M-1636

J. Chem. Thermodynamics **1984**, 16, 423–426

The enthalpies of formation of bis-benzyl mercury and bis-phenylethynyl mercury and some associated bond-dissociation enthalpies

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(Received 12 September 1983)

The two compounds $Hg(C_6H_5CH_2)_2$ and $Hg(C_6H_5C{\equiv}C)_2$ have been burnt in a static combustion bomb and their vapour pressures have been measured by an effusion method: $\Delta_f H^\circ_m\{Hg(C_6H_5CH_2)_2, cr\} = (189.3 \pm 4.1)\ kJ \cdot mol^{-1}$; $\Delta_{sub} H_m\{Hg(C_6H_5CH_2)_2\} = (88.7 \pm 2.1)\ kJ \cdot mol^{-1}$; $\Delta_f H^\circ_m\{Hg(C_6H_5C{\equiv}C)_2, cr\} = (621.3 \pm 5.2)\ kJ \cdot mol^{-1}$; $\Delta_{sub} H_m\{Hg(C_6H_5C{\equiv}C)_2\} = (99.2 \pm 1.4)\ kJ \cdot mol^{-1}$. These values have been used to obtain the mean Hg–C bond-dissociation enthalpies.

1. Introduction

The enthalpies of formation of $Hg(C_6H_5CH_2)_2$ and $Hg(C_6H_5C{\equiv}C)_2$ are of interest because of the information they give on the way in which the Hg–C dissociation enthalpies are affected by interaction between the mercury and the ethyne groups and by the stability of the radicals concerned.

2. Experimental

Bis-benzyl mercury was prepared by the method of Jones and Werner.(1) Benzyl mercury chloride was first prepared by adding mercury(II) chloride to the Grignard reagent: benzyl magnesium chloride, in either solution. The benzyl mercury chloride was then added to a new sample of the Grignard reagent and after being refluxed for 4 h the ether layer was separated and the ether removed by distillation. The product was recrystallized from an aqueous-ethanolic solution of sodium thiosulphate and then from 90 mass per cent aqueous ethanol. The bis-benzyl mercury was washed with distilled water and dried *in vacuo*. The melting temperature was 385.6 K and analysis gave carbon and hydrogen mass percentages of 43.85 and 3.65 respectively, compared with the theoretical values 43.92 and 3.68. Melting-temperature curves were obtained using d.s.c., but it was difficult to estimate the purity unambiguously from these, since the peak shape indicated that the compound tended to decompose in the melting-temperature region. The indication was, however, that the purity was at least 99.7 moles per cent.

0021–9614/84/160423+04 $02.00/0

Bis-phenylethynyl mercury was prepared by the method of Johnson and McEwan,(2) in which phenylethyne is added to a cooled dilute alkaline solution of mercury(II) iodide:

$$2\mathrm{PhC{\equiv}CH} + \mathrm{K_2HgI_4} + 2\mathrm{KOH} = 4\mathrm{KI} + 2\mathrm{H_2O} + \mathrm{Hg(PhC{\equiv}C)_2}.$$

The precipitate was filtered off, washed with 50 mass per cent aqueous ethanol, and recrystallized from 90 mass per cent aqueous ethanol. The melting temperature was 397.6 K and analysis gave carbon and hydrogen mass percentages of 47.65 and 2.5 respectively, compared with the theoretical values 47.7 and 2.5. Melting-temperature curves obtained using d.s.c. indicated that the purity was 99.96 moles per cent.

The combustion calorimeter has been described previously in its original(3) and modified forms.(4) The mercury compounds were burnt in sealed Melimex bags and the extent of the combustion was checked by collecting and weighing the carbon dioxide produced. Small amounts of mercury(II) oxide and mercury(I) nitrate were also formed during the combustion and these were estimated by the methods previously described.(3)

3. Results and discussion

In table 1 which refers to the combustion of bis-benzyl mercury, $\mathrm{Hg(C_6H_5CH_2)_2}$: m, mass; M, molar mass; ρ, density; q_{T}, total energy change; q_{m}, energy correction for the combustion of Melinex; q_{f}, energy correction for the cotton fuse; $q_{\mathrm{HgNO_3}}$, the energy correction for the mercury(I) nitrate formation; q_{i}, the correction involved in reducing the combustion process to 298.15 K; q_{W}, the Washburn correction; q_{HgO}, the energy correction for the mercury(II) oxide formation.

A combined mass-loss torsional-recoil effusion method(6) was used to measure the equilibrium vapour pressure in the temperature range 350 to 390 K and the molar enthalpy of sublimation was found to be $(88.7 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}$. Therefore

$$\Delta_{\mathrm{f}} H^{\ominus}_{\mathrm{m}}\{\mathrm{Hg(C_6H_5CH_2)_2, g}\} = (278.0 \pm 4.6)\ \mathrm{kJ \cdot mol^{-1}}.$$

Table 2 contains the corresponding values for bis-phenylethynyl mercury,

TABLE 1. Results of measurements of the energy of combustion of bis-benzyl mercury, $\mathrm{Hg(C_6H_5CH_2)_2}$: $M = 382.858\ \mathrm{g \cdot mol^{-1}}$, $\rho = 1.94\ \mathrm{g \cdot cm^{-3}}$

m(cpd)/g	m\{Melinex\}/g	q_{T}/kJ	q_{m}/kJ	q_{f}/kJ	q_{HgO}/kJ	$q_{\mathrm{HgNO_3}}$/kJ	q_{i}/kJ	q_{W}/kJ	$-\Delta u^{\ominus}_{\mathrm{c}}/(\mathrm{kJ \cdot g^{-1}})^{a}$
1.453675	0.066650	30.7915	1.5221	0.0676	0.0062	0.0059	0.0396	0.0172	20.0953
1.486719	0.066551	31.4274	1.5198	0.0675	0.0074	0.0029	0.0403	0.0176	20.0795
1.404023	0.067688	29.8093	1.5458	0.0623	0.0047	0.0056	0.0383	0.0167	20.0940
1.403382	0.068429	29.7978	1.5627	0.0635	0.0079	0.0061	0.0389	0.0167	20.0799

$-\Delta_{\mathrm{c}} U^{\ominus}_{\mathrm{m}} = (7690.6 \pm 3.5)\ \mathrm{kJ \cdot mol^{-1}}$, where the uncertainty is twice the standard deviation of the mean and includes the uncertainties in the Melinex combustions and the calibration experiments; $-\Delta_{\mathrm{c}} H^{\ominus}_{\mathrm{m}} = (7699.2 \pm 3.5)\ \mathrm{kJ \cdot mol^{-1}}$. Using $\Delta_{\mathrm{f}} H^{\ominus}_{\mathrm{m}}(\mathrm{CO_2, g}) = -(393.51 \pm 0.13)\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_{\mathrm{f}} H^{\ominus}_{\mathrm{m}}(\mathrm{H_2O, l}) = -(285.830 \pm 0.042)\ \mathrm{kJ \cdot mol^{-1}}$,(5) $\Delta_{\mathrm{f}} H^{\ominus}_{\mathrm{m}}\{\mathrm{Hg(C_6H_5CH_2)_2, cr}\} = (189.3 \pm 4.1)\ \mathrm{kJ \cdot mol^{-1}}$.

[a] $-\Delta u^{\ominus}_{\mathrm{c}} = \{q_1 - q_{\mathrm{m}} - q_{\mathrm{f}} - q_{\mathrm{HgO}} - q_{\mathrm{HgNO_3}} + q_{\mathrm{i}} - q_{\mathrm{W}}\}/m(\mathrm{cpd})$.

TABLE 2. Results of measurements of the energy of combustion of bis-phenylethynyl mercury, $Hg(C_6H_5C{\equiv}C)_2$: $M = 402.848\ \mathrm{g \cdot mol^{-1}}$, $\rho = 1.72\ \mathrm{g \cdot cm^{-3}}$

m(cpd)/g	m\{Melinex\}/g	q_T/kJ	q_m/kJ	q_f/kJ	q_{HgO}/kJ	$q_{\mathrm{HgNO_3}}$/kJ	q_i/kJ	q_W/kJ	$-\Delta u_c^\circ/(\mathrm{kJ \cdot g^{-1}})$
1.411422	0.056635	30.5578	1.2934	0.0662	0.0135	0.0049	0.0388	0.0201	20.6871
1.457672	0.053987	31.4906	1.2329	0.0641	0.0114	0.0073	0.0398	0.0210	20.7136
1.428140	0.052158	30.8525	1.1911	0.0710	0.0233	0.0059	0.0392	0.0204	20.7123
1.377083	0.059143	29.9290	1.3506	0.0655	0.0181	0.0047	0.0376	0.0200	20.7015
1.407320	0.059207	30.5589	1.3521	0.0693	0.0164	0.0023	0.0387	0.0204	20.7040

$-\Delta_c U_m^\ominus = (8340.4 \pm 4.8)\ \mathrm{kJ \cdot mol^{-1}}$; $-\Delta_c H_m^\ominus = (8346.6 \pm 4.8)\ \mathrm{kJ \cdot mol^{-1}}$; $\Delta_f H_m^\ominus\{Hg(C_6H_5C{\equiv}C)_2, \mathrm{cr}\} = (621.3 \pm 5.2)\ \mathrm{kJ \cdot mol^{-1}}$.

$Hg(C_6H_5C{\equiv}C)_2$. The molar enthalpy of sublimation is $(99.2 \pm 1.4)\ \mathrm{kJ \cdot mol^{-1}}$, and so

$$\Delta_f H_m^\ominus\{Hg(C_6H_5C{\equiv}C)_2, g\} = (720.5 \pm 5.4)\ \mathrm{kJ \cdot mol^{-1}}.$$

$\Delta_f H_m^\ominus\{C_6H_5C{\equiv}CH, g\}$ may be obtained by combining the liquid-phase molar enthalpy of formation of $283.3\ \mathrm{kJ \cdot mol^{-1}}$,(7) with a calculated molar enthalpy of vaporization of $44.2\ \mathrm{kJ \cdot mol^{-1}}$.† If it is then assumed that the C–H molar dissociation enthalpy in ethynylbenzene is about the same as that in ethyne (about $532\ \mathrm{kJ \cdot mol^{-1}}$),(9) a molar enthalpy of formation of about $642\ \mathrm{kJ \cdot mol^{-1}}$ may be found for the radical $C_6H_5C{\equiv}C^\bullet$. Also $\Delta_f H_m^\ominus(C_6H_5CH_2^\bullet) = 188.3\ \mathrm{kJ \cdot mol^{-1}}$,(10) and $\Delta_f H_m^\ominus(Hg, g) = 61.3\ \mathrm{kJ \cdot mol^{-1}}$.(11)

The mean carbon–metal bond dissociation enthalpies in these compounds may be represented by

$$\langle D \rangle(Hg-R) = \tfrac{1}{2}\{\Delta_f H_m^\ominus(Hg) + 2\Delta_f H_m^\ominus(R) - \Delta_f H_m^\ominus(HgR_2, g)\}.$$

By using the above enthalpies, $\langle D \rangle(Hg{-}CH_2C_6H_5) = 80.0\ \mathrm{kJ \cdot mol^{-1}}$, and $\langle D \rangle(Hg{-}C_2H_6H_5) = 312\ \mathrm{kJ \cdot mol^{-1}}$, may be obtained. When the dissociation enthalpy of the benzyl compound is compared with, for example, $\langle D \rangle(Hg{-}CH_2CH_3) = 100.0\ \mathrm{kJ \cdot mol^{-1}}$,(3) it is seen that the Hg–C bond has been considerably weakened. This effect has been observed in other organometallic compounds(12) and is presumably due to the stability of the benzyl radical.

If we assume that the molar dissociation enthalpy of a bond is increased by about $120\ \mathrm{kJ \cdot mol^{-1}}$ in going from an essentially sp^3 configuration to an sp one, then the $\langle D \rangle$ value in the ethynyl case is unusually large, about $90\ \mathrm{kJ \cdot mol^{-1}}$ above the expected value. This would seem to indicate that the inner electrons in the mercury are interacting in some way with the π electrons of the triple bond.

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† $\Delta_{\mathrm{vap}} H_m/(\mathrm{kJ \cdot mol^{-1}}) = 20.9 + 0.163\{(T_b/\mathrm{K}) - 273.15\}$.(8)

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