

sufficient for use on submilligram quantities.

### Experimental Section

NMR experiments were carried out on a Nicolet 500-MHz spectrometer, equipped with a 10-mm  $^{13}\text{C}$  probe and a 5-mm  $^1\text{H}$  probe. Eight milligrams of sample were dissolved in 0.4 mL of  $^2\text{HCCl}_3$ , and a 5-mm Wilmad-528pp sample tube was used throughout. All spectra were recorded at 25 °C.  $^{13}\text{C}$  shifts are indirectly referenced to tetramethylsilane ( $\text{Me}_4\text{Si}$ ) by using the central line of the  $^2\text{HCCl}_3$  triplet as an internal reference (77.0 ppm).  $^1\text{H}$  shifts are relative to a small amount of internal  $\text{Me}_4\text{Si}$ .

**Double-Quantum Filtered COSY.**  $t_1$  values (480) ranging from 0 to 175 ms were used and two FID's consisting of 512 complex data points each were acquired per  $t_1$  value. The acquisition time in the  $t_2$  dimension was 188 ms. Data were zero-filled in both dimensions, to yield a  $1024 \times 1024$  data matrix for the absorptive part of the 2D spectrum. Gaussian line broadening was used in both dimensions to avoid truncation. The phase cycling of the  $90_{\phi}-t_1-90_{\psi}-90_{\phi}-\text{acq.}(t_2)$  sequence was the following:

$\phi$ : x, y, -x, -y, x, y, -x, -y, x, y, -x, -y, x, y, -x, -y

$\psi$ : x, x, x, x, x, x, x, x, x, x, x, x, x, x, x, x

$\theta$ : x, x, -x, -x, y, y, -y, -y, -x, -x, x, x, -y, -y, y, y

acq.: x, x, x, x, -y, -y, -y, -y, -x, -x, -x, -x, y, y, y, y

Additionally, CYCLOPS phase cycling<sup>53</sup> was used by repeating the entire 16-step experiment four times with the phases of all radio-frequency pulses and of the receiver incremented by 90° each time. The delay time between scans (including the data acquisition time,  $t_2$ ) was 1.98 s and

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the total data accumulation time was 17 h. Small artifacts on the lines  $F_1 = NF_2$  ( $N = -2, -1, 0, 1, 2$ ) are due to an insufficiently long delay period between scans ( $\sim T_1$ ). For longer delay periods these artifacts rapidly decrease in intensity, but this requires unacceptably long data accumulation times.

**$^1\text{H}-^{13}\text{C}$  Heteronuclear Chemical Shift Correlation.**  $t_1$  values (100) ranging from 0 to 59.4 ms were used and two FID's consisting of 1024 complex data points each were acquired per  $t_1$  value. The acquisition time in the  $t_2$  dimension was 152 ms. Data were zero-filled in both dimensions, to yield a  $2048 \times 512$  data matrix for the absorptive part of the 2D spectrum. Gaussian line broadening was used in both dimensions to avoid truncation. Ninety six scans were acquired per  $t_1$  value and a delay time of 1.8 s was used between the end of data acquisition and the 90° pulse of the next scan. The total measuring time was 6 h.

**HOHAHA Experiments.** Each of the HOHAHA spectra results from 128 accumulations ( $\sim 4$  min). A 10-Hz decoupler radio frequency field strength (50 ms 180° pulse) was used to selectively invert the  $^1\text{H}$  multiplet of interest. A tuned Henry class A radioamplifier was used to generate 4-W radio-frequency power for the observe channel, corresponding to a 6-kHz radio-frequency field strength. Tuned diodes and a band-pass filter were used in the transmitter line to avoid sensitivity loss and to prevent perturbation of the  $^2\text{H}$  lock channel by the long spin-lock pulse. To avoid poor cancellation in the difference spectra, the sample was not spun.

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## Theoretical Study of the Addition of Hydrogen Halides to Olefins: Reaction of Dimeric Hydrogen Fluoride with Ethylene

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**Abstract:** This paper presents a theoretical study of the addition of  $(\text{HF})_2$  to ethylene using ab initio methods with the 3-21G basis set. Thermodynamical calculations to obtain  $\Delta G^\circ_{298}$  values were also made. Comparison with the bimolecular addition of HF to ethylene shows a larger stabilization of the transition state obtained, reflected in a decrease of the potential barrier. This fact, along with an analysis of the energy components and the mechanism, allows us to assert the catalytic activity of the second HF molecule. From the thermodynamics of the reaction, the need for a "bimolecular" collision between  $(\text{HF})_2$  and ethylene and not a termolecular one is deduced, and the ability of this mechanism to explain data in the gas phase and in nonpolar solvents is sustained.

Addition of hydrogen halides to olefins belongs to the classic reactions of organic chemistry. It is generally accepted that three distinct pathways are possible in those processes, although not all of them are applicable to all olefins and all hydrogen halides. The first one, ionic addition, takes place in polar solvents and is assumed to proceed through protonation, yielding a carbonium intermediate that later evolves to the product.<sup>1</sup> This is always a normal Markovnikov addition. The second mechanism, present only in HBr additions,<sup>2</sup> is the anti-Markovnikov addition, usually explained by the so-called peroxide effect,<sup>3</sup> which suggests a radical chain mechanism,<sup>4</sup> and has been verified in the gas phase and in solution. Finally, we have the direct bimolecular addition, which

occurs in gas phase, that is, the reverse of the much-studied elimination of HX from haloalkanes by pyrolysis; it has been examined in detail in the case of hydrogen iodide reaction with olefins.<sup>5</sup>

In nonpolar solvents without radical initiators, experimental facts seem not to be explainable by any of the aforementioned

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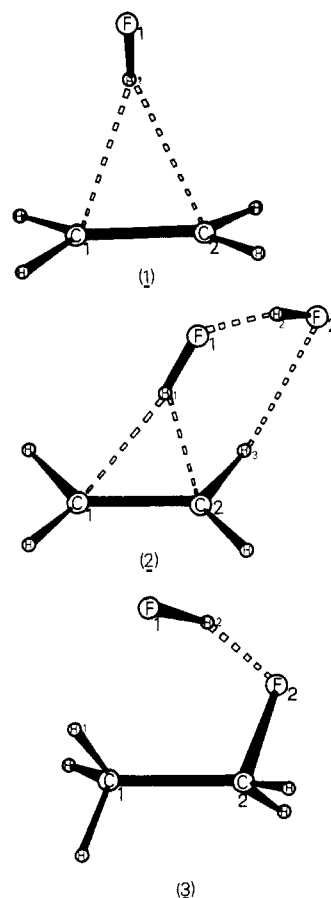
mechanisms. For instance, for the addition of HBr to 1-heptene in *n*-hexane/ $\text{CH}_2\text{Cl}_2$  mixtures, it has been shown that the variation of the dielectric constant by the change in the relative composition of the solvent affects the addition rate only slightly.<sup>6</sup> This fact makes it possible to discard the ionic mechanism. On the other hand, the use of radical inhibitors does not affect the reaction rate either,<sup>6</sup> an argument against the radical chain mechanism. Also some older work of Mayo and Katz<sup>7</sup> exists on the addition of HCl to propylene in heptane solution, pointing toward the presence of complexes between hydrogen halide and olefin as well as toward a high order of the reaction rate with regard to hydrogen halide concentration. Thus it seems that a fourth mechanism may be acting in nonpolar solvents and perhaps also in the gas phase. In the last decade this point of view has emerged, for instance, in the work of Sergeev et al.<sup>6</sup> and of Haugh and Dalton.<sup>8</sup> In the first of these papers the aforementioned addition of HBr to 1-heptene was investigated and the experimental results interpreted by a mechanism involving cyclic structures with participation of HBr dimers. In the second paper, the net gas-phase addition of HCl to propylene was studied by means of  $^1\text{H}$  NMR. It was determined that the results were best fitted by kinetic expressions first order in propylene and third order in HCl, and a reaction scheme including a six-center intermediate was proposed. Thus, from an experimental point of view, a fourth mechanism involving the reaction with dimers of hydrogen halides has appeared in recent years, with the interesting proposal of complexed cyclic transition-state structures built in.

From a theoretical point of view, several reports have been published on the addition of hydrogen halides to olefins. Some of them refer to partial aspects of ionic or radical<sup>9</sup> mechanisms, such as addition of  $\text{H}^+$  or  $\text{Br}^-$  to olefins, but the most complete papers are concerned with the elimination of hydrogen halides from haloalkanes.<sup>10</sup> This latter reaction is the reverse of the bimolecular gas-phase addition of HX to olefins. These reports stress specifically the role of a four-center transition state in the unimolecular pathway of the reaction. To our knowledge no theoretical work has been undertaken on the new molecular mechanism mentioned above.

It is known that, in a sense, addition of HX to olefins is similar to its hydration. From our experience and the work of other people on the participation of water dimers in hydration<sup>11</sup> and tautomeric<sup>12</sup> reactions, we know of the large decrease of the potential energy barriers obtained by allowing the dimer instead of the monomer to take part in the reaction. Thus, on the basis of the similarity mentioned above and our experience with water dimers, we carried out a theoretical study, reported in this paper, involving HX complexes for the addition of hydrogen halides to olefins.

### Methodology

The first step to reach the goal previously described is to define a model system to carry on research. We chose the HF and  $\text{C}_2\text{H}_4$  molecules, the simplest hydrogen halide and olefin, respectively. Perhaps this choice is not the best possible one from an experimental point of view, but it allows an easy interpretation not provided by more complex systems. The existence of a theoretical



**Figure 1.** 3-21G structure of reactants and products: (1)  $\text{C}_2\text{H}_4\cdot\text{HF}$ ; (2)  $\text{C}_2\text{H}_4\cdot(\text{HF})_2$ ; (3)  $\text{CH}_3\text{CH}_2\text{F}\cdot\text{HF}$ .

study<sup>10b</sup> on the decomposition of  $\text{CH}_3\text{CH}_2\text{F}$  with which to compare the internal consistency of our results is also an important reason for choosing this system.

Ab initio SCF calculations were made with the GAUSSIAN 82 series of programs<sup>13</sup> using the 3-21G basis set.<sup>14</sup> The structures of all the stable species considered were obtained by full geometry optimization with either the Murtagh-Sargent<sup>15</sup> or Schlegel<sup>16</sup> algorithms.

For geometry optimizations of transition states we adopted the following strategy: in the case of the bimolecular reaction between HF and  $\text{C}_2\text{H}_4$  the four-centered transition state was located with Schlegel's<sup>16</sup> method starting from the 4-31G structure determined by Kato and Morokuma.<sup>10b</sup> In the case of the termolecular reaction between  $(\text{HF})_2$  and ethylene the constrained optimization method using the F2C2 distance (see Figure 1) as the leading parameter was employed to generate an energy profile whose maximum was used as a starting point for the direct location of the transition state in the potential energy hypersurface by Schlegel's method.

To prevent error in relation to basis set superposition, we corrected the stabilization energies of the complexes between the olefin and HF using the counterpoise method.<sup>17</sup> In the present work, the correction has been taken into account by evaluating the difference between the sum of the energies of each distorted fragment, calculated once with its own basis set and again with the basis of the whole supermolecule. This method has been shown

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Table I. Most Relevant Bond Lengths (Å) for the Different Species Involved in the Bimolecular and the Trimolecular Additions

|  | C1-C2 | C1-H1 | H1-F1 | F1-C2 | F1-H2 | H2-F2 | F2-C2 |
|--|-------|-------|-------|-------|-------|-------|-------|
| C <sub>2</sub> H <sub>4</sub>                    | 1.315 |       |       |       |       |       |       |
| HF   |       |       | 0.937 |       |       |       |       |
| C <sub>2</sub> H <sub>4</sub> ·HF                | 1.320 | 2.418 | 0.940 | 3.333 |       |       |       |
| TS1  | 1.406 | 1.413 | 1.199 | 1.856 |       |       |       |
| C <sub>2</sub> H <sub>5</sub> F                  | 1.520 | 1.082 | 2.364 | 1.410 |       |       |       |
| (HF) <sub>2</sub>                                |       |       | 0.940 |       | 1.675 | 0.942 |       |
| C <sub>2</sub> H <sub>4</sub> ·(HF) <sub>2</sub> | 1.322 | 2.364 | 0.948 |       | 1.624 | 0.948 | 3.099 |
| TS2  | 1.397 | 1.352 | 1.207 |       | 1.225 | 1.064 | 1.948 |
| C <sub>2</sub> H <sub>5</sub> F·HF               | 1.519 | 1.079 | 2.212 |       | 0.946 | 1.639 | 1.438 |

by Maggiora and Williams<sup>18</sup> to be necessary for chemically reacting systems that undergo significant geometry changes.

The influence of correlation energy on the different species in the reaction was looked at with the aid of the second- and third-order Møller-Plesset perturbation theory,<sup>19</sup> taking into account all the molecular orbitals arising from the SCF.

$\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  values, including zero-point correction, were calculated to obtain results more readily comparable to the experimental ones. These magnitudes were computed by using the partition functions as provided by the statistical thermodynamic formulae within the ideal gas, rigid-rotor, and harmonic oscillator approximations<sup>20</sup> as implemented in the GAUSSIAN 82 package. A pressure of 1 atm and temperature of 298.15 K were assumed in the calculations. Analytical second derivatives of energy with respect to the Cartesian coordinates were used for the determination of vibrational frequencies.

## Results and Discussion

**Structures of Reactants and Products.** In order to compare the addition of (HF)<sub>2</sub> to ethylene with the bimolecular reaction of HF with C<sub>2</sub>H<sub>4</sub>, we first determined the structures of the reactants and the expected products. These optimized geometries are compiled in Table I and the general appearance of the species depicted in Figure 1.

With respect to the structure of the complex between HF and ethylene (1 in Figure 1), our results fully agree with already published theoretical work using different basis sets.<sup>21</sup> A symmetrical  $\pi$ -complex was formed, with the hydrogen of HF pointing toward ethylene; a fact explainable on the basis of the leading charge-transfer interaction from the HOMO of the olefin to the LUMO of the hydrogen halide, whose largest part is localized on the hydrogen atom. From a Mulliken population analysis, this charge transfer was determined to be 0.029 electrons. In the same way, the product coincides with previous results,<sup>10b</sup> since we obtained the alternate conformation as the most stable one.

To study the interaction of (HF)<sub>2</sub> with the olefin, we first found the structure of the hydrogen fluoride dimer. The geometry is quite coincident with the results obtained with other basis sets<sup>22</sup> and with experimental data.<sup>23</sup> Some more detailed discussion is needed, however, on the structure of C<sub>2</sub>H<sub>4</sub>·(HF)<sub>2</sub> (2 in Figure 1) since it is presented in this paper for the first time. Although

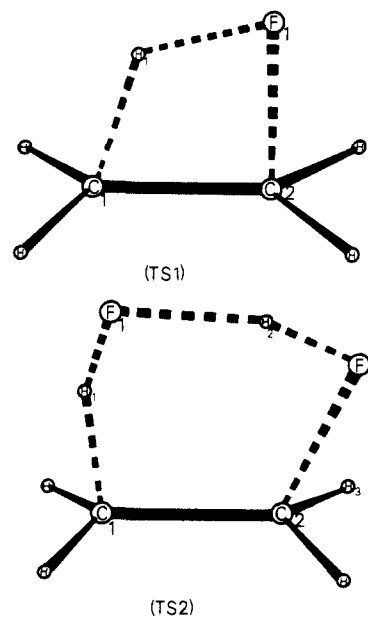


Figure 2. 3-21G structure of transition states of the bimolecular (TS1) and trimolecular (TS2) additions.

at first sight it may seem that the complex would be formed by the arrangement of (HF)<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> in perpendicular planes—with one end hydrogen of (HF)<sub>2</sub> interacting with one of the carbon atoms and the fluorine of the other end of the chain interacting with the other carbon atom—this is not so. As a matter of fact, we initially located a stationary point with the structure just mentioned by using Schlegel's method of energy minimization, but its force constant matrix had one negative eigenvalue. Following its associated eigenvector, the same method reached a true energy minimum with no negative eigenvalues of the Hessian matrix that was 2.22 kcal/mol below the first one. This final structure shows some similarity with the C<sub>2</sub>H<sub>4</sub>·HF complex. The first HF molecule again forms a  $\pi$ -complex, but now its symmetry is destroyed by the interaction of its fluorine atom with the hydrogen of the other halide molecule, whose fluorine atom in turn forms a hydrogen bond with one H atom of C<sub>2</sub>H<sub>4</sub>. The quality of the hydrogen bond of this interaction is shown by the F2H3 distance, 2.1 Å, and its Mulliken population, 0.045, compared with the 0.050 of the HF·HF bond.

In the structure of the product (3 in Figure 1) we notice that a new HF molecule has been formed with the F1 and H2 atoms in such a way that it comes from what was previously the hydrogen bond in the dimer. A strong hydrogen bond is seen between F2 and H2, as proved by the bond distance, 1.64 Å, and its Mulliken population, 0.046.

**Transition States.** In Figure 2 we have drawn the structures of the transition states of the bimolecular (TS1) and trimolecular (TS2) additions, whose most relevant geometric parameters are given in Table I.

With respect to the first transition state, we notice that it is very similar to the one found by Morokuma<sup>10b</sup> using the 4-31G basis set. The incipient change in hybridization undergone by the carbons and the four-centered character of this transition state are apparent in the figure. The six-center transition state for the

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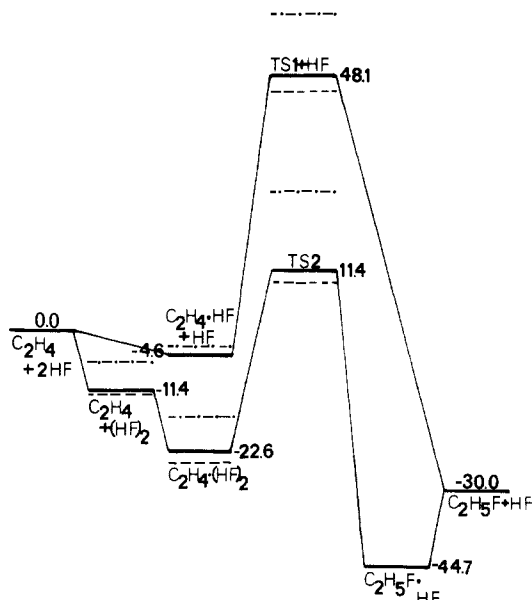
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**Figure 3.** Relative 3-21G potential energies (kcal/mol) for the bimolecular (via TS1) and trimolecular (via TS2) reactions. For reactants and transition states, energies corrected at the MP3 level (lower dashed lines) and MP3 + BSSE (upper broken lines) are also shown.

**Table II.** SCF and MP Correction Energies (au) of Reactants, Intermediates, Transition States, and Products by Using 3-21G Optimized Geometries

|  | ESCF        | E2        | E3                           | EMP3        |
|--|-------------|-----------|------------------------------|-------------|
| C <sub>2</sub> H <sub>4</sub>                    | -77.600 99  | -0.182 37 | -0.167 44 × 10 <sup>-1</sup> | -77.800 10  |
| HF   | -99.460 22  | -0.123 22 | -0.460 22 × 10 <sup>-3</sup> | -99.583 90  |
| C <sub>2</sub> H <sub>4</sub> ·HF                | -177.068 60 | -0.305 69 | -0.169 02 × 10 <sup>-1</sup> | -177.391 19 |
| TS1  | -176.984 53 | -0.318 42 | -0.929 63 × 10 <sup>-2</sup> | -177.312 25 |
| C <sub>2</sub> H <sub>3</sub> F                  | -177.108 97 | -0.304 00 | -0.159 06 × 10 <sup>-1</sup> | -177.428 87 |
| (HF) <sub>2</sub>                                | -198.938 60 | -0.248 53 | 0.176 29 × 10 <sup>-3</sup>  | -199.186 96 |
| C <sub>2</sub> H <sub>4</sub> ·(HF) <sub>2</sub> | -276.557 43 | -0.435 35 | -0.150 05 × 10 <sup>-1</sup> | -277.007 81 |
| TS2  | -276.503 22 | -0.442 63 | -0.798 65 × 10 <sup>-2</sup> | -276.953 84 |
| C <sub>2</sub> H <sub>3</sub> F·HF               | -276.592 61 | -0.430 78 | -0.148 30 × 10 <sup>-1</sup> | -277.038 22 |

addition of (HF)<sub>2</sub> to C<sub>2</sub>H<sub>4</sub> exhibits an increased interaction between C2 and F2, as shown by the 0.075 Mulliken bond population vs. a nonbonding -0.012 one in the reactant. It is interesting to note that the previous hydrogen bond interaction between F2 and H3 has now almost disappeared and that the HF dimer plane lies almost perpendicular to the one that contains the four hydrogen atoms.

**Energy Profile.** Using the optimized structures described earlier, we calculated the total energies of the species involved in the bimolecular and termolecular reactions. These energies are given in Table II and the diagram is depicted in Figure 3.

We see in this figure that, at the 3-21G level, a large decrease in the potential energy barrier is brought about by the use of the dimer instead of the monomer. This is one of the fundamental results of this paper, which will be discussed extensively. In the figure we have also drawn the levels corresponding to the formation of the different reactant and product complexes involved in the course of the reaction.

Two shortcomings may be seen in the results. In the first place, it is known that with a small basis set, calculations suffer from so-called basis set superposition error,<sup>24</sup> that is, an overstabilization of fragments in a complex provided by the basis functions of all the other fragments forming it. Although this is particularly noticeable in minimal basis sets like STO-3G, in double- $\zeta$  basis like the one we are using here it may also have some influence. The second objection concerns the importance that correlation effects may have on the reaction. To overcome these possible

**Table III.** Relative Energies (kcal/mol) of the Distinct Species with Respect to Ethylene Plus Two HF Molecules Infinitely Apart

|   | $\Delta E^a$ | $\Delta E_{\text{MP3}}^b$ | $\Delta E_{\text{BSSE}}^c$ | $\Delta E_{\text{BSSE}}^{\text{MP3}}^d$ |
|---|--------------|---------------------------|----------------------------|---|
| C <sub>2</sub> H <sub>4</sub> + HF + HF           | 0.0          | 0.0                       | 0.0                        | 0.0                                     |
| C <sub>2</sub> H <sub>4</sub> ·HF + HF            | -4.6         | +0.1                      | +1.5                       | -3.0                                    |
| C <sub>2</sub> H <sub>4</sub> + (HF) <sub>2</sub> | -11.4        | -0.6                      | +5.9                       | -6.1                                    |
| C <sub>2</sub> H <sub>4</sub> ·(HF) <sub>2</sub>  | -22.6        | -2.4                      | +8.7                       | -16.3                                   |
| TS1 + HF  | +48.1        | -3.1                      | +14.4                      | +59.4                                   |
| TS2   | +11.4        | -2.6                      | +17.3                      | +26.1                                   |
| C <sub>2</sub> H <sub>3</sub> F·HF                | -44.7        | +0.6                      |                            |   |
| C <sub>2</sub> H <sub>3</sub> F + HF              | -30.0        | +1.8                      |                            |   |

<sup>a</sup>Hartree-Fock relative energies. <sup>b</sup>Only correlation energy corrections (at MP3 level). <sup>c</sup>Only counterpoise corrections. <sup>d</sup> $\Delta E_{\text{BSSE}}^{\text{MP3}} = \Delta E + \Delta E_{\text{MP3}} + \Delta E_{\text{BSSE}}$ .

shortcomings in the calculations, we corrected the 3-21G energies, for the first of them using the counterpoise<sup>17</sup> method as explained in Methodology. For the second one, we used second- and third-order Møller-Plesset perturbation theory.<sup>19</sup>

In Table II we show the SCF energies, the energy corrections due to second- and third-order MP perturbation theory, and the total energies including these corrections. In Table III we give the relative energies of the species with respect to ethylene and two hydrogen fluoride molecules infinitely apart at the Hartree-Fock level plus the corrections due to correlation energy and to basis set superposition. In Figure 3 we have also given the corrected and uncorrected relative energies for reactants and transition states in order to compare the influence of the corrections on the potential energy barriers.

As seen in Table III and Figure 3, the decrease in the potential energy barrier when passing from the bimolecular to the termolecular reaction is only slightly affected by both corrections. In Table II one can see that the third-order corrections are lower than the second-order ones. In the (HF)<sub>2</sub> dimer the third-order perturbation energy correction is even positive, showing that reaching only the MP2 level of theory may lead sometimes to overcorrections in correlation energy. If we look at the relative energies of Table III, we can observe that the barriers of both reactions become slightly lower. For the bimolecular reaction, this agrees with the results found by Kato and Morokuma.<sup>10b</sup>

With regard to BSSE corrections, the unusually high values obtained for  $\Delta E_{\text{BSSE}}$  in the transition states can be understood by the proximity of the two intervening fragments. Nevertheless, it must be remarked that in transition states several bonds are being formed or broken, so some ambiguity arises for the definition of the fragments.

It is clear that the utilization of a large basis set is the best way to correct BSSE. However, in large systems like the one studied here, where small basis sets must be employed, the counterpoise method may be a good way to correct that BSSE. For instance, for the (HF)<sub>2</sub> dimer we found that the BSSE correction lowers the stabilization energy from 11.4 to 5.5 kcal/mol. Taking into account correlation energy, that value becomes 6.1 kcal/mol, which is close to the experimental data ( $5.7 \pm 1.0$  kcal/mol), and is a little higher than the best values found in several theoretical results (ref 22c,d and 24c) recently published with large basis sets along with correlation energy. The net effect of the BSSE correction on potential barriers is to increment both of them.

From the analysis we have made with the BSSE and correlation energy corrections, one can see that the energy changes due to both effects go in opposite directions and are somewhat offset. Some cancellation of correlation and basis set size corrections are also found in different chemical reactions, as, for instance, in the nucleophilic reaction between formic acid and ammonia.<sup>25</sup> Taking into account the mentioned effects and that the energy differences are sizeable enough, further refinements from higher level calculations would not change the qualitative conclusions of this work.

**Mechanism.** While the mechanism of the bimolecular addition has already been studied, the reaction of (HF)<sub>2</sub> with C<sub>2</sub>H<sub>4</sub> is

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(25) Oie, T.; Loew, G. H.; Burt, S. K.; Binkley, J. S.; MacElroy, R. D. *Int. J. Quantum Chem., Quantum Biol. Symp.* **1982**, *9*, 223-245.

Table IV. Mulliken Bond Populations and Percentages of Bond-Forming or -Breaking

|  | C1-C2 | C1-H1 | H1-F1 | F1-C2  | F1-H2 | H2-F2 | F2-C2  |
|--|-------|-------|-------|--------|-------|-------|--------|
| C <sub>2</sub> H <sub>4</sub> ·HF                | 0.502 | 0.010 | 0.206 | -0.002 |       |       |        |
| TS1  | 0.290 | 0.140 | 0.098 | 0.087  |       |       |        |
| C <sub>2</sub> H <sub>5</sub> F                  | 0.213 | 0.374 | 0.001 | 0.210  |       |       |        |
| % forming or breaking                            | 74    | 35    | 53    | 42     |       |       |        |
| C <sub>2</sub> H <sub>4</sub> ·(HF) <sub>2</sub> | 0.478 | 0.012 | 0.198 |        | 0.050 | 0.190 | -0.012 |
| TS2  | 0.264 | 0.040 | 0.146 |        | 0.106 | 0.120 | 0.081  |
| C <sub>2</sub> H <sub>5</sub> F·HF               | 0.207 | 0.335 | 0.027 |        | 0.192 | 0.046 | 0.175  |
| % forming or breaking                            | 79    | 9     | 30    |        | 39    | 49    | 50     |

presented here for the first time. Therefore, a thorough analysis of the results seems appropriate in order to understand the mechanism involved. A first approach to the problem may be to look at the geometries of the transition states depicted in Figure 2, whose most relevant parameters are given in Table I. From these data it may be seen that a chain of hydrogen fluorides has been established between both carbon atoms with which one end hydrogen and one end fluorine atom will be bonded. Breakage of the HF bonds is suggested by comparison of the values of the H1F1 and H2F2 bond distances in the transition state with those in the reactant, while the incipient formation of a new HF molecule starting from the central H and F atoms is also apparent from the shortening of the F1H2 distance. From a purely geometric point of view, it seems as if the H1F1 and F1H2 bonds were weaker than the H2F2 one, that is, more broken and less formed, respectively. However, we will see in the following paragraph how a more thorough analysis of the electronic structure of the transition states supports a slightly different conception.

Table IV contains the Mulliken population for the bonds involved in the reaction. The last row in this table shows the evolution of the bonds according to the ratio

$$r = 100 \frac{\text{MP}(\text{TS}) - \text{MP}(\text{R})}{\text{MP}(\text{P}) - \text{MP}(\text{R})}$$

where MP stands for the Mulliken population of the bond in the transition state (TS), reactants (R), and products (P), respectively. Also included in the table are the bond populations and the corresponding ratios for the bimolecular addition since they have not been presented in the literature yet.

The analysis of the Mulliken bond populations in the case of the bimolecular addition is straightforward. In fact, we see that in the first place the two bonds being broken, C1C2 and H1F1, are more advanced in the process than the pair being formed—C1H1 and F1C2. It is also clear that the F1C2 bond is more fully formed than the C1H1 one, suggesting that in the transition state the driving force is more of a nucleophilic character than electrophilic. This is confirmed by the electron transfer from ethylene to HF, which decreases from 0.029 in the reactant to 0.014 in the transition state.

Some subtle details are shown in the data corresponding to the termolecular addition. First, we notice a kind of propagation of bond-breaking and forming activity from the percentage of F2C2 formation (50%) to the unexpectedly low percentage of C1H1 formation (9%). These extreme values show again the larger interaction between the end fluorine and the carbon atoms than between the end hydrogen and the other carbon. Moreover, we can compare the percentage of rupture of both HF bonds in the termolecular transition state with that of the bimolecular one and see that the H2F2 bond is broken almost as much as the HF in the four-centered transition state of the bimolecular addition. The lower percentage of breakage of the H1F1 bond in the six-centered transition state combined with the low figure of 9% formation of C1H1 bond confirms our belief that the leading interaction in the transition state is the nucleophilic one between F2 and C2 and not the electrophilic one between H1 and C1. Finally, as we said before, from electronic structure analysis we see that the H2F2 bond is broken more than F1H1, which contrasts with the less accurate indication of bond distances. In fact, an analysis of Mulliken charges on the fragments shows that in the transition state a kind of ionic pair of the type FH<sub>2</sub><sup>+</sup>·F<sup>-</sup> is halfway formed,

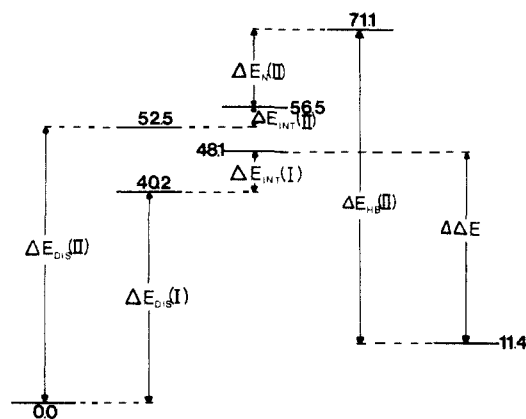


Figure 4. Formal decomposition of the relative energies of the transition states with respect to ethylene and two HF molecules infinitely apart.

since the electron transfer from FH<sub>2</sub> to F is 0.5, and the main interaction between FH<sub>2</sub><sup>+</sup> and C<sub>2</sub>H<sub>4</sub> is through F<sup>-</sup> and not through the end hydrogen of the chain.

**Energetic Analysis.** The decrease in the potential energy barrier provided by the mechanism analyzed above suggests that the second HF molecule is acting as a bifunctional catalyst strongly stabilizing the transition state and only slightly the initial reactant complex. This behavior is analogous to that of H<sub>2</sub>O, as demonstrated by us in tautomeric reactions<sup>12c,d</sup> and by others in addition of water to formaldehyde,<sup>11a</sup> and we can use a formal energy decomposition, much in the spirit of Maggiora's work,<sup>11a</sup> to understand the lowering of the barrier.

In Figure 4 we present a diagram of potential energy barriers referring to one ethylene and two isolated HF molecules following the energy decomposition mentioned above. In it, (I) refers to the bimolecular and (II) to the trimolecular addition. Furthermore, ΔE<sub>DIS</sub> represents the distortion energies of the fragments and ΔE<sub>INT</sub> corresponds to the interaction energy between C<sub>2</sub>H<sub>4</sub> and the first (H1F1) molecule. For the termolecular reaction, ΔE<sub>HB</sub> is the interaction energy arising from the hydrogen bond (F1H2) interaction, while ΔE<sub>N</sub> is the interaction energy between the second HF molecule and ethylene.

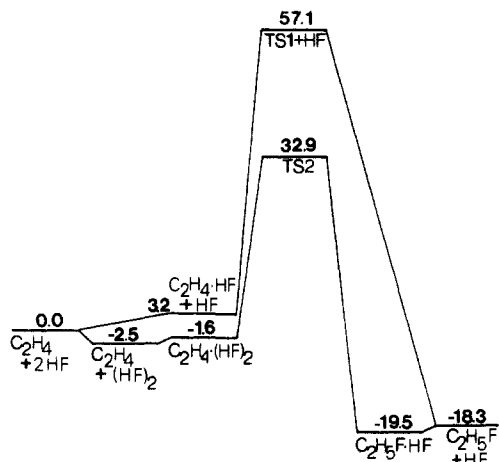
The barriers in our work and that of Kato and Morokuma<sup>10b</sup> with the 4-31G basis set for the bimolecular reaction are appreciably similar (52.3 and 48.1 kcal/mol), but the latter found a negative ΔE<sub>INT</sub>, most probably due to the greater distortion energy found for the HF fragment. With respect to the termolecular addition, ΔE<sub>DIS</sub>, ΔE<sub>INT</sub>, and ΔE<sub>N</sub> are repulsive, the distortion energy being the dominant term. The only negative contribution to the barrier comes from the ΔE<sub>HB</sub> term, which is more than capable of compensating for the increased deformation and interaction energies as compared to the bimolecular reaction, since the barrier diminishes from 48.1 to 11.4 kcal/mol. In this way, the catalytic action of the second HF molecule is due to the strong stabilization provided by the formation of the resulting HF (F1H2) molecule. Thus, the second HF molecule acts as a bifunctional catalyst, since it simultaneously accepts and releases a proton.

**Thermodynamical Analysis.** It is clear that in calculations involving such ordered structures as the ones we have here, energetic considerations are somewhat doubtful since entropic contributions may be almost as important as enthalpic ones.

**Table V.** Relative Gibbs Free Energies and Its Components for the Different Species Involved in the Reaction<sup>a</sup>

|                        | $\Delta E^b$ | $\Delta E_t^{b,d}$ | $\Delta H^b$ | $\Delta S^c$ | $-T\Delta S^b$ | $\Delta G^b$ |
|------------------------|--------------|--------------------|--------------|--------------|----------------|--------------|
| $C_2H_4 + HF + HF$     | 0.0          | 0.0                | 0.0          | 0.0          | 0.0            | 0.0          |
| $C_2H_4 \cdot HF + HF$ | -4.6         | 1.9                | -2.7         | -19.85       | 5.9            | 3.2          |
| $C_2H_4 + (HF)_2$      | -11.4        | 2.2                | -9.2         | -22.54       | 6.7            | -2.5         |
| $C_2H_4 \cdot (HF)_2$  | -22.6        | 5.0                | -17.7        | -53.87       | 16.1           | -1.6         |
| TS1 + HF               | 48.1         | -0.5               | 47.7         | -31.60       | 9.4            | 57.1         |
| TS2                    | 11.4         | 2.0                | 13.4         | -65.29       | 19.5           | 32.9         |
| $C_2H_3F \cdot HF$     | -44.7        | 7.3                | -37.4        | -60.06       | 17.9           | -19.5        |
| $C_2H_3F + HF$         | -30.0        | 4.6                | -25.4        | -23.75       | 7.1            | -18.3        |

<sup>a</sup>With respect to ethylene plus two hydrogen fluoride infinitely apart. <sup>b</sup>In kcal/mol. <sup>c</sup>In eu. <sup>d</sup>Thermal energies including zero-point energy and vibrational excited states and rotational contributions.

**Figure 5.** Relative 3-21G Gibbs free energies (kcal/mol) for bimolecular (via TS1) and trimolecular (via TS2) additions.

Therefore, a thermodynamical analysis is necessary to fully support the conclusions reached above on an energy basis.

In Table V we show the different contributions to  $\Delta G^\circ_{298}$ , and Figure 5 is a diagram of the relative values of that magnitude. The most noteworthy fact is the greater importance of the entropic term in the trimolecular reaction than in the bimolecular one. It is interesting to note that the HF dimer is stable even in a free energy analysis. The barriers to transformation, which must now be measured starting from ethylene plus HF and ethylene plus HF dimer, are 57.1 and 35.4 kcal/mol, and the free energy decrease, 21.7 kcal/mol, is even more pronounced that the internal

energy one, 18.7 kcal/mol. This strengthens the analysis given in the preceding section and shows that in the gas phase and in nonpolar solvents the termolecular reaction is a chemically more favorable pathway than the bimolecular one for the addition of HF to ethylene.

### Conclusions

On the basis of the discussion presented above, we have obtained a clear picture of the reaction mechanism. Two different regions are present in the concerted pathway for the addition of  $(HF)_2$  to ethylene, just before and after the transition state, which can be distinguished by the processes taking place. The path from the hydrogen-bonded reactant to the transition state involves a semi-ion pair formation with the attack of fluorine on carbon being more advanced than the transfer of the proton to ethylene. This may be interestingly linked to the ionic mechanism in polar solvents, where effective formation of ion pairs would be involved. After the transition state is passed, this semi-ion pair situation goes back to a neutral one by the transfer of the hydrogen to the other carbon atom and the final products, where there is one HF molecule hydrogen bonded to  $CH_3CH_2F$ .

The catalytic intervention of the second hydrogen fluoride molecule in the termolecular reaction is supported not only by the increased stabilization of the transition state, but by an analysis of the energy components. The importance of the HF bond being formed is thus clearly seen and explains the catalytic activity referred to before.

The decrease in the potential energy barrier is confirmed also at the chemically significant level of  $\Delta G^\circ_{298}$ . Although the formation of the termolecular complexes is entropically unfavorable for both the reactant and the transition state due to the higher order compared with the bimolecular complexes, the relations among them remain almost unchanged. Indeed, the formation of the  $(HF)_2$  dimer is possible even at the free energy level, showing that the reaction requires a collision between only two species,  $(HF)_2$  and ethylene, and not three, which would have lowered its possibility of success.

As a general conclusion we can then say that the theoretical study, within the limitations of the model and methods employed, strongly supports the termolecular reaction as opposed to the bimolecular one, in line with part of the experimental suggestions. Theoretical studies with more complicated models are at present under investigation in our laboratory.

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