Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THERMODYNAMIC FUNCTIONS FOR MONOSUBSTITUTED HALONITROBENZENES

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(Received September 7th, 1971)

ABSTRACT

Thermodynamic functions*, C_p°, S°, $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H_0^\circ)/T$, have been calculated for monosubstituted halonitrobenzenes: *o*-, *m*-, and *p*-$XC_6H_4NO_2$ (X = F, Cl, Br, or I) in the ideal gas state from 298.15° to 800°K, at 1 atm pressure. The restricted internal rotational contribution has been treated by means of the Pitzer–Gwinn method.

Thermodynamic functions for monosubstituted halonitrobenzenes

The recent availability of molecular structural and spectroscopic data[1-3] has enabled the calculation of thermodynamic functions—heat capacity, enthalpy, entropy and free energy—for 12 halonitrobenzenes: *o*-, *m*-, *p*-$XC_6H_4NO_2$ (X = F, Cl, Br, I) in the ideal gas state at 1 atm pressure. Table I presents the calculated thermodynamic functions obtained by treating the restricted internal rotational contribution by Pitzer–Gwinn's method[4]. The results presented in Table I are fitted to Eqn. (1):

$$\Lambda = a + bT + cT^2 \qquad (1)$$

where Λ is the thermodynamic function and T is the temperature (°K). The constants a, b, c in Eqn. (1) were evaluated using least-squares curve fitting methods[5] and are given in Table II. The use of Eqn. (1) causes standard error (Table II) in the calculated thermodynamic function values from those shown in Table I. Table III gives the values of the molecular parameters used in the calculation of the thermodynamic functions.

Although there are no available calorimetric data, the overall reliability of the frequency assignments[1], even if few frequency values were estimated (see Table III, footnotes *a* and *b*), suggests that the presented thermodynamic function values (Table I) may well be within the bounds of experimental accuracy.

*For nomenclature see p. 398.

TABLE I

HEAT CAPACITY, ENTROPY, FREE ENERGY FUNCTION AND ENTHALPY FUNCTION

	Temp. (°K)	*o-F-Nitro-benzene*	*o-Cl-Nitro-benzene*	*o-Br-Nitro-benzene*	*o-I-Nitro-benzene*	*p-F-Nitro-benzene*
Heat capacity	298.15	31.28	32.30	32.71	33.31	31.24
C_p° (cal/mole/°K)	300.00	31.44	32.47	32.87	33.47	31.41
	350.00	35.83	36.75	37.11	37.60	35.82
	400.00	39.87	40.70	41.01	41.43	39.88
	450.00	43.51	44.26	44.53	44.89	43.53
	500.00	46.74	47.42	47.66	47.97	46.77
	550.00	49.60	50.22	50.42	50.70	49.63
	600.00	52.12	52.67	52.86	53.10	52.15
	650.00	54.33	54.83	55.00	55.21	54.36
	700.00	56.29	56.75	56.89	57.09	56.31
	750.00	58.03	58.44	58.58	58.75	58.05
	800.00	59.58	59.96	60.08	60.23	59.59
Entropy	298.15	85.18	88.63	91.47	94.24	84.55
S° (cal/mole/°K)	300.00	85.37	88.83	91.67	94.45	84.75
	350.00	90.56	94.17	97.06	99.92	89.93
	400.00	95.60	99.34	102.28	105.20	94.98
	450.00	100.52	104.34	107.31	110.28	99.89
	500.00	105.28	109.17	112.17	115.18	104.66
	550.00	109.87	113.82	116.84	119.88	109.25
	600.00	114.29	118.30	121.34	124.39	113.68
	650.00	118.55	122.60	125.66	128.73	117.94
	700.00	122.65	126.74	129.80	132.89	122.04
	750.00	126.60	130.71	133.79	136.89	125.99
	800.00	130.39	134.53	137.62	140.73	129.78
Enthalpy fu- :tion	298.15	18.06	19.11	19.58	20.35	18.11
$(H^\circ - H_0^\circ)/T$	300.00	18.14	19.19	19.66	20.43	18.20
(cal/mole/°K)	350.00	20.36	21.50	21.85	22.59	20.41
	400.00	22.54	23.71	24.01	24.71	22.59
	450.00	24.68	25.68	26.09	26.77	24.72
	500.00	26.73	27.70	28.10	28.74	26.77
	550.00	28.68	29.62	30.00	30.61	28.72
	600.00	30.53	31.44	32.81	32.38	30.57
	650.00	32.27	33.15	33.52	34.06	32.31
	700.00	33.92	34.78	35.12	35.64	33.96
	750.00	35.48	36.30	36.63	37.13	35.51
	800.00	36.93	37.73	38.05	38.53	36.96
Free energy function	298.15	67.12	69.52	71.89	73.89	66.44
$-(F^\circ - H_0^\circ)/T$	300.00	67.23	69.64	72.01	74.02	66.55
(cal/mole/°K)	350.00	70.20	72.67	75.21	77.33	69.52
	400.00	73.06	75.63	78.27	80.49	72.39
	450.00	75.84	78.66	81.22	83.51	75.17
	500.00	78.55	81.47	84.07	86.44	77.89
	550.00	81.19	84.20	86.84	89.27	80.53
	600.00	83.76	86.86	89.53	92.01	83.11
	650.00	86.28	89.45	92.14	94.67	85.63
	700.00	88.73	91.96	94.68	97.25	88.08
	750.00	91.12	94.41	97.16	99.76	90.48
	800.00	93.46	96.80	99.57	102.20	92.82

p-Cl-Nitro-benzene	*p-Br-Nitro-benzene*	*p-I-Nitro-benzene*	*m-F-Nitro-benzene*	*m-Cl-Nitro-benzene*	*m-Br-Nitro-benzene*	*m-I-Nitro-benzene*
32.42	32.64	32.89	31.31	32.25	32.71	32.97
32.59	32.80	33.06	31.47	32.41	32.88	33.13
36.91	37.09	37.30	35.88	36.73	37.12	37.34
40.88	41.03	41.20	39.93	40.69	41.03	41.23
44.44	44.57	44.72	43.57	44.26	44.56	44.73
47.60	47.71	47.84	46.80	47.43	47.69	47.84
50.38	50.49	50.60	49.66	50.22	50.45	50.59
52.83	52.92	53.02	52.17	52.68	52.88	53.01
54.98	55.07	55.15	54.38	54.84	55.02	55.14
56.88	56.96	57.04	56.33	56.75	56.91	57.02
58.57	58.64	58.71	58.06	58.44	58.59	58.70
60.07	60.13	60.20	59.61	59.95	60.09	60.19
87.76	90.53	92.52	85.85	89.15	92.71	95.01
87.96	90.74	92.72	86.04	89.35	92.92	95.22
93.31	96.12	98.14	91.23	94.68	98.31	100.65
98.50	101.33	103.38	96.29	99.84	103.52	105.89
103.53	106.37	108.44	101.21	104.84	108.56	110.95
108.38	111.24	113.32	105.97	109.68	113.43	115.83
113.05	115.92	118.01	110.57	114.33	118.10	120.52
117.64	120.42	122.52	115.00	118.81	122.60	125.03
121.85	124.74	126.85	119.27	123.11	126.92	129.36
126.00	128.89	131.01	123.37	127.25	131.07	133.52
129.98	132.88	135.00	127.31	131.22	135.05	137.51
133.81	136.71	138.84	131.11	135.04	138.88	141.35
19.11	19.48	19.86	18.10	19.01	19.60	19.98
19.19	19.57	19.93	18.18	19.09	19.69	20.07
21.42	21.76	22.11	20.40	21.31	21.88	22.24
23.60	23.93	24.26	22.59	23.48	24.03	24.38
25.73	26.03	26.34	24.73	25.59	26.12	26.44
27.76	28.04	28.34	26.77	27.62	28.13	28.43
29.70	29.97	30.24	28.73	29.55	30.03	30.32
31.62	31.78	32.04	30.58	31.38	31.84	32.12
33.24	33.49	33.74	32.33	33.10	33.54	33.81
34.87	35.10	35.34	33.98	34.73	35.15	35.40
36.39	36.61	36.84	35.52	36.25	36.65	36.90
37.82	38.03	38.36	36.98	37.68	38.07	38.31
68.65	71.05	72.66	67.75	70.14	73.11	75.03
68.77	71.17	72.79	67.86	70.26	73.23	75.15
71.89	74.36	76.03	70.83	73.37	76.43	78.41
74.90	77.40	79.12	73.70	76.36	79.49	81.51
77.80	80.34	82.10	76.48	79.25	82.44	84.51
80.62	83.20	84.98	79.20	82.06	85.30	87.40
83.35	85.95	87.77	81.84	84.78	88.07	90.20
86.02	88.64	90.48	84.42	87.43	90.76	92.91
88.61	91.25	93.11	86.94	90.01	93.38	95.55
91.13	93.79	95.67	89.39	92.52	95.92	98.12
93.59	96.27	98.16	91.79	94.97	98.40	100.61
95.99	98.68	100.48	94.13	97.36	100.81	103.04

TABLE II

CALCULATED[a] CONSTANTS a, b, AND c IN EQN (1)

Function	a	$b \times 10^2$	$c \times 10^5$	*Standard deviation*[b] (*cal mole*$^{-1}$ °K^{-1}	a	$b \times 10^2$	$c \times 10^5$	*Standard deviation*[b] (*cal mole*$^{-1}$ °K^{-1})
	o-Fluoronitrobenzene				*o*-Chloronitrobenzene			
C_p°	1.9821	11.55	−5.374	0.3693	3.6583	11.30	−5.260	0.3620
$(H^\circ - H_0^\circ)/T$	2.4583	5.76	−1.812	0.0319	3.7550	5.70	−1.808	0.0301
$-(F^\circ - H_0^\circ)/T$	48.5280	6.63	−1.256	0.0345	49.8816	7.02	−1.441	0.0496
S°	50.9863	12.39	−3.068	0.0371	53.6367	12.72	−3.249	0.0555
	p-Fluoronitrobenzene				*p*-Chloronitrobenzene			
C_p°	1.8278	11.61	−5.416	0.3780	3.7111	11.34	−5.301	0.3767
$(H^\circ - H_0^\circ)/T$	2.5358	5.75	−1.807	0.0330	3.4272	5.79	−1.866	0.0459
$-(F^\circ - H_0^\circ)/T$	47.8042	6.64	−1.263	0.0332	49.0712	7.01	−1.430	0.0486
S°	50.3400	12.39	−3.071	0.0370	52.5485	12.80	−3.296	0.0680
	m-Fluoronitrobenzene				*m*-Chloronitrobenzene			
C_p°	1.9600	11.58	−5.401	0.3760	3.5116	11.34	−5.292	0.3716
$(H^\circ - H_0^\circ)/T$	2.4684	5.77	−1.820	0.0314	3.5053	5.74	−1.825	0.0298
$-(F^\circ - H_0^\circ)/T$	49.1214	6.64	−1.261	0.0343	50.6589	6.98	−1.420	0.0494
S°	51.5898	12.41	−3.081	0.0362	54.1643	12.71	−3.245	0.0536

[a]Constants for Eqn. (1) calculated using input data for temperature range 298.15–1000°K. Note that Table I gives temperature range from 298.15 to 800°K only. [b]Standard deviation of residuals, s.

$$s = \sqrt{\frac{\sum_{i=1}^{n} (Y_{i'} - Y_i)^2}{n-m-1}}$$

where n is the number of observations, m is the number of independent variables, $Y_{i'}$ is the ith observed value of Y (Table I) and Y_i is the ith predicted value of Y (Eqn. 1).

a	$b \times 10^2$	$c \times 10^5$	Standard deviation[b] (cal $mole^{-1}°K^{-1}$)	a	$b \times 10^2$	$c \times 10^5$	Standard deviation[b] (cal $mole^{-1}°K^{-1}$)
o-Bromonitrobenzene				*o*-Iodonitrobenzene			
4.3894	11.17	−5.192	0.3553	5.5060	10.95	−5.076	0.3395
4.2492	5.67	−1.805	0.0286	5.2842	5.57	−1.770	0.0268
51.9265	7.17	−1.513	0.0606	53.2546	7.44	−1.647	0.0743
56.1757	12.84	−3.318	0.0635	58.5389	13.02	−3.417	0.0793
p-Bromonitrobenzene				*p*-Iodonitrobenzene			
4.1001	11.27	−5.261	0.3706	4.5921	11.17	−5.204	0.3626
4.0505	5.71	−1.825	0.0306	4.5534	5.65	−1.793	0.0308
51.1663	7.14	−1.492	0.0576	52.4751	7.27	−1.566	0.0858
55.2169	12.85	−3.317	0.0607	57.0285	12.92	−3.359	0.0663
m-Bromonitrobenzene				*m*-Iodonitrobenzene			
4.3607	11.18	−5.207	0.3612	4.7896	11.11	−5.170	0.3541
4.2598	5.68	−1.812	0.0285	4.7815	5.62	−1.788	0.0266
53.1302	7.18	−1.513	0.0595	54.7190	7.31	−1.579	0.0666
57.3899	12.86	−3.325	0.0630	59.5006	12.94	−3.367	0.0669

TABLE III

MOLECULAR PARAMETERS OF MONOSUBSTITUTED HALONITROBENZENES

o-F-Nitro-benzene	*o-Cl-Nitro-benzene*	*o-Br-Nitro-benzene*	*o-I-Nitro-benzene*	*p-F-Nitro-benzene*	*p-Cl-Nitro-benzene*
Fundamental frequencies, ν, cm^{-1} (Ref. 1)[a,b,c]					
3113, 3090,	3097, 3097,	3094, 3094,	3092, 3092,	3120, 3120,	3104, 3104,
3060, 3060,	3076, 3076,	3074, 3074,	3071, 3071,	3086, 3086,	3081, 3081,
1607, 1598,	1590, 1581,	1588, 1580,	1586, 1575,	1621, 1531,	1606, 1578,
1527, 1484,	1536, 1474,	1536, 1470,	1533, 1459,	1496, 1429,	1525, 1479,
1456, 1352,	1442, 1353,	1440, 1353,	1434, 1352,	1347, 1295,	1424, 1343,
1313, 1270,	1301, 1259,	1297, 1257,	1294, 1256,	1285, 1244,	1279, 1228,
1242, 1162,	1167, 1147,	1160, 1143,	1160, 1142,	1150, 1111,	1169, 1109,
1142, 1091,	1130, 1058,	1120, 1041,	1107, 1039,	1090, 1011,	1095, 1095,
1034, 987,	1036, 985,	1035, 985,	1025, 984,	950, 863,	1014, 965,
956, 863,	954, 853,	953, 852,	952, 852,	853, 806,	953, 855,
856, 809,	774, 734,	852, 775,	850, 777,	748, 682,	847, 829,
776, 741,	726, 853,	730, 703,	728, 693,	678, 619,	741, 741,
684, 657,	687, 651,	690, 645,	693, 635,	1596, 966,	677, 535,
570, 515,	568, 473,	568, 462,	544, 464,	805, 526,	535, 524,
541, 440,	457, 406,	413, 399,	410, 298,	493, 409,	468, 406,
393, 351,	361, 303,	317, 275,	240, 194,	406, 356,	324, 313,
260, 228,	197, 180,	199, 163,	194, 163,	307, 231,	281, 197,
150	137	132	139	130	112
Principal moments of inertia, g $cm^2 \times 10^{39}$ (Refs. 1 and 3)					
I_A 34.658	52.405	67.064	68.568	20.495	20.495
I_B 65.680	66.147	83.662	113.592	105.027	147.587
I_C 100.338	118.553	150.726	182.160	125.522	168.079
I_{red} 15.326	25.487	37.435	45.032	28.595	41.980
Symmetry number, σ (Ref. 8)					
2	2	2	2	4	4
Molecular weight, M					
141.10	157.56	212.02	249.01	141.10	157.56

For physical constants, see Ref. 9

[a]The missing frequencies, ν_3 and ν_4 for *o*- and *m*-isomers were assumed the same as frequencies ν_1 and ν_2 for the same isomers (see Ref. 1). [b]We have estimated the missing frequency in the region 194–298 cm^{-1} for *o*-I-Nitrobenzene (Ref. 1) to be as 240 cm^{-1}. [c]Refs. 1 and 2 suggest that the NO_2 torsional frequency is most likely to be 170 cm^{-1}, corresponding to a barrier of 5.4 kcal/mole. In this work we used this barrier height (5.4 kcal/mole) for all of the 12 halogenated nitrobenzenes. It should be noted that this is an approximation and neglects the symmetry and substituent atom effects on the torsional barrier[6,7] of NO_2 groups. However, the uncertainty in the choice of correct-NO_2 group barrier is much larger[1,2] than apparently the neglected effects[6,7]

p-Br-Nitro-benzene	*p-I-Nitro-nenzene*	*m-F-Nitro-benzene*	*m-Cl-Nitro-benzene*	*m-Br-Nitro-benzene*	*m-I-Nitro-benzene*
3099, 3099,	3095, 3095,	3115, 3115,	3104, 3104,	3105, 3105,	3097, 3097,
3079, 3079,	3074, 3074,	3096, 3096,	3097, 3097,	3083, 3083,	3065, 3065,
1603, 1579,	1599, 1574,	1605, 1595,	1601, 1581,	1600, 1578,	1600, 1574,
1532, 1474,	1527, 1472,	1537, 1482,	1540, 1470,	1537, 1467,	1534, 1464,
1414, 1344,	1410, 1344,	1446, 1355,	1432, 1348,	1429, 1346,	1423, 1345,
1280, 1225,	1280, 1236,	1313, 1274,	1308, 1272,	1303, 1272,	1295, 1272,
1171, 1108,	1176, 1107,	1230, 1154,	1153, 1134,	1152, 1117,	1144, 1110,
1101, 1068,	1102, 1059,	1104, 1080,	1100, 1067,	1097, 1064,	1098, 1058,
1012, 965,	1009, 965,	1005, 980,	1004, 981,	1003, 980,	1002, 980,
951, 851,	849, 814,	925, 909,	921, 893,	922, 891,	925, 893,
843, 820,	734, 954,	883, 810,	879, 795,	869, 797,	864, 798,
737, 737,	841, 734,	802, 737,	750, 731,	729, 729,	728, 714,
674, 622,	673, 618,	672, 665,	665, 656,	664, 647,	663, 640,
525, 481,	523, 458,	553, 526,	537, 491,	530, 478,	532, 466,
459, 405,	452, 405,	504, 431,	420, 415,	418, 398,	414, 397,
300, 276,	288, 260,	416, 377,	382, 326,	311, 295,	298, 252,
256, 182,	214, 165,	248, 218,	204, 178,	193, 147,	186, 129,
102	96	172	164	147	129
20.495	20.495	34.658	52.405	83.662	113.592
223.358	289.663	82.470	99.166	129.148	154.324
243.854	310.157	117.128	151.572	212.810	267.916
54.248	60.066	24.806	37.680	50.279	56.692
4	4	2	2	2	2
212.02	249.01	141.10	157.56	212.02	249.01

NOMENCLATURE

a, b, c	constants
C_p°	ideal gas heat capacity at constant pressure (cal/mole/°K)
$-(F^\circ - H_0^\circ)/T$	ideal gas free energy function (cal/mole/°K)
$(H^\circ - H_0^\circ)/T$	ideal gas enthalpy function (cal/mole/°K)
I_A, I_B, I_C	principal moments of inertia (g cm^2)
I_{red}	reduced moment of inertia (g cm^2)
M	molecular weight
S°	ideal gas entropy (E.U.)
T	absolute temperature (°K)
A	any of the thermodynamic functions (cal/mole/°K)
ν	wave number (cm^{-1})
σ	molecular symmetry number

Superscripts ° refer to the ideal gas state. Subscripts p refer to pressure.

ACKNOWLEDGEMENT

The financial assistance of the National Research Council of Canada is gratefully acknowledged.

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