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Ab initio MP2 study of the reaction mechanisms of C_2 with halogens and hydrohalides

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The *ab initio* MP2 method was used to calculate the activation energy of vinylidene and its derivatives formation, and their decisive role in the detailed mechanism of C_2 ($X^1\Sigma_G^+$) reactions with halogen and hydrohalide molecules was shown.

The quantum chemical calculations were performed according to the perturbation theory, Møller–Plesset second order (MP2), taking into account zero-point energy. The GAUSSIAN-03 program was used with correlated Dunning bases (aug-cc-pVDZ) to calculate the interaction of C_2 ($X^1\Sigma_G^+$) with the molecules of HF, F_2, HCl and Cl_2. To calculate the interaction of C_2 with HBr and Br_2, we had to use the bases 6-311+G*, which take into account polarizing and diffusive components and their quality is on a par with the Dunning bases. Unfortunately, Dunning bases are not represented in the GAUSSIAN-03 program for systems with the Br atom. All calculations were performed with full geometry optimization.

Transition states of elementary reactions were calculated by synchronous transit method QST2 and QST3 and refined by the gradient computation and the computation of the normal vibration frequencies followed with revision of the transition state structure by Hessian matrix calculation. The last step was to set up a correspondence of the transition state to the initial compounds and to the products using the IRC method. The main results of the calculations are summarized in Tables 1 and 2.

The energy released during the transition from TS1 to vinylidene intermediate is sufficient for the 1,2-shift in its hydrogen atom or halogen (Table 1, entry 3). In this case, it turns into a final product (haloacetylene) with a large surplus of energy on the internal degrees of freedom. For example, this energy for HBr (124 kcal mol^{-1}, Table 1, entry 7) is more than sufficient to break bromoacetylene into the bromine atom and the C_2H radical.

The activation energy of 1,2-halogen shift is much larger than that of 1,2-hydrogen shift and it decreases from 33 to 5 kcal mol^{-1} on going from fluorine to bromine. Transitions from halogen-substituted vinylidene to haloacetylene are exothermic and their enthalpies are practically equal for all halogens (Table 1, entry 6). According to the calculated enthalpies of the overall reactions of hydrohalides HX with dicarbene C_2, it can be concluded that a large amount of heat is released during these reactions, which increases on going from HF to HBr (Table 1, entry 7). Similar results were obtained for reactions of molecular halogens with dicarbene (Table 2).

Data in Tables 1 and 2 were obtained as a result of calculations, in which the centers of gravity of the molecules were closed, without specifying their orientation in space. The total energy of the system initially goes through a maximum, which corresponds to the transition state TS1. Among the hydrohalides, the activation energy decreases rapidly symbatically with a

Table 1 Energy characteristics (kcal mol^{-1}) for the interaction of hydrohalides HX with dicarbene C_2 (data based on zero point energy).

Entry	Parameter	HF	HCl	HBr
1	The activation energy of the first stage of the reaction of free molecules HX and C_2	29.87	7.22	2.45
2	The bond energy of HX (experiment)[1]	135.3	102.2	87.8
3	The enthalpy of formation of vinylidene intermediates from molecules HX and C_2	–48.63	–62.44	–73.67
4	The activation energy of conversion of intermediates to the final product HC≡CX with migrating H atom	0.56	0.44	2.28
5	The activation energy of conversion of intermediates to the final product HC≡CX with migrating X atom	33.10	11.35	5.00
6	The enthalpy of transformation of the intermediate to the final product HC≡CX[a]	–49.95	–51.71	–49.89
7	The enthalpy of the overall reaction of molecules HX and C_2	–98.58	–114.14	–123.56
8	The enthalpy of the reaction $HC\equiv CX \rightarrow {}^{\bullet}C\equiv CX + H^{\bullet}$	142.19	135.35	132.97
9	The enthalpy of the reaction $HC\equiv CX \rightarrow HC\equiv C^{\bullet} + X^{\bullet}$	140.75	119.54	115.59

[a] Involves the formation of vibrationally excited molecules of haloacetylenes.

Table 2 Energy characteristics (kcal mol^{-1}) for the interaction of halogens X_2 with dicarbene C_2 (data based on zero point energy).

Entry	Parameter	F_2	Cl_2	Br_2
1	The activation energy of the first stage of the reaction of free molecules X_2 and C_2	25.54	11.30	9.29
2	The bond energy of X_2 (experiment)[1]	37.0	57.2	45.4
3	The enthalpy of formation of vinylidene intermediate from X_2 and C_2 molecules	–153.24	–93.19	–88.04
4	The activation energy of transformation of the intermediate to the final product XC≡CX	34.03	6.97	0.31
5	The enthalpy of transformation of the intermediate to the final product XC≡CX[a]	–32.98	–49.20	–49.51
6	The enthalpy of the overall reaction between X_2 and C_2	–186.22	–142.39	–137.55
7	The enthalpy of the reaction $XC\equiv CX \rightarrow {}^{\bullet}C\equiv CX + X^{\bullet}$	136.86	114.33	105.47

[a] Includes the formation of vibrationally excited molecules of dihaloacetylenes.

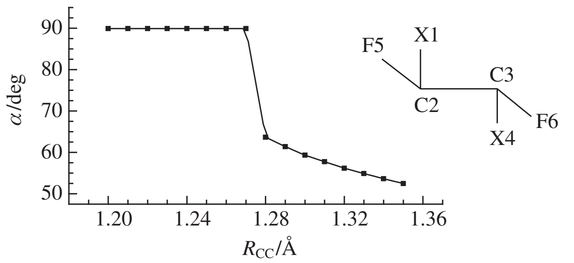


Figure 1 Dependence of the angle $\alpha = \alpha$(F5–C2–X1) = α(F6–C3–X4) on the R_{CC} distance in the difluoroacetylene molecule. Insert: geometric structure of difluoroacetylene with dummy atoms X1 and X4.

decrease in the experimental values of bond energies of HF, HCl and HBr.

We have previously shown[2] that, as a result of the Renner–Teller effect, the acetylene molecule changes its geometry from linear to transoid when it reaches a certain threshold energy and, correspondingly, the C≡C distance. This pattern holds for all dihaloacetylenes XC≡CX*, as illustrated in Figure 1 for difluoroacetylene.

Figure 1 shows that the structure of the difluoroacetylene molecule at the distances C≡C < 1.27 Å does not change and the angle α is 90°, which corresponds to the linear geometry of the molecule. At the distance C≡C ≥ 1.27 Å, the angle α abruptly changes as a result of the Renner–Teller effect. For haloacetylene molecules, this pattern is not observed. Note that acetylene and dihaloacetylene belong to the same symmetry group, while haloacetylenes belong to the lower symmetry group.

For the first time, it is established that the spatial orientation of molecules that react with molecular carbon precedes the formation of vinylidenecarbene and its derivatives. All investigated reactions involving dicarbene C_2 go through this intermediary stage rather than a one-stage reaction mechanism.[3] An example of such orientation during the interaction of C_2 and HF is shown in Figure 2. HF joins C_2 by the hydrogen atom so that, in the transition state TS1, the halogen atom is significantly farther from the carbene center C_2 than a hydrogen atom. This structure of TS1 is typical of all hydrohalides.

To quantify the orientation of molecules interacting with dicarbene C_2, we used the following logic. Let the molecule HX with the interatomic distance a approach the C_2 carbene center so that the distances from the H and X atoms, l_1 and l_2, become equal. Then, there is an isosceles triangle with base a and sides l_1 and l_2. If this is not true and l_1 is not equal l_2, the molecule HX rotates by a certain angle and one needs to select a measure that characterizes this orientation. We draw the median m in the triangle, shown in Figure 3, which forms the angle $\alpha = 90°$ with the base a when $l_1 = l_2$.

Table 3 demonstrates the results of the calculation of the geometry of interaction of C_2 with HX and X_2. Based on these data, one can make a qualitative conclusion that the larger dipole moment (μ) of HX molecules, the greater the deviation of angle α from 90°. Thus, for the first time, it is demonstrated that the spatial orientation of molecules with permanent dipole moment precedes the formation of TS1 during the interaction with molecular carbon. A deviation of angle α from 90° for X_2 molecules without permanent dipole moment is apparently accidental. Indeed, the obvious regularity of the angle α changes at the different values of polarizability β_{ZZZ}, which defines the possibility of appearance of the induced dipole moment in these X_2 molecules.

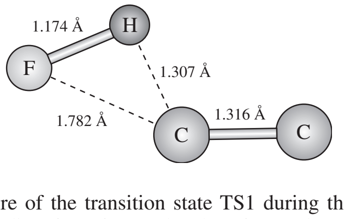


Figure 2 Structure of the transition state TS1 during the formation of a vinylidene intermediate from free molecules of C_2 and HF.

Table 3 Calculation of the geometry of interaction of C_2 with HX and X_2.

Molecule	a/Å	l_1/Å	l_2/Å	μ/D	cosα	α/deg	β_{ZZZ}/ Q M^2 V$^{-1\,a}$
HF	1.174	1.307	1.782	1.9	0.43	65	6.28
HCl	1.352	1.739	1.813	1.1	0.06	87	17.68
HBr	1.497	1.804	1.928	0.8	0.09	85	18.26
F_2	1.443	2.041	2.340	0	0.23	77	10.97
Cl_2	2.119	2.574	3.039	0	0.24	76	41.17
Br_2	2.564	2.080	2.252	0	0.09	85	51.67

[a] β_{ZZZ} is the diagonal element of the tensor of molecular polarizability.

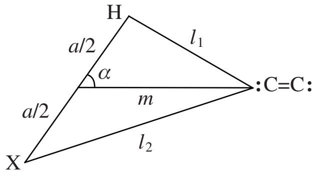


Figure 3 The orientation of HX and C_2 during the interaction.

Figures 4 and 5 show that the formation of vinylidene intermediates is an indispensable stage of the reactions involving molecular carbon C_2.

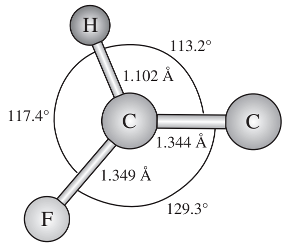
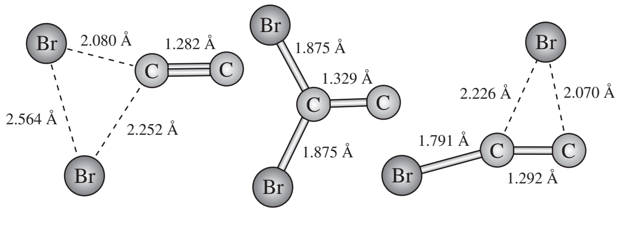


Figure 4 Vinylidene intermediate in the reaction of C_2 with HF.



TS1 Intermediate TS2

Figure 5 Transition states (TS1, TS2) and the intermediate of the reaction $Br_2 + C_2$.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2011.11.003.

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