In the inverse process, rotational energy has a special contribution to bond breaking. Thus, in the pyrolysis of C_2H_6 into $2CH_3$, at 1000°K the typical excited $C_2H_6^*$ molecule which reacts contains about 10 kcal of rotational energy and a minimum of 78 kcal of internal vibrational energy which do not exchange with each other.

Another consequence of the formation of rotationally hot species in association reactions is that the quenching or stabilization of these species, which has been presumed to be vibrational in nature, can more likely be by a much faster path, namely by rotational quenching. The author has shown[8] that the N_2 afterglow can be quantitatively accounted for by a near-pseudo-equilibrium of rotationally cooled $N_2(^3B^{12})$ species with rotationally hot species and with N atoms.

In similar fashion, the recombination reactions $M + O + O_2 \rightarrow O_3 + M$ and $NO + O + M \rightarrow M + NO_2$, which must almost certainly take place *via* a two-step mechanism

$$O + O_2 \overset{1}{\rightleftarrows} O_3^*;\quad O_3^* + M \overset{2}{\rightleftarrows} O_3 + M;\quad \text{etc.}$$

involve rotational quenching of nascent O_3^* and NO_2^*. If estimates can be made of the absolute over-all rate constant k_r from a two-step mechanism, the calculated rates are smaller by a factor of from 20 to 50 than the observed rates. If, however, a more complex mechanism is used[9]

$$O_2 + O \overset{1}{\rightleftarrows} O_3^{V,R} \qquad \text{(fast)}$$

$$O_3^{V,R} + M \overset{2}{\rightleftarrows} O_3^{V} + M \qquad \text{(slow)}$$

$$O_3^{V} + M \overset{3}{\rightleftarrows} O_3 + M \qquad \text{(slower)}$$

Then, because steps 1 and 2 are virtually at equilibrium, the over-all rate constant is approximately $k_r \leq K_1K_2k_3$, where K_2 is the equilibrium constant for an exothermic reaction and contributes a large negative activation energy of the order of about $4RT$ to k_r. A similar analysis gives values of k_r very close to experimental for NO_2 recombination and chemiluminescence and for O_3 formation. Further details will be reported later.

A final example is provided by dissociative recombination, such as

$$e^- + NO^+ \overset{1}{\rightleftarrows} (NO)^* \overset{2}{\rightleftarrows} N + O$$

Since these reactions are strongly exothermic and have extremely large cross sections, the reverse reactions (O + N) have large activation energies.[10] In this case, the reverse reaction can be shown to have very small impact parameters less than or equal to the internuclear distance in the cation. Larger impact parameters will produce rotationally hot cations, which are energetically not possible.[11] Using the cation bond length for a collision diameter, one can calculate upper limits for dissociative recombination which are larger than the measured rate constants[12] by less than a factor of 2 or 3.

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[7] Using a simple potential energy function, such as Morse or Lennard-Jones, yields an even larger impact parameter for the collision, and hence more rotational energy; see, S. W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1968, p 105.

[8] S. W. Benson, *J. Chem. Phys.*, **47**, 4199 (1967). This effect also makes possible depletion of states below the dissociation threshold.

[9] Superscripts E, V, and R denote electronic, vibrational, and rotational excitation, respectively.

[10] Typical values are from 2 to 5 eV, even when excited electronic states are produced.

[11] Current data indicate no activation energy for $e^- + AB^+$. Some evidence does exist that rotationally excited cations do have slightly higher cross sections than normal cations: W. L. Fite, personal communication.

[12] S. W. Benson, unpublished work. This model also appears to give the proper ratio of production of the different allowed excited states of the product of atoms. H_2^+ and He_2^+ are not predicted accurately by this method.

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Reaction of Carbon Vapor Produced by Laser Evaporation of Graphite[1]

Sir:

Evaporation of solid substances by a focused laser pulse offers a useful method of producing highly reactive and unusual reagents. For example, Howe[2] has reported that a 1-J pulse of 6943-Å light on graphite was shown to vaporize about 1 μg of carbon; he observed only C_2 molecules spectroscopically. In contrast, Berkowitz and Chupka[3] in a study of laser-produced carbon vapor that had been ionized in a mass spectrometer showed that various carbon species (C_1, C_2, C_3, C_4, C_5) were present in the amounts that conformed well to the equilibrium concentration over graphite at 4000°K. The carbon molecules formed *via* laser evaporation should be highly interesting chemical reagents available for reaction under unusual conditions of very rapid heating and quenching.

We have shown that carbon vapor produced from graphite by a 1.06-μ laser pulse of 7 J reacts in high yield with hydrogen to produce acetylene as the principal product. Methane, ethylene, and propyne are minor products of the reaction. In addition, 1,3-butadiyne is present in the reaction products and is apparently the result of reaction of additional carbon vapor with acetylene. In an experiment in which graphite in an atmosphere of hydrogen was irradiated with ten laser pulses, a mass spectrometric analysis showed that acetylene constituted 95% of the accumulated volatile products. In a separate experiment, 1.5 mg of carbon was evaporated by 13 7-J pulses on graphite in a calibrated infrared cell containing 70 cm of H_2, and over 90% of the evaporated carbon was converted to acetylene. The buildup of acetylene was followed *via* infrared scans after individual bursts. With succeeding laser bursts, 1,3-butadiyne formed and appeared in greater quantity per burst late in the experiment. At lower hydrogen pressure (10 cm),

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. A. Howe, *J. Chem. Phys.*, **39**, 1362 (1963).

[3] J. Berkowitz and W. A. Chupka, *ibid.*, **40**, 2735 (1964).

carbon was deposited on the walls of the cell, and the yield of acetylene fell correspondingly.

To further confirm the fact that acetylene was formed by reaction of the evaporated carbon,[4] the experiment was carried out with carbon evaporated into deuterium, and the corresponding deuterated products were identified. When carbon was evaporated into an argon atmosphere *via* focused laser bursts, no volatile products were formed, and a black deposit of carbon coated the walls of the cell.

Evidence that butadiyne results from reaction of acetylene with carbon vapor was obtained from an experiment in which carbon was evaporated in an infrared cell containing acetylene at 10 cm pressure. Under these conditions, 1,3-butadiyne was produced in much larger quantity than in the above reactions of hydrogen with carbon vapor, but the yield was not quantitative since some of the carbon was deposited on the walls of the cell.

It has been found that carbon vaporized by laser pulses on graphite undergoes a variety of reactions with oxygen, hydrogen chloride, sulfur, nitric oxide, nitrous oxide, carbon tetrachloride, silane, and olefins. Further experimentation is continuing in these studies and details will be reported at a later date.

The generality of the technique has further been demonstrated by formation of boron trichloride from laser-evaporated boron in a hydrogen chloride atmosphere.

Acknowledgment. The authors wish to thank Dr. James Swain for making the laser facility at the Lawrence Radiation Laboratory available for this work.

[4] It has been shown that a laser pulse on coal produces a variety of hydrocarbon products: A. G. Sharkey, Jr., J. L. Shultz, and R. A. Friedel, "Gases from Flash and Laser Irradiation of Coal," Advances in Chemistry Series, No. 55, American Chemical Society, Washington, D. C., 1966, pp 643–649.

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A Novel Synthesis of Methyl Trimethylsilanecarboxylate. The n → π^* Transition of Silanecarboxylates

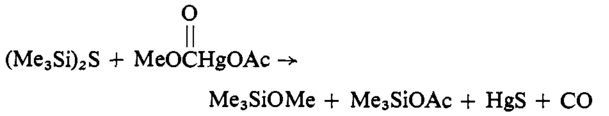
Sir:

We wish to report a novel synthesis of methyl trimethylsilanecarboxylate (**1**). Previously reported[1,2] silanecarboxylates have been prepared *via* the silyllithium reagent and have had phenyl groups present to facilitate the formation of the lithium compound.[3,4] As a result **1** is the first silanecarboxylate for which the electronic spectrum attributable to the n → π^* transition of the carbonyl group has been observed. There is a great deal of current interest in the effect of the silicon on the n → π^* transition in the ultraviolet absorption spectra of the related acylsilanes,[6-10] and it seemed of considerable interest to determine if a similar effect was present in **1**.

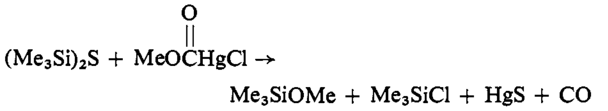
When hexamethyldisilthiane[11] (13.5 mmol) was slowly added to a mechanically stirred mixture of bis(carbomethoxy)mercury[12] (13.5 mmol) in 10 ml of ether effervescence of carbon monoxide occurred and a gray-white solid precipitated. Gas–liquid partition chromatography[13] indicated that the only volatile components were ether, hexamethyldisilthiane, and a small amount of trimethylmethoxysilane. When the mixture was refluxed for 40 hr under a nitrogen atmosphere the solid slowly turned black. Filtration gave 3.1 g (98%) of mercuric sulfide. Glpc of the filtrate showed, in addition to solvent, trimethylmethoxysilane and **1** in a 1:2 molar ratio. Preparative-scale glpc[14] gave 1.1 g (35%) of **1**.

Bis(trimethylsilyl)mercury,[16] (**2**) reacted rapidly at room temperature with carbomethoxymercuric chloride[12] to give **1** (30%), trimethylmethoxysilane (60%), and trimethylchlorosilane (10%). Since **2** is considerably more difficult to prepare and handle than hexamethyldisilthiane, this preparation is less useful than the first one.

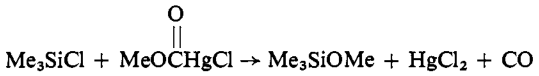
A number of unsuccessful attempts to prepare **1** are outlined below in eq 1–3. All of these reactions proceeded under mild conditions to give virtually quantitative yields of the products shown. No other products were detected by glpc or nmr in any of these systems.



$$(Me_3Si)_2S + MeO\overset{O}{\overset{\|}{C}}HgOAc \rightarrow Me_3SiOMe + Me_3SiOAc + HgS + CO \quad (1)$$



$$(Me_3Si)_2S + MeO\overset{O}{\overset{\|}{C}}HgCl \rightarrow Me_3SiOMe + Me_3SiCl + HgS + CO \quad (2)$$



$$Me_3SiCl + MeO\overset{O}{\overset{\|}{C}}HgCl \rightarrow Me_3SiOMe + HgCl_2 + CO \quad (3)$$

Methyl trimethylsilanecarboxylate (**1**) was a volatile, sweet smelling liquid. Complete decarbonylation of **1** occurred within 0.5 hr at 200°. The infrared carbonyl

$$1 \xrightarrow[200^\circ]{} Me_3SiOMe + CO$$

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[1] A. G. Brook, *J. Amer. Chem. Soc.*, **77**, 4827 (1955); A. G. Brook and R. J. Mauris, *ibid.*, **79**, 971 (1957).

[2] H. Gilman and W. J. Trepka, *J. Org. Chem.*, **25**, 2201 (1957).

[3] D. Wittenberg and H. Gilman, *Quart. Rev.* (London), **13**, 116 (1959).

[4] The carbonation of triethylsilyllithium to give triethylsilanecarboxylic acid in low yield has been claimed, but no experimental details or properties of the acid have been reported.[5]

[5] N. S. Vyazankin, G. A. Razuvaev, E. N. Gladyshev, and S. P. Korneva, *J. Organometal. Chem.*, **7**, 353 (1967).

[6] A. G. Brook, *Advan. Organometal. Chem.*, **7**, in press.

[7] H. Bock, A. Alt, and H. Seidl, *J. Amer. Chem. Soc.*, **91**, 355 (1969).

[8] P. A. Jones and R. West, *ibid.*, **90**, 6978 (1968).

[9] G. J. D. Peddle, *J. Organometal. Chem.*, **14**, 139 (1968).

[10] F. Agolini, S. Kleimenko, J. G. Csizmadia, and K. Yates, *Spectrochim. Acta*, **24A**, 169 (1968).

[11] G. Champetier, Y. Etienne, and R. Kullman, *Compt. Rend.*, **234**, 1985 (1952).

[12] F. E. Paulik and R. E. Dessy, *Chem. Ind.* (London), **15**, 1650 (1962).

[13] All analytical glpc was done on an Aerograph A90-P3 instrument using a 20 ft × $\frac{1}{8}$ in. i.d. stainless steel column packed with 5% SE-30 on 60–80 mesh Chromosorb W.

[14] Preparative-scale glpc was done on an Aerograph A90-P3 instrument using a 10 ft × $\frac{3}{8}$ in. i.d. column packed with 30% SE30 on 60–80 mesh Chromosorb P. The retention volume of **1** was 1700 ml at a column temperature of 100°. *Anal.* Calcd for $C_5H_{12}O_2Si$: C, 45.4; H, 9.15; molecular ion: 132.0606. Found: C, 45.4; H, 9.03; molecular ion: 132.0606.[15]

[15] The mass spectrum was determined on an A.E.I. MS9 spectrometer at 70 eV.

[16] E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler, and E. Staude, *Angew. Chem. Intern. Ed. Engl.*, **2**, 507 (1963).