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## Calorimetric and Computational Study of Enthalpy of Formation of Acetone Diperoxide

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### ABSTRACT

A rather simple thermochemical experimental technique was applied to determine the enthalpy of formation of Diperoxide of acetone. The study is complemented with theoretical calculations *ab initio* and by the density functional theory (DFT) procedure.

**KEYWORDS:** DPAC, heat of formation, DFT calculation.

### RESUMEN

Una técnica experimental sencilla y rápida se emplea para determinar la entalpía de formación de acetona diperoxido. El estudio se complementa con cálculos teóricos en *ab initio* y los niveles de funciones de densidad (DFT).

**PALABRAS CLAVE:** DPAC, calor de formación, cálculo DFT.

## INTRODUCTION

Peroxides are widely used in several areas of chemistry due to their high reactivity with organic and inorganic substrates [1]. Their specific properties as free radical reaction initiators are widely employed in synthetic chemistry [2], especially in polymerization processes. [3] More recently, tetroxanes have been found to possess impressive antimalarial activity [4]. As a result of an apparent association between the peroxide functional group and antimalarial activity, a substantial effort has been devoted to developing new peroxide antimalarial drugs [4-6]. Unfortunately, several members of this compound class are very unstable; only a small number are easy to manipulate with adequate safety and are available as commercial products.

Among these peroxides is a large number of peroxyacids and peroxyesters [7]. Although the importance of these compounds is well known in chemistry, several aspects of their structure and reactivity modelling remain to be precisely defined [8].

Ketone and aldehyde diperoxides (1,2,4,5-tetroxanes) contain two peroxy groups in a six membered heterocycle and they are readily formed by acid-catalysed oxidation of carbonyl compounds with hydrogen peroxide. These compounds are also described as carbonyl dimers since they can be generated by dimerization of a carbonyl oxide intermediate derived from ozonolysis of olefins [9-11].

In this article, we report on the experimental determination of the enthalpy of formation of diperoxide of acetone (DPAC) (Figure 1) as well as the theoretical results calculated *ab initio* by the Hartree-Fock and density functional theory (DFT) methods.



## EXPERIMENTAL PROCEDURE

### Material

Acetone diperoxide (DPAC) was prepared by dropwise addition of acetone in acetonitrile to a vigorously stirred, cooled (-20 °C) solution of 69.7% hydrogen peroxide and sulphuric acid (18 M). After stirring for 2 h at -20 °C, filtration, thorough water washing, and drying, the crude product (71% yield) was purified by recrystallizing from ethyl acetate until a constant melting point was attained (132 – 132.5 °C [lit., 133-135 and 132-133 °C]). The product purity was also checked by GC and IR analyses (KC1) 2910 (s), 2850 (s), 1200 (m), 940 (w), 860 (w), 814 (w) and 682 (w)  $\text{cm}^{-1}$ .

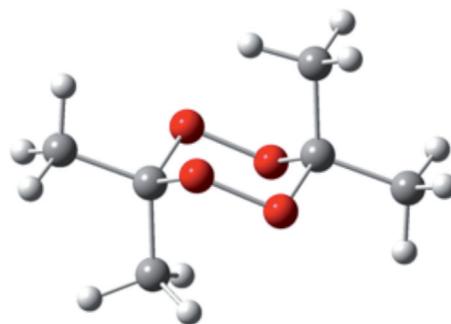


Figure 1. Diperoxide of acetone (DPAC)

### Thermochemical measurements

The measurement of the heat of combustion of diperoxide of acetone was made in an isoperibol macrocalorimeter fitted with a stirred water bath. The substance was burned in oxygen at  $p = 25$  atm. The current of ignition was determined to be 2 Amp. The heat capacity of the calorimeter (E) was determined with a standard reference sample of benzoic acid (Sample SRM 39i, NIST) for all experiments. E was measured to be  $(1808.17 \pm 1.5)$  cal/K. The crystalline compounds were pressed into capsules of masses  $\approx 10^{-2}$  g. The reduction of the data to standard conditions was made through conventional procedures [12]. The atomic weights used were those recommended by the IUPAC Commission [13].

Vapour pressures as a function of temperature of DPAC were measured by a mercury manometer using a Bodestein differential equipment and the enthalpy of sublimation was deduced from the temperature dependence of the vapour pressures (Clausius-Clapeyron equation).

### Theoretical calculations

The most important reason for calorimetric studies was to determine the molecular energy of a set of structurally and functionally related molecules in order to establish the corresponding structure-activity relationships and to be able to assess the main electronic features determining chemical reactivity.

It is well known that in order to make theoretical calculations of molecular enthalpy of formation it is necessary to find suitable isodesmic chemical reactions 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 chose the Gaussian 03 package [14] to perform the theoretical calculations *ab initio* and using Density Functional Theory (DFT).



In order to determine 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 03 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

### Experimental enthalpy of formation

Results for a typical combustion experiment on compound DPAC are given in Table 1. The individual values of the standard specific energy of combustion ( $\Delta U_c^0$ ), enthalpies of combustion (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 combustion and formation of the compound DPF are given in Table 2.

To derive  $\Delta H_f^0(g)$  from  $\Delta H_f^0(c)$ , the following molar enthalpies of formation were used [13]: for  $H_2O(g)$ :  $-(244.83 \pm 0.17)$  kJ/mol and for  $CO_2(g)$ :  $-(393.50 \pm 0.54)$  kJ/mol.

Table 2 shows the standard molar energy and enthalpy of combustion and formation of diperoxide of acetone, in the crystalline state at  $T = 298.15$  K, and it corresponds to the chemical reaction:



The uncertainties of the standard molar energy are four times the final overall standard deviation of the mean and they were estimated as outlined by statistical methods. Vapour pressure was determined at different temperatures and the enthalpy of sublimation was calculated as pointed out before.

Table 1. Results from typical combustion experiments at 298.15 K

	1	2	3	4	5	6	7	8
$M_{DPAC}/g$	0.0311	0.0492	0.0413	0.0487	0.0484	0.0488	0.0495	0.0490
$m_{Fe}/g$	0.0025	0.0098	0.0119	0.009	0.0081	0.0130	0.0113	0.0116
$\Delta T/K$	0.09615	0.15835	0.13440	0.14770	0.15411	0.15789	0.15879	0.15761
$(m_{water}+E)\Delta T/J^a$	1445.067	2409.950	1990.478	2211.864	2361.253	1570.532	1750.319	2368.765
$m_{Fe} \Delta U_{Fe}/J^b$	29.085	108.300	138.445	10.471	94.235	138.985	131.464	134.954
$\Delta U_c/J/g^c$	22901.960	23165.751	22915.423	22927.966	23091.932	22900.635	22915.218	22931.164
$\Delta H_c/kJ/mol$	-3376.842	-3415.883	-3378.836	-3380.691	-3404.958	-3376.646	-3378.804	-3381.165

<sup>a</sup> mwater=2700g

<sup>b</sup> DUFe (heat of combustion of iron wire)=1800.00 ± 0.70 cal/g

<sup>c</sup> DUc standard specific heats of combustion

The standard molar enthalpies of formation for both crystalline and gaseous states of DPAC at  $T = 298.15$  K are also given in Table 2. No combustion enthalpy and enthalpy of sublimation have been found in the standard literature for comparison purposes.



Table 2. Summary of experimental specific heats of combustion and standard molar thermodynamic function of DPAC at T = 298.15 K.

Experiment N°	$\Delta U_c^0(c)^a$ J/mol	$-\Delta H_c^0(c)^b$ kJ/mol	$-\Delta H_f^0(c)^c$ kJ/mol	$-\Delta H_f^0(g)^d$ kJ/mol
1	22901.960	-3376.842	-435.10	-370.40
2	23165.751	-3415.883	-396.06	-331.36
3	22915.423	-3378.836	-433.11	-368.41
4	22927.966	-3380.691	-431.25	-366.55
5	23091.932	-3404.958	-406.98	-342.28
6	22900.635	-3376.646	-435.30	-370.60
7	22915.218	-3378.804	-433.14	-368.44
8	22931.164	-3381.165	-430.78	-366.08
Average value	22968,7561	-3386.728	-425.21	-360.51
Standard deviation	1.057055	0.241008	0.241008	0.241008

<sup>a</sup> Standard molar heat of combustion

<sup>b</sup> Standard enthalpy of combustion

<sup>c</sup> Standard enthalpy of formation in crystalline state

<sup>d</sup> Standard enthalpy of formation in gas phase obtained from the sublimation molar enthalpy ( $\Delta H_s = 64.66$  kJ/mol)

### Theoretical Calculation of the enthalpy of formation

In the case of diperoxide of acetone, the suitable isodesmic chemical reaction, is:



In order to calculate enthalpy values at 298 K, the difference between the enthalpy at temperature T and 0 K can be evaluated according to standard thermodynamic formula 2. The sum of electronic and enthalpy energies at 298 K calculated *ab initio* using the Hartree-Fock and Density Functional Theory (DFT) procedures with different basis sets for the studied compounds, are also shown in Table 3.

The heats of formation calculated through atomization reaction are given in Table 4. The analysis of theoretical results show that *ab initio* and DFT procedures yield better results. Besides, the best agreement among experimental data and theoretical predictions happens for the 3-21G\*\* basis set.

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

	$-(\epsilon_0 + H_{corr})^a$ [Hartree]			
	RHF 3-21G**	RHF 6-31G**	B3LYP 3-21G**	B3LYP 6-31G**
DPAC	-530.393261	-533.276675	-533.624866	-536.434576
CH <sub>4</sub>	-39.945747	-40.151095	-40.271061	-40.477542
C <sub>3</sub> H <sub>8</sub>	-117.536449	-118.162074	-118.427441	-119.050393
CH <sub>3</sub> OOCH <sub>3</sub>	-227.520094	-228.748400	-228.895519	-230.091622
$\Delta H_r^b$	-0.063188	-0.060110	-0.063204	-0.060718

<sup>a</sup> Sum of electronic and thermal enthalpies calculated using *ab initio* Hartree-Fock and Density Functional Theory (DFT) techniques with different basis sets levels;

<sup>b</sup> Heat of reaction obtained with *ab initio* Hartree-Fock and Density Functional Theory (DFT) techniques at different basis sets levels:  $\Delta H_r = \sum (\epsilon_0 + H_{corr})_{products} - \sum (\epsilon_0 + H_{corr})_{reactants}$



Table 4. Enthalpy of formation of DPAC

$-\Delta H_f^0(g)$ [kJ mol <sup>-1</sup> ]			
RHF 3-21G**	RHF 6-31G**	B3LYP 3-21G**	B3LYP 6-31G**
-326.58	-318.52	-326.62	-320.10

<sup>a</sup> Standard enthalpy of formation in gas phase calculated *ab initio* by the Hartree-Fock and Density Functional Theory (DFT) techniques and with different basis sets.

## CONCLUSIONS

We have reported a simple and accurate experimental method to determine the enthalpy of formation of the title compound and we have complemented it with the theoretical calculation of the property under study via *ab initio* Molecular Orbital methods and DFT procedures. The theoretical value of the enthalpy of formation of diperoxide of acetone, -360.51 kJ mol<sup>-1</sup>, evaluated by the Hartree-Fock and DFT methods at the 3-21G\*\* basis set level, is in very good agreement with the experimental value, -326.62 kJ mol<sup>-1</sup>. This methodology, consisting in the experimental determination of the thermochemical property and its complementation with theoretical procedures, represents a prudent way to study similar oxane derivative molecules and further studies along this line are currently under development.

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