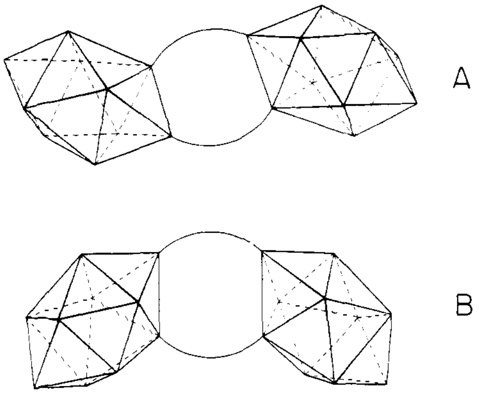

Fig. 1.—Proposed structures for $B_{20}H_{18}^{-2}$ ions A and B. The low field singlet and doublet in the B^{11} n.m.r. spectra of ions A and B are essentially identical, but the high field regions are different enough to indicate different structures for A and B, but not different enough to indicate that the B_{10} units have been destroyed in the preparations for A and B. Each curved line is a bridge hydrogen. Terminal hydrogens are not shown.

(n.m.r.) spectrum[1] of ion A is similar enough to that of $B_{10}H_{10}^{-2}$ to suggest that the polyhedron is retained, and is strongly suggestive of modification of one apex BH bond and at least one equatorial BH bond of each original $B_{10}H_{10}^{-2}$. The proposed structure (Figure 1) is the only one consistent with the present form of the valence theory.[4]

We now wish to report that oxidation of the triethylammonium salt of $B_{10}H_{10}^{-2}$ with two equivalents of cold acidified aqueous Ce^{+4} ion precipitates the triethylammonium salt of another $B_{20}H_{18}^{-2}$ ion, B. Ion B has been converted quantitatively into ion A in aqueous solutions containing a catalytic amount of HCl, and we therefore suspect that Ce^{+4} attack at a more negative apical region of $B_{10}H_{10}^{-2}$ leads mechanistically to ion B. Probably also, isolation of A from the Fe^{+3} oxidation results from the acid catalyzed conversion of B to A at higher temperatures at which the $HNEt_3^+$ salt of B is more soluble. At higher temperatures ion A is formed exclusively in these oxidations.

The idea that the B_{10} units are preserved in ions A and B is supported (a) by infrared spectra which have a 1890 cm.$^{-1}$ band in B and a 2500 cm.$^{-1}$ band in A suggestive of symmetrical and unsymmetrical H bridges, respectively, and (b) by the B^{11} n.m.r. spectra which are strongly indicative in both ions of modification of one apex and at least one equatorial BH group of each B_{10} unit. Hence, the proposed structure of isomer B involves one apex–apex H bridge and one equatorial–equatorial H bridge. The acid catalyzed isomerization of B to A is presumed to occur by an unusual process[1] in which the bridges are not broken, but in which changes from 4 to 5 and from 5 to 4 coördination occur by slight movement (0.5 Å. or less) of the appropriate B atoms.[1] Further studies of these structures and of the isomerization mechanism have been initiated.

This new triethylammonium salt of $B_{20}H_{18}^{-2}$ (B) melts at 203–204°, shows ion aggregation in various somewhat polar solvents, and has an X-ray diffraction pattern unlike that of the corresponding salt of ion A. *Anal.* for this salt of ion B: Calcd. for $C_{12}H_{50}B_{20}N_2$: C, 32.85; H, 11.40; N, 6.39; B, 49.36. Found: C, 32.70; H, 11.80; N, 6.35; B, 49.20. Visible and ultraviolet absorption maxima are at 292 mμ (ϵ = 10,800) and 232 mμ (ϵ = 23,800) for ion A, at 292 mμ (ϵ = 4,880) and < 200 mμ for ion B, and < 210 mμ for $B_{10}H_{10}^{-2}$, all taken in acetonitrile solutions. The similarity of the 292 mμ band in A and B is striking, and is apparently associated with polyhedron–polyhedron interaction, since it is not present in the $B_{10}H_{10}^{-2}$ spectrum.

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THE RELATIVE IMPORTANCE OF C–H BOND ENERGY AND ALKYL INTERFERENCE IN RECOIL TRITIUM REACTIONS WITH ALKANES[1]

Sir:

The radioactive products have been analyzed for the reactions of recoil tritium atoms with many individual hydrocarbons, and have been shown to be formed predominantly by reactions occurring at above-thermal energies.[2–6] The detailed course of such atomic reactions in the low electron-volt region is not very well known, and further information concerning the mechanism and energetics of these processes is very desirable. Since approximately 90% of all of the recoil tritium atoms which react with alkanes while "hot" lead to HT or the labeled parent molecule[2] by (1) or (2), these two reactions are of central importance in the understanding of the chemistry of such energetic species.

$$T^* + RH \longrightarrow HT + R\cdot \qquad (1)$$

$$T^* + RH \longrightarrow RT + H\cdot \qquad (2)$$

The relative yields of HT and labeled parent have previously been measured for ten alkanes with yield ratios (HT/RT) between 1.0 and 3.6. These ratios have been shown to correlate satisfactorily with the formula

$$\frac{HT}{RT} = \frac{\Sigma n_i}{\Sigma n_i(1 - \Omega)^x} \qquad (A)$$

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[1] This research supported by A.E.C. Contract No. AT-(11-1)-407.

[2] D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2982 (1961).

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[5] J. K. Lee, B. Musgrave and F. S. Rowland, *Canad. J. Chem.*, **38**, 1756 (1960).

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in which n_i is the number of primary, secondary, or tertiary hydrogen atoms, x is 1, 2, or 3, respectively, and Ω is an empirical parameter with the value 0.45. The agreement between the experimental values and those calculated values has been interpreted as evidence for interference with reaction (2) by the substituent alkyl groups, and Ω has been designated as an "obstruction parameter."[2,3]

The increase in HT/RT ratio for more highly substituted carbon atoms can also be rationalized by the hypothesis that reaction (1) occurs more frequently as the C–H bond strength is weakened by alkyl substitution, and the experimental ratios can also be correlated with empirical functions attributing some or all of the change to variations in the yield of HT. A direct experimental test seemed desirable to ascertain whether the alkyl substituents were hindering reaction (2), facilitating reaction (1), or perhaps both.

We have carried out such a test through competitive recoil tritium reactions,[7,3] in which two parent molecules, CH_4 and n-C_4H_{10}, are simultaneously present in a gaseous system and the relative yields of the two labeled parent compounds are measured. The techniques of irradiation[2–6] and counting[8] as developed earlier can then be used without modification. The irradiations were carried out in the presence of O_2 or I_2 scavenger molecules to suppress the production of HT and labeled hydrocarbons from thermal processes.[2–6]

The ratio of *specific* radioactivities expected from formula (A) for n-C_4H_9T and CH_3T from the respective parent compounds is 1.13, if the assumption is made that the hydrogen atoms in both molecules are equally accessible to abstraction by hot tritium atoms.[9] An extreme alternate approximation can be made that all C—H substitutions are equally likely and the HT/RT variations result solely from increasing yields of HT with increasing values of x. The expected ratio of specific radioactivities from such an approximation is then just the ratio of H atoms per molecule, or 2.5 for n-C_4H_9T/CH_3T. The results given in the last column of Table 1 show good agreement with this simple ratio of numbers of C—H bonds per molecule.

The implications of these experimental observations for the explanations of recoil tritium reactions with alkanes seem to us to be: (1) The *average* probability of T for H substitution *per hydrogen atom* is closely comparable in methane and n-butane. While intramolecular variations in specific tritium activity may yet be observed in the alkanes, the steric obstruction implied in formula (A) is clearly not the dominant factor affecting these substitutions, and is probably of minor importance.[10]

(2) The previously observed variations in HT/RT ratios must then chiefly result from increases in the relative frequency of reaction (1) with increasing alkyl substitution,[11] and the conclusion readily follows that the hot hydrogen abstraction reaction is rather sensitive to C–H bond energy differences. These conclusions are consistent with the indications from experiments with isotopic methanes that the hot abstraction reaction occurs predominantly in a lower kinetic energy region, but still above thermal energies.[12] Bond strength is certainly not the determining criterion for the probability of occurrence of all hot tritium reactions, however, as shown by the comparatively low yields corresponding to the breakage of the weaker C—C bonds.[2,3]

TABLE I

DISTRIBUTION OF RADIOACTIVITY IN GAS PHASE COMPETITIVE RECOIL TRITIUM REACTIONS WITH CH_4 AND n-C_4H_{10}

Exp.[a]	Pressure ratio CH_4 C_4H_{10}	Scavenger	Activity ratio $C_4H_9T/$ CH_3T	Specific activity ratio Uncorrected	Corrected[b]
287 S	8.72	O_2	0.286	2.50	2.55
306 P	4.02	O_2	.547	2.20	2.29
307 S	4.32	O_2	.578	2.50	2.60
289 S	7.40	I_2	.313	2.32	2.37
308 P	3.81	I_2	.604	2.30	2.40
309 S	3.76	I_2	.600	2.26	2.36

[a] All samples contained approximately 1 cm. He^3 and a total pressure of 100 cm. Hg. **S** = 1 hour at 10^{11} n./cm.^{2}/sec., P = 1 pulse (about 6×10^{15} n./cm.^{2}/sec. for 10^{-2} secs.). [b] Corrected for CH_3T formed from T reaction with n-butane, taken as 0.067 times the yield of n-C_4H_9T.

(3) The rough geometrical division of recoil tritium reactions with alkanes into hydrogen abstraction in energetic collisions along the C—H axis, and T for H substitution through approach at larger angles loses one of the stronger arguments in its support, *i.e.*, the correlation of HT/RT ratios with formula (A). While this separation into two general geometric approaches is supported by other arguments, and may well be correct, there does not now appear to be any experimental evidence that adjacent alkyl groups seriously interfere with the larger angles of approach hypothesized for T for H substitution.

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(9) This should be a reasonable approximation for the conditions specified in references (2) and (3) for formula (A).

(10) The intramolecular variations in specific tritium activity already observed (*e.g.*, see ref. 6) are not comparable to the alkanes because additional mechanisms are available leading to labeling of aromatic and olefinic positions.

(11) The hot yields of HT and lower alkanes from these experiments are in good agreement with the sums of yields calculated from the parent molecules separately, if the total reaction probability of a methane molecule is weighted as 0.22 relative to n-butane.

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