Submitted to Chemical
Physics Letters

UCRL-20531
Preprint

BARRIER TO COMPLEX FORMATION IN THE HYDROGEN ATOM-CHLORINE MOLECULE REACTION

Charles Maltz

March 1971

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-20531 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

BARRIER TO COMPLEX FORMATION IN THE HYDROGEN ATOM-CHLORINE MOLECULE REACTION

CHARLES MALTZ

Department of Chemistry and Lawrence Radiation Laboratory,
University of California, Berkeley, California USA

ABSTRACT

The absence of formation of the stable hydrogen dichloride as an intermediate in the beam studies of the hydrogen atom-chlorine molecule reaction is explained in terms of a symmetry imposed barrier accompanying the broadside attack of a hydrogen atom on a chlorine molecule.

The gas phase hydrogen atom-chlorine molecule reaction has of late been carefully scrutinized by several groups choosing from two different experimental techniques. The results of two recent crossed molecular beam investigations [1,2] and those of an earlier infrared chemiluminescence study [3] are all in good agreement with one another and indicate that the reaction $H + Cl_2 = HCl + Cl$ proceeds in a direct manner with no evidence for the formation of any long-lived intermediate complex. This outcome is rather unexpected when viewed in light of the matrix isolation experiment [4] involving the trapping of the hydrogen dichloride radical, this study showing that HCl_2 is a stable, linear, centrosymmetric species with a potential basin of about 15 kcal/mole (to dissociation to $Cl + HCl$). Perhaps equally surprising are indications from both measurements of the energy partitioning in the reaction [1-3], and the product angular distributions [1,2], that the reaction is governed by predominantly repulsive forces between the products with no evidence of any reactant attraction that one might expect to be associated with a system in which the formation of a stable intermediate is not deemed unlikely. This seeming paradox has been duly noted by the beam experimenters, and

the reaction has been discussed by Herschbach utilizing a valence bond approach [2b]. In this paper it is demonstrated by a simple molecular orbital argument that regardless of the incoming hydrogen velocity, symmetry requirements impose a barrier to the bimolecular formation of ClHCl from $H + Cl_2$.

Although a mainstay for many years in the calculation of molecular orbitals for isolated molecules [5], the power and simplicity of the group theoretical approach to the investigation of reactive systems has only quite recently been adequately appreciated [6]. The presence of a symmetry imposed barrier in a bimolecular reaction can most easily be demonstrated by constructing a correlation diagram between the molecular orbitals of the reactant(s) and product(s). In this procedure, the direction of approach of the reactants must be specified, and the caveat must be kept in mind that in the final analysis it is the correlation of molecular states and not molecular orbitals which must be examined for symmetry imposed activation energy.

Fig. 1 depicts the molecular orbital correlation diagram for the reaction $H + Cl_2 = Cl\text{-}H\text{-}Cl = Cl + HCl$. The bonding in the hydrogen dichloride species can be treated as a three center bond formed from combination of the hydrogen 1s orbital and chlorine 3p orbitals [7]. This results in one bonding, one non-bonding, and one antibonding orbital, the qualitative features of which are illustrated in fig. 2. The quantitative values of these orbital energies are uncertain, but reasoning by analogy to HCl, in which the $\sigma^2\pi^3\sigma^*$ configuration is

repulsive [9], one expects the σ_g^* antibonding orbital to be at a very high energy. Orbital energies for the chlorine molecule and hydrogen chloride are obtained from photoelectron spectroscopy [10]. The reactant orientation most likely to lead to the formation of the intermediate complex Cl-H-Cl is that of a broadside attack of a hydrogen atom on a chlorine molecule. This results in a triangular transition state of C_{2v} symmetry and produces the orbital correlations between H + Cl_2, Cl-H-Cl, and Cl + HCl as indicated in fig. 1, where actual orbital crossings are avoided when electron correlation and deviations from ideal C_{2v} symmetry are taken into account. This reactant approach results in an increase in energy of the filled Cl_2 π_g orbitals and the half filled hydrogen 1s orbital accompanying the decrease in energy of the filled Cl_2 σ_g orbital. Whether or not this mode of reactant approach involves a symmetry imposed activation energy depends upon whether the electronic state of Cl-H-Cl containing one electron in the antibonding σ_g^* orbital is of higher or lower energy than the separated reactants (i.e., ground state H + Cl_2). Again referring to the analogous HCl $\sigma^2\pi^3\sigma^*$ (repulsive) configuration, one would expect the excited Cl-H-Cl molecule to be of higher energy than the separated reactants and thus an activation energy barrier is anticipated. In any case, the argument does not rest on this but only upon whether symmetry considerations indicate that a linear approach of an hydrogen atom is more likely to lead to reaction to Cl + HCl than the broadside attack, since only in the latter case can the complex Cl-H-Cl be formed. Fig. 3 illustrates the orbital correlations for the linear case. A comparison of

figs. 1 and 3 does indicate that the linear reactive channel is energetically favored over that of the hydrogen attacking broadside, thus explaining why formation of Cl-H-Cl is not observed in the beam studies.

The orbital correlation diagrams also make clear the formation of Cl-H-Cl in the matrix isolation experiment, in which the relevant reaction has been postulated as Cl + HCl = Cl-H-Cl [4]. Reference to the right hand side of fig. 1 indicates that this reaction is indeed symmetry allowed.

I thank Professors Ronald R. Herm and Bruce H. Mahan for useful discussions. Support by the U.S. Atomic Energy Commission is gratefully acknowledged.

References

[1] J. Grosser and H. Haberland, Chem. Phys. Letters 7 (1970) 442.

[2] a) P. R. LeBreton, Ph.D. Thesis, Harvard University (1969);

b) D. R. Herschbach, Proceedings of the Conference on Potential Energy Surfaces in Chemistry (IBM, San Jose, California 1971).

[3] K. G. Anlauf, P. J. Kuntz, D. H. Maylotte, P. D. Pacey, and J. C. Polanyi, Discussions Faraday Soc. 44 (1967) 183; K. G. Anlauf, J. C. Polanyi, W. H. Wong, and K. B. Woodall, J. Chem. Phys. 49 (1968), 5189.

[4] P. N. Noble and G. C. Pimentel, J. Chem. Phys. 49 (1968) 3165.

[5] G. Herzberg, Electronic Spectra of Polyatomic Molecules (D. Van Nostrand Co., New York, 1966).

[6] R. B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, (Academic Press, 1970).

[7] G. C. Pimentel, J. Chem. Phys. 19 (1951) 446.

[8] R. S. Mulliken, Phys. Rev. 61 (1942) 277; J. Romand, Ann. Physique 4 (1949) 527.

[9] D. C. Frost, C. A. McDowell, and D. A. Vroom, J. Chem. Phys. 46 (1967) 4255.

Figure Captions

Figure 1. Molecular orbital correlation diagram for the reaction $H + Cl_2 = Cl\text{-}H\text{-}Cl = Cl + HCl$. Dashed lines indicate avoided crossings and closed and open circles denote electronic configuration for ground state $H + Cl_2$ and $Cl + HCl$ respectively.

Figure 2. Qualitative forms for the bonding, non-bonding and anti-bonding three center orbitals in Cl-H-Cl. Shaded and unshaded areas denote different phases of the wave function.

Figure 3. Molecular orbital correlation diagram for the reaction $H + Cl_2 = (H\text{-}Cl\text{-}Cl) = HCl + Cl$. The orbital energies for the intermediate (H-Cl-Cl) are estimates.

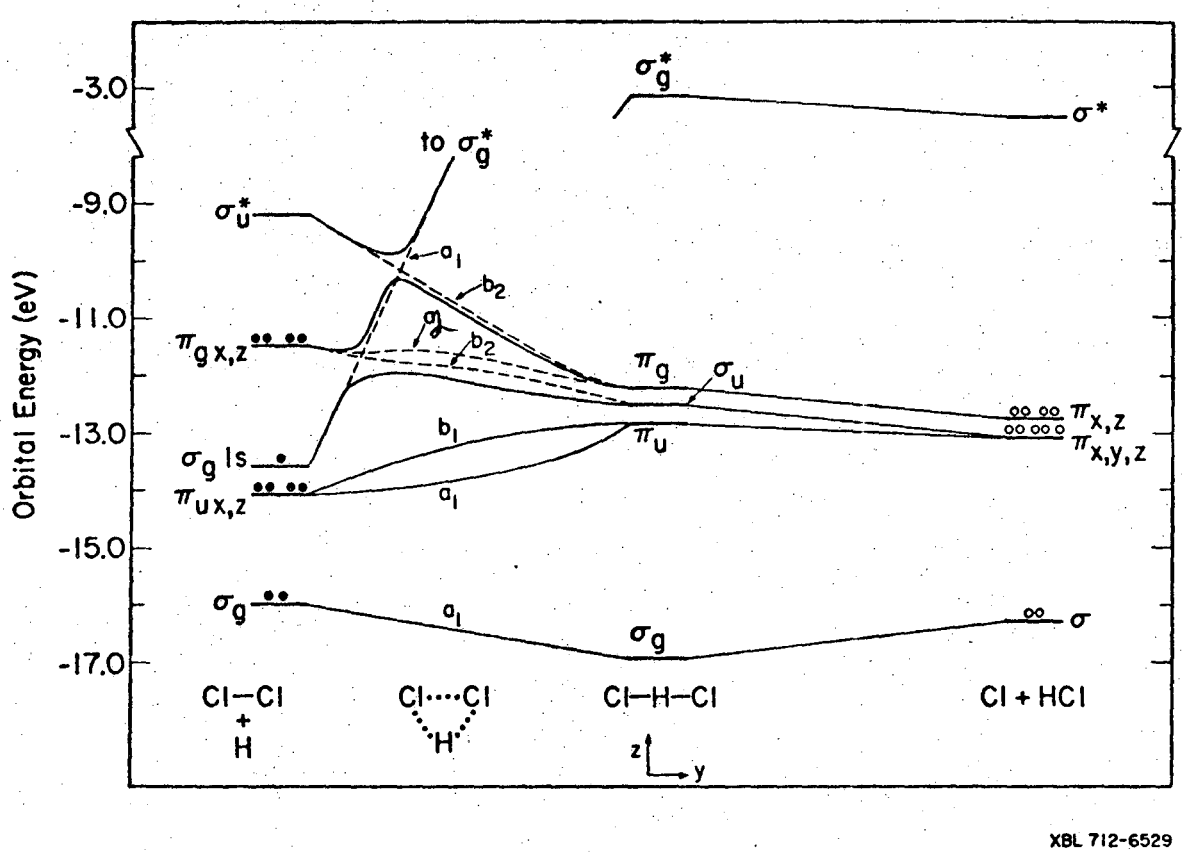
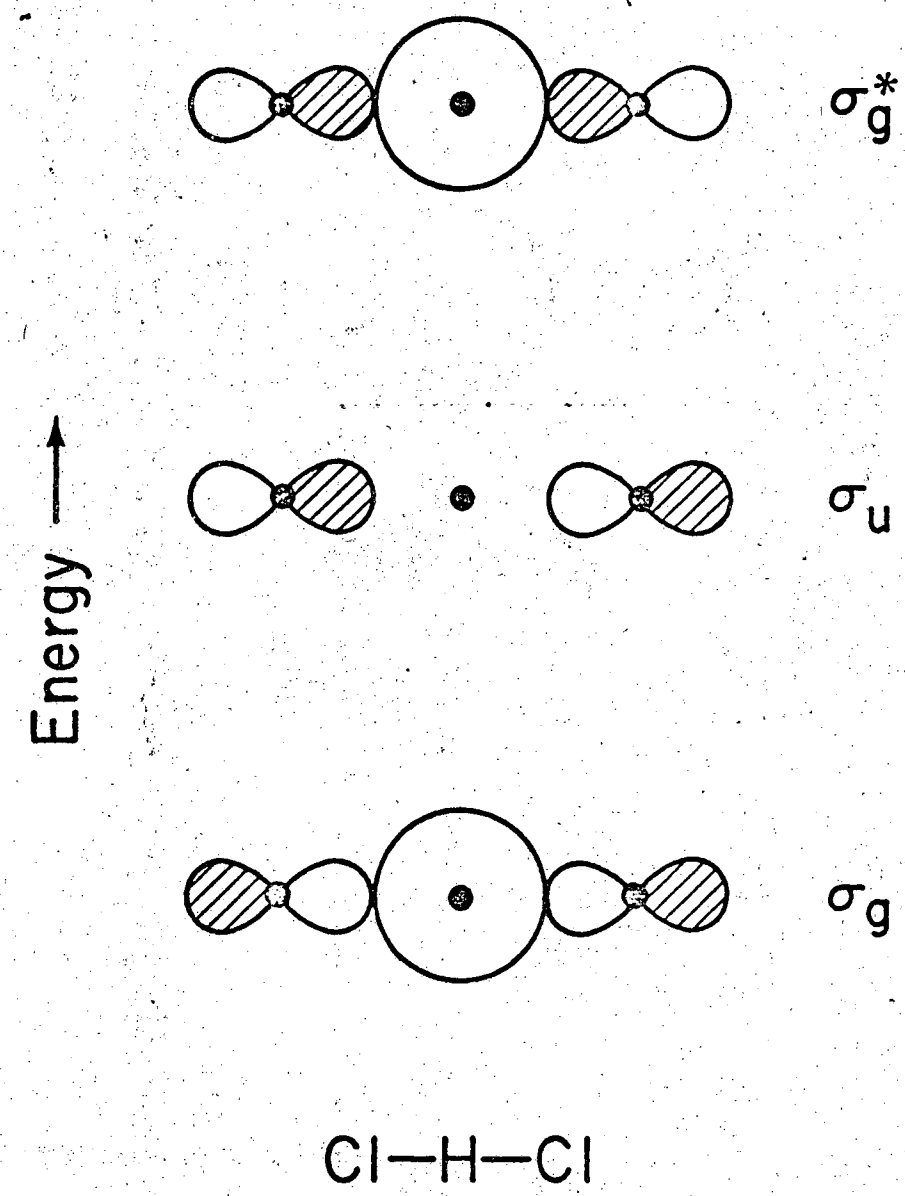

Orbital Energy (eV)
-3.0
-9.0
-11.0
-13.0
-15.0
-17.0
σ_g^*
σ^*
to σ_g^*
σ_u^*
a_1
b_2
a_1
b_2
$\pi_{g\,x,z}$
π_g
σ_u
$\pi_{x,z}$
$\pi_{x,y,z}$
b_1
π_u
σ_g 1s
$\pi_{u\,x,z}$
a_1
σ_g
a_1
σ_g
σ
Cl—Cl
+
H
Cl····Cl
H
Cl—H—Cl
Cl + HCl
z
y
XBL 712-6529

Fig. 1.



XBL 712-6528

Fig. 2.

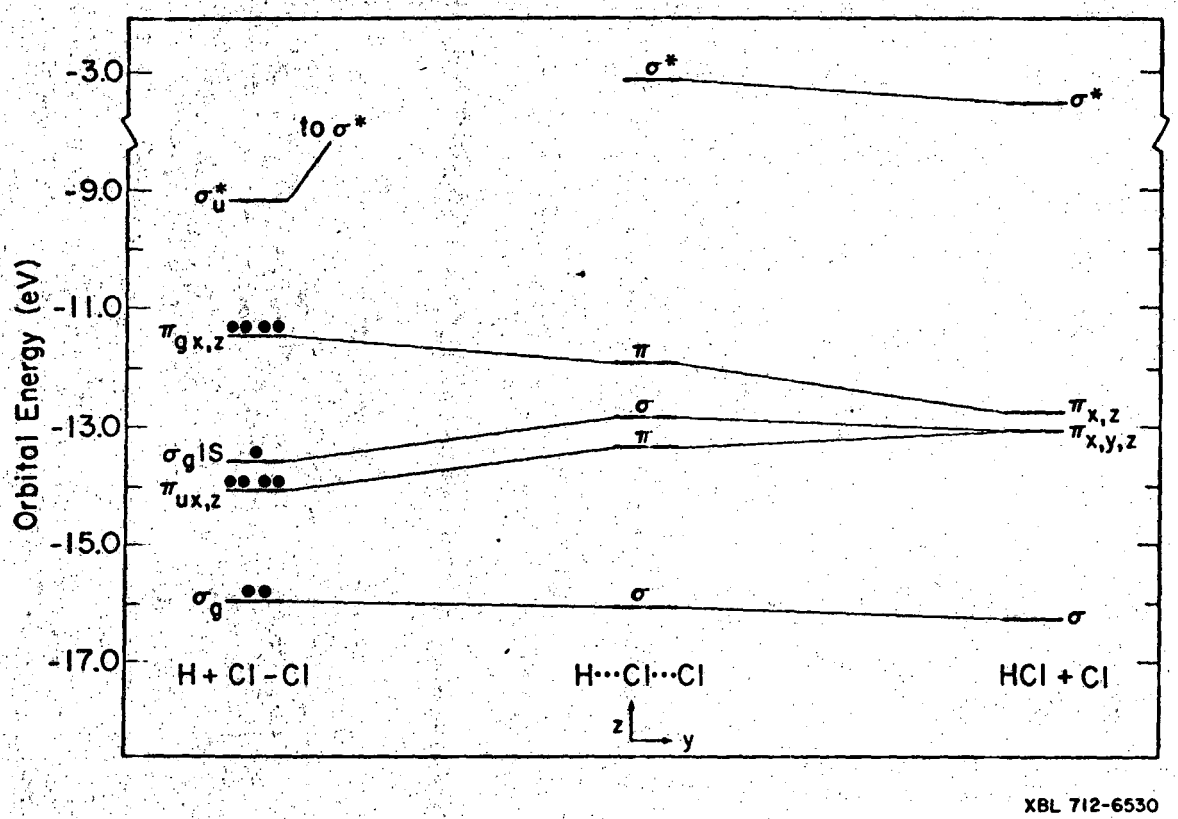

Orbital Energy (eV)
-3.0
-9.0
-11.0
-13.0
-15.0
-17.0
to σ*
σ*u
πg x,z
σg 1S
πux,z
σg
σ*
σ*
π
σ
π
σ
πx,z
πx,y,z
σ
H + Cl - Cl
H···Cl···Cl
HCl + Cl
z
y
XBL 712-6530

Fig. 3.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720