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Modeling of the Mechanism of One-Electron Transfer from the Perylene Molecule to the Oxygen Molecule $^3O_2$ in the HF Medium

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Abstract—The thermodynamic parameters of the formation of the perylene radical cation in anhydrous hydrogen fluoride containing dissolved dioxygen were calculated by the ab initio method MP2. The protonated product of HF autoprotolysis was modeled as the $H(FH)_3^+$ cluster. The $^3O_2$ molecule was found to bind to the linear $H(FH)_3^+$ cluster via a hydrogen bond. As the charge and multiplicity of the system change upon the capture of an electron, the oxygen–hydrogen fluoride cluster complex undergoes rearrangement to yield the hydroperoxyl radical OOH incorporated in a cycle formed by HF molecules. The free energy of electron transfer from the perylene molecule to the $^3O_2$ molecule in the HF medium is about –38 kcal/mol.

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Aromatic hydrocarbons oxidize in solutions of strong Brønsted acids to yield hydrocarbon radical cations [1]. This method of generating aromatic radical cations is widely used in EPR studies of their electronic structure and properties. Nevertheless, there are some obscure issues in the mechanism of this one-electron transfer. One cause of this uncertainty is that it is usually impossible to identify the reduction products. Some structural diversity should apparently be expected of these products because, in some media, such as anhydrous hydrogen fluoride, one-electron transfer occurs only in the presence of dissolved dioxygen [2–5]. The formation of perylene radical cations in HF upon admission of dioxygen was observed by EPR and UV spectroscopy, and it was found that the radical cation concentration increases as the oxygen pressure is raised [4, 5]. In view of this, it is of interest to construct a simple model for the processes taking place in perylene oxidation with dioxygen in the HF medium. Because of the high laboriousness of the calculation of the joint molecular system in the construction of the model, we will make two assumptions. Firstly, we will consider the perylene ionization step separate from electron capture by the complex between oxygen and a protonated hydrogen fluoride cluster. Secondly, we will use the protonated product of HF autoprotolysis as the proton donor model. We think that these assumptions cannot lead to an unreliable qualitative conclusion as to the thermodynamic possibility of the one-electron transfer process. Using this model, we will calculate, by the MP2 ab initio method, the thermodynamic parameters of the formation of the perylene radical cation in the anhydrous hydrogen fluoride medium containing dissolved dioxygen.

COMPUTATIONAL PROCEDURE

Quantum chemical calculations were performed using the GAUSSIAN 03 program [6] by the unrestricted Hartree–Fock method [7–9], DFT method with the B3LYP functional [10–12], and MP2 [13–19] and MP4(SDQ) methods [20–22] with a number of Pople basis sets.

In order to find the optimum method and basis set, we carried out a series of calculations for the energy of excitation of the singlet state of molecules whose ground state is triplet (O_2 and HO_2^+) and for the ionization potentials of 1,3-butadiene and benzene. The oxygen molecule and HO_2^+ cation were chosen as the test species for the reason that solvated oxygen molecules and the $HO_2^{\bullet}$ radical were to be examined in this study.

Singlet oxygen ($^1O_2$) and the $^1HO_2^+$ cation are the first excited states ($a^1\Delta_g$) of dioxygen and the HO_2^+ cation, with an excitation energy of 22.4 kcal/mol [23] and 3.4 kcal/mol [24], respectively. The electronic excitation energies and the enthalpies and free energies of excitation from the ground, triplet state to the first excited state, $a^1\Delta_g$, for the O_2 and HO_2^+ molecules,

Table 1. Electronic energies ΔE, enthalpies ΔH, and free energies ΔG ($T = 298$ K, $P = 1$ atm) for the excitation $X^3\Sigma_g^- \longrightarrow a^1\Delta_g$ of dioxygen and the HO_2^+ cation, calculated using different methods (all energies are in kcal/mol)

Level of theory	$^3O_2 \longrightarrow {}^1O_2$			$^3HO_2^+ \longrightarrow {}^1HO_2^+$		
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
UHF/6-31G	52.773	52.773	53.425	41.810	41.792	42.505
UHF/6-311G	52.987	52.987	53.639	42.056	42.044	42.746
UHF/6-311++G	53.271	53.271	53.926	42.305	42.292	42.997
UHF/6-311G**	53.233	53.234	53.888	35.530	35.521	36.222
UHF/6-311++G**	53.299	53.299	53.954	35.715	35.707	36.408
B3LYP/3-21G	39.439	39.439	40.086	21.456	21.432	22.133
B3LYP/6-31G	39.381	39.381	40.029	20.361	20.337	21.004
B3LYP/6-311G	39.103	39.104	39.752	20.233	20.212	20.872
B3LYP/6-311++G	38.803	38.803	39.451	20.203	20.181	20.845
B3LYP/6-311G**	39.000	39.000	39.650	15.424	15.408	16.085
B3LYP/6-311++G**	38.552	38.552	39.203	15.412	15.397	16.073
MP2/3-21G	24.487	24.569	25.027	1.026	1.003	1.612
MP2/3-21+G	22.432	22.570	22.918	1.401	1.375	1.979
MP2/6-21G	24.156	24.258	24.680	0.611	0.589	1.196
MP2/6-311G	25.405	25.509	25.930	3.706	3.690	4.286
MP2/6-311++G	25.031	25.121	25.568	3.705	3.690	4.289
MP2/6-311G**	30.792	30.796	31.417	3.488	3.473	4.130
MP2/6-311++G**	30.222	30.226	30.848	3.495	3.480	4.138
MP4/6-31G	31.579	31.587	32.205	8.666	8.663	9.256
MP4/4-31G	31.325	31.333	31.948	8.302	8.301	8.887
MP4/6-21G	29.420	29.425	30.047	5.261	5.250	5.850
MP4/3-21G	29.510	29.514	30.136	5.597	5.586	6.188
MP4/3-21+G	29.288	29.295	29.912	6.212	6.199	6.798

calculated for the fully optimized singlet and triplet structures, are listed in Table 1. According to these data, the most accurate estimates of the excitation energies are provided by the MP2 method with the 3-21+G and 6-21G basis sets. The second criterion in selecting a computational method was the photoionization energy of benzene and 1,3-butadiene. Vertical ionization energies were obtained by applying the SCF procedure to the fully optimized ground states of the molecules with a fixed charge of +1 and one unpaired electron. The atomic coordinates were frozen to conserve the Coulomb field and molecular orbital configurations. Relaxation was carried out by full optimization of the structures up to the corresponding stationary points, for which vibrations were calculated. The optimization procedure indicated the isomerization of the butadiene radical cation into the *cis* isomer, and it turned out that the *trans*-1,3-butadiene radical cation is a transition state executing imaginary vibrations corresponding to torsional rotation about the C–C bond.

The data presented in Table 2 were compared with the experimental ionization potentials measured by photoionization methods—213.31 kcal/mol for ben-

Table 2. Calculated vertical ionization energies (E_{PI}) and adiabatic thermodynamics of ionization (enthalpy ΔH_r and free energy ΔG_r, $T = 298$ K, $P = 1$ atm) for benzene and 1,3-butadiene (all energies are in kcal/mol)

Level of theory	1,3-Butadiene			Benzene		
	E_{PI}	ΔH_r	ΔG_r	E_{PI}	ΔH_r	ΔG_r
UHF/6-31G	175.451	171.471	170.922	183.505	176.219	196.833
UHF/4-31G	175.333	171.060	170.518	183.265	176.449	186.799
UHF/6-21G	178.400	173.914	173.373	186.592	179.315	189.756
UHF/3-21G	179.405	174.887	174.348	187.642	179.737	203.919
UHF/3-21+G	182.237	178.758	178.199	190.658	183.170	200.600
B3LYP/6-31G	199.907	199.379	198.665	209.476	203.482	212.406
B3LYP/4-31G	199.547	198.851	198.155	209.090	203.000	211.796
B3LYP/6-21G	201.278	200.332	199.618	211.154	204.849	213.894
B3LYP/3-21G	202.368	201.345	200.627	212.298	205.950	214.907
B3LYP/3-21+G	206.874	206.634	205.879	216.685	209.272	229.218
MP2/6-31G	171.282	200.111	199.584	180.535	203.698	203.302
MP2/4-31G	171.164	199.257	198.737	180.399	202.786	202.350
MP2/6-21G	174.560	200.177	199.655	183.799	204.262	203.782
MP2/3-21G	175.585	201.121	200.603	184.875	205.268	204.782
MP2/3-21+G	178.665	206.976	206.374	187.991	211.311	210.911

zene and 209.39 kcal/mol for 1,3-butadiene [25]. This comparison demonstrated that the MP2 and B3LYP methods with the 3-21+G basis set ensure the closest fits to the experimental data.

All optimized geometries were checked for the presence of negative vibration frequencies and were found to be local minima on the potential energy surface. The enthalpies and free energies were calculated for 298 K and 1 atm. The anhydrous hydrogen fluoride medium was modeled as a linear protonated cluster consisting of three hydrogen fluoride molecules, $H(FH)_3^+$. Within the model used in our analysis, the electron donor and electron acceptor were considered separately.

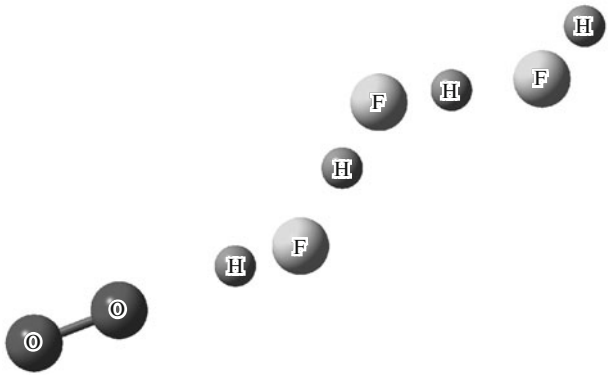


Fig. 1. Optimized geometry of the $^3O_2$ molecule solvated by an $H(FH)_3^+$ cluster. The total charge of the system is +1, and the multiplicity is 3.

RESULTS AND DISCUSSION

The calculated data make it possible to evaluate the acid solvation of triplet oxygen with anhydrous HF by optimizing the $^3O_2$ molecule combined with the protonated cationic cluster $H(FH)_3^+$. It was demonstrated earlier [26] that this $H(FH)_3^+$ cluster is among the likely products of the autoprotolysis of anhydrous HF. In the optimized structure, the oxygen molecule is bound to the hydrogen fluoride cluster by a hydrogen bond 1.80 Å in length (Fig. 1),

$$H(FH)_3^+ + {}^3O_2 = [{}^3O_2...H(FH)_3]^{+0}. \quad (I)$$

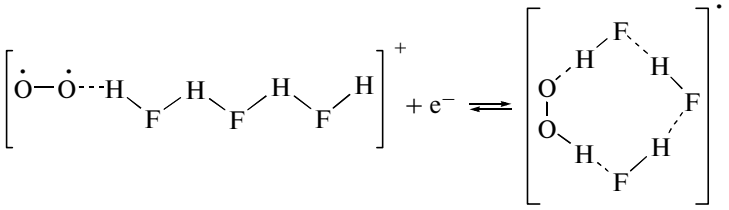
Thermodynamic data for this solvation processes are listed in Table 3. Clearly, the free energy and enthalpy of solvation are negative.

Electron capture was modeled as a change in the charge and multiplicity of the system; accordingly,

Table 3. Enthalpies (ΔH) and free energies (ΔG) at $T = 298$ K and $P = 1$ atm for the processes occurring in electron transfer between perylene and oxygen

Reaction	ΔH, kcal/mol	ΔG, kcal/mol
$H(FH)_3^+ + {}^3O_2 = [{}^3O_2\cdots H(FH)_3]^+$ (I)	1.1	8.3
$[{}^3O_2\cdots H(FH)_3]^+ + e^- = [O_2H\cdots(HF)_3]^{\bullet}$ (II)	−197.4	−193.9
$C_{20}H_{12} = C_{20}H_{12}^+ + e^-$ (III)	155.2	155.6

thereafter we considered the electroneutral doublet corresponding to the complex $[O_2...H(FH)_3]$. The optimization of this complex gave a cyclic structure with a well-defined covalent O–H bond 1.02 Å in length (Fig. 2). The formation of this structure can be represented as



(II)

The thermodynamics of process (II) (Table 3) was calculated by the MP2 method as the difference between the energies of the charged and electroneutral states, and it was found that the change in enthalpy is $\Delta H_0 = -197.4$ kcal/mol and the change in free energy is $\Delta G_0 = -193.49$ kcal/mol.

The above results can be interpreted as follows: electron transfer to the oxygen molecule in the Brønsted acid medium is accompanied by proton migration from the solvent to oxygen with the formation of the hydroperoxyl radical $HOO^{\bullet}$. An electron donor is necessary for this electron transfer to take place. Taking into account earlier experimental data [4, 5], we considered perylene as the electron donor.

We failed to attain a satisfactory degree optimization of the electroneutral and radical cation forms of perylene by the MP2/3-21+G method, so the thermodynamic functions of the ionization reaction were estimated by the DFT method with the B3LYP/3-21+G functional. Comparative calculations of the same quantities for benzene and 1,3-butadiene by the MP2/3-21 and DFT/3-21+G methods gave similar results (Table 2). The B3LYP/3-21+G method predicts the enthalpy of ionization of perylene (reaction (III)) to be $\Delta H_0 = 155.2$ kcal/mol and the free energy of ionization of perylene to be $\Delta G_0 = 155.6$ kcal/mol (Table 3). Note that the experimental vertical ionization potential of perylene is 162.8 kcal/mol [5] and the adiabatic ionization potential cannot exceed this value; therefore, our theoretical estimate can be used in subsequent calculations. By combining reaction (II) with the perylene ionization reaction

$$C_{20}H_{12} = C_{20}H_{12}^+ + e^-, \qquad \text{(III)}$$

we obtain

$$C_{20}H_{12} + [{}^3O_2\ldots H(FH)_3]^+ = C_{20}H_{12}^{\bullet+} + [O_2H\ldots(HF)_3]^{\bullet}. \qquad \text{(IV)}$$

For the overall reaction (Table 3), $\Delta H_0 = -42.2$ kcal/mol and $\Delta G_0 = -38.3$ kcal/mol. These data suggest that the equilibrium in reaction (IV) is fully shifted toward the products. The perylene radical cation concentration will depend strongly on the concentration of dissolved oxygen. The free energy of solution of oxygen in hydrogen fluoride via reaction (I) is +8.3 kcal/mol

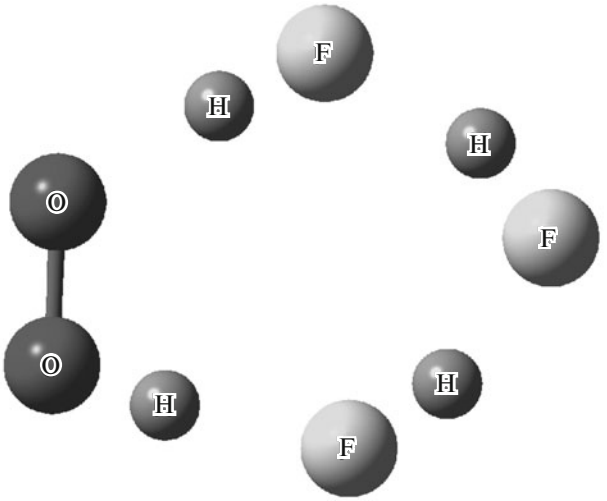


Fig. 2. Optimized geometry of the electroneutral cluster $[O_2...H(FH)_3]^{\bullet}$ with a multiplicity of 2.

(Table 3), and that is why a high oxygen pressure is necessary for dissolution.

The thermodynamic estimates obtained here demonstrate that, as an electron is transferred to the oxygen molecule in the Brønsted acid medium, the oxygen molecule can readily be protonated into the hydroperoxyl radical $HOO^{\bullet}$. It remains unclear whether it is possible to observe, e.g., by EPR spectroscopy, the hydroperoxyl radical in this system. Serious difficulties should be expected here a priori because this radical is likely very reactive and its concentration may, therefore, be low. Another complication in the spectroscopic observation of this radical may come from rapid hydrogen exchange, which should be expected to take place in the HF medium. Nevertheless, it is quite important to carry out such experiments.

Thus, it was demonstrated using perylene as an example that the electron transfer reaction between a hydrocarbon with a low ionization potential and oxygen in anhydrous hydrogen fluoride is thermodynamically possible. The products of this reaction are a hydrocarbon radical cation and the hydroperoxyl radical $HOO^{\bullet}$.

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