Thermochimica Acta 585 (2014) 10–15

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermochemistry of cyclic acetone peroxides

V.P. Sinditskii[a,*], V.I. Kolesov[a], V.Yu. Egorshev[a], D.I. Patrikeev[a], O.V. Dorofeeva[b]

[a] Mendeleev University of Chemical Technology, 9 Miusskaya Square, 125047 Moscow, Russia
[b] Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia

ARTICLE INFO

Article history:
Received 28 January 2014
Received in revised form 27 March 2014
Accepted 28 March 2014
Available online 6 April 2014

Keywords:
Diacetonediperoxide (DADP)
Triacetonetriperoxide (TATP)
Enthalpy of formation

ABSTRACT

Two potentially initiating explosive peroxides, diacetonediperoxide (DADP) and triacetonetriperoxide (TATP), were studied in respect to their thermochemical properties. To get the internally self-consistent estimations of gas-phase enthalpy of formation of DADP and TATP, their values were calculated by combining Gaussian-4 (G4) theory with an isodesmic reaction scheme. The energies of combustion ($\Delta_c U$) were measured and the standard enthalpies of formation ($\Delta_f H^\circ_{298}$) of DADP and TATP were derived using the standard enthalpies of formation of the combustion products. The heat of explosion was measured for small low-pressed charges of the peroxides. The obtained enthalpies of formation of DADP and TATP were found to agree well with quantum chemical calculations and reasonably account for the observed derivative parameters: heats of decomposition, combustion, and detonation.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Organic peroxides find numerous applications; they serve as accelerators, activators, cross-linking agents, curing and vulcanization agents, hardeners, polymerization initiators, and promoters. Depending on the peroxide unit concentration in the molecule, organic peroxides may possess explosive properties to a greater or lesser extent. Explosive peroxides have been never used in civilian or military applications mainly due to their high sensitivity, volatility, and sometimes tendency to explode spontaneously without apparent reasons [1]. The cyclic acetone peroxides are characteristic examples. These substances are produced in the reaction of acetone with hydrogen peroxide generally as a mixture of two cyclic isomers [2,3], diacetonediperoxide (DADP) and triacetonetriperoxide (TATP) (Fig. 1).

Despite the fact that explosive acetone peroxides have been known since the 19th century [4–6], the substances are being intensively studied in recent years [7–12] to provide new information on physical, chemical and explosive properties. However, the information on the thermochemical properties of the acetone peroxides is most contradictory and knotty. All available information on thermochemical properties of acetone peroxides is presented in Table 1.

Muraour [5] reported the heat of TATP explosion as 5665 kJ kg^{-1}. This value seems to be unreal as it is comparable with the heat of explosion of such high explosives as RDX and HMX. The heat of explosion of both small pressed and cast TATP samples was measured in 1985 to be only 2803 kJ kg^{-1} [13].

Heats of DADP and TATP combustion (under nitrogen atmosphere) can be approximately calculated from maximum combustion temperatures (1125 and 1300 K, respectively) measured by using thin thermocouples [14,15] and assuming average specific heat of combustion products to be 2.4 J g^{-1} K^{-1}. The calculated values are 1985 kJ kg^{-1} and 2405 kJ kg^{-1} for DADP and TATP, respectively.

The heat of TATP decomposition can be estimated from the enthalpies of formation ($\Delta_f H^\circ_{298}$) of TATP and its decomposition products. According to Muraour [5], the enthalpy of TATP formation is equal to −90.8 kJ mol^{-1}. Thermolysis of TATP, according to data of Oxley et al. [7], results mainly in acetone and CO_2 (1.83 mol of acetone and 1.43 mol of CO_2/mol of TATP at 230 °C). Assuming other minor products of decomposition to have negative enthalpies of formation, the calculated decomposition heat effect will exceed 3765 kJ kg^{-1}. At fast heating rates, the dominant decomposition product of TATP is methane rather than acetone [12]. In this case, the heat of TATP decomposition is calculated to be around 4853 kJ kg^{-1}.

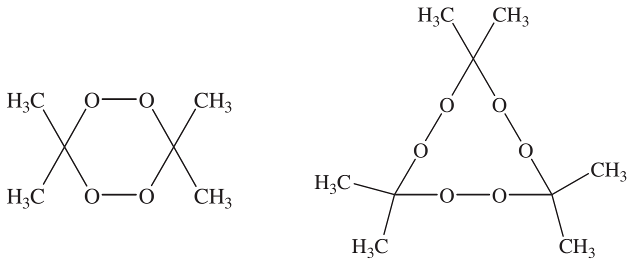
A comparison of rather moderate experimental heats of TATP explosion and combustion with large heats of TATP decomposition (calculated with the enthalpy of formation taken from [5]), casts some doubt upon the correctness of the used enthalpy of TATP formation.

Indeed, a simple estimation of the enthalpy of TATP formation by semi-empirical AM1 method, taking into account experimental heat of sublimation [14], gives a significantly less value

---

* Corresponding author. Tel.: +7 495 4966027; fax: +7 495 4966027.
E-mail address: vps@rctu.ru (V.P. Sinditskii).

http://dx.doi.org/10.1016/j.tca.2014.03.046
0040-6031/© 2014 Elsevier B.V. All rights reserved.



DADP TATP

Fig. 1. Structural formulas of acetone peroxide isomers.

(-395 kJ mol^{-1}) than reported in [5]. The enthalpy of DADP formation estimated by the same way is -281 kJ mol^{-1} [14].

The enthalpies of TATP and DADP formation were measured recently in [16] using the semi-micro oxygen bomb calorimetry. According to the data obtained, DADP had a negative enthalpy of formation $\Delta_f H^{\circ}_{298} = -598.5 \pm 39.7$ kJ mol^{-1} (-4043.9 kJ kg^{-1}), while TATP all of a sudden appeared to be endothermic compound with a positive $\Delta_f H^{\circ}_{298} = +151.4 \pm 32.7$ kJ mol^{-1} (+682.0 kJ kg^{-1}).

However, this article has not made things clear. Based on the published data, one has to believe that the transition from the six-membered cycle to the related nine-membered one is accompanied by a tremendous increase in the endothermicity of the compound (4725.9 kJ kg^{-1}). Some increase in the endothermicity may be thought to result from the internal strain of TATP cycle. Indeed, the thermocouple-aided experiments showed somewhat higher combustion temperature for TATP than for DADP that might confirm this suggestion [14,15]. However a calculated difference in the heat effects during combustion of TATP and DADP (~420 kJ kg^{-1}) proved to be many times less than it could be expected from data obtained in [16].

The paper of Keinan et al. [17] adds more intrigue to the thermochemistry of TATP. These authors predicted the preferential formation of acetone and oxygen (or even ozone) at thermal initiation of TATP based only on theoretical calculations without taking into account the experimental data on the decomposition products [7]. According to these calculations, the conversion of TATP to acetone and oxygen is almost energy-neutral, because there is no redox reaction. Imagining the TATP decomposition reaction to be energy-neutral, the authors [17] have made an unrealistic assumption that the detonation of peroxide-containing materials, including TATP, is an entropic explosion rather than an exothermic process.

The purpose of this work is to address the issue of DADP and TATP enthalpies of formation again, basing on both calorimetric measurements and quantum chemical calculations. To calculate the gas-phase enthalpies of formation, the composite Gaussian-4 (G4) [18] method was used. This method is one of the most successful today in calculating enthalpies of formation of large molecules.

2. Experimental

2.1. Preparation

Triacetonetriperoxide was synthesized by methods published elsewhere [2] as a white crystalline solid. Dissolving TATP in chloroform with a catalytic amount of p-toluenesulfonic acid and keeping the solution at room temperature for a week afforded pure crystalline DADP [17]. Both substances were recrystallized from hot ethanol. The purity of DADP and TATP was checked at high-performance gas–liquid chromatography combined with selective mass spectrometer. Melting points were run in sealed capillary tubes at 3 °C/min using Boitus melting point apparatus and were 95–97 °C for TATP (lit. 94–98.5 °C [2]) and 132–133 °C for DADP (lit. 131–133 °C [2,19]).

2.2. Calorimetric measurements

The calorimetric measurements were carried out using a standard bomb calorimeter B-08M equipped by a modified oxygen bomb with 210.5 mL volume, which was capable of withstanding an explosion of 2 g of a powerful explosive. Distilled water was added to the calorimetric bucket to the total mass of 4587 ± 0.1 g; the temperature of the filled calorimetric bucket was brought to 298 ± 0.1 K. The temperature growth was measured with a Beckmann thermometer to the nearest 5×10^{-3} K, providing the accuracy of measurements less than 1%. The calorimeter was calibrated using thermochemical grade benzoic acid with a quoted internal energy of combustion $\Delta_c U = -26{,}454 \pm 5$ J g^{-1} [20,21]. The heat equivalent of the calorimeter was measured as $\varepsilon = 14{,}958 \pm 8$ J K^{-1}.

Samples of TATP and DADP were burned both in the pure form at the oxygen pressure of 0.5 MPa and as a mixture of the crystalline peroxides with liquid (tetradecane, Vaseline mineral oil) or solid (benzoic acid) phlegmatizers at the oxygen pressure of 2.0 MPa. All liquid mixtures were placed into NiCr stainless steel crucibles whereas pure peroxides and solid mixture with benzoic acid were tested in the form of pressed annular pellets strung on the ignition wire. Ignition of all samples was performed using electrically heated steel firing wires of about 9 cm length with a quoted internal energy of combustion $\Delta_c U = 6690$ J g^{-1} [20]. A contribution of the combustion energy from the ignition wire (along with the Joule heat) was accounted for by measuring the weight of unburned wire fragments and calculating the combustion energy of the burned wire. In some experiments a small length of thin cotton thread tying a tested pellet to the firing wire and having an internal energy of combustion $\Delta_c U = -16{,}240$ J g^{-1} [20] was used as the ignition aid.

Table 1
Thermochemical parameters of acetone peroxide isomers.

Parameter	DADP	TATP	Comments
Heat of explosion (kJ kg^{-1})		5665	Published in 1932 [5]
		2803	Experiment, 1985 [13]
Heat of combustion (kJ kg^{-1})	1985	2405	Calculated from measured flame temperatures, 2009 [14]
Heat of decomposition (kJ kg^{-1})		>3765	Calculated from decomposition products at low heating rates [7] and $\Delta_f H^{\circ}_{298} = -90.8$ kJ mol^{-1} [5], 2009 [14]
		4853	Calculated from decomposition products at fast heating rates [12] and $\Delta_f H^{\circ}_{298} = -90.8$ kJ mol^{-1} [5], 2009 [14]
Enthalpy of formation (kJ mol^{-1})		−90.8	Published in 1932 [5]
	−281	−395	Estimated by semi-empirical AM1 with allowance for heat of sublimation, 2009 [14]
	−598.5 ± 39.7	+151.4 ± 32.7	Experiment, 2012 [16]

Download English Version:

https://daneshyari.com/en/article/673324

Download Persian Version:

https://daneshyari.com/article/673324

Daneshyari.com