ever, longer than that (1.412 Å) in SF_2O (S→O stretch[17] at 1331 cm^{-1}) and near that (1.45 Å) of Cl_2SO (S→O stretch[18] at 1229 cm^{-1}) and that of CF_3SFO (S→O stretch[5] at 1269 cm^{-1}). The boiling point, 36°, of $(CF_3)_2SO$ is slightly higher than one would have expected based on the value of 15.6° for $(CF_3)_2SO_2$ mentioned by Banks and Haszeldine[19] and the much lower values of perfluorosulfur compounds of comparable molecular weights (*e.g.*, CF_3SF_5: mol wt 196; bp −20°). The Trouton constant, however, indicates that $(CF_3)_2SO$ is, unlike DMSO,[17] an unassociated liquid. The $(CF_3)_2SO$ therefore appears to have a sizable dipole moment, but it is probably nearer those[20] of Cl_2SO (1.452 D) and SF_2O (1.618 D) than that (4.3 D) of DMSO.[17] The $(CF_3)_2SO$ should prove to have some interesting solvent properties.

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(17) E. L. Pace and H. V. Samuelson, *J. Chem. Phys.*, **44**, 3682 (1966).

(18) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **39**, 2171 (1961).

(19) R. E. Banks and R. N. Haszeldine, *Advan. Inorg. Chem. Radiochem.*, **3**, 410, 413 (1961).

(20) A. L. McClellan, "Table of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS 60637

Mechanism of the Tris(triphenylphosphine)platinum(0)-Catalyzed Oxidation of Triphenylphosphine

BY JACK HALPERN*[1] AND A. L. PICKARD

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We have previously interpreted the $Pt(P(C_6H_5)_3)_3$-catalyzed oxidation of $P(C_6H_5)_3$ in terms of the stepwise mechanism depicted by[2]

$$Pt(P(C_6H_5)_3)_3 + O_2 \xrightarrow{k_1} Pt(P(C_6H_5)_3)_2O_2 + P(C_6H_5)_3 \quad (1)$$

$$Pt(P(C_6H_5)_3)_2O_2 + P(C_6H_5)_3 \xrightarrow{k_2} [Pt(P(C_6H_5)_3)_3O_2] \xrightarrow[\text{fast}]{2P(C_6H_5)_3} Pt(P(C_6H_5)_3)_3 + 2(C_6H_5)_3PO \quad (2)$$

$$2P(C_6H_5)_3 + O_2 \xrightarrow{Pt(P(C_6H_5)_3)_3} 2(C_6H_5)_3PO \quad (3)$$

Our conclusions were based upon kinetic investigations of the two separate component reactions, each of which was followed spectrally by monitoring the concentration of $Pt(P(C_6H_5)_3)_3$. The kinetic results yielded by these investigations are summarized by the two rate laws

$$-d[Pt(P(C_6H_5)_3)_3]/dt = k_1[Pt(P(C_6H_5)_3)_3][O_2] \quad (4)$$

$$d[Pt(P(C_6H_5)_3)_3]/dt = k_2[Pt(P(C_6H_5)_3)_2O_2][P(C_6H_5)_3] \quad (5)$$

These results are consistent with the mechanism postulated above but do not unambiguously establish (i) whether the initial reaction between $Pt(P(C_6H_5)_3)_3$ and O_2 involves the displacement of $P(C_6H_5)_3$ as depicted above or (as has been suggested elsewhere),[3] in part at least of $(C_6H_5)_3PO$, in accord with the alternative overall stoichiometry of

$$Pt(P(C_6H_5)_3)_3 + 1.5O_2 \longrightarrow Pt(P(C_6H_5)_3)_2O_2 + (C_6H_5)_3PO \quad (6)$$

or (ii) whether the formation of $Pt(P(C_6H_5)_3)_2O_2$ results exclusively from the reaction of O_2 with $Pt(P(C_6H_5)_3)_3$ in accord with eq 1 (or eq 6) or whether there is an *additional* contribution (eq 7) from a reaction with $Pt(P(C_6H_5)_3)_2$ which is known to coexist in solution in equilibrium with $Pt(P(C_6H_5)_3)_3$.[2,4] Since the reactions of several other molecules, *e.g.*, acetylenes, with $Pt(P(C_6H_5)_3)_3$ to form adducts such as $Pt(P(C_6H_5)_3)_2$(acetylene) have been shown to proceed through mechanisms of the latter type, it is not unreasonable to expect a similar reactive path for O_2. The obvious criterion for distinguishing between these two alternative pathways, namely, the dependence of the rate on the $P(C_6H_5)_3$ concentration, could not be adequately examined in our earlier study because, when excess $P(C_6H_5)_3$ was added, the simultaneous occurrence of reaction 2 interfered with the study of reaction 1.

$$Pt(P(C_6H_5)_3)_3 \xrightleftharpoons{-P(C_6H_5)_3} Pt(P(C_6H_5)_3)_2 \xrightarrow{O_2} Pt(P(C_6H_5)_3)_2O_2 \quad (7)$$

In order to resolve these residual mechanistic questions concerning this important system, we have performed the additional experiments described in this paper in which the kinetics of reaction 3 were examined (under conditions of the simultaneous occurrence of eq 1 and 2) by monitoring the consumption of O_2. The results support the mechanism described by eq 1–3.

Experimental Section

Solutions of $Pt(P(C_6H_5)_3)_3$ were prepared by dissolving $Pt(P(C_6H_5)_3)_4$ (synthesized as described earlier[4]) in deoxygenated reagent grade benzene, the dissociation of $Pt(P(C_6H_5)_3)_4$ to $Pt(P(C_6H_5)_3)_3 + P(C_6H_5)_3$ having previously been shown to be complete.[2,4]

The kinetic experiments were performed at 25.0 ± 0.3° by measuring the volume of oxygen taken up at constant pressure, using the gas buret apparatus and procedure described previously.[5] The same apparatus was also used to determine the solubility of oxygen in benzene, by measuring the successive volumes of oxygen taken up as the partial pressure was incrementally increased.[5] The solubility of O_2 in benzene at 25° was thus determined to be $(6.5 \pm 0.4) \times 10^{-3}$ mol $l.^{-1}$ atm^{-1}.

Results and Discussion

Our earlier kinetic studies of the reaction that we interpreted as corresponding to eq 1 were based on spectral measurements of the rates of consumption of $Pt(P(C_6H_5)_3)_3$ by reaction with O_2.[2] The initial $Pt(P(C_6H_5)_3)_3$ concentrations in these experiments, ranging from 2×10^{-3} to 8×10^{-3} *M*, were at least 20 times greater than the O_2 concentration, so that the small overall decrease in the $Pt(P(C_6H_5)_3)_3$ concentration (which could be accurately measured at wavelengths in the 420–450-nm range, using the expanded scale of a Cary 14 spectrophotometer) exhibited pseudo-first-

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(1) To whom correspondence should be addressed.

(2) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, **90**, 4491 (1968).

(3) G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, **6**, 92 (1967).

(4) J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, **7**, 2672 (1968).

(5) A. J. Chalk and J. Halpern, *J. Amer. Chem. Soc.*, **81**, 5846 (1959).

TABLE I

KINETIC DATA IN BENZENE AT 25°

	O_2 partial	Initial concn, M				10^6rate(O_2), M sec^{-1}		[Rate(O_2)]$_{calcd}$/
Expt no.	press, atm	$10^3[O_2]$	$10^4[Pt]_{total}$	$10^2[P(C_6H_5)_3]$	$10^4[Pt(P(C_6H_5)_3)_3]$	Exptl	Calcd	[rate(O_2)]$_{exptl}$
I	0.83	5.38	4.02	5.35	1.46	1.8	2.0	1.11
II	0.90	5.83	4.02	5.35	1.39	1.8	2.1	1.16
III	0.87	5.64	4.82	11.2	2.57	3.7	3.7	1.00
IV	0.87	5.64	4.82	11.2	2.57	3.6	3.7	1.03
V	0.38	2.45	4.82	11.2	3.49	2.0	2.2	1.10
VI	0.61	3.98	4.31	11.3	2.67	2.8	2.8	1.00
VII	0.72	4.69	13.6	11.3	7.90	9.6	9.6	1.00
VIII	0.34	2.23	13.6	11.3	10.1	6.2	5.9	0.95
IX	0.53	3.42	13.6	11.3	8.91	7.8	7.9	1.01
							Av	1.04

order kinetics. The initial concentrations of free $P(C_6H_5)_3$ were maintained below 8×10^{-3} M to minimize interference from reaction 2. These experiments yielded the rate law corresponding to eq 4 with $k_1 = 2.6 \pm 0.1$ M^{-1} sec^{-1} in benzene at 25°. The earlier kinetic experiments on reaction 2 were performed by adding a large excess (ranging from 5×10^{-3} to 1×10^{-1} M) of $P(C_6H_5)_3$ to a benzene solution of $Pt(P(C_6H_5)_3)_2O_2$ (typically $\sim 3 \times 10^{-4}$ M initially) and spectrally measuring the resulting pseudo-first-order formation of $Pt(P(C_6H_5)_3)_3$. These experiments yielded the rate law corresponding to eq 5 with $k_2 = 0.15 \pm 0.01$ M^{-1} sec^{-1}.[2]

Assuming the mechanism corresponding to eq 1 and 2, the kinetic behavior of the system, under conditions such that both reactions are occurring simultaneously, is described by eq 8 and 9, where rate(O_2) is the rate of consumption of O_2.

$$\text{rate}(O_2) = k_1[Pt(P(C_6H_5)_3)_3][O_2] \qquad (8)$$

$$-d[Pt(P(C_6H_5)_3)_3]/dt = k_1[Pt(P(C_6H_5)_3)_3][O_2] - k_2(Pt(P(C_6H_5)_3)_2O_2][P(C_6H_5)_3] \qquad (9)$$

Under experimental conditions such that $[O_2]$ remains constant (because of equilibration with a constant partial pressure of O_2) and $P(C_6H_5)_3$ (initially 5×10^{-2} to 11×10^{-2} M) is in large excess over the combined concentrations of $Pt(P(C_6H_5)_3)_3$ and $Pt(P(C_6H_5)_3)_2O_2$ ($[Pt]_{total} = 4 \times 10^{-4}$ to 13×10^{-4} M), a steady state is reached early in the reaction (when less than 1% of the $P(C_6H_5)_3$ initially present is consumed) during which reactions 1 and 2 are occurring at equal rates and thus maintaining a constant concentration of $Pt(P(C_6H_5)_3)_3$. Under these conditions, eq 8 and 9 may be combined with the steady-state approximation (eq 10) and with the conservation relation (eq 11) to yield eq 12 and 13.

$$d[Pt(P(C_6H_5)_3)_3]/dt = 0 \qquad (10)$$

$$[Pt(P(C_6H_5)_3)_3] + [Pt(P(C_6H_5)_3)_2O_2] = [Pt]_{total} \qquad (11)$$

$$[Pt(P(C_6H_5)_3)_3] = \frac{k_2[Pt(P(C_6H_5)_3)_2O_2][P(C_6H_5)_3]}{k_1(O_2]} = \frac{k_2[Pt]_{total}[P(C_6H_5)_3]}{k_1[O_2] + k_2[P(C_6H_5)_3]} \qquad (12)$$

$$\text{rate}(O_2) = \frac{k_1k_2[Pt]_{total}[P(C_6H_5)_3][O_2]}{k_1[O_2] + k_2[P(C_6H_5)_3]} \qquad (13)$$

If the measurements of the rate of O_2 uptake are confined to the first 10% or so of the reaction (*i.e.*, of the consumption of the initial $P(C_6H_5)_3$), then both $[P(C_6H_5)_3]$ and $[O_2]$ remain essentially constant, and pseudo-zero-order kinetic behavior should be observed. Typical initial zero-order rate plots consistent with this behavior are depicted in Figure 1. The experimental values of rate(O_2) (determined from the slopes of such plots), together with the corresponding values calculated from eq 13, using the values of k_1 and k_2 determined earlier, are listed in Table I.

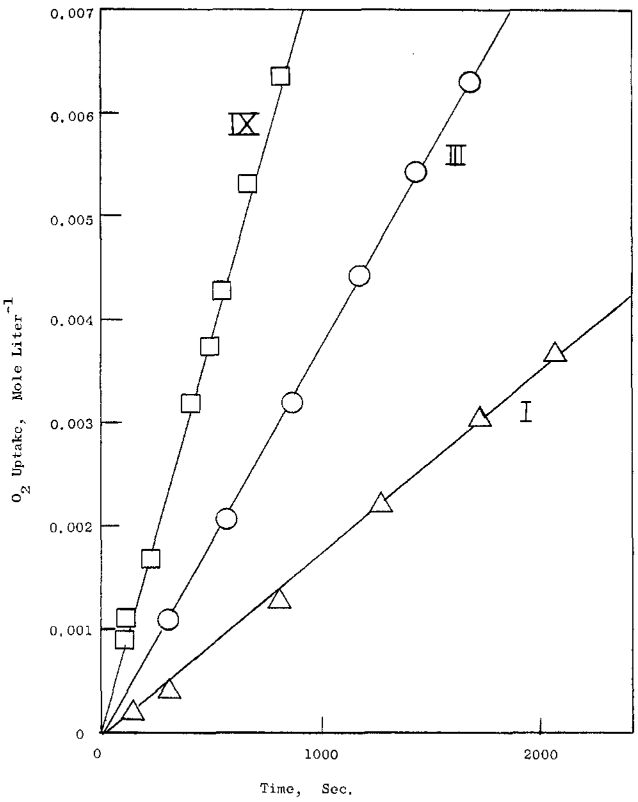

Figure 1.—Representative pseudo-zero-order rate plots. Experiment numbers refer to Table I.

The excellent agreement between the measured and calculated values of rate(O_2), over the wide range of conditions examined, lends strong support to the mechanism depicted by eq 1–3. A significant contribution from a step with stoichiometry corresponding to eq 6 (instead of eq 1) would be reflected in a higher value of rate(O_2) than calculated by our procedure. The other mechanistic uncertainty cited earlier, namely, the possibility of a significant contribution from a reaction with $Pt(P(C_6H_5)_3)_2$ (eq 7), would be reflected in a departure (which was not observed) from the dependence on $[P(C_6H_5)_3]$ described by eq 13.

We thus conclude that the results of this investigation, together with our earlier observations, firmly establish the general features of the mechanism depicted by eq 1–3 for the $Pt(P(C_6H_5)_3)_3$-catalyzed oxidation of $P(C_6H_5)_3$. The detailed mechanisms of the individual steps, particularly of step 2, which we have previously interpreted in terms of a dissociative "oxygen insertion" sequence, *i.e.*

$$Pt(P(C_6H_5)_3)_2O_2 \xrightarrow{P(C_6H_5)_3} [Pt(OP(C_6H_5)_3)_2(P(C_6H_5)_3)] \xrightarrow{2P(C_6H_5)_3} Pt(P(C_6H_5)_3)_3 + 2(C_6H_5)_3PO$$ [2]

remain to be more fully elucidated.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
LOYOLA UNIVERSITY OF CHICAGO,
CHICAGO, ILLINOIS 60626

Nickel Complexes with Long-Chain Primary Amines

BY B. RAPP AND S. F. PAVKOVIC*

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Although methyl-, ethyl-, and propylamine readily form stable nickel(II) complexes,[1] isopropylamine does not.[2] We report the preparation and characterization of new complexes with higher alkylamine members, which clarify effects of chain length and branching on complex formation. The ligand system consists of straight-chain primary amines containing four through eight and eighteen carbon atoms, as well as isobutyl-, isopentyl-, and isohexylamine.

TABLE I

ANALYTICAL AND MAGNETIC INFORMATION FOR $[Ni(ligand)_6](ClO_4)_2$

Ligand	% carbon		% hydrogen		% nickel		μ_{eff}, BM
	Calcd	Found	Calcd	Found	Calcd	Found	
n-$C_4H_9NH_2$	41.30	41.34	9.57	9.03	8.42	8.36	3.23
i-$C_4H_9NH_2$	41.30	40.28	9.57	9.25	8.42	7.29	Paramag
n-$C_5H_{11}NH_2$	46.16	45.91	10.09	9.65	7.52	7.63	3.22
i-$C_5H_{11}NH_2$	46.16	46.06	10.09	9.66	7.52	7.48	3.19
n-$C_6H_{13}NH_2$	49.99	49.64	10.51	9.99	6.78	6.62	3.24
i-$C_6H_{13}NH_2$	49.99	49.64	10.51	10.50	6.78	6.78	3.18
n-$C_7H_{15}NH_2$	53.16	53.12	10.76	10.50	6.18	6.16	3.21
n-$C_8H_{17}NH_2$	55.69	55.49	11.14	10.66	5.68	5.64	3.18
n-$C_{18}H_{37}NH_2$	69.15	69.35	12.48	12.34	(4.49)[a]	(4.60)[a]	Paramag

[a] These are figures for per cent nitrogen.

Experimental Section

Preparation of Compounds.—Ligands were distilled over BaO and charcoal immediately before use and diluted with *n*-hexane. Hydrated nickel perchlorate was dehydrated with 2,2-dimethoxypropane (DMP) and diluted with 1-butanol. This alcohol solution was distilled under reduced pressure to remove excess DMP and dehydration products, filtered, and added dropwise to ligand solution at 0° while stirring. Light blue solids formed, which were separated by filtration, washed with hexane, and dried in a moisture-free air stream. A chloroform–hexane mixture was used to dissolve *n*-octadecylamine.

Analyses.—Carbon–hydrogen analyses were obtained using a Coleman Model 33 analyzer in conjunction with a Mettler M-5 balance. Nickel was estimated as dimethylglyoximate, and per cent nitrogen for the octadecylamine complex was determined by Micro-Tech Laboratories, Skokie, Ill.

Physical Measurements.—Magnetic susceptibilities were determined at two field strengths by the Gouy method at room temperature. A Perkin-Elmer Model 457 grating spectrophotometer measured infrared spectra from 4000 to 250 cm^{-1} on samples mulled with Nujol and Fluorolube. A Cary Model 14 spectrophotometer marked electronic spectra from 3500 to 17,000 Å for mulled samples supported on filter paper and immersed in optical cells containing Fluorolube.

Results and Discussion

Elemental content clearly demonstrates the formation of hexakis-amine complexes in all cases (Table I). Poor results for isobutylamine reflect instability of that product. They all exhibit magnetic moments of 3.20 ± 0.05 BM (excessive magnetic dilution for *n*-octadecylamine prevented quantitative results with our equipment). Amine infrared bands appear more intense, sharper, and at lower frequencies after complexation, and T_d perchlorate frequencies remain intact. Visible–uv spectra of the complexes are remarkably similar in detail (Table II) and consist of three weak absorptions plus a shoulder. Minor band splitting is noted only for *n*-octadecylamine. Ligand field parameters[3] of $Dq = 1030$ cm^{-1} and $\beta \sim 900$ cm^{-1}, obtained from mull spectra, closely match solution information for isobutylamine. Slight energy changes in solution as observed here are not uncommon.[4] This evidence shows the complexes are paramagnetic, six-coordinate species of O_h symmetry,[5] bound through amine nitrogen

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* To whom correspondence should be addressed.

(1) R. J. Fitzgerald and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 2523 (1968).

(2) R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, *Inorg. Chem.*, **2**, 1056 (1963).

(3) A. P. B. Lever, *J. Chem. Educ.*, **45**, 711 (1968).

(4) L. F. Lindoy and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4694 (1969).

(5) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 220.