

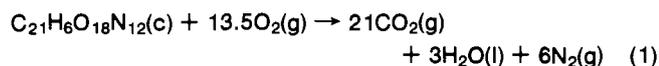
Enthalpy of Formation of 2,4,6-Tripcryltriazine

Edward E. Baroody* and George A. Carpenter

U.S. Naval Surface Weapons Center, Research Department, Naval Ordnance Station, Indian Head, Maryland 20640

The enthalpy of formation of 2,4,6-tripicryltriazine (TPTA) was determined by combustion calorimetry, using a platinum-lined rotating-bomb calorimeter. A mixture of TPTA and diethyl oxalate (DEO) was used to desensitize and ensure complete combustion of TPTA. The enthalpy of formation was determined to be $+70.87 \pm 1.68$ kcal/mol at 298.15 K.

The enthalpy of formation of 2,4,6-tripicryltriazine (TPTA) was determined by combustion calorimetry, using a platinum-lined rotating-bomb calorimeter. A mixture of approximately 40/60% of TPTA to diethyl oxalate (DEO) was burned in an oxygen atmosphere (30 atm pressure). After a series of preliminary runs on a Parr stationary adiabatic-bomb calorimeter, this ratio was selected to produce a smooth and clean combustion. Since TPTA was considered shock sensitive, the DEO also served as a desensitizer. The enthalpy of formation (298.15 K) was determined from the following idealized equation at 1 atm:



Experimental Section

Apparatus. The combustion experiments were carried out in a platinum-lined rotating-bomb calorimeter, built according to a design of the Bureau of Mines, Bartlesville, Okla. (6). The modifications to the original instrumentation with the basic procedure were as previously reported¹⁶ with the exception that the platinum resistance thermometer and Mueller bridge were replaced by a quartz crystal thermometer with a resolution of 0.0001 °C coupled to a digital clock recorder. With this arrangement, time and temperature could be recorded automatically at predetermined intervals throughout the run.

The thermometer-probe was calibrated (by Dymec Division, Hewlett Packard, Palo Alto, Calif.) against a reference thermometer in a variable-temperature bath. The probe was placed in a well-stirred temperature-controlled liquid bath. Use of stirred liquids as calibrating mediums with large volumes eliminated heat-transfer effects. The liquids used were alcohol at low temperatures, water at medium temperatures, and oil at high temperatures. The probe was connected to an oscillator, and its outputs were scanned and measured by a quartz thermometer. A strip chart recorder was used to verify stabilization of the baths at each temperature setting. Nine calibration temperatures were used, ranging from -80 to $+240$ °C in 40 °C steps. The calibration baths were monitored by a transfer standard calibrated against an NBS-certified platinum resistance thermometer and a Mueller bridge. The transfer standard was regularly checked for drift in a triplepoint cell and in a certified tin freezing-point standard, and drift against the freezing point of triple-distilled mercury. If excessive drift was noted, the transfer standard could be recalibrated against the certified thermometer. These checks, plus the short-term stability of the temperature-controlled baths, achieved a calibration accuracy of 0.02 °C

relative to NBS at all nine points. The internal volume of the rotating bomb was 0.346 l.

The density measurements of DEO were made with a 5-ml Gay-Lussac pycnometer calibrated with distilled water. DEO was distilled through a 14-in. glass bead column and collected on a water condenser. The complete apparatus was assembled at this station.

Procedure

TPTA and DEO mixtures were sealed in polypropylene bags resistant to organic halides. The bag was placed in a platinum crucible in the bomb. Ten cubic centimeters of distilled water was placed in the bomb that was assembled, purged, pressurized to 30 atm with oxygen, and then submerged in a weighed quantity of water into the calorimeter bucket, which, in turn, was placed in a constant-temperature jacket. When the temperature of the bucket reached a predetermined value calculated to obtain a final bucket temperature slightly below the jacket temperature of 25 °C, the mixture was ignited by a thread connected to a heated wire and polypropylene bag. Following ignition, the bomb was rotated to ensure a uniform final state of the products. The temperature was recorded at 1-min intervals 10 min before ignition and 25 min after ignition with predetermined time intervals for the rate of change in the temperature. The experimental results are listed in Table II.

Materials

The TPTA sample investigated was obtained from Dr. P. N. Hall, Naval Surface Weapons Center, White Oak, Md. (7). The compound was recrystallized from acetone and methanol solutions and filtered under heat and vacuum conditions to obtain a sample of high purity. Elemental analysis showed that the actual and theoretical formulas were in agreement within the limits of the apparatus.

Anal. Calcd for $\text{C}_{21}\text{H}_6\text{O}_{18}\text{N}_{12}$: C, 35.3; H, 0.85; O, 40.25; N, 23.6; mol wt, 714.35157. Found: C, 35.41; H, 0.91; O, 40.90; N, 22.78.

Diethyl Oxalate. The ester was a commercial grade distilled several times until the boiling point became constant at 105 °C at 55 mm pressure. An elemental analysis of the purified material was also performed. Results were in agreement with the theoretical formula within limits of the determination.

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{O}_4$: C, 49.30; H, 6.90; O, 43.79; mol wt, 146.14. Found: C, 49.72; H, 7.19; O, 43.45. The energy of combustion was $E_c^\circ/M = -4875.78 \pm 1.13$ cal/g (mean standard deviation for nine runs).

Benzoic Acid. NBS sample 39i was used to calibrate the calorimeter. The benzoic acid has a heat of combustion of 26.434 ± 0.003 abs kJ/g under certified conditions. Conversion to standard conditions (9) gives $E_c^\circ/M = -6312.96 \pm 0.72$ cal/g.

Polypropylene Film. Material was burned in the calorimeter and its energy of combustion determined at this station to be $E_c^\circ/M = -11083.14 \pm 1.66$ cal/g (mean and standard deviation for eight runs). Elemental analysis showed that the actual and

Table I. Density, Heat Capacity, and $(\partial E/\partial P)T$ for TPTA and Auxiliary Materials

	Density, g/ml	Cp, cal/(deg g)	$(\partial E/\partial P)T$, cal/(atm g)
TPTA	1.67 ^a	0.2 ^b	-0.006 ^b
DEO	1.08 ^c	0.466 ^d	-0.006 ^b
Polypropylene	0.9 ^e	0.315 ^b	-0.008 ^b
Thread	1.5 ^f	0.4 ^g	-0.007 ^h

^a Determined by Mrs. I. P. Mosher, NSW, Indian Head, Md. ^b Estimated.
^c Reference 8. ^d Reference 5. ^e Determined by authors. ^f Reference 11.
^g Reference 12. ^h Reference 9.

theoretical formulas were in agreement within the limits of the apparatus.

Anal. Calcd for C₃H₆: C, 85.63; H, 14.37; mol wt, 42.081.

Found: C, 85.39; H, 14.34.

The fuse used to ignite the materials was a commercial grade of cotton thread with an energy of combustion, $E_c^\circ/M = -4050$ cal/g (13) with an empirical formula of C₁H_{1.744}O_{0.884}.

Analytical. Complete combustions were evidenced by ir analysis, titration of the acid solution, and absorption of carbon dioxide on Ascarite. The gaseous reaction products were passed through a train of magnesium perchlorate and Ascarite to absorb water and carbon dioxide. The carbon dioxide recovery was 99.7% or better of the theoretical value of the runs tested. Gas samples were taken directly from the bomb without passing through any type of absorbent and were analyzed by ir spectra. There was no indication of gases other than CO₂, N₂, and O₂ (N₂ and O₂ cannot be detected by ir spectra). The NO₃ ion was reduced to ammonia by Devard's alloy distilled into excess standardized MCl. The total acidity of the bomb washings was determined by titration with NaOH after carbon dioxide had been removed by boiling, using phenolphthalein as an indicator.

Units of Measurements and Auxiliary Quantities. All data reported are based on the 1961 atomic weights (3) and the 1963 fundamental constants and definition of the thermodynamic

temperature scale and of the thermochemical calories; 1 cal = 4.184 (exactly) abs J (4).

The physical properties of the compound and auxiliary material are listed in Table I. The calorimeter was calibrated with benzoic acid, NBS sample 39i, and $\xi(\text{calor})$ was determined to be 4121.95 ± 0.58 cal/deg (mean and standard deviation for nine calibration experiments).

Results and Discussion

The enthalpies of formation of sensitive compounds by combustion have been determined by dissolving them in desensitizing compounds such as diethyl phthalate (DEP) and diethyl oxalate (7). TPTA in an atmosphere of oxygen alone burned too rapidly to control. At times it would react with metal parts in the calorimeter. The compound had to be burned with an auxiliary material to help desensitize and control the burning.

Several trial runs were conducted on TPTA with DEP, DEO, and other solvents in a Parr stationary adiabatic-bomb calorimeter to determine the best auxiliary material to use with TPTA, the proper weight ratios to approximate the heat released for initial temperature settings on the rotating bomb, and to test for ignitability and good combustion of TPTA mixtures. Such trial runs on a stationary bomb saved time and reduced damage in the event of a detonation.

The experimental results for nine combustion runs are given in Table II. All data reduction was performed on a digital computer (2). To correct for the heat of solution of CO₂ in acid solutions, the data of Rossini (10) were used. Heats of formation used were CO₂(g) = -94 051 cal/mol; H₂O(l) = -68 317.5 cal/mol(l) (14). The uncertainties assigned to gaseous carbon dioxide and liquid water are 0.011 and 0.0144, respectively (15).

Nomenclature

m = mass of (') compound, (') auxiliary material, (') polypropylene film, and (') fuse in g

n = number of moles of (') compound, (') auxiliary material, (') polypropylene film, and (') fuse

*n*ⁱ = initial number of moles of water in bomb

*t*_i = initial temperature of calorimeter, °C

Table II. Summary of Calorimetric Data for 2,4,6-Tripropyltriazine

	Run no.					
	44871	44873	44887	44888	44890	44891
<i>m</i> '(cpd), g	0.937377	0.851316	0.867709	0.809549	0.862530	0.841119
<i>m</i> '(DEO), g	1.091936	1.102389	1.417670	1.442634	1.426637	1.441193
<i>m</i> '''(polypropylene), g	0.064649	0.069653	0.071254	0.064389	0.055197	0.077509
<i>m</i> '''''(fuse), g	0.008597	0.008026	0.00816	0.009477	0.009577	0.009392
<i>n</i> (H ₂ O), mol	0.55605	0.55921	0.55544	0.56059	0.55981	0.55655
Δt_c , deg	2.1957	2.1561	2.5459	2.5130	2.5088	2.5694
Δt_{corr} , deg	0.02989	0.02781	0.02950	0.02543	0.02686	0.02923
$\xi(\text{calor})(-\Delta t_c)$, cal	-9050.57	-8887.34	-10494.07	-10358.46	-10341.15	-10590.94
$\xi^i(\text{cont})$, cal	-29.76	-29.26	-34.20	-34.10	-34.11	-34.66
$\xi^i(\text{cont})$, cal	1.23	1.14	0.82	0.94	1.03	0.91
ΔE_{ign} , cal	1.19	1.19	1.19	1.19	1.19	1.19
ΔE_{corr} , cal	13.38	12.82	15.27	15.06	15.29	15.33
$\Delta E_{dec}(\text{HNO}_3)$, cal ^a	25.73	30.75	27.71	26.08	26.74	27.68
<i>n</i> ' ΔE_c° (DEO), cal	-5324.03	-5374.99	-6912.23	-7033.95	-6955.95	-7026.93
<i>n</i> ''' ΔE_c° (polypropylene), cal	-716.51	-771.97	-789.72	-713.63	-611.76	-859.04
<i>n</i> ''''' ΔE_c° (fuse), cal	-34.82	-32.50	-33.05	-38.38	-38.79	-38.04
$\Delta E_c^\circ(\text{cpd})/M$, cal/g	-3161.45	-3161.20	-3167.29	-3166.22	-3158.55	-3158.13

Averages: $\Delta E_c^\circ(\text{cpd})/M$, cal/g, -3162.14 ± 1.60 ; ^b $\Delta E_c^\circ(\text{cpd})$, kcal/mol, -2258.88 ± 1.68 ; $\Delta H_c^\circ(\text{cpd})$, kcal/mol, -2250.88 ± 1.68 ; $\Delta H_f^\circ(\text{cpd})$, kcal/mol, $+70.87 \pm 1.68$

^a The heat released from the TPTA/DEO mixtures was determined in a separate experiment. The average value for these runs is 0.74 cal that is included in the HNO₃ corrections. ^b Standard deviation of the mean. Uncertainty corrections for all auxiliary materials are included as well as the assigned uncertainty values for CO₂ and H₂O.

t_f = final temperature of calorimeter, °C
 t_h = reference temperature to which combustion reaction is referred (25 °C)
 Δt_{corr} = rise in temperature of calorimeter because of thermal leakage of outer jacket
 $\Delta t_c = t_f - t_i + \Delta t_{\text{corr}}$
 $\xi(\text{calor})$ = energy equivalent of calorimeter, cal/deg
 $\xi(\text{cont})$ = energy equivalent of contents, cal/deg ($\xi^i(\text{cont})(t_i - 25) + \xi^f(\text{cont})(25 - t_f + \Delta t_{\text{corr}})$ where $\xi^i(\text{cont})$ and $\xi^f(\text{cont})$ are energy equivalents of contents before and after combustion, respectively)
 ΔE_{ign} = energy released because of ignition, cal
 E_c°/M = standard energy of idealized combustion reaction, cal/g
 ΔE_{corr} = energy reduction to standard states, cal (10, 13)
 $\Delta E_{\text{dec}}(\text{HNO}_3)$ = energy released from formation of nitric acid, cal
 ΔE_c° = standard energy of idealized combustion reaction, cal/mol
 ΔH_c° = standard heat of combustion of compound at constant pressure, kcal
 ΔH_f° = enthalpy of formation of TPTA, kcal/mol

Literature Cited

- (1) Baroody, E. E., Carpenter, G. A., Robb, R. A., Zimmer, M. F., *J. Chem. Eng. Data*, **13** (2), 215 (1968).
- (2) Baroody, E. E., Wynne, J., Zimmer, M. F., U.S. Naval Propellant Plant, Naval Weapons Rep. 8686, Tech. Rep. 154 (1964).
- (3) Cameron, A. E., Wichers, E., *J. Am. Chem. Soc.*, **84**, 4175 (1962).
- (4) Cohen, E. R., DuMond, J. W. M., *Rev. Mod. Phys.*, **37**, 537 (1965).
- (5) Dornalski, E. S., National Bureau of Standards, Gaithersburg, Md., private communication, Jan 1970.
- (6) Good, W. D., Scott, E. W., Waddington, G., *J. Phys. Chem.*, **63**, 1080 (1959).
- (7) Hall, P. N., Naval Surface Weapons Center, White Oak, Md., private communication, Nov 1974.
- (8) "Handbook of Chemistry and Physics", 43d ed, Chemical Rubber Co., Cleveland, Ohio, 1961-1962, p 1165.
- (9) Hubbard, W. N., Scott, D. W., Waddington, G., in "Experimental Thermochemistry", F.D. Rossini, Ed., Interscience, New York, N.Y., 1956, Chapter 5, pp 75, 128.
- (10) Rossini, F. D., ref 9, Vol. I, 1962, pp 90, 107.
- (11) Rossini, F. D., ref 9, p 81.
- (12) Rossini, F. D., ref 9, p 93.
- (13) Skinner, H. A., ref 9, Vol. II, pp 25-28.
- (14) Wagman, D. D., Kilpatrick, J. E., Taylor, W. J., Pitzer, S. P., Rossini, F. D., *J. Res. Natl. Bur. Stand.*, **34**, 143 (1945).
- (15) Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., *Natl. Bur. Stand. (U.S.), Tech. Note* 270-3, 22 (1968).
- (16) Zimmer, M. F., Baroody, E. E., Schwartz, M., McAllister, M. P., *J. Chem. Eng. Data*, **9**, 527 (1964).

Received for review March 20, 1975. Accepted February 23, 1976.

Liquid Diffusivities in Normal Paraffin Solutions

Walter Hayduk* and Sotirios Ioakimidis

Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

An apparatus was constructed for measuring diffusivities in miscible liquid solutions which has all the essential features of a diaphragm cell but with two additional features. The diaphragm is composed of uniform stainless steel precision capillaries imbedded in a Teflon plug. As a result, the physical system for the diffusion process is clearly defined and can be mathematically described so that the diffusion cell requires no prior calibration. The diffusion cell was also designed for operation in the transient mode when the transfer rates are much higher than those obtained at steady state. As a result diffusivities can be measured in relatively short times. Diffusivities of tetracosane and dotriacontane (C₂₄ and C₃₂) at low concentrations were measured in hexane and octane at 25 °C. Diffusivities were also measured at 25 °C for dilute solutions of cyclohexane in carbon tetrachloride and dodecane in hexane. Data from the literature, along with those reported here, were used to construct a viscosity-diffusivity map for normal paraffin solutes of carbon content from 1 (methane) to 32 (dotriacontane).

In the absence of strong molecular interactions, diffusivities of a substance dissolved in a number of different solvents tend to diminish with increasing solvent viscosity. This relation may usually be represented by a straight line on a log-log plot of diffusivity vs. solvent viscosity as expressed by Hayduk and Cheng (11) in the form:

$$D = A\mu^{-B} \quad (1)$$

The slope, B , of the log D -log μ relation usually increases for diffusing substances of larger molecular size. Similarly, diffusivities of a number of substances in the same solvent tend

to decrease with increasing solute molecular size or molar volume. Both of the above relations can be observed for solutions of normal paraffins. It is possible to summarize the above generalizations for normal paraffins by way of a diffusivity-viscosity map. While experimental data, as reported in the literature for all the possible solute-solvent combinations, are far from complete, enough data are available to construct the viscosity-diffusivity relationship by interpolation. While at least one attempt has been made to quantitatively describe the diffusivity behavior in liquid n -paraffins, Shieh and Lyons (22), it appears of questionable value for application to gaseous or solid solutes using parameters such as liquid density and liquid viscosity. The diffusivity-viscosity map can be used directly, however, to estimate most probable diffusivities at 25 °C in any dilute normal paraffin solution.

A diaphragm cell consisting of uniform capillaries was first reported by Ross and Hildebrand (20) for use at steady state in measuring diffusivities of gases dissolved in carbon tetrachloride. The capillaries consisted of holes drilled 1 mm in diameter in a 0.9 cm thick plate. A subsequent variation of the diaphragm, as reported by Nakanishi et al. (19), consisted of a bundle of hypodermic tubes held together in a close-packed formation by a solder plug. In both cases, diffusion occurred from a gas-saturated liquid layer above the plate to a reservoir of initially deaerated liquid below the plate, while the rate of diffusion was measured volumetrically by observing the change in the enclosed volume of gas held at constant pressure above the liquid. Malik and Hayduk (16) described a steady-state volumetric method for measuring diffusivities of gases in liquids utilizing a column of liquid solvent confined in a single glass capillary.

The steady-state diaphragm cell method was adapted for elevated temperatures by Sanni and Hutchison (21). The cells were actually used in the temperature range from 25 to 60 °C. Provision was made for preheating fresh solvent, replacing the