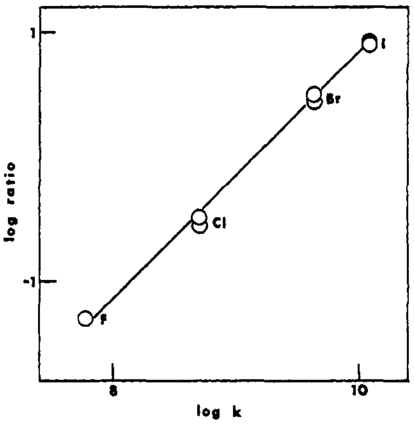


Figure 1. Correlation of log (phenylacetone/1-phenyl-2-propanol product ratio) with log *k* for reactions with the hydrated electron in water,[9] for the four halobenzenes. Most of the data are from experiments not listed in Table I. The alkali metal was K except that it was Na for one of the two points for iodobenzene.

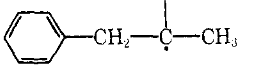
Arylation occurs without isomerization in the aryl group. When arylation was effected with *p*-bromotoluene, *p*-bromoanisole, or *p*-tolyl- or *p*-anisyltrimethylammonium iodide, the arylacetones obtained were in all cases para isomers uncontaminated by ortho or meta isomers, as shown by comparison of properties with those of authentic samples.

To date, only one other ketone enolate ion has been investigated, namely, that from cyclopentanone. It was para tolylated with *p*-tolyltrimethylammonium iodide in ammonia at −33°. By glpc, the yields of 2-(*p*-tolyl)cyclopentanone and 2-(*p*-tolyl)cyclopentanol were 28 and 37%, respectively; after oxidation[7] and work-up, the isolated yield of ketone was 34%.

The fact that aryltrimethylammonium ions and aryl diethyl phosphates may be employed is of special significance because of the ease with which these can be obtained from aromatic amines and phenols,[8] respectively.

We suspect this principle of synthesis to have much wider validity than actually demonstrated in our experiments. We anticipate that yet other aromatic substituents may have sufficient nucleofugicity to be useful, that the method is applicable to ketone enolate ions and carbanions from nitriles[4] in general, and that other types of carbanions as well as other solvents and other sources of electrons may be employed.

In our experiments, the proportions of arylacetone and 1-aryl-2-propanol obtained varied according to the identity of X in ArX. The naive view that the alcohol product is derived simply by reduction of the ketone in an electron-rich environment is refuted by the fact that phenylacetone is not reduced to 1-phenyl-2-propanol by potassium in liquid ammonia under the conditions of our experiments. It is converted to an enolate ion instead.



$C_6H_5CH_2\overset{O^-}{\dot{C}}CH_3$

1

The ratios of phenylacetone to 1-phenyl-2-propanol, as obtained from the four halobenzenes, correlate linearly (in log–log fashion) with their rates of reaction with the hydrated electron;[9] see Figure 1. The slope is 1.01 and the correlation coefficient is 0.998. We suggest that the immediate product of combination of phenyl radical with acetonate ion is ketyl-like radical anion **1** which is then involved in competing reactions: electron transfer to ArX as in eq 4 or reduction to the alcohol. The mechanism of the latter is uncertain, but presumably its rate is independent of the identity of the halogen atom of the original halobenzene. On the other hand, the rate of electron transfer according to eq 4 depends on the identity of the halogen much the same as when the halobenzene reacts with the hydrated electron.

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(10) Grateful recipient of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

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Molecular Magnetic Moments, Magnetic Susceptibility Anisotropy, Molecular Quadrupole Moment, and Sign of the Electric Dipole Moment in Methylsilane

Sir:

We report here the molecular Zeeman effect in CH_3SiH_3 and CH_3SiD_3. The results give the magnitudes and relative signs of the molecular *g* values, the magnetic susceptibility anisotropy, and the molecular quadrupole moments of the molecule.

The microwave spectra of both $H_3{}^{28}SiCH_3$ and $D_3{}^{28}SiCH_3$ have been studied previously and a substitutional structure is also available.[1] The equations describing the linear and quadratic Zeeman effect in a symmetric top have been developed in detail[2–4] and the experimental apparatus involving the high-field electromagnet has been described previously.[5] $J = 0 \rightarrow 1$ transitions in both H_3SiCH_3 and D_3SiCH_3 were observed with $\Delta M = \pm 1$ selection rules. The $J = 0 \rightarrow 1$ transition of CH_3SiH_3 was split by 962 ± 3 kHz at a field of 17,603 ± 20 G, and the center frequency of the doublet was shifted by −14 ± 5 kHz from the zero field frequency of 21,937.93 MHz. The $J = 0 \rightarrow 1$ transition of CH_3SiD_3 was split by 830 ± 5 kHz at a field of 17,602 ± 20 G, and the center frequency of the doublet was shifted by −12 ± 5 kHz from the zero field frequency of 19,245.46 MHz. From eq 1 of ref 3 the splitting of the doublet is given by $2\mu_0 g_\perp H/h$ and the shift is given by $-H^2(\chi_\perp - \chi_\parallel)/15h$. Thus we obtain the following values for $g_\perp$

$$\begin{aligned} &CH_3SiH_3 \quad |g_\perp| = 0.03583 \pm 0.00012 \\ &CH_3SiD_3 \quad |g_\perp| = 0.03092 \pm 0.00019 \end{aligned} \tag{1}$$

Notice that the sign of $g_\perp$ cannot be determined from this analysis. From the center frequency shifts a value

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of $(\chi_\perp - \chi_\parallel) \cong 0.40 \times 10^{-29}$ erg/G^2 is obtained. A much more accurate value will be obtained below from the $\Delta M = 0$ transition.

The $J = 0 \rightarrow 1$, $\Delta M = 0$ transition of CH_3SiH_3 was also examined under high resolution. A single line shifted by $+38.5 \pm 3.4$ kHz from the zero field line was found at a field of 21,173 ± 20 G. From eq 1 of ref 3, this shift is given by $2H^2(\chi_\perp - \chi_\parallel)/15h$. Therefore

$$(\chi_\perp - \chi_\parallel) = (0.398 \pm 0.035) \times 10^{-29}\ \text{erg/G}^2$$
$$= (2.40 \pm 0.21) \times 10^{-6}\ \text{erg/(G}^2\ \text{mol)} \qquad (2)$$

This result is valid for $(\chi_\perp - \chi_\parallel)$ in CH_3SiD_3 also, since $(\chi_\perp - \chi_\parallel)$ is independent of the position of the center of mass.

In order to obtain $g_\parallel$, the $J = 1 \rightarrow 2$, $K = 1$ transition of CH_3SiD_3 at 38,490.50 MHz was observed. These $K = 1$ spectra are difficult to obtain because the lines are very susceptible to pressure broadening, power saturation, and improper zero basing of the Stark modulation voltage. These effects are all due to the fact that $K \neq 0$ transitions have a first-order Stark effect. However, an assignment of the $\Delta M = 0$ and $\Delta M = \pm 1$ transitions was finally made as follows. The $\Delta M = 0$, $J = 1 \rightarrow 2$, $K = 1$ transition was found to be a partially resolved triplet with a splitting of approximately 425 kHz between the two outermost peaks at 17,800 G. From eq 1 of ref 3 we find that this splitting is given by $2\mu_0 H(g_\perp - g_\parallel)/3$. Since the magnitude of $g_\perp$ is known, $g_\parallel$ can be calculated to be about 0.079 if $g_\perp$ and $g_\parallel$ have the same sign and about 0.017 if $g_\perp$ and $g_\parallel$ have opposite signs.

With $\Delta M = \pm 1$ selection rules, the $J = 1 \rightarrow 2$, $K = 1$ transition shows a single broad unresolved peak near the zero field frequency and a well-resolved doublet further out with a splitting of 1045 ± 25 kHz at 17,525 G. This spectra is consistent only with $g_\perp$ and $g_\parallel$ having opposite signs. This choice identifies the doublet peaks as the $M = 1 \rightarrow 2$ and $M = -1 \rightarrow -2$ transitions. Equation 1 of ref 3 gives this splitting as $\mu_0 H \cdot (7g_\perp - g_\parallel)/3$. From this we calculate $g_\parallel$ for CH_3SiD_3

$$|g_\parallel| = 0.0182 \pm 0.0069 \qquad (3)$$

We also know that $g_\perp$ and $g_\parallel$ have opposite signs. The details of fitting this spectra are given elsewhere.[4] The molecular quadrupole moment along the parallel axis (Si–C bond axis) is given by[3]

$$Q_\parallel = \frac{|e|}{M_p}[g_\perp I_\perp - g_\parallel I_\parallel] + \frac{4Mc^2}{|e|}(\chi_\perp - \chi_\parallel) \qquad (4)$$

Using the known perpendicular and parallel moments of inertia ($I_\perp$ and $I_\parallel$),[1] the value of $\chi_\perp - \chi_\parallel$ in eq 2 and the $g_\perp$ and $g_\parallel$ values given above gives the following molecular quadrupole moments.

$g_\perp$ negative, $g_\parallel$ positive

$$Q_\parallel = -(6.31 \pm 0.46) \times 10^{-26}\ \text{esu cm}^2 \qquad (5)$$

$g_\perp$ positive, $g_\parallel$ negative

$$Q_\parallel = +(11.74 \pm 0.46) \times 10^{-26}\ \text{esu cm}^2 \qquad (6)$$

The electric dipole moment of CH_3SiH_3 along the symmetry axis, μ_z, is related to the perpendicular molecular g values as follows[3]

$$g_\perp^D/B^D - g_\perp^H/B^H = -\frac{8\pi M_p}{\hbar|e|}Z\mu_z \qquad (7)$$

$g_\perp^D$ and $g_\perp^H$ are the g values in CH_3SiD_3 and CH_3SiH_3, respectively, and B^D and B^H are the corresponding rotational constants. M_p is the mass of the proton and Z is the center of mass shift from the CH_3SiH_3 molecule to the CH_3SiD_3 molecule ($Z = +0.0692$ Å). In this axis system the molecular electric dipole moment has values of

$$\mu_z = -(0.96 \pm 0.40)\ \text{D} \quad \text{for } g_\perp \text{ negative; } +CH_3SiH_3- \qquad (8)$$

$$\mu_z = +(0.96 \pm 0.40)\ \text{D} \quad \text{for } g_\perp \text{ positive; } -CH_3SiH_3+ \qquad (9)$$

The magnitude of the dipole moment given here is in agreement with the magnitude determined by more accurate Stark effect measurements: $|\mu| = 0.73 \pm 0.02$.[1]

We are unable, on the basis of our experimental results, to choose the correct quadrupole moment from eq 5 or 6 or the correct sign of the electric moment from eq 8 or 9. However, there are several arguments which favor the negative value of $g_\perp$ and the corresponding $Q_\parallel = -(6.31 \pm 0.46) \times 10^{-26}$ esu cm^2, and $+CH_3SiH_3-$. We will numerically list these arguments below.

1. The sign of the dipole moment in methylsilane is expected to be $+CH_3SiH_3-$. The molecular octapole moment of CH_4 is positive[6] which indicates that the C–H bond dipole has −C–H+ polarity. The corresponding octapole moment for SiH_4 is negative[7] indicating +Si–H− bond polarity. If we assume the −C–H+ and +Si–H− bond polarities in CH_3SiH_3 we obtain a $+CH_3SiH_3-$ dipole moment sign even in the presence of a +Si–C− moment. It is also well known that the hydrogen atoms on SiH_4 are hydridic and the hydrogen atoms on CH_4 are protonic (which is reflected in the signs of the molecular octapole moments). Thus, one would expect the dipole sign to be $+CH_3SiH_3-$ which is obtained with a negative $g_\perp$.

2. The sign of the electric dipole moment has been measured by a deuterium isotope effect to be $+CH_3SiH_3-$.[8]

3. Using a point charge model[9] to compute the molecular dipole and quadrupole moments with +1 esu on the carbon hydrogen and −1 esu on the silicon hydrogens leads to a negative value of $Q_\parallel$. The assignment of the point charges is expected on the basis of the signs of the molecular octapole moments.

In conclusion, the above three arguments favor the negative value of $g_\perp$, $+CH_3SiH_3-$, and $Q_\parallel = -(6.31 \pm 0.46) \times 10^{-26}$ esu cm^2. However, we emphasize again that this conclusion on the sign of $g_\perp$ is not based on experimental facts. It would be useful to perform an *ab initio* calculation on CH_3SiH_3 in order to determine which value of $Q_\parallel$ is correct. The large difference between the two choices ($Q_\parallel = -6.3$ or $+11.7$)

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as shown in eq 5 and 6, should make an *ab initio* calculation useful in the differentiation.

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Production of a Dinitrogen Complex *via* the Attack of Nitric Oxide upon a Metal-Ammine Complex

Sir:

We wish to report a novel preparation of the now familiar $Ru(NH_3)_5N_2^{2+}$ ion. Some previous methods of preparation have included direct substitution by N_2 into $Ru(NH_3)_5OH_2^{2+}$ [1] and the use of such nitrogen-containing compounds as N_2H_4,[2] N_2O,[3] and NO^+.[4] While pursuing our interests in the chemistry of nitrosylammineruthenium complexes,[5] we have now discovered that saturation of alkaline solutions (pH >9) of $Ru(NH_3)_6^{3+}$ with nitric oxide results in the rapid and quantitative formation of $Ru(NH_3)_5N_2^{2+}$.

Solutions of $Ru(NH_3)_6^{3+}$ (2.96×10^{-3} *M*) were saturated with argon using an all-glass system. Argon-purged solutions of NaOH (0.01 *M*) were then introduced into the reaction flask with a Teflon needle. The gas flow could be switched rapidly to NO, which had been vigorously scrubbed through towers of molecular sieve, solid KOH, and 5 *M* NaOH.[6] All gases were passed through a final, common scrubber of 0.1 *M* NaCl (room temperature, ~1 atm). At the conclusion of the NO gas flow, argon was readmitted to the system (~20 min) to remove residual NO. The product solution was acidified (HCl or HBr) and $Ru(NH_3)_5N_2^{2+}$ was analyzed by the characteristic uv spectrum (λ_{max}, 221 nm (ϵ 1.8×10^4 M^{-1} cm^{-1}))[7] (97%) and by gas chromatographic techniques (molecular sieve column)[6] using Fe^{3+} to liberate N_2 (95 ± 5%). The complex isolated as the bromide salt (>75% yield) displayed the identical ir spectrum as alternative preparations of $[Ru(NH_3)_5N_2]Br_2$. Rotary evaporation to dryness of the product solution (acidified with HCl) indicated no products other than $[Ru(NH_3)_5N_2]Cl_2$ as identified by ir and uv-visible spectroscopy.

Treatment of NO with $Ru(NH_3)_6^{3+}$ in acid media results in the quantitative, facile production of $Ru(NH_3)_5NO^{3+}$.[5a] For the most part, substitution or redox reactions of ruthenium ammines have been confined to studies in acid media. Only recently, Rudd and Taube[8] have suggested that some Ru(III) pentaammines undergo disproportionation in alkaline media. Using $Ru(NH_3)_5Cl^{2+}$ (3.38×10^{-3} *M*) and a NO saturated (15 min) solution of 0.01 *M* NaOH, we did not observe any $Ru(NH_3)_5N_2^{2+}$. Instead, at least 82% of the product was identified[6] as $[Ru(NH_3)_4(NO)(OH)]^{2+}$.

From Latimer[9] one can calculate that NO is thermodynamically capable of undergoing disproportionation in alkaline solution into NO_2^- and N_2. The rapidity of the reaction negated the possibility of N_2 (from the disproportionation of NO)[9] being the source of our dinitrogen product.[10] With $Ru(NH_3)_6^{3+}$ or $Ru(NH_3)_6^{2+}$ (2.96×10^{-3} *M*), NaOH (0.01 *M*), and $NaNO_2$ (4.7×10^{-3} *M*), no $Ru(NH_3)_5N_2^{2+}$ was observed. In addition, the reaction of $Ru(NH_3)_6^{2+}$ (2.96×10^{-3} *M*) with NO in 0.01 *M* solutions of NaOH did not produce the dinitrogen complex.

The reaction was studied as a function of pH using the following buffer solutions: pH 6–8, $H_2PO_4^-$–OH^-; pH 8–9.2, Borax–HCl; pH 9.2–10.8, Borax–OH^-; pH 11.5–12, HPO_4^{2-}–OH^-. A small volume of $Ru(NH_3)_6^{3+}$ solution was added to the buffer solutions which had been saturated with NO. Using gas chromatography and the uv spectrum of the product, $Ru(NH_3)_5N_2^{2+}$, no dinitrogen complex was detected at pH 6, 31% at pH 7.5, 41% at pH 7.76, 100% at pH 8.45 and 9.03. Both a 0.01 *M* NaOH solution and a HPO_4^{2-}–OH^- buffer (pH 12) gave quantitative yields of $Ru(NH_3)_5N_2^{2+}$.

Attempts at measuring the rate of the reaction have been complicated because of the rapidity of the reaction. Preliminary kinetic studies performed by injecting $Ru(NH_3)_6^{3+}$ solutions (1×10^{-3} *M*) into alkaline NO solutions indicate that the rate increased markedly while increasing the pH of buffer solution (pH 7.0 → 9.0).

In order to gain further insight into the mechanism of our reaction, N-15 labeled NO (99% enriched, Mallinckrodt Nuclear) was used in place of the tank NO. The experiment was performed using a vacuum line to admit controlled amounts of NO into the reaction vessel containing frozen 0.01 *M* NaOH and solid $[Ru(NH_3)_6]Br_3$ (contained in a side arm mounted on the reaction vessel). The NaOH solution and NO were allowed to thaw (5 min) with vigorous stirring. The $[Ru(NH_3)_6]Br_3$ was then tipped into the solution. After 20 min the NO was pumped off, the solution was evaporated to dryness, and the residue was washed with absolute methanol to remove NaBr. The labeled sample produced only a single, strong band at 2080 ± 5 cm^{-1}. The unlabeled sample produced a band at 2114 ± 5 cm^{-1}. The doubly labeled complex, $Ru(NH_3)_5{}^{30}N_2^{2+}$ has recently been prepared as the bromide salt[11] and gives a band at 2035 ± 10 cm^{-1}. Earlier work[6,12] producing equilibrium mixtures of $Ru(NH_3)_5{}^{29}N_2^{2+}$ demonstrated that the dinitrogen stretch occurs at 2075 ± 10 cm^{-1}.

The evidence presented above suggests that nitrogen(II) as NO (rather than nitrogen(III), or N_2) attacks the metal-ammine complex. The dependence of the product yield on pH points to the possibility of amide

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