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Vapor Pressures and Enthalpies of Vaporization of Benzyl Halides and Benzyl Ethers

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Molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ of seven benzyl halides and seven benzyl ethers have been obtained from the temperature dependence of the vapor pressure measured by the transpiration method. These values and the correlation-gas chromatography method, based on Kovat's index, have been applied for the determination of $\Delta_l^g H_m^\circ$ of three cumyl halides (Cl, Br, and I). The data obtained for $\Delta_l^g H_m^\circ$ of benzyl derivatives have been checked successfully for internal consistency using enthalpies of formation of alkyl halides and alkyl ethers available from the literature.

1. Introduction

Knowledge of the thermochemical properties of benzyl derivatives is required to determine the radical stabilization energies and strength of a C−C or C−X (X = halide) bond in these compounds.[1] Benzyl radicals, produced by the thermal decomposition of benzyl derivatives, are widely used as initiators of radical polymerization. They also play an important role in stimulating spontaneous ignition, both in diesel and petrol engines.[2] Thus, a systematical study of the thermochemistry of benzyl derivatives seems to be important for practical and theoretical reasons. In our previous works[3−8] the thermochemical properties of benzyl derivatives of ethers,[3−5] esters,[6] nitriles,[7] alkohols,[8] and amines[8] were measured. In a continuation of this research line, vapor pressures and the standard molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ of seven benzyl halides (F, Cl, Br, and I) and seven benzyl ethers (see Figure 1) have been obtained from the temperature dependence of the vapor pressure measured by the transpiration method. These values and the correlation-gas chromatography method, based on Kovat's indices,[9] have been applied for the determination of $\Delta_l^g H_m^\circ$ of three cumyl halides **3a**−**c** (see Figure 1). To check our results for internal consistency, we have used new experimental results $\Delta_l^g H_m^\circ$ for benzyl derivatives together with data already available from the literature[3−5,10] for correlating the enthalpies of vaporization of benzyl derivatives with the $\Delta_l^g H_m^\circ$ of alkyl halides and alkyl ethers.

2. Experimental Section

2.1. Materials. Benzyl fluoride **1a** was prepared from benzyl chloride and potassium fluoride.[11] Benzyl halides **1b** and **1c** were of commercial origin (Aldrich). Benzyl iodide **1d**, (1-iodoethyl)benzene (**2c**), and cumyl iodide (**3c**) were prepared from KI and the corresponding benzyl chloride **(1b)**, (1-chloroethyl)benzene **(2a),** and cumyl bromide **(3b)**.[13] Benzyl ethers **1e** and **1f** were prepared according to procedures given in the literature.[14,15] *tert*-Amyl benzyl ether (**1g)** and benzyl ethers **2e**−**g** were synthesized via alkylation of appropriate alcohol with 2-methyl-butene-2 or styrene in the presence of a catalytic amount of cation-exchange resin in H^+ form (Amberlist 15, Aldrich) at room temperature.[4,5] Prior to the experiments, the cation-exchange resin Amberlist 15 in H^+ form was dried in a vacuum oven for 8 h at 383 K at reduced pressure.

The liquid benzyl derivatives were purified by repeated distillation under reduced pressure. GC analyses of the samples **1** and **2** for thermochemical measurements gave a purity >99.9%. We used the following equipment: GLC (Carlo Erba Fraktometer Vega Series GC 6000), Hewlett-Packard Integrator 3390A, N_2 flow of 0.333 $cm^3 \cdot s^{-1}$, SE-30 capillary columns of length 25 m. The standard temperature program of the GC was T = 303 K for 5 min followed by a heating rate of 0.167 $K \cdot s^{-1}$ to T = 523 K. Sample of benzyl iodide and (1-iodoethyl)benzene were recrystallized from ethanol and immediately used for the vapor pressure measurements. Because of the very low selectivity and yield of cumyl halides (**3a**−**c**) synthesis reactions, the purification of these compounds to a degree appropriate for the thermochemical measurements was not possible. Consequently, no transpiration experiments were performed with cumyl halides (**3a**−**c**), and their enthalpies of vaporization were obtained only from the results of gas-correlation methods.

2.2. Measurements of the Enthalpies of Vaporization. The enthalpies of vaporization of benzyl derivatives were determined by using the method of transference in a saturated N_2 stream. The method has been described before[3−5] and has proved to give results in excellent agreement with other established techniques for determining vapor pressures of pure substances. About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of length 20 cm and diameter 0.5 cm. A nitrogen stream was passed through the U-tube at constant temperature (±0.1 K), and the transported amount of material was condensed in a cooled trap. The mass of condensed product was determined by GC analysis using an internal standard (hydrocarbons). Assuming that Dalton's law of partial pressures of ideal gaseous mixtures applied to the saturated nitrogen stream is valid, values of the vapor pressure p were calculated according to

$$p = mRT_a/V(N_2)M \qquad (1)$$

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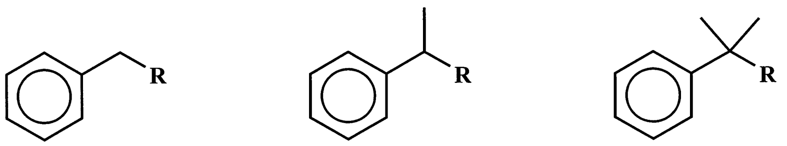

1

R= F : benzyl fluoride (**1a**) [350-50-5]]
R= Cl : benzyl chloride (**1b**) [100-44-7]
R= Br : benzyl bromide (**1c**) [100-39-0]
R= I : benzyl iodide (**1d**) [620-05-3]
R= O-Me : benzyl methyl ether (**1e**) [538-86-3]
R= O-Et : benzyl ethyl ether (**1f**) [539-30-0]
R= O-tAm : benzyl tert-amyl ether (**1g**) [27674-74-4]

2

R= Cl : (1-chloroethyl) benzene (**2a**) [672-65-1]
R= Br : (1-bromoethyl) benzene (**2b**) [585-71-7]
R= I : (1-iodoethyl) benzene (**2c**) [10604-60-1]
R= O-iPr : (1-iso-propoxyethyl) benzene (**2d**) [65757-61-1]
R= O-sBu : R*S*-(1-sec-butoxy-ethyl)-benzene (**2e**) [6857851]
R= O-sBu : S*S*-(1-sec-butoxy-ethyl)-benzene (**2f**) [8760638]
R= O-cHex: (1-cyclo-hexyl-oxy-ethyl)-benzene (**2g**) [61812-55-3]

3

R= Cl: cumyl chloride (**3a**) [934-53-2]
R= Br: cumyl bromide (**3b**) [3575-19-7]
R= I: cumyl iodide (**3c**) [54290-22-1]

Figure 1. Structures of benzyl derivatives and their Chemical Abstracts Service registry numbers (CAS).

where $R = 8.31451\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, m is the mass of transported compound, $V(\mathrm{N_2})$ is the volume of transporting gas, M is the molar mass of the compound, and T_a is the soap bubble meter temperature. The volume of the gas $V(\mathrm{N_2})$ transferred through the tube was determined from the flow rate and time measurements.

The results for $p-T$ measurements have been treated by the Clausius–Clapeyron equation, which was integrated, and the temperature dependence of the vapor pressure was described by the equation

$$R\ln(p) = a + \frac{b}{T} + \Delta_g^l C_{p,m}^\circ \ln\left(\frac{T}{T_0}\right) \tag{2}$$

which is fitted to the experimental p,T data using a and b as adjustable parameters. The following equation gives the value of the molar vaporization enthalpy at temperature T,

$$\Delta_l^g H_m^\circ(T) = -b + \Delta_g^l C_{p,m}^\circ T \tag{3}$$

where $\Delta_g^l C_{p,m}^\circ = C_{p,m}^g - C_{p,m}^l$ is the difference of the molar heat capacities of the liquid and the gaseous phase, respectively. Values of $\Delta_g^l C_{p,m}^\circ$ are based on the molar heat capacities calculated according to a procedure developed by Domalski and Hearing.[16] These values together with the coefficients a and b according to eq 3 are listed in Table 1. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature. The molar enthalpies of vaporization $\Delta_l^g H_m^\circ$ have been calculated as function of temperature using eq 3 and are listed in Table 1. To assess the uncertainty of the $\Delta_l^g H_m^\circ$ (298.15 K), the experimental data were approximated with the linear equation $\ln(p) = f(T^{-1})$ using the method of least squares. The errors in the thermodynamic functions were defined as deviations of experimental $\ln(p)$ from this linear correlation.

2.3. GC-Correlation Method. The second method used was the method of correlation-gas chromatography.[9,17] This method[9] correlates the gas-chromatographical behavior (retention time in the form of Kovat's index[18]) of a compound of interest with the net of the Kovat's indices of some standard compounds from which enthalpies of vaporization are known. Correlation-gas chromatography has several advantages over other methods. It is a fast and easy method where low concentrations are used and relatively impure substances are tolerated. A detailed description of the method used can be found elsewhere.[9,17] Measurements were made using a Hewlett-Packard Series 5890 gas chromatograph, equipped with a FID and Hewlett-Packard Integrator 3390A. GC runs were done isothermally on a SE-30 capillary column of length 30 m and diameter 0.32 mm with a film thickness of the stationary phase of 0.25 μm. Nitrogen was used as the carrier gas. At each temperature the corrections of retention times with the value for the nonretained solvent (methanol) were made. The temperature was maintained constant within ±0.1 K. All substances were dissolved in methanol. Retention times were generally reproducible within (1 to 2) s. Experimental values of Kovat's indices (see Table 2) were obtained according to the equation[18]

$$J_x = \frac{\lg(t_x) - \lg(t_N)}{\lg(t_{N+1}) - \lg(t_N)} \times 100 + 100N \tag{4}$$

where t_x is the retention time of the compound of interest x, t_N is the retention time of n-alkane, which is eluated after the compound x, t_{N+1} is the retention time of n-alkane, which is eluated just before the compound x, and N is the number of carbon atoms in n-alkane.

3. Results and Discussion

3.1. Enthalpies of Vaporization from the Transpiration Method. Results obtained by the transpiration method for the vapor pressures p and molar vaporization enthalpies of benzyl halides and benzyl ethers are presented in Table 1. The available data for comparison are scarce. Benzyl halides are very reactive and thermolabile (especially benzyl iodide); that is why these compounds are often used for determination of the bond dissociation enthalpies (BDE).[21-23] The few values of $\Delta_l^g H_m^\circ$ (298.15 K) of benzyl halides cited in the experimental works dealing with the determinations of BDE[21-23] are only rough estimates, and they cannot be used for comparison with our results. Some vapor pressure measurements on benzyl halides have been reported by Ashcroft[19] and Stull.[20] The comparison of the vapor pressures reported by these authors with our results is presented in Figures 2–5. The vapor pressures measured for benzyl halides in this work are not always in agreement (except for benzyl chloride) with those from the literature. Our results are systematically lower than previously published data by Stull[20] and Ashcroft.[19] The discrepancy could be explained with the ill-defined purity of the compounds reported by Stull,[20] who compilated experimental results made as early 1947. More recent results on vapor pressures and the standard molar enthalpy of vaporization $\Delta_l^g H_m^\circ$ (298.15 K) of benzyl halides measured using an isoteniscope have been reported by Ashcroft.[19] This author claimed the purity of the samples

Table 1. Results for the Vapor Pressure *p* and $\Delta_l^g H_m^\circ$ Obtained by the Transpiration Method

T^a	m^b	$V(N_2)^c$	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m^\circ$	T^a	m^b	$V(N_2)^c$	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m^\circ$
K	mg	dm^3	Pa	Pa	kJ·mol^{-1}	K	mg	dm^3	Pa	Pa	kJ·mol^{-1}
Benzyl Fluoride (**1a**), $\Delta_l^g H_m^\circ$ (298.15 K) = (46.22 ± 0.26) kJ·mol^{-1}											
$\ln(p/\mathrm{Pa}) = \frac{279.641}{R} - \frac{66549.829}{R(T/\mathrm{K})} - \frac{68.20}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
278.1	16.20	1.690	229.4	2.91	47.58	298.2	22.90	0.606	864.5	−24.6	46.21
280.1	8.95	0.810	261.8	−0.48	47.45	303.1	8.99	0.170	1203.0	2.49	45.88
283.2	19.10	1.370	327.2	−0.45	47.24	303.2	17.10	0.319	1217.0	9.3	45.87
288.0	19.20	0.956	465.5	8.30	46.91	308.2	16.00	0.224	1618.0	−2.71	45.53
293.2	11.80	0.797	635.5	−10.8	46.55	313.2	15.50	0.159	2209.0	59.0	45.19
293.3	22.00	0.410	659.7	9.19	46.55	318.3	12.00	0.096	2832.0	−4.11	44.84
298.1	7.50	0.200	856.7	−26.9	46.22						
Benzyl Chloride (**1b**), $\Delta_l^g H_m^\circ$ (298.15 K) = (50.12 ± 0.27) kJ·mol^{-1}											
$\ln(p/\mathrm{Pa}) = \frac{281.417}{R} - \frac{71588.799}{R(T/\mathrm{K})} - \frac{72.00}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
276.0	1.730	1.256	26.95	−0.56	51.72	292.1	1.485	0.297	97.84	3.79	50.56
278.0	1.665	1.009	32.31	−0.05	51.58	293.2	1.581	0.305	101.60	−0.09	50.48
280.0	1.614	0.818	38.60	0.66	51.43	294.3	0.561	0.099	111.00	1.13	50.40
282.0	1.660	0.742	43.78	−0.59	51.29	295.2	1.485	0.247	117.44	0.45	50.34
284.0	1.652	0.628	51.48	−0.27	51.14	297.2	1.423	0.209	133.06	−1.22	50.19
286.0	1.813	0.590	60.14	−0.07	51.00	299.2	1.493	0.190	153.53	−0.27	50.05
286.1	2.085	0.673	60.61	−0.05	50.99	301.3	1.882	0.209	175.98	−0.93	49.90
287.1	1.563	0.476	64.27	−1.09	50.92	303.3	1.594	0.152	204.90	3.19	49.75
288.1	1.783	0.495	70.50	0.12	50.85	305.3	1.359	0.114	232.87	3.35	49.61
289.1	1.612	0.419	75.36	−0.38	50.78	307.3	1.877	0.143	257.42	−3.18	49.47
291.1	1.745	0.381	89.72	2.16	50.63	309.3	1.390	0.095	285.92	−9.40	49.32
Benzyl Bromide (**1c**), $\Delta_l^g H_m^\circ$ (298.15 K) = (53.27 ± 0.67) kJ·mol^{-1}											
$\ln(p/\mathrm{Pa}) = \frac{286.257}{R} - \frac{75306.669}{R(T/\mathrm{K})} - \frac{73.9}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
284.2	1.462	1.023	20.70	0.99	54.31	294.2	1.652	0.532	44.99	2.15	53.57
286.2	1.031	0.614	24.32	1.18	54.16	297.3	1.560	0.409	55.21	1.40	53.34
287.3	1.494	0.819	26.44	1.20	54.08	300.3	0.991	0.205	70.17	3.45	53.12
290.3	1.362	0.614	32.14	0.25	53.86	303.3	1.192	0.205	84.41	2.09	52.90
291.2	0.955	0.409	33.81	−0.35	53.79	306.3	1.494	0.205	105.72	4.67	52.67
293.2	1.718	0.614	40.54	0.79	53.64						
Benzyl Iodide (**1d**), $\Delta_l^g H_m^\circ$ (298.15 K) = (57.38 ± 0.34) kJ·mol^{-1}											
$\ln(p/\mathrm{Pa}) = \frac{284.944}{R} - \frac{77912.128}{R(T/\mathrm{K})} - \frac{70.10}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
301.1	2.067	1.110	21.15	0.07	57.29	316.2	1.955	0.351	63.37	1.07	56.24
303.1	1.733	0.818	24.07	−0.45	57.15	319.0	1.921	0.292	74.71	−0.44	56.04
303.1	1.733	0.818	24.07	−0.45	57.15	322.1	2.145	0.263	92.69	0.63	55.82
305.2	1.697	0.688	28.02	−0.63	57.01	325.2	2.024	0.205	112.47	0.21	55.60
305.2	1.697	0.672	28.70	0.04	57.01	328.2	2.093	0.175	135.68	0.24	55.39
307.2	1.863	0.628	33.70	0.53	56.87	331.2	2.070	0.146	160.99	−1.74	55.18
309.1	1.777	0.526	38.39	0.37	56.73	334.2	2.477	0.146	192.66	−2.09	54.97
311.2	1.930	0.482	45.50	1.37	56.59	337.2	2.978	0.146	231.63	−0.52	54.76
(1-Chloroethyl)benzene (**2a**), $\Delta_l^g H_m^\circ$ (298.15 K) = (52.79 ± 0.24) kJ·mol^{-1}											
$\ln(p/\mathrm{Pa}) = \frac{301.565}{R} - \frac{78876.853}{R(T/\mathrm{K})} - \frac{87.50}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
280.8	1.743	1.413	21.74	−0.73	54.31	301.0	1.434	0.245	103.24	−1.24	52.54
282.8	1.509	1.001	26.56	0.08	54.14	303.0	1.597	0.234	120.46	0.47	52.37
284.8	1.433	0.812	31.08	−0.04	53.96	305.1	1.678	0.211	139.88	1.46	52.18
286.8	1.408	0.690	35.96	−0.52	53.79	307.1	1.203	0.134	158.75	0.51	52.01
288.8	1.413	0.579	43.04	0.41	53.61	309.1	1.346	0.134	177.69	−2.80	51.83
290.9	1.463	0.512	50.39	0.31	53.43	311.1	1.303	0.111	206.39	0.94	51.66
292.9	1.568	0.467	59.13	0.90	53.25	313.1	1.459	0.111	231.11	−2.25	51.48
294.9	1.455	0.378	67.78	0.26	53.08	315.1	1.845	0.122	265.68	1.16	51.31
297.0	1.572	0.345	80.32	1.65	52.89	317.2	1.897	0.111	300.42	−0.67	51.13
299.0	1.405	0.267	92.71	1.94	52.72	319.2	2.106	0.111	333.53	−6.39	50.95
(1-Bromoethyl)benzene (**2b**), $\Delta_l^g H_m^\circ$ (298.15 K) = (56.38 ± 0.28) kJ·mol^{-1}											
$\ln(p/\mathrm{Pa}) = \frac{296.149}{R} - \frac{79905.093}{R(T/\mathrm{K})} - \frac{78.90}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
298.1	2.060	0.937	29.45	0.16	56.39	317.3	2.221	0.263	112.90	−1.14	54.87
300.1	2.295	0.907	33.86	−0.23	56.23	319.3	2.354	0.234	134.63	4.74	54.72
302.1	2.235	0.761	39.32	−0.24	56.07	321.3	2.557	0.234	146.19	−1.45	54.56
304.1	2.276	0.673	45.28	−0.54	55.92	323.4	2.708	0.220	165.19	−3.37	54.39
306.2	2.354	0.585	53.85	0.54	55.75	325.4	2.896	0.205	189.30	−1.55	54.23
308.2	2.219	0.483	61.52	0.07	55.59	327.4	2.630	0.161	218.76	3.08	54.08
310.2	2.497	0.468	71.39	0.73	55.43	329.4	2.648	0.146	242.31	−0.98	53.92
312.2	1.605	0.263	81.61	0.53	55.28	331.4	3.055	0.146	279.52	5.57	53.76
315.2	2.364	0.322	98.30	−0.96	55.04	333.5	3.326	0.146	304.32	−5.39	53.60

Table 1 (Continued)

T^a	m^b	$V(N_2)^c$	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H^\circ_m$	T^a	m^b	$V(N_2)^c$	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H^\circ_m$
K	mg	dm^3	Pa	Pa	$kJ \cdot mol^{-1}$	K	mg	dm^3	Pa	Pa	$kJ \cdot mol^{-1}$
(1-Iodoethyl)benzene (**2c**), $\Delta_l^g H^\circ_m$ (298.15 K) = (59.90 ± 0.35) $kJ \cdot mol^{-1}$											
$\ln(p/Pa) = \frac{289.502}{R} - \frac{83097.671}{R(T/K)} - \frac{77.80}{R}\ln\left(\frac{T/K}{298.15}\right)$											
303.1	3.836	7.643	5.34	−0.07	59.52	323.3	3.041	1.403	23.05	−0.16	57.95
305.1	3.154	5.332	6.29	−0.02	59.36	325.3	3.011	1.227	26.08	−0.41	57.79
307.1	3.393	4.799	7.52	0.17	59.21	327.3	3.014	1.096	29.24	−0.94	57.64
309.1	2.772	3.555	8.29	−0.24	59.05	330.4	3.313	0.933	37.75	0.95	57.40
311.1	3.466	3.814	9.66	−0.23	58.90	332.4	3.002	0.755	42.24	0.51	57.24
313.1	3.063	2.805	11.61	0.17	58.74	334.5	3.136	0.711	46.89	−0.62	57.08
315.2	3.946	3.068	13.67	0.38	58.58	336.5	3.576	0.706	53.86	0.19	56.92
317.2	4.023	2.762	15.49	0.18	58.42	338.5	3.029	0.529	60.83	0.31	56.77
319.2	3.090	1.841	17.84	0.27	58.27	340.5	1.394	0.221	67.16	−0.96	56.61
321.2	2.940	1.534	20.38	0.23	58.11						
Benzyl Methyl Ether (**1e**), $\Delta_l^g H^\circ_m$ (298.15 K) = (51.40 ± 0.29) $kJ \cdot mol^{-1}$											
$\ln(p/Pa) = \frac{292.546}{R} - \frac{73909.071}{R(T/K)} - \frac{75.49}{R}\ln\left(\frac{T/K}{298.15}\right)$											
274.3	0.988	0.604	33.16	−1.14	53.20	292.3	3.172	0.456	141.11	−0.60	51.84
276.3	1.328	0.684	39.38	−1.22	53.05	293.2	2.681	0.353	153.94	2.64	51.78
278.3	1.623	0.684	48.13	0.21	52.90	293.2	3.248	0.433	152.05	0.75	51.78
278.6	6.389	2.548	50.85	1.73	52.88	293.7	6.979	0.898	157.56	0.70	51.74
279.4	3.439	1.342	51.96	−0.47	52.82	294.3	1.468	0.182	163.19	−0.60	51.69
280.3	1.924	0.707	55.21	−1.19	52.75	296.2	2.862	0.313	185.34	−2.18	51.55
282.3	1.700	0.536	64.33	−1.86	52.60	298.1	3.587	0.330	220.67	6.43	51.41
283.1	2.459	0.699	71.38	0.86	52.54	298.7	7.122	0.636	227.08	3.73	51.36
283.7	7.505	2.009	75.78	1.85	52.49	300.3	1.377	0.114	245.06	−4.28	51.24
285.3	1.395	0.342	82.71	−1.03	52.37	303.3	4.020	0.267	305.53	0.22	51.01
288.2	2.964	0.565	106.37	1.85	52.15	303.7	7.074	0.450	318.76	5.21	50.98
288.3	1.595	0.308	105.12	−0.20	52.15	308.2	5.300	0.267	402.81	−17.84	50.64
288.8	8.428	1.520	112.49	3.13	52.11	308.6	4.575	0.218	426.40	−5.16	50.61
291.3	3.711	0.553	136.19	4.49	51.92	313.8	4.480	0.154	588.59	−9.06	50.22
Benzyl Ethyl Ether (**1f**), $\Delta_l^g H^\circ_m$ (298.15 K) = (53.49 ± 0.43) $kJ \cdot mol^{-1}$											
$\ln(p/Pa) = \frac{305.859}{R} - \frac{79968.084}{R(T/K)} - \frac{88.80}{R}\ln\left(\frac{T/K}{298.15}\right)$											
278.3	1.721	1.611	19.44	0.09	55.26	298.6	4.785	0.912	95.44	−0.15	53.45
278.7	3.935	3.654	19.59	−0.43	55.22	300.1	2.860	0.495	105.16	−1.28	53.32
283.8	4.768	2.880	30.11	−0.56	54.77	302.3	2.721	0.421	117.65	−6.66	53.12
285.1	2.043	1.053	35.31	1.22	54.65	303.2	2.190	0.311	128.09	−4.27	53.04
288.8	5.363	2.179	44.78	−0.98	54.32	303.6	4.797	0.645	135.21	−0.87	53.01
290.2	1.973	0.678	52.97	1.93	54.20	307.4	2.885	0.295	177.63	1.37	52.67
292.6	3.587	1.060	61.54	0.20	53.99	308.4	3.233	0.312	188.48	0.05	52.58
293.7	4.640	1.288	65.53	−1.12	53.89	310.2	2.940	0.239	223.55	11.34	52.42
295.2	1.977	0.462	77.81	3.26	53.75	312.2	2.718	0.202	244.83	3.17	52.24
297.3	3.405	0.701	88.33	1.33	53.57	313.7	3.156	0.221	259.37	−6.67	52.11
Benzyl *tert*-Amyl Ether (**1e**), $\Delta_l^g H^\circ_m$ (298.15 K) = (61.81 ± 0.23) $kJ \cdot mol^{-1}$											
$\ln(p/Pa) = \frac{342.035}{R} - \frac{96243.25}{R(T/K)} - \frac{115.48}{R}\ln\left(\frac{T/K}{298.15}\right)$											
276.2	0.367	3.647	1.40	0.06	64.35	298.2	1.102	1.468	10.41	0.26	61.81
278.3	0.604	5.083	1.65	0.00	64.11	298.2	1.528	2.105	10.09	−0.06	61.81
280.3	0.571	4.034	1.97	−0.04	63.87	299.2	0.714	0.912	10.89	−0.14	61.69
283.2	3.536	18.347	2.68	0.02	63.54	301.2	0.599	0.638	13.05	0.05	61.46
284.3	0.550	2.598	2.94	−0.01	63.41	303.2	0.269	0.241	15.49	0.21	61.23
288.0	1.000	3.368	4.13	−0.03	62.99	303.2	1.548	1.382	15.57	0.29	61.23
288.3	0.550	1.778	4.30	0.02	62.95	303.2	1.922	1.776	15.04	−0.24	61.23
290.1	1.261	3.480	5.04	0.01	62.74	307.1	0.493	0.319	21.47	0.69	60.78
292.3	0.579	1.322	6.09	−0.03	62.49	308.1	1.338	0.827	22.48	0.03	60.66
293.4	1.101	2.379	6.43	−0.31	62.36	308.2	1.297	0.801	22.51	−0.11	60.65
293.5	1.292	2.725	6.59	−0.21	62.35	310.1	0.765	0.410	25.92	−0.22	60.43
295.2	0.555	0.980	7.87	0.00	62.15	313.0	0.972	0.416	32.47	0.01	60.10
298.2	0.387	0.531	10.13	−0.02	61.81	313.1	1.365	0.572	33.18	0.48	60.09
(1-Isopropoxyethyl)benzene (**2d**), $\Delta_l^g H^\circ_m$ (298.15 K) = (55.41 ± 0.27) $kJ \cdot mol^{-1}$											
$\ln(p/Pa) = \frac{320.981}{R} - \frac{84982.865}{R(T/K)} - \frac{99.20}{R}\ln\left(\frac{T/K}{298.15}\right)$											
278.3	2.99	3.254	14.73	−0.15	57.38	298.2	3.81	0.766	76.04	0.31	55.40
278.4	3.26	3.290	15.44	0.42	57.37	298.3	5.70	1.120	77.37	1.07	55.39
283.2	2.84	1.993	22.37	−0.45	56.89	303.2	3.16	0.431	111.60	2.31	54.91
283.4	3.67	2.380	23.77	0.56	56.87	303.3	3.33	0.462	109.20	−0.88	54.90
288.2	2.04	0.957	33.12	−1.51	56.39	308.0	5.77	0.550	159.20	5.97	54.43
288.4	3.46	1.470	35.98	0.78	56.37	308.2	3.26	0.331	149.30	−6.06	54.41
293.2	2.32	0.718	49.63	−2.02	55.90	313.1	2.83	0.198	216.30	0.02	53.92
293.3	4.49	1.300	52.67	0.62	55.89						

Table 1 (Continued)

T^a	m^b	$V(N_2)^c$	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H^\circ_m$	T^a	m^b	$V(N_2)^c$	p^d	$(p_{exp} - p_{calc})$	$\Delta_l^g H^\circ_m$
K	mg	dm^3	Pa	Pa	kJ·mol^{-1}	K	mg	dm^3	Pa	Pa	kJ·mol^{-1}
R^*S^*-(1-*sec*-Butoxyethyl)benzene (**2e**)), $\Delta_l^g H^\circ_m$ (298.15 K) = (58.70 ± 0.46) kJ·mol^{-1}											
$\ln(p/\mathrm{Pa}) = \frac{325.528}{R} - \frac{90514.905}{R(T/\mathrm{K})} - \frac{106.7}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
296.5	2.65	3.042	12.20	−0.06	58.88	317.2	3.25	0.794	57.00	0.36	56.67
299.5	2.93	2.619	15.63	0.06	58.56	320.2	3.30	0.661	69.42	0.19	56.35
305.4	3.97	2.249	24.62	0.16	57.93	323.2	3.20	0.529	84.13	−0.09	56.03
308.4	3.29	1.524	30.12	−0.40	57.61	326.2	3.33	0.476	97.41	−4.55	55.71
311.3	4.12	1.508	38.06	0.45	57.30	329.2	2.53	0.291	121.20	−1.69	55.39
314.3	3.59	1.069	46.79	0.36	56.98	332.2	3.21	0.291	153.40	5.95	55.07
S^*S^*-(1-*sec*-Butoxyethyl)benzene (**2f**), $\Delta_l^g H^\circ_m$ (298.15 K) = (59.13 ± 0.48) kJ·mol^{-1}											
$\ln(p/\mathrm{Pa}) = \frac{326.163}{R} - \frac{90945.564}{R(T/\mathrm{K})} - \frac{106.7}{R}\ln(\mathrm{T/K}/298.15)$											
296.5	2.40	3.042	11.04	−0.08	59.31	317.2	2.98	0.794	52.27	0.34	57.10
299.5	2.66	2.619	14.19	0.05	58.99	320.2	3.03	0.661	63.78	0.21	56.78
305.4	3.62	2.249	22.45	0.16	58.36	323.2	2.94	0.529	77.42	−0.02	56.46
308.4	3.00	1.524	27.51	−0.34	58.04	326.2	3.06	0.476	89.56	−4.34	56.14
311.3	3.77	1.508	34.83	0.46	57.73	329.2	2.34	0.291	111.80	−1.53	55.82
314.3	3.28	1.069	42.82	0.32	57.41	332.2	2.96	0.291	141.60	5.43	55.50
(1-Cyclohexyloxyethyl)benzene (**2g**), $\Delta_l^g H^\circ_m$ (298.15 K) = (69.75 ± 0.45) kJ·mol^{-1}											
$\ln(p/\mathrm{Pa}) = \frac{378.975}{R} - \frac{112061.294}{R(T/\mathrm{K})} - \frac{141.9}{R}\ln\left(\frac{T/\mathrm{K}}{298.15}\right)$											
286.0	1.36	38.38	0.43	0.00	71.48	323.2	2.05	2.034	12.23	0.02	66.20
303.5	0.955	4.830	2.40	0.02	68.99	326.2	2.03	1.627	15.11	−0.19	65.77
308.4	1.28	4.220	3.69	0.02	68.30	328.3	1.95	1.322	17.93	0.07	65.48
311.4	1.43	3.661	4.74	0.00	67.87	331.3	2.43	1.322	22.29	0.11	65.05
314.4	1.52	3.026	6.08	−0.01	67.45	334.3	2.50	1.093	27.77	0.38	64.62
317.3	1.60	2.542	7.64	−0.06	67.04	335.2	14.70	5.933	30.00	0.84	64.50
320.3	1.94	2.415	9.75	−0.01	66.61	338.2	2.67	0.941	34.47	−1.31	64.07

[a] Temperature of saturation. N_2 gas flow (0.22 to 0.69) cm^3·s^{-1}. [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen used to transfer mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at T = 243 K.

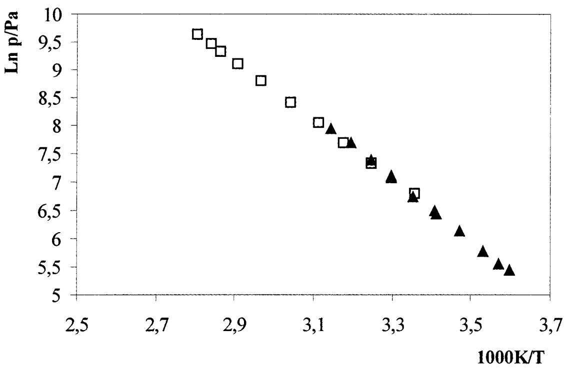

Figure 2. Experimental data of the vapor pressures of benzyl fluoride. (□) Ashcroft, 1976; (▲) this work.

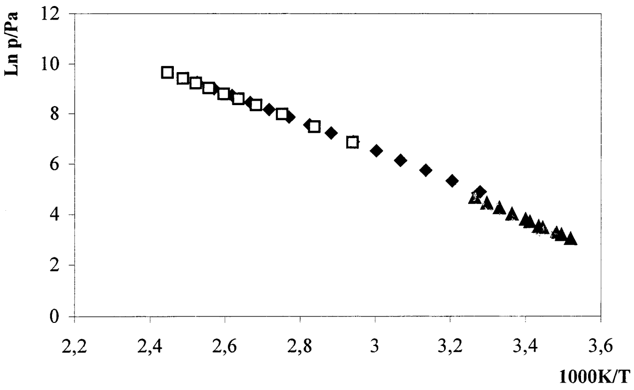

Figure 4. Experimental data of the vapor pressures of benzyl bromide. (●) Stull, 1947; (□) Ashcroft, 1976; (▲) this work.

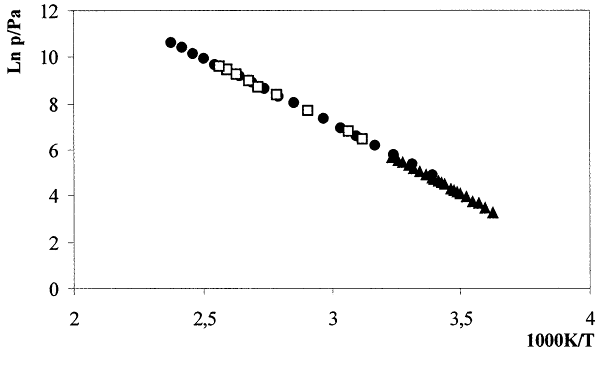

Figure 3. Experimental data of the vapor pressures of benzyl chloride. (●) Stull, 1947; (□) Ashcroft, 1976; (▲) this work.

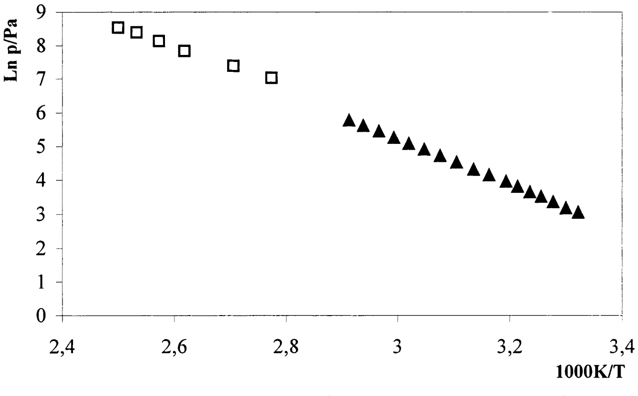

Figure 5. Experimental data of the vapor pressures of benzyl iodide. (●) Ashcroft, 1976; (▲) this work.

Table 2. Benzyl Halides: Results from Measurements of the Kovat's Indices J_x and Vaporization Enthalpies $\Delta_l^g H_m^\circ$ (in kJ·mol^{-1}) Derived from Correlation-Gas Chromatography; Temperature of the GC Experiments, 393.2 K

compound	J_x	$\Delta_l^g H_m^\circ$ (exp)[a] (298.15 K)	$\Delta_l^g H_m^\circ$ (calc.)[b] (298.15 K)	Δ[c]
benzyl fluoride (**1a**)	935.3	46.22	46.5	0.3
benzyl chloride (**1b**)	1007.5	50.12	49.9	−0.2
benzyl bromide (**1c**)	1087.3	53.27	53.7	0.4
benzyl iodide (**1d**)	1173.9	57.50	57.7	0.2
(1-chloroethyl)benzene (**2a**)	1059.5	52.79	52.4	−0.4
(1-bromoethyl)benzene (**2b**)	1139.2	56.38	56.1	−0.3
(1-iodoethyl)benzene (**2c**)	1222.1	59.90	60.0	0.1
cumyl chloride (**3a**)	1109.3		54.7	
cumyl bromide (**3b**)	1181.3		58.0	
cumyl iodide (**3c**)	1293.6		63.3	

[a] Values derived from the transpiration method and correlated with the Kovat's indicies. [b] Calculated from the linear relationship: $\Delta_l^g H_m^\circ(\text{calc.}) = 0.0468 J_x + 2.74$. [c] Calculated as the difference $\Delta = \Delta_l^g H_m^\circ(\text{calc.}) - \Delta_l^g H_m^\circ(\text{exp.})$.

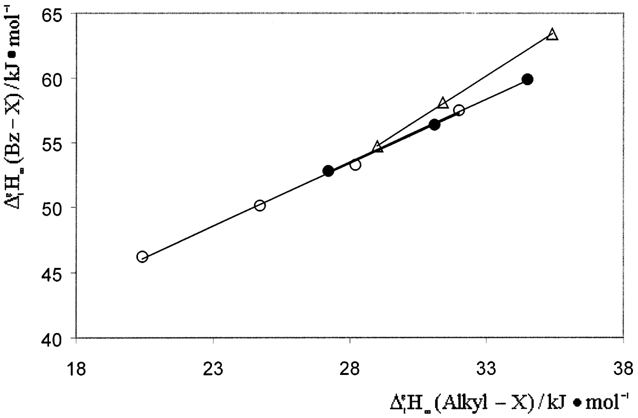

Figure 6. Relation between $\Delta_l^g H_m^\circ$ of alkyl halides (data from Pedley et al.[10] except for $\Delta_g^l H_m^\circ = 20.4$ in kJ·mol^{-1} for ethyl fluoride calculated from results in ref 24) and $\Delta_l^g H_m^\circ$ of benzyl halides (in kJ·mol^{-1}). (○) (Pr−X) and PhCH$_2$−X; (●) (iPr−X) and PhCH(CH$_3$)−X; (△) (tBu−X) and PhC(CH$_3$)$_2$−X.

in the range of (99.5 to 99.8) mass%, established by GC. He obtained the following results for $\Delta_l^g H_m^\circ$ (298.15 K): (44.5 ± 0.4) kJ·mol^{-1} for **1a**; (50.1 ± 0.5) kJ·mol^{-1} for **1b**; (50.5 ± 0.5) kJ·mol^{-1} for **1c**; and (50.6 ± 1.4) kJ·mol^{-1} for **1d**. The agreement with our values $\Delta_l^g H_m^\circ$ (298.15 K) listed in Table 1 for compounds **1a**−**c** is acceptable within (1 to 3) kJ·mol^{-1} but disagrees for benzyl iodide by 6 kJ·mol^{-1}. However, Ashcroft[19] detected some thermal decomposition of his sample **1d** during the measurements. Surprisingly, molar vaporization enthalpies for **1b**−**d**, derived by Ashcroft,[19] are not different from each other, as should be expected, because Cl, Br, and I contribute to increasing the intermolecular interactions. In contrast to Ashcroft's[19] results, our values of $\Delta_l^g H_m^\circ$ (298.15 K) from Table 1 for **1a**−**d**, demonstrate enhancing of the vaporization enthalpy from **1a** to **1d**. It also should be noticed that the transpiration method applied in this work has a crucial advantage for the vapor pressure measurements of thermolable and reactive compounds because the nitrogen stream, which is used for transportation of the sample, at the same time serves as protection against oxidation.

To the best of our knowledge, molar enthalpies of vaporization of benzyl ethers **1e** and **1g** (see Figure 1) have been measured for the first time. Vapor pressure measurements on ethyl benzyl ether **1f** reported by Stull[20] are in disagreement with those from this work.

3.2. GC-Correlation Method. As already mentioned above, sufficient purification of the samples **3a**−**c** was not possible. However, to accomplish thermochemical information on the chemical family of benzyl derivatives, the GC-

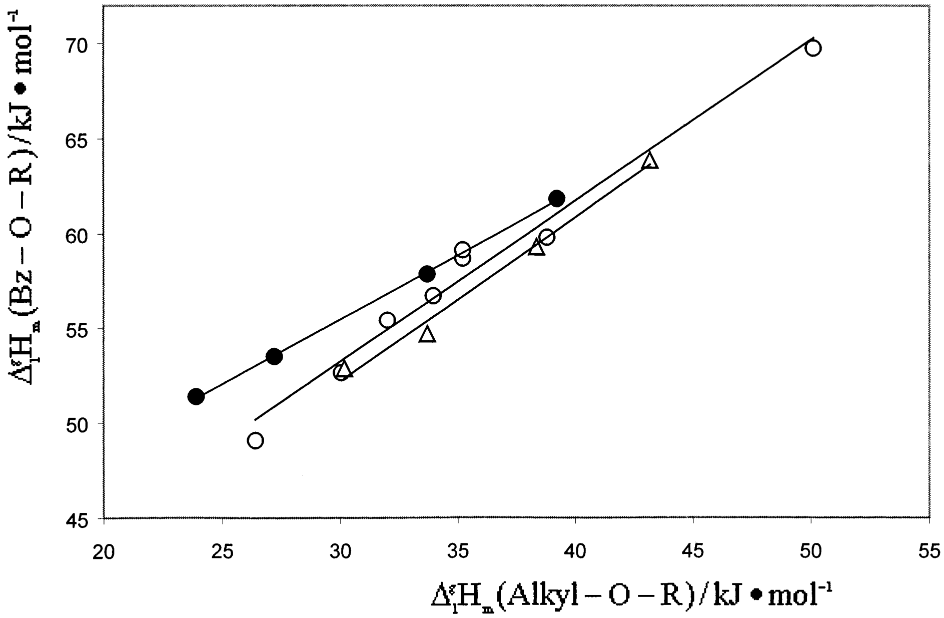

Figure 7. Relation between $\Delta_l^g H_m^\circ$ of alkyl ethers (data from Pedley et al.[10]) and $\Delta_l^g H_m^\circ$ of benzyl ethers (data from this work and for cumyl ethers from ref 4. (●) (Et−O−R) and PhCH$_2$−O−R; (○) (iPr−O−R) and PhCH(CH$_3$)−O−R; (△) (tBu−O−R) and PhC(CH$_3$)$_2$−O−R.

correlation method[18] has been applied to derive enthalpies of vaporization $\Delta_l^g H_m^\circ$ (298.15 K) of **3a**−**c**. With use of this method, impurities do not impact the results. We used our experimental results for $\Delta_l^g H_m^\circ$ (298.15 K) of the benzyl halides obtained from the transpiration method as standards for the GC-correlation method. The following linear correlation was obtained,

$$\Delta_l^g H^\circ_m \text{ (298.15 K)/kJ·mol}^{-1} = 0.0468 J_x + 2.74 \qquad (r = 0.9948) \quad (5)$$

for the molar vaporization enthalpies of benzyl halides (see Table 1) using their Kovat's indices (see Table 2). With eq 5, the values $\Delta_l^g H_m^\circ$ (298.15 K) of compounds **3a**−**c** have been calculated and are presented in Table 2. The error in the enthalpies of vaporization obtained by this method is assumed to be within ±(0.3 to 0.6) kJ·mol^{-1}.

3.3. Correlation of $\Delta_l^g H_m^\circ$ of Benzyl Derivatives with Those $\Delta_l^g H_m^\circ$ of Alkyl Analogs. Taking into account the high chemical reactivity and thermal lability of the benzyl derivatives, which could aggravate thermochemical measurements, evidence of the reliability of the results derived in this work seems to be desirable. Values of $\Delta_l^g H_m^\circ$ of benzyl derivatives derived in this work could be checked for internal consistency using enthalpies of formation of alkyl halides and alkyl ethers available from the literature.[10] Considering structures of the benzyl derivatives presented in Figure 1, it is obvious that benzyl derivatives (**1**) are parent to the structure of the ethyl derivatives C_2H_5−X, for example, $PhCH_2$−Cl (**1b**) and C_2H_5−Cl. Benzyl derivatives (**2**) are parent to the structure of the isopropyl derivatives iso-C_3H_7−X. Benzyl derivatives (**3**) are parent to the structure of the *tert*-butyl derivatives *tert*-C_4H_9−X. Thus, the correlation of the enthalpies of vaporization of **1**−**3** with those of alkyl derivatives alkyl−X, where X = Hal or O−R, should give a linear correlation if the data used for the correlation are reliable. It can be seen from Figures 6 and 7 that our data for both families (halides and ethers) of the compounds studied fit very well in the linear correlation specific for each type of branching. This relationship can subsequently be used at least as an indication of the internal consistency of our experimental results.

Note Added after ASAP Posting

This article was posted in error on 7/27/2002 before all author corrections had been made. The corrected version was posted on 9/30/2002.

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