Dissociation Constants of Pyro- and Tripolyphosphoric Acids at 25°C

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Thermodynamic dissociation constants of pyro- and tripolyphosphoric acids were determined from the pH and concentration of solutions in the systems $[(CH_3)_4N]_4P_2O_7$–$H_4P_2O_7$–H_2O, and $[(CH_3)_4N]_5P_3O_{10}$–$H_5P_3O_{10}$–H_2O. In the method of calculation, starting values for the dissociation constants were assumed and the corresponding molalities of the aqueous species were calculated iteratively. From these data, improved values of the constants were calculated by a least-squares procedure that minimized the differences between the observed and calculated values of pH. The dissociation constants for pyrophosphoric acid are $pk_1^\circ = 0.70 \pm 0.40$, $pK_2^\circ = 2.19 \pm 0.05$, $pK_3^\circ = 6.80 \pm 0.02$, and $pK_4^\circ = 9.59 \pm 0.03$, and for tripolyphosphoric acid are $pK_2^\circ = 0.89 \pm 0.57$, $pK_3^\circ = 4.09 \pm 0.08$, $pK_4^\circ = 6.98 \pm 0.02$, and $pK_5^\circ = 9.93 \pm 0.04$.

The dissociation constants of pyro- and tripolyphosphoric acids that have been reported in the literature were reviewed by Sillén and Martell *(18)*. Most of the values are only approximations, as very few are given limits of precision.

Reliable values of dissociation constants of pyro- and tripolyphosphoric acids are required for calculating stability constants of complex polyphosphates of magnesium and other metals. This paper describes a method for determining thermodynamic dissociation constants of condensed phosphoric acids and presents values for the four constants of pyrophosphoric acid and for four of the constants of tripolyphosphoric acid. The limits of precision of the constants are assigned.

Solutions in the systems $[(CH_3)_4N]_4P_2O_7$–$H_4P_2O_7$–H_2O and $[(CH_3)_4N]_5$–P_3O_{10}–$H_5P_3O_{10}$–H_2O were prepared at several concentrations of total phosphorus and at several atomic ratios N:P. At each ratio, measurements were made of the pH of the initial solution and of solutions prepared by successive dilutions of the initial samples. The solutions contained the noncomplexing tetramethylammonium ion instead of alkali metal ions, which form complexes with polyphosphates *(12)*. Concentrations of the electrolytes approached infinite dilution in each series.

In the method of calculation, starting values for the dissociation constants of the various species were assumed and the corresponding molalities were estimated from the pH and concentration by an iterative procedure. The differences between the calculated and observed pH values then were minimized by a least-squares procedure, and improved values of the dissociation constants were calculated. The computation methods, for which computer programs were developed, are described briefly here; the detailed procedure has been deposited with the ACS Microfilm Depository Service.

Experimental

Reagent sodium pyrophosphate and technical sodium tripolyphosphate were purified by dissolving each salt in cold (10°C) conductance water and then precipitating the salt by slow addition of cold methyl alcohol. The dissolution and precipitation procedure was repeated several times. The extraneous phosphate species in the purified salts were shown by paper chromatography *(9, 11)* to be no more than 0.7% of the total phosphate.

Reagent tetramethylammonium chloride was purified by recrystallization from a mixture of methyl alcohol and acetone *(17)*. A jacketed 30-mm glass tube 1 meter long with a stopcock at the bottom was packed with 450 grams of Dowex 50W-X2 cation exchange resin which was then leached with 1*m* HCl, washed free of chloride, converted to the noncomplexing tetramethylammonium form by percolating 1*m* $(CH_3)_4NCl$ solution through the column, and then washing the resin free of electrolytes.

The tetramethylammonium polyphosphate solutions were prepared by passing a solution of the sodium salt (about 0.1*m*) through the quaternary-form resin that was maintained at 10°C by a stream of cold water through the column jacket. The input and effluent solutions were chilled in ice baths and kept under an atmosphere of nitrogen. The eluates were frozen and stored at −10°C until portions were taken for analysis and pH measurements. The pyrophosphate eluates were 0.091*m* in P_2O_7 and had an atomic ratio N:P of 1.93. The tripolyphosphate eluates were 0.022*m* in P_3O_{10} and had an atomic ratio N:P of 1.35.

The phosphorus contents of most samples were determined by the gravimetric quimociac method *(1)* and those in other samples were determined by the photometric vanadomolybdate *(2)* or heteropoly blue *(6)* methods. Replicate analyses were reproducible to within 0.8% of the phosphorus content or about 50 mg P per sample by each of the methods.

The nitrogen of the quaternary tetramethylammonium salts resisted decomposition by usual Kjeldahl techniques, and prolonged digestion at elevated temperatures was required. Nitrogen in the most concentrated solutions (at least 100 mg N per sample) was determined by the Raney catalyst powder method *(3)* and in higher dilutions by the method adapted to a micro scale *(21)*. The nitrogen determinations were reproducible within 1 or 2%. Uncertainties in the nitrogen and phosphorus contents of the test solutions are major factors affecting the reliability of the dissociation constants.

Portions of each solution were taken for pH measurements without further treatment. Other portions were treated at 3°C with the amounts of hydrogen-form resin (Dowex 50W-X2, acid-treated and washed) required to replace tetramethylammonium ion with hydrogen to produce selected atomic ratios N:P. The mixtures of resin and solution were shaken frequently for 8 hr, stored overnight at 3°C, and then filtered on a fritted-glass funnel. The treatment with ion-exchange resin adjusted the pH and the ratio N:P without introducing foreign ions.

For the pH measurements, a 50-ml sample of the initial or adjusted solution was equilibrated at 25°C and weighed in a capped weighing bottle to within 0.1 mg. The pH of the solutions was measured with a Beckman

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Research pH meter, Model 101900, equipped with glass and saturated-calomel electrodes *(4)*. Half of the sample was removed for analysis and the rest was weighed, diluted with 25 ml of recently boiled distilled water, reweighed, mixed thoroughly, and equilibrated at 25°C for measurement of pH. This procedure was repeated for six or more dilution-pH measurements. The composition of each solution in a series was calculated from replicate analyses of the initial solution and the weights of succeeding portions before and after dilution.

The pH meter was mounted on a foam rubber pad and grounded. It was connected to the 110-V house supply through a 250-W voltage stabilizer. Double-shielded leads connected the electrodes to the meter. The 50-ml weighing bottle containing the test solution was mounted in a water bath maintained at 25.00° ± 0.01°C. The pH meter was standardized against four buffer solutions that were prepared from NBS salts: No. 188, tartrate, pH 3.639; No. 185d, phthalate, pH 4.008; Nos. 186-Ic and 186-IIb, phosphate, pH 6.862; and No. 187a, borate, pH 9.180. The temperature compensator of the pH meter was adjusted so that the indicated pH of each buffer solution was within 0.001 pH unit of the standard value. The temperature compensator thus was used as a slope control and the response of the meter was linear over the range of pH covered by the buffers. A rubber cap with three ports replaced the glass cap of the weighing bottle during the pH measurements. The electrodes were inserted through two of the ports and immersed to the same depth (2.5 cm) in each of the test solutions. A stream of nitrogen was admitted through the third port in the cap to shield the solutions from atmospheric carbon dioxide. Before each series of measurements, the meter was standardized against freshly prepared buffers (not more than two days old), first against the phosphate buffer, then against the phthalate and borate buffers. In addition, before each measurement the meter was calibrated against the standard cell and against the buffer whose pH was nearest that of the sample. In all measurements the final readings were taken after equilibration for 3 min. The pH measurements were reproducible within 0.001 pH unit.

Dissociation Constants of Pyrophosphoric Acid

Measurements were made of the pH of each of 51 solutions grouped in nine series of dilutions in the system $[(CH_3)_4N]_4P_2O_7–H_4P_2O_7–H_2O$. As shown in Table I, the total phosphorus contents (as P_2O_7) ranged from 1.2×10^{-1} to 1.5×10^{-4} *m*, the atomic ratios N:P ranged from 1.93 to 0.08, and the measured pH ranged from 1.192 to 9.824.

The method of calculation is outlined in this section and described in detail in the document deposited with ACS Microfilm Depository Service. The species, equations, and symbols are identified in Table II. The activity coefficient, f_i, of each species was calculated by the equation

$$\log f_i = Az_i^2 \{[-(\mu)^{1/2}/1 + \mathring{a}_i B (\mu)^{1/2}] + b\mu\} + u_i\mu \quad (1)$$

where A and B are the usual Debye-Hückel parameters at 25°C; $A = 0.5116$, $B = 0.3291 \times 10^8$; μ, the ionic strength, $= 0.5\ \Sigma_i m_i z_i^2$; m is the concentration, molality; z is the ionic charge; $\mathring{a}$ is the ionic size, Å; b is an empir-

Table I. pH of Solutions in the System $[(CH_3)_4N]_4P_2O_7–H_4P_2O_7–H_2O$ at 25°C

		pH					pH		
			Calcd by iteration					Calcd by iteration	
Atomic ratio N:P	Concn P_2O_7, $m \times 10^3$	Obsd	1st	4th	Atomic ratio N:P	Concn P_2O_7, $m \times 10^3$	Obsd	1st	4th
1.927	23.140	9.602	9.146	9.603	1.146	86.61	5.896	5.664	5.877
	7.251	9.824	9.320	9.732		20.91	6.002	5.797	5.972
	2.332	9.792	9.477	9.839		3.995	6.108	5.996	6.161
	0.8937	9.696	9.528	9.835		1.240	6.188	6.097	6.259
						0.3832	6.250	6.164	6.325
1.780	90.15	8.981	8.533	9.104		0.1455	6.214	6.203	6.362
	25.11	9.052	8.494	8.952					
	8.245	9.166	8.671	9.099	0.980	84.88	3.366	3.176	3.316
	3.159	9.238	8.835	9.248		18.04	3.560	3.479	3.566
	1.132	9.232	8.969	9.363		5.485	3.838	3.813	3.867
						1.913	4.157	4.159	4.195
1.579	87.95	8.238	7.717	8.227		0.6179	4.544	4.551	4.584
	20.52	8.368	7.783	8.202		0.1829	4.979	4.956	4.999
	5.662	8.468	8.000	8.401					
	1.209	8.512	8.216	8.607	0.888	120.2	2.478	2.384	2.495
						38.51	2.650	2.566	2.649
1.466	86.49	7.317	6.975	7.284		12.18	2.905	2.846	2.906
	21.75	7.425	7.053	7.299		4.439	3.218	3.157	3.196
	8.970	7.505	7.177	7.408		1.572	3.571	3.530	3.550
	3.009	7.556	7.319	7.541		0.4340	4.090	4.038	4.047
	1.006	7.504	7.426	7.644		0.1313	4.604	4.528	4.536
1.248	90.93	6.310	6.037	6.263	0.0792	94.50	1.192	1.318	1.202
	15.18	6.481	6.194	6.368		48.85	1.418	1.487	1.414
	7.391	6.534	6.285	6.454		27.53	1.624	1.645	1.604
	2.729	6.592	6.394	6.559		15.56	1.833	1.814	1.798
	1.580	6.642	6.442	6.606		4.311	2.212	2.239	2.249
	0.4457	6.602	6.523	6.686		1.871	2.518	2.547	2.559
						0.7392	2.866	2.912	2.921
						0.2698	3.313	3.327	3.332

Table II. Dissociation Equilibria of Pyrophosphoric Acid

Equilibrium	Species	Activity	Dissociation constants
$H_2O \rightleftarrows H^+ + OH^-$	H^+	a_1	$K_w^\circ = a_1a_2/a_9 = a_1a_2$[a]
$H_4P_2O_7 \rightleftarrows H^+ + H_3P_2O_7^-$	OH^-	a_2	$K_1^\circ = a_1a_6/a_7$
$H_3P_2O_7^- \rightleftarrows H^+ + H_2P_2O_7^{2-}$	H_2O	a_9	$K_2^\circ = a_1a_5/a_6$
$H_2P_2O_7^{2-} \rightleftarrows H^+ + HP_2O_7^{3-}$	$H_4P_2O_7$	a_7	$K_3^\circ = a_1a_4/a_5$
$HP_2O_7^{3-} \rightleftarrows H^+ + P_2O_7^{4-}$	$H_3P_2O_7^-$	a_6	$K_4^\circ = a_1a_3/a_4$
	$H_2P_2O_7^{2-}$	a_5	
	$HP_2O_7^{3-}$	a_4	
	$P_2O_7^{4-}$	a_3	
	$[(CH_3)_4N]^+$	a_8	

[a] Since $a_9 = 1$, by convention.

Table III. Dissociation Constants of Pyrophosphoric Acid at 25°C

		Ref.						
Constants	Present work	*(12)*	*(14)*	*(8)*	*(5)*	*(15)*	*(16)*	*(20)*
pK_1°	0.70 ± 0.40	$-\infty$	0.91	1.52	...	...	...	...
pK_2°	2.19 ± 0.05	2.64	2.10	2.36	2.27	...	2.28	...
pK_3°	6.80 ± 0.02	6.76	6.70	6.60	6.63	6.57	6.70	...
pK_4°	9.59 ± 0.03	9.42	9.32	9.25	9.29	9.62	9.37	9.53

ical constant; and u is a constant, 0.076 for uncharged species, zero for charged species *(19)*.

The values of $\mathring{a}$ were taken as 6.0 for H^+, 3.0 for OH^-, 4.5 for $(CH_3)_4N^+$, and 5.0 for all phosphate species *(19)*. Equation 1 has been used to calculate activity coefficients of many species in solutions *(19)*, and is similar to the Davies equation *(7)*.

The logarithmic forms of the equations that define the constants (Table II), where a_i is replaced by m_if_i are

$$\log K_w = \log m_1 + \log m_2 + \log f_1 + \log f_2 \quad (2)$$

$$\log K_4 = \log m_1 + \log m_3 - \log m_4 + \log f_1 + \log f_3 - \log f_4 \quad (3)$$

$$\log K_3 = \log m_1 + \log m_4 - \log m_5 + \log f_1 + \log f_4 - \log f_5 \quad (4)$$

$$\log K_2 = \log m_1 + \log m_5 - \log m_6 + \log f_1 + \log f_5 - \log f_6 \quad (5)$$

$$\log K_1 = \log m_1 + \log m_6 - \log m_7 + \log f_1 + \log f_6 - \log f_7 \quad (6)$$

The concentrations of the phosphatic species are given by

$$m_3 + m_4 + m_5 + m_6 + m_7 - T_p = 0 \quad (7)$$

where T_p is total phosphorus and the subscripts correspond to those for activity listed in Table II. The total phosphorus content of each solution was determined by analysis.

The other equation required by the seven unknowns is the electroneutrality relation

$$m_1 - m_2 - 4\,m_3 - 3\,m_4 - 2\,m_5 - m_6 + m_8 = 0 \quad (8)$$

where m_8, the total nitrogen content, was determined by analysis.

The values of the four dissociation constants and of b of Equation 1 were calculated by a two-step procedure. In the first step, approximate values of the dissociation constants and b in Equation 1 were taken from the literature or were assumed. The concentrations of the species in each solution were calculated by an iterative process from the approximate dissociation constants in terms of molalities, activities, and activity coefficients. Partial derivatives were evaluated to accumulate the matrices for the least-squaring process as described in the document deposited with the ACS Microfilm Depository Service.

In the second step, improved values of the constants and of b were found by a least-squares fit of observed values of pH and those calculated from the revised molalities and the matrices obtained from the first calculation. The procedure was continued, through the two steps, until changes in the constants and in b were not significant. The measured values of pH are compared with those calculated after the first and fourth (final) iterations in Table I.

The dissociation constants are compared in Table III with the values reported in the literature. Since dissociation of $H_4P_2O_7$ to form $H_3P_2O_7^-$ is virtually complete, the value of K_1 is large and cannot be determined with high precision *(12)*. The new dissociation constants with their limits of precision will be used to calculate formation constants of metallic pyrophosphates. The value of the parameter b in the extended Debye-Hückel expression, Equation 1, was calculated to be 0.264 ± 0.019 as compared with the value 0.3 given by Davies *(7)* for 1:1, 1:2, and 2:1 electrolytes.

Dissociation Constants of Tripolyphosphoric Acid

The method of calculation was modified to determine four of the dissociation constants of tripolyphosphoric acid from the data for the system $[(CH_3)_4N]_5P_3O_{10}$-$H_5P_3O_{10}$-H_2O in Table IV. The total phosphorus contents of the solutions ranged from 2.2×10^{-2} to 1.3×10^{-5} m in P_3O_{10} and the atomic ratios N:P of the 14 series of solutions ranged from 1.6 to 0.5. A total of 65 data points was used in the computer program. The symbols and equations are shown in Table V.

Four of the dissociation constants (K_2, K_3, K_4, and K_5) of tripolyphosphoric acid and their standard errors are compared in Table VI with values from the literature. The value of K_1 was not determined because the required strongly acid solutions (N:P approaching 0) could not be prepared by the exchange method that was used to pre-

Table IV. pH of Solutions in the System $[(CH_3)_4N]_5P_3O_{10}$–$H_5P_3O_{10}$–H_2O at 25°C

Atomic ratio N:P	Concn P_3O_{10}, $m \times 10^3$	pH Obsd	pH Calcd by iteration 1st	pH Calcd by iteration 4th
1.589	16.1197	9.760	9.757	9.882
	7.9591	9.841	9.671	9.768
	3.7748	9.885	9.712	9.792
	1.7421	9.875	9.777	9.843
	0.7988	9.765	9.799	9.853
	0.3649	9.659	9.753	9.796
1.365	8.9185	8.331	8.273	8.354
	4.3991	8.426	8.343	8.413
	2.1006	8.490	8.450	8.514
	1.0214	8.498	8.549	8.608
1.329	22.3886	7.977	7.837	7.887
	0.7261	8.190	8.070	8.072
1.320	16.0672	7.663	7.647	7.665
	8.0212	7.766	7.647	7.649
	3.9895	7.861	7.719	7.713
	1.9583	7.928	7.813	7.801
	0.9036	7.948	7.907	7.892
1.086	16.0543	5.916	6.063	6.021
	7.9660	6.020	6.104	6.051
	3.9276	6.119	6.184	6.127
	1.9332	6.211	6.270	6.210
	0.9451	6.288	6.347	6.287
	0.4613	6.357	6.411	6.351
	0.2238	6.406	6.461	6.401
	0.1056	6.431	6.501	6.442
1.059	8.9029	5.789	5.915	5.850
	4.3096	5.882	5.995	5.925
	2.1643	5.980	6.077	6.006
	1.0584	6.054	6.155	6.083
	0.5143	6.118	6.220	6.149
	0.2480	6.147	6.272	6.202
	0.0562	6.220	6.352	6.286

Atomic ratio N:P	Concn P_3O_{10}, $m \times 10^3$	pH Obsd	pH Calcd by iteration 1st	pH Calcd by iteration 4th
0.583	15.8093	2.440	2.469	2.425
	7.8806	2.635	2.729	2.672
	3.9081	2.854	2.990	2.917
	1.9214	3.089	3.247	3.157
	0.9393	3.352	3.498	3.392
	0.4556	3.630	3.740	3.624
	0.2197	3.935	3.976	3.856
	0.1046	4.252	4.212	4.098
0.536	17.5490	2.356	2.252	2.229
	8.5297	2.560	2.531	2.500
	3.9287	2.786	2.832	2.789
	1.7892	3.048	3.134	3.074
	0.7460	3.330	3.461	3.380
	0.3401	3.626	3.741	3.646
	0.1507	3.954	4.020	3.918
	0.0674	4.308	4.288	4.192
	0.0294	4.650	4.568	4.488
0.520	18.0993	2.216	2.192	2.173
	8.6372	2.442	2.480	2.454
	3.9103	2.683	2.790	2.753
	1.5161	2.990	3.158	3.101
	0.5805	3.329	3.519	3.440
	0.2181	3.693	3.868	3.774
	0.0931	4.076	4.159	4.063
	0.0344	4.500	4.497	4.415
	0.0125	4.934	4.853	4.798
0.510	15.6247	2.118	2.222	2.203
	7.7918	2.350	2.493	2.469
	0.4527	3.392	3.590	3.511
	0.2181	3.690	3.852	3.761
	0.1045	4.008	4.107	4.013
	0.0497	4.344	4.360	4.273
	0.0235	4.704	4.618	4.547

Table V. Dissociation Constants of Tripolyphosphoric Acid

Equilibrium	Species	Activity	Dissociation constants
$H_2O \rightleftharpoons H^+ + OH^-$	H^+	a_1	$K_w° = a_1a_2/a_{10} = a_1a_2$[a]
$H_5P_3O_{10} \rightleftharpoons H^+ + H_4P_3O_{10}^-$	OH^-	a_2	$K_1° = a_1a_7/a_8$
$H_4P_3O_{10}^- \rightleftharpoons H^+ + H_3P_3O_{10}^{2-}$	H_2O	a_{10}	$K_2° = a_1a_6/a_7$
$H_3P_3O_{10}^{2-} \rightleftharpoons H^+ + H_2P_3O_{10}^{3-}$	$H_5P_3O_{10}$	a_8	$K_3° = a_1a_5/a_6$
$H_3P_3O_{10}^{3-} \rightleftharpoons H^+ + HP_3O_{10}^{4-}$	$H_4P_3O_{10}^-$	a_7	$K_4° = a_1a_4/a_5$
$HP_3O_{10}^{4-} \rightleftharpoons H^+ + P_3O_{10}^{5-}$	$H_3P_3O_{10}^{2-}$	a_6	$K_5° = a_1a_3/a_4$
	$H_2P_3O_{10}^{3-}$	a_5	
	$HP_3O_{10}^{4-}$	a_4	
	$P_3O_{10}^{5-}$	a_3	
	$[(CH_3)_4N]^+$	a_9	

[a] Since $a_{10} = 1$, by convention.

pare the solutions with higher ratios N:P. The measured values of pH and those calculated after the first and fourth (final) iterations are shown in Table IV.

The new dissociation constants with their limits of precision will be used in calculating formation constants of metallic tripolyphosphates. The value of the parameter b in the extended Debye-Hückel expression used in our computation was calculated to be 0.659 ± 0.058 as compared with the value 0.264 ± 0.019 for the pyrophos-

Table VI. Dissociation Constants of Tripolyphosphoric Acid at 25°C

Constants	Present work	Ref. *(5)*	Ref. *(13)*	Ref. *(12)*	Ref. *(20)*
$pK_2°$	0.89 ± 0.57	. . .	. . .	$-\infty$	. . .
$pK_3°$	4.09 ± 0.08	2.79	. . .	2.30	. . .
$pK_4°$	6.98 ± 0.02	6.47	6.10	6.50	. . .
$pK_5°$	9.93 ± 0.04	9.24	9.12	9.24	9.52

phate system or with the value 0.3 given by Davies *(7)* for 1:1, 1:2, and 2:1 electrolytes.

The physicochemical relationships used in the computation describe a model somewhat different from the model described by the measurements. Thus, plots of log total phosphorus concentration vs. calculated values of pH for the several series of solutions form a family of sigmoid curves, whereas plots of the observed values of pH form a family of smooth parabolic arcs that approach pH 7 at infinite dilution. The difference in shapes of the curves is attributed, at least in part, to the use of an expression for the activity coefficient that contained the Debye-Hückel relationship and only one additional adjustable parameter, a form used by Davies *(7)*; Farr and Elmore *(10)* successfully used three adjustable parameters in adapting the Debye-Huckel relationship to their data. Moreover, in the single-ion activity coefficient expression used in our computer program, the ionic size, $\mathring{a}$, was fixed at 5Å for all polyphosphate species. This constant probably is not correct for all polyphosphate species, since $\mathring{a}$ by definition is an adjustable parameter.

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Enthalpies of Formation of Some Fluorodinitroethyl Derivatives and 2,2′,4,4′,6,6′-Hexanitroazobenzene

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The enthalpies of formation of bis(2-fluoro-2,2-dinitroethyl)nitrosamine (BFDNO), bis(2-fluoro-2,2-dinitroethyl)nitramine (BFDNAM), *N,N′*-bis(2-fluoro-2,2-dinitroethyl)oxamide (BFDNOX), 2,2′,4,4′,6,6′-hexanitroazobenzene (HNAB), *N,N,O*-tris(2-fluoro-2,2-dinitroethyl)carbamate (TFDC) and bis(2-fluoro-2,2-dinitroethyl)oxalate (REX-17) were determined to be −102.041 ± 0.21, −120.735 ± 0.56, −232.335 ± 0.82, +61.087 ± 0.26, −266.926 ± 0.22, and −288.862 ±0.67 kcal/mol, respectively, by combustion calorimetery using a platinum-lined rotating-bomb calorimeter. The compounds were burned with either diethyl phthalate or diethyl oxalate to desensitize and to ensure complete combustion.

The enthalpies of formation of bis(2-fluoro-2,2-dinitroethyl)nitrosamine (BFDNO), bis(2-fluoro-2,2-dinitroethyl)nitramine (BFDNAM), *N,N′*-bis(2-fluoro-2,2-dinitroethyl)oxamide (BFDNOX), 2,2′,4,4′,6,6′-hexanitroazobenzene (HNAB), *N,N,O*-tris(2-fluoro-2,2-dinitroethyl)carbamate (TFDC), and bis(2-fluoro-2,2-dinitroethyl)oxalate (REX-17) were determined by combustion calorimetry using a platinum-lined rotating-bomb calorimeter. A mixture of these compounds with either diethyl phthalate (DEP) or diethyl oxalate (DEO) was burned in an oxygen atmosphere (30 atm). The ratios of the compounds to DEP or DEO were selected after a series of preliminary runs on a Parr stationary adiabatic-bomb calorimeter indicated the amounts needed to produce a smooth and clean combustion. Since these compounds were considered shock sensitive, DEP and DEO served as desensitizers. The enthalpies of formation (298.15K) were determined from the following idealized equations at 1 atm:

BFDNO:

$$C_4H_4O_9N_6F_2(c) + 179\ H_2O(l) \rightarrow 4\ CO_2(g) + 2\ (HF{\cdot}90H_2O)(l) + 3\ N_2(g) \qquad (1)$$

BFDNAM:

$$C_4H_4O_{10}N_6F_2(c) + C_6H_{10}O_4(l) + 6\ O_2(g) + 194\ H_2O(l) \rightarrow 10\ CO_2(g) + 2\ (HF{\cdot}100H_2O)(l) + 3\ N_2(g) \qquad (2)$$

BFDNOX:

$$C_6H_6O_{10}N_6F_2(c) + 2\ O_2(g) + 238\ H_2(l) \rightarrow 6\ CO_2(g) + 2\ (HF{\cdot}120H_2O)(l) + 3\ N_2(g) \qquad (3)$$

HNAB:

$$C_{12}H_4O_{12}N_8(c) + 7\ O_2(g) \rightarrow 12\ CO_2(g) + 2\ H_2O(l) + 4\ N_2(g) \qquad (4)$$

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