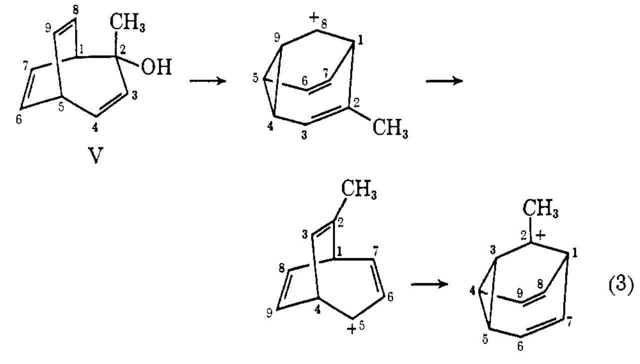
−5°.[23] This remarkable influence of the charge on the Cope rearrangement will probably be enhanced in III. This suggests an even higher barrier for a Cope averaging process for III than for VII. The barrier of 7.3 kcal/mol observed for III thus is suggested to be the barrier for the concerted divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl rearrangement (eq 2).[22]

Formation of III from V can be rationalized by invoking mechanisms (eq 3)[23] that involve the interconversion of barbaralyl and bicyclo[3.2.2]nonatrienyl cations. If bicyclo[3.2.2]nonatrienyl cations are intermediates in the transformation of V to III, these by necessity have to be less stable than III. The exclusive rearrangement of III to VI shows that VI is the most stable of the species studied in this investigation, possibly because of its bishomoaromatic character.[5]



V

III

(3)

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[21] $\Delta S^{\ddagger}$ is assumed to be *ca.* 0 eu.

[22] The concerted divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl rearrangement for VII is considered to be a high-energy process compared to the same process for III.

[23] Equation 3 is one of several possible mechanisms that contain the bicyclo[3.2.2]nonatrienyl cation.

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The Gas to Condensed Phase Transition in Hot Atom Chemistry

Sir:

Interpretation of hot atom phenomena in gaseous media has become relatively straightforward.[1] In saturated systems primary products are formed by abstraction or displacement occurring by direct mechanisms (*i.e.*, single-step processes not involving persistent intermediates[1]). Secondary decomposition of such products may often occur but is usually identifiable. Condensed-phase hot atom phenomena are less well understood. While hot hydrogen reactions are normally relatively phase independent,[2,3] yield spectra of hot halogen processes are often drastically different in gas and condensed media.[4] Despite much discussion of these differences their origin remains speculative.[4] This is largely because scavenger methods are unable to distinguish between direct hot reactions and thermal processes occurring in solvent cages.

We have approached this problem by taking a relatively well-understood low-pressure gas system and observing the effect of a continuous increase in density to that of a close-packed liquid or solid. A pioneering study of this type found an apparently linear rise in yields.[5] Interpretation of this, and related experiments on phase effects,[4] was hampered by lack of information regarding both primary processes (including possible reactions of the recoil species as ions) and the scavenging of thermalized entities.

Absolute yields of ^{18}F-labeled products from the reactions

$$^{18}\mathrm{F}^* + \mathrm{CH_3F} \longrightarrow \mathrm{CH_3{}^{18}F} + \mathrm{F} \text{ and } \mathrm{CH_2F^{18}F} + \mathrm{H} \quad (1)$$

were measured for densities from 0.0014 g cm^{-3} (gas at 1.1 atm) to 1.1 g cm^{-3}. This system was chosen because these and similar gas-phase reactions have now been studied quite extensively,[6–10] and because of the low critical temperature of CH_3F (44.9°).

Samples in sealed Pyrex ampoules at 55° were run up to twice the critical density. Beyond this it was necessary to lower the temperature to avoid excessive pressures.

Hot ^{18}F was produced by the ^{19}F(n,2n)^{18}F process, occurring within the ampoules. (The requisite fast neutrons resulted from 26-MeV protons causing p(d,n)2p reactions in heavy water.[11]) There was no apparent radiation damage; acetylene–benzene dosimeters indicated energy deposition $<10^{-2}$ eV/molecule.

Analysis was by radiogas chromatography.[7,12] $CH_3{}^{18}F$, $CH_2F^{18}F$, and other low-boiling products were separated on a combined (3-m 40% hexamethylphosphoramide, 8-m 30% silicone oil (GE SF97) on chromosorb P) column at 25°. A thin-window flow-proportional counter[13] provided assays of ^{18}F-labeled products. Absolute yields are based on total available ^{18}F, as estimated using monitor samples irradiated simultaneously under the same or similar conditions.

In one series of runs, iodine at its saturation concentration and 6 mol % ethylene were both present as scavengers;[14] in another only iodine was used. Results

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[1] R. Wolfgang, (a) *Progr. React. Kinet.*, **3**, 99 (1965); (b) *Annu. Rev. Phys. Chem.*, **16**, 15 (1965).

[2] M. Menzinger and R. Wolfgang, *J. Phys. Chem.*, **72**, 1789 (1968).

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[10] Y. N. Tang, T. Smail, and F. S. Rowland, *ibid.*, **91**, 2130 (1969).

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[14] We have no absolute assurance that in the dense samples the

were similar, except that in the presence of ethylene individual yields were uniformly reduced by a factor of about 0.1. This indicates that ethylene acts primarily as a diluent and that thermal fluorine atoms are scavenged otherwise, as suggested previously,[7b] probably by the reaction

$$^{18}F + CH_3F \longrightarrow H^{18}F + CH_2F \qquad (2)$$

Results obtained in the absence of ethylene are shown in Figure 1. Absolute yields of two substitution products are plotted against density and estimates of the corresponding mean intermolecular distance.[15]

Both $CH_3{}^{18}F$ and $CH_2F^{18}F$ show sharp rises in yields from the lowest gas densities, leveling off at about 0.2 g cm^{-3} (50–100 atm). This behavior is characteristic of improving collisional deexcitation of primary products formed with such high internal energy that they would otherwise undergo secondary decomposition. Applying simple unimolecular decay theory to the results indicates that a substantial fraction of the primary substitution processes yield labeled molecules with internal energies of the order of 10 eV. This finding is consistent with early results indicating that reactions of hot fluorine tend to leave much more highly excited products[16] than do analogous hot hydrogen processes, and with more recent findings on C_2F_6[17] and on CH_3CF_3.[18]

Of even greater magnitude is a second rise in yields at higher densities. It is unlikely that this is a temperature- rather than a density-dependent phenomenon, since temperature effects of this magnitude are neither expected nor have been found for true hot atom processes. Experiments at approximately 0.55 g/cm^3 indicate temperature coefficients of yields near zero and smaller than required to account for the rise at high densities. It is also implausible to ascribe this phenomenon to collisional stabilization of excited molecules. At these densities this would require that a large fraction of product molecules would have to be stabilized before they moved more than a few tenths of an ångström. This would imply lifetimes of the order of a vibrational period or less, meaning that the entity involved was not bound in the first place.

The most natural explanation of the final rise in yields is that it is due to caging effects. Fluorine atoms having more energy than is optimum for the one-step substitution reactions (1) can nevertheless rupture bonds, *e.g.*

$$^{18}F^{**} + CH_3F \longrightarrow CH_3 + F + {}^{18}F^{*} \qquad (3)$$

$$\longrightarrow CH_2F + H + {}^{18}F^{*} \qquad (4)$$

In the gas phase the products of such processes will separate, but at higher densities they may be mutually confined in the same solvent cage. The $^{18}F^*$ can then lose the remainder of its excess energy and undergo a secondary recombination to form the same products that resulted from the direct processes.

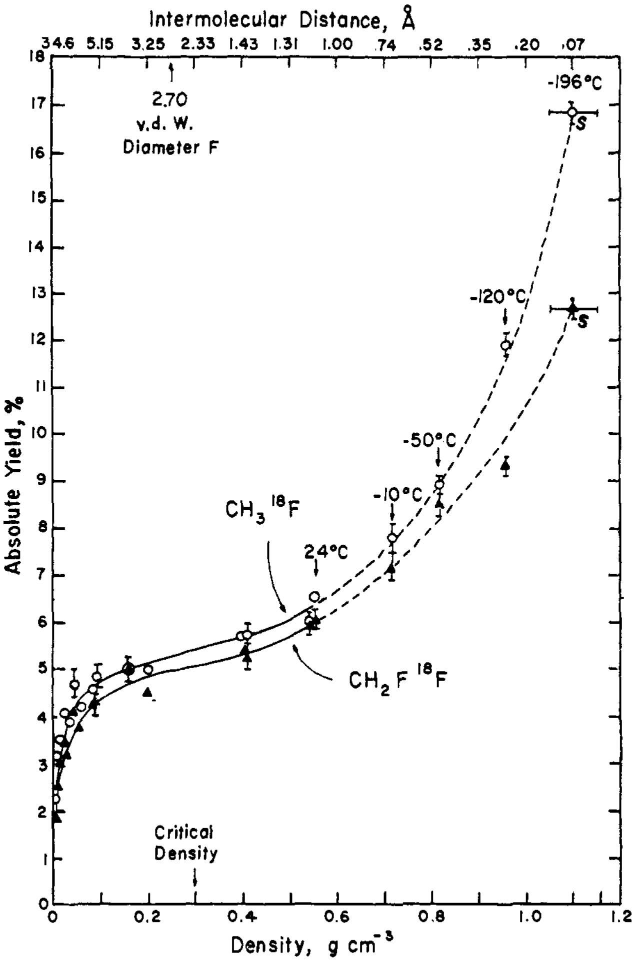

Figure 1. Absolute yields of single displacement products as a function of density in the $CH_3F–I_2$ system: $CH_3{}^{18}F$, ○; $CH_2F^{18}F$, ▲. Temperature at 55° unless otherwise specified. Iodine either at vapor pressure at 55° or at saturated solution concentration at the specified temperature. S indicates sample was solid, otherwise it was fluid.

$$CH_3 + {}^{18}F \longrightarrow CH_3{}^{18}F \qquad (5)$$

$$CH_2F + {}^{18}F \longrightarrow CH_2F^{18}F \qquad (6)$$

Such Franck–Rabinowitsch caging[19] has long been postulated as a central concept in condensed-phase hot atom chemistry.[4,20,21] However, evidence for it has been quite indirect and subject to other plausible interpretations,[4] such as attribution to ionic or unscavenged thermal processes.

Figure 1 indicates that caging becomes important only when mean intermolecular distances shrink to about half the diameter of the fluorine atom. That is reasonable, since there will always be some larger interstices in the cage wall through which the energetic atom can squeeze. It is also consistent with the earlier finding that in hydrocarbons the small hydrogen atoms cannot be effectively caged at all.[2]

Acknowledgment. The authors are indebted to Dr. John Hawke for design of the irradiation facility, to the

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ethylene was in solution. Since it seems to act as diluent only, this uncertainty is not critical.

[15] The "mean intermolecular distance" is computed as $(4.30\rho^{1/3} - 4.10)10^{-8}$ cm. The first term is the mean distance between molecular centers assuming closest packing of spheres. The second is an estimate of the viscosity diameter of CH_3F.

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staff of the University of Colorado cyclotron, and to the U. S. Atomic Energy Commission for its support.

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The Diammoniate of Pentaborane(9)

Sir:

It is known that diborane(6), tetraborane(10), and pentaborane(11) react with ammonia to give diammoniates containing the $H_2B(NH_3)_2^+$ cation, *i.e.*, $[H_2B(NH_3)_2^+][BH_4^-]$,[1] $[H_2B(NH_3)_2^+][B_3H_8^-]$,[2] and $[H_2B(NH_3)_2^+][B_4H_9^-]$,[3] respectively. Structural features of these parent boranes are similar in that each of them contains a BH_2 group bonded by two hydrogen bridge bonds. Pentaborane(9), not having this particular structural feature, has been regarded as a compound that belongs to another category.[4,5] A different kind of reaction might be anticipated.

In 1924 Stock reported[6] the tetraammoniate of pentaborane(9), $B_5H_9 \cdot 4NH_3$, as a stable, white solid. Characterization of the compound, however, was not complete. More recent work by various investigators has revealed that pentaborane(9) reacts with bases in both the Lewis acid and Brønsted acid sense.[7–13] In the present study it has been shown that pentaborane(9) will also react with ammonia under controlled conditions to give the ionic compound $[H_2B(NH_3)_2^+][B_4H_7^-]$. The $B_4H_7^-$ anion has not been isolated previously.

An ethereal solution of pentaborane(9) was stirred at −78° while ammonia gas was introduced slowly above the surface of the solution. The ammonia was absorbed and a white precipitate separated slowly from the initially clear solution. The molar ratios of ammonia and pentaborane(9) used in the reaction vessel varied from run to run and ranged from two up to eight. After a given mixture had been standing at −78° for several days, the volatile components were pumped out while the temperature of the system was held at −78°. The temperature was then raised to −45° and to 25° for *a very few minutes*. The white residue which remained in the reaction vessel was stable below 0°, but decomposed spectacularly on standing at room temperature. For this reason prolonged exposure to the pumps at 25° must be avoided.

The reaction of the solid with *excess* hydrogen chloride in ether at −78° gave a precipitate of $H_2B(NH_3)_2^+Cl^-$.[1] The yield of $H_2B(NH_3)_2^+Cl^-$ accounted quantitatively for all of the ammonia consumed in the reaction. No hydrogen gas was evolved, and X-ray diffraction did not indicate the presence of ammonium chloride in the precipitate.

When hydrogen chloride was added to the ammoniate of pentaborane(9) in a *one-to-one molar ratio* (no excess HCl used), $H_2B(NH_3)_2^+Cl^-$ separated again as a white precipitate. To the supernatant liquid an equivalent amount of $(CH_3)_2NPF_2$ was added at −78°. After standing for about 12 hr at −78° the system was fractionated by a trap-to-trap distillation. A good yield of $(CH_3)_2NPF_2B_4H_8$[14] resulted.

The foregoing observations can be summarized by the following equations.

$$B_5H_9 + 2NH_3 \xrightarrow[\text{ether}]{-78°} [H_2B(NH_3)_2^+][B_4H_7^-]$$

$$[H_2B(NH_3)_2^+][B_4H_7^-] + HCl \xrightarrow[\text{ether}]{-78°} H_2B(NH_3)_2^+Cl^- + B_4H_8 \cdot O(C_2H_5)_2$$

$$B_4H_8 \cdot O(C_2H_5)_2 + (CH_3)_2NPF_2 \xrightarrow[\text{ether}]{-78°} (CH_3)_2NPF_2B_4H_8 + O(C_2H_5)_2$$

The details of characterization of the diammoniate and the work on related systems will be described in subsequent publications.

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Structure and Stereochemical Nonrigidity of Six-Coordinate Complexes

Sir:

Earlier[1] we described the stereochemical nonrigidity of two six-coordinate metal hydrides, $H_2Fe[P(OC_2H_5)_3]_4$

Table I. Phosphinometal Dihydrides

$H_2Fe[P(OC_2H_5)_3]_4$	**1**	$H_2Ru[P(OCH_3)_3]_4$	**7**
$H_2Fe[C_6H_5P(OC_2H_5)_2]_4$	**2**	$H_2Ru[P(OC_2H_5)_3]_4$	**8**
$H_2Fe[P(OCH(CH_3)_2)_3]_4$	**3**	$H_2Ru[P(OCH(CH_3)_2)_3]_4$	**9**
$H_2Fe[C_6H_5P(OCH(CH_3)_2)_2]_4$	**4**	$H_2Ru[C_6H_5P(OC_2H_5)_2]_4$	**10**
$H_2Fe[P(OCH_2)_3CC_2H_5]_4$	**5**	$H_2Ru[C_6H_5P(CH_3)_2]_4$	**11**
$H_2Fe[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$	**6**	$H_2Ru[C_6H_5P(C_2H_5)_2]_4$	**12**
		$H_2Ru[(C_6H_5)_2PCH_3]_4$	**13**
		$H_2Ru[(C_6H_5)_2POCH_3]_4$	**14**

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