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Activation Energies for Reactions of Atoms in Different States

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A slight modification of Eyring's method enables the activation energy for the reaction of iodine monochloride with normal or with excited chlorine atoms to be calculated. The calculations indicate that normal chlorine atoms are much more reactive with respect to iodine chloride than are chlorine atoms excited to the $^2P_{3/2}$ state. Experimental evidence supporting these calculations is obtained from the

results of Rollefson and Lindquist with mixtures of hydrogen, chlorine and iodine monochloride.

In the modified method, the atomic interactions—which give rise to the activation energy—are obtained from the potential energies of those molecular states which may be adiabatically formed from atoms in the particular electronic states to be considered.

A SHORT time ago Rollefson and Lindquist¹ concluded from their experiments on mixtures of hydrogen, chlorine and iodine monochloride that the reaction chains yielding hydrogen chloride were started by chlorine atoms in the $^2P_{3/2}$ state. Recent work,² especially that by Rodebush and Klingelhoefer, has shown that the reaction between chlorine atoms and hydrogen has a heat of activation sufficiently large that there should be time enough for the two lowest states of the chlorine atom to reach statistical equilibrium. Therefore, no matter what source of chlorine atoms was used, hydrogen chloride formation should be observed. Rodebush and Klingelhoefer suggest that the results (of the experiments of Rollefson and Lindquist) with iodine chloride are due to chlorine atoms reacting more readily with some other substance than hydrogen. The truth of this is apparent since iodine chloride is a powerful inhibitor for hydrogen chloride formation. It has been suggested¹ that this may be caused by a reaction such as $\text{ICl} + \text{Cl} = \text{Cl}_2 + \text{I}$. To account for the observed phenomena fulfillment of a second condition is necessary: normal chlorine atoms must be removed more readily than excited ones. This second requirement is readily fulfilled by postulating that $\text{ICl} + \text{Cl} = \text{Cl}_2 + \text{I}$ is very much faster than $\text{ICl} + \text{Cl}^* = \text{Cl}_2 + \text{I}$. This

may seem to be very improbable since it requires an excited atom to be less reactive than the corresponding unexcited atom. We shall show that considerations based on thermodynamics and the quantum theory of activation lead to just this conclusion.

The use of quantum mechanics in the calculation of activation energies has been presented in great detail in papers by Eyring and Polanyi^{3, 4}; the second reference deals especially with the reactions of the halogen atoms. However, in Eyring's calculations, no distinction is made between the reactions of halogen atoms in the $^2P_{3/2}$ state and those in the $^2P_{1/2}$ state. The calculations are all made for the halogen atoms in the $^2P_{3/2}$ state.

The approximate values of the interaction terms in the equation

potential energy

$$= Q + \frac{1}{2}(2)^{\frac{1}{2}}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2]^{\frac{1}{2}}$$

are usually obtained from the potential energy functions for the corresponding diatomic molecules. Now if we consider the reaction $\text{ICl} + \text{Cl}^* = \text{I} + \text{ClCl}^*$, the interaction terms are to be derived from the energies of the molecules ICl , ClCl^* , and ICl^* . If Cl^* is in the $^2P_{3/2}$ state and the other two atoms are in the $^2P_{3/2}$ state, then we must obtain our interaction terms from $\text{ICl} (^1\Sigma)$,

¹ Rollefson and Lindquist, *J. Am. Chem. Soc.* **52**, 2793 (1930); **53**, 1184 (1931).

² Rodebush and Klingelhoefer, *J. Am. Chem. Soc.* **55**, 130 (1933); H. v. Hartel, *Zeits. f. physik. Chemie* **B11**, 96 (1930).

³ Eyring and Polanyi, *Zeits. f. physik. Chemie* **B12**, 279 (1931).

⁴ Eyring, *J. Am. Chem. Soc.* **53**, 2537 (1931).

Cl_2 ($^3\Pi_0$), and ICl ($^3\Pi_0$).^{5, 6} The reasons for this choice of states are: (1) ICl ($^1\Sigma$), case under consideration. (2) Cl_2 ($^3\Pi_0$), a $^2P_{3/2}\text{Cl}$ atom and a $^2P_{3/2}\text{Cl}$ atom cannot form a normal molecule. (3) ICl ($^3\Pi_0$), a $^2P_{3/2}\text{I}$ atom and a $^2P_{3/2}\text{Cl}$ atom cannot form a normal molecule. This treatment permits us to differentiate between the reaction of an ICl molecule with a chlorine atom in the $^2P_{3/2}$ state and one in the $^2P_{1/2}$ state, for in the latter case all the interactions would be obtained from the $^1\Sigma$ terms.

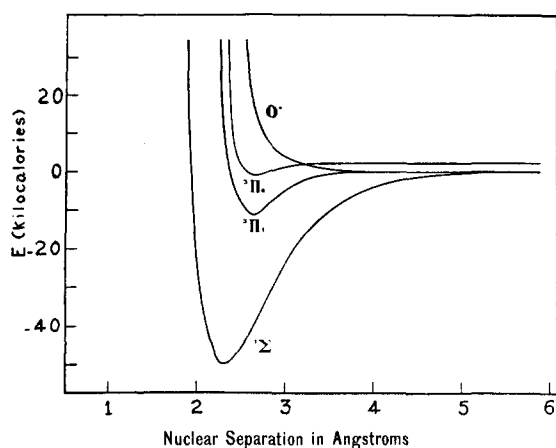


FIG. 1. Potential energy diagram for ICl . The states marked $^1\Sigma$, $^3\Pi_1$, and O^+ are formed by an iodine atom in the $^2P_{3/2}$ state and a chlorine atom in the $^2P_{3/2}$ state; the $^3\Pi_0$ state is formed by a normal iodine atom ($^2P_{3/2}$) and an excited $^2(P_{3/2})$ chlorine atom. The diagram for the chlorine molecule is similar⁸ except that transitions involving the $^3\Pi_1$ and O^+ states have never been observed experimentally.

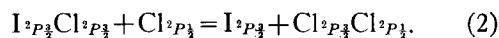
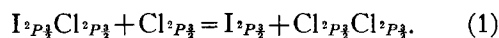
In order to explain the experimental results of Rollefson and Lindquist it is not necessary to make the activation energy calculations for both of the reactions,

⁵ See Fig. 1.

⁶ Providing no electronic change takes place as the atoms approach.

⁷ Weitzel, *Handbuch der Experimental Physik, Ergänzungswerk I*, 383–385 (1931). Akademische Verlagsgesellschaft, Leipzig.

⁸ Mullikan, *Phys. Rev.* **36**, 669, 1440 (1930); *Rev. Mod. Phys.* **4**, 17, 70 (1930).



Reaction (1) is exothermic by an amount equal to the difference between the heats of formation of ICl and Cl_2 (from normal atoms), approximately 7 kilocalories. We calculate the corresponding heat of activation to be about 4 kilocalories. To calculate the heat of reaction (2) we use the heat of formation of iodine chloride (from normal atoms) and the heat of formation of the $^3\Pi_0$ state of Cl_2 . This latter⁷ is only 9.6 kilocalories which makes reaction (2) endothermic to the extent of 40 kilocalories. According to the first law of thermodynamics it would be necessary to supply at least this much energy if the reaction is to proceed. Hence this is a minimum value for the heat of activation and without further calculation we may say that reaction (2) is very slow compared with reaction (1). Expressed in other words, by activating the chlorine atom to the $^2P_{1/2}$ state we have rendered it much less reactive toward ICl . This does not mean that if we introduce a large number of $^2P_{1/2}$ chlorine atoms into some iodine chloride vapor that no reaction would occur; we must remember that collisions would eventually transfer the chlorine atoms to the $^2P_{3/2}$ state and then the reaction would proceed according to (1). From the experimental results of Rollefson and Lindquist we conclude that such energy transfers have a probability sufficiently low so that many of the excited atoms survive long enough to react with hydrogen.

At the present time the possibility of extending these considerations to other reactions is limited by insufficient knowledge of the higher electronic states of most molecules. It may be that in those cases where there is a marked discrepancy between the experimental activation energies and those calculated by Eyring that the discrepancy would be greatly reduced if the calculation, in which the higher states are considered, could be made.