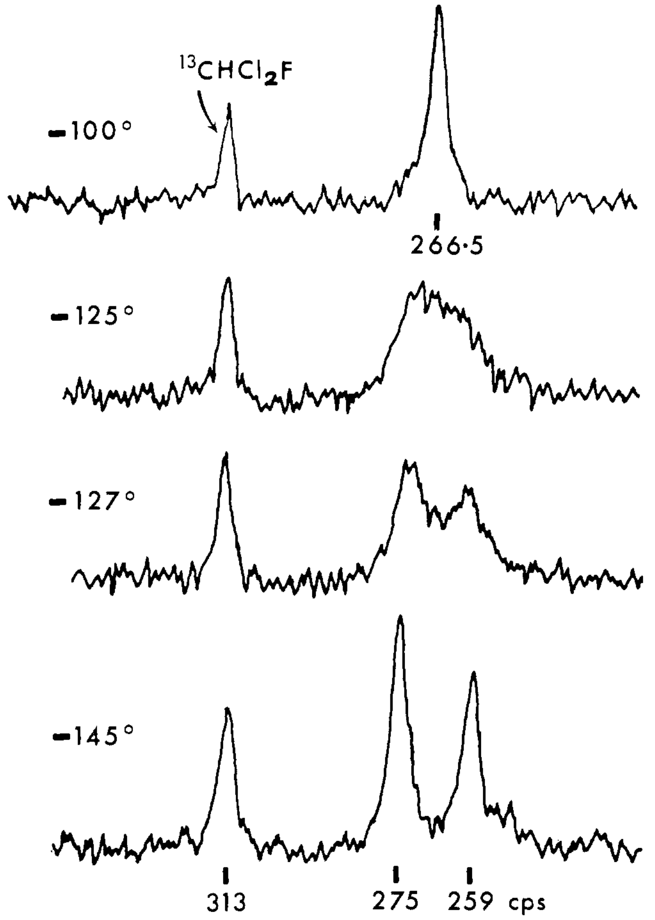
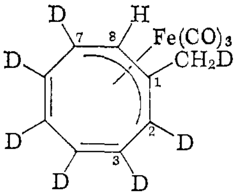
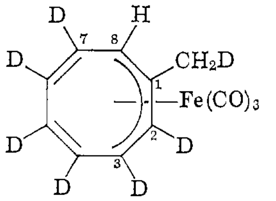


Figure 1. Proton spectrum (60 Mc/sec, deuterons decoupled) of II in $CHCl_2F$ at various temperatures. Only the olefinic region is shown. The scale is cps downfield from internal tetramethylsilane.

ature (−125°) for the ring-proton bands, the rate constant for the valency tautomerism, IIa $\rightleftarrows$ IIb, is 35 sec^{-1}, and the free energy of activation (ΔF^*) is 7.5 kcal/mole, a value close to the 7.2 kcal/mole observed[8] for the parent compound.



Ia (D replaced H)
IIa



Ib (D replaced H)
IIb

The average of the chemical shifts of the two ring-proton bands at −150° is very close to the chemical shift of the coalesced bands (*e.g.*, at −100° or higher). This is in agreement with the conclusion based on the chemical shift of the ring proton that tautomers other than IIa or IIb must be present in very small amounts.

Tautomers other than IIa or IIb should show a ring-proton band at low field (*ca.* τ 4) at −145°, but ununfortunately this region is partly obscured by a ^{13}C satellite of the solvent as well as being very close to an intense solvent peak. We plan to examine the spectrum further in a deuterated solvent, which should allow the detection of small peaks in this region. On the basis of the present evidence, it appears that more than 90% of II is in the form of IIa and IIb.

The present work does not allow an unambiguous assignment to be made to the ring-proton bands in the low-temperature spectrum of II. Since the ring proton in IIb would be expected to be upfield from that in IIa,[9] the bands at τ 5.42 and 5.68 can be assigned tentatively to IIa and IIb, respectively.

The origin of the low energy of IIa and IIb is of interest. In IIa or IIb the methyl group is attached to a ring carbon atom which in cyclooctatetraeneiron tricarbonyl[10] has an internal angle of 124.6°. In other tautomers of II the methyl group would be attached to carbon atoms having internal angles greater than 130°. From previous work[3,11] on the rates of ring inversion and bond shift in derivatives of cyclooctatetraene (COT), it is known that large groups, and even methyl groups,[12] destabilize the planar form of COT (bond angles of 135°) relative to the tub form (bond angles of about 125°). This effect was ascribed to the greater steric repulsions existing between a substituent and adjacent hydrogen atoms in the planar form relative to the tub form. Although II is nonplanar, these steric effects should operate to make IIa and IIb more stable than other tautomers. Steric repulsions between the $Fe(CO)_3$ and the methyl group would destabilize IIa and IIb and therefore do not appear to be important. Inductive and hyperconjugative effects of the methyl group may be significant in stabilizing IIa and IIb; experimental investigations of this possibility are planned.

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group and relaxation by the direct spin-spin interactions modulated by molecular rotation.

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[12] The rate constant for bond shift[4] in III at −10° is not more than one-tenth of that[11] in cyclooctatetraene.

Mass Spectrometric Evidence for the Gaseous Si_2N Molecule

Sir:

Optical spectroscopic studies[1] and ionic-model calculations[2] have indicated that the binding energies of gaseous nitrides should be of the order of 100 kcal mole^{-1}, and thus one expects that gaseous nitrides should be relatively stable. Most of the refractory nitrides have been reported, however, to dissociate when heated under vacuum.[3–7] Only gaseous gallium

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Table I. Partial Pressures of Gaseous Species over the Si-BN System and Heat of the Reaction $Si_2N(g) = 2Si(g) + 0.5N_2(g)$

Temp, °K	Pressure, atm: Si	Pressure, atm: N_2	Pressure, atm: Si_2N	$-4.576 \log K$, cal deg^{-1} mole^{-1}	$-\Delta\left(\frac{F°_T - H°_{298}}{T}\right)$, cal deg^{-1} mole^{-1}	$\Delta H°_{298}$, kcal mole^{-1}
1846	8.03×10^{-6}	2.82×10^{-4}	2.17×10^{-7}	24.3	(43)	124
1806	4.34×10^{-6}	1.91×10^{-4}	1.08×10^{-7}	25.7	(43)	124
1765	2.30×10^{-6}	1.19×10^{-4}	4.20×10^{-8}	26.8	(43)	123
1742	1.66×10^{-6}	1.05×10^{-4}	2.83×10^{-8}	27.4	(43)	123
						$\Delta H°_{298} = 123.5 \pm 1.0$

nitride has been observed mass spectrometrically,[8] but no attempt was made to establish its stability. Optical spectra have been cited as evidence for gaseous MoN[9] and TiN.[10]

In the course of a mass spectrometric study of the vaporization of silicon from a boron nitride Knudsen cell, the Si_2N molecule has been identified in the gas phase. This species is isoelectronic with the well-established gaseous species C_2N for which both the CCN and CNC isomers are known from optical spectra.[11]

The experiments were performed on a 12-in. radius, 60°-sector mass spectrometer, similar to that described by Chupka and Inghram.[12] The Knudsen cell was machined from a high-purity boron nitride rod and was tightly fitted into a heavy tantalum crucible. The cell was heated by electron bombardment, and the temperature was measured with an optical pyrometer sighted into the blackbody hole in the bottom of a tantalum crucible.

With the cell heated above 1500°K, the main peaks in the mass spectrum were N_2^+ and Si^+, both increasing with temperature. At temperatures above 1700°K, the ions Si_2^+, Si_3^+, and Si_4^+, as well as peaks at *m/e* 70, 71, and 72, were observed. From the isotopic abundance calculations the peaks at masses 70, 71, and 72 were identified with the Si_2N^+ ion. The appearance potential, determined by the vanishing-current method, using the ionization potential of Si as standard was 9.4 ± 0.3 ev. This value suggests that the Si_2N^+ ion is formed by direct ionization of the Si_2N molecule and not by fragmentation.

It was impossible in these experiments to decide unambiguously whether the molecules Si_2N_2 or Si_2N_4 existed in the vapors, because of interference of Si_3^+ and Si_4^+ ions at the same mass.

The ion intensities of Si^+, N_2^+, and Si_2N^+ were measured at several temperatures in the range 1742–1846°K and were used to calculate the equilibrium constant for the reaction

$$Si_2N(g) = 2Si(g) + 0.5N_2(g) \qquad (1)$$

With the JANAF[13] free-energy functions for Si(g) and N_2(g), values for Si_2N(g), estimated by analogy with Al_2O(g), and equilibrium constants derived from the ion-current data with the aid of a silver calibration, one can derive the heat of reaction 1 by the third-law method. The results are given in Table I.

From the heat of reaction 1 and the heat of sublimation of silicon, $\Delta H_s°_{298} = 108.4 \pm 3.0$ kcal mole^{-1},[14] one calculates $\Delta H_f°[Si_2N(g)] = 93 \pm 5$ kcal mole^{-1}. The heat of atomization of Si_2N(g), as calculated from the heat of reaction 1 and the dissociation energy of N_2, $D_0° = 225.0 \pm 2$ kcal mole^{-1},[13] is $\Delta H_a[Si_2N(g)] = 236 \pm 10$ kcal mole^{-1}, close to the atomization energy for Al_2O of 248 kcal mole^{-1}.[15]

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Sulfur Dioxide Insertion. IV. A New Allylic Rearrangement[1]

Sir:

The unusual paucity of data on insertion reactions of σ-bonded allylic complexes of the transition elements[2] prompted us to examine the behavior of several such organometallics toward sulfur dioxide. Reported now are some preliminary results on a new type of rearrangement which accompanies insertion of SO_2 into metal–carbon bonds.

The qualitative observation of one of us (F. A. H.) that allylmanganese pentacarbonyl inserts sulfur dioxide at a rate much faster than do the methyl and benzyl analogs[3] suggested a possibility of mechanistic differences between these reactions. Particularly inviting was a path involving an allylic rearrangement resulting from cleavage of the Mn–C(1) bond and formation of the Mn–S and S–C(3) bonds (eq 1). In order to test for this possibility we have examined the reaction of

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(1) For part III of this series, see J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, **88**, 4862 (1966).

(2) The only example of such reactions known to the authors is the reversible carbonylation of allylmanganese pentacarbonyl: T. H. Coffield, J. Kozikowski, and R. D. Closson, Lecture to International Conference on Coordination Chemistry, London, England, April 1959; quoted by G. E. Coates, "Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960, p 280.

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