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IDEAL GAS THERMODYNAMIC PROPERTIES OF BENZENEDIOLS: PYROCATECHOL, RESORCINOL AND HYDROQUINONE

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ABSTRACT

The vibrational fundamentals have been selected using the available literature data. −271.96, −274.89 and −261.71 kJ mole^{-1} are selected for the enthalpies of formation (g, 298.15 K) for pyrocatechol, resorcinol and hydroquinone, respectively. The ideal gas thermodynamic properties are obtained assuming one, three and two rotational isomers for 1,2-, 1,3-, and 1,4-benzenediol, respectively.

INTRODUCTION

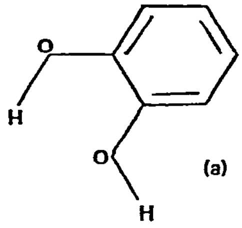
In continuation of the calculations of ideal gas thermodynamic properties of coal chemicals (phenol[1], cresols[1], xylenols[2], naphthol[3], naphthalene[4], anthracene[5], phenanthrene[5], furans[6]), this work was carried out. It was found that no ideal gas thermodynamic properties are available for benzenediols. This is due to the lack of information regarding the vibrational assignments, stability of the rotational isomers and the potential barrier heights (V_2).

In this work we have selected a complete set of fundamental frequencies using the data from the literature[7–13]. Our molecular orbital calculations[14] gave us the information regarding the stability of the various rotational isomers for pyrocatechol (1,2-benzenediol), resorcinol (1,3-benzenediol) and hydroquinone (1,4-benzenediol). In turn the ideal gas thermodynamic properties were calculated.

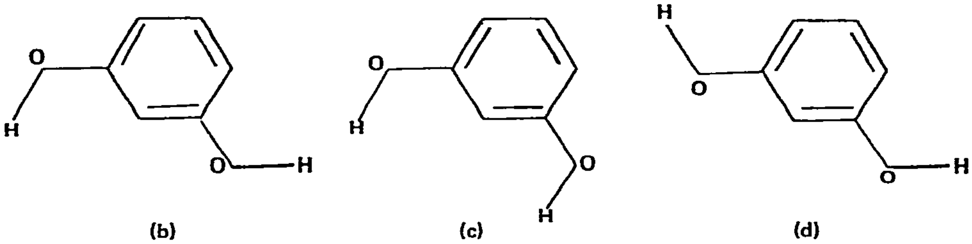
VIBRATIONAL FUNDAMENTAL FREQUENCIES

Pyrocatechol

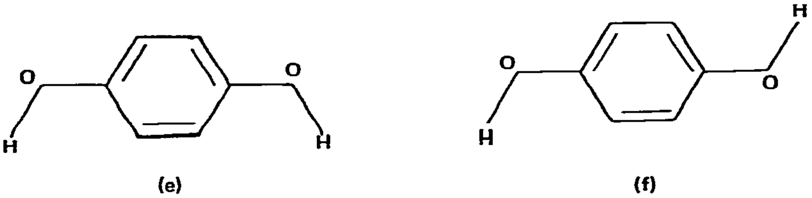
Pyrocatechol has two OH groups in the *ortho* position and three orientations are possible for these groups giving rise to three rotational isomers. According to Wilson[7], the rotational isomer having intramolecular hydrogen bonding does not exist in the vapor phase as he did not observe much shift in the OH stretching frequency. On the contrary our MO calculations show that the rotational isomer with intramolecular hydrogen bonding is the most stable isomer and the other two isomers may be assumed to be non-existing. Calculations of Snyder et al.[15] on the shifts



Pyrocatechol



Resorcinol



Hydroquinone

Fig. 1. Stable rotational isomers of pyrocatechol, resorcinol and hydroquinone.

of OH stretching frequencies of the hydrogen bonded systems favor our results. They obtained the shift of 44 cm^{-1} for pyrocatechol which had excellent agreement with the experimental shift of 42 cm^{-1} observed by Robinson et al.[16] in CCl_4 solution. Wilson's result gives a shift of 49 cm^{-1} in the gas phase which agrees well with Snyder et al.'s calculated value.

The intramolecular hydrogen bond $(\mathrm{O}{-}^{\mathrm{H}}{\cdots}\mathrm{O})$ is bent and hence is weaker than the colinear interhydrogen bond (O–H---O). This causes it to have a lower shift. The preceeding observation enabled us to conclude that an intramolecular hydrogen bonded structure is present in pyrocatechol (Fig. 1). Additionally, pyrocatechol has a very high value for torsional frequency which could be due to the presence of an intrahydrogen bond.

Using the vibrational assignments reported by Wilson[7], Hidalgo and Otero[11], Nonnenmacher and Mecke[9], and Sechkarev and Timoshenko[8], a complete set of fundamentals was obtained. The same torsional frequency[13] was assumed for both the OH groups. The adopted frequencies are presented in Table 1. They compare well with those for *o*-cresol[17].

TABLE 1

VIBRATIONAL FREQUENCIES FOR PYROCATECHOL, RESORCINOL AND HYDROQUINONE (cm^{-1})

Pyrocatechol *In-plane*	*Resorcinol*	*Hydroquinone*
3663	3654	3652
3605	3651	3652
3069	3064	3030
3060	3053	3030
3051	3039	3020
3051	3036	3020
1616	1614	1616
1607	1607	1611
1504	1502	1521
1479	1486	1455
1365	1332	1332
1324	1304	1324
1275	1299	1264
1251	1225	1249
1195	1190	1236
1151	1146	1178
1151	1140	1158
1092	1075	1087
1035	1000	1001
859	845	853
768	745	754
563	565	648
553	542	519
501	494	468
277	356	385
Out-of-plane		
968	956	937
916	929	918
850	837	829
742	768	821
741	680	700
522	531	531
450	458	412
299	243	322
204	200	211
411[a](2)	318[a](2)	266[a](2)

[a] OH torsional frequency, same for both the OH groups.

Resorcinol

Wilson[7] has assumed the rotational isomer with C_s symmetry to be present in resorcinol. The MO calculations[14] show that all of the three possible rotational isomers (Fig. 1) are almost equally stable. We have adopted the same set of fundamentals for all three isomers.

Using the vibrational assignments reported by Wilson[7], Hidalgo and Otero[11], Nonnenmacher and Mecke[9], and Sechkarev and Timoshenko[8], a complete set of fundamentals was obtained and is presented in Table 1. They compare well with those for *m*-cresol[17]. The same torsional frequency[13] was assumed for both the OH groups.

Hydroquinone

Wilson[7] has assigned the frequencies according to C_{2h} symmetry. From our MO calculations it is seen that both of the isomers, one with C_{2h} and the other with C_{2v} symmetry, are equally stable (Fig. 1). From their calculations Radom et al.[18] found the *trans* isomer to be more stable by only 0.29 kJ mole^{-1}.

A complete set of fundamentals was evaluated using the assignments reported by Wilson[7], Jakobsen and Brewer[10], Hidalgo and Otero[11], and Sechkarev and Timoshenko[8]. This set compared well with that for *p*-cresol[17]. The same set of fundamentals was assumed for both isomers and is presented in Table 1. The same torsional frequency[13] was assumed for both the OH groups.

MOLECULAR STRUCTURE

The structural parameters for pyrocatechol are reported by Brown[19] and Wunderlich and Mootz[20]. Here we have adopted those of Wunderlich and Mootz as they are refined values which are for the intramolecular hydrogen bonded conformer. Bacon and Curry[21] and Bacon and Jude[22] reported some of the structural parameters for resorcinol. Using these values and those for phenol[23] and *m*-cresol[24], we estimated all the parameters for resorcinol. Structural parameters are not available for hydroquinone. In this work they are assumed to be the same as those for phenol[23] and *p*-cresol[24].

ENTHALPIES OF FORMATION

No reliable values of enthalpies of formation are available for these compounds. For hydroquinone, Cox and Pilcher[25] recommended ΔH_f° (g, 298.15) = -265.18 ± 2.09 kJ mole^{-1}. They used the ΔH_{sub} (99.16 kJ mole^{-1}) reported by Wolf and Trieschmann[26]. However, they erroneously attributed this value to Magnus[27]. We feel that ΔH_{sub} = 103.76 kJ mole^{-1} reported by Magnus from vapor pressure data of Coolidge and Coolidge[28] is more reliable. With the above value of ΔH_{sub} and ΔH_f (c, 298.15) = -365.47 ± 1.26 kJ mole^{-1} (ref. 29) we obtained ΔH_f° (g, 298.15) = -261.71 ± 2.09 kJ mole^{-1}.

For pyrocatechol (-353.13 kJ mole^{-1}) and resorcinol (-368.19 kJ mole^{-1}) the enthalpies of formation of solids were obtained from Zwolinski et al.[29] and Desai et al.[30], respectively. Using the only available value of enthalpy of sublimation[27] (81.17 kJ mole^{-1}) for pyrocatechol we obtained ΔH_f° (g, 298.15) = -271.96 ± 5 kJ mole^{-1}. For resorcinol, ΔH_f° (g, 298.15) = $274.89 \pm 5.$ kJ mole^{-1} was obtained using ΔH_{sub} (93.30 kJ mole^{-1}) deduced from the vapor pressure equation of Hoyer and Peperle[31].

TABLE 2

IDEAL GAS THERMODYNAMIC PROPERTIES OF PYROCATECHOL

T (*K*)	C_p^0	S^0 (*J K*$^{-1}$ *mole*$^{-1}$)	$-(G^0-H_0^0)/T$	$H^0-H_0^0$ (*kJ mole*$^{-1}$)	ΔH_f^0 (*kJ mole*$^{-1}$)	ΔG_f^0 (*kJ mole*$^{-1}$)	*Log* K_f
0	0.00	0.00	0.00	0.00	−251.44	−251.44	Infinite
50	34.39	224.86	191.43	1.67	−257.57	−248.00	259.077
100	45.32	251.48	215.25	3.62	−260.61	−237.26	123.929
150	62.77	273.03	230.97	6.31	−263.70	−224.91	78.321
200	82.10	293.72	244.08	9.93	−266.73	−211.56	55.253
273.15	110.62	323.55	261.37	16.98	−270.74	−190.57	36.443
298.15	120.09	333.64	267.01	19.87	−271.96	−183.24	32.103
300	120.78	334.39	267.42	20.09	−272.05	−182.68	31.808
400	155.47	374.02	289.15	33.95	−276.08	−152.31	19.890
500	183.90	411.89	309.94	50.97	−278.89	−120.96	12.637
600	206.30	447.48	329.94	70.53	−280.74	−89.20	7.765
700	223.91	480.66	349.12	92.07	−281.91	−57.14	4.264
800	237.92	511.50	367.52	115.19	−282.53	−25.04	1.635
900	249.27	540.20	385.13	139.57	−282.71	7.24	−0.420
1000	258.60	566.97	401.99	164.98	−282.45	39.55	−2.066
1100	266.38	591.99	418.14	191.24	−281.89	71.42	−3.392
1200	272.93	615.46	433.61	218.21	−281.19	103.60	−4.510
1300	278.49	637.53	448.46	245.79	−280.36	135.71	−5.453
1400	283.25	658.34	462.72	273.88	−279.44	168.03	−6.269
1500	287.35	678.03	476.42	302.42	−278.42	199.80	−6.958

I_a = 154.077 μÅ², I_b = 225.020 μÅ², I_c = 379.097 μÅ², I_r = 0.8578 μÅ² (average value for two OH rotors), σ = 1.
V_2 = 28.56 kJ mole^{-1}.

TABLE 3

IDEAL GAS THERMODYNAMIC PROPERTIES OF RESORCINOL

T (*K*)	C_p^0	S^0 (*J K*$^{-1}$ *mole*$^{-1}$)	$-(G^0-H_0^0)/T$	$H^0-H_0^0$ (*kJ mole*$^{-1}$)	ΔH_f^0 (*kJ mole*$^{-1}$)	ΔG_f^0 (*kJ mole*$^{-1}$)	*Log* K_f
0	0.00	0.00	0.00	0.00	−255.07	−255.07	Infinite
50	34.69	231.45	197.97	1.67	−261.20	−251.38	262.611
100	47.46	258.83	221.98	3.69	−264.18	−240.41	125.574
150	65.81	281.46	238.08	6.51	−267.14	−227.88	79.354
200	85.45	303.08	251.64	10.29	−270.01	−214.40	55.994
273.15	114.24	333.99	269.57	17.60	−273.76	−193.29	36.962
298.15	123.75	344.40	275.41	20.57	−274.89	−185.94	32.575
300	124.44	345.17	275.84	20.80	−274.97	−185.38	32.276
400	158.69	385.82	298.29	35.01	−278.64	−154.98	20.238
500	185.86	424.28	319.68	52.30	−281.19	−123.69	12.921
600	206.73	460.10	340.14	71.97	−282.93	−92.02	8.011
700	222.95	493.23	359.67	93.49	−284.12	−60.07	4.483
800	235.90	523.88	378.31	116.46	−284.90	−28.06	1.832
900	246.52	552.30	396.08	140.59	−285.32	4.14	−0.241
1000	255.42	578.74	413.04	165.70	−285.36	36.42	−1.902
1100	262.97	603.45	429.24	191.63	−285.13	68.29	−3.243
1200	269.45	626.62	444.73	218.26	−284.77	100.49	−4.374
1300	275.04	648.41	459.57	245.49	−284.30	132.65	−5.330
1400	279.88	668.97	473.80	273.24	−283.71	165.05	−6.158
1500	284.11	688.43	487.46	301.45	−283.02	196.93	−6.858

1b: I_a = 135.570 μÅ², I_b = 280.492 μÅ², I_c = 416.063 μÅ², I_r = 0.8556 μÅ², σ = 1.
1c: I_a = 139.397 μÅ², I_b = 275.297 μÅ², I_c = 414.694 μÅ², I_r = 0.8518 μÅ², σ = 2.
1d: I_a = 131.849 μÅ², I_b = 285.549 μÅ², I_c = 417.398 μÅ², I_r = 0.8599 μÅ², σ = 2.
V_2 = 17.45 kJ mole^{-1}.

TABLE 4

IDEAL GAS THERMODYNAMIC PROPERTIES OF HYDROQUINONE

T (K)	C_p^0	S^0 $(J K^{-1} mole^{-1})$	$-(G^0-H_0^0)/T$	$H^0-H_0^0$ $(kJ mole^{-1})$	ΔH_f^0 $(kJ mole^{-1})$	ΔG_f^0 $(kJ mole^{-1})$	$Log K_f$
0	0.00	0.00	0.00	0.00	−241.98	−241.98	Infinite
50	34.52	230.73	197.28	1.67	−248.11	−238.83	249.503
100	47.69	258.06	221.24	3.68	−251.09	−228.40	119.302
150	66.48	280.88	237.36	6.53	−254.03	−216.42	75.362
200	86.13	302.69	250.98	10.34	−256.86	−203.48	53.144
273.15	114.40	333.75	269.01	17.69	−260.58	−183.20	35.033
298.15	123.60	344.17	274.87	20.66	−261.71	−176.13	30.857
300	124.27	344.94	275.30	20.89	−261.79	−175.59	30.573
400	157.14	385.35	297.81	35.02	−265.55	−146.32	19.107
500	183.26	423.34	319.16	52.09	−268.31	−116.11	12.130
600	203.62	458.63	339.50	71.48	−270.34	−85.48	7.442
700	219.74	491.27	358.88	92 67	−271.85	−54.52	4.068
800	232.82	521.50	377.34	115.32	−272.94	−23.45	1.531
900	243.67	549.56	394.94	139.16	−273.66	7.86	−0.456
1000	252.83	575.72	411.72	164.00	−273.97	39.28	−2.051
1100	260.64	600.20	427.76	189.68	−273.99	70.30	−3.338
1200	267.36	623.17	443.09	216.09	−273.85	101.68	−4.426
1300	273.17	644.81	457.79	243.13	−273.57	133.04	−5.346
1400	278.22	665.24	471.88	270.70	−273.17	164.65	−6.143
1500	282.61	684.59	485.42	298.75	−272.63	195.75	−6.817

1e: $I_a = 90.963\ \mu Å^2$, $I_b = 341.649\ \mu Å^2$, $I_c = 432.612\ \mu Å^2$, $I_r = 0.8586\ \mu Å^2$, $\sigma = 2$.
1f: $I_a = 90.857\ \mu Å^2$, $I_b = 341.789\ \mu Å^2$, $I_c = 432.645\ \mu Å^2$, $I_r = 0.8590\ \mu Å^2$, $\sigma = 2$.
$V_2 = 12.62$ kJ mole^{-1}.

THERMODYNAMIC PROPERTIES

The ideal gas thermodynamic properties were calculated by usual procedure and are presented in Tables 2, 3 and 4. As mentioned earlier, pyrocatechol was assumed to be present as a single rotational isomer, resorcinol as a mixture of the three and hydroquinone as a mixture of two rotational isomers. The internal rotation contributions to the thermodynamic properties were obtained by the use of a partition function formed by summation of the calculated internal rotation energy levels. These energy levels were obtained from an approximate solution of the Schroedinger equation using the potential function

$$V_{OH} = \frac{1}{2} V_2(1 - \cos 2\theta)$$

where V_2 was derived from the torsional frequency by usual procedure[32].

The reliability of the calculated thermodynamic properties could be checked only for hydroquinone. The third law entropy at 298.15 K is compared with spectroscopically calculated values in Table 5. The agreement seems to be satisfactory.

TABLE 5

COMPARISON OF THIRD LAW ENTROPY WITH SPECTROSCOPIC ENTROPY ($\text{J K}^{-1}\ \text{mole}^{-1}$) AT 298.15 K FOR HYDROQUINONE

		Ref.
S (solid	140.16	29
$\Delta H_{\text{sub}}/T$	348.01	28
$R \ln P$	−145.10	28
Gas imperfection correction	0.0	
S^0 (third law)	343.07 ± 5.	
S^0 (spectroscopic)	344.17 ± 5.	

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