tivation were calculated by using the Eyring equation from absolute rate theory.[15]

The interaction of aliphatic nitriles, RCN [R = CCl_3, CH_3, $C(CH_3)_3$], with iodine was studied by the method described by Person and co-workers.[8] The equilibrium constants of interactions were determined for acetonitrile and trimethylacetonitrile by the use of the Rose–Drago equation[16] employing an IBM 1620 computer.

The enthalpies of formation (uncertainty of ±1 kcal $mole^{-1}$) of the 1:1 complexes were calculated from the equilibrium constants at different temperatures. The transformation of outer complexes of nitriles to the inner complexes was studied by employing the I_3^- bands. It is interesting that even though the interaction of trichloroacetonitrile with iodine is very weak,[8] the rate of formation of I_3^- is comparable with that of other nitriles.

Acknowledgment. The authors' thanks are due the Council of Scientific and Industrial Research (India) for the grant of a research project.

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On the Jahn–Teller Effect in Vanadium Hexacarbonyl

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Abstract: It is suggested that the odd-electron species $V(CO)_6$ should experience a Jahn–Teller effect. Comparison of the infrared spectra of gaseous $V(CO)_6$ and $Cr(CO)_6$ gives strong evidence for such an effect because the P, Q, and R branches present in the CO stretching band structure of $Cr(CO)_6$ are absent in $V(CO)_6$. The greater complexity of the electronic spectrum of $V(CO)_6$ compared with that of $Cr(CO)_6$ may be additional evidence for this effect. It is suggested that *probably* there is no static distortion of the O_h symmetry in $V(CO)_6$ but a dynamic Jahn–Teller effect in which the molecule still transforms in its initial higher symmetry group in spite of the coupling between nuclear and electronic motions.

After the discovery of $V(CO)_6$ there existed considerable confusion about the structure of this molecule. The initial investigators suggested a dimeric formula,[1] since no effects of paramagnetism were found in the nmr spectrum in the hydrocarbon solvent even at high carbonyl concentrations. The compound was independently discovered by another group[2] and formulated as monomeric, since it was found to be isomorphous with $Cr(CO)_6$. A later attempt to observe the paramagnetic resonance spectrum was unsuccessful and favored the dimeric formula.[3] Finally, however, exact magnetic measurements showed[4] that the species was paramagnetic in both solid and dissolved states. This, together with the molecular weight determination, proved that the monomeric formula is correct. Recently the esr spectrum was obtained, and a g factor close to 2 was found. This is the value expected for one free electron.

In all these investigations it has been silently assumed that the structure of monomeric $V(CO)_6$ is octahedral in similarity to the other metal hexacarbonyls. This assumption must be questioned because of the existence of the Jahn–Teller rule. This rule states that a molecular configuration with an electronically degenerate ground state is not stable. For the group VI-B carbonyls, in which the central metal has six d electrons, the ground state is A_{1g} in the field of a strong ligand such as CO. On the other hand, the ground state of vanadium(0), a d^5 case, must be $^2T_{2g}$ in the octahedral configuration. If a tetragonal distortion is assumed, for example, this is split into $^2B_{2g}$ and ^2E_g terms. The three degenerate d_π orbitals d_{xy}, d_{yz}, and d_{zx} are split in this way into d_{xy} and a degenerate set d_{yz} and d_{zx}. For an elongation along the z axis, d_{yz} and d_{zx} should have lower energy, and the state $^2B_{2g}$ made up of $(d_{yz}, d_{zy})^4d_{xy}$ should be the ground state.

On the other hand, previous experience[5] suggests a dynamic rather than a static Jahn–Teller effect. Even though there is coupling between the nuclear and electronic motions, the molecule still transforms in its initial higher symmetry group.[6]

Whereas the dynamic Jahn–Teller effect has been observed for the molecules ReF_6, TcF_6, OsF_6, and RuF_6 (see, for example, ref 6), this is the first attempt to observe it in a metal carbonyl.

Experimental Section

A. The Shape of the CO Stretching Band in $V(CO)_6$. The infrared spectrum of vanadium hexacarbonyl in solution has been reported, and the single CO stretching absorption observed at 1980 cm^{-1} has been described as "broad."[1] This is not expected because the CO stretching band is very sharp for all group VI-B metal hexacarbonyls dissolved in inert solvents such as hydrocarbons. In view, however, of the possible Jahn–Teller effect in $V(CO)_6$, it seemed worthwhile to investigate further this band structure in gaseous $V(CO)_6$.

The infrared spectra calibrated against the known peaks of polystyrene were taken with a Perkin-Elmer Model 521 spectrometer. A heated infrared cell used for gases was alternately filled with $V(CO)_6$ and $Cr(CO)_6$, and the spectra were recorded from 4000 to 700 cm^{-1}. Only the CO stretching absorptions could be detected in $V(CO)_6$ and $Cr(CO)_6$. Figure 1 shows the analogous bands of gaseous $V(CO)_6$ and $Cr(CO)_6$ for comparison. The P, Q, and R branches of the rotational structure are easily distinguishable in the CO stretching vibration of $Cr(CO)_6$ even though the separate rotational lines are not resolved. This is exactly what is expected for a

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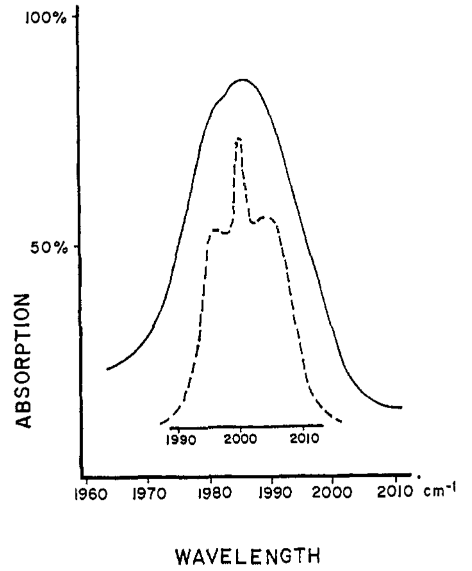

Figure 1. The infrared spectrum of the CO stretching band in gaseous V(CO)$_6$ (solid line) and Cr(CO)$_6$ (insert and dashed line).

molecule with octahedral symmetry with the resolution available from a Perkin-Elmer 521 spectrometer.

The spectrum of V(CO)$_6$, on the other hand, shows only one broad band. We believe that this is a clear indication of a Jahn-Teller effect. Since only a single band is observed in an infrared-active C-O stretching region, it seems *probable* that there is no static distortion and that, therefore, we are dealing with the dynamic Jahn-Teller effect in this molecule. However, this conclusion must be considered tentative because a small amount of tetragonal distortion, for example, would give rise to two close-lying infrared-active C-O stretching bands. It is conceivable that the overlapping rotational structures of two such close lying bands could produce the one broad band experimentally observed. The present experiment with moderate (0.3 cm^{-1}) resolution gives no basis for a complete interpretation of the band shape. Although it is only an empirical quantitative measurement, it is interesting to note that the full width at half-maximum for the CO stretching vibration increases from ~14 cm^{-1} in Cr(CO)$_6$ to 22 cm^{-1} in V(CO)$_6$. The significant difference between Cr(CO)$_6$ and V(CO)$_6$ is, however, strong evidence for the Jahn-Teller effect in the vanadium carbonyl molecule that is required from theoretical arguments.

B. Ultraviolet Spectrum of Vanadium Hexacarbonyl. A second less conclusive test of the Jahn-Teller effect in V(CO)$_6$ utilizes a comparison of the electronic levels observed in the ultraviolet spectra of V(CO)$_6$ and Cr(CO)$_6$. The Jahn-Teller effect should considerably complicate the electronic spectrum of V(CO)$_6$ relative to that of Cr(CO)$_6$. Since the five d electrons of the vanadium molecule will give rise to transitions different from those for the six electrons of Cr(CO)$_6$, the interpretation of the visible and ultraviolet spectrum cannot give such conclusive evidence for the effect as the vibrational spectrum. It is, therefore, not possible to accept the yellow-green color of V(CO)$_6$ solutions or the blue of the solid as an indication for such an effect.

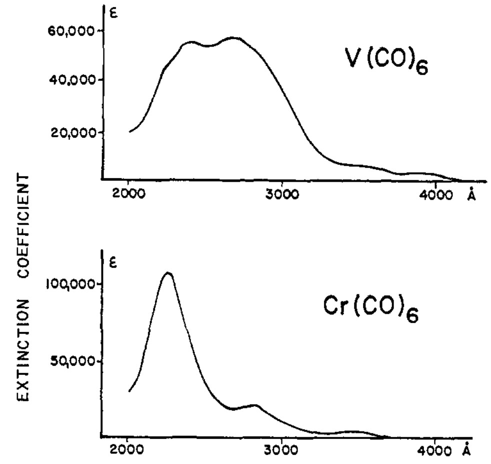

Figure 2. The ultraviolet spectrum of gaseous V(CO)$_6$ and Cr(CO)$_6$.

The ultraviolet spectrum of gaseous V(CO)$_6$ taken on a Cary Model 14 spectrometer is shown in Figure 2, together with the spectrum of Cr(CO)$_6$. The higher complexity of the d^5 case is evident. Qualitatively it may be seen that some of the bands in the Cr(CO)$_6$ are shifted or split in the corresponding ultraviolet spectrum of V(CO)$_6$. The two weak bands at the low-energy side of the spectrum are probably such a pair having mainly d-d character. The blue color of solid V(CO)$_6$ remains unexplained and apparently has no direct relation to the Jahn-Teller effect. It is evidently connected with the crystalline state, since solutions in hydrocarbons are yellow-green, quite natural for the strong absorption in the near-ultraviolet region.

Conclusion

These spectroscopic observations give strong evidence for a Jahn-Teller effect in V(CO)$_6$. In view of the probable existence of a dynamic Jahn-Teller effect rather than a static distortion of the O_h symmetry of the V(CO)$_6$ molecule, it would appear to be worthwhile to make a complete analysis of the vibration spectrum.

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