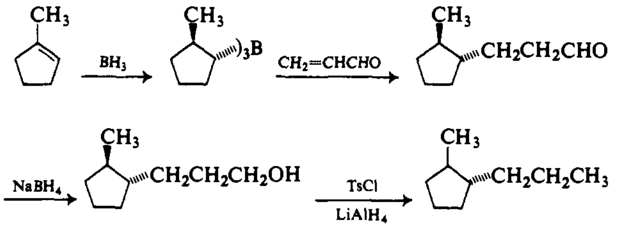
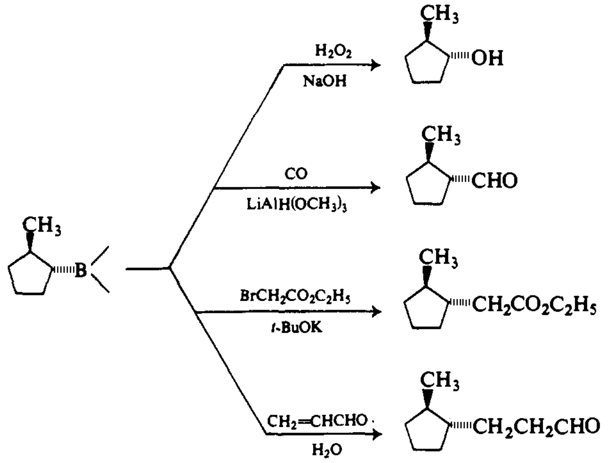

(6)

Consequently, the conversion of the *trans*-2-methylcyclopentylboron moiety into the alcohol (7), the aldehyde (8), the ester (9), and the γ-propanol derivative (10) all proceed with retention at the carbon atom undergoing substitution.

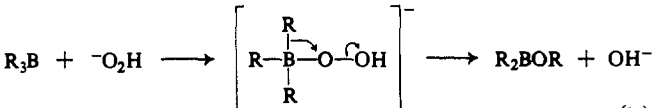

(7)

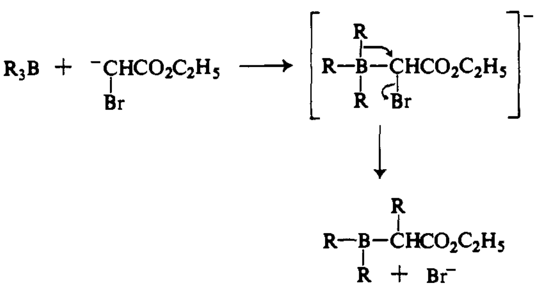
(8)

(9)

(10)

In these reactions the alkyl group is believed to migrate with its bonding pair from boron to another electron-deficient atom, as illustrated for oxidation[2] and the carbethoxymethylation[5] reactions (11, 12).


$$R_3B + {}^{-}O_2H \longrightarrow \left[R{-}\overset{R}{\underset{R}{B}}{-}O{-}OH \right]^{-} \longrightarrow R_2BOR + OH^{-}$$
(11)


$$R_3B + {}^{-}\underset{Br}{C}HCO_2C_2H_5 \longrightarrow \left[R{-}\overset{R}{\underset{R}{B}}{-}\underset{Br}{C}HCO_2C_2H_5 \right]^{-} \longrightarrow R{-}\overset{R}{\underset{R}{B}}{-}CHCO_2C_2H_5 + Br^{-}$$
(12)

This mechanism suggests that the migration of the group R from boron to carbon should involve an inversion at the receiving center. Indeed, Pasto and Hickman have demonstrated such an inversion in the rearrangement of α-haloorganoboranes obtained in the hydroboration of appropriate vinyl halides.[14]

It is evident that it is now becoming possible to control substitution processes to achieve either substitution with inversion or substitution with retention merely by controlling the reagents and reactions utilized. These developments greatly add to the versatility of the available procedures for organic synthesis.

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(14) D. J. Pasto and J. Hickman, *J. Am. Chem. Soc.*, **89**, 5608 (1967).

(15) Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

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Some Consequences of the Conservation of Angular Momentum in Chemical Kinetics

Sir:

Unimolecular fission reactions in which two radicals are formed have a "loose" transition state in which the two largest moments of inertia of the reactant molecule are appreciably larger than they are in the "ground" state.[1,2] One consequence of this, which has been discussed recently,[2,3] is that the rate constants for such reactions tend to be faster, both at the high- and low-pressure limits, than those for tight transition states.

A further consequence which has not been discussed explicitly is that the average reacting molecule undergoing fission is rotationally "hot." This effect has been demonstrated in the photolysis of NO_2[4] by showing that NO_2 could be photodissociated into NO + O by 4047 Å, which was about 1.3 kcal lower in energy than the bond dissociation energy. The energy deficit was provided by rotational energy.

The converse of this behavior should be exhibited by association reactions. Methyl radical recombination provides an excellent example. The measured rate of CH_3 recombination is about $10^{10.5}$ l./(mole sec).[5] If we count only singlet collisions as effective (*i.e.*, $^1/_4$), this rate constant at 400°K corresponds to a "hard-sphere" collision diameter of 3.5 Å. If we compare this to the ground-state C–C bond length of 1.54 Å, and treat the collision as a hypothetical diatomic pair, this corresponds to $r^{\ddagger}/r = 2.27$ and $I^{\ddagger}/I = 5.2$.[6] Now the average relative translational energy of an approaching $CH_3\cdots CH_3$ pair will be RT, so that the newly formed $C_2H_6{}^{*}$ molecule will be rotationally hot by $5.2RT$. At 400°K this corresponds to 4.2 kcal and at 1000°K, with the same recombination diameter, to 10.4 kcal.[7] Similar values apply to C_2H_5 recombination.

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(1) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964).

(2) R. A. Marcus, *J. Chem. Phys.*, **43**, 2658 (1965); **20**, 364 (1952); R. A. Marcus and O. K. Rice, *J. Phys. Colloid. Chem.*, **55**, 894 (1951).

(3) W. Forst, *J. Chem. Phys.*, **48**, 3665 (1968).

(4) J. N. Pitts, Jr., J. H. Sharp, and S. I. Chan, *ibid.*, **42**, 3655 (1964). The authors estimated that about 85% of the total rotational energy was available for bond breaking. This would suggest an increase in moment of inertia of about a factor of 6.

(5) G. B. Kistiakowsky and E. K. Roberts, *ibid.*, **21**, 1637 (1953). We are ignoring here the small corrections suggested by A. Shepp, *ibid.*, **24**, 939 (1956), since they yield an unreasonably higher value for CD_3 recombination than for CH_3.

(6) $r^{\ddagger}$ and $I^{\ddagger}$ correspond to internuclear distance and moment of inertia in the transition state.

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.

Acknowledgment. This work has been sponsored in part by Grants AP00353-04 and AP00698-01 from the National Air Pollution Control Administration, Consumer Protection and Environmental Health Service of the Public Health Service.

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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).