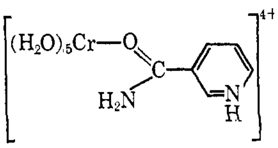
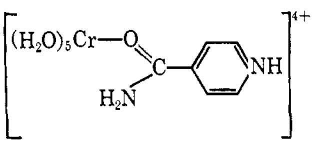
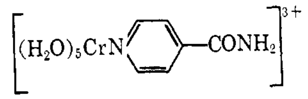
isonicotinamide complex as was done for the nicotinamide complex we conclude that the complex has structure IV. Preliminary estimates indicate that this


III


IV

chromic complex of isonicotinamide constitutes at least 90% of the chromium(III) product under these conditions.

If, however, the isonicotinamidepentaammine is reduced in the presence of $>10^{-3}$ *M* Cr^{2+} and <0.1 *M* H^+, a different chromic product appears. This complex may also be isolated by ion-exchange chromatography, although with more difficulty than before because it is retained on the column only slightly more strongly than $Cr(H_2O)_6^{3+}$. Its absorption maxima are at 400 mμ (ε 18.2) and 558 mμ (ε 18.7). Its aquation rate is very slow, $k = 4.3 \times 10^{-5}$ sec^{-1} at 70° (for chromic complex III k would be 7×10^{-3} sec^{-1} at 70°). The infrared spectrum of the chromic complex has peaks at 1660 and 1435 cm^{-1}, very close to those of the free ligand indicating that the amide group is not coordinated. Visible bands for this complex appear at shorter wavelengths than for $Cr(H_2O)_6^{3+}$, implying coordination by a ligand higher in the spectrochemical series than H_2O. The ion-exchange behavior indicates that it probably has the same charge as $Cr(H_2O)_6^{3+}$. These observations support the assignment of structure V to this last


V

chromic complex. The characterization of this isomer strengthens by contrast the arguments made for the assignment of structure IV (and III).

Despite the complexities in the product distributions the reduction of the isonicotinamidepentaammine can be described by a single term rate law, $d(Co^{III})/dt = -k(Co^{III})(Cr^{2+})$; it is furthermore found that complex IV does not react with Cr^{2+} at low (H^+) to form complex V.

These kinetic data in conjunction with the other observations cited imply that the rate-determining step leads to a metastable complex which can react to form either IV or V. In view of the Cr^{2+} and H^+ dependence, it is reasonable to supposet hat the metastable chromic complex is closely related to IV and can itself undergo attack by Cr^{2+} at the remote pyridinyl nitrogen (after loss of its proton) to produce complex V. Work in progress should settle this point and yield information about the metastable complex.

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[10] National Institutes of Health Predoctoral Fellow, 1964–1966.

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The Temperature Dependence of Fluorine and Carbon-13 Hyperfine Interactions of Hexakis(trifluoromethyl)benzene Anion

Sir:

We have observed the effect of temperature on ^{19}F and both ^{13}C hyperfine splittings of the hexakis(trifluoromethyl)benzene anion (I).

The variations with temperature of the ^{19}F and ^{14}N hyperfine splittings in bis(trifluoromethyl) nitroxide (II) were described recently by Scheidler and Bolton,[1] who found that a^F increased and a^N decreased linearly as the temperature was lowered. These temperature effects were explained by assuming that configurations leading to increased conjugation between nitrogen and fluorine are favored at lower temperatures.[1]

I was produced by reducing the fluorocarbon with potassium in tetrahydrofuran *in vacuo*.[2] Sample concentrations were about 10^{-3} *M*. The esr spectra of I were measured on a Varian V-4502 spectrometer operating at about 9.3 Gcps with a field modulation of 100 kcps. Constant temperatures were obtained by passing cold nitrogen through a quartz dewar running the length of the rectangular cavity. The temperature was monitored using a copper-constantan thermocouple located alongside the sample tube outside the cavity, but well within the dewar. During the course of an experiment there was no discernible change in temperature. The potentiometer could be read to ±1°. The field was determined from the frequency of a proton resonance probe inserted between one face of the magnet and the side of the cavity and was monitored with a Hewlett-Packard 5245L frequency counter. During the course of these experiments the probe and sample tube were kept at fixed positions in the magnetic field.

The esr spectrum of I consists of 19 lines with a binomial intensity distribution due to 18 equivalent fluorine nuclei. Each line has four satellites, each of which is 0.033 times as intense as the main line.[3] The ^{19}F splittings were determined by setting the field at the center of a line and simultaneously measuring the proton resonance frequency. The coupling constants were calculated from the difference in frequency between two lines. The ^{13}C splittings were determined from calibrated spectra presented on a chart recorder. Overlap of the ^{13}C satellites was compensated for with the aid of the calculated spectra of Lebedev, *et al.*[4] The estimated uncertainty in determination of ^{13}C coupling constants ranges from ±0.005 gauss at room temperature to ±0.020 gauss at 207°K, when the overlap of the satellites was the largest.

Table I gives the values of the coupling constants at several temperatures. A least-squares treatment of the data gives the following equations for the linear variation of the coupling constants with temperature.

$$a^F = 7.827 - 0.00100T \tag{1}$$

$$a^{C_1} = 4.110 + 0.00205T \tag{2}$$

$$a^{C_2} = 5.338 + 0.00162T \tag{3}$$

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[1] P. J. Scheidler and J. R. Bolton, *J. Am. Chem. Soc.*, **88**, 371 (1966).

[2] D. E. Paul., D. Lipkin, and S. I. Weissman, *ibid.*, **78**, 116 (1956).

[3] M. T. Jones, *J. Chem. Phys.*, **42**, 4054 (1965).

[4] Y. S. Lebedev, D. M. Chernikova, N. N. Tikhomirova, and V. V. Voevodskii, "Atlas of Electron Spin Resonance Spectra," Consultants Bureau, New York, N. Y., 1963.

Table I. Coupling Constants (Gauss) of Hexakis(trifluoromethyl)benzene Anion in Tetrahydrofuran

Temp, °K	a^F	a^C_1	a^C_2
299		4.721	5.836
297	7.530		
274		4.669	5.775
273	7.554		
243		4.603	5.743
239	7.596		
216		4.559	5.701
208	7.615		
207		4.540	5.651
185	7.643		

Bolton and Fraenkel[5] indicate that line-width variations among sets of equivalent ^{13}C nuclei having the same statistical weights can be used in assigning coupling constants. The lines belonging to the set of nuclei having the larger local π-electron spin density should be broader under conditions where the anisotropic dipole interactions affect the line width. As the temperature was lowered, the amplitudes of the ^{13}C satellites with the larger splitting were found to decrease more than the amplitudes of the other pair. Therefore, we assign the larger coupling constant to the ring carbon nuclei, since only these atoms should have a significant local π-electron spin density.

Of particular interest in these data is the magnitude of a^C_2. Bolton[6] has reported a value of 2.8 gauss for a^C in the benzene anion at $-100°$. Our extrapolated value of 5.62 is about twice as large. This larger coupling may be explained if the benzene ring of I is slightly nonplanar. In this case, either changes in hydridization or bond polarization effects could influence the magnitude of a^C. Karplus and Fraenkel[7] predict an increase of about 20 gauss in the ^{13}C splitting for a 5° deviation from planarity of the methyl radical. At lower temperatures an increase in the planarity of the benzene ring would cause a decrease in the ^{13}C coupling constant, as observed here.

It has been suggested[1,8] that a p orbital of fluorine can undergo direct conjugation with the π orbital containing the unpaired spin. An enhancement of the conjugation as the temperature is lowered would lead to an increase in a^F. Our results are thus consistent with those obtained by Scheidler and Bolton[1] for II.

The decrease in a^C_1 and a^C_2 as the temperature is lowered could then arise partially from a transfer of π-spin density to the fluorine p orbitals. It is difficult to draw any quantitative conclusions from this work and that of Scheidler and Bolton, however, because of the possibility of at least two mechanisms contributing to the temperature dependence of the coupling constants.

Acknowledgment. This work was supported by the National Science Foundation through Grant GP-3398.

(5) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 944 (1964).
(6) J. R. Bolton, *Mol. Phys.*, **6**, 219 (1963).
(7) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).
(8) W. A. Sheppard, *J. Am. Chem. Soc.*, **87**, 2410 (1965).

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A Thiopolyphosphine Heterocycle[1]

Sir:

The existence of the homocyclic polyphosphines $(CF_3P)_4$ and $(CF_3P)_5$[2] suggests the possibility of heterocycles in which CF_3P is replaced by another bifunctional unit. However, various attempts to make CF_3P–O heterocycles have failed, and recent attempts toward CF_3P–NR heterocycles fared no better.[3] One may argue that the $(CF_3P)_n$ rings are stabilized by circumannular delocalization of the phosphorus lone-pair electrons *via* the P_{3d} orbitals (enhanced by the electron-withdrawing CF_3 groups), whereas the insertion of N or O into the ring would block such delocalization. Hence a $(CF_3P)_nO$ or $(CF_3P)_nNR$ ring might be far less stable than other arrangements of the same atoms.

However, the insertion of sulfur into the P_n ring would not block the 3d delocalization; rather, S_{3d} would contribute only a little less π-bonding energy than P_{3d} aided by CF_3.

Accordingly, the stable compound $(CF_3P)_4S$ can be made by direct addition of S_8 to $(CF_3P)_4$ at temperatures in the μ-sulfur range. Although this inorganic thiophene analog is the first clearly recognized product of the reaction, other P–S heterocycles apparently are formed in larger yield.

Synthesis. Each of the two main experiments employed 1 g-atom of sulfur[4] per $(CF_3P)_4$, in sealed tubes at 170–250° for as long as 5 hr. The colorless liquid mixture consisted mostly of an oil which could be refluxed under high vacuum only by heating toward 100°. However, about 15% of it was a liquid having 1-mm vapor tension at 25°, separable from the 27–35% of unconsumed $(CF_3P)_4$ by a high-vacuum microcolumn (boiler, 50°; reflux, 0°). It showed the vapor-phase molecular weight (437 or 432) and chemical behavior expected for a heterocyclic $(CF_3P)_4S$. Its strong infrared spectrum in the C–F stretching region lacked certain intense peaks characteristic of $(CF_3P)_n$: the tetramer had been removed and the pentamer had not been formed at the reaction temperature.

A less volatile fraction (*ca.* 0.5 mm at 25°) showed a different infrared spectrum (*e.g.*, a single main C–F stretching peak at 1153 cm^{-1}). It was heated in a sealed tube with mercury (48 hr, 145°), forming HgS and nearly pure $(CF_3P)_4S$, but no $(CF_3P)_n$. Removal of one S from a P–S–S–P situation is suggested.

Chemical Proof of Formula. The most direct proof of the formula $(CF_3P)_4S$ is described by the following equation with mmole stoichiometry.

$$\begin{array}{cccc} (CF_3P)_4S + & (CH_3)_3P \longrightarrow & (CH_3)_3PS + & 4CF_3P \\ 0.359 & 0.399 & 0.352 & 1.432 \\ & \underline{-0.036} & & (99.7\%) \\ & 0.363 & & \end{array}$$

The sample was from the mercury-treated product. A more direct column distillate (mol wt obsd 432) slowed slightly more sulfur and less CF_3P per mole, suggesting impurities such as $(CF_3P)_4S_2$ and $(CF_3P)_3S$. The principle of the method relates to the reversible

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[1] Supported by Grant No. GP-3812 from the National Science Foundation, which contributed also through Grants GP-199 and G-14665 toward the purchase of the Beckman IR7 spectrophotometer with NaCl and CsI optics.
[2] W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).
[3] J. Heners and A. B. Burg, *ibid.*, **88**, 1677 (1966).
[4] A spectroscopically pure crystalline product of American Smelting and Refining Co., kindly supplied by Professor J. Donohue.