O-O BOND DISSOCIATION ENTHALPY IN PERFLUOROMETHYL FLUOROCARBONYL PEROXIDE, $CF_3OOC(O)F$. A DENSITY FUNCTIONAL QUANTUM CHEMICAL ANALYSIS

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Abstract

Density functional at the B3LYP levels of theory using the Pople's 6-311+G(3df) basis sets and the Dunning's aug-cc-pVTZ correlation consistent basis sets have been employed to determine the enthalpy of formation ($\Delta H_f^0(298)$) of $CF_3OOC(O)F$ at 298 K, using the isodesmic reaction $CF_3OOCF_3 + FC(O)OOC(O)F \rightarrow 2\ CF_3OOC(O)F$. Thus, the B3LYP/6-311+G(3df) and B3LYP/aug-cc-pVTZ methods yield $\Delta H_f^0(298)$ values of –273.3 and –273.2 kcal mol⁻¹, respectively. From the reported $\Delta H_f^0(298)$ for $CF_3O\cdot$ and $FC(O)O\cdot$ radicals, bond energy dissociation (D_{O-O}) values of 38.3 and 38.2 kcal mol⁻¹ are deduced for $CF_3OOC(O)F$, which are in agreement with the reported value for related peroxides. Also, calculations for the enthalpy change in the peroxide bond excision reaction were performed at the B3LYP and B3PW91 using several basis sets. The corresponding D_{O-O} values obtained using these enthalpy changes are too low independently of both basis sets and method of calculation used for the calculation.

Resumen

El método B3LYP de los funcionales de la densidad con la base de Pople 6-311+G(3df) y con la base de correlación consistente de Dunning aug-cc-pVTZ, fue empleado para determinar la entalpía de formación a 298 K ($\Delta H_f^0(298)$) del $CF_3OOC(O)F$, utilizando la reacción isodésmica $CF_3OOCF_3 + FC(O)OOC(O)F \rightarrow 2\ CF_3OOC(O)F$. Es así que se obtienen valores de $\Delta H_f^0(298)$ de –273,3 y –273,2 kcal mol⁻¹ para los métodos B3LYP/6-311+G(3df) y B3LYP/aug-cc-pVTZ respectivamente. A partir de los valores de $\Delta H_f^0(298)$ reportados para los radicales $CF_3O\cdot$ y $FC(O)O\cdot$, se obtienen valores de energía de disociación de enlace D_{O-O} igual a 38,3 y 38,2 kcal mol⁻¹, que acuerdan con los valores reportados para peróxidos similares. El cambio de entalpía en la reacción de escisión del enlace peróxido fue calculado a los niveles B3LYP y B3PW91 utilizando varias funciones bases. Los

correspondientes valores de D_{O-O} obtenidos utilizando estos cambios de entalpía son demasiado bajos, con independencia tanto del conjunto de funciones base, como del método utilizados en el cálculo.

Introduction

CF$_3$OOC(O)F was synthesized for the first time in 1967 by Cauble and Cady by photochemical reaction of FC(O)OOC(O)F with fluorine [1] with a yield of about 5% (based upon the amount of peroxide consumed). In a separated [2] article these authors reported some physical and spectroscopic characteristic of CF$_3$OOC(O)F. At the same time, Talbot [3] reported the synthesis of CF$_3$OOC(O)F by photochemical reaction of a mixture containing FC(O)OOC(O)F and CF$_2$N$_2$ in a yield close to 18%. Later, in 1970 Anderson and Fox [4] and DesMarteau [5] synthesized CF$_3$OOC(O)F using the reaction between CF$_2$(OF)$_2$ and C(O)F$_2$ catalyzed by CsF. At the same time, Blesa and Aymonino [6] reported in this journal an improved method for the preparation of CF$_3$OOC(O)F by photolysis of gaseous mixtures of perfluorocyclobutanone, fluorine and oxygen, upon UV irradiation, with the yield being ca. 35%.

Species containing only carbon, oxygen and fluorine atoms have renewed its attraction and many of them are being investigated or even re-investigated since they have shown to play an important role in atmospheric chemistry [7].

Recently [8], we have reported a structural and conformational study of CF$_3$OOC(O)F structural and conformational features, which included the use of gas electron diffraction (GED) technique, vibrational spectroscopy (IR of both gas phase and isolated in Ar-matrix, and liquid Raman) and quantum chemical calculations. The dihedral angle around the peroxide bond in CF$_3$OOC(O)F (δ(COOC) = 111(5)°) with one sp^2- and one sp^3- hybridized carbon substituent is intermediate between those found in FC(O)OOC(O)F (83.5(14)°) [9] with two sp^2- hybridized carbon substituents and in CF$_3$OOCF$_3$ (123(4)°) [10] with two sp^3- hybridized carbon substituents. Furthermore, syn orientation of the C=O double bond relative to the O-O single bond is preferred in CF$_3$OOC(O)F. The MP2 $\Delta G°$ (G$^0_{anti}$ − G$^0_{syn}$) value ($\Delta G°$ = 2.03 kcal/mol) is in excellent agreement with the experimental $\Delta G°$ value of 2.09(22) kcal/mol as derived from the matrix IR experiment. The O-O bond length in CF$_3$OOC(O)F (1.422(15)Å) is within experimental uncertainties equal to those in CF$_3$OOCF$_3$ (1.419(20) Å) and FC(O)OOC(O)F (1.419(9) Å).

Furthermore, when Ar/CF$_3$OOC(O)F mixtures are passed thought the spray-on nozzle held at temperatures higher than 300 °C, new bands appear in the IR spectra superposed to those belonging to the parent CF$_3$OOC(O)F peroxide. These bands belong to CF$_3$O· and FC(O)O· radicals [11]. No characteristic bands of CF$_3$OO· nor FC(O)OO· peroxi radicals [12] were found in the IR spectra. These features agree with the previous finding of Argüello and Willner [11]. Quantum chemical calculations performed at the B3LYP/6-311G* level of the theory for bond energy dissociations predict the peroxide bond weaker than the C-O bonds. Thus, the computed values for D_{O-O}, $D_{C(sp2)-O}$ and $D_{C(sp3)-O}$ are 21.3, 70.2 and 75.5 kcal mol^{-1}, respectively. However, this computed D_{O-O} bond energy dissociation is too low, as compared with reported values for related peroxides [8].

In the present contribution, we report a theoretical study concerning thermodynamic properties of CF$_3$OOC(O)F, specially those related with the D_{O-O} bond energy dissociation.

Quantum Chemical Calculations

Electronic structure calculations using Becke's three-parameters functional [13] with the correlation functional of Lee, Yang and Parr (B3LYP) hybrid functional were performed with the GAUSSIAN 98 program [14]. The Pople's triple-zeta split valence 6-311+G(3df) basis sets which include diffuse and polarization function [15] and the Dunning's triple-zeta diffuse function augmented correlation consistent basis sets, denoted as aug-cc-pVTZ, [16] were used to calculate fully optimized equilibrium geometries and harmonic vibrational frequencies of the molecules under investigation. The syn conformer was taken as the more stable conformation for $CF_3OOC(O)F$ [8] (syn with respect to C=O and O-O bonds) and C_2 molecular symmetry with syn conformation was adopted in $FC(O)OOC(O)F$ [17] (syn with respect to C=O and O-O bonds). A good agreement was found between calculated and experimental geometrical parameters and fundamental vibrational frequencies [18], [19].

The enthalpy of formation of the $CF_3OOC(O)F$ molecule was estimated using the following isodesmic reaction:

$$CF_3OOCF_3 + FC(O)OOC(O)F \rightarrow 2\ CF_3OOC(O)F$$

In a isodesmic reaction, reactants and products contain the same number of the same type of bonds and errors due to inherent limitations in the basis set and electron correlation energy nearly cancel [20]. Total energies are corrected by zero-point vibration energies (ZPVE) (without any scaling factor). Thermal corrections, 0 K to 298.15 K, are calculated to estimate the reaction enthalpy at 298.15 K ($\Delta H_r^0(298)$). $\Delta H_f^0(298)$ values for CF_3OOCF_3 and $FC(O)OOC(O)F$ were taken from the literature [21], [22].

A second model was employed for the calculation of bond dissociation enthalpies taking into account the difference between the corrected enthalpies at 298 K for reactants and products. Thus, the bond dissociation enthalpy for the $CF_3OOC(O)F \rightarrow CF_3O\cdot + FC(O)O\cdot$ dissociation, is then determined by: $D_{O-O} = (H_{298}^0(CF_3O\cdot) + H_{298}^0(FC(O)O\cdot)-H_{298}^0(CF_3OOC(O)F)$. B3LYP and B3PW91 hybrid functionals with Pople's type basis sets up to 6-311+G(3df) and the Dunning's cc-pVDZ and aug-cc-pVTZ basis sets were applied. These results are listed in Table 1.

Table 1. *Calculated D_{O-O} bond energy dissociations, in kcal mol^{-1}, for $CF_3OOC(O)F$ as the enthalpy reaction change at 298 K for the process $CF_3OOC(O)F \rightarrow CF_3O\cdot + FC(O)O\cdot$.[a]*

	6-31G*	6-31+G*[b]	6-311+G*	6-311+G(3df)	cc-pVDZ	aug-cc-pVTZ
B3LYP	28.8	-	24.0	26.8	28.1	26.8
B3PW91	29.2	26.9	25.0	28.2	28.1	28.1

[a] *$CF_3O\cdot$ was optimized assuming C_s geometry.* [b] *The convergence criteria are not reach for $CF_3OOC(O)F$ at the B3LYP/6-31+G* level of calculation.*

Results and Discussion

The enthalpy of formation of $CF_3OOC(O)F$ was evaluated using the calculated isodesmic reaction enthalpies $\Delta H_r^0(298)$ and the experimental enthalpy of formation of CF_3OOCF_3 of -343±3 kcal mol^{-1} [21] and the computed enthalpy of formation for $FC(O)OOC(O)F$ of -202.9 kcal mol^{-1} [22]. From the B3LYP/6-311+G(3df) and B3LYP/aug-cc-pVTZ levels of calculations, $\Delta H_f^0(298)$ values of –273.3 and –273.2 kcal mol^{-1} were calculated for $CF_3OOC(O)F$. According to the experimental uncertainties, an error level of ±4 kcal mol^{-1} is estimated for the above value [21].

The predicted $\Delta H_f^0(298)$ values, in conjunction with the $\Delta H_f^0(298)$ values of –149±2 kcal mol^{-1} for $CF_3O\cdot$ [23] and of -86.0 kcal mol^{-1} for $FC(O)O\cdot$ [24], lead to reaction enthalpies values of 38.3 and 38.2 kcal mol^{-1} for $CF_3OOC(O)F \rightarrow FC(O)O\cdot + CF_3O\cdot$ at the B3LYP/6-311+G(3df) and B3LYP/aug-cc-pVTZ, respectively. The mean D_{O-O} value for $CF_3OOC(O)F$ of 38.2 kcal mol^{-1} lies in between of the experimentally determined bond dissociation energy values for the symmetrically substituted peroxides, which are 47.5±0.5 kcal mol^{-1} for CF_3OOCF_3 [25], and 31±3 [26] and 29.5 kcal mol^{-1} for $FC(O)OOC(O)F$ [27]. In addition, the experimental D_{O-O} value for $CF_3OOC(O)OCF_3$ is 34 kcal mol^{-1} [27]. It is interesting to note that this molecule displays a similar D_{O-O} value as calculated in this work for $CF_3OOC(O)F$.

Thus, our previously calculated D_{O-O} value at the B3LYP/6-311G* level of calculation of 21.3 kcal mol^{-1} [8] seem to be low. It should be noted that this value was calculated by using the enthalpy change in the dissociation reaction $CF_3OOC(O)F \rightarrow CF_3O\cdot + FC(O)O\cdot$. In order to study both the role of the basis set and the calculation method in the computed D_{O-O} value, several basis sets at the B3LYP and B3PW91 methods were used (Table 1). D_{O-O} values depend strongly on the basis sets. With the two levels of approximation used in this work, both 6-311+G(3df) and aug-cc-pVTZ, (351 and 414 basis function for $CF_3OOC(O)F$, respectively) basis sets display better results than the previously reported [8] B3LYP/6-311G* method (162 basis function for $CF_3OOC(O)F$), but are still too low (ca. 10 kcal mol^{-1}) as compared with the value obtained by using an isodesmic reaction scheme and experimental data reported for related peroxides [25], [28]. Similar discrepancies were reported for the computed thermodynamic properties of $FC(O)OOC(O)F$. Strong dependencies on the basis set were calculated for the D_{O-O} value obtained as enthalpy differences ($FC(O)OOC(O)F \rightarrow 2\ FC(O)O\cdot$) by using the B3LYP level of approximation [22], [29]. Even at higher level of calculations (B3LYP/6-311+G(3df)//B3LYP/6-311+G*), the D_{O-O} value is around 14 kcal mol^{-1} lower that the experimental one. The use of a scheme of isodesmic reactions leads to a D_{O-O} which agrees fairly well with that determined experimentally. In the Reference [22], it was suggested that for the description of a non-isodesmic reaction the B3LYP method results inadequate probably due to deficiencies in the treatment of electron correlation effects. In the present study for $CF_3OOC(O)F$ a coincidence with the reported result was found. In addition it is shown that the B3PW91 hybrid method has similar limitations even by using larger basis sets. Therefore, the use of an isodesmic reaction scheme for a reliable description of these systems can be considered as necessary.

Acknowledgements

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