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Enthalpies of Formation of Bitetrazole and Bis(2,2,2-trinitroethyl)formal

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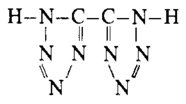
The enthalpies of formation of bitetrazole and bis(2,2,2-trinitroethyl)formal were determined by combustion calorimetry, using a platinum-lined rotating-bomb calorimeter. Mixtures of methanol/bitetrazole and diethyl oxalate/bis(2,2,2-trinitroethyl)formal were used to desensitize and ensure complete combustion of the compounds investigated. The enthalpies of formation were determined to be +127.08 ± 0.23 and -96.40 ± 0.64 kcal/mol, respectively, for bitetrazole(c) and bis(2,2,2-trinitroethyl)formal(c).

The combustions of bitetrazole and bis(2,2,2-trinitroethyl)formal (TEFO) were carried out in oxygen at a pressure of 30 atm. The enthalpies of formation were calculated in their standard states at 25 °C and 1 atm from the following equations of the idealized reactions:

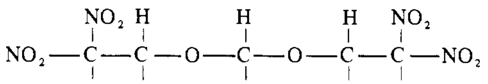
$$C_2H_2N_8(c) + 2.5O_2(g) \rightarrow 2CO_2(g) + H_2O(l) + 4N_2(g$$

$$C_5H_6O_{14}N_6(c) \rightarrow 5CO_2(g) + 3H_2O(l) + 3N_2(g) + 0.5O_2(g)$$

Both compounds are sensitive explosives that were burned in solution of desensitive materials. To achieve clean combustions without explosions, approximately 37%/63% methanol/bitetrazole and 32%/68% diethyl oxalate/TEFO mixtures by weight were used. Bitetrazole and TEFO have the following structural formulas.



bitetrazole



$$NO_2-\underset{NO_2}{\overset{NO_2}{C}}-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{NO_2}{\overset{NO_2}{C}}-NO_2$$

TEFO

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.[8] The modifications to the original instrumentation with the basic procedure were as previously reported[19] 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 counting instrument. 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 monitered 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 triple-point 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.

Procedure. Bitetrazole and TEFO were mixed with methanol and diethyl oxalate (DEO), respectively, in a polypropylene bag and sealed. The quantities burned gave a temperature rise in the calorimeter of approximately 1.8–2.0 °C. The bags were placed in a platinum crucible in the bomb. Ten milliliters 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 in the calorimeter bucket, which 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 for 25 min after ignition at a predetermined time interval for the rate of change in temperature.

Materials. Bitetrazole and bis(2,2,2-trinitroethyl)formal were prepared at the Naval Surface Weapons Center, White Oak, Md.[1] They were recrystallized several times, chemically analyzed, checked by gas chromatography and nuclear magnetic resonance, and found to have a purity of better than 99%.[1]

Benzoic acid, NBS sample 39i, was used to calibrate the calorimeter. The benzoic acid had a heat of combustion of 26.434 ± 0.003 abs kJ/g under certified conditions. Conversion to standard conditions gives $\Delta E°_c/M$ = -6312.96 ± 0.72 cal/g.[12]

Polypropylene film was burned in the calorimeter and its energy of combustion determined to be $\Delta E°_c/M$ = -11 083.14 ± 1.66 cal/g (mean and standard deviation for eight runs). Elemental analyses showed that the actual and theoretical formulas were in agreement within the limits of the determination.

The fuse used to ignite the materials was a commercial grade of cotton thread with an energy of combustion of $\Delta E°_c/M$ = -4050 cal/g[16] and with an empirical formula of $C_1H_{1.744}O_{0.884}$.

Diethyl oxalate was a commercial grade distilled several times until the boiling point became constant at 105 °C and at 55 mm pressure. The density measurements of DEO were made with a 5-mL Gay-Lussac pycnometer calibrated with distilled water.

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

	density, g/mL	C_p, cal/(deg g)	$(\partial E/\partial P)T$, cal/(atm g)
bitetrazole	1.28[a]	0.21[b]	−0.006[b]
TEFO	1.69[a]	0.21[b]	−0.006[b]
DEO	1.08[c]	0.466[d]	−0.006[b]
thread	1.5[e]	0.4[f]	−0.007[g]
polypropylene film	0.9[a]	0.315[b]	−0.008[b]
methanol	0.796[h]	0.566[i]	−0.006[b]

[a] Determined at NSWC, Indian Head, Md. [b] Estimated. [c] Reference 9. [d] Reference 7. [e] Reference 14. [f] Reference 15. [g] Reference 16. [h] Reference 10. [i] Reference 11.

DEO was distilled through a 14-in. glass bead column and collected on a water condenser. The complete apparatus was assembled at this station. An elemental analyses of the purified material was also performed. Results were in agreement with the theoretical formula within limits of the determination. The energy of combustion was $\Delta E°_c/M = -4875.78 \pm 1.13$ cal/g (mean standard deviation for 9 runs).

Methanol, a commercial grade, was purified by distillation and the elemental composition of the material was checked after several distillations. This procedure was continued until the elemental composition agreed with the theoretical values within experimental error. The energy of combustion was determined at this laboratory to be $\Delta E°_c/M = -5412.24 \pm 1.15$ cal/g and its enthalpy of formation was determined to be −56.97 ± 0.04 kcal/mol. This is in good agreement with the literature value of −57.01 ± 0.05 kcal/mol.[6]

***Analytical Procedure*.** Complete combustions were evidenced by IR analyses, titration of the acid solutions, 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 on the runs tested. Gaseous 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 CO_2 (N_2 and O_2 cannot be detected by IR spectra). The NO_3^- ion was reduced to ammonia by Devard's alloy distilled into excess standardized HCl. 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[4] and 1963 fundamental constants and definition of the thermodynamic temperature scale and of the thermochemical calories; 1 cal = 4.184 (exactly) absolute J.[5]

The physical properties of the compounds and auxiliary materials are listed in Table I. The calorimeter was calibrated with benzoic acid, NBS sample 39i, and ξ(calor) was determined to be 4121.95 ± 0.58 cal/deg (mean and standard deviation for nine calibration experiments).

Results and Discussion

In previous work conducted at this laboratory, sensitive compounds were burned by dissolving them in desensitizing compounds.[2] Several trial runs were conducted on bitetrazole and TEFO with several desensitizers in a Parr stationary adiabatic-bomb calorimeter before methanol and diethyl oxalate were chosen to burn with bitetrazole and TEFO, respectively. A number of mixtures, using different weight ratios of compounds to desensitizers, were burned in the adiabatic-bomb calorimeter to determine initial temperature settings for the isoperibol rotating-bomb calorimeter and to test for ignitability and combustibility of the bitetrazole and TEFO mixtures. Since the adiabatic-bomb calorimeter is less expensive and easier to operate, the trial runs save time and reduce damage to the equipment in the event of a detonation.

The experimental results for both compounds are given in Tables II, III, and IV. All data reduction was performed on a digital computer.[3] To correct for the heat of solution of CO_2 in acid solutions, the data of Rossini[13] were used. Heats of formation used were $CO_2(g) = -94\,051$ cal/mol and $H_2O(l) = -68\,317.5$ cal/mol.[17] The uncertainties assigned to gaseous carbon dioxide and liquid water are 0.011 and 0.0144 kcal/mol, respectively.[18]

Glossary

m	mass of (′) compound, (″) auxiliary material, (‴) polypropylene film, and (⁗) fuse in grams
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
t^f	final temperature of calorimeter, °C
t^h	reference temperature to which combustion reaction is referred (25 °C)
Δt_{cor}	rise in temperature of calorimeter because of thermal leakage of outer jacket

Table II. Summary of Calorimetric Data for Bitetrazole

	run no.					
	43435	43436	43438	46637	46638	46640
m'(compd), g	1.332880	1.366096	1.331249	1.479027	1.559859	1.594475
m''(methanol), g	0.770251	0.920705	0.867669	0.778496	0.699575	0.636707
m'''(polypropylene), g	0.061177	0.069353	0.065490	0.053796	0.054557	0.067807
m''''(fuse), g	0.006976	0.007386	0.007556	0.007436	0.007176	0.008652
$n^i(H_2O)$, mol	0.56059	0.61338	0.56712	0.55157	0.55810	0.54781
$\Delta t_c(t_f - t_i - \Delta t_{cor})$, deg	2.0884	2.3293	2.2247	2.1774	2.1263	2.1098
Δt_{cor}, deg	0.0256	0.0288	0.0284	0.0250	0.0243	0.0252
$\xi(\text{calor})(-\Delta t_c)$, cal	−8608.28	−9601.26	−9170.10	−8975.13	−8764.50	−8696.49
ξ^i(cont), cal	−27.98	−33.42	−30.27	−30.18	−28.75	−27.87
ξ^f(cont), cal	0.76	0.71	0.96	2.15	1.12	0.86
ΔE_{ign}, cal	1.19	1.19	1.19	1.19	1.19	1.19
ΔE(cor std states), cal	10.52	11.74	10.92	11.09	11.24	11.02
$\Delta E_{dec}(HNO_3)$,[a] cal	16.13	20.22	20.83	19.21	17.17	27.73
$n''\Delta E°_c$(methanol), cal	−4178.47	−4983.00	−4695.97	−4213.33	−3786.21	−3445.96
$n'''\Delta E°_c$(propylene), cal	−678.03	−768.65	−725.83	−596.23	−604.66	−751.51
$n''''\Delta E°_c$(fuse), cal	−28.25	−29.91	−30.60	−30.11	−29.06	−35.04
$\Delta H°_c(\text{compd})/M$, cal/g	−2794.03	−2796.67	−2790.77	−2794.62	−2784.66	−2792.61

[a] The heat released from the methanol/bitetrazole mixtures was determined in a separate experiment and is included in the HNO_3 corrections.

Table III. Summary of Calorimetric Data for Bis(2,2,2-trinitroethyl)formal

	run no.								
	44909	44911	44921	44923	44924	44925	43426	43427	43428
m'(compd), g	1.689933	1.824970	1.901951	1.928606	1.890057	1.886249	2.024529	1.883487	1.799713
m''(diethyl oxalate), g	0.882725	0.867524	0.889606	0.875510	0.923717	0.876726	0.874329	0.878708	0.901175
m'''(polypropylene film), g	0.064459	0.064549	0.066010	0.059711	0.064739	0.063764	0.068647	0.062648	0.067176
m''''(fuse), g	0.008716	0.008186	0.007886	0.007611	0.007856	0.007696	0.007236	0.007806	0.007996
$n^{i}(H_2O)$, mol	0.5634	0.5576	0.5538	0.5621	0.55880	0.58809	0.55511	0.55510	0.56203
$\Delta t_c(t_f - t_i - \Delta t_{cor})$, deg	1.8674	1.9013	1.9576	1.9375	1.9948	1.9347	1.9907	1.9322	1.9351
Δt_{cor}, deg	0.0243	0.0288	0.0314	0.0272	0.02806	0.0286	0.0300	0.0246	0.0266
ξ(calor)($-\Delta t_c$), cal	−7697.33	−7837.06	−8069.13	−7986.28	−8222.47	−7974.74	−8205.57	−7964.43	−7976.38
ξ^{i}(cont), cal	−25.52	−25.60	−26.46	−26.48	−27.13	−27.34	−28.11	−26.18	−26.45
ξ^{f}(cont), cal	0.88	0.66	0.86	0.86	0.85	0.47	1.63	0.54	0.53
ΔE_{ign}, cal	1.19	1.19	1.19	1.19	1.26	1.19	1.27	1.27	1.27
ΔE(cor std states), cal	14.72	15.25	15.70	15.76	15.90	15.82	16.19	15.15	15.40
$\Delta E_{dec}(HNO_3)$,[a] cal	18.11	15.78	18.52	17.83	19.90	19.21	19.90	19.21	17.83
$n''\Delta E^\circ_c$(diethyl oxalate), cal	−4303.96	−4229.85	−4337.61	−4268.78	−4503.83	−4274.71	−4263.03	−4284.38	−4393.92
$n'''\Delta E^\circ_c$(polypropylene film), cal	−714.41	−715.40	−731.60	−661.78	−717.51	−706.71	−760.82	−694.34	−744.52
$n''''\Delta E^\circ_c$(fuse), cal	−35.29	−33.15	−31.94	−30.82	−31.82	−31.17	−29.31	−31.61	−32.38
ΔE°_c(compd)/M, cal/g	−1559.48	−1563.07	−1555.94	−1564.21	−1566.03	−1565.84	−1552.07	−1563.41	−1554.59

[a] The heat released from the TEFO/DEO mixtures was determined in a separate experiment and is included in the HNO_3 corrections.

Table IV. Summary of Bitetrazole and TEFO

averages	bitetrazole	TEFO
ΔE°_c(compd)/M, cal/g	−2792.19 ± 1.72[a]	−1560.50 ± 1.73[a]
ΔE°_c(compd), kcal/mol	−385.56 ± 0.23	−583.84 ± 0.64
ΔH°_c(compd), kcal/mol	−383.52 ± 0.23	−578.81 ± 0.64
ΔH°_f(compd), kcal/mol	+127.08 ± 0.23	−96.40 ± 0.64

[a] Standard deviation of the mean. Uncertainty corrections for all auxiliary materials are included as well as the assigned uncertainty values for CO_2 and H_2O.

Δt_c	$t_f - t_i + \Delta t_{cor}$
ξ(calor)	energy equivalent of calorimeter, cal/deg
ξ(cont)	energy equivalent of contents, cal/deg, $\xi^{i}(\mathrm{cont})(t_i - 25) + \xi^{f}(\mathrm{cont})(25 - t_f + \Delta t_{cor})$ where ξ^{i}(cont) and ξ^{f}(cont) are energy equivalents of contents before and after combustion, respectively
ΔE_{ign}	energy released because of ignition, cal
$\Delta E^\circ_c/M$	standard energy of idealized combustion reaction, cal/g
ΔE(cor std state)	energy reduction to standard states, cal[13,16]
$\Delta E_{dec}(HNO_3)$	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 bitetrazole and TEFO, kcal/mol

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Vapor–Liquid Equilibria: Systems Methyl Ethyl Ketone–*p*-Xylene and Chlorobenzene–*p*-Xylene

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Vapor–liquid equilibrium data have been measured for the binary systems methyl ethyl ketone–*p*-xylene and chlorobenzene–*p*-xylene, at 685 mmHg pressure. The activity coefficients have been evaluated taking into consideration the vapor-phase nonideality. The *t–x–y* data have been subjected to a thermodynamic consistency test and the activity coefficients have been correlated by the Wilson equation.

Introduction

In continuation with our attempts to separate a *p*-xylene and *m*-xylene mixture by azeotropic distillation techniques, the vapor-liquid equilibria of the systems methyl ethyl ketone–*p*-xylene and chlorobenzene–*p*-xylene have been determined at 685 mmHg pressure.

Experimental Section

p-Xylene "Labchem" grade, obtained from E. Merck, and chlorobenzene, supplied by M/s. Sarabhai M. Chemicals, were purified by repeatedly shaking with concentrated sulfuric acid until the acid layer was no longer colored. These were washed with water, alkali, and water and then dried over anhydrous calcium chloride. Methyl ethyl ketone, supplied by M/s. B.D.H. Chemicals, was purified by the bisulfite method. All the liquids purified by chemical methods were distilled in a 30-mm glass column packed with 10-mm Raschig rings to a height of 1 m. The column was operated at total refulx for 30 min. The low boiling impurities were drawn off at a very low rate as rejects. When the desired boiling temperature was reached and remained constant for 15 min, the fraction was collected, while the column was operated at nearly total reflux. The physical properties of the materials used are listed in Table I.

Apparatus and Analytical Procedure

A vapor-recirculation type equilibrium still described by Brown (*2*, *3*) was used to study the vapor-liquid equilibrium. The still was operated for 3 h after recirculation was stabilized. A mercury-in-glass thermometer with an accuracy of ±0.1 °C calibrated against vapor pressure measurements was used for temperature measurements. The pressure was maintained at 685 ± 0.5 mmHg. The pressure was measured with a precision of ±0.1 mm. After the attainment of equilibrium, the vapor and liquid samples were withdrawn without disturbing the operation of the still.

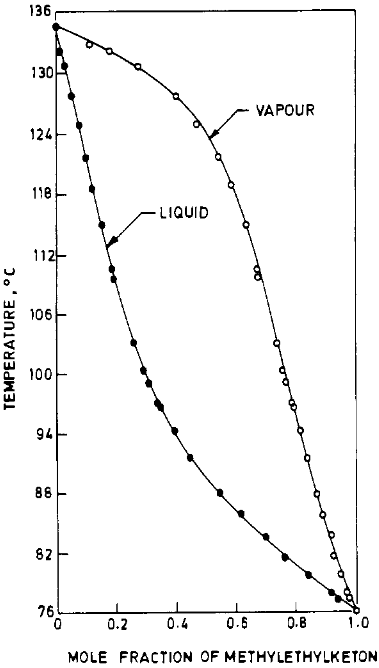

Figure 1. Boiling point-composition diagram for the methyl ethyl ketone–*p*-xylene system.

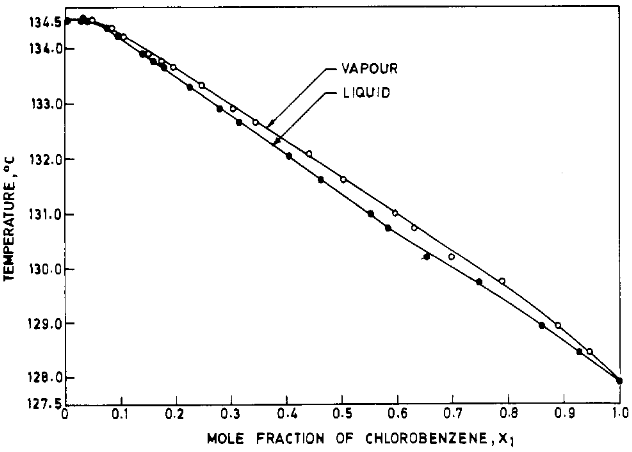

Figure 2. Boiling point-composition diagram for the chlorobenzene–*p*-xylene system.

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