were calculated, according to their spectra, as

$$g_{\mathrm{av}} = 2.0136 \qquad A_{\mathrm{av}} = 8.9\ \mathrm{G}$$

The "average" g and A values are the isotropic ones computed from the three g-values ($g_1 = 2.025$, $g_2 = 2.011$, $g_3 = 2.005$) and from the three hf coupling constants ($A_1 = 13.2 \times 10^{-4}\mathrm{cm}^{-1}$, $A_2 = 6.4 \times 10^{-4}\mathrm{cm}^{-1}$, $A_3 = 5.6 \times 10^{-4}\mathrm{cm}^{-1}$) reported in Ref. (*8*) according to the formulas:

$$\begin{aligned} g_{\mathrm{av}} &= \tfrac{1}{3}(g_1 + g_2 + g_3) = 2.0136, \\ A_{\mathrm{av}} &= \tfrac{1}{3}(A_1 + A_2 + A_3) \\ &= 8.4 \times 10^{-4}\mathrm{cm}^{-1} = 8.9\ \mathrm{G}. \end{aligned}$$

These values are somewhat different from those obtained for the $VOSO_4$–H_2O_2 system.

The radical species of Fig. 1 may probably be ascribable to the HO_2 radical rather than the OH radical because the g value (2.0116) is much less than those (2.0267–2.0388) reported by Gunter (*9*) for the OH radical generated in various hydrate crystals. The HO_2 radical is expected to ionize depending on pH as

$$HO_2 \rightleftarrows O_2^- + H^+$$

Since the pK of HO_2 has been estimated as 4.4 ± 0.4 (*10*), the ionized form or O_2^- should be excluded under the present pH, unless complexing affects the pK of HO_2 to a great extent.

Consequently, we can consider that the VO^{3+}–HO_2 complex radicals are formed upon mixing vanadium(IV) oxysulfate and hydrogen peroxide. The VO^{3+}–HO_2 complex would have been produced via $VO^{2+} + H_2O_2 \rightarrow VO^{3+} + OH + OH^-$, $OH + H_2O_2 \rightarrow H_2O + HO_2$, $VO^{3+} + HO_2 \rightarrow VO^{3+}$–$HO_2$. The complex was rather stable and may not be regarded as active intermediates in the reactions with organic additives. Kinetic evidence of this sort will be reported elsewhere.

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Some Acid Properties of H_2PtCl_6

In studying the relation between the catalytic properties of Pt–Al_2O_3 and the reaction of Al_2O_3 with the H_2PtCl_6 impregnation solution, we found it necessary to answer two questions concerning aqueous H_2PtCl_6: (i) How can the acid content of a solution of H_2PtCl_6 be determined, since at least one side reaction occurs when a strong base is used to titrate? (ii) How strong an acid is H_2PtCl_6? One might expect H_2PtCl_6 to be a strong acid, but there seems to be no evidence in the literature that this question has actually been answered. Because of the extensive use of aqueous H_2PtCl_6 in the preparation of platinum catalysts, our answers to these questions may be of general interest.

EXPERIMENTAL METHODS

The H_2PtCl_6 was Baker Analyzed Reagent $H_2PtCl_6 \cdot 6H_2O$, assayed (by the manufacturer) to be 37.6% Pt (calc: 37.67%), with 0.04% alkalies and other salts, as sulfates. Our Pt analyses were made by the spectrophotometric method of Ayres and Meyer (*1*). The 4-nitrodiphenylamine (NDA), research grade, mp 132–135°, was obtained from the Aldrich Chemical Co. The pH measurements were made on a Beckman GS pH meter, using glass and calomel electrodes. The spectra were obtained using a Spectronic 20 spectrophotometer.

RESULTS

Titration with NaOH gave for H_2PtCl_6 an apparent H/Pt value greater than two when no special precautions were taken. Phenolphthalein and pH measurements indicated the same end point. Typical of several such experiments was the titration of 28.00 ml of 0.01095 *M* H_2PtCl_6 with 0.1023 *N* NaOH, in which a value of 2.33 for H/Pt was obtained. The high value can be a consequence of OH^-–Cl^- exchange during the titration. It was possible to reproduce a given titration to within 1%.

Postulating that high values of H/Pt are a consequence of OH^-–Cl^- exchange, we titrated H_2PtCl_6 with NaOH in the presence of an excess of Cl^- to repress exchange. In a typical experiment, 25 g of NaCl was mixed with 35.00 ml of 0.0355 *M* H_2PtCl_6. This mixture was titrated with a 0.0136 *N* NaOH-0.5 *M* NaCl solution, and a value of 2.02 for H/Pt was obtained. Values close to two for H/Pt could be obtained only for fresh H_2PtCl_6 solutions, since solutions several days old were obviously partially hydrolyzed.

Three experiments indicating H_2PtCl_6 is a very strong acid are reported. First, plots of pH titrations (not shown) are those characteristic of strong acids. In such plots initial pH values were low because the excess of NaCl removes "free" water via ion hydration, thereby effecting an increase in the activity coefficient of the hydrogen ion. In other respects, general shapes of the plots of non-NaCl and NaCl titrations are the same.

Since at the end point in such plots both hydrogen ions of H_2PtCl_6 have been neutralized, the absence of an inflection point at lower pH values suggests that the two hydrogen ions are equivalent. Thus, such plots provide no evidence that $HPtCl_6^-$ existed in these solutions.

Second, a comparison of the pH values (using the same electrodes) of solutions of H_2PtCl_6 with those of H_2SO_4 solutions of the same concentration indicates H_2PtCl_6 is a very strong acid. H_2SO_4 is chosen for comparison because it is of the same charge type, and therefore ionic strengths are equal at equal concentrations. The results are given in Table 1. The pH values in the last column are calculated (assuming 100% ionization) by means of the Debye-Huckel equation, useful up to ~0.1 *M*, $\log \gamma_{H_+} = -0.5085\ \mu^{1/2}/(1 + 0.3281\ \alpha_{H_+}\ \mu^{1/2})$, for water at 25°, where α_{H_+} is taken to be 9 Å (*2*). Over the whole concentration range studied, up to 1 *M* H^+, $PtCl_6^{2-}$ is evidently a weaker base than SO_4^{2-}; and in the range in which the calculated activities can be given, H_2PtCl_6 may be almost completely ionized.

The third indication that H_2PtCl_6 is a very strong acid is provided by its inter-

TABLE 1
pH VALUES OF H_2PtCl_6 AND H_2SO_4

M[a]	Observed (pH)		Calc[b]
	H_2PtCl_6	H_2SO_4	
0.02	1.81	1.81	1.76
0.04	1.56	1.63	1.47
0.10	1.17	1.32	1.09
0.14	1.03	1.21	0.95
0.20	0.84	1.08	—
0.40	0.63	0.86	—
0.60	0.56	0.75	—
0.80	0.51	0.69	—
1.00	0.48	0.63	—

[a] H^+ molarity, assuming 100% dissociation.

[b] Assuming 100% dissociation; see text.

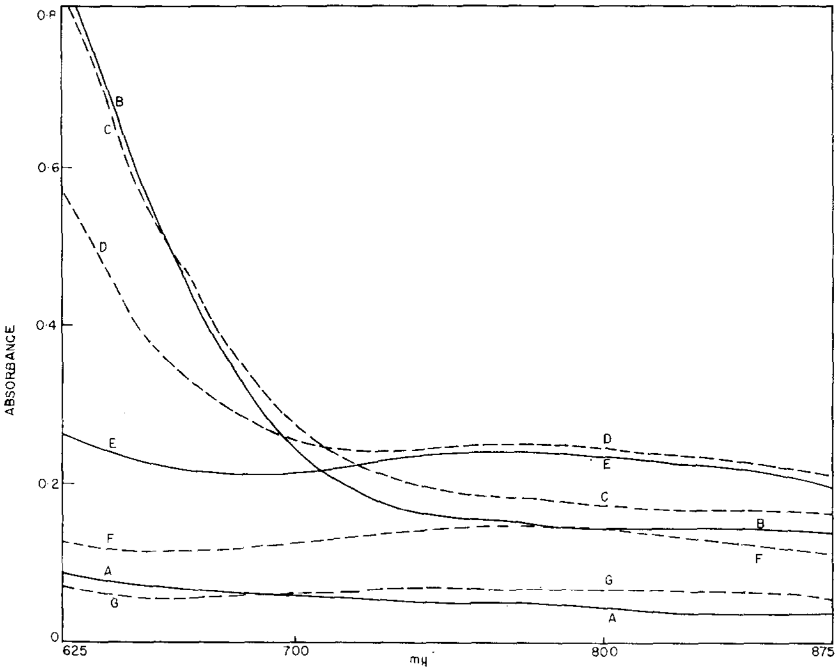

FIG. 1. Partial spectra: A, 2.35 *M* H_2PtCl_6; B, A with NDA added; C, D, E, F, and G are B diluted by factors of 1.10, 1.30, 1.67, 2.72, and 5.44, respectively.

action with NDA, a very weak base. Our results are summarized in Fig. 1, which shows partial spectra of aqueous H_2PtCl_6 and H_2PtCl_6–NDA solutions. Absorption maxima due to the presence of NDA could not be observed, since they appear at shorter wavelengths, where H_2PtCl_6 absorbs intensely. Solution A is 2.35 *M* H_2PtCl_6; Solution B is Solution A to which 0.6 mg of NDA/ml has been added. Excess solid

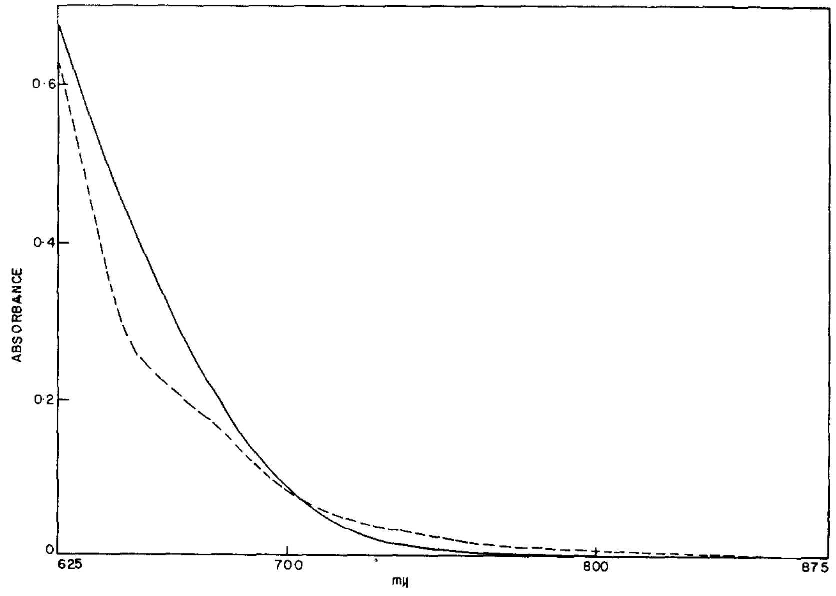

FIG. 2. Partial spectra: ——, corrected partial spectrum of Solution B of Fig. 2; - - -, NDA in H_2SO_4.

was removed from Solution B and the product was diluted with water stepwise to produce Solutions C–G. The time elapsed between the mixing of solid $H_2PtCl_6 \cdot 6H_2O$ with water and the determination of the partial spectrum of Solution G was 150 min. Each partial spectrum was obtained only after the solution was stirred thoroughly with a magnetic stirrer in the absorption cell. After 112 hr a fine, dark precipitate at the bottom of the cell containing Solution G could be seen. The absorbance of this solution, measured without prior agitation and thus without interference by the solid, was 0.000–0.003 everywhere. Dilution, slow decomposition, and adsorption on the solid account for the absence of H_2PtCl_6 absorbance. After thorough stirring of this mixture, dispersed solid was barely visible, and the absorbance was 0.053–0.065 in the same wavelength range.

From these results certain deductions about H_2PtCl_6–NDA interaction can be made. Since H_2PtCl_6 was in great excess in any H_2PtCl_6–NDA interactions, the absorbances of Solution A can be subtracted from those of Solution B to obtain the partial spectrum of the other species in Solution B. The resulting difference spectrum has a flat "tail," apparently caused by light scattering by finely divided particles. If the absorbances of both this "tail" and that of Solution A are subtracted from the partial spectrum of Solution B, there is produced the partial spectrum of the NDA-related soluble species of Solution B, given in Fig. 2. The remaining features of the partial spectra of Fig. 1 can be explained by assuming H_2PtCl_6 reacts rapidly with NDA to produce a violet, soluble species, absorbing in the 625–775 mμ range, with a maximum at some lower wavelength, but which slowly decomposes to the insoluble material previously referred to.

The second partial spectrum in Fig. 2 is that of a violet, NDA–concentrated H_2SO_4 solution, in which the NDA concentration is (because of the precipitation in H_2PtCl_6 already discussed) only approximately the same as in Solution B. Even though the absorbance units of Fig. 2 must therefore be arbitrary, it seems very likely that the two spectra are of the same violet species.

While the conjugate acid of NDA, which forms in moderately concentrated H_2SO_4, is colorless, it has long been known that NDA-concentrated H_2SO_4 solutions are violet (*3*). The NDA decomposes in concentrated H_2SO_4 (*4*). The NDA also decomposes in $HClO_4$, yielding a violet solution and a brown, flocculent precipitate (*4*). Bugai *et al.* (*5*) conclude from spectroscopic studies that NDA forms an ionic complex in concentrated H_2SO_4. Thus, it seems certain that the violet species forms in concentrated H_2SO_4 because H_2SO_4 is a very strong acid. Similarly, the formation of a violet species and a dark precipitate when NDA reacts with 2.35 M H_2PtCl_6 almost certainly indicates that that solution is very strongly acidic.

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