

mean that aquation (with Os^{III}-N₂ cleavage) is more rapid.

We have performed temperature-dependent electronic absorption and MCD measurements over the entire spectral region from the UV to the NIR for both I and II. A detailed report and analysis of electronic absorption spectra and MCD of I is given elsewhere.¹³ Figure 1 shows the absorption spectrum of II at two temperatures for the near-IR and vis regions in a KCl disk. The bands at 4670, 4950, and 17 000 cm⁻¹ belong to II⁶ and those at 4700, 5400, 5700, and 14 000 cm⁻¹ are due to I. Careful comparison of MCD signals and absorption spectra of different samples of II confirmed that the observed MCD was due to impurity of I, and no signals from II could be identified. This confirms the diamagnetic nature of the complex and the presence of a strong antiferromagnetic exchange coupling between the osmium ions. The lack of any appreciable temperature dependence in the absorption spectrum of II shows that the exchange coupling is much greater than kT at room temperature, in contrast to the case of the corresponding pyrazine complex.¹⁴

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Flow Adsorption Calorimetry with Supercritical Fluids on Silica Gel

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The supercritical state has long held a fascination for chemists as a "fourth state of matter",^{1,2} and supercritical fluids are a lively area of current interest for fundamental and industrial chemistry³ as well as for geochemistry and extraterrestrial chemistry.⁴ Of particular significance is the use of supercritical carbon dioxide for tertiary oil recovery, coal extraction, and chromatography in all of which supercritical fluids interact with solid phases.⁵⁻⁸ The present study evolved from an investigation of the thermodynamics of adsorption on silica gel during supercritical HPLC separations.

The apparatus shown in Figure 1 may be assembled, for the most part, from readily available components following recent accounts of high-pressure and high-temperature flow calorimeters assembled for heats of mixing.⁹⁻¹¹

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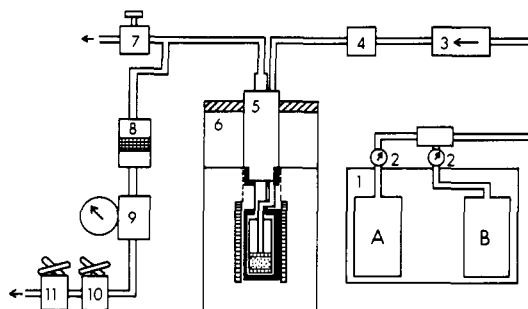


Figure 1. Schematic of adsorption flow calorimeter: (1) Perkin-Elmer Model 601 dual piston pumps, (2) Perkin-Elmer Bourden pressure gauges, (3) High Pressure Equipment Co. check valve, (4) High Pressure Equipment Co. safety valve, (5) high-pressure cell, (6) C-80 Setaram calorimeter, (7) Butech Pressure Systems high-temperature valve, (8) Valco filter, (9) Pilgrim Instruments Bourden pressure gauge, (10, 11) Tescom back-pressure regulators, Model 26-1724-24.

Table I. ΔH_{imm} (Batch Mode) of Silica Gel in Some Liquids at 26 °C

liquid	$\Delta H_{imm}/\text{cal g}^{-1}$	$T_c/^\circ\text{C}^a$	P_c/psi^a
(1) isopentane	-4.83 ± 0.63	187.8	483.5
(2) 10% isopropylamine	-21.66 ± 0.81	190.0 ^b	527.0 ^b
(3) isopropylamine	-20.33 ± 0.30	209.7	700.0 ^c
(2) - (1) = $\Delta H_{ads} = -16.83 \pm 1.02 \text{ cal g}^{-1}$			
$\Delta H_{ads}(\text{flow mode})$ at 30 psi = $-17.97 \pm 0.27 \text{ cal g}^{-1}$			

^a Reference 16. ^b Reference 17. ^c Reference 18.

Table II. Heats of Adsorption, ΔH_{ads} of Isopropylamine on Silica Gel at Different Temperatures and Pressures by Flow Calorimetry

temp, °C	P/psi	$\Delta H_{ads}/\text{cal/g}$
26	30	-17.97 ± 0.27
	1000	-17.44 ± 0.84
80	500	-15.79 ± 0.22
	1000	-15.34 ± 0.23
160	500	-12.52 ± 0.80
	200	-9.86 ± 1.30
250	1000	-11.52 ± 0.72
	1500	-13.61 ± 0.16
	1000	-4.30 ± 0.16

After preliminary calibration of the calorimeter under various batch conditions by heats of solution by KCl and BaCl₂ in water¹² and heats of immersion of silica gel in water,¹³ the ΔH_{ads} of isopropylamine from an isopentane solution was determined on silica gel using again heats of immersion (batch mode) at ambient temperature (Table I) to establish standards of reference for the more difficult flow studies.

Table II presents ΔH_{ads} values of isopropylamine on the same sample of silica gel (Fisher grade 62) from an isopentane carrier stream over a range of temperatures and pressures from subcritical to supercritical. Results are given in terms of calories per gram of silica gel. Since this is a saturation experiment, the observed values at a given temperature and pressure should be (and are) independent of flow rate (7-30 mL/h) or concentration (10-20%) of isopropylamine.

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(12) Our ΔH_{soln} values for KCl and BaCl₂ of $4.25 \pm 0.04 \text{ kcal mol}^{-1}$ at 25 °C and $-6.65 \pm 0.30 \text{ kcal mol}^{-1}$ at 75 °C agree well with the literature values of 4.20 and $-6.76 \text{ kcal mol}^{-1}$, respectively (Gunn, S. *J. Phys. Chem.* 1965, 69, 2902; and Criss, C. M.; Cobble, J. W. *J. Am. Chem. Soc.* 1961, 83, 3223).

(13) Our ΔH_{imm} value of $-12.55 \text{ cal g}^{-1}$ for silica gel in water agrees with the range of values -11.95 to $-13.14 \text{ cal g}^{-1}$ obtained at Bartlesville Laboratory (Noll, L. A., private communication) by using different samples of silica gel (Fisher, grade 62).

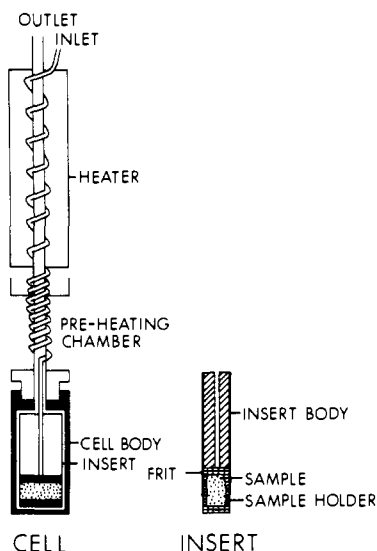


Figure 2. Detail of adsorption cell 5 (Figure 1) showing preheater coil.

The most obvious results from Table II are (a) the insignificant effect of pressure on ΔH_{ads} in the subcritical range, (b) the decrease of ΔH_{ads} in response to increasing temperature at a given pressure, and (c) the significant increase in ΔH_{ads} with increase in pressure above the supercritical threshold at 200 °C. These observations are consistent with the notion that isopropylamine, a strong base, is primarily chemisorbed on the silica gel surface by hydrogen bonds.¹⁴ Increasing the temperature weakens this interaction. The peculiar variations of ΔH_{ads} around the critical point are probably related to complicated changes in the heats of mixing in the fluid phase, such as those reported by Izatt, Christensen, and their co-workers,⁹ rather than direct effects on the solid silica.

A crucial component for extending flow calorimetry into the supercritical range is the use of a Setaram-80 heat flow calorimeter which may be operated in the flow mode at temperatures up to 300 K using the sample cell (5) in Figure 1. This was designed for adsorption thermochemistry so that a bed of adsorbent in cell 5 can be placed downstream from the switching valves in the pumps so that either of the fluid streams leaving the piston pumps (A and B) may be directed through the adsorbent bed. An important problem in flow calorimetry (even at ambient conditions) is to balance mass transfer and heat transfer.¹⁵ Unless the stream of fluid containing the adsorbate has been brought to exactly the temperature of the adsorbent (in cell 5) the observed ΔH_{ads} will contain a contribution due to incomplete thermal equilibration of the streams. Figure 2 shows how this problem was solved by forcing the stream through a coil of $\frac{1}{8}$ in. (o.d.) \times 0.60 in. (i.d.) 316 stainless steel tubing positioned in the preheating chamber of the calorimeter.

In each experiment, about 100–150 mg of silica gel was used. Once the appropriate pressure was obtained, the solvent (isopentane) flow rate was reduced from 75 mL/h to either 7 or 15 mL/h and then the system was thermally equilibrated. Once a steady recorder base line was achieved, the reactive liquid in pump B was pressurized, and, simultaneously, pump A was turned off and pump B was opened to the system at the same flow rate as that of pump A. Heat evolved during the process of interaction of the isopropylamine with the silica gel was monitored by both

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(15) It is also important to reduce dead space in cell 5 by the use of a machined metal insert so that mixing of the flow streams is minimized following switching from pure solvent to the solution of base.

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(18) P_c (isopropylamine) is an average value from estimates using Riedel's and Lydersen's methods reported in ref 17.

digital and analog outputs and was presented as an exothermic release of heat up to the point of surface saturation after which the system returned to its original base-line temperature in about 30 min.

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Registry No. Isopropylamine, 75-31-0.

New Modes of Ligation for a Phosphorus–Nitrogen Double Bond

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The recent availability of stable compounds with element phosphorus multiple bonds¹ has prompted a surge of interest in the use of these species as ligands. Iminophosphines (RN=PR) have been shown capable of acting as two- or four-electron donors toward transition metals.² We report (i) the first example of an iminophosphine behaving as a six-electron donor and (ii) a novel interaction between an RN=PR ligand and a bound carbon monoxide.

In a typical preparation, a mixture of 0.33 g (2.07 mmol) of *t*-BuN=P-*t*-Bu³ and 1.5 g (4.12 mmol) of Fe₂(CO)₉ in 25 mL of *n*-hexane was stirred for 20 h at 25 °C. Separation by column chromatography (silica gel, 1:1 toluene/*n*-hexane) afforded two thermochromic solids, **1** (orange, 35% yield) and **2** (red, 60% yield). The EI MS (70 eV) of **1** exhibited a parent peak at *m/e* 439 and a 100% intensity peak at *m/e* 271 assignable to [(*t*-BuNP-*t*-Bu)Fe₂(CO)₆]⁺ and [(*t*-BuNP-*t*-Bu)Fe]⁺, respectively. Interestingly, the EI-MS of **2** was identical with that of **1** due to the thermal elimination of 2CO. However, the 32.384-MHz ³¹P{¹H} NMR spectra of **1** (s, +81) and **2** (s, +269) were quite different; moreover, in contrast to that of **1**, the IR spectrum of **2** featured a low-energy C–O stretch (1645 cm⁻¹). The structures of both compounds were established by X-ray crystallography.⁴

As shown in Figure 1, the structure of **1** involves a distorted tetrahedral Fe₂PN core. The iminophosphine ligand serves as a six-electron donor and adopts a *cis* conformation (C(11)–P(1)–N–C(7) dihedral angle = 0.3°). By analogy with the isostructural

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(4) Compound **1**: C₁₄H₁₈Fe₂NO₆P; *M_r* = 438.97. Crystal data: monoclinic, *P*2₁/*m*; *a* = 8.198 (1) Å, *b* = 15.331 (2) Å, *c* = 15.242 (2) Å, β = 93.05 (1)°; *V* = 1913 (1) Å³; *Z* = 4; *D*(calcd) = 1.524 g cm⁻³. Compound **2**: C₁₆H₁₈Fe₂NO₈P; *M_r* = 494.99. Crystal data: monoclinic, *P*2₁/*c*; *a* = 19.839 (10) Å, *b* = 12.787 (7) Å, *c* = 26.578 (10) Å, β = 110.49 (3)°; *V* = 6316 (1) Å³; *Z* = 12, *D*(calcd) = 1.562 g cm⁻³. Intensity data: Enraf-Nonius CAD-4F diffractometer, ω–2θ scan modes in the range 2.0 ≤ 2θ ≤ 50.0; 3506 and 11 805 unique reflections for **1** and **2**, respectively. The structures of **1** and **2** were solved (Patterson and difference Fourier) and refined (full matrix, least squares) by using 2496 and 6384 data, respectively. Final residuals were **1**, *R* = 0.0496 and *R_w* = 0.0564 and **2**, *R* = 0.0674 and *R_w* = 0.0710.