in the data collection at Durham University. Calculations were performed on the IBM 370/168 and Hewlett-Packard 2000E computers at Newcastle University. I am grateful to Dr. J. K. Burdett for his interest and for the use of his molecular orbital calculations.

Registry No. $[Fe(NO)_2P(CF_3)_2]_2$, 36486-27-8.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Notes

Contribution from the Department of Chemistry,
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Preparation of Finely Divided VCl_3 by Decomposition of VCl_4 in an Electrical Discharge

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Vanadium trichloride complexed with certain organometalic compounds is often used to promote various polymerization reactions. The activity of heterogeneous catalysts, such as VCl_3, is greatly influenced by their surface characteristics. High specific surface (hence small particle size) and irregularly shaped particles are desirable. This is achieved when crystals develop at high supersaturation, i.e., in conditions far from the crystallization equilibrium. Pure VCl_3 can be prepared by thermal decomposition[2] of VCl_4 at 150–170 °C. This reaction yields crystals larger than 10 μm^3. Since the solid-state texture of vanadium trichloride cannot be altered by the traditional postsynthesis treatments[4] it is desirable to devise reaction methods which yield smaller particles of VCl_3.

We have recently found that very finely divided VCl_3 is produced when VCl_4 vapors are excited in an electrical discharge

$$2VCl_4(g) \rightarrow 2VCl_3(s) + Cl_2(g)$$

Exploratory experiments have shown that this reaction is very fast; its rate in the discharge is many times higher than the rate of thermal decomposition of VCl_4 vapors observed in our laboratories.[5] Examination of the product in a transmission electron microscope revealed very small ($\sim$0.1 μm) round particles. Despite the small particle size, the discharge-made VCl_3 and the commercial VCl_3 (made by thermal decomposition of VCl_4) give the same x-ray powder diagram.

Although vanadium tetrachloride is an unstable compound and decomposes slowly to VCl_3, even at room temperature, the ease of decomposition in the discharge appears surprising in the light of known thermodynamic data. Heating of gaseous VCl_4 by the discharge energy accelerates the reaction, but as the temperature increases, the equilibrium shifts to the VCl_4 side. At 160 and 180 °C the equilibrium constant K_p ($P_{Cl_2}/P_{VCl_4}{}^2$) assumes the values of 6.8×10^{-4} and 3.3×10^{-4} (in $mmHg^{-1}$) respectively.[6] Since we have used pressures lower than 1 mmHg, very little VCl_4 should have decomposed if the transfer of thermal energy were the only important effect of the discharge. At low temperatures, when the equilibrium lies on the VCl_3 side,[7] the decomposition is very slow; at 20 °C liquid VCl_4 has a half-life of 4150 months.[8]

Formation of VCl_3 can be rationalized if one considers interaction of excited species with the reactor wall. If an excited molecule remains in the discharge zone without colliding with the reactor wall, probability of back-reaction is high.[9] On the other hand, when an excited molecule collides with and is absorbed on a cold reactor wall, equilibrium conditions favor the formation of VCl_3. This interpretation is also supported by differences in the behavior of VCl_4 and $TiCl_4$ in the discharge. Both can be reduced to their respective trichlorides by atomic hydrogen generated in the discharge[10,11] but all reported attempts to reduce titanium tetrachloride (which is thermodynamically stable[7]) in hydrogen-free discharges have failed.[11,12]

Experimental Section

VCl_4 (Stauffer; highest purity) was added to a round-bottom flask under an inert atmosphere. The flask was connected to a grease-free vacuum system; VCl_4 was cooled to about −20 °C and degassed for approximately 1 h by slow pumping. It was then cooled to liquid nitrogen temperature and the whole system was thoroughly evacuated (to 10^{-4} mmHg or less). The vanadium tetrachloride was then allowed to heat up and was distilled through a 700 mm long, 31-mm o.d. glass tube (made from Pyrex 7740). When radiofrequency power (5.2 MHz, 100 W, 2000 V) was applied using a coil applicator, a pale blue-green glow developed and VCl_3 started immediately to deposit on the tube walls. If the power was interrupted after a few seconds, a fine iridescent coating was obtained. After about 1 min the whole discharge tube was covered with an opaque purple layer of VCl_3. However, the discharge could be maintained despite the VCl_3 deposit. The pronounced color of VCl_4 vapors allowed an estimation of the pressure within the reaction tube. The best results were obtained when the pressure was between 0.1 and 1 mmHg. Alternatively, a Tesla coil could be used instead of a radiofrequency generator, if the discharge tube had a constriction (3–5 mm in diameter) and the discharge was applied at that point.

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Registry No. VCl_3, 7718-98-1; VCl_4, 7632-51-1.

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Influence of Internal Hydrogen Bonding on the Kinetics of Complex Formation with Nickel(II)

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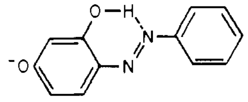
We have recently become interested in the reactivity of internally hydrogen-bonded acids.[1-3] These substances are known to lose their proton to bases at rates far below the normal.[4] The rates are also abnormally low when such acids act as ligands to form labile complexes.[5] It seemed interesting to investigate the possible correlation between the strength of a given acid, its rate of proton loss to bases, and its rate of complex formation. For this purpose, we chose 4-(phenylazo)resorcinol, tropaeolin O (2,4-dihydroxy-4′-azobenzenesulfonate), and 4-(*m*-nitrophenylazo)resorcinol, which had served in our previous investigations concerning the mechanism of proton loss.[1,2] Unfortunately, 4-(*p*-nitrophenylazo)resorcinol proved insufficiently soluble in the pH range suitable for the measurement of the complexation reaction.

Our substances differ from each other only in the meta or para substituent on the benzene ring and have in common the structure



The acid forms will be designated by HL, and the forms which have lost the last proton by L, omitting charges for the sake of brevity.

As cation we chose Ni(II) which has been the subject of many kinetic investigations (see, for instance, ref 5–7).

It would have been instructive to investigate also the reaction of the much more labile Cu(II), but experiments under the same conditions of pH and concentration cannot be carried out.[8]

Experimental Section

Materials. 4-(Phenylazo)resorcinol and 4-(*m*-nitrophenylazo)resorcinol were from Eastman Organic Chemicals, the 4-(*p*-nitrophenylazo) resorcinol was from Eastman Kodak Co., and tropaeolin O was from BDH. These substances were purified as described by previous authors.[9] Nickel(II) was used in the form of $Ni(NO_3)_2 \cdot 6H_2O$, Baker Analyzed reagent. The concentration of the Ni(II) stock solution was determined by adding excess EDTA and back-titrating with zinc sulfate solution, using EBT as indicator.

All measurements were carried out at 25 °C and at an ionic strength of 0.2 M, regulated by the addition of potassium nitrate.

Static Measurements. The pH was measured with a Radiometer PHM52 pH meter having an accuracy of ±0.005 pH unit. It was again[1] assumed that pH equals $-\log [H^+]\gamma_{H^+}$, with $\gamma_{H^+} = 0.75$, calculated from the Davies equation[10] for our ionic strength.

Spectrophotometric measurements were carried out with a Hilger-Gilford spectrophotometer.

Kinetic Experiments. All experiments were carried out by the *T*-jump method, using an apparatus equipped with a reference photomultiplier (Messanlagenstudiengesellschaft m.b.H., Göttingen).

Relaxation times were again evaluated with the aid of a simple mechanical device developed in our department.[11]

Results

Formation Constants. From our kinetic results (see below) we conclude that the phenolic group is not the active site. Furthermore, we shall make the simplifying assumption[8]—derived essentially from kinetic evidence[8,12-14]—that the phenolic hydrogen has the same p*K* in the complex as it has in the free ligand. When considering the formation constants of the complexes we therefore write $[HL_T]$ for $[HL] + [H_2L]$, with an analogous notation for the complexes.

The determinations were carried out spectrophotometrically. At constant pH, plots of $b/(A - \bar{\epsilon}_{HL}b - \bar{\epsilon}_{Ni}a)$ as a function of $1/a$ should be straight lines. [See, for instance, ref 16; here, a is the total concentration of the metal ion, and b is that of the ligand, with $a >> b$; A is the absorbance, and $\bar{\epsilon}_{HL}$, $\bar{\epsilon}_{Ni}$, $\bar{\epsilon}_{NiHL}$, and $\bar{\epsilon}_{NiL}$ are apparent molar extinction coefficients. (For example, $\bar{\epsilon}_{HL} \equiv (\epsilon_{HL}[HL] + \epsilon_{H_2L}[H_2L])/b$.) The first two of these quantities were determined experimentally at each wavelength employed. They depend on pH because of the changing protonation of the phenolic hydrogen and because $NiOH^+$, though present in very small concentration,[15] has a much higher extinction coefficient than has Ni^{2+}]. For solutions in which b was 3×10^{-5} M and a was varied between 1×10^{-2} and 5×10^{-2} M, this was indeed found to be the case. In the pH range between 6.8 and 7.7 (regulated by the addition of small amounts of potassium hydroxide or nitric acid solution) the ratio between the intercept and the slope of these lines showed no trend with pH. This shows that our complex cannot be NiL_T, because this would require[16] this ratio to be inversely proportional to $[H^+]$. We conclude that the proton adjacent to the azo group is retained in the complex, and the above ratio is equal to

$$K_1 = [NiHL_T]/[Ni^{2+}][HL_T] \qquad (I)$$

where $[NiOH^+]$ is neglected in comparison with $[Ni^{2+}]$.

The results are shown in Table I, together with the acid dissociation constants for the last proton which we determined earlier.[1,2]

Kinetic Results. The value of b was kept constant at 10^{-4} M and a was varied between 4×10^{-2} and 7×10^{-2} M. (At lower values of a the relaxation amplitude was too small for reliable results to be obtained, whereas at higher values $Ni(OH)_2$ precipitated.) The reciprocal relaxation time $1/\tau$ increased linearly with increasing a. Furthermore, $1/\tau$ increased with increasing pH. A reaction scheme compatible with these findings is

$$\begin{array}{lcccr}
Ni^{2+} + & HL & \rightleftharpoons & NiHL & (1a)\\
 & \updownarrow & & \updownarrow & \\
Ni^{2+} + & H_2L & \rightleftharpoons & NiHLH & (1b)\\
 & \updownarrow & & \updownarrow & \\
NiOH^+ + & HL & \rightleftharpoons & NiHL + OH^- & (2a)\\
 & \updownarrow & & \updownarrow & \\
NiOH^+ + & H_2L & \rightleftharpoons & NiHLH + OH^- & (2b)
\end{array}$$

The vertical reactions involve the phenolic hydrogen and the