

shifted by  $-23\text{ cm}^{-1}$  from the dominant original band. Its formation kinetics establishes that this band is due to complexes of composition  $\text{BBXHQ-Ar}$ .<sup>7</sup> The most striking feature of the new band is that it is only monitored by red fluorescence. Blue fluorescence only observes the original band at  $4178\text{ \AA}$  of the bare molecule, disregarding the overwhelming presence of complexed molecules.

Fluorescence excitation of BBXHQ was also examined at higher resolution in pulsed expansions of He mixed with Ne, Ar, Kr, or Xe (Figure 1). Two bands are generally observed—by their red fluorescence only—for complexes BBXHQ-R with a single noble atom R. Through the dependence of their spectral position on the polarizability of R, the stronger band must be associated with the original excitation band for dual fluorescence at  $4178\text{ \AA}$ . It is therefore due to a complex formed by the molecule in its favored conformation shown in Figure 1.

Why does complexation with a single noble gas atom R effectively remove the blue fluorescence associated with the excited molecule prior to proton transfer? A possible explanation is the preferred stabilization of the excited tautomer by dipole-induced dipole interaction with R. This should lower the barrier for ES IPT. In cooperation with proton tunneling,<sup>4</sup> a relatively small stabilization would be needed for a strong enhancement of the transfer rate.

Regardless of interpretation, the observations reported here suggest that the relative short-wavelength fluorescence of BBXHQ in noble gas matrices may be quite reduced by comparison with the isolated molecule. Conversely, the dual character of fluorescence may be significantly more pronounced in a supersonic jet, for similar molecules<sup>8</sup> which have previously been studied in noble gas matrices.

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### Crystal and Molecular Structure of $[(\text{CH}_3)_2\text{N}]_3\text{S}^+\text{CF}_3\text{O}^-$ . Evidence for Negative Fluorine Hyperconjugation

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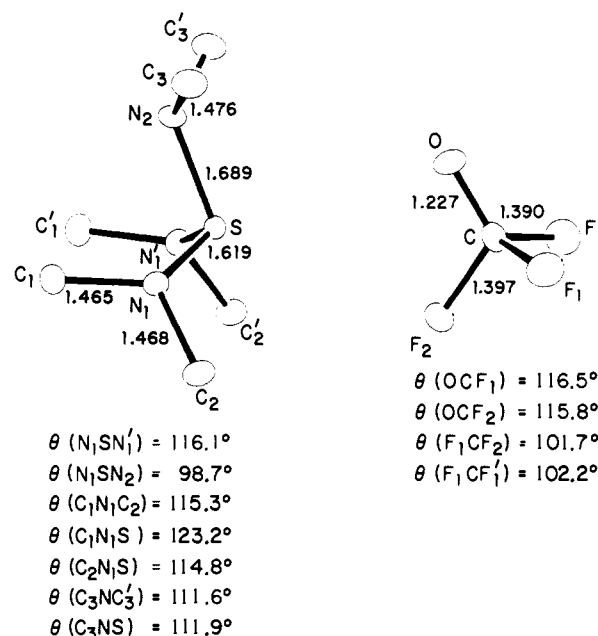
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Perfluorinated alkoxide anions are well-known reactive intermediates<sup>1</sup> and have been the subject of limited theoretical study,<sup>2</sup> but except for the infrared vibrational frequencies of some  $\text{Cs}^+$  and  $\text{Rb}^+$  salts,<sup>1f,3</sup> no experimental structural data have been re-

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**Figure 1.** X-ray crystal structure of tris(dimethylamino)sulfonium trifluoromethoxide (1). Bond distances in Å. The mirror plane relates atoms bearing primed and unprimed labels.

ported. We now report the first single-crystal X-ray structure of a perfluoroalkoxide salt, tris(dimethylamino)sulfonium (TAS) trifluoromethoxide, and we present our theoretical studies of the structure and bonding in  $\text{CF}_3\text{O}^-$  and related perfluoroalkoxides.

The X-ray single-crystal diffraction analysis of  $\text{TAS}^+\text{CF}_3\text{O}^-$  (1)<sup>4</sup> shows that the TAS cation and the  $\text{CF}_3\text{O}^-$  anion both lie on a crystallographic mirror plane<sup>5</sup> (Figure 1). The C-F bond lengths (1.390 (3), 1.397 (4) Å) are exceptionally long and the C-O bond length (1.227 (4) Å) is quite short compared with the corresponding gas-phase experimental values for  $\text{CF}_3\text{OR}$  (R = F, Cl,  $\text{CF}_3$ ) derivatives ( $r(\text{C}-\text{F}) = 1.319\text{--}1.327\text{ \AA}$ ,  $r(\text{C}-\text{O}) = 1.365\text{--}1.395\text{ \AA}$ ).<sup>7</sup> In fact, the C-O bond length in 1 approaches that for the C=O bond in  $\text{CF}_2=\text{O}$  (1.171 Å).<sup>8</sup> Moreover, the FCF bond angles (101.7 (2)°, 102.2 (3)°) are extraordinarily small.<sup>9</sup>

(4) The  $\text{TAS}^+\text{CF}_3\text{O}^-$  salt (1) was prepared by adding  $\text{COF}_2$  to a slurry of 11.0 g (39.5 mmol) of tris(dimethylamino)sulfonium difluorotrimethylsiliconate ( $\text{TASF}^6$ ) in 100 mL of anhydrous tetrahydrofuran at  $-75\text{ }^\circ\text{C}$  until the exothermic reaction subsided. The mixture was warmed to  $25\text{ }^\circ\text{C}$  and filtered with the rigorous exclusion of moisture to give 8.81 g (88%) of 1: mp  $214\text{--}216\text{ }^\circ\text{C}$  dec; IR ( $\text{CH}_2\text{Cl}_2$ ) 1553 ( $\nu_1$ ), 805 ( $\nu_2$ )  $\text{cm}^{-1}$ ;  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  -21.3 (br s,  $w_{1/2} = 430$  (23  $^\circ\text{C}$ ), 110 Hz ( $-1\text{ }^\circ\text{C}$ ));  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  2.88(s). Anal. C, H, N, F, S. Crystals for X-ray analysis were grown by slowly diffusing an 8:1 mixture of tetrahydrofuran/diethyl ether into a solution of 1 in 1,2-dichloroethane. The solvent mixture was then removed and replaced with tetrahydrofuran to afford crystals which were mounted in glass capillaries in an atmosphere of dry nitrogen.

(5) Crystal structure information: orthorhombic; space group  $Pnma$  (No. 62);  $a = 14.547$  (2) Å,  $b = 11.125$  (1) Å,  $c = 7.310$  (1) Å,  $V = 1183\text{ \AA}^3$ ,  $Z = 4$ ;  $T = -100\text{ }^\circ\text{C}$ . Data collected on Syntex R3 diffractometer, graphite monochromator, Mo K $\alpha$ ,  $\lambda = 0.71069\text{ \AA}$ ; 1643 reflections,  $4.6^\circ < 2\theta < 55.0^\circ$ ; 895 unique reflections with  $I > 3.0\sigma(I)$ . Structure solved by direct methods (MULTAN); full-matrix, least-squares refinement. All hydrogens refined isotropically, other atoms, anisotropically. Final  $R = 0.036$ ,  $R_w = 0.039$  for 112 independent variables.

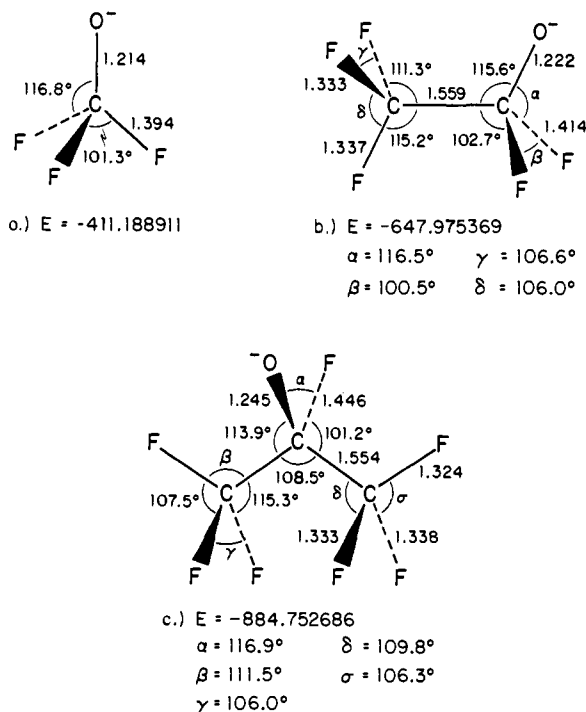
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(9) For  $\text{CF}_3\text{OR}$  (R = F, Cl,  $\text{CF}_3$ ),  $\angle\text{FCF} = 108.8\text{--}109.4^\circ$ . The  $\angle\text{FCF}$  for the  $\text{CF}_3$  group in saturated derivatives normally ranges from  $108.1^\circ$  to  $109.5^\circ$ .<sup>10</sup>

(10) Typke, V.; Dakkouri, M.; Oberhammer, H. *J. Mol. Struct.* **1978**, *44*, 85.



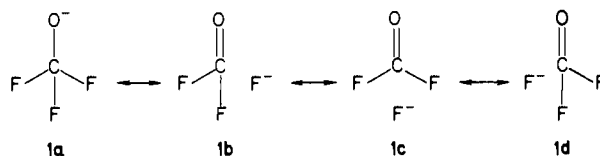
**Figure 2.** Calculated molecular structures (bond distances in Å) and total energies (au): (a) trifluoromethoxide anion; (b) pentafluoroethoxide anion; (c) heptafluoro-2-propoxide anion.

Ab initio Hartree-Fock calculations were performed on  $\text{CF}_3\text{O}^-$ ,  $\text{CF}_3\text{CF}_2\text{O}^-$ , and  $(\text{CF}_3)_2\text{CFO}^-$  using the program HONDO.<sup>11</sup> The (9,5)/[3,2] double- $\zeta$  basis set of Dunning and Hay augmented by a set of d polarization functions on C and O<sup>12</sup> was used. The geometry of  $\text{CF}_3\text{O}^-$  was gradient optimized<sup>13</sup> in  $C_{3v}$  symmetry;  $C_s$  symmetry was employed for the other ions. The calculated structure for  $\text{CF}_3\text{O}^-$  (Figure 2) agrees well with both experiment and previous calculations,<sup>2a-c</sup> although the C-O bond length is somewhat too short as is expected with this polarized basis set.<sup>14</sup>

The force field for  $\text{CF}_3\text{O}^-$  was determined using gradient techniques<sup>13</sup> to verify the  $C_{3v}$  symmetry of the isolated ion. The observed  $C_{2v}$  symmetry in the crystal thus is presumably due to packing forces. The calculated frequencies for  $\text{CF}_3\text{O}^-$  are  $\nu_1(\text{A}) = 1748$ ,  $\nu_2(\text{A}) = 912$ ,  $\nu_3(\text{A}) = 662$ ,  $\nu_4(\text{E}) = 1077$ ,  $\nu_5(\text{E}) = 643$ , and  $\nu_6(\text{E}) = 461 \text{ cm}^{-1}$ , which reasonably agree with values calculated with a 3-21G basis set<sup>2a</sup> but are slightly higher than the matrix values and those for solid  $\text{Cs}^+\text{CF}_3\text{O}^-$ .<sup>3</sup>

The unusual molecular structure predicts  $\text{CF}_3\text{O}^-$  can be attributed largely to negative hyperconjugation (H CJ).<sup>15</sup> The role

of HCJ can be estimated by comparing the electronic charge on F in  $\text{CF}_3\text{O}^-$  with that for model  $\text{CF}_3$  compounds. From Mulliken population analyses, the charge on F ( $q_F$ ) in a  $\text{CF}_3$  group is normally between  $-0.15e$  and  $-0.20e$  for  $\text{CF}_3\text{X}$  derivatives.<sup>16,17</sup> For  $\text{CF}_3\text{O}^-$ ,  $q_F = -0.35e$  ( $q_C = 0.64e$ ,  $q_O = -0.59e$ ) which compares with  $q_F = -0.15e$  in the isoelectronic molecule  $\text{CF}_4$ . Thus there is an additional charge of  $-0.2e$  on each F in  $\text{CF}_3\text{O}^-$ . This excess charge implies that each of the hyperconjugative resonance structures **1b-d** contributes approximately 20% to the bonding



in  $\text{CF}_3\text{O}^-$ . From the ab initio CO bond lengths of 1.307 Å in  $\text{CF}_3\text{OH}$  and 1.157 Å in  $\text{CF}_2=\text{O}$ ,<sup>16</sup> and assuming 40% single- and 60% CO double-bond character in  $\text{CF}_3\text{O}^-$ , the C-O bond length in  $\text{CF}_3\text{O}^-$  calculates to be 1.217 Å, in excellent agreement with experiment. The observed 0.07–0.08 Å increase in the C-F bond length over the normal values in  $\text{CF}_3\text{OR}$  derivatives also is consistent with negative HCJ since an increase in CO bond order requires a simultaneous decrease in bond order of the C-F bonds.<sup>21</sup>

Although the HCJ model predicts a somewhat reduced  $\angle\text{FCF}$  in  $\text{CF}_3\text{O}^-$  ( $\angle\text{FCF} = 107.7^\circ$  in  $\text{CF}_2=\text{O}$ )<sup>8</sup> compared with the normal values for  $\text{CF}_3$  groups,<sup>9</sup> it does not account for the observed angle shrinkage of about  $7^\circ$ . The origin of the small  $\angle\text{FCF}$  in  $\text{CF}_3\text{O}^-$  is unclear.<sup>22</sup>

Electrostatic (polar) effects also are likely to be important to the bonding in  $\text{CF}_3\text{O}^-$ . The very electropositive  $\text{O}^-$  substituent on a  $\text{CF}_3$  group will withdraw electron density from the C-F bonds, increase the p character in the carbon hybrid orbitals directed toward the fluorines, and consequently lengthen the C-F bonds and reduce the FCF bond angles. The magnitude of the electrostatic effect and its importance relative to HCJ, however, are difficult to ascertain.<sup>24</sup>

A comparison of the  $\text{C}_1\text{-F}$  bond lengths in the series  $\text{CF}_3\text{O}^-$ ,  $\text{CF}_3\text{CF}_2\text{O}^-$ , and  $(\text{CF}_3)_2\text{CFO}^-$  further reveals the importance of negative HCJ. The  $\text{C}_1\text{-F}$  bonds in  $\text{CF}_3\text{CF}_2\text{O}^-$  and  $(\text{CF}_3)_2\text{CFO}^-$  are respectively 0.02 and 0.05 Å longer than the C-F bond in  $\text{CF}_3\text{O}^-$  (Figure 2).<sup>27</sup> The alkoxide  $(\text{CF}_3)_2\text{CFO}^-$  expectedly has

(16) Dixon, D. A., unpublished results, using same basis set as described in text.

(17) Ab initio (STO-3G)<sup>18</sup> and semiempirical calculations<sup>10,19,20</sup> give  $q_F = -0.18e$  to  $-0.22e$  for saturated  $\text{CF}_3\text{X}$  and  $(\text{CF}_3)_2\text{Y}$  derivatives. It should be noted that the charge distributions obtained by Mulliken population analyses are used here only for comparative purposes. For criticism of this method, see, for example: (a) Streitwieser, A., Jr.; Williams, J. E., Jr.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778. (b) Lüthi, H. P.; Ammeter, J. H.; Almlöf, J.; Faegri, K., Jr. *J. Chem. Phys.* **1982**, *77*, 2002.

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(21) The C-F bond order in  $\text{CF}_3\text{O}^-$  is 0.8 from this model, but the corresponding bond length cannot be derived since the relationship between  $\sigma$ -CF bond order and bond length is unknown.

(22) The small bond angle is not unprecedented. The C-F bond length and  $\angle\text{FCF}$  in  $\text{CF}_3\text{O}^-$  are similar to those calculated for  $\text{CF}_3^-$ :  $r(\text{C-F}) = 1.417$ ,<sup>16</sup>  $1.434$  Å;<sup>23</sup>  $\angle\text{FCF} = 99.5^\circ$ ,<sup>16</sup>  $99.6^\circ$ .<sup>23</sup>

(23) Marynick, D. S. *J. Mol. Struct.* **1982**, *87*, 161.

(24) The increase in C-F bond lengths in  $\text{CF}_3\text{X}$  (X = F, Cl, Br, I, H) from 1.319 (X = F) to 1.334 Å (X = H) has been attributed solely to polar effects,<sup>10,20</sup> but this undoubtedly is oversimplified since resonance is known to be important in  $\text{CF}_4$ .<sup>25,26</sup> The FCF bond angles in  $\text{CF}_3\text{X}$  (X = Cl, Br, I, H) are nearly identical within experimental error, however.<sup>10</sup> Without a value for the effective electronegativity of  $\text{O}^-$ , the influence of polar effects on the structure of  $\text{CF}_3\text{O}^-$  remains moot.

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(14) With a fully polarized basis set (d polarization functions on F added),  $r(\text{C-O}) = 1.220$  Å,  $r(\text{C-F}) = 1.385$  Å, and  $\angle\text{FCF} = 101.5^\circ$  in  $\text{CF}_3\text{O}^-$ . Total  $E = -411.215524$  au.

(15) Negative HCJ has been invoked to explain the IR spectral data for  $\text{Cs}^+\text{CF}_3\text{O}^-$ .<sup>2a,3</sup> For leading references on negative HCJ in carbanions, see: (a) Schleyer, P. v. R.; Kos, A. *J. Tetrahedron* **1983**, *39*, 1141. (b) Streitwieser, A., Jr.; Berke, C. M.; Schriver, G. W.; Grier, D.; Collins, J. B. *Tetrahedron, Suppl.* **1981**, *37*, (1)345. (c) Sleight, J. H.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc., Chem. Commun.* **1979**, 921. (d) Sleight, J. H.; Stephens, R.; Tatlow, J. C. *J. Fluorine Chem.* **1980**, *15*, 411. (e) Streitwieser, A., Jr.; Holtz, D.; Ziegler, G. R.; Stoffer, J. O.; Brokaw, M. L.; Guibe, F. *J. Am. Chem. Soc.* **1976**, *98*, 5229. (f) Stock, L. M.; Wasielewski, M. R. *Prog. Phys. Org. Chem.* **1981**, *13*, 253. (g) Holtz, D. *Prog. Phys. Org. Chem.* **1971**, *8*, 1. Evidence has also been offered for negative HCJ in the related  $\text{CH}_3\text{O}^-$  system: (h) DeFrees, D. J.; Bartmess, J. E.; Kim, J. K.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 6451. (i) DeFrees, D. J.; Taagepera, M.; Levi, B. A.; Pollack, S. K.; Summerhays, K. D.; Taft, R. W.; Wolfsberg, M.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 5532. (j) Steigerwald, M. L.; Goddard, W. A., III; Evans, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1994.

the longest C<sub>1</sub>-F bond since only one fluorine hyperconjugative resonance structure is available to delocalize charge, whereas in CF<sub>3</sub>CF<sub>2</sub>O<sup>-</sup> and CF<sub>3</sub>O<sup>-</sup> there are two and three, respectively. The increase in C<sub>1</sub>-F bond lengths, however, might simply reflect the well-known dependence of C-F bond length on the number of fluorines attached to the carbon atom.<sup>7a,28</sup> For CF<sub>3</sub>-F, CF<sub>3</sub>CF<sub>2</sub>-F, and (CF<sub>3</sub>)<sub>2</sub>CF-F the calculated bond lengths are 1.306, 1.312, and 1.328 Å, respectively.<sup>29</sup> The C-F bond lengths in the perfluoroalkoxides show a much larger change than in the perfluoroalkanes, which clearly supports the importance of negative HCl in the alkoxides.

**Registry No.** (Me<sub>2</sub>N)<sub>3</sub>S<sup>+</sup>CF<sub>3</sub>O<sup>-</sup>, 96898-10-1; F<sub>2</sub>CO, 353-50-4; (Me<sub>2</sub>N)<sub>3</sub>S<sup>+</sup>Me<sub>3</sub>F<sub>2</sub>Si<sup>-</sup>, 59218-87-0; CF<sub>3</sub>O<sup>-</sup>, 57178-38-8; CF<sub>3</sub>CF<sub>2</sub>O<sup>-</sup>, 94295-10-0; (CF<sub>3</sub>)<sub>2</sub>CFO<sup>-</sup>, 44967-50-2.

**Supplementary Material Available:** Tables of atomic coordinates, thermal parameters, and structure amplitudes (5 pages). Ordering information is given on any current masthead page.

(27) The TAS salts of CF<sub>3</sub>CF<sub>2</sub>O<sup>-</sup> and (CF<sub>3</sub>)<sub>2</sub>CFO<sup>-</sup> were easily prepared by adding CF<sub>3</sub>C(O)F and (CF<sub>3</sub>)<sub>2</sub>C=O, respectively, to TASF following the procedure to make 1;<sup>4</sup> TAS<sup>+</sup>CF<sub>3</sub>CF<sub>2</sub>O<sup>-</sup>: mp 189-191 °C dec; <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, -80 °C) δ -83.52 (s, CF<sub>3</sub>), -34.56 (s, CF<sub>2</sub>); TAS<sup>+</sup>(CF<sub>3</sub>)<sub>2</sub>CFO<sup>-</sup>: mp 129 °C dec; <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, -30 °C) δ -81.24 (d, J = 4.5 Hz, CF<sub>3</sub>), -71.17 (sept, J = 4.5 Hz, CF); δ (20 °C) -81.21 (s, CF<sub>3</sub>), -69.30 (s, CF, w<sub>1/2</sub> = 12 Hz). Unfortunately we have not yet been able to obtain crystals of either salt suitable for X-ray analysis. Unlike their Rb<sup>+</sup> and Cs<sup>+</sup> salts, which rapidly decompose at or below 50 °C,<sup>1f</sup> the TAS<sup>+</sup> salts of CF<sub>3</sub>CF<sub>2</sub>O<sup>-</sup> and (CF<sub>3</sub>)<sub>2</sub>CFO<sup>-</sup> are both stable up to their respective melting points. Solution dynamic properties and synthetic use of TAS perfluoroalkoxides and related stable TAS perfluorocarbanions will be discussed in a forthcoming publication: Smart, B. E.; Middleton, W. J.; Farnham, W. B., unpublished results.

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## Changes in the Electronic Structure of Ni/TiO<sub>x</sub> Composites as a Function of Reduction Temperature<sup>†</sup>

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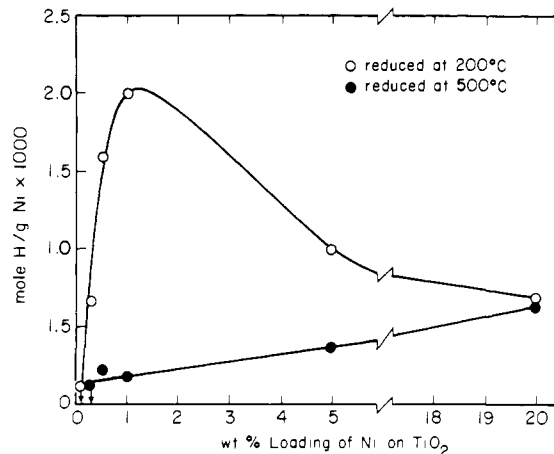
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Transition-metal catalysts are dispersed on high surface area oxide supports in order to obtain a large catalytic activity per metal atom. Many supports, such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, are considered to be inert; that is, these supports do not alter the intrinsic activity of the metal significantly but only serve to increase the surface area of the metal and prevent sintering. For some oxide supports, however, there is a strong interaction between the metal and the support.<sup>1</sup> In particular, TiO<sub>2</sub> can affect the activity of the supported metal depending on the conditions under which the metal-titanium dioxide composite is prepared. It is our goal to learn how to control the chemistry of supported metals by mod-

<sup>†</sup> In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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**Figure 1.** Dependence of H<sub>2</sub> chemisorption at room temperature on the weight percent of Ni supported on TiO<sub>2</sub>.

ifying the support composition and the composite preparation temperature.

Typically, transition metals are dispersed on oxide supports by impregnation of the support with a metal salt and subsequent reduction to the metal in flowing hydrogen. The catalytic activity and chemisorption properties of group 8-10 metals supported on TiO<sub>2</sub> depend on the reduction temperature used to prepare the catalyst. In particular, the chemisorption of H<sub>2</sub> and CO at 295 K decreases sharply as the reduction temperature is increased from 473 to 773 K. This suppression of chemisorption can be attributed to (1) the migration of TiO<sub>x</sub> species from the support onto the metal particles, thereby decreasing the number of metal sites exposed for chemisorption,<sup>2</sup> (2) an electronic effect, due to charge transfer from the reduced support to the metal,<sup>3</sup> or (3) the formation of a new metastable Ni-Ti-O phase. We have studied the magnetic properties of Ni/TiO<sub>2</sub> and have shown that an electronic change occurs as a function of reduction temperature.

We chose to study nickel supported on TiO<sub>2</sub> because the magnetic properties of the nickel provide an excellent probe of changes in the electronic properties of the Ni/TiO<sub>2</sub> composites. Nickel is ferromagnetic below its Curie temperature of 627 K with a saturation magnetization  $M_s = 57.50 \text{ emu/g}$  at absolute zero.<sup>4</sup> By measuring the saturation magnetization of the Ni/TiO<sub>2</sub> samples, the amount of Ni present as bulk metal can be determined. TiO<sub>2</sub>, on the other hand, is an insulator and is diamagnetic. It can be reduced, however, in hydrogen to a series of paramagnetic phases known as the Magneli phases of formula Ti<sub>n</sub>O<sub>2n-1</sub> for  $n \geq 3$ .<sup>5</sup> Whereas this reduction does not occur for pure TiO<sub>2</sub> below ~1000 K, it occurs at much lower temperatures in the presence of metal impurities.<sup>6</sup> These Magneli phases are all paramagnetic due to the presence of Ti<sup>3+</sup> species.<sup>7</sup> By measuring the paramagnetic moment of the Ni/TiO<sub>2</sub> samples it is possible to determine the degree of support (TiO<sub>2</sub>) reduction. Therefore, in a single magnetic measurement one can determine both changes in the electronic properties of the nickel and the degree of reduction of the support.

Samples of Ni/TiO<sub>2</sub> were prepared from TiO<sub>2</sub> (Cerac, 99.9% pure) which was 15-20% rutile and 80-85% anatase with a surface area of 51 m<sup>2</sup>/g. Samples with nickel loadings from 0.1% to 20% by weight were prepared by incipient wetness techniques using

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