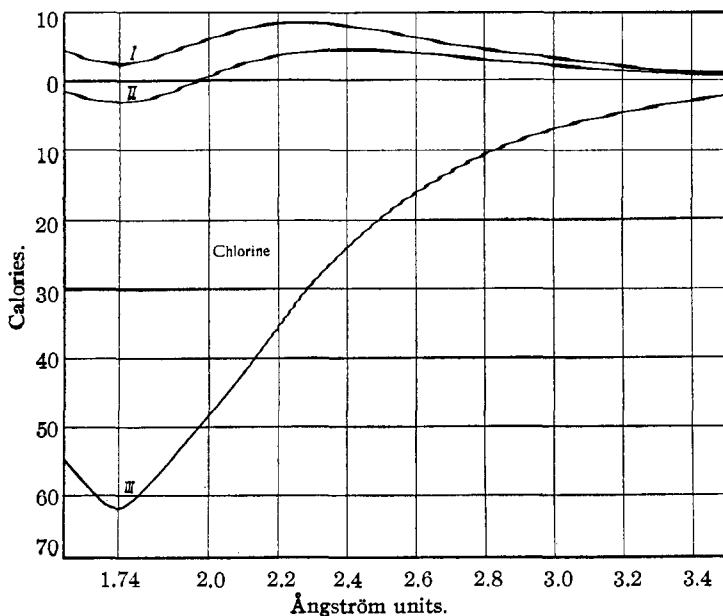


Fig. 2.

This may be seen in the following way. If the two distances between the outer atoms and the central atom of a linear X₃ molecule be taken as axes making an angle of 120° with each other and the corresponding energy E_3 of Equation 1 be plotted, a contour map is obtained. If the corresponding

energy surface is constructed, it can be shown, by the method of Wigner⁴ (pp. 305-309) that a ball rolling on this surface will describe the behavior of the X_3 molecule. The surface consists essentially of a roughly triangular basin lying in the pass separating two valleys which make an angle of 120° with each other. The formation of an X_3 molecule corresponds to a ball rolling up one valley passing over a pass into the basin. The ball will not find its way through the other pass into the adjoining valley on the first trial. For such a triangular basin this will require many trials. In fact, the ball may after repeated trials return over the pass by which it entered. In any case the quasimolecule will have a very long life as compared with the duration of an ordinary collision. The gentle slopes contribute to the long life by making the individual vibrations slow.⁶

Another point which this surface reveals is that all the activation energy is translational. This is apparent because the gap into the basin is almost exactly along the axis of the valley and the ball will require only longitudinal motion along the valley (translational energy) to pass into the basin. Transverse motion which represents vibration of the X_2 molecule is not helpful. The fact that the gap lies along the axis of the valley corresponds to the fact that the activation energy is for a configuration in which there is no expansion of the original X_2 molecule due to the presence of the third atom.

The negative values of ΔH for the reaction $X_2 + X = X_3$ in Table II point to the stability of X_3 at low temperatures. The equilibrium for this reaction may be calculated if we have a value for the entropy change. This entropy change must lie between zero and the value for $X = \frac{1}{2}X_2$ which is about minus ten. A reasonable estimate,¹ which we shall use, is minus six. This gives for the equilibrium constant K_p

$$K_p = \frac{(X_3)}{(X)(X_2)} = e^{-\Delta H/RT} e^{\Delta S/R} = 0.05e^{-\Delta H/RT}$$

To apply this to a particular case consider the data for iodine for which the dissociation $I_2 = 2I$ has been investigated by Starck and Bodenstein⁷ on the assumption that there is no I_3 . Using the value of ΔH given in Table II for $I + I_2 = I_3$, according to Curve 2

$$K_p = \frac{(I_3)}{(I)(I_2)} = 0.05e^{2400/2 \times T}$$

For

$$T = 300$$

$$K_p = 2.75$$

$$T = 1200$$

$$K_p = 0.14$$

This shows that at room temperature the principal molecule, other than I_2 , is I_3 but at high temperatures it is I . The amount of I_3 calculated for 1200°A .

⁶ An example of a triatomic quasimolecule of long life has been pointed out recently by Volmer, [*Z. physik. Chem.*, **13B**, 299 (1931)].

⁷ Starck and Bodenstein, *Z. Elektrochem.*, **16**, 965 (1910).

on the basis of the data given above is large enough so that it might have been detected in the experiments of Starck and Bodenstein but not with any great certainty. The absolute values obtained by these calculations are, however, too sensitive to slight changes in ΔH or ΔS to be considered very accurate. For the other halogens where the ΔH is larger and the ΔS is practically the same, the percentage in the form of X_3 would be considerably greater.

From what has been said it follows that all reactions such as photochemical reactions at room temperature, in which a dissociation of the chlorine molecule has been postulated as a primary step, should be considered as involving Cl_3 molecules. If this is the case we should expect to find chlorine atoms in the first excited state, the $^2P_{1/2}$ state, more reactive than normal atoms since they possess some of the activation energy necessary to form Cl_3 . Whether all of the difference in energy between the $^2P_{1/2}$ and the $^2P_{3/2}$ states of the atom can be considered as available for a process of this kind cannot be stated definitely but it is possible to say that at least a considerable portion is available. For example, let us consider that the excited chlorine atom collides with some molecule and the excitation energy is converted into translational energy; the division of the energy between the two colliding molecules will depend upon their masses. For a collision between a chlorine atom and a chlorine molecule, the atom will acquire two-thirds of the energy. Lacking more definite information, let us assume that the total energy difference, $^2P_{3/2} - ^2P_{1/2}$, amounting to 2.5 kcal. for Cl atoms is available as activation energy for the reaction to form Cl_3 . Then we should expect the excited atoms to react $e^{2500/600} = 65$ times as often as the normal atoms. This is quite in accord with the experiments of Rollefson and Lindquist⁸ in which they demonstrated that the excited atoms would cause the formation of hydrochloric acid at an easily measurable rate, whereas the normal atoms produced no effect under the same conditions. In those experiments the situation was somewhat more complicated in that the chlorine atoms had a chance to react with ICl before acquiring sufficient energy to form Cl_3 . This resulted in the observed difference in rates being greater than the factor given above. These arguments would hold for any other mechanism in which an activation energy was required for the chlorine atom to react. The difference would disappear if the following reactions were so slow that Cl_3 was at its equilibrium concentration.

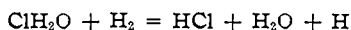
The next stage in the photosynthesis of hydrochloric acid by visible light must involve water. In a previous paper⁹ one of us has postulated that the chlorine atom forms an addition compound with water which is capable of reacting with hydrogen. This possibility has been discussed

⁸ Rollefson and Lindquist, *THIS JOURNAL*, **52**, 2793 (1930).

⁹ Rollefson, *ibid.*, **51**, 770 (1929).

also by Franck and Rabinowitsch¹⁰ and by Bodenstein.¹¹ In the latter paper it is argued that the ClH₂O molecule is formed so slowly that its only function must be to start rather long chains yielding HCl. Let us examine these arguments in detail.

Coehn and Jung found that in a particular experiment in which the concentration of water vapor was 10⁻⁹ mole/liter, the rate of formation of HCl was 3 × 10⁻⁵ mole/sec. If half of this was due to reaction of ClH₂O with hydrogen, then $k'(\text{ClH}_2\text{O})(\text{H}_2) = 10^{-5}$ mole/sec. Now it would be necessary for ClH₂O to be formed with this same speed so we could say that $k(\text{Cl})(\text{H}_2\text{O}) = 10^{-5}$ mole/sec., in which case Bodenstein says that the maximum value of k is 10¹¹, the collision number for a bimolecular reaction, neglecting the fact that a three-body collision is needed to stabilize the molecule formed. From the standpoint of the results we have presented the equation should be written $k_1(\text{Cl}_3)(\text{H}_2\text{O}) = 10^{-5}$ mole/sec., in which case 10¹¹ instead of being considered the maximum value of k_1 must be considered as a reasonable value. Using unpublished data Bodenstein takes 10⁻¹⁰ as the concentration of chlorine atoms; this seems like a reasonable value, so we shall use the same for the concentration of Cl₃. This gives $k_1(\text{Cl}_3)(\text{H}_2\text{O}) = 10^{-8}$ mole/sec., a value a thousand-fold too small for the ClH₂O molecule to be involved in the formation of half the HCl. That would mean that the chains started by ClH₂O would have to result in the formation of 1000 moles of HCl. Bodenstein's suggestion for this is that the hydrogen atom formed in the reaction



catalyzes the reaction between hydrogen and chlorine molecules. Regardless of what mechanism is postulated for such a catalysis, we can say that the quantum yield obtained in the study of the reaction with very dry gases indicates that the yield must be very much less than 1000 molecules of HCl for each hydrogen atom produced. Coehn and Heymer¹² give the quantum yield of the dry reaction as less than seven; if we are more liberal we can say that as many as ten molecules may be formed but that still leaves the rate of formation of ClH₂O too small by a factor of one hundred. Probably at least a factor of ten in this could be put onto uncertainties in the water and Cl₃ concentrations, the remaining factor of ten must be attributed to larger collisional diameters or other factors which might increase k_1 .¹³

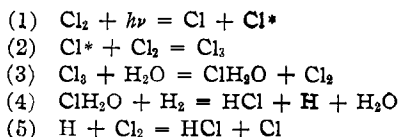
¹⁰ Franck and Rabinowitsch, *Z. Elektrochem.*, **36**, 794 (1930).

¹¹ Bodenstein, paper presented at the meeting of the Faraday Society, April 16-17, 1931.

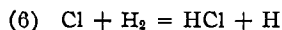
¹² Coehn and Heymer, *Naturwissenschaften*, **14**, 299 (1926).

¹³ A recent paper by Schumacher and Stieger, [*Z. physik. Chem.*, **B13**, 169-189 (1931)] on the chlorine sensitized photosynthesis of carbon dioxide reports chlorine atom concentrations of 2 to 6 × 10⁻⁹ mole/liter. If we use these values instead of the 10⁻¹⁰ reported by Bodenstein the desired rates are obtained without difficulty.

We would suggest the following mechanism for the reaction between hydrogen and chlorine

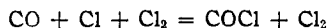


The reaction of H with Cl_2 is exothermic to the extent of approximately 45 k. cal. If we consider this amount as divided approximately equally between the products, the chlorine atom will have kinetic energy equivalent to 22.5 k. cal. According to calculations by Eyring,¹⁴ this is greater than the probable activation energy necessary for the atom to react with H_2 without the intervention of water. Therefore we would say that the chain proceeded by (5) and

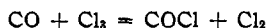


until the atoms are removed by some other reaction. Or a chlorine atom loses so much of its energy by ineffective collisions that it is no longer able to react with hydrogen. According to these views the reaction with dry gases is brought about by light of such frequencies that the Cl atoms produced have enough energy to react with hydrogen. Such being the case, the measurements of Coehn and Heymer give the length of the chains due to (5) and (6) as being of the order of magnitude of ten. This gives the same mechanism to the union of the dry and the moist gases except that in the dry gases there is no way to continue the chain if the kinetic energy of the chlorine atom drops below a critical value, whereas in the moist gases the chain may be continued through the formation of ClH_2O .

Another reaction of interest is the photochemical formation of phosgene. A mechanism for this reaction has been proposed by Lenher and Rollefson³ which involves the formation of an intermediate molecule COCl according to the equation



Opponents of this mechanism have objected to this step on the ground that it involved a more specific effect on the part of the chlorine molecule than had been found in any other reaction. In the light of the results which have been presented in this paper we see that the above equation should be replaced by



which is equivalent to saying that the chlorine molecule has an effect which could be duplicated only by molecules capable of forming loose addition products with chlorine atoms. Therefore it is not surprising that this effect has not been found with other molecules. The calculations of this

¹⁴ Eyring, THIS JOURNAL, 53, 2537 (1931).

paper must be considered as giving a very definite justification for the assumption of a very specific action of chlorine molecules in reactions of the type written above.

Next let us consider what explanation may be offered for the results of Senftleben and Germer,¹⁵ who carried out experiments to demonstrate the dissociation of the halogens by light. Their experiments consisted of illuminating the halogens in a Pirani gage and measuring the change in heat conductivity of the gas. Due to disturbing factors no quantitative data were given but if we assume that the apparatus used had the same sensitivity as that used by Senftleben and Riechemeier¹⁶ in their work on atomic hydrogen, then we can say that the concentration of halogen atoms necessary to give a pronounced effect would be of the order of 10^{-7} or 10^{-8} mole/liter. This is a much higher value than that given by Bodenstein and must be considered as too high to be compatible with the results from photochemical reactions. According to the views we have expressed, the principal product formed by the light in the experiments of Senftleben and Germer would be X_3 and not halogen atoms; therefore, the increased loss in heat from the hot wire of the Pirani gage could not be attributed to an increase in heat conductivity of the gas due to a decrease in the average molecular weight. The observed effect can be explained as due to dissociation of the X_3 molecules at the hot wire, thus causing more heat to be taken from the wire than would be the case if only X_2 molecules were present.

Summary

By using the quantum mechanics equation for the potential energy of systems of three atoms, it has been shown that for all the halogens the molecules of the type X_3 are stable at room temperature with respect to the decomposition into X_2 and X . The significance of this fact has been discussed in connection with the mechanism for the reactions between chlorine and hydrogen and between chlorine and carbon monoxide. For the hydrogen-chlorine reaction it has been shown that the mechanism of the reaction is essentially the same for dry gases as for moist. The results of Senftleben and Germer on the optical dissociation of the halogens have been interpreted from the standpoint of the conclusions presented in this paper.

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¹⁵ Senftleben and Germer, *Ann. Physik*, [5] 2, 847 (1929).

¹⁶ Senftleben and Riechemeier, *ibid.*, [5] 6, 105 (1930).