the mean coordinate bond dissociation energies given in Table IV. For the tetrahedral complexes of cobalt, zinc, and cadmium the bond strengths are of the same order as previously found (*2*) for other tetrahedral sulfur-bonded complexes. The highest value, for cobalt, may reflect the additional ligand field stabilization present in this species. Although the silver complex has a distorted structure, the bond energy is close to that of the other tetrahedral complexes. The mercury complex displays considerably weaker bonding. Direct comparison is probably unwise, however, owing to the uncertainty in the value of the enthalpy of sublimation and to the unusual structure of the complex.

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Registry No. tu, 62-56-6; $[Cotu_2Cl_2]$, 14240-49-4; $[Zntu_2Cl_2]$, 14239-75-9; $[Cdtu_2Cl_2]$, 15021-53-1; $[Agtu_2Cl]$, 15631-39-7; $[Hgtu_2Cl_2]$, 15020-97-0; Co, 7440-48-4; Zn, 7440-66-6; Cd, 7440-43-9; Ag, 7440-22-4; Hg, 7439-97-6.

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Vapor Pressures of Methyl, Ethyl, *n*-Propyl, Isobutyl, and *n*-Butyl Benzoates at Reduced Pressures

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The vapor pressures of methyl, ethyl, *n*-propyl, isobutyl, and *n*-butyl benzoates were measured over the pressure range of 0.50-30 kPa. The results were examined by fitting with a Chebyshev polynomial and with Miller, Florst-Kalkwarf, and Antoine equations. The percent root mean square deviations of pressures of these five benzoates for the Miller fit were 0.30, 0.30, 0.25, 0.16, and 0.24, respectively. The enthalpies of vaporization of the benzoates were also obtained by using a Chebyshev polynomial with mean errors of ±0.2 kJ/mol.

Experimental Section

As few experimental data for alkyl benzoates have been published, the vapor pressure of five benzoates were measured at 0.5-30 kPa.

All the special grade materials from Tokyo Kasei Co., Ltd., were used without further purification. The purities of the materials were determined to exceed 99% by a gas chromatographic analysis with a 3 mm i.d. and 2 m length column packed with 5% silicone (SE52) on celite. Table I shows the densities and refractive indexes compared with the literature values (*1-5*).

The experimental apparatus and procedure were already described elsewhere (*6*). The Multi-Range Model 157/100 pressure standard with a spiral quartz Bourdon tube attached a calibration table from Texas Instruments Inc. was used as a pressure gauge. As the gauge was essentially a difference meter, a McLeod gauge was used in determining zero pressure (less than 0.001 kPa) as a standard pressure. The accuracies of pressures were ±0.002 kPa for the 10-30 kPa range and ±0.001 kPa for 0.50-10 kPa range. Three mercury thermometers with immersion lines marked at the 18-cm points from their bulb ends, i.e., sets of 40-100, 100-150, and 150-200 °C graduations, were used for temperature measurements. They were calibrated in 5-°C intervals with accuracies of ±0.04 K by Watanabe Keiki Seisakusho Co. Ltd., Tokyo. The intermediate temperatures in the intervals were interpolated.

Results and Discussion

The experimental results are presented in Table II. The results are also plotted in Figure 1 including a comparison with values from the literature (*2*, 7-13).

The Chebyshev polynomial (*14*) and Miller (*15*), Frost-Kalkwarf (*16*), and Antoine equations were used to fit the results.

The Chebyshev polynomial is

$$t \ln P = a_0/2 + \sum a_i E_i(x)$$

where $t = T - 273.15$ K, $E_1(x) = x$, $E_2(x) = 2x^2 - 1$, $E_i(x) = 2xE_{i-1}(x) - E_{i-2}(x)$, and x is a function of temperature defined as

$$x = \frac{2T - (T_{max} + T_{min})}{T_{max} - T_{min}}$$

where T_{max} and T_{min} are the maximum and minimum temperatures of the related substances. The polynomial with four

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Table I. Physical Properties of Five Benzoates

	density, g/cm³			n_D[a]		
	temp, K	exptl	lit.	temp, K	exptl	lit.
methyl benzoate	298.15	1.0833	1.0832[b]	293.15	1.51873	1.51701[c]
ethyl benzoate	298.15	1.0421	1.04214[d]	293.15	1.50672	1.50519[c]
n-propyl benzoate	293.15	1.0227	1.0232[c]	293.15	1.50087	1.50031[c]
isobutyl benzoate	293.15	0.9957	0.9989[e]	293.15	1.49451	1.4934[e]
n-butyl benzoate	293.15	1.0056	1.0057[f]	293.15	1.49782	1.49720[c]

[a] Refractive index. [b] Reference 1. [c] Reference 2. [d] Reference 3. [e] Reference 4. [f] Reference 5.

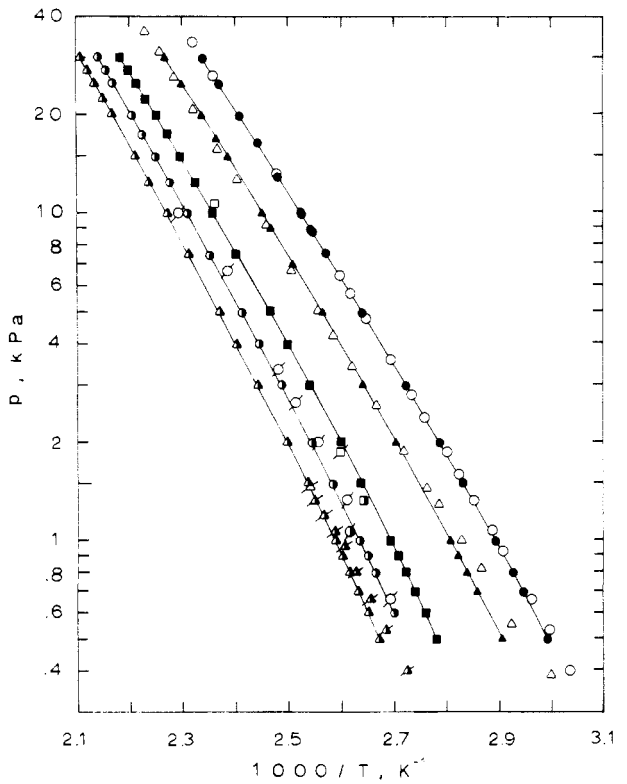

Figure 1. Vapor pressures of five benzoates vs $1/T$: ●, ▲, ■, ◑, ▲, values from this work for methyl, ethyl, *n*-propyl, isobutyl, and *n*-butyl benzoates respectively; methyl benzoate (○, Kahlbaum (1898) (*7*)); ethyl benzoate (△, Hieber and Reindl (1940) (*8*)); *n*-propyl benzoate (◨, Matsuno and Han (1983) (*9*); ⊡, Price and Belanger (1954) (*10*); □, Negoro and Saheki (1956) (*11*)); isobutyl benzoate (◌, Kahlbaum (1884) (*12*); ◌, Matsuno and Han (1933) (*9*)); *n*-butyl benzoate (◭, Hickman and Weyerts (1930) (*13*); ◭, Vogel (1948) (*2*)).

parameters is equivalent to the Miller equation.

The Miller equation is

$$\ln P = A_m + B_m/t + C_m t + D_m t^2$$

or

$$t \ln P = A_m t + B_m + C_m t^2 + D_m t^3$$

The Frost–Kalkwarf equation is

$$\ln P = A_f + B_f/t + C_f \ln t + D_f P/t^2$$

or

$$t \ln P = A_f t + B_f + C_f t \ln t + D_f P/t$$

The Antoine equation is

$$\ln P = A_a - B_a/(t + C_a)$$

or

$$t \ln P = A_a t + D_a - C_a \ln P$$

where $D_a = A_a C_a - B_a$.

All the constants of the expression mentioned above were determined by least-squares fits of $t \ln P$.

Table II. Vapor Pressures of Five Benzoates (from Experiment)

T, K	P, kPa	ΔH,[a] kJ/mol	T, K	P, kPa	ΔH,[a] kJ/mol
		Methyl Benzoate			
428.33	30.000	46.7	389.16	7.604	49.9
422.70	25.000	47.3	378.99	5.000	50.7
415.77	20.000	47.9	367.42	3.000	51.7
410.09	16.499	48.3	358.86	2.000	52.7
403.47	13.000	48.9	353.18	1.500	53.6
396.41	10.113	49.3	345.47	1.000	55.0
396.19	10.000	49.3	341.66	0.800	56.0
393.15	9.000	49.5	339.26	0.700	56.6
392.97	8.851	49.6	333.86	0.500	58.7
		Ethyl Benzoate			
440.55	30.000	48.7	390.05	5.000	52.6
434.58	25.000	49.2	378.49	3.000	53.8
427.68	20.000	49.8	369.73	2.000	54.8
422.87	17.000	50.2	356.00	1.000	57.0
419.13	15.000	50.5	354.25	0.900	57.5
407.82	10.000	51.3	352.14	0.800	58.0
404.95	9.000	51.5	349.66	0.700	58.6
398.47	7.000	52.0	344.05	0.500	60.4
		n-Propyl Benzoate			
457.80	30.000	51.1	405.58	5.000	55.3
454.49	27.500	51.4	400.15	4.000	55.9
451.28	25.000	51.7	393.51	3.000	56.9
447.92	22.500	52.1	384.67	2.000	58.6
444.20	20.000	52.4	378.89	1.500	60.2
440.02	17.500	52.7	371.04	1.000	62.8
435.40	15.000	53.1	369.21	0.900	63.6
430.10	12.500	53.4	367.20	0.800	64.6
423.85	10.000	53.9	364.80	0.700	65.8
416.05	7.500	54.4	362.24	0.600	67.2
			359.42	0.500	69.0
		Isobutyl Benzoate			
466.76	30.000	53.9	414.35	5.000	56.7
463.77	27.500	53.9	408.89	4.000	57.4
460.59	25.000	54.0	402.04	3.000	58.6
453.47	20.000	54.2	393.07	2.000	60.4
449.29	17.500	54.4	387.14	1.500	62.0
444.71	15.000	54.6	379.32	1.000	64.3
439.18	12.500	55.0	377.32	0.900	64.9
432.80	10.000	55.3	375.27	0.800	65.6
424.92	7.500	55.7	370.21	0.600	67.8
		n-Butyl Benzoate			
474.61	30.000	54.9	416.08	4.000	59.2
471.58	27.500	54.8	409.29	3.000	60.1
468.42	25.000	54.9	400.12	2.000	61.7
464.97	22.500	54.9	394.06	1.500	63.2
461.19	20.000	55.0	386.14	1.000	65.8
452.11	15.000	55.7	384.21	0.900	66.6
446.67	12.500	56.1	382.14	0.800	67.6
440.18	10.000	56.6	379.70	0.700	68.9
432.16	7.500	57.4	376.98	0.600	69.3
421.62	5.000	58.5	374.07	0.500	70.8

[a] Enthalpy of vaporization obtained from the Chebyshev polynomial.

The percent root square deviations of pressure (prms) obtained by using Chebyshev polynomials with 3–10 parameters were estimated as 1.78, 0.30, 0.32, and 0.25 with 3, 4, 5, and 6 parameters, respectively, and 0.24 with 7–10 parameters for

Table III. Constants of Miller and Frost-Kalkwarf Equations and Chebyshev Polynomial

Chebyshev const		Miller const		Frost-Kalkwarf const	
		Methyl Benzoate			
a_0	426.203	A_m	−2.44360	A_f	−24.8763
a_1	286.834	B_m	−72.7929	B_f	105.6931
a_2	29.587	C_m	0.537278×10^{-1}	C_f	5.46692
a_3	−2.1712	D_m	-0.841657×10^{-4}	D_f	13.527
a_4	0.10866				
a_5	0.26194				
prms[a]	0.25	prms[a]	0.30	prms[a]	0.38
		Ethyl Benzoate[b]			
a_0	462.309	A_m	−2.58158	A_f	−27.2845
a_1	311.396	B_m	−100.8819	B_f	113.8421
a_2	28.922	C_m	0.521035×10^{-1}	C_f	5.86491
a_3	−2.1414	D_m	-0.762554×10^{-4}	D_f	−22.121
prms[a]	0.30	prms[a]	0.30	prms[a]	0.32
		n-Propyl Benzoate			
a_0	517.119	A_m	−0.62873	A_f	−23.0225
a_1	344.359	B_m	−249.0629	B_f	−24.1904
a_2	25.361	C_m	0.359278×10^{-1}	C_f	5.07250
a_3	−1.0535	D_m	-0.364276×10^{-4}	D_f	110.424
a_4	−0.27131				
prms[a]	0.21	prms[a]	0.25	prms[a]	0.32
		Isobutyl Benzoate			
a_0	562.122	A_m	−0.19841	A_f	−23.3338
a_1	355.074	B_m	−308.0472	B_f	−55.8869
a_2	23.521	C_m	0.321218×10^{-1}	C_f	5.11238
a_3	−0.7730	D_m	-0.273834×10^{-4}	D_f	131.424
a_4	−0.09274				
a_5	−0.15467				
prms[a]	0.14	prms[a]	0.16	prms[a]	0.18
		n-Butyl Benzoate			
a_0	567.691	A_m	−0.10668	A_f	−23.4476
a_1	378.352	B_m	−353.2868	B_f	−93.6105
a_2	24.090	C_m	0.317416×10^{-1}	C_f	5.13256
a_3	−0.8787	D_m	-0.278936×10^{-4}	D_f	113.474
a_4	−0.17728				
a_5	0.15110				
prms[a]	0.19	prms[a]	0.24	prms[a]	0.28

[a] Percent root mean square deviation defined by $100(\sum_i((P_{expt} - P_{calcd})/P_{expt})_i^2/n)^{1/2}$. [b] In this case, the Chebyshev polynomial equals the Miller equation.

methyl benzoate. For ethyl benzoate the prms of pressure were 1.45 with 3 parameters, 0.30 with 4–5 parameters, 0.29, 0.28, and 0.27 with 6–8 parameters, respectively, and 0.26 with 9–10 parameters. For *n*-propyl benzoate the prms of pressure were 0.59 and 0.25 with 3 and 4 parameters, respectively, 0.21 with 5–6 parameters, 0.19 with 7 parameters, and 0.17 with 8–10 parameters. For isobutyl benzoate the prms of pressure were 0.43, 0.16, 0.16, 0.14, and 0.14 with 3–7 parameters, respectively, and 0.12 with 8–10 parameters. For *n*-butyl benzoate the prms of pressure was 0.45, 0.24, 0.20, 019, 0.19, 0.18, 0.17, and 0.16 with 3–10 parameters, respectively. As listed in Table III, 6, 4, 5, 6, and 6 parameters for methyl, ethyl, *n*-propyl, isobutyl, and *n*-butyl benzoates, respectively, were selected to provide satisfactory fitness with relatively few parameters.

The prms of the Miller, Frost–Kalkwarf, and Antoine equations were found to be 0.30, 0.38, and 0.46, respectively, for methyl benzoate; 0.30, 0.32, and 0.38, respectively, for ethyl benzoate; 0.25, 0.32, and 0.79, respectively, for *n*-propyl benzoate; 0.16, 0.18, and 0.65, respectively, for isobutyl benzoate; and 0.24, 0.28, and 0.71, respectively, for *n*-butyl benzoate. The constants of the Miller and Frost–Kalkwarf equations are listed in Table III. The Antoine constants were not listed because of the large errors of *n*-propyl, isobutyl and *n*-butyl benzoates.

The enthalpies of vaporization, which were obtained from the Chebyshev polynomial with constants shown in Table III and the Clausius–Clapeyron relation, have been also presented in Table II. The errors of the enthalpies were estimated as ±0.2 kJ/mol from the Chebyshev polynomial with higher parameters.

Conversely, the temperatures were calculated from the pressures by using the Miller and Frost–Kalkwarf equations. The mean temperature differences of the Miller and Frost–Kalkwarf equations were taken as 0.06 and 0.07 K, respectively, for methyl benzoate; 0.05 K in both cases for ethyl benzoate; 0.05 and 0.06 K, respectively, for *n*-propyl benzoate; 0.04 K in both cases for isobutyl benzoate; and 0.04 and 0.05 K, respectively, for *n*-butyl benzoate. The Miller equation gives a somewhat better correlation than the Frost–Kalkwarf equation.

Glossary

ΔH	enthalpy of vaporization, kJ/mol
P	pressure, kPa
T	temperature, K
t	T − 273.15, K

Registry No. Methyl benzoate, 93-58-3; ethyl benzoate, 93-89-0; *n*-propyl benzoate, 2315-68-6; *n*-butyl benzoate, 136-60-7; isobutyl benzoate, 120-50-3.

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