References and Notes

(1) The complete names of 1 and 2 are (±)-7β,8α-dihydroxy-9β,10β-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene and (±)-7β,8α-dihydroxy-9α,10α-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene, respectively.

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(7) Diol epoxide **2** was reported (ref 6) to be ca. three times more reactive than **1** toward acid-catalyzed hydrolysis in 50% dioxane–water.

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Enthalpy of Vaporization Measurements by Gas Chromatography[1]

Sir:

Recent studies of reactivity and acidity in the gas phase and comparisons with the corresponding solution properties have provided major insights into the importance of intrinsic properties vs. solvation phenomena in determining solution behavior.[2] Essential to the thermodynamic cycles involved in many such studies are heats of vaporization (evaporation) (ΔH_v^{25}) of organic reactants or products, relatively few of which are presently known with reasonable accuracy.[3]

We now wish to report a simple method for the measurement of heats of vaporization. It has been applied to liquid substances boiling between 100 and 360°, and there is reason to believe that this range could be considerably extended in both directions. It is possibly the easiest method for making such measurements, and, for substances boiling above 150-200°, we believe that this method will prove to be the most accurate available. The equipment required is a gas chromatograph and a solution calorimeter, and the amount of sample used is 200-500 μL.

Table I. Enthalpies of Evaporation of Some Organic Liquids at 25 °C

Compound	Expl ΔH_v[a]	Lit. ΔH_v[b]
2,2,4,4-Tetramethylpentane	9.23	9.12 ± 0.10[c]
tert-Butylbenzene	11.34	11.50 ± 0.05[c]
1-Butanol	12.08	12.27 ± 0.02,[d] 12.19 ± 0.01[e]
2-Pentanone	9.05	9.14 ± 0.05,[c] 9.18[f]
2-Hexanone	10.17	10.1 ± 0.1,[c] 10.25[f]
2-Octanone	12.36	12.38[f]
2-Nonanone	13.48	13.48[f]
3-Pentanone	9.20	9.22[f]
4-Heptanone	11.17	11.16[f]
5-Nonanone	13.16	12.74 ± 0.02,[c] 13.1[f]
2,2,4,4-Tetramethyl-3-pentanone	10.87	10.84 ± 0.01[c]
Methyl octanoate	13.84	13.6 ± 0.4[c]
Tetraethylgermane	10.93	10.7 ± 0.3[c]

[a] kcal/mol. Estimated accuracy ±0.10. [b] kcal/mol. [c] Reference 9. [d] E. M. Arnett and D. Oancea, *J. Chem. Educ.*, **52**, 269 (1975). [e] K. G. McCurdy and K. J. Laidler, *Can. J. Chem.*, **41**, 4867 (1963). [f] D. Ambrose, J. H. Ellender, E. B. Lees, C. H. S. Sprake, and R. Townsend, *J. Chem. Thermodyn.*, **7**, 453 (1975).

The method is derived from reported[4,5] gas chromatographic determinations of $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$, the enthalpy of transfer from vapor to solution:

$$\Delta H(\mathrm{v} \rightarrow \mathrm{S}) = -R \frac{\mathrm{d} \ln V_g}{\mathrm{d}(1/T)}$$

V_g is the retention volume,[6] defined by the equation

$$V_g = \frac{F_c j}{w_t}(t_r - t_a)\frac{273.15}{T_m P_o}(P_o - P_w)$$

where F_c is the carrier gas flow rate at room temperature (T_m) and j is the compressibility factor, w_t is the weight of stationary phase, t_r is the sample retention time, t_a is the retention time of air, P_o is the outlet pressure, and P_w is the vapor pressure of water at room temperature.

Consider a system where F_c, j, w_t, T_m, and P_o are held constant.[7] The specific retention volume would then be given by a constant times the corrected retention time ($\Delta t = t_r - t_a$). If ln Δt is plotted vs. $1/T$ the intercept of the straight line passing through these points will differ from that obtained in the plot of ln V_g vs. $1/T$, but the slope will be unchanged. The resulting enthalpy change will be the same whether Δt or V_g is used.

We have taken advantage of this relationship to obtain enthalpies of transfer from vapor to solution in DC-200 silicone fluid for a number of compounds. The values are corrected from the mean temperature of the range studied to 25 °C using the equation

$$\Delta H^{25}(\mathrm{v} \rightarrow \mathrm{S}) = \Delta H^{T_m}(\mathrm{v} \rightarrow \mathrm{S}) + \int_{T_m}^{298.15} [C_p(\mathrm{l}) - C_p(\mathrm{g})]\, \mathrm{d}t$$

Liquid heat capacities [$C_p(\mathrm{l})$] at 25 °C were calculated by the group contribution method,[8] and the additivity rules of Benson[9] were used to determine gas-phase heat capacities at 25 °C, [$C_p(\mathrm{g})$].

The enthalpy of evaporation is not equal to $-\Delta H(\mathrm{v} \rightarrow \mathrm{S})$

(unless the sample and stationary phase form an athermal solution), but the two quantities are related by the equation

$$\Delta H_v = \Delta H_s - \Delta H(\mathrm{v} \rightarrow \mathrm{S}).$$

where ΔH_s is the heat of solution of the sample in the solvent (DC-200) measured calorimetrically at 25 °C.

The ΔH_v values obtained in this way are not exactly identical with the correct values[10] but are linearly related. We have established the relationship by plotting the GC-calorimetry values of ΔH_v vs. a group of six ΔH_v values determined (mainly by direct vaporization calorimetry) with high accuracy (generally ±0.02 kcal/mol).[10] The compounds are *n*-octane, *n*-nonane, mesitylene, *n*-decane, *n*-dodecane, and 1-hexadecene. The plot has the slope 0.9696, an intercept of 0.8374, and a correlation coefficient (*R*) of 0.99990.

We have measured GC-calorimetry values for a number of other compounds and have calculated corrected ΔH_v values[11] by the equation

$$\Delta H_v(\mathrm{cor}) = 0.9696\Delta H_v(\mathrm{expl}) + 0.8374$$

Not surprisingly, values for some nonpolar aliphatic and aromatic hydrocarbons were in good agreement with literature values. More noteworthy is that measurements on polar compounds, mainly ketones, also gave excellent agreement with the best literature values (Table I). The determination with H-bonding 1-butanol is satisfactory, but slightly less accurate, owing in part to tailing of the GC peaks. We are investigating the use of more highly polar stationary phases to overcome this behavior.

Retention times were determined using capillary columns (30 m × 0.5 mm i.d.) at six temperatures over a 50 °C temperature range. The relationship of $\ln \Delta t$ vs. $1/T$ was deemed satisfactory when the correlation coefficient exceeded 0.9995. Essentially equivalent results were obtained for several samples using a lightly loaded column and a heavily loaded column, and using 10 or 5 psi pressure of nitrogen carrier gas. Because the flame ionization detector used does not respond to air, methane was used to measure t_a. DC-200 silicone fluid of 100 cSt viscosity was used both in column loading and as the calorimetric solvent. The use of less viscous (5 cSt) DC-200 in the calorimetric determinations gives somewhat different values of ΔH_s. The calorimetric procedure was essentially that previously described,[12] excepting that a somewhat reduced sensitivity was usually used (500 μV full-scale recorder deflection), and stronger magnetic stirring must be provided.

We believe that the present method offers substantial advantages over previous techniques, in that measurement of flow rate, w_t, and vapor pressure are avoided. Provided that measurements involve "infinitely dilute" solutions, a variety of liquid phases and a wide range of temperatures should be suitable.

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Solar Energy Storage. Production of Hydrogen by 546-nm Irradiation of a Dinuclear Rhodium(I) Complex in Acidic Aqueous Solution

Sir:

We have reported[1] previously on the synthesis and characterization of a novel dinuclear rhodium(I) complex, $[\mathrm{Rh_2(bridge)_4}]^{2+}$ (bridge = 1,3-diisocyanopropane). The orbital interactions between the directly coupled rhodium(I) centers give rise to striking electronic absorption spectral properties,[1,2] the most prominent being a low-lying system (λ_{max} 553 nm (ϵ 14 500), $[\mathrm{Rh_2(bridge)_4}](\mathrm{BPh_4})_2$ in acetonitrile solution) attributable to the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($1a_{2u} \rightarrow 2a_{1g}$) excitation. A logical avenue for exploratory research on $[\mathrm{Rh_2(bridge)_4}]^{2+}$ involves its excited-state reactivity behavior, as a directly coupled dinuclear redox center might be able to channel charge-transfer excitation energy into redox-substrate chemical bond formation at rates that are competitive with back electron transfer. The purpose of the present communication is to report that we have achieved this goal in one important case, namely, in the reduction of protons to hydrogen through 546-nm irradiation of $[\mathrm{Rh_2(bridge)_4}]^{2+}$ in aqueous HCl solution.

The electronic absorption spectrum of $[\mathrm{Rh_2(bridge)_4}](\mathrm{BF_4})_2$[3] in aqueous 12 M HCl solution exhibits an intense band at 578 nm (ϵ 52 700) that may be assigned to the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ transition in the blue protonated species, $[\mathrm{Rh_2(bridge)_4H}]^{3+}\cdot\mathrm{Cl^-}$.[4] The proton stoichiometry was determined by measuring the change in pH upon dissolution of a known quantity of $[\mathrm{Rh_2(bridge)_4}](\mathrm{BF_4})_2$ in each of six standard aqueous HCl solutions. Initial pH values varied from 3.77 to 3.88. In all six experiments the pH increased as predicted for the binding of 1.05 ± 0.10 protons to $[\mathrm{Rh_2(bridge)_4}]^{2+}$. The fact that the principal absorption maximum in the spectrum of $[\mathrm{Rh_2(bridge)_4H}]^{3+}\cdot\mathrm{Cl^-}$ is very near that of $[\mathrm{Rh_2(bridge)_4}]^{2+}$ shows that a relatively small electronic perturbation has occurred upon protonation. In contrast, a related oxidative-addition product, $[\mathrm{Rh_2(bridge)_4(CH_3)(I)}]^{2+}$, exhibits an intense absorption band at much higher energy (397 nm in acetonitrile solution; assigned to the $\sigma \rightarrow \sigma^*$ transition $1a_{1g} \rightarrow 1a_{2u}$ in a $[\mathrm{I\text{-}Rh^{II}\text{-}Rh^{II}\text{-}CH_3}]^{2+}$ species).[1] Thus we prefer to formulate the ground state of $[\mathrm{Rh_2(bridge)_4H}]^{3+}\cdot\mathrm{Cl^-}$ as a protonated dinuclear $\mathrm{Rh^I}$ complex, $[(\mathrm{Cl^-})\mathrm{Rh^I}\text{---}\mathrm{Rh^I}(\mathrm{H^+})]^{2+}$, rather than the hydrido $\mathrm{Rh^{II}}$ oxidative-addition product, $[\mathrm{Cl\text{-}Rh^{II}\text{-}Rh^{II}\text{-}H}]^{2+}$.

Irradiation of $[\mathrm{Rh_2(bridge)_4H}]^{3+}\cdot\mathrm{Cl^-}$ in 12 M HCl solution at 546 nm leads to clean conversion to a yellow product (Figure 1) and a gas. The absorption spectrum of the yellow product (λ_{max} 338 nm (ϵ 56 200)) is identical with that of a sample of $[\mathrm{Rh_2(bridge)_4Cl_2}]^{2+}$ prepared by $\mathrm{Cl_2}$ oxidation of $[\mathrm{Rh_2(bridge)_4}]^{2+}$ in 12 M HCl solution. Characterization of several oxidative-addition products of the type $[\mathrm{Rh_2(bridge)_4X_2}]^{2+}$ has been reported previously.[1] The gas was identified as $\mathrm{H_2}$ both by mass spectroscopic analysis and by