Experimental and Theoretical Standard Enthalpies of Formation of 3,6-dibutanal-1,2,4,5-tetroxane

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Abstract: We describe the synthesis of 3,6-dibutanal-1-2-4-5-tetroxane and we present the results of the experimental determination and the theoretical calculation of its standard enthalpy of formation. The 3,6-dibutanal-1-2-4-5-tetroxane is synthesized by oxidation of glutaraldehyde with oxygen peroxide in presence of concentrated sulfuric acid. Theoretical calculations are performed with the ab initio Hartree Fock method at different basis set levels. Theoretical results at 3-21+G basis set level agree quite well with the experimental data since they differ in just 1.90 kcal mol^{-1}, which is the regular uncertainty associated to the experimental determination.

INTRODUCTION

The chemistry of organic peroxides, which entails the synthesis, characterization and transformation of derivatives of hydrogen peroxide, has a long history and strong tradition [1-3]. The unusual reactivity of peroxides is generally attributed to the weakness of the O-O bond linkage and hence to the fact that it is homolytically cleaved. Cyclic di- and triperoxides derived from aliphatic ketones and aldehydes which were prepared in our laboratory have been the object of numerous studies related to their application as initiators for the polymerization of vinyl monomers [4-5].

The effects of the nature of these peroxide initiators on polystyrene conversion and molecular weigth have been evaluated [6].

In this work, we report the synthesis and the experimental enthalpy of formation of the 3,6-dibutanal-1,2,4,5-tetroxane (DBT), as well as the results calculated through theoretical semiempirical and ab-initio methods.

MATERIALS AND METHODS

Synthesis of glutaraldehyde diperoxide (DBT): The DBT is synthesized by oxidation of glutaraldehyde with oxygen peroxide in presence of concentrated sulfuric acid, following the Bayer and Viller Method modified by Jorge *et al.,* [7].

Sixty eight percent H_2O_2 (0.102 mol, 1.95 g) and glutaraldehyde (0.0354 mol, 4.02 g) were added by consecutive dropwise addition to a stirred solution of water (15 mL), EtOH (25 mL) and H_2SO_4 (35 mL) at-10°C. Stirring was continued for 1 h at -10°C. The resulting white precipitate was filtered, washed with water and air-dried. The precipitate was recrystallized in methanol and carefully dried under vacuum.

Melting points were determined with a Electrothermal Capillary Melting Point apparatus, obtaining a melting point equal to 95°C

Thermochemical measurements: The measurement of the heat of combustion of 3,6-dibutanal-1,2,4,5-tetroxane (DBT) was made with an isoperibol macrocalorimeter fitted

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with a stirred water bath. The substance were 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) in all experiments. E was measured to be (856.17 ± 1.5) cal K^{-1}. The crystalline compounds were pressed into gelatine capsules. For the data reduction to standard conditions conventional procedures were used [8]. The atomic weights used were those recommended by the IUPAC Commission [9].

The heats of sublimation of the DBT was determined using measurements of the vapor pressure at different temperatures resorting to the Clapeyron -Clausius equation. Measurements were carried out with a gauge of mercury through a differential Bodestein.

Theoretical calculations: One of the most important purposes of the calorimetric studies is to find out the molecular energy of the molecules, which enables one to derive significant conclusions when they are analyzed in depth for a family of related ones. It is well known that in order to perform theoretical calculations of the 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 [10] to perform the calculations at the semiempirical and *ab initio* levels.

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 the forces are null and all frequencies are real.

RESULTS AND DISCUSSION

Experimental enthalpy of formation: Table 1 gives the results for a typical combustion experiment on compound DBT. Table 2 gives the standard molar energy and enthalpy of combustion and formation of 3,6-dibutanal-1,2,4,5-tetroxane, in the crystaline state at T = 298.15 K and correspond to the reaction:

$$C_{10}H_{16}O_6(c)+11O_2(g) \rightarrow 10CO_2(g)+8H_2O(l) \qquad (1)$$
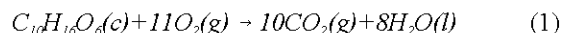
The uncertainties of the standard molar energy is four time the final overall standard deviation of the mean and were estimated as outlined by stadistic methods. Vapor pressure were determined at different temperatures and the enthalpy of sublimation was calculated. The standard molar enthalpies of formation for both crystalline and gaseous states of the DBT at T = 298.15 K are also given in Table 2.

No combustion enthalpy and enthalpy of sublimation have been found in the literature for comparison with our results.

Theoretical enthalpies of formation: In the case of the 3,6- dibutanal- 1,2,4,5 -tetroxane, the isodesmic reaction, is:

$2 H_3C-CH_2-O-O-CH_2CH_3$ (DEP) (g)+ 2 CH_3-CH_2-CO (g) $\rightarrow$ DBT (g) + 4 CH_4 (g)
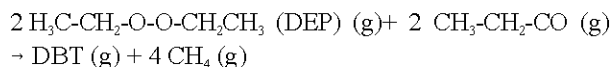
In order to calculate enthalpy values at 298 K, the difference between the enthalpy at temperature T and 0 K can be evaluated according to standard thermodynamic. The sum of electronic energy and heat of reaction at 298 K calculated with the Hartree Fock *ab initio* method at different basis set levels for the studied compound, are also collected in Table 3. The heat of formation calculated

Table 1: Results for typical combustion experiments of 3,6-dibutanal-1,2,4,5-tetroxane (DBT) at 298.15 K

	1	2	3	4	5	6	7	8
$m_{DBT} \times 10^3 g^{-1}$	20.00	18.80	9.10	11.10	10.30	0.50	0.30	0.50
$m_{gel} g^{-1}$	0.0227	0.0275	0.0240	0.0169	0.0242	0.040	0.0366	0.0400
$m_{Fe} g^{-1}$	0.0328	0.0381	0.0352	0.0267	0.0296	0.0108	0.0175	0.0119
$\Delta T/K$	0.05619	0.08121	0.05996	0.05066	0.05962	0.05469	0.05322	0.05518
$(m_{water}E)\Delta T/cal^a$	266.32	288.05	213.37	180.03	211.84	194.49	189.22	203.73
$m_{gel} \Delta U_{gel}/cal^b$	98.93	119.86	104.61	73.66	105.47	174.34	159.52	174.33
$m_{Fe} \Delta U_{Fe}/cal^c$	52.48	60.96	56.32	42.72	47.36	17.28	28.00	19.04
$\Delta U_c/cal\ g^{d-1}$	5745.33	5743.69	5747.64	5744.27	5746.21	5744.27	5744.88	5744.88
$\Delta H_c/Kcal\ mol^{-1}$	-1334.83	-1334.45	-1335.37	-1334.58	-1331.03	-1334.58	-1334.72	-1334.72

$^a m_{water} = 2700g$, $^b \Delta U_{gel}$(heat of combustion of gelatine capsules) = 4358.30 ± 0.65 cal g^{-1}, $^c \Delta U_{Fe}$(heat the combustion of iron wire)= 1600.00 ± 0.75 cal g^{-1}, $^d \Delta U_c$ standard specific energy of combustion.

Table 2: Standard molar energy of combustion and enthalpies of combustion and formation of 3,6-dibutanal-1,2,4,5-tetroxane (DBT) at T = 298.15 K

Experiment N°	ΔU^0_c (c)[a] kcal mol^{-1}	ΔH^0_c (c)[b] cal mol^{-1}	ΔH^0_f (c)[c] kcal mol^{-1}	ΔH^0_f (g)[d] kcal mol^{-1}
1	5745.33	-1334.83	-153.61	-116.91
2	5743.69	-1334.45	-153.99	-117.29
3	5747.64	-1335.37	-153.07	-116.37
4	5744.27	-1334.58	-153.86	-117.16
5	5746.21	-1335.03	-153.41	-116.71
6	5744.27	-1334.58	-153.86	-117.16
7	5744.88	-1334.73	-153.71	-117.01
8	5744.88	-1334.73	-153.71	-117.01
Average value	5745.15	-1334.79	-153.68	-116.9
Standerd deviation	1.26	0.29	0.29	0.29

[a]Standard molar energy of combustion, [b]Standard enthalpy of combustion, [c]Standard enthalpy of formation in crystalline state, [d]Standard enthalpy of formation in gas phase obtained from the sublimation molar, enthalpy ($\Delta H_S = 36.70$ kcal mol?[l])

Table 3: Calculated electronic energy and heat of reaction (Hartree) of 3,6-dibutanal-1,2,4,5-tetroxane (DBT)

$(\varepsilon_0 + H_{corr})^a$ [Hartree]

	AM1	PM3	RHF 3-21+G	RHF 3-21+G	RHF 6-31G	RHF 6-31+G
DBT	-0.2116383	-0.2267866	-832.021751	-832.134845	-836.264171	-836.287781
DEP	0.088909	0.127295	-305.069212	-305.112382	-306.622051	-306.631078
CH$_4$	0.034185	0.028432	-39.925067	-39.927109	-40.128804	-40.129575
Propanal	-0.097462	-0.095528	-190.781106	-190.805892	-191.766334	-191.771146
Δhr[b]	0.012356	-0.113977	0.048479	-0.018302	-0.011609	-0.009736

[a]Sum of electronic and thermal enthalpies at semiempirical and Hartree Fock *ab initio* techniques and different basis sets levels

[b]Heat of reaction at semiempirical and Hartree Fock *ab initio* techniques and different basis sets levels:

Table 4: Theoretical enthalpy of formation of 3,6-dibutanal-1,2,4,5-tetroxane (DBT)

ΔH^0_f (g)[a] [kcal mol^{-1}]

AM1	PM3	RHF3-21 G	RHF 3-21+G	RHF 6-31 G	RHF 6-31+G
-132.81	-142.31	-124.24	-115.05	-112.46	-111.85

[a]Standard Enthalpy of Formation in gas phase at the Semiempirical and Hartree Fock *ab initio* technique and different basis set levels.

through atomization reaction is given in Table 4. We can see that the best agreement with experimental result is obtained from the *ab initio* method with the 3-21+G basis set.

CONCLUSION

The method employed to determine the DBT enthalpy of formation and which is described in this article is simple enough but at the same time it makes up a reliable procedure which can be employed for other similar substances. The similarity of experimental and theoretical values of enthalpy of formation reveals that both methods are suitable for DBT.

In fact, the theoretical value of the enthalpy of formation of 3,6-dibutanal-1,2,4,5-tetroxane, -115.05 kcal mol^{-1}, evaluated at the Hartree Fock level with a 3-21+G basis set, is in very good agreement with the experimental value, -116.95kcal mol^{-1}. At present we are performing the experimental determinations and theoretical calculations of other similar tetroxane derivatives and results will be presented elsewhere in the near future.

REFERENCES

1. McCullough, K.J., A.R. Morgan, D.C. Nonhebel, P.L. Pauson and G.J.J. White, 1980. Chem. Res. Synop., 34: M0601.
2. McCullough, K.J., A.R. Morgan, D.C. Nonhebel and P.L. Pauson, 1981. Chem. Res. Synop., 35: M0629.
3. Adam, W., L.P. Hadjiarapoglou, R. Curci and R. Mello, 1992. In Organic Peroxides. Ando, W., Ed., John Wiley and Sons, Chichester, England, Chapt. 4.
4. Eyler, G.N., C.M. Mateo, E.E. Alvarez, A.I.J. Cañizo, 2000. Org. Chem., 65: 2319-2321.

5. Eyler, G.N., C.M. Mateo, E.E. Álvarez, A.I. Cañizo, L.F.R. Cafferata, 1999. J. Org. Chem., 64: 8457-8460.

6. Morales, G., G.N. Eyler and A.I. Cañizo, (submitted).

7. Leiva, L.C.A., J.M. Romero, N.L. Jorge, M.E. Gómez Vara and L.F.R. Cafferata, 2002. Revista Internacional Información Tecnológica, 13: 23-26.

8. Hubbart, W.N., D.W. Scott and G. Waddington, 1956. In Experimental Thermochemistry, F.D. Rossini, Ed. Interscience, New York, pp: 75-127.

9. Cox, J.D., D.D. Wagman and V.A. Medvedev, Eds., 1989. CODATA Key Values for Thermodynamics. Hemisphere, New York.

10. Frisch, M.J., G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, A. Robb, J.R. Cheeseman, T.A. Keith, G. A. Petersson, J.A. Montgomery, K. Kaghavachari, M.A. Al-Laham, V.G. Kakrewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andrés, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. DeFrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. González, J.A. Pople, Gaussian 94, rev D3, SGI; Gaussian, Inc., Pittsburgh, PA., 1995.