octadecane (mass spectrum, molecular ion m/e 252).

The nmr spectrum of **3** (CCl_4, 100 Mcps) consisted of a singlet at τ 2.98. Compared with the *cis*-enediyne **5** (τ 4.11) as a model, the downfield shift in the $(4n + 2)$ π-electron system **3** is therefore τ 1.13, and the upfield shift in the $4n$ system **2** is τ 1.47. This provides strong evidence for the existence of a diamagnetic ring current in **3** and a paramagnetic ring current in **2**.[13]

Acknowledgment. We are indebted to Professor Dr. O. Bayer and Dr. H. Oediger, Farbenfabrik Bayer, Leverkusen, for a generous gift of 1,5-diazabicyclo-[4.3.0]non-5-ene.

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[13] The results appear not to be in accord with the ideas of J. I. Musher, *J. Chem. Phys.*, **43**, 4081 1965; **46**, 1219 (1967); *Advan. Magnetic Resonance*, **2**, 177 (1966).

[14] Supported by the Air Force Office of Scientific Research and the National Academy of Sciences, National Research Council.

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Beam Studies of Energy Dependence of Hot-Atom Reactions

Sir:

The reactions of neutral species above threshold have been explored using nuclear recoil[1] and photochemical techniques.[2] These methods, while uncovering the richness of the field, can only provide limited data on the energy dependences of hot processes. We report here on beam experiments aimed toward providing such information on reactions of hot tritium.[3]

The apparatus ADAM was used to generate beams of monoenergetic tritium ions in the energy range 1–200 ev (Figure 1). Bombardment with 150-ev electrons was used to produce T_2^+ from T_2 gas and T^+ from T_2 which had been dissociated in a tungsten oven at 2500°K. The ions were extracted, accelerated to 200 ev, focused by a series of electrostatic lenses, and mass-analyzed by a simple Wien filter. After deceleration to the desired energy by a 12-element exponential lens, the beam was monitored by passing through a grid intercepting a known fraction of the current. Finally, it impinged on a liquid-nitrogen-chilled target of a solid hydrocarbon, cyclohexane being used as a prototype. The target surface was continually renewed by deposition of fresh material. Positive charge build-up was prevented by electrons from a filament near and slightly negative with respect to the target.

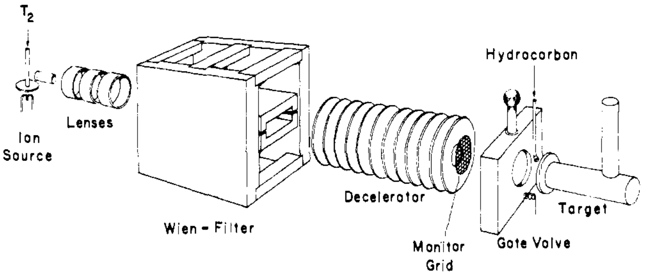

Figure 1. Schematic representation of ADAM apparatus.

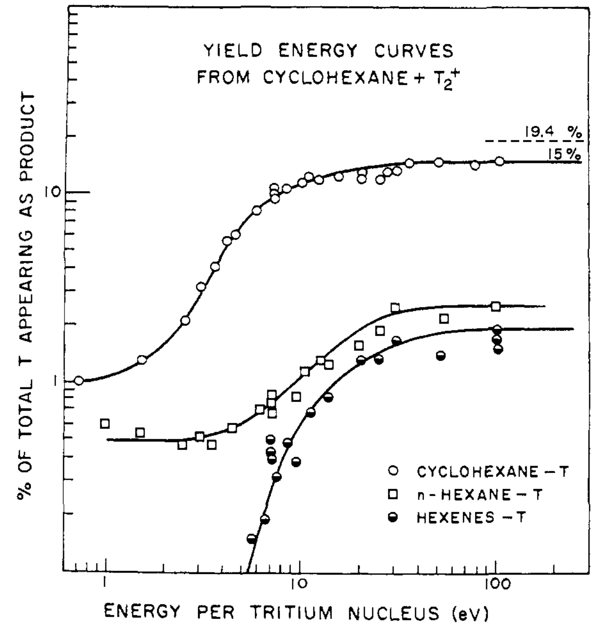

Figure 2. Log–log plot of yields of labeled products from T_2^+ beam interacting with solid cyclohexane. Yield of cyclohexane-*t* from recoil tritium is indicated by dashed line.

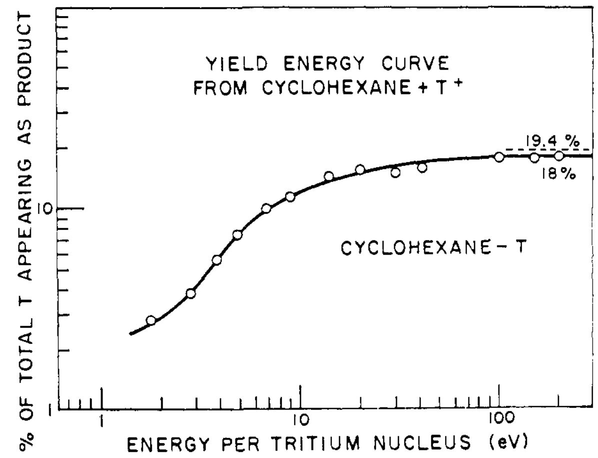

Figure 3. Log–log plot of yields of labeled cyclohexane-*t* from T^+ beam interacting with solid cyclohexane. Yield from recoil tritium is indicated by dashed line.

At the end of a run, the target was volatilized and analyzed for tritiated products by radio gas chromatography.[1,4] Absolute yields of cyclohexane-*t* and other products are shown in Figures 2 and 3 as a function of kinetic energy per T atom. Cyclohexane-*t* yields obtained in separate experiments with recoil tritium and solid cyclohexane[5] are also indicated.

Other studies have shown that the dominant reaction of hydrogen ions with hydrocarbons is charge transfer, proceeding with large cross section.[6,7] This process,

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[1] R. Wolfgang, *Ann. Rev. Phys. Chem.*, **16**, 15 (1965).

[2] (a) R. M. Martin and J. E. Willard, *J. Chem. Phys.*, **40**, 2999, 3007 (1964); (b) A. Kuppermann and J. M. White, *ibid.*, **44**, 4352 (1966); (c) C. C. Chou and F. S. Rowland, *J. Am. Chem. Soc.*, **88**, 2612 (1966).

[3] The first work on low-energy tritium beams was carried out by J. M. Paulus and J. P. Adloff (*Radiochim. Acta*, **4**, 146 (1965); J. M. Paulus, Thesis, Université de Strasbourg, 1966) using T^+ interacting with butane gas. A variety of processes presumably including hot-atom, ion–molecule, and surface interactions appear to be involved in this system, and the authors do not offer a definitive interpretation of their results.

[4] R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

[5] The technique used to obtain absolute yields from recoil tritium interacting with solids will be discussed elsewhere.

[6] W. A. Chupka and E. Lindholm, *Arkiv Fysik*, **25**, 349 (1963).

[7] J. Futrell, F. P. Abramson, and T. O. Tiernan, private communication.

occuring on the surface of the target, converts T^+ to hot T atoms of essentially the same kinetic energy. T_2^+ is expected to yield hot T atoms of the same average velocity in a transition to the repulsive $^3\Sigma_u^+$ state and $T_2(^1\Sigma_g^+)$ molecules. Since a fraction of the latter species is likely to be in a high vibrational state, due to its formation by a Franck–Condon transition, it may undergo collision-induced dissociation upon further collision.[8] The tritium atoms thus formed should then react further to yield labeled products by normal hot abstraction and displacement mechanisms.[1]

These expectations are borne out by the following data. (1) Yields increase with energy, which is normal for hot-atom processes. (2) The yield of cyclohexane-*t* from a high-energy T^+ beam is within experimental error of that from hot atoms produced by nuclear recoil (Figure 3). As expected, the yield is somewhat lower for T_2^+ since not all of these ions are converted to hot atoms (Figure 2). (3) The shape of the yield function is, after appropriate normalization, similar for initial T_2^+ and T^+ beams.[8]

Some salient results of this study may be pointed out. The efficiency for hydrogen displacement to form cyclohexane-*t* rises steeply from a threshold at about 1 ev to the vicinity of 10 ev. (Excitation functions derived from these results will be discussed in the full report on the work.) Hexene-*t* and *n*-hexane-*t* production, which involve rupture of a C–C as well as a C–H bond, have a threshold of about 5 ev.[9] This appears to be the first measurement of the threshold of a reaction not occurring at thermal energies which involves only neutral species.

Acknowledgments. This work owes much to Professors R. Fink and R. Beringer, who helped develop a prototype of ADAM. (Details on this apparatus will be published separately.) Technical assistance by Mr. S. Y. Tang is greatly appreciated. We are grateful to Dr. J. Futrell for permission to cite his results prior to publication. The work was supported by the U. S. Atomic Energy Commission.

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[8] The yield of cyclohexane-*t* production at low energies appears to be lower for T_2^+ than for T^+ beams. This may result from a decreased efficiency of hot-T-atom production when the energy is so low that collision-induced dissociation of excited $T_2(^1\Sigma_g^+)$ (as produced by neutralization) becomes ineffective.

[9] As is emphasized by the log–log plots of the data, there appear to be small but finite yields of *n*-hexane-*t* and cyclohexane-*t* as the energy approaches zero. This would be due to nonhot-atom processes having low or zero thresholds. Examples of such would be ionic or radical reactions on the surface of the target.

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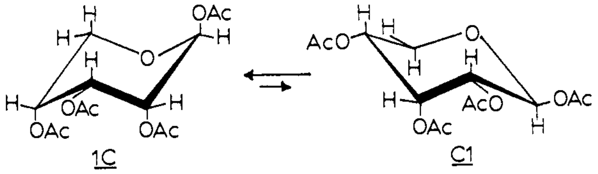
Conformational Inversion of Pyranoid Ring Sugars. The Conformational Equilibrium of β-D-Ribopyranose Tetraacetate[1]

Sir:

Pyranoid ring sugars and their derivatives may be formulated in two energetically nonequivalent chairlike conformations, interconversion between which involves an energy barrier, and in a "flexible cycle" of skew forms interconvertible through energy barriers corresponding to the boat forms.[2,3] Steric and electronic interactions between substituents on the tetrahydropyran ring usually cause one chair conformer to be favored strongly over the alternative chair form.[4–6] Nmr spectroscopic and other evidence indicates that most pyranoid sugars and their derivatives exhibit a high degree of conformational homogeneity in one of the two chairlike conformations;[4,5] convincing evidence for major contributions from nonchair conformers has been presented only in the case of systems having other rings fused to the pyranose ring.[7]

It has not been established directly whether the conformational homogeneity indicated for pyranoid sugar derivatives by nmr spectroscopy reflects a time-averaged spectrum of conformers in rapid interconversion, with a preponderant contribution from the favored chair conformation, or whether interconversion is slow, so that spectra of the separate conformers are obtained but the proportion of the minor conformer is so small that its signals are lost in the background noise of the spectrum. Available evidence[4,5,8] suggests that the energy barrier for chair–chair interconversion is small, so that interconversion is rapid and a time-averaged spectrum is seen, because, in a few examples where the energy difference between the two chair conformers is predictably small, the nmr spectral parameters appear to be intermediate between those predicted for each separate chair conformer. Such an example[5a] is β-D-ribopyranose tetraacetate (**1**). The present communication reports direct observation of separate conformers of **1** by low-temperature nmr spectroscopy, thereby establishing that **1**, and presumably other pyranoid sugar derivatives, indeed exists in rapid conformational equilibrium at room temperature. Such conformational equilibria have been observed with cyclohexane[9] and some of its derivatives.[10]



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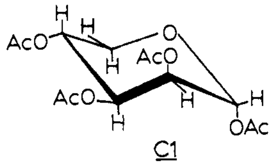

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[1] This paper is part of a series "Application of 220-MHz Nmr to the Solution of Stereochemical Problems." For previous, related papers, see (a) N. S. Bhacca and D. Horton, *Chem. Commun.*, 867 (1967); (b) C. V. Holland, D. Horton, M. J. Miller, and N. S. Bhacca, *J. Org. Chem.*, 32, 3077 (1967); (c) C. V. Holland, D. Horton, and J. S. Jewell, *ibid.*, 32, 1818 (1967).

[2] D. Horton, in "Handbook of Biochemistry and Biophysics," H. C. Damm, Ed., World Publishing Co., Cleveland, Ohio, 1966, pp 128–131.

[3] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1965, Chapter 6.

[4] L. D. Hall, *Advan. Carbohydrate Chem.*, **18**, 51 (1964).

[5] (a) R. U. Lemieux and J. D. Stevens, *Can. J. Chem.*, **43**, 2059 (1965); (b) *ibid.*, 44, 249 (1966).

[6] Reference 3, p 370.

[7] C. Cone and L. Hough, *Carbohydrate Res.*, 1, 1 (1965); compare S. J. Angyal and R. M. Hoskinson, *J. Chem. Soc.*, 2991 (1962).

[8] M. Rudrum and D. F. Shaw, *J. Chem. Soc.*, 52 (1965).

[9] F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin,