Enthalpies of Formation and Calculated Detonation Properties of Some Thermally Stable Explosives

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As part of a study of thermally stable explosives, the heats of combustion and standard enthalpies of formation of 22 experimental organic explosives and of one standard explosive, TNT, were determined. The results of these measurements, together with the reported crystal densities, were used to calculate the detonation velocities and pressures by two different methods. The calculated velocities were compared with experimental velocities where suitable values of the latter were available.

The properties of a number of thermally stable explosives are being studied at the Los Alamos Scientific Laboratory. Among the properties of interest are the detonation velocity and pressure and the heat of explosion. These can be calculated with reasonable accuracy by any of several methods if the heat (enthalpy) of formation and density of the explosive are known. The velocity and pressure are not sensitive functions of the heat of formation, and usually one simply estimates this quantity by some semiempirical method. In some cases, however, this can lead to significant errors, and we therefore decided to obtain experimental values for the compounds of interest. High-precision values were not required, nor were they justified in terms of the probable purity of the samples; therefore, commercial equipment capable of giving a standard deviation of about 0.1% in the heat of combustion was used. The results of these measurements and of the detonation calculations are presented in this paper.

Experimental

Apparatus. The combustion experiments were carried out in a stationary-bomb calorimeter having an automatically controlled adiabatic jacket (Parr Instrument Co. Model 1241). The oxygen bomb used was a Parr Model 1104B high-pressure bomb, which had an internal volume of 250 ml. The temperatures of the bucket and jacket were measured with Parr Model 1622 mercury-in-glass thermometers (smallest graduation 0.01°C), which were calibrated by Parr at half-degree intervals from 24° to 30°C by comparison with a platinum resistance thermometer certified by the National Bureau of Standards. With these thermometers the temperatures could be measured with a resolution of 0.001°C.

Procedure. An approximately 1-g sample of the explosive was pressed to form a coherent pellet either $\frac{3}{8}$ or $\frac{1}{2}$ in. in diameter. The pellet was weighed on an ordinary analytical balance in the stainless steel or platinum–rhodium crucible in which it was to be burned. The weight of the pellet was corrected to vacuum. A 10-cm piece of Parr fuse wire (No. 45C10) was weighed, attached to the bomb electrodes, and bent down into firm contact with the upper surface of the pellet. A measured quantity of water, either 1 or 5 ml, was placed in the bomb which was then assembled, purged, pressurized to 30 atm with oxygen, and tested for leaks by submersion in trichlorotrifluoroethane. The bomb was then placed in a volumetrically measured quantity of water in the calorimeter bucket, which was in turn placed in the adiabatic jacket. When the automatic control of the jacket had brought the temperature of the jacket to within 0.003°C of the temperature of the water in the bucket (about 25°C) and both temperatures had been constant for at least 3 min, the initial temperature of the bucket was recorded and the charge ignited. When the two temperatures were again within 0.003°C of each other and had been constant for at least 3 min (approximately 20 min after ignition), the final temperature of the bucket was recorded. Corrections for the temperature of the emergent stem were made.

Caution. Although none of the explosives studied showed any tendency to detonate upon ignition in the combustion bomb, they must be considered hazardous materials. While pressing the pellets the operator was protected from possible accidents by a steel shield surrounding the press.

Analysis. After thermal equilibrium was attained, the gases in the bomb were released at a rate of 200 to 300 ml/min through an absorption-combustion train consisting of an Anhydrone–P_2O_5 absorber; an Ascarite absorber; a tube packed with CuO heated to 650°C; a second Anhydrone–P_2O_5 absorber; a second Ascarite absorber; a buffer absorber charged with P_2O_5, Anhydrone, and Ascarite; and a flow meter. The amount of CO in the products of combustion was calculated from the increase in weight of the second Ascarite absorber.

The interior and contents of the bomb were washed with distilled water, and the washings were divided into two equal portions. One portion was titrated with standard NaOH solution, with methyl orange as indicator, to determine the total of the nitric and nitrous acids formed. The other portion was added to a solution of nitric acid, which had been brought to an end-point with standard $KMnO_4$ solution, and titrated with the standard permanganate to determine the amount of nitrous acid formed.

The pieces of fuse wire remaining attached to the electrodes and any loose pieces found in the bomb were weighed to determine the amount of fuse wire burned. The heat of combustion of the fuse wire is given by Parr as 1400 cal/g (1 cal = 4.184 J).
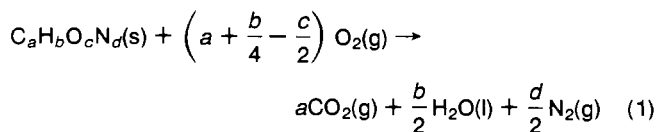
The crucible was dried in an oven, weighed, heated in the flame of a gas burner, and reweighed. The loss in weight of the crucible was taken to be the weight of residual carbon formed in the combustion.

Materials. Most of the explosives included in this study were synthesized at Los Alamos or at the Naval Surface Weapons Center, White Oak, Md. Exceptions are the TNT, which was obtained from Army sources and repurified here; the TACOTS, which originated at Du Pont; and the BTF, which was synthesized for the Lawrence Livermore Laboratory, Livermore, Calif., by Aldrich Chemical Co. The chemical names of the explosives, their abbreviations, and the physical properties used in the conversion of the measured energies of combustion to standard conditions are presented in Table I.

Elemental analyses of each of these explosives gave results in agreement with the empirical formula within the limits of accuracy of the determination. Nuclear magnetic resonance spectra of all the explosives except TATB and BTF were recorded, and none gave evidence of any impurities. Levels of impurity are probably below 1%, except for TATB.

The TATB contained about 0.2% chlorine by weight, which implies that the sample contained 1.4% by weight of the known impurity 1,3-diamino-2-chloro-4,6-dinitrobenzene, $C_6H_6N_5O_4Cl$.

Bomb reaction. The idealized equation of the bomb reaction is

$$C_aH_bO_cN_d(s) + \left(a + \frac{b}{4} - \frac{c}{2}\right) O_2(g) \rightarrow$$

$$aCO_2(g) + \frac{b}{2}H_2O(l) + \frac{d}{2}N_2(g) \quad (1)$$

Calibration of calorimeter. The calorimeter was calibrated by combustion of samples of NBS standard benzoic acid 39i and of Parr benzoic acid 3404, 3413, and 3414. No significant difference was found between the results obtained with the NBS and Parr samples. At various times during the course of the measurements on the explosives, seven calibrations were carried out with 0.2-g samples, 15 with 0.4-g samples, 41 with 0.5- to 0.6-g samples, and eight with 1.0-g samples. Also, since no corrections were applied for electrical energy of ignition, heat of stirring, or heating by the thermistor probe in the bucket (used to control the jacket temperature), five blank runs were made. All these data were used to determine the constants A and B in a least-squares fit to the equation

$$wt_{BA} = \frac{A + B \cdot \Delta t - \Delta E_a - \Delta E_w + \Delta E_c}{\Delta E_{BA}} \quad (2)$$

where wt_{BA} is the weight of the benzoic acid sample used, ΔE_{BA} is the quantity of heat evolved in the combustion of 1 g of benzoic acid under actual bomb conditions, Δt is the measured temperature rise of the calorimeter, ΔE_a is the calculated energy released by the formation of nitric acid, ΔE_w is the energy released by combustion of the fuse wire, and ΔE_c is the energy that would be released by combustion of the residual carbon (taken to be 7930 cal/g) (17). ΔE_c was significant only for the 0.2-g samples, which left about 0.1 mg of carbon. The value found for A was −8.8 cal with a standard

deviation of 1.2 cal. This term affords a composite correction for the energies mentioned above for which separate corrections were not made. The calculated value of B was 2624.6 cal/K, which includes the energy equivalent of the calorimeter and its contents (ignoring the 0.01% variation resulting from differences in sample weights) together with a correction for the loss of energy resulting from the lag of the jacket temperature behind that of the calorimeter.

Calculations

The calorimeter calibration constants A and B were used to calculate $\Delta E_c^\circ/M$ in cal/g for each explosive sample from the equation

$$-\Delta E_c^\circ/M =$$

$$\frac{A + (B + \delta) \cdot \Delta t - \Delta E_a - \Delta E_w + \Delta E_c + \Delta E_{co} - W}{m} \quad (3)$$

where δ is the increase in energy equivalent of the bomb contents over that existing during the calibration experiments, ΔE_{co} is the energy which would be released by combustion of the residual CO (taken to be 2415 cal/g) (17), W is the correction to standard states calculated by the standard procedure (5), m is the weight of the sample of explosive, and the other symbols have the same meanings as given for Equation 2. Results obtained from the computer program used to calculate the values of A and B indicate that the effective uncertainty (15) of the energy equivalent of the calorimeter in using Equation 3 is from 0.05 to 0.06% for the values of Δt produced by combustion of the explosives.

The standard enthalpy of combustion of the explosive in cal/mol was calculated for each sample by use of the equation

$$\Delta H_c^\circ = \Delta E_c^\circ + 592.47 \left(\frac{d}{2} - \frac{b}{4} + \frac{c}{2}\right) \quad (4)$$

where b, c, and d are subscripts in the formula $C_aH_bO_cN_d$ of the explosive.

Table I. Explosives and Their Properties

Name	Empirical formula	Abbrev	Density, g/ml	Heat capacity,[a] cal/deg g	$(\partial E/\partial P)_T$,[a] cal/atm g
3-Picrylamino-1,2,4-triazole	$C_8H_5O_6N_7$	PATO	1.94	(0.3)	(−0.007)
2,6-bis(Picrylamino)-3,5-dinitropyridine	$C_{17}H_7O_{16}N_{11}$	PYX	1.77	(0.3)	(−0.007)
2,4,6-Tripicryl-s-triazine	$C_{21}H_6O_{18}N_{12}$	TPT	1.67	(0.3)	(−0.007)
3,3′-Diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl	$C_{12}H_6O_{12}N_8$	DIPAM	1.79	0.25	(−0.007)
2,2″,4,4′,4″,6,6′,6″-Octanitro-m-terphenyl	$C_{18}H_6O_{16}N_8$	ONT	1.80	(0.3)	(−0.007)
1,4,5,8-Tetranitronaphthalene	$C_{10}H_4O_8N_4$	TNN	1.80	(0.3)	(−0.007)
2,2′,4,4′,6,6′-Hexanitrobiphenyl	$C_{12}H_4O_{12}N_6$	HNBP	1.74	(0.3)	(−0.007)
2,2′,4,4′,6,6′-Hexanitrostilbene	$C_{14}H_6O_{12}N_6$	HNS	1.74	0.23	(−0.007)
2,2′,2″,4,4′,4″,6,6′,6″-Nonanitroterphenyl	$C_{18}H_5O_{18}N_9$	NONA	1.78	0.23	(−0.007)
2,2′,2″,2‴,4,4′,4″,4‴,6,6′,6″,6‴-Dodecanitroquatraphenyl	$C_{24}H_6O_{24}N_{12}$	DODECA	1.81	(0.3)	(−0.007)
5,7-Dinitro-1-picrylbenzotriazole	$C_{12}H_4O_{10}N_8$	BTX	1.74	(0.3)	(−0.007)
2,2′,4,4′,6-Pentanitrobenzophenone	$C_{13}H_5O_{11}N_5$	PENCO	1.86	(0.3)	(−0.007)
1,3,5-Tripicrylbenzene	$C_{24}H_9O_{18}N_9$	TPB	1.670	(0.3)	(−0.007)
Benzotrifuroxane	$C_6O_6N_6$	BTF	1.901	(0.3)	(−0.007)
1,3-Diamino-2,4,6-trinitrobenzene	$C_6H_5O_6N_5$	DATB	1.837	0.23	(−0.007)
1,3,5-Triamino-2,4,6-trinitrobenzene	$C_6H_6O_6N_6$	TATB	1.938	0.25	(−0.007)
Azo-bis(2,2′,4,4′,6,6′-hexanitrobiphenyl)	$C_{24}H_6O_{24}N_{14}$	ABH	1.78	(0.3)	(−0.007)
2,2′,4,4′,6,6′-Hexanitroazobenzene	$C_{12}H_4O_{12}N_8$	HNAB	1.775	(0.3)	(−0.007)
2,2′,2″,2‴,4,4′,4″,4‴,6,6′,6″,6‴-Dodecanitro-3,3′-bis(phenylazo)biphenyl	$C_{24}H_6O_{24}N_{16}$	bis-HNAB	1.81	(0.3)	(−0.007)
2,6-bis(Picrylazo)-3,5-dinitropyridine	$C_{17}H_5O_{16}N_{13}$	PADP	1.86	(0.3)	(−0.007)
1,3,7,9-Tetranitrobenzotriazolo[2,1-a]benzotriazole	$C_{12}H_4O_8N_8$	Z-TACOT	1.85	(0.3)	(−0.007)
1,3,8,10-Tetranitrobenzotriazolo[1,2-a]benzotriazole	$C_{12}H_4O_8N_8$	T-TACOT	1.81	(0.3)	(−0.007)
2,4,6-Trinitrotoluene	$C_7H_5O_6N_3$	TNT	1.654	0.25	(−0.007)

[a] Values in parentheses are estimates.

The standard heat of formation in cal/mol was calculated for each sample by use of the equation

$$\Delta H_f^{\circ} = a\Delta H_f^{\circ}(CO_2, g) + \frac{b}{2} \Delta H_f^{\circ}(H_2O, l) - \Delta H_c^{\circ} \qquad (5)$$

taking $\Delta H_f^{\circ}(CO_2, g)$ and $\Delta H_f^{\circ}(H_2O, l)$ equal to -94051 and -68315 cal/mol (18), respectively.

Results

Typical results illustrating the magnitude of the quantities involved are given for each explosive in Table II. All runs on BTX, DODECA, BTF, PENCO, TPB, bis-HNAB, ABH, PADP, Z-TACOT, T-TACOT, all but the first run on HNAB, and the last five runs on DATB were carried out in a platinum–rhodium crucible. The other experiments were done in stainless-steel crucibles, and these generally produced larger amounts of residual carbon and carbon monoxide. This is presumably the result of the greater specific heat of the stainless steel.

For no sample did the titration of the nitrous acid generated by combustion require more than one drop of $0.1N$ KMnO$_4$ solution. Accordingly, no corrections were made for formation of nitrous acid.

A summary of all the results is given in Table III. The values given for TATB include an empirical correction for the presence of 1.4% of $C_6H_6O_4N_5Cl$. This correction was calculated from an estimate from bond energies (10) that the enthalpy of formation of $C_6H_6O_4N_5Cl$ is 2.8 kcal/mol more positive than the enthalpy of formation of TATB. This assumption leads to the conclusion that the enthalpy of combustion per gram of pure TATB would be 1.9 cal/g more positive than the enthalpy of combustion per gram of mixture.

The agreement between the first six and the last five results for DATB indicates that, for that material at least, we have adequately compensated for the incomplete combustion caused by use of a stainless-steel crucible.

Enthalpies of Formation

Mean values of the enthalpies of formation, together with their uncertainties (15), are presented in Table IV. The uncertainties include the contributions from the calibration of the calorimeter, the combustion experiments on the explosive, the value of the heat of combustion of benzoic acid (assuming that NBS sample 39i and Parr samples have the same value), the value of the heat of formation of $CO_2(g)$, and the value of the heat of formation of $H_2O(l)$. The uncertainties of the last two quantities were taken as ± 11 and ± 10 cal/mol, respectively (19). In general, only the contributions of the first two factors are significant. The uncertainties stated in Table IV contain no special contributions for the corrections for incomplete combustion or for the empirical correction for the chlorine-containing impurity in TATB.

Literature values for the enthalpies of formation of eight of these explosives have been found. Cox and Pilcher (3) list three measurements for TNT and give as their selected value -16.03 ± 0.65 kcal/mol. A more recent measurement by Lenchitz et al. (7) gave -19.25 ± 0.74 kcal/mol. A determination by Stegeman (16) resulted in the value -14.84 ± 0.73 kcal/mol. Our value disagrees significantly only with the value of Lenchitz et al.

The heat of combustion of HNS was measured by Marantz and Armstrong (12). The enthalpy of formation calculated from their result is $+13.88 \pm 1.09$ kcal/mol. Our result does not differ significantly from this value.

Baroody and Carpenter (1) report an enthalpy of formation of HNAB of $+61.087 \pm 0.26$ kcal/mol. Dobratz (4) quotes a value of $+57.8$ kcal/mol. Since our result does not agree with either of these values, we initiated tests of our sample for acetonitrile and tetrachloroethane, the solvents used in its purification (13). Neither mass spectrometry nor gas-liquid chromatography revealed any trace of either solvent. Thin-layer chromatography of the HNAB sample also gave no evidence of impurities.

Values of the enthalpy of formation of five of the other explosives, tabulated by Dobratz (4), are as follows: TATB, -36.85 kcal/mol; DATB, -29.23 kcal/mol; DIPAM, -20.1 kcal/mol; BTF, $+144.5$ kcal/mol; and Z-TACOT, $+128$ kcal/ mol. The values for DIPAM and Z-TACOT are in serious disagreement with our results. The value for BTF agrees well with our result and with the value $+144.54 \pm 0.19$ kcal/mol obtained by Popolato (14).

Table II. Typical Experimental Results

Explosives	m, g	Δt, °C	W, cal	ΔE_a, cal	ΔE_w, cal	ΔE_c, cal	ΔE_{co}, cal	$\Delta E_c^{\circ}/M$ sample, cal/g	ΔE_c° sample, kcal/mol	ΔH_c° sample, kcal/mol	ΔH_f° sample, kcal/mol
PATO	1.0999	1.380	4.3	15.8	16.5	7.9	1.5	-3261	-962.6	-959.5	36.3
PYX	0.9839	1.138	3.9	15.4	13.6	4.7	4.0	-3003	-1865.8	-1858.8	20.9
TPT	0.9892	1.205	4.1	13.8	13.7	5.5	2.6	-3165	-2261.2	-2253.2	73.2
DIPAM	0.9922	1.122	3.9	14.9	16.1	4.7	2.5	-2932	-1331.8	-1326.8	-6.8
ONT	0.9592	1.204	4.0	13.2	16.2	6.3	1.1	-3259	-1923.8	-1917.6	19.7
TNN	0.9868	1.345	4.2	13.7	14.1	8.7	0.9	-3547	-1093.0	-1090.0	12.9
HNBP	0.9822	1.147	4.0	12.8	17.2	5.9	0.0	-3028	-1284.6	-1279.9	14.6
HNS	0.9837	1.296	4.1	12.8	13.3	7.1	4.5	-3431	-1544.8	-1540.3	18.7
NONA	0.9644	1.109	4.0	12.8	14.2	9.9	0.2	-2988	-1898.4	-1891.2	27.4
DODECA	0.9624	1.109	5.1	12.8	20.3	0.0	0.0	-2980	-2522.5	-2512.8	50.6
BTX	0.9836	1.210	5.2	14.9	17.9	4.7	0.0	-3191	-1340.9	-1336.2	70.9
PENCO	0.9752	1.265	5.4	13.3	15.4	0.0	0.5	-3366	-1370.9	-1366.9	-26.6
TPB	0.9734	1.323	5.6	13.6	16.5	0.0	0.0	-3527	-2509.2	-2502.6	-62.1
BTF	0.9906	1.082	5.0	18.8	16.0	0.0	0.3	-2823	-711.6	-708.1	143.8
DATB	0.9834	1.112	3.5	17.0	16.1	11.0	2.8	-2937	-714.0	-711.5	-23.6
TATB	0.9954	1.097	3.4	18.5	14.6	7.9	3.4	-2859^a	...	...	...
ABH	0.9971	1.143	4.1	13.5	20.6	0.0	0.0	-2961	-2588.8	-2578.4	116.3
HNAB	0.9926	1.135	5.1	15.1	17.8	0.0	0.0	-2960	-1338.5	-1333.2	67.9
bis-HNAB	0.9910	1.133	4.0	15.2	20.7	0.0	0.0	-2952	-2664.2	-2653.3	191.1
PADP	1.0017	1.153	4.0	15.6	18.3	0.8	0.0	-2974	-1925.2	-1917.4	147.7
Z-TACOT	0.9966	1.366	4.2	15.1	16.5	1.2	0.0	-3554	-1379.9	-1375.7	110.5
T-TACOT	0.9977	1.368	4.2	14.0	13.9	1.2	0.0	-3559	-1381.8	-1377.7	112.4
TNT	0.9990	1.382	3.9	14.2	15.5	13.4	3.5	-3606	-819.1	-817.2	-12.0

a To correct for the heat evolved by formation of a small amount of HCl by combustion of the chlorine-containing impurity, 0.4 cal has been added algebraically to this value.

Table III. Summary of Combustion Runs

Explosive	\multicolumn{11}{c}{$-\Delta H_c^\circ$, kcal/mol}										Mean	SD of mean
	1	2	3	4	5	6	7	8	9	10	11		
PATO	959.5	959.5	961.4	959.0	959.2	958.5	958.8					959.4	0.4
PYX	1858.8	1855.2	1856.6	1858.1								1857.2	0.8
TPT	2253.2	2255.3	2259.6									2256.0	1.9
DIPAM	1326.8	1330.4	1327.9	1335.0	1332.8	1327.1						1330.0	1.4
ONT	1917.6	1916.4	1925.6	1922.4								1920.5	2.1
TNN	1090.0	1086.3	1087.5	1090.1								1088.5	1.0
HNBP	1279.9	1282.7	1280.0	1282.6	1289.8	1283.7						1281.6	0.9
HNS	1540.3	1538.7	1534.9	1537.4								1537.8	1.2
NONA	1891.2	1896.4	1896.9	1897.7	1894.4							1895.3	1.2
DODECA	2512.8	2510.9	2514.8	2510.4	2513.5	2515.9						2513.1	0.9
BTX	1336.2	1337.1	1335.3	1337.4	1338.6							1336.9	0.6
PENCO	1366.9	1365.5	1367.3	1364.7	1366.1							1366.1	0.5
TPB	2502.6	2503.8	2504.0	2499.6	2500.0	2507.2	2511.0	2512.7	2515.6			2506.3	1.9
BTF	708.1	710.3	709.4	709.3	710.0	708.2						709.2	0.4
DATB	711.5	712.0	712.8	712.7	712.8	711.7	711.6	712.1	709.4	710.1	712.2	711.7	0.3
TATB	734.9	734.7	737.7	737.3	735.2	735.4						735.9	0.5
ABH	2578.4	2577.0	2576.4	2575.5	2577.4							2576.9	0.5
HNAB	1333.2	1335.7	1336.0	1334.1	1334.8	1333.2						1334.5	0.5
bis-HNAB	2653.3	2651.4	2648.7	2652.1								2651.4	1.0
PADP	1917.4	1917.1	1917.1									1917.2	0.1
Z-TACOT	1375.7	1374.3	1377.0	1376.6	1373.5							1375.4	0.7
T-TACOT	1377.7	1374.2	1373.3	1377.3	1372.7							1375.0	1.0
TNT	817.2	811.7	811.7	812.7	812.5	812.8	816.1	814.8	815.7	813.4	815.4	814.0	0.6

Table IV. Enthalpies of Formation, Detonation Properties

Explosive	ΔH_f°, kcal/mol	Mader[a] D, km/sec	Mader[a] P, kbar	Kamlet and Jacobs[b] D, km/sec	Kamlet and Jacobs[b] P, kbar	D exp,[c] km/sec
BTF	144.9 ± 0.9	8.28	341	8.50	331	8.62
TATB	−33.4 ± 1.2	7.99	316	7.95	293	7.99
PATO	36.2 ± 0.9	7.84	307	7.78	281	
PADP	147.5 ± 1.2	7.62	284	7.96	286	
DATB	−23.4 ± 0.8	7.64	276	7.71	267	7.69
bis-HNAB	189.2 ± 2.6	7.49	270	7.88	276	
Z-TACOT	110.2 ± 1.5	7.42	263	7.44	250	7.25
DODECA	50.9 ± 2.4	7.34	258	7.70	264	
HNAB	69.2 ± 1.3	7.40	257	7.73	263	
PENCO	−27.4 ± 1.2	7.32	257	7.43	249	
DIPAM	−3.6 ± 2.9	7.38	255	7.63	257	7.50
ABH	114.8 ± 1.9	7.34	254	7.69	261	(7.60)
T-TACOT	109.8 ± 2.2	7.31	250	7.33	239	
NONA	31.6 ± 2.6	7.27	249	7.61	255	(7.56)
ONT	22.6 ± 4.4	7.25	247	7.46	247	(7.33)
PYX	19.2 ± 2.0	7.26	243	7.48	246	
TNN	11.3 ± 2.0	7.22	243	7.30	236	
HNBP	16.3 ± 2.0	7.19	239	7.50	244	
BTX	71.7 ± 1.4	7.17	234	7.34	234	
HNS	16.2 ± 2.5	7.13	231	7.27	230	7.13
TNT	−15.1 ± 1.2	7.01	211	7.02	207	6.98
TPT	76.0 ± 4.0	6.90	210	7.08	212	
TPB	−58.4 ± 4.0	6.65	189	6.64	187	

[a] Computed by Mader (11), BKW equation of state (8, 9) with TNT parameters except BTF. [b] Computed by method of Kamlet and Jacobs (6). [c] Values in parentheses were obtained in small-diameter, heavily confined charges and may be low.

Detonation Properties

Also given in Table IV are the detonation properties calculated for crystal density by the methods of Mader (8, 9) and of Kamlet and Jacobs (6). Most of these compounds consist largely of substituted polynitroaromatic groups; therefore, Mader's calculations were done with his TNT parameters except for BTF, for which his RDX parameters were used. The experimental velocities given were obtained from AEC or DOD sources. In converting the reported values to crystal density, a correction factor of 3.2 km·ml/sec·g was used unless this quantity had been determined. The validity of these velocities varies, but for the most part we consider them good to within about 0.1 km/sec.

With respect to the calculated velocities, there is a systematic difference between the Mader and Kamlet and Jacobs values, the latter being higher than the former for all but three of the 23 compounds. The differences (Kamlet and Jacobs-Mader) range from −0.06 to +0.39 km/sec, with an average of 0.176 and a standard deviation of 0.145. In most cases the experimental values lie between the two computed numbers. The two methods are in somewhat better agreement for the computed pressures. Here, the differences range from −26 to +7 kbar, with an average of 2.7 kbar and a standard deviation of 9.2 kbar.

Nomenclature

wt_{BA} = mass of sample of benzoic acid, g
m = mass of sample of explosive, g
A = correction for unmeasured contributions to rise in temperature of calorimeter, cal
B = effective energy equivalent of calorimeter in calibration experiments, cal/K
δ = excess of energy equivalent of bomb contents over that existing during calibration, cal/K

Δt = rise in temperature of calorimeter, K

ΔE_a = energy released by formation of nitric acid, cal

ΔE_w = energy released by combustion of fuse wire, cal

ΔE_c = energy that would have been released by combustion of residual carbon, cal

ΔE_{co} = energy that would have been released by combustion of residual carbon monoxide, cal

W = sum of the terms in the correction of the internal energy of combustion to standard states that are essentially constant for all experiments on one explosive, cal; W is designated as ΔE_Σ in ref. 5

ΔE_c^o = standard internal energy of idealized combustion reaction at 298K, cal/mol

M = molecular weight of explosive, g/mol (2)

ΔH_c^o = standard enthalpy of idealized combustion reaction at 298K, cal/mol

a, b, c, d = subscripts in the formula $C_aH_bO_cN_d$ of an explosive

ΔH_f^o = standard enthalpy of formation at 298K, cal/mol

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Gas Sweetening Data: Equilibrium Solubility of Hydrogen Sulfide and Carbon Dioxide in Aqueous Monoethanolamine and Aqueous Diethanolamine Solutions

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Equilibrium solubility data for hydrogen sulfide, carbon dioxide, and mixtures of the two acid gases in methane are collected for water solutions of monoethanolamine (MEA) and also diethanolamine (DEA). The experimental procedures, experimental apparatus, and analytical methods are described. The resulting equilibrium solubility data are presented for 15 wt % MEA and 25 wt % DEA over ranges of temperature and acid gas composition encountered in commercial MEA and DEA gas treating units. Some of the data are plotted and compared to data from other sources.

Knowledge of the equilibrium solubility of hydrogen sulfide, carbon dioxide, and their mixtures in water solutions of monoethanolamine (MEA) and diethanolamine (DEA) is essential in the design of natural gas and refinery gas absorption systems which remove these acid gases. The equilibrium solubility of the acid gases determines the amount of amine feed solution to be circulated to treat a given feed gas and the

maximum amount of residual acid gases which can be present in the regenerated amine feed solution to the contactor to produce the desired acid gas specification for the treated gas. The equilibrium solubility of either acid gas is a function of temperature, hydrogen sulfide and carbon dioxide partial pressure in the vapor phase, amine type (MEA or DEA), and amine concentration in the liquid phase. The data presented provide a partial definition of the effects of these variables upon acid gas solubility.

Several investigators have measured hydrogen sulfide and carbon dioxide solubility in MEA and DEA solutions. Much of the past work, however, has limited utility for engineering design because the concentration and temperature ranges of the data are too narrow, the data are not consistent with other independent work, and/or the data are for only hydrogen sulfide or only carbon dioxide, but not for mixtures of the two acid gases. The most usable data collections are those of Jones et al. (7), Muhlbauer and Monaghan (19), Atwood et al. (2), Bocard (3), Leibush and Shneerson (15), Dow (6), Pearce (22), Mason and Dodge (17), and Lee et al. (11). Other solubility data are presented by Atadan (1), Bottoms (4), Lyndkovskaya and Leibush (16), Murzin et al. (20, 21), Reed (24), Reed and Wood (25), Lee et al. (10–14), and Riegger et al. (26).

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