

# A CNDO/2 STUDY OF THE ETHYLENE-CHLORINE REACTION

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**Abstract**—CNDO/2 calculations have been carried out of the energies of reaction and changes in charge distribution for some reactions involving the ethylene chlorine complex. The addition of chlorine to ethylene may involve the attack of a chloride ion on the ethylene chlorine complex.

The charge transfer complex between ethylene and chlorine has recently been studied by CNDO calculations<sup>1-3</sup> and by UV<sup>3,4</sup> and IR spectroscopy.<sup>3</sup> It has been suggested that complex formation between halogen and olefine represents the first step in the addition of halogen to the double bond.<sup>2,5</sup> The second step is thought to be the dissociation of this complex into a positive halogen olefin ion and a halogenide ion.<sup>2-5</sup> (Reaction I, see Fig 1) In Ref 2 this energy of dissociation was calculated to be 220.8 kcal/mole. When the influence of a solvent of dielectric constant 6.15 was taken into account a slightly more realistic value, 147 kcal/mole, was obtained. Considering the very limited experience with CNDO calculations on ions, I have repeated this calculation\* and compared it to the direct dissociation of chlorine into ions (Reaction II, see Fig 1) and to the formation of a Cl<sub>3</sub><sup>+</sup> ion and a Cl<sub>3</sub><sup>-</sup> ion from three chlorine molecules. (Reaction III, see Fig 1). The results are given in Fig 1.



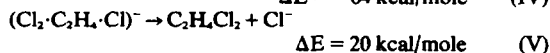
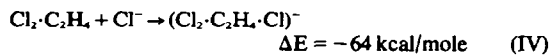
The energy of reaction is considerably smaller for reaction I than for reaction II but of the same order of magnitude as that of reaction III. However, reaction III has never been observed, which may serve as an indication that the heterolytic dissociation of the complexed chlorine may require too much energy even if solvation energies are taken into account.

We may obtain a very rough estimate of the energy of heterolytic dissociation of the complexed chlorine molecule by multiplying the result of the CNDO calculation with the ratio of the measured (272 kcal/mole<sup>7</sup>) and CNDO value (439 kcal/mole) for the dissociation of chlorine into ions, and finally

take the solvent effect into account using the estimate of Ref 2.

We then get 62 kcal/mole, still rather high for such a rapid reaction. It therefore seemed to be of interest to explore a direct attack of chloride ion on the ethylene chlorine complex.

When a chloride ion is brought closer to an ethylene chlorine complex along the C<sub>2</sub> axis of the complex (on the opposite side of the ethylene plane from the chlorine molecule) the CNDO calculations give a decrease in energy and significant charge transfer from the chloride ion to the most distant chlorine atom (Fig 2). However, it was found that the axially symmetric configuration is unstable against unsymmetrical displacements of the chlorine molecule and the chloride ion. After a series of calculations, in which groups of structural parameters were simultaneously varied,<sup>†</sup> a structure was found, which is stable against small simultaneous displacements of the structural parameters. The resulting structure may be described as trans 1,2 dichloro ethane with a chloride ion attached to one of the chlorine atoms (Fig. 3). The negative charge is shared between the initial chloride ion and the outer chlorine atom of the former chlorine molecule with somewhat more charge on the molecular chlorine. Only a rather small energy of reaction separates this ternary complex from 1,2 dichloro ethane plus a chloride ion. To summarise the CNDO calculations predict:



However, while the overall energy of reaction from ethylene and chlorine (-50 kcal/mole) compares favourably with experiment<sup>8</sup> (-43.5 kcal/mole, 298 K) (note that the energy of complex formation for the ethylene chlorine complex is -6 kcal/mole in the CNDO approximation) it seems unlikely that the errors for the individual steps are this small, and furthermore the solvation of the

\*All calculations reported in this paper were carried out with the CNDO/2 program described in reference 1 using the original parameters. The sp. approximation was used.<sup>6</sup>

†This variation was carried out using the program package described.<sup>8</sup>

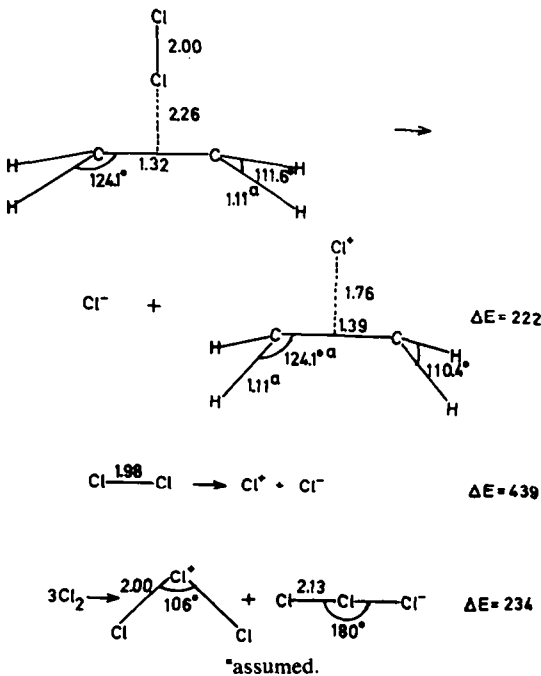


Fig. 1. Energies of reaction for some heterolytic dissociations of chlorine (CNDO calculations). The CNDO equilibrium structures are given.

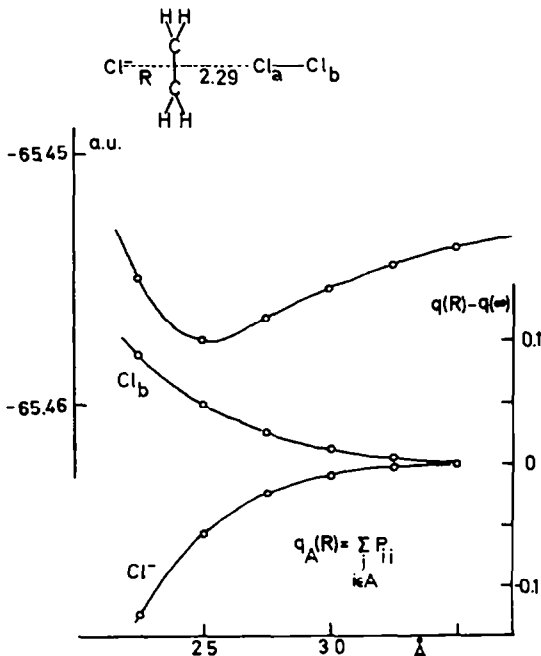


Fig. 2. Energy and charge transfer for an axial Cl<sup>-</sup> · C<sub>2</sub>H<sub>4</sub> · Cl<sub>2</sub> complex.

ionic species will alter the energetic relations considerably.<sup>2</sup> It seems, however, fair to conclude that the CNDO results indicate that a direct attack of a

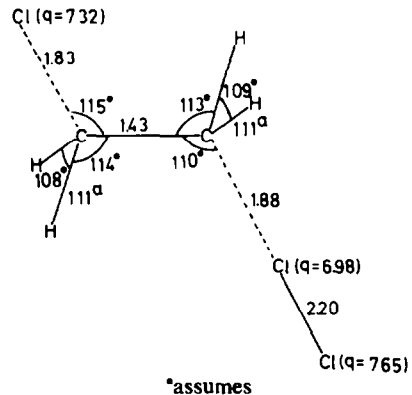
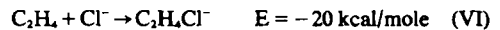


Fig. 3. Equilibrium structure for the Cl<sup>-</sup> · C<sub>2</sub>H<sub>4</sub> · Cl<sub>2</sub> complex (CNDO).

chloride ion on the ethylene chlorine complex is an energetically more favourable route for the addition that the heterolytic dissociation of the complex into ions.

Some indication of the influence of the chlorine molecule on the addition of the chloride ion addition may be obtained from a comparison with the direct attack of a chloride ion on ethylene. The CNDO calculations predict the formation of a stable ion with the structure given in Fig. 4.



Thus, the ethylene chlorine complex seems to be considerably more sensitive to the attack of a chloride ion than is free ethylene.

A comparison between the electron distributions of the ethylene chlorine complex and those of the ethylene chloride anion, the ethylene chloride ion and ethylene chloride, indicates that it is a rather strong electron acceptor, when interacting with a chloride ion. It seems likely that this electron acceptor strength is effective also against other, neutral electron donors, which may explain the addition of solvent molecules as a competing

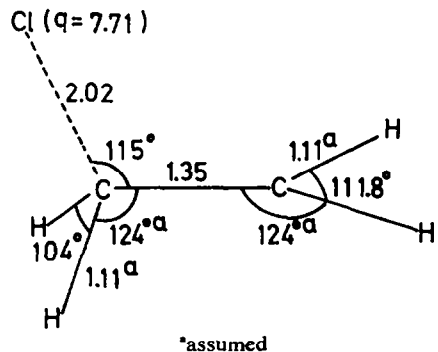


Fig. 4. Equilibrium structure for the C<sub>2</sub>H<sub>4</sub> · Cl<sup>-</sup> complex (CNDO) (q, see Fig. 2).

reaction in many solvents. CNDO calculations of course can never prove that the addition of halogen to double bonds involves a charge transfer complex between halogen and olefin which is attacked by a halogenide ion to give the final product. It may be noted, however, that the existence of the facile electron transfer within the complex, necessary for this mechanism, is indicated by the appearance of the Cl—Cl stretching and C=C stretching vibrations in the IR-spectrum of the complex.<sup>3</sup>

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