

The Enthalpies of Formation of Trioxane and Tetroxane

MARGRET MÅNSSON, ERNST MORAWETZ,
YOSHIAKI NAKASE* and STIG SUNNER

*Thermochemistry Laboratory,** University of Lund, Chemical Center, S-220 07 Lund 7, Sweden*

The enthalpies of combustion and sublimation of 1,3,5-trioxane and 1,3,5,7-tetroxane have been measured and enthalpies of formation at 25.0°C derived. The obtained data for the crystalline, $\Delta H_f^\circ(c)$, and the gaseous, $\Delta H_f^\circ(g)$, states are

trioxane -124.84 ± 0.09 and -111.32 ± 0.12 ;
tetroxane -167.27 ± 0.12 and -148.24 ± 0.16

kcal-mole⁻¹, respectively.

EXPERIMENTAL

Compounds. Trioxane. The sample of trioxane was supplied by Perstorp AB through the courtesy of Dr. P. Flodin. The purity of the sample was stated as: ~70 ppm water; 3-5 ppm monomer; the sum of all other impurities (HCOOH, HCOOCH₃, CH₃OH, CH₂(OCH₃)₂) less than 20 ppm. In order to remove any water present trioxane was sublimed through a layer of activated Molecular Sieves Type 4A on to a cold finger (covered with Al-foil in order to simplify removal of the layer of trioxane) in a closed glass apparatus, which was then opened in a glove box where the relative humidity was less than 5%. The sublimation was performed at a pressure of about 100 mm Hg with a temperature difference of a few degrees. Appropriate amounts of the dried trioxane were made into pellets, using a balance and a pellet press inside the "dry box". The pellets were placed individually in small weighing bottles that were stored in a desiccator.

During the sublimation, and probably also when pelleting the material, some polymer formed in the trioxane. In order to determine quantitatively the amount of polymer, trioxane pellets of known mass were dissolved in excess methanol, the residue collected on a glass filter, rinsed with fresh methanol and dried at 105°C overnight before weighing. The amount of polymer found was 6.1 ± 0.3 %.

Trioxane polymer. In order to make it possible to apply corrections for the polymer content in trioxane the enthalpy of combustion of trioxane polymer had to be determined. Therefore a polymer sample was prepared by carefully removing the monomer by sublimation in vacuum, 0.1 mm Hg.

Tetroxane. The sample of tetroxane was given to us by Toyo Koatsu Co. Ltd., Japan, through Professor K. Hayashi. It had been produced by thermal decomposition of

* Present address: Japan Atomic Energy Research Institute, Takasaki, Japan.

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polyoxymethylene diacetate over a catalyst and then recrystallized from CS_2 . The material was pelleted and then stored over Molecular Sieves in a desiccator. When performing the first series of calorimetric experiments small amounts of incombustible material were found in the crucible after combustion. The origin and identity of this residue could not be properly established and therefore a second series of combustions was considered desirable. Prior to this the tetroxane was treated in the same way as the trioxane sample (sublimation through Molecular Sieves; pelleting in dry atmosphere) $d_{20}^{20}=1.441$, $d_{25}^{25}=1.424$. Polymer content $\leq 0.03\%$.

Combustion calorimetry; apparatus and procedure. The Thermochemistry Laboratory rotating-bomb calorimeter TKL-3 with bomb 3A was used.¹ Calibration experiments were performed according to standard procedure using the National Bureau of Standards sample 39i of benzoic acid.

The volatile samples of trioxane as well as tetroxane had to be enclosed before combustion. For this purpose polyester bags made from Du Pont's 100 gauge Mylar Type A were used, using the technique described by Good *et al.*² Unfortunately, the high vapour pressure of trioxane (13 mm Hg at 25°C; Ref. 3) as well as its high solubility in the Mylar contributed to a rapid penetration of the film. To overcome this obstacle the trioxane pellet was put into the Mylar bag as late as possible prior to the combustion experiment. The Mylar bag was sealed immediately and put into a second bag, which was then sealed as quickly as possible and weighed after 10 to 15 min. Blank experiments were carried out to determine whether the weight of Mylar changed due to insufficient time for humidity equilibration between sealing operations. No significant change in weight was observed. The tetroxane pellets were enclosed in single Mylar bags approximately 20 min before filling the bomb for the combustion experiments.

The combustions were carried out under standard conditions with 0.79 ml of water in the bomb and $P^i(\text{gas})=30.0$ atm. The substances burned well in all experiments, with no trace of any soot deposit. The paraffin oil used as auxiliary material with the trioxane polymer was designated USBM-P3a.⁴ Calorimeter data are given in Ref. 1. All weighings were reduced to mass and the molecular weights computed from the 1961 table of atomic weights.⁵ The density of trioxane was taken as 1.39⁶ and that of the trioxane polymer 1.5.

Vaporization calorimetry. The enthalpies of sublimation at 25.0°C for trioxane and tetroxane were determined by isothermal evaporation using the calorimeter previously described.⁷ Since the vapour pressure of trioxane at 25°C is 13 mm Hg³ the evaporation of this compound can only be performed at a vapour flow Mach number close to zero, and the systematic error, $\delta\Delta H$, is therefore 0.014 ± 0.016 kcal-mole⁻¹. About 0.3 g of trioxane was sublimed into the calorimeter under vacuum. One series of measurements was performed using a steel capillary, diam. 0.1₃ mm, length 4.0 mm.

No literature value for the vapour pressure of tetroxane is available. It has been shown that the flow rate obtained in a vaporization experiment can be used in calculating the saturation pressure, when the outflow of vapour occurs through an orifice.⁸ A preliminary experiment proved that the saturation pressure is $0.1 > P_s > 0.01$ mm Hg. The vapour flow in the calorimeter then occurs at a Mach number close to unity, irrespective of the diameter, d , of the orifice and its distance, l , from the evaporating surface. Accordingly, the systematic error under these conditions is 0.214 ± 0.014 kcal-mole⁻¹. Two series of measurements were performed, the values of d and l (in mm) being (I) $d=0.8_3$, $l\sim 10$; (II) $d=0.6_4$, $l\sim 1$. The average saturation pressure calculated is $0.05_4 \pm 0.01_1$ mm Hg at 25°C.

The enthalpy of sublimation for trioxane was also determined using the Wadsö calorimeter.⁹

RESULTS

The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 abs.joules. All symbols used are those introduced by Hubbard, Scott and Waddington.¹⁰ The ΔE_Σ values were calculated using SMIL, electronic computer of the University of Lund, and therefore the calculational procedure given by Hubbard *et al.*¹⁰ has been slightly modified.

The values used for the specific heat, c_p , and $(\delta V/\delta T)_p$ for trioxane and tetroxane were $0.27 \text{ cal}\cdot\text{deg}^{-1}\cdot\text{g}^{-1}$ ¹¹ and $0.00166 \text{ ml}\cdot\text{deg}^{-1}\cdot\text{g}^{-1}$, respectively. The final over-all precision of the ΔE_c° mean values was estimated following the scheme presented by Bjellerup¹² with one modification. The quantity q_5 in these calculations stands for the energy of decomposition of nitric acid in the final bomb solution. The ratio s_5/q_5 has been estimated as 0.02. For trioxane an extra quantity was added to account for the uncertainty in the correction for polymer contamination of the sample.

Table 1. Results of combustion experiments.

$$\begin{aligned} \varepsilon^\circ(\text{calor}) &= 6771.07 \pm 0.34 \text{ cal}\cdot\text{deg}^{-1} \\ -\Delta E_c^\circ/M(\text{Mylar}) &= (5472.49 - 0.2524\cdot\text{RH}) \pm 0.79 \text{ cal}\cdot\text{g}^{-1} \\ -\Delta E_c^\circ/M(\text{Oil}) &= 10984.4 \pm 0.9 \text{ cal}\cdot\text{g}^{-1} \\ t_h &= 25.00^\circ\text{C} \end{aligned}$$

m'	m''	Δt	$\Delta E_{\text{dec}}^f(\text{HNO}_3)$	ΔE_Σ	$-\Delta E_c^\circ/M$
g	g	deg	cal	cal	cal·g ⁻¹
Trioxane ^a		M = 90.079			
	At RH = 40				
1.098265	0.093801	0.731178	1.06	3.69	4018.73
1.089191	0.096339	0.728232	0.89	3.68	4019.96
1.084967	0.094805	0.724361	1.04	3.65	4019.49
1.095908	0.092780	0.729287	0.96	3.68	4020.57
1.088574	0.094443	0.726276	1.04	3.66	4019.16
1.080522	0.096350	0.722863	1.03	3.64	4019.25
1.086618	0.095825	0.725941	1.03	3.66	4018.66
1.077164	0.094971	0.719755	1.03	3.63	4018.89
					$-\Delta E_c^\circ/M = 4019.34 \pm 0.23 \text{ * cal}\cdot\text{g}^{-1}$ ^a
Tetroxane		M = 120.106			
	At RH = 54				
1.177493	0.046266	0.73936	0.95	3.70	4015.83
1.176698	0.046174	0.73884	1.02	3.70	4016.08
1.178957	0.046610	0.74037	0.93	3.71	4014.95
1.179529	0.047349	0.74130	0.99	3.72	4015.70
1.179622	0.047452	0.74104	0.99	3.72	4013.29
1.183753	0.046051	0.74371	0.61	3.73	4014.70
1.180726	0.046259	0.74209	2.42	3.70	4014.38
1.181278 ^b	0.047000	0.741919	0.92	3.72	4013.87
1.177669 ^b	0.046233	0.739662	1.03	3.71	4014.91
0.916762 ^b	0.046293	0.583864	0.82	2.83	4013.07
					$-\Delta E_c^\circ/M = 4014.68 \pm 0.33 \text{ * cal}\cdot\text{g}^{-1}$
Trioxane polymer					
0.240811	0.365404	0.73791	0.86	1.93	3983.21
0.457552	0.285762	0.73609	0.88	2.30	3985.66
					$-\Delta E_c^\circ/M = 3984.4 \pm 1.2 \text{ cal}\cdot\text{g}^{-1}$

* The given uncertainties are the standard deviations of the mean.

^a Trioxane sample with 6.1 % polymer.

^b Second sample of tetroxane.

Table 2. Results of vaporization experiments. $t=25.0^{\circ}\text{C}$.

	Numbers of experiments	$G_{\text{adiab.}}^a$ $\mu\text{g}\cdot\text{sec}^{-1}$	$\Delta H_{\text{subl.}}(\text{obs})$ $\text{kcal}\cdot\text{mole}^{-1}$	$\delta\Delta H$ $\text{kcal}\cdot\text{mole}^{-1}$	$\Delta H_{\text{subl.}}$ $\text{kcal}\cdot\text{mole}^{-1}$
Trioxane	5	9.4097 ± 0.0115	13.506 ± 0.014	0.014 ± 0.016	13.520 ± 0.022 *
Trioxane ^b	5	—	13.54 ± 0.03	-0.02	13.52 ± 0.03
Tetroxane I	6	14.767 ± 0.019	18.796 ± 0.017	0.214 ± 0.014	19.010 ± 0.018
Tetroxane II	5	8.825 ± 0.016	18.833 ± 0.011	0.214 ± 0.014	19.047 ± 0.022

^a Amount vaporized per second.

^b Measured using the Wadsö calorimeter.

* The given uncertainties are the standard deviations of the mean.

Enthalpies of formation at 25.0°C for gaseous CO_2 and liquid water have been taken from Ref. 13.

Table 1 gives the results of the combustion experiments. No significant difference was found in the energies of combustion of the two samples of tetroxane and they were therefore treated as one series of measurements. The ΔE_c° values refer to the idealized combustion reaction in which all reactants and products are in their thermodynamic standard states at 25.0°C . The results from the vaporization measurements are summarized in Table 2. The two independently determined values for trioxane are in excellent agreement. Table 3 gives the standard energies, ΔE_c° , and enthalpies, ΔH_c° , of combustion for trioxane (corrected for polymer content) and tetroxane in the crystalline state together with enthalpies of sublimation, $\Delta H_{\text{subl.}}$, and derived enthalpies of formation, ΔH_f° , at 25.0°C .

DISCUSSION

In 1943 Walker and Carlisle³ reported an experimentally determined value for the "heat of combustion" of trioxane at 23°C . The value given was $356.7 \pm 0.9 \text{ kcal}\cdot\text{mole}^{-1}$, a figure that within the given limits of error may be taken as valid also for 25°C . This corresponds to an enthalpy of formation, $\Delta H_f^{\circ}(\text{c})$, for crystalline trioxane of $-130.4 \text{ kcal}\cdot\text{mole}^{-1}$, which is $5.6 \text{ kcal}\cdot\text{mole}^{-1}$ different from that of the present investigation, -124.84 . However, no details are given on experimental technique, neither was it explicitly stated whether corrections to standard states had been applied. The high volatility of trioxane necessitates very careful enclosure of the substance prior to ignition to prevent

Table 3. Results and derived data at 25.0°C . In $\text{kcal}\cdot\text{mole}^{-1}$.

	$\Delta E_c^{\circ} = \Delta H_c^{\circ}$	$\Delta H_f^{\circ}(\text{c})$	$\Delta H_{\text{subl.}}$	$\Delta H_f^{\circ}(\text{g})$
Trioxane	-362.26 ± 0.07^a	-124.84 ± 0.09^a	13.52 ± 0.04^b	-111.32 ± 0.12^a
Tetroxane	-482.19 ± 0.11	-167.27 ± 0.12	19.03 ± 0.05	-148.24 ± 0.16

^a The uncertainties given in this column are twice the final over-all standard deviations of the mean.

^b The uncertainties given in this column are the final over-all standard deviations of the mean.

loss of material to the gas phase after the weighing until the end of the equilibration period. A value that is as much as one per cent low might well be obtained if the proper precautions are not taken.*

Snelson and Skinner¹⁴ calculated the enthalpy of formation for gaseous trioxane to be -120.8 ± 1.5 kcal-mole⁻¹ apparently using the enthalpy of vaporization for liquid trioxane at its boiling point 115°C, 9.6 kcal-mole⁻¹, reported by Walker and Carlisle.

The data obtained in this work for gaseous trioxane and tetroxane lead to enthalpies of formation for the $-\text{CH}_2-\text{O}-$ groups of -37.11 and -37.06 kcal, respectively. In connection with the publication of recent work on acyclic compounds with "next-neighbour oxygens"¹⁵ a more detailed discussion of the results from this investigation will be given.

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* *Added in proof.* Dr. G. Pilcher, University of Manchester, kindly pointed out to us a value published in 1942 by M. Delépine and M. Badoche for " α -trioxymethylene" (*Compt. Rend.* **214** (1942) 777). Their figure for the enthalpy of combustion for crystalline trioxane is -362.30 kcal-mole⁻¹ (after correction to modern energy units).