EXPERIMENTAL AND THEORETICAL STUDY OF THE HEAT OF FORMATION OF FORMALDEHYDE DIPEROXIDE

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Abstract

We report the results obtained from the experimental determination and theoretical calculation of the diperoxide formaldehyde molecule.

Experimental work was performed using a macrocalorimeter to get the combustion heat and sublimation enthalpy was determined measuring the equilibrium vapor pressure in equilibrium with the vapor phase at different temperatures through the Clapeyron-Claussius equation.

Theoretical calculations were made resorting to the semiempirical AM1 procedure as well as via RHF *ab initio* and DFT B3LYP methods at the 3-21 G, 3-21+G, 6-311 G(d,p) and 6-311 +G(d,p) basis set levels.

Introduction

During the last decade, the chemistry of cyclic peroxides has enjoyed a renaissance with the increasing appreciation that such compounds occur widely in nature and often possess desirable pharmacological properties.[1] In the past decade remarkable progress has been made in theoretical chemistry, particularly in computational procedures for elucidation of the structures of unstable molecules and transition states and those of stable molecules.[2] These advanced theoretical methods have been applied to the determination of fully optimized geometries of unstable intermediate species and also to the location of structures in oxidation reaction of organic compounds with various peroxy compounds. The mechanisms of many newly developed oxidation reactions have been elucidated by the use of such modern techniques.[3]

Although 1,2,4,5-tetroxane (DPF) have been know for some time, there has been renewed interest in this class of cyclic peroxide on account of the significant antimalarial

activity exhibited by some of these compounds,[4] and their comparative ease of synthesis.[5]

The enthalpy of formation of 3,6-diphenyl-1,2,4,5-tetroxane at 298 K has been estimated by semiempirical and ab initio calculations and similar calculations have also been carried out for related saturated cyclic peroxides.[6-8]

The aim of this paper is to report the experimental enthalpy of formation of the 1,2,4,5-tetroxane (DPF), as well as the results calculated through the theoretical semiempirical, Density Functional (DFT) and ab-initio methods.

Experimental Procedure

Materials

Sample were synthesized by the known procedures,[5] the crystalline compounds were purified by repeated crystallization from ethyl acetate (boiling point 350 K). The purity of the samples was also determined by gas chromatography and ultraviolet (UV) spectra.

Combustion Calorimetric

The measurement of the enthalpy of combustion of the 1,2,4,5-tetroxane was made with an isoperibol macrocalorimeter fitted with a stirred water bath. The samples were pressed into gelatin capsules of mass $\approx$ 100 mg and burned in oxygen at under a pressure equal to 25 atm. The ignition current was 2 amperes. The combustion products were examined for carbon dioxide and water (visual inspection), but neither was detected. The energy equivalent of the calorimeters E_{calor} was determined (855.45 $\pm$ 1.5 cal/°C) with a standard reference sample of benzoic acid (Sample SRM 39i, NIST). For reduction of the data to standard conditions conventional procedures were used.[9] The atomic weights used were those recommended by the IUPAC Commission.[10]

The enthalpy of sublimation was determined using the measurements the vapor pressure at equilibrium with the vapor phase at different temperatures resorting to the Classius-Clapeyron equation. Measurements were made with the mercury manometer through Bodestein differential equipment.

Theoretical Calculations

One of the most important purposes of the calorimetric studies is to find out the molecular energy of the substituted molecules. Thermochemical relationships are very important because in some cases the formation heats, for example those corresponding to hydrocarbon species, are known with a very good accuracy degree, but usually the heat of formation of substituted compounds are not known due to practical drawbacks, or they are known with a rather low accuracy degree. A way to surmount these difficulties when one introduces substitutes in a parent molecule is to making suitable theoretical calculations.

It is well known that in order to make theoretical calculations of molecular enthalpy of formation it is necessary to find a suitable isodesmic chemical reaction to optimize the corresponding molecular structure and to perform the frequency calculations from the optimized equilibrium molecular geometries applying the corresponding theoretical method to obtain the total electronic energy at 298 K. Here we have chosen the Gaussian 94 package to perform the calculations.[11]

When one tries to get the equilibrium molecular geometries, it is necessary to localize the absolute minimum at the potential energy hypersurface. The optimization procedure is complete when the numerical process converges, i.e. when forces are null. Convergence criteria employed in the Gaussian 94 package are:

- Forces are practically zero.
- The square root of the average forces must be zero.
- The shifting calculation for the next step in the calculation cycle must be small enough.
- The second derivative of the shifting must be zero.

Results and Discussion

Combustion Calorimetric

Results for a typical combustion experiment on compound DPF are given in Table 1. The individual values of the standard specific energy of combustion (ΔU_c^0), enthalpies of combustion (ΔH_c^0) (the given standard deviations of the mean include the uncertainties from calibration and the uncertainties from the combustion energies of the

auxiliary materials), and enthalpies of formation (ΔH_f^0) of the compound DPF are given in Table 2.

Table 1. Result for Typical Combustion Experiment at 298.15 K.

Experience Nº	m_{DPF} g	m_{gel} g	m_{Fe} g	ΔT K	$(m_{agua}+E)\Delta T$ cal [a]	$m_{gel}.\Delta U_{gel}$ cal [b]	$m_{Fe} \Delta U_{Fe}$ cal [c]	ΔU_c^o cal g^{-1} [d]
1	0.07	0.12	0.03	0.23	801.75	540.81	54.72	3101.09
2	0.05	0.12	0.04	0.21	763.36	533.76	62.72	3078.79
3	0.13	0.15	0.05	0.32	1141.80	662.80	78.88	3104.07
4	0.05	0.13	0.04	0.22	797.44	583.53	66.88	3095.32
5	0.06	0.13	0.05	0.24	840.76	570.76	79.68	3099.66
6	0.09	0.14	0.05	0.27	968.11	624.49	80.00	3086.96
7	0.12	0.14	0.03	0.29	1034.31	634.18	43.20	3087.69
8	0.06	0.14	0.04	0.24	837.51	598.50	62.08	3103.90
9	0.06	0.14	0.03	0.24	848.40	604.67	49.60	3096.25
10	0.05	0.14	0.05	0.25	877.63	628.89	83.84	3093.88

[a]m_{water} = 2700g; [b]ΔU_{gel} (heat the combustion of gelatine capsules) = 4400±0.55 cal/g; [c]ΔU_{Fe} (heat the combustion of iron wire) = 1600±0.75 cal/g; [d]ΔU_c, standard specific energy of combustion.

Table 2. Summary of Experimental Specific Energies of Combustion and Standard Molar Thermodynamic Function of DPF at T=298.15 K. Denote average value.

Experience Nº	ΔU_c^0 (c) [a] cal mol^{-1}	ΔH_c^0 (c) [b] kcal mol^{-1}	ΔH_f^0 (c) [c] kcal mol-1	ΔH_f^0 (g) [d] kcal mol^{-1}
1	3101.09	-285.89	-38.84	-36.16
2	3078.79	-283.84	-40.89	-38.22
3	3104.07	-286.17	-38.57	-35.89
4	3095.32	-285.36	-39.37	-36.69
5	3099.66	-285.76	-38.97	-36.30
6	3086.96	-284.59	-40.14	-37.46
7	3087.69	-284.66	-40.07	-37.40
8	3103.9	-286.15	-38.58	-35.90
9	3096.25	-285.45	-39.29	-36.61
10	3093.88	-285.23	-39.50	-36.83
Average value	3094.76	-285.31	-39.42	-36.75
Standard deviation	± 2.05	± 0.75	±0.75	± 0.75

[a]ΔU_c, Standard Molar Energy of Combustion.

[b]Standard Enthalpy of Combustion.

[c]Standard Enthalpy of Formation in crystaline state.

[d]Standard Enthalpy of Formation in gas phase obtained from the Sublimation Molar Enthalpy (ΔH_S = 2.676 kcal/mol).

Table 3. Calculated electronic energy and heat of reaction (Hartree).

	$(\varepsilon_0 + H_{corr})^a$ [Hartree] RHF			
	3-21G	3-21 +G	6-311 G(d,p)	6-311 +G(d,p)
DPF	-375.1391	-375.1979	-377.3039	-377.3103
H_2O	-75.5604	-75.5939	-76.0202	-76.0265
CH_4	-39.9251	-39.9271	-40.1583	-40.1584
HP	-188.6994	-188.7383	-189.7928	-189.7977
MeOH	-114.3393	-114.3677	-115.0167	-115.0214
ΔHr^b	-0.03275	-0.027889	-0.041677	-0.04173

[a]Sum of Electronic and Thermal Enthalpies at the Hartree Fock ab initio technique and diferents basis sets levels. [b]Heat of reaction at the Hartree Fock ab intio technique and diferents basis sets levels $\Delta Hr = \Sigma(\varepsilon_0 + H_{corr})_{products} - \Sigma(\varepsilon_0 + H_{corr})_{reactants}$.

	$(\varepsilon_0 + H_{corr})^a$ [Hartree] B3LYP			
	3-21G	3-21 +G	6-311 G(d,p)	6-311 +G(d,p)
DPF	-377.1643	-377.2440	-379.3367	-379.3465
H_2O	-75.9504	-75.9965	-76.4224	-76.4334
CH_4	-40.2522	-40.2566	-40.4854	-40.4856
HP	-189.7457	-189.8010	-190.8509	-190.8594
MeOH	-115.0186	-115.0563	-115.7020	-115.7096
ΔHr^b	-0.040948	-0.035678	-0.04618	-0.046481

[a]Sum of electronic and thermal Enthalpies at the B3LYP Density Functional technique and diferents basis sets levels. [b]Heat of reaction at the B3LYP Density Functional technique and diferents basis sets levels $\Delta Hr = \Sigma(\varepsilon_0 + H_{corr})_{products} - \Sigma(\varepsilon_0 + H_{corr})_{reactants}$.

Table 4. Molecular formation energy of DPF (kcal/mol).

AM1	ΔH_f^0 (g)^a (kcal mol^{-1}) RHF			
	3-21 G	3-21+G	6-311 G (d,p)	6-311+ G (d,p)
-38.24	-34.25	-34.53	-33.53	-33.56

[a] Standard Enthalpy of Formation in gas phase at the AM1 semiempirical and Hartree Fock ab initio technique and diferents basis sets levels.

ΔH_f^0 (g)^a (kcal mol^{-1}) B3LYP			
3-21 G	3-21+G	6-311 G (d,p)	6-311+ G (d,p)
-36.53	-36.85	-36.35	-36.54

[a] Standard Enthalpy of Formation in gas phase at the B3LYP Density Functional technique and diferents basis sets levels.

To derive ΔH_f^0 (c) from ΔH_c^0 (c), the following molar enthalpies of formation were used:[10] for H_2O(l): -(68.38± 0.04) kcal mol^{-1} and for CO_2(g): (94.14±0.13) kcal mol^{-1}.

Theoretical Calculations

The isodesmic reaction chosen for the present calculation of the enthalpy of formation of DPF is

$$2\,CH_3OOH \;+\; 2\,CH_3OH \longrightarrow 2\,CH_4 \;+\; 2\,H_2O \;+$$
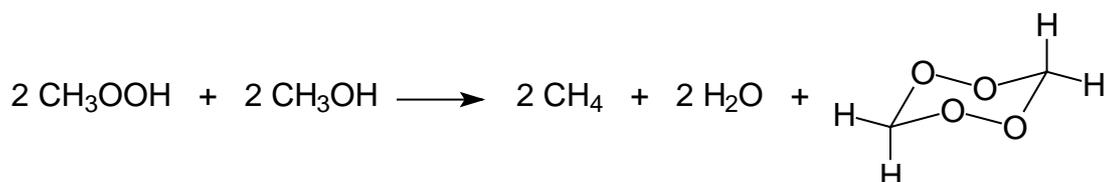
We made the complete optimization procedure for each molecule involved in the precedent chemical reaction via the AM1 semiempirical method as well as from the RHF ab initio technique and B3LYP DFT method at the 3-21 G, 3-21+G, 6-311 G(d,p) and 6-311 +G(d,p) basis sets levels. In Table 3 we display the electronic energy and heat of reaction in Hartree, using data associated to each molecule in the previous isodesmic chemical reaction.

Conclusions

The comparison of theoretical results and experimental determination shows that there is a rather good agreement among them. In order to judge suitably these data, one must take into account that, in general, experimental uncertainties are about 1-2 kcal/mol. The best predictions are obtained from the DFT methods, so that it seems convenient to employ them to make a structural analysis and chemical reactivity for this sort of molecules. However, in order to achieve more definitive conclusions it should be advisable to make similar calculations on similar molecules. Work along this line in under development in our laboratories and results will be published elsewhere in the near future.

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Povzetek

Poročamo o rezultatih eksperimentalnih meritev in teoretičnih izračunov za molekulo formaldehid diperoksida.

Sežigno toploto in sublimacijsko entalpijo smo eksperimentalno določili z makrokalorimetrom, z merjenjem parnih tlakov in uporabo Clapeyron-Claussius enačbe. Teoretični izračuni so bili narejeni s semiempiričnimi in *ab initio* metodami.