O-O BOND DISSOCIATION ENTHALPHY IN
PERFLUOROMETHYL FLUOROCARBONYL PEROXIDE,
CF$_3$OOC(O)F. A DENSITY FUNCTIONAL QUANTUM
CHEMICAL ANALYSIS

Erben$^1$, M. F.; Della Védova, C. O.$^{1,2}$

Departamento de Química. Facultad de Ciencias Exactas. Universidad Nacional de La
Plata, 47 esq. 115 (1900) La Plata, Argentina.
$^1$CEQUINOR Centro de Química Inorgánica (CONICET-UNLP).
$^2$LaSeSiC, Laboratorio de Servicios a la Industria y al Sistema Científico
(UNLP-CIC-CONICET) Camino Centenario, Gonnet, Argentina

FAX: +54 221 425 9485; email: carlosdv@quimica.unlp.edu.ar

Received March 16, 2004. In final form April 17, 2004
Dedicated to Prof. Pedro J. Aymonino on the occasion of his 75th birthday

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 ($\Delta H_f^{\text{a}}$(298)) of CF$_3$OOC(O)F at 298 K, using the isodesmic reaction
CF$_3$OOCF$_3$ + FC(O)OOC(O)F $\rightarrow$ 2 CF$_3$OOC(O)F. Thus, the B3LYP/6-311+G(3df) and
B3LYP/aug-cc-pVTZ methods yield $\Delta H_f^{\text{a}}$(298) values of $-273.3$ and $-273.2$ kcal mol$^{-1}$, respectively.
From the reported $\Delta H_f^{\text{a}}$(298) for CF$_3$O$^*$ and FC(O)O$^*$ radicals, bond energy dissociation ($D_{O-O}$)
values of 38.3 and 38.2 kcal mol$^{-1}$ are deduced for CF$_3$OOC(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
enthalpía de formación a 298 K ($\Delta H_f^{\text{a}}$(298)) del CF$_3$OOC(O)F, utilizando la reacción isodésmica
CF$_3$OOCF$_3$ + FC(O)OOC(O)F $\rightarrow$ 2 CF$_3$OOC(O)F. Es así como se obtienen valores de $\Delta H_f^{\text{a}}$(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 $\Delta H_f^{\text{a}}$(298) reportados para los radicales CF$_3$O$^*$ y
FC(O)O$^*$, 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

CF₃OOC(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 CF₃OOC(O)F. At the same time, Talbot [3] reported the synthesis of CF₃OOC(O)F by photochemical reaction of a mixture containing FC(O)OOC(O)F and CF₂N₂ in a yield close to 18%. Later, in 1970 Anderson and Fox [4] and DesMarreau [5] synthesized CF₃OOC(O)F using the reaction between CF₂(OF)₂ and C(O)F₂ catalyzed by CsF. At the same time, Blesa and Aymonino [6] reported in this journal an improved method for the preparation of CF₃OOC(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 CF₃OOC(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 CF₃OOC(O)F (δCOOC) = 111(5)°) with one sp²- and one sp³- hybridized carbon substituent is intermediate between those found in FC(O)OOC(O)F (83.5(14)°) [9] with two sp²- hybridized carbon substituents and in CF₃OOCF₃ (123(4)°) [10] with two sp³- hybridized carbon substituents. Furthermore, syn orientation of the C=O double bond relative to the O-O single bond is preferred in CF₃OOC(O)F. The MP2 ΔG° (G°₀⁻⁻⁻−G°₀⁺⁺⁺) value (ΔG° = 2.03 kcal/mol) is in excellent agreement with the experimental ΔG° value of 2.09(22) kcal/mol as derived from the matrix IR experiment. The O-O bond length in CF₃OOC(O)F (1.422(15)Å) is within experimental uncertainties equal to those in CF₃OOCF₃ (1.419(20) Å) and FC(O)OOC(O)F (1.419(9) Å).

Furthermore, when Ar/CF₃OOC(O)F mixtures are passed through a nozzle held at temperatures higher than 300 °C, new bands appear in the IR spectra superposed to those belonging to the parent CF₃OOC(O)F peroxide. These bands belong to CF₃O- and FC(O)O- radicals [11]. No characteristic bands of CF₃OO- 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 D̃O-O, D̃C(sp²)-O and D̃C(sp³)-O are 21.3, 70.2 and 75.5 kcal mol⁻¹, respectively. However, this computed D̃O-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 CF₃OOC(O)F, specially those related with the DO-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 CF₃OOC(O)F [8] (syn with respect to C=O and O-O bonds) and C₂ 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 CF₃OOC(O)F molecule was estimated using the following isodesmic reaction:

\[ \text{CF}_3\text{OOCF}_3 + \text{FC(O)OOC(O)F} \rightarrow 2 \text{CF}_3\text{OOC(O)F} \]

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 (\( \Delta H_r^0(298) \)). \( \Delta H_r^0(298) \) values for CF₃OOCF₃ 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 \( \text{CF}_3\text{OOC(O)F} \rightarrow \text{CF}_3\text{O}^- + \text{FC(O)O}^- \) dissociation, is then determined by: \( \delta D_{O-O} = (H_{298}^0(\text{CF}_3\text{O}^-) + H_{298}^0(\text{FC(O)O}^-) - H_{298}^0(\text{CF}_3\text{OOC(O)F}) \). 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$_3$OOC(O)F as the enthalpy reaction change at 298 K for the process CF$_3$OOC(O)F $\rightarrow$ CF$_3$O$^-$ + FC(O)O$^-$.$^a$

<table>
<thead>
<tr>
<th></th>
<th>6-31G*</th>
<th>6-31+G*</th>
<th>6-311+G*</th>
<th>6-311+G(3df)</th>
<th>cc-pVDZ</th>
<th>aug-cc-pVTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td>28.8</td>
<td>-</td>
<td>24.0</td>
<td>26.8</td>
<td>28.1</td>
<td>26.8</td>
</tr>
<tr>
<td>B3PW91</td>
<td>29.2</td>
<td>26.9</td>
<td>25.0</td>
<td>28.2</td>
<td>28.1</td>
<td>28.1</td>
</tr>
</tbody>
</table>

$^a$CF$_3$O$^-$ was optimized assuming $C_s$ geometry. $^b$The convergence criteria are not reach for CF$_3$OOC(O)F at the B3LYP/6-31+G* level of calculation.

Results and Discussion.

The enthalpy of formation of CF$_3$OOC(O)F was evaluated using the calculated isodesmic reaction enthalpies $\Delta H_f^0$ (298) and the experimental enthalpy of formation of CF$_3$OOCF$_3$ of $-343\pm3$ 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$_3$OOC(O)F. According to the experimental uncertainties, an error level of $\pm4$ kcal mol$^{-1}$ is estimated for the above value [21].

The predicted $\Delta H_f^0$(298) values, in conjunction with the $\Delta H_f^\circ$(298) values of $-149\pm2$ kcal mol$^{-1}$ for CF$_3$O$^-$ [23] and of $-86.0$ kcal mol$^{-1}$ for FC(O)O$^-$ [24], lead to reaction enthalpies values of 38.3 and 38.2 kcal mol$^{-1}$ for CF$_3$OOC(O)F $\rightarrow$ FC(O)O$^-$+CF$_3$O$^-$ at the B3LYP/6-311+G(3df) and B3LYP/aug-cc-pVTZ, respectively. The mean $D_{O-O}$ value for CF$_3$OOC(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$\pm0.5$ kcal mol$^{-1}$ for CF$_3$OOCF$_3$ [25], and 31$\pm3$ [26] and 29.5 kcal mol$^{-1}$ for FC(O)OOC(O)F [27]. In addition, the experimental $D_{O-O}$ value for CF$_3$OOC(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$_3$OOC(O)F.

Thus, our previously calculated DO-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 CF3OOC(O)F $\rightarrow$ CF3O$^-$ + FC(O)O$^-$. In order to study both the role of the basis set and the calculation method in the computed DO-O value, several basis sets at the B3LYP and B3PW91 methods were used (Table 1). DO-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 CF3OOC(O)F, respectively) basis sets display better results than the previously reported [8] B3LYP/6-311G* method (162 basis function for CF3OOC(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 DO-O value obtained as enthalpy differences (FC(O)OOC(O)F $\rightarrow$ 2
FC(O)O·) 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 DO-O value is around 14 kcal mol⁻¹ lower that the experimental one. The use of a scheme of isodesmic reactions leads to a DO-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 CF3OOC(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

The authors thank ANPCYT-DAAD for the German-Argentine cooperation Awards. They also thank the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), Argentina. They are indebted to the Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Argentina for financial support.

They also thank the FONCyT (Agencia Nacional de Promoción Científica y Tecnológica) and to the following institutions: LNLS (Brazil), British Council (U.K), Jesus College (Oxford), DAAD, AvH and VW Stiftung (Germany)

References


