with 15 mL of dichloromethane. Crystallization from dichloromethane/ether at −20 °C afforded 405 mg (0.29 mmol, 76%) of light-yellow fine crystals: ^1H NMR (80 MHz, CD_3NO_2) δ 1.38 (t, 36, $POCH_2CH_3$), 4.28 (sym. m, 13 lines, 24, $POCH_2$), 5.49 (s, 10, C_5H_5). Anal. Calcd for $C_{34}H_{70}Co_2F_{12}O_{18}P_8Ti$: C, 28.99; H, 5.01. Found: C, 28.90; H, 5.24.

Bis[(cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]oxovanadium (13). To a solution of 0.92 g (1.60 mmol) of $NaL \cdot H_2O$ in 10 mL of water was added $VOSO_4 \cdot 5H_2O$ in small portions until no more precipitation occurred. The product was separated by centrifugation, washed with water, and dried in vacuo. Repeated crystallization from pentane yielded 0.50 g (0.44 mmol, 55%) of greenish yellow crystals: IR (CCl_4) $\nu(V{=}O)$ 965 cm^{-1}. Anal. Calcd for $C_{34}H_{70}Co_2O_{19}P_6V$: C, 35.90; H, 6.20; Co, 10.36; P, 16.34; V, 4.48. Found: C, 36.05; H, 6.11; Co, 10.40; P, 16.16; V, 4.30.

[(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]trichlorotin (14). To a freshly prepared solution of 254 mg (0.44 mmol) of $NaL \cdot H_2O$ in 5 mL of 2 M hydrochloric acid was added dropwise a solution of 267 mg (0.73 mmol) of $(NH_4)_2SnCl_6$ in 5 mL of 2 M hydrochloric acid. A yellow precipitate formed which was extracted into 10 mL of dichloromethane. The organic phase was separated and pumped to dryness at reduced pressure. Crystallization from dichloromethane/ether afforded 175 mg (0.23 mmol, 52%) of light-yellow crystals: ^1H NMR (270 MHz, CD_2Cl_2) δ 1.31 (t, 18, $POCH_2CH_3$), 4.19 (sym. m, 13 lines, 12, $POCH_2$), 5.20 (s, 5, C_5H_5); MS (200 °C), *m/e* (relative intensity) 760 (M^+, 68%), 725 ($M^+ - Cl$, 96%). Anal. Calcd for $C_{17}H_{35}Cl_3CoO_9P_3Sn$: C, 26.85; H, 4.64. Found: C, 26.68; H, 4.47.

[(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]trichlorozirconium (15). A suspension of 120 mg (0.51 mmol) of $ZrCl_4$ and 285 mg (0.51 mmol) of NaL in 20 mL of dry tetrahydrofuran was stirred at room temperature for 48 h. The residue after evaporaion of the solvent was extracted three times with 10 mL of hexane to remove any unreacted NaL. The product was taken up in chloroform and crystallized from hexane/chloroform: yield 242 mg (0.33 mmol, 65%) of large-yellow crystals; ^1H NMR (80 MHz, $CDCl_3$) δ 1.32 (t, 18, $POCH_2CH_3$), 4.21 (sym. m, 13 lines, 12, $POCH_2$), 5.20 (s, 5, C_5H_5); MS (165 °C), *m/e* (relative intensity) 732 (M^+, 56%), 697 ($M^+ - Cl$, 88%). Anal. Calcd for $C_{17}H_{35}Cl_3CoO_9P_3Zr$: C, 27.86; H, 4.82. Found: C, 27.68; H, 5.11.

Tetraphenylphosphonium [(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]trichlororhodate(1−) (16). To a stirred solution of 407 mg (0.71 mmol) of $NaL \cdot H_2O$ in 20 mL of tetrahydrofuran was added 200 mg (0.73 mmol) of $RhCl_3 \cdot xH_2O$ (37.8% Rh). After 24 h the precipitate was filtered off, washed with a little tetrahydrofuran, and dried in vacuo to give a light-red powder. The filtrate contains the dimeric complex **17** and another not yet identified oxygen tripod ligand–rhodium complex. The dry powder was dissolved in 20 mL of water and precipitated with a saturated aqueous solution of PPh_4Cl. The precipitate was separated by centrifugation, washed with water, and dried in vacuo. Recrystallization from acetone/ether afforded 332 mg (0.31 mmol, 43%) of red shiny plates: ^1H NMR (80 MHz, CD_2Cl_2) δ 1.23 (t, 18, $POCH_2CH_3$), 4.10 (sym. m, 13 lines, 12, $POCH_2$), 5.00 (s, 5, C_5H_5). Anal. Calcd for $C_{41}H_{55}Cl_3CoO_9P_4Rh$: C, 45.43; H, 5.11. Found: C, 45.53; H, 5.10.

Di-μ-chlorobis{[(cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]chlororhodium} (17). A mixture of 400 mg (0.69 mmol) of $NaL \cdot H_2O$ and 200 mg (0.73 mmol) of $RhCl_3 \cdot xH_2O$ (37.8% Rh) in 20 mL of methanol was heated to reflux for 18 h. The resulting dark-red solution was separated from black solid decomposition products and concentrated to ca. 10 mL. Addition of 20 mL of ether precipitated NaCl and presumably some $Na[LRhCl_3]$. The supernatant solution was concentrated to yield a red oil which was dried in high vacuum. A chloroform solution of the oil was covered with hexane and kept at −20 °C. After a few days, dark-red crystals had grown which were separated and dried in vacuo: ^1H NMR (80 MHz, CD_2Cl_2) δ 1.24, 1.28, 1.31 (3 overlapping t, 36, $POCH_2CH_3$, $^3J(HCCH) = 7$ Hz), 3.9–4.4 (unsym. m, br, 24, $POCH_2$), 5.06 (q, 10, C_5H_5, $^3J(PCoCH) = 0.4$ Hz). Anal. Calcd for $C_{34}H_{70}Cl_4Co_2O_{18}P_6Rh_2$: C, 28.79; H, 4.97; Cl, 10.00; Rh, 14.51. Found: C, 28.65; H, 5.10; Cl, 9.88; Rh, 14.35.

[(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]dichlorooxomolybdenum (18). A suspension of 224 mg (0.70 mmol) of $[MoCl_4(CH_3CN)_2]$ and 400 mg (0.72 mmol) of dry NaL in 15 mL of tetrahydrofuran was stirred for 24 h at room temperature. The dark-red solution was separated from insoluble NaCl and concentrated at reduced pressure to yield a red–brown sticky residue. This was extracted with hexane to give immediately a blue hexane solution and a small amount of a viscous red–brown oil. Long green needles crystallized from the hexane solution at −78 °C, which were collected: yield 260 mg (0.36 mmol, 52%); MS (150 °C), *m/e* (relative intensity) 719 (M^+, 63%), 684 ($M^+ - Cl$, 5%), 649 ($M^+ - 2Cl$, 3%). Anal. Calcd for $C_{17}H_{35}Cl_2CoMoO_{10}P_3$: C, 28.43; H, 4.91; Cl, 9.87; Mo, 13.36. Found: C, 28.16; H, 5.25; Cl, 9.79; Mo, 13.27.

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Supplementary Material Available: Tables II–IV listing anisotropic thermal parameters, bond lengths, and bond angles (8 pages); tables of calculated and observed structure factors (45 pages). Ordering information is given on any current masthead page.

Thermodynamic Studies of Donor Binding to Heterogeneous Catalysts

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Abstract: The thermodynamic data for the adsorption of pyridine, *N*-methylimidazole, and dimethylcyanamide from cyclohexane onto palladium oxide crystallites supported on carbon (5% w/w) were obtained by calorimetric and adsorption studies. The data indicated that there are at least two acceptor sites on the palladium oxide surface. Both the calorimetric and adsorption experiments give the same saturation adsorption capacity for site 1. Its magnitude suggests that the adsorbed pyridine is normal to the surface plane of palladium oxide, indicating that the adsorption process involves a Lewis acid–base type of interaction. In the low-coverage region, the adsorption quotients of base onto palladium oxide are considerably larger than those of carbon, indicating a preferential adsorption of base onto the palladium oxide surface.

Reactions of gases and liquids at solid interfaces are an important, fundamental process in heterogeneous catalysis.[1] Relatively little information is available concerning the binding of any but the simplest gas molecules to a solid interface. Consequently, little is known about the electronic nature of the gas–solid or liquid–solid interaction. Uncertainty often exists about the geometry of the adsorbate relative to the metal surface and whether or not to describe the interaction as Lewis acid–base in nature.[2] The relationship of the metal–ligand bond strength to

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0002-7863/87/1509-0169$01.50/0

the metal surface d-level occupancy has received little attention,[3] as has the influence of the covalent and electrostatic donor and acceptor properties of the adsorbate on these trends. Attaining this level of understanding is essential to understanding the subsequent reactions that occur in catalysis.

The correlation of donor–acceptor bond energies measured in poorly solvating solvents into the *E* and *C* equation has provided a quantitative standard for determining what constitutes normal σ bond formation in an interaction.[4] This approach has uncovered several systems in which additional contributions to coordinate bond energies exist.[5] Combination of the *E* and *C* analysis and results from spectroscopic and electrochemical studies have led to an identification of the extra repulsive or attractive interactions that often accompany coordination.[5] We propose that a determination of the energetics of interaction of the organic donor and acceptor molecules in our *E* and *C* correlation with metal surfaces has the potential of characterizing the nature of the donor–metal center interaction and indicating irregularities in the thermodynamic data from those expected for normal σ bond formation. The interactions of donors and acceptors with solid catalysts are expected to be much more complex than donor–acceptor interactions in poorly solvating solvents, and this model is capable of demonstrating this complexity. The recently reported successes by Fowkes[6] in using the *E* and *C* approach to understand phenomena as complicated as adhesive also suggests that comparable insights may be obtained in surface science and catalysis.

"The heat of chemisorption, the major thermodynamic quantity determined by experiment, is a critical target in theoretical models that address issues of direct interest to surface scientists."[1] Estimates of the heat of chemisorption are often made from thermal desorption studies, and these experiments are typically not very accurate. In this article we present a method for the calorimetric determination of interaction energies. The procedure is more involved than that employed in our earlier solution studies because multiple coordination sites exist on most solid catalysts. Consequently, in contrast to the solution case, more information is needed than the heat evolution accompanying addition of the donor to the solid catalyst to define the system. The measurements described in this article permit a determination of the number of active sites, the equilibrium constant, and the enthalpy of a binding to each site. Data obtained in this fashion are compared with results from thermal desorption studies, and our procedure is seen to be more sensitive and accurate.

Experimental Section

Purification of Materials. Palladium on carbon (5%) (lot 11890-11A; 50% wet) and the corresponding carbon support (lot 11890-11B) supplied by Englehard Inc. Preliminary drying of PdO/C was done by drying it over anhydrous phosphorus pentoxide in a vacuum desiccator. Final drying was accomplished by storing over fresh P_2O_5 in vacuo for several days. The corresponding carbon support was similarly dried over P_2O_5 under vaccum.

Pyridine (Fischer; certified ACS) was stored over BaO and redistilled over CaH_2 by using a 12-in. Vigreaux column. *N*-Methylimidazole (Aldrich Chemical; 99%) (*N*-MeIm) was distilled over CaH_2 under reduced pressure. Dimethylcyanamide (Alfa; 99%) (DMCA) was distilled once under reduced pressure. In all cases, only the middle fraction was collected.

Cyclohexane (Fischer; certified ACS) was treated with activated charcoal 3 times in order to remove traces of benzene and was distilled once. The distillate was stored over a 4A molecular sieve at least 24 h prior to use. Water used in the spectrophotometric analysis of *N*-MeIm and DMCA were doubly distilled (the first distillation over $KMnO_4$) or purified by the Barnstead NONO pure system.

Calorimetric Studies. Calorimetry was performed by the modified procedure as previously described.[7] The slurry of PdO/C or carbon powder was magnetically stirred in a Dewar cell and a solution of base injected into the slurry with a precalibrated gas-tight syringe. The temperature of the solution for the pyridine experiment was 25 (±1) °C while the temperatures of *N*-MeIm and DMCA were 26 (±1) °C. All measured heats of adsorption of base onto PdO/C and carbon powder were corrected for the heats of dilution of base. As the adsorbents and the bases are hygroscopic, all handling of these materials was carried out in a dry N_2 bag or a drybox.

Analysis of the Concentration of Base after Adsorption. After the injection of the base solution into the slurry of adsorbent and the establishment of a good base line, an aliquot of the solution was withdrawn from the calorimeter cell by using a Swinney filter. Withdrawal of all solutions began ~100 s after the injection of base. An average of 20 s was required to withdraw approximately 6 mL of solution.

The concentration of pyridine in the aliquot was determined by UV spectrophotometry at 252 nm using a Perkin-Elmer 330 spectrophotometer. The determination of the concentrations of *N*-MeIm and DMCA required a different procedure. Sample solutions (5 mL each) of *N*-MeIm and DMCA were shaken vigorously with an equal volume of 0.01 M HCl (for *N*-MeIm) and water (for DMCA) for several minutes. Two layers were allowed to separate and equilibrate overnight. The absorbance of the aqueous layer was determined at 212 (*N*-MeIm) and 202 nm (DMCA). Controls were run to verify this procedure and to establish that Beer's law is obeyed for these bases in the concentration range studied.

Adsorption Isotherm of Pyridine at Equilibrium. A measured amount of pyridine solution was mixed thoroughly with 0.3 mg of adsorbent in 25 mL of cyclohexane in a stoppered flask, and the mixture was allowed to equilibrate for 24 h at 25 (±0.5) °C in a water bath. Aliquots of solution were then withdrawn for UV determination at the end of the 24th hour.

Procedure for Finding the Heat of Adsorption of Base onto the Palladium Crystallites in PdO/C. For PdO/C, the measured heat in cyclohexane solvent, h', is the displacement heat for the process in eq 1,

$$\text{base}_{\text{soln}} + \text{S}_{\text{ad}} \rightarrow \text{base}_{\text{ad}} + \text{S}_{\text{soln}} \qquad (1)$$

where $\text{base}_{\text{soln}}$ is the base in solution, S_{ad} the adsorbed cyclohexane solvent, base_{ad} the adsorbed base, and S_{soln} the return of the adsorbed solvent to solution. The measured heat, h', is the combined contribution from the processes described in eq 1 for both carbon and palladium oxide adsorption, i.e.,

$$h' = h'_{\text{C}} + h'_{\text{PdO}} \qquad (2)$$

where h'_{C} and h'_{PdO} are the contributions to the measured heats from carbon and palladium adsorption, respectively. In order to factor out the contribution from carbon adsorption, a plot of the number of moles of base adsorbed per gram of carbon vs. the base concentration (molarity) of the solution in equilibrium with it for a given carbon sample size was determined experimentally. After the injection of base solution into the PdO/C slurry, the molarity of base left in solution was determined and the number of moles absorbed by the PdO/C support determined by the difference of the added amount and that left in solution. The number of moles of base adsorbed by the charcoal was determined by using the solution molarity of base and the corresponding value for the moles of base adsorbed, B'_{C}, from the plot described above. The difference between the total amount of base adsorbed by PdO/C and the estimated amount of base adsorbed by the carbon support is the moles of base adsorbed by palladium oxide (B'_{PdO}). This same approach was used to factor the total measured heat, h', to obtain the heat of adsorption by only palladium oxide, h'_{PdO}. The heat of adsorption, ΔH, per mole of base adsorbed from a given solvent onto palladium oxide is therefore given by $h'_{\text{PdO}}/B'_{\text{PdO}}$.

Thermal Analysis. The thermogravimetric analysis data were obtained by using a Cahn Thermogravimetric Analysis System 113. The samples were run at a rate of temperature increase of 4 °C/min under static air conditions. Sample sizes ranged from 4 to 16 mg. Weight loss of pyridine was complete at 225 °C. The mass sensitivity of the microbalance at 1-mg full scale on the recorder is 0.001 mg.

The gas–solid calorimetric data were obtained by using a Du Pont Thermoanalyzer Model 1090 in the differential scanning calorimeter mode. Sample sizes range from 6.4 to 7.3 mg, and the samples were run under flowing dry nitrogen. These samples were run to 225 °C at a heating rate of 5 °C/min.

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Table I. Adsorption Enthalpy of Adsorbed Base as a Function of Base Concentration

	$[B] \times 10^4$, M	B'_{PdO},[a] mmol		$-h'_{PdO}$, cal[b]		B'_C,[a] mmol	$-h'_C$ (measd), cal[b]
		measd	calcd	measd	calcd		
pyridine[c]	0.380	0.0458	0.0458	0.59	0.61	0.027	0.27
	0.496	0.0581	0.0523	0.76	0.69	0.032	0.30
	1.00	0.0690	0.0688	0.90	0.91	0.050	0.41
	1.15	0.0707	0.0719	0.93	0.95	0.054	0.43
	2.34	0.0790	0.0860	1.03	1.12	0.078	0.62
	4.39	0.104	0.0977	1.27	1.26	0.097	0.73
	7.33	0.116	0.108	1.41	1.38	0.116	0.83
	10.3	0.129	0.116	1.51	1.46	0.130	0.93
	19.4	0.142	0.133	1.67	1.64	0.163	1.14
	26.7	0.151	0.143	1.74	1.74	0.185	1.25
	39.3	0.162	0.155	1.86	1.86	0.213	1.36
	63.8	0.171	0.169	1.96	2.01	0.252	1.58
	107	0.191	0.182	2.10	2.14	0.305	1.90
	167	0.196	0.191	2.18	2.23	0.367	2.18
	269	0.218	0.197	2.38	2.30	0.442	2.58
N-MeIm[c]	0.040	0.041	0.041	0.648	0.638	0.0250	0.280
	0.070	0.052	0.052	0.765	0.788	0.0243	0.280
	0.128	0.044	0.063	0.689	0.929	0.0290	0.325
	0.160	0.069	0.067	0.985	0.975	0.0306	0.340
	0.200	0.067	0.072	0.963	1.019	0.0330	0.362
	0.268	0.080	0.077	1.104	1.074	0.0365	0.396
	0.351	0.082	0.083	1.127	1.123	0.0399	0.431
DMCA[c]	0.269	0.0660	0.0672	0.848	0.861	0.0230	0.210
	0.385	0.0730	0.0758	0.942	0.966	0.0270	0.243
	0.508	0.0914	0.0823	1.169	1.044	0.0300	0.270
	0.515	0.0780	0.0826	0.977	1.048	0.0310	0.280
	1.73	0.114	0.114	1.386	1.386	0.0470	0.368
	3.95	0.129	0.142	1.548	1.673	0.080	0.612
	4.41	0.149	0.146	1.750	1.717	0.0818	0.620
	6.02	0.165	0.159	1.946	1.843	0.0840	0.630
	10.95	0.180	0.184	2.060	2.088	0.1140	0.818

[a] B'_{PdO} and B'_C are the millimoles of base adsorbed onto PdO and carbon, respectively, in the PdO/C sample. [b] Uncertainties in h'_{PdO} and h'_C are ±0.03 and ±0.02 cal, respectively. [c] Although the error in ΔH varies from ca. 6% in the extremely low-concentration region to ca. 3% in high concentration regions, the precision obtained is much smaller, ca. 2%. The sample sizes of PdO/C for pyridine, *N*-methylimidazole, and dimethylcyanamide adsorption were 0.750, 0.440, and 0.599 g, respectively. Volume of solution was approximately 50 cm^3.

Initial temperature in all thermal studies was 25 °C, and all samples were loaded and initially weighed in a glovebag under dry argon. At least duplicate determinations were carried out on all samples.

Results and Discussion

The definition of the equilibrium system for a heterogeneous catalyst requires the determination of the number of different types of active sites, n_1, n_2, etc., the total number of sites for each type, $n_1{}^s$, $n_2{}^s$, etc., the equilibrium constant for each site, and the enthalpy of binding to each site. The approach to be employed here involves a typical Langmuir type[9] evaluation of the equilibria coupled with an enthalpy titration to provide more information to help determine the unknowns.

Treatment of Adsorption Data with the Langmuir Equation. The equilibrium constant for the absorption of base in solution onto a solid is given by eq 3, where B_{PdO} is the number of moles of base on PdO in units of mol/g of PdO, [B] is the equilibrium molar concentration of base in solution, and $n_1{}^s$ is the total number of moles of active site 1 per gram of PdO. The term $n_1{}^s - B_{PdO}$ gives the concentration of free sites at equilibrium. Rearrangement of eq 3 produces the familiar[10] Langmuir equation (eq 4). For a homogeneous adsorbent with only one type of adsorption site, the plot of $[B]/B_{PdO}$ vs. [B] gives a straight line in the whole concentration range (constrained by the condition that the solute concentration be dilute). For a heterogeneous adsorbent with more than one kind of adsorption site, curvature is found in the plot with regions approximating straight lines with different slopes.[11]

$$K_1 = \frac{B_{PdO}}{[B][n_1{}^s - B_{PdO}]} \tag{3}$$

$$\frac{[B]}{B_{PdO}} = \frac{1}{n_1{}^s K_1} + \frac{[B]}{n_1{}^s} \tag{4}$$

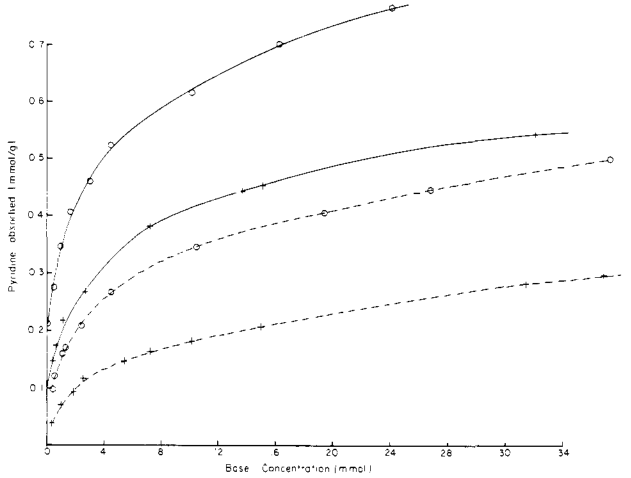

Figure 1. Adsorption isotherms for pyridine obtained immediately after (---) and 24 h after (—) the calorimetric experiment: (O) pyridine onto PdO/C; (+) pyridine onto carbon.

The pyridine adsorption isotherms from cyclohexane obtained immediately after the calorimetric experiment and 24 h later are shown in Figure 1. They exhibit Type I behavior according to the classification scheme of Brunauer.[9] The same type of behavior is also observed for *N*-methylimidazole and dimethylcyanamide. The change with time indicates that a rapid equilibrium is es-

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Table II. Thermodynamic Data for the Adsorption of Base onto the Two Sites in Palladium Oxide[a]

base	$K_1 \times 10^{-4}$, M^{-1}	n_1^s, mmol g^{-1}	ΔH_1, kcal/mol	$K_2 \times 10^{-2}$, kcal/mol	n_2^s, mmol g^{-1}	ΔH_2, kcal/mol
pyridine	2.5 ± 0.20 (2.1)	2.5 (2.6)	13 (13)	2.9 ± 0.19 (2.7)	3.2 (3.3)	10 (9)
N-methylimidazole	34 ± 2.3 (34)	3.0 (3.0)	16 (16)	79 ± 12 (79)	4.6 (4.6)	6 (7)
dimethylcyanamide	8.2 ± 1.7 (8.8)	3.0 (2.9)	13 (13)	13 ± 1.3 (14)	5.4 (5.4)	10 (10)

[a] All n^s values have errors less than 5% except n_2^s for DMCA, which is 20%. All heats have errors less than 0.5 kcal/mol except ΔH_2 values for *N*-meIm and DMCA, which are 1.0 and 1.5 kcal/mol, respectively. The ± errors on *K*'s are standard deviations. Values in parentheses were obtained from individual fits of eq 5 for *K* and *n* values and a least-squares fit for ΔH_1 and ΔH_2 using *K* and *n* from eq 5.

tablished in this system that involves Lewis acid–base reactions, and this is followed by a slower reaction involving less accessible sites. All of our results pertain to the initial coordination processes, and when we use the term equilibrium it should be understood that we mean the initial coordination process and not a true, final equilibrium for the system.

The pyridine–PdO/C adsorption data are corrected for the carbon adsorption by the procedure previously described. The results are summarized in Table I for all three bases studied. Langmuir plots of the PdO adsorption do not give straight lines, indicating the existence of multiple sites. In analyzing this data it is common[11] to select straight-line portions of the curve and from the corresponding slopes and intercepts of eq 4 determine K_n and n_n^s. For reasons similar to those raised in Benesi–Hildebrand type analysis of homogeneous equilibria,[12] these procedures can introduce errors in the data analysis. Accordingly, we decided on a rigorous solution of the consecutive equilibrium constant expressions and a fit of all the adsorption data by a simplex routine to obtain K_1, K_2, n_1^s, and n_2^s for a two-site system. The resulting equation is

$$B_{\mathrm{PdO}} = \frac{n_1^s K_1[\mathrm{B}]}{1 + K_1[\mathrm{B}]} + \frac{n_2^s K_2[\mathrm{B}]}{1 + K_2[\mathrm{B}]} \tag{5}$$

Similar equations can be derived for an additional number of different sites. Each site adds another term of the same form as for the first and second terms shown in eq 5. The results of this analysis for the three bases studied are contained in Table II.

At this point we should clarify the interpretation of two separate sites. For practical reasons, we shall define a site as either one or more types of metal centers whose equilibrium constants and enthalpies of base binding are the same within the detection limits of the experiment. In order to distinguish separate sites, the equilibrium constants for the interaction of base with these sites must differ enough that at low concentration only the most active site is filled (we call it site 1). As the base concentration increases, the second site (site 2) will begin to be filled, etc. A very small number of highly active sites (≪0.05 mM/g of catalyst) would be incorporated into site 1 if they existed.

Our next objective is to evaluate the enthalpy data. We shall first determine if it is consistent with the absorption data analysis and then describe the procedure for a simultaneous best fit of absorption and calorimetric results.

Enthalpy Studies. The changes in the measured heats of adsorption of pyridine from cyclohexane onto 0.750 g of PdO/C and 0.712 g of C powders, respectively, as the pyridine concentration in solution increases are depicted in Figure 2. As can be observed, initially, $-h'$ values increase rapidly with the pyridine concentration. The increase is more abrupt in the case of adsorption on PdO/C. The heat evolved levels off in the higher concentration region. Similar behavior is also observed for *N*-methylimidazole (*N*-MeIm) and dimethylcyanamide (DMCA). With the calibration plot of base adsorbed vs. the base concentration described earlier, the values of B_{PdO}, B_{C}, etc., as a function of base concentration were obtained and are summarized in Table I for the three bases investigated in this work. For this system, we will assume that there is no adsorbate–adsorbate interaction. In the region where only site 1 is being filled, ΔH corresponds to the molar enthalpy of adsorption of base from a given solvent onto site 1. When contributions from site 2 being filled occur, the observed experimental heat, h'_{PdO}, is the sum of ΔH_1 and ΔH_2 weighted by the respective number of moles of base adsorbed onto site 1 and site 2. It follows that

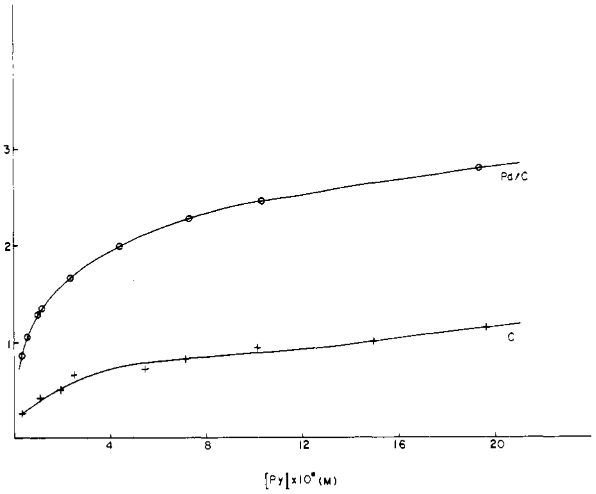

Figure 2. Plot of the measured heat ($-h'$) of adsorption of pyridine from cyclohexane vs. the pyridine concentrations, [Py], in solution. Data in the more concentrated region are not included for reason of clarity.

Table III. Pyridine Adsorption Parameters Obtained as a Function of Time

time	n_1^s, mmol g^{-1}	K_1, M^{-1}
105 s	2.5 ± 0.10	2.5×10^4
9 min	2.5 ± 0.10	2.5×10^4
equilibrium[a] (24 h)	4.1 ± 0.2	$4.5 \pm 0.7 \times 10^4$

[a] This may be a slowly attained equilibrium value or could result from a slow reaction of water or pyridine with the surface creating more metal acid sites.

$$\frac{h'_{\mathrm{PdO}}}{\text{g of PdO}} = B_{\mathrm{PdO(1)}}\Delta H_1 + B_{\mathrm{PdO(2)}}\Delta H_2 \tag{6}$$

The total number of moles of base adsorbed by palladium, B_{PdO}, equals $B_{\mathrm{PdO(1)}} + B_{\mathrm{PdO(2)}}$. Substituting the values for $B_{\mathrm{PdO(1)}}$ and $B_{\mathrm{PdO(2)}}$ from the equilibrium constant expression (eq 5) leads to eq 7. Substituting n_1^s, K_1, n_2^s, and K_2 from the adsorption data

$$\frac{h'_{\mathrm{PdO}}}{\text{g of PdO}} = \frac{n_1^s K_1[\mathrm{B}]}{1 + K_1[\mathrm{B}]}\Delta H_1 + \frac{n_2^s K_2[\mathrm{B}]}{1 + K_2[\mathrm{B}]}\Delta H_2 \tag{7}$$

fit, a least-squares fit for the best values of ΔH_1 and ΔH_2 needed to reproduce the h'_{PdO} values is found. The results are reported in Table II. The excellent fit of the experimental h'_{PdO} values provides support for the authenticity of the *K* and n^s results from the absorption data.

As an additional check on our analysis, no change in the magnitude of our ΔH_1 value (13 kcal mol^{-1}) was observed when the sample size was changed from 0.75 to 1.2 g and a quantity of base added to bind only to site 1 ([Py] = 4.66×10^{-5} M, B'_{PdO} = 0.0816 mmol, and h'_{PdO} = 1.05 cal for a ΔH_1 of 12.9 kcal mol^{-1}).

The best solution to the problem is to simultaneously fit the enthalpy and the adsorption data to n^s, *K*, and ΔH for each site. These results are also summarized in Table II.

Pyridine adsorption parameters as a function of time are summarized in Table III. The number of the active sites measured in the first 9 min is constant but increases over a longer period of time. The calorimetric experiment provides a rapid response

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(12) Drago, R. S.; Rose, N. J. *J. Am. Chem. Soc.* **1959**, *81*, 6141.

to the properties of the adsorption site at the time the adsorbent comes in contact with the base. The time dependence of our adsorption studies shows that any treatment of adsorption heats determined calorimetrically based on adsorption measurements in which the residence time was not the same or about the same time interval as the calorimetric experiment can produce incorrect results. This oversight may have introduced inaccuracy in some recent work.[13]

The magnitude of the n_1^s value for pyridine (Table II) provides information about the mode of coordination of this donor to the surface. We propose that the base is normal to the surface plane of the palladium oxide. If the pyridine molecule coordinated parallel to the surface, 2000 m^2 of surface would be required compared to the 127 m^2 available (indicated by Englehard Inc.). These calculations are based on an average particle size[8] of 4 nm and a 0.68-nm van der Waals radius of pyridine. The normal orientation of the base molecule would be consistent with donor–acceptor bond formation between the basic nitrogen donor and the acidic palladium site and would strengthen our claim that the adsorption process often involves a Lewis acid–base type of interaction.

Characterization of Surface Sites. The ESCA spectrum of the dried PdO/C sample showed two palladium peaks at 336.8 ($3d_{5/2}$) and 342.1 eV ($3d_{3/2}$). The non-Gaussian nature of the peaks suggests the presence of Pd(0) and Pd(II) so our representation PdO/C refers to this mixture. The spectrum of the PdO/C sample containing adsorbed pyridine could not be obtained because the pyridine was removed by the high vacuum system of the spectrometer (no nitrogen peak was detected). The positions of the two peaks mentioned above are the same in the sample from which pyridine is desorbed.

Preliminary *E* and *C* Analysis of the Data. Since the adsorption of the bases studied on the palladium oxide surface is dominated by the Lewis acid–base interaction, it is of interest to determine if E and C values can be obtained for sites 1 and 2 by solving eq 8,[4] where W would correspond to the desorption of solvent and E_A and C_A to the Lewis acid site.

$$-\Delta H + W = E_A E_B + C_A C_B \qquad (8)$$

As shown in recent work, π back-bonding causes deviations from this equation. When acid parameters for a π back-bonding acid are obtained with σ-only donors, the enthalpies predicted when both pyridine and acetonitrile are used as donors are lower than those measured experimentally. The enhanced interaction is attributed to π back-bonding from the metal onto the ligand. When the enthalpies and corresponding E_B and C_B parameters for pyridine, *N*-methylimidazole, and dimethylcyanamide are substituted into eq 8, a large set of E_A and C_A parameters can be found to fit the data. A more complete data set is needed to draw conclusions about the nature of the acid center.

Comparison of PdO and C Adsorption. The K_1 values which measure the extent of adsorption at the time of the calorimetric experiment are all extremely large for site 1 for the three bases, and they decrease appreciably for site 2. The n_1^s values are the same for all donors, and experimental error prevents conclusions about n_2^s being drawn. The very large K_1 values for *N*-methylimidazole are mirrored in ΔH_1.

The Langmuir plot based on the carbon adsorption data shows that more than two straight lines can be drawn, indicating its heterogeneous character. It is of interest to observe that in the low-coverage region, the K value for the pyridine adsorption onto the carbon support is estimated to be 7.8×10^3 M^{-1} and n_1^s = 0.16 mmol/g of carbon. Both of these values are considerably smaller than those in the pyridine–palladium oxide interaction. The other two bases show the same trend. This implies that at low coverage, the base is preferentially adsorbed by the palladium oxide crystallites. The data summarized in Table I show more than 60% of the pyridine introduced was adsorbed onto palladium oxide in spite of the relatively small amount of PdO compared to the carbon support. For pyridine and DMCA, the relative amount of base adsorbed onto the palladium oxide (i.e., the ratio B_{PdO}/B_C) decreases with increasing base concentration. This is a reflection of a smaller K_2 value for adsorption onto palladium and that the K values for adsorption onto the carbon support are comparable to the corresponding K_2 value for palladium oxide.

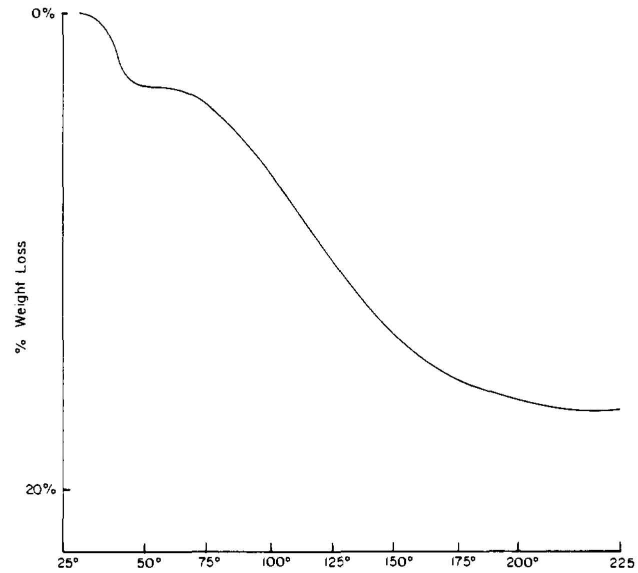

Figure 3. TGA of PdO/C with adsorbed pyridine and cyclohexane under static air.

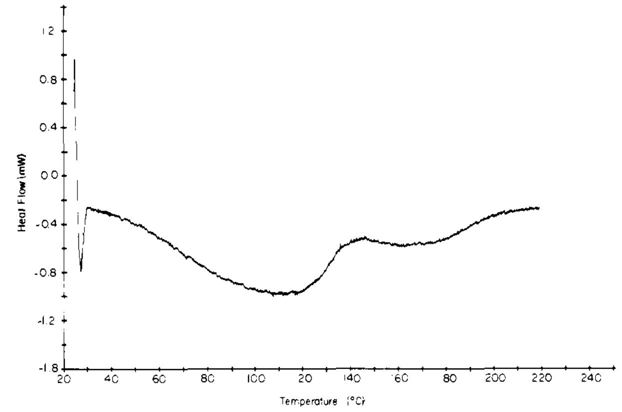

Figure 4. DSC of PdO/C with adsorbed pyridine under flowing nitrogen.

Thermoanalytical Results. The sample used for thermogravimetric analysis TGA, was prepared by adding 0.750 g of PdO/C to a cyclohexane solution of pyridine. The weight increase of the dried solid and the analysis of the residual solution indicated 0.105 g of cyclohexane and 0.0595 g of pyridine were adsorbed. In the TGA results (see Figure 3), two-site binding of pyridine is not detected during a steady temperature increase even though the weight loss is consistent with all the pyridine and cyclohexane being removed. the first low-temperature process detected in the TGA, beginning at about 28 °C, represents loss of a very volatile, loosely bound component such as cyclohexane (from sample preparation). The only other possibility would be water, but this is a very low temperature for water to be lost at the rate observed under static air conditions. The broad feature in the TGA curve involves pyridine and cyclohexane, corresponding to 15.9% of the original sample mass. This result is consistent with our absorption studies.

The differential scanning calorimetry (DSC) studies were very difficult to interpret due to the broad temperature range throughout which the desorption phenomenon occurred and the subsequent inability to obtain a good base line (see Figure 4). As a result, the enthalpy error limits are rather large. DSC clearly shows a range of processes occurring over the temperature range studied. Pyridine and cyclohexane were both desorbed within the

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[13] Hey, M. J.; Mactaggart, J. W.; Rochester, C. H. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 699.

temperature range used, but separation of the effects ascribed to each component was not possible. The total enthalpy change measured is 25.9 ± 1.5 J/g of sample where the reported error is the average deviation of the runs performed. This result was converted to 11.6 ± 0.8 kcal/mol of adsorbed substance both by using an average mole mass for pyridine and cyclohexane of 81.5 g/mol and by using the initial composition of the sample as prepared with no appreciable difference in result.

Furthermore, blank determinations were used on the PdO/C catalyst to check for any other processes which might have occurred, and these were subtracted as background (the effect was negligible).

An interesting feature of the TGA is observed if the temperature rise is interrupted during the run and the temperature held constant. The weight loss also stops quickly, which is somewhat unusual in this type of run. Subsequent temperature increase results in more weight loss. This implies extremely rapid equilibration during the desorption-adsorption process and is not inconsistent with desorption from activated carbon itself. Both DSC and TGA results are consistent with a multiple-site model for PdO.

Conclusion

In summary, the thermodynamic data for adsorption of base from a solvent onto a metallic crystallite supported on carbon powder were obtained from our work. The results show unequivocally the multiple-site character of the palladium oxide crystallites. It also shows that there is a preferential adsorption of base onto the palladium oxide surface in spite of the good adsorbing power of the carbon support. Our adsorption method provides more resolution of the two sites than TGA and a more accurate value for the binding enthalpy than DSC because of the multiple processes observed. The calorimetric titration procedure and data analysis reported in this paper can be extended to other heterogeneous catalysts.

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Registry No. *N*-MeIm, 616-47-7; DMCA, 1467-79-4; PdO, 1314-08-5; C, 7440-44-0; pyridine, 110-86-1.

Polyethylene-Bound Rhodium(I) Hydrogenation Catalysts

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Abstract: Homogeneous, recoverable hydrogenation catalysts were prepared with use of functionalized ethylene oligomers as ligands. Phosphine groups were introduced onto ethylene oligomers following anionic oligomerization of ethylene. The product polyethylenediphenylphosphine ligands were then exchanged with triphenylphosphine or ethylene ligands to prepare ethylene oligomer ligated rhodium(I) complexes. These Rh(I) complexes had the solubility of polyethylene and dissolved at 90-110 °C in hydrocarbon solvents but quantitatively precipitated at 25 °C. Less than 0.1% of the charged rhodium was lost in each dissolution precipitation cycle. The rhodium(I) complexes so prepared were shown to have about 80% of the activity of tris(triphenylphosphine)rhodium chloride in hydrogenation of various alkenes including 1-octene, Δ^2-cholestene, cyclooctene, cyclododecene, styrene, and α-methylstyrene. ^{31}P NMR spectroscopy and reactivity studies were used to characterize these catalysts.

Wilkinson's catalyst is one of the most reliable and widely used transition-metal catalysts in laboratory-scale catalytic hydrogenation reactions.[1] Versions of this catalyst were also among the first to be "immobilized" on insoluble cross-linked polymers.[2] Recently we have described soluble, polyethylene-bound catalysts and reagents.[3-6] Here we describe in detail the preparation and use of a polyethylene-bound analogue of Wilkinson's catalyst.

While homogeneous catalysts are desirable because of their high activity and selectivity, separation of a homogeneous catalyst from the products of reaction and/or recovery of the catalyst (and ligand) are inherent problems with conventional soluble catalysts. In small scale laboratory reactions, catalyst recovery can be ignored. In other cases, distillation can be used to separate volatile products from a catalyst. While each of these strategies works in some circumstances, efforts have continued to develop general strategies to separate and recover homogeneous catalysts at a reaction's end. Solutions to this separation problem with use of water-soluble hydrogenation catalysts and catalysts bound to insoluble gel-type polymers have been described.[2,7] While these approaches are conceptually attractive, each in practice has some limitations. These approaches depend on the differences between the solid polymeric phase or an aqueous solution phase and the organic solution of product at the reaction's end to recover the catalyst and to separate it from the reaction product. The disadvantages of either of these approaches largely arise from problems encountered because of the needless but unavoidable phase difference which also exists *during* the reaction in each of these cases.[8] Here we describe an alternative, general strategy using the temperature-dependent solubility properties of polyethylene to prepare catalyst ligands which are soluble during a reaction yet insoluble at a reaction's end. The semicrystalline nature of polyethylene which makes it insoluble at room temperature in all solvents[9] but soluble at elevated temperatures

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