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Trapping of Hydrogen and Deuterium Atoms Produced by the Photolysis of Hydrogen Iodide in 3-Methylpentane-d_{14}[1]

Sir:

Photolysis of HI in 3-methylpentane (3MP) glass at 77°K produces hot hydrogen atoms, which abstract hydrogen from the matrix to form C_6H_{13} radicals,[2-4] and thermal H atoms which add to olefins present as dilute solutes.[3] The quantum yield[4] of thermal atoms, which is *ca.* 0.8 in liquid 3MP at 300°K, drops to *ca.* 0.1 at 77°K, as a result of increasing geminate recombination. Using esr detection, we have sought to determine whether thermal H atoms can be produced by photolysis of HI in 3MP glass at temperatures below 77°K, and, if so, whether there are conditions under which they can be trapped. The work was initiated to assist in determining[5] whether the absence of esr signals for H atoms in γ-irradiated solid hydrocarbons means that such atoms are not produced, or simply that they are not trapped.

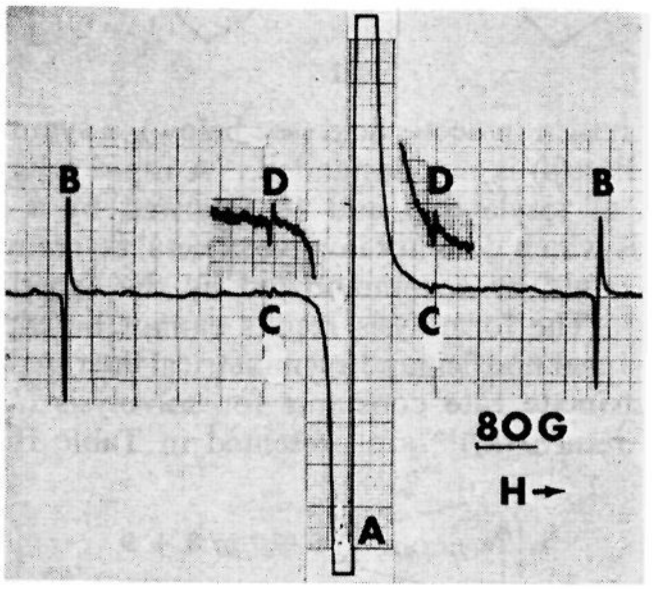

Figure 1. Esr spectrum produced by photolys is of HI in perdeuterated 3-methylpentane at 27°K, showing lines due to the C_6D_{13} radical (A), ^{1}H (B), and ^{2}H (C). The inserts (D) show the ^{2}H lines recorded at a fivefold higher amplifier gain. The microwave power was 3.9 mW.

In initial tests 0.1 mole % HI was photolyzed in perdeuterated 3-methylpentane (3MP-d_{14}), with 0.3 mole % isobutylene (iB) present to serve as a detector for thermal H atoms (by forming t-C_4H_9 radicals observable by esr). 3MP-d_{14} rather than 3MP-h_{14} was used as the matrix because the outer lines of the t-C_4H_9 spectrum (~150 G) are free of overlap with the C_6D_{13} spectrum (~50 G), whereas the C_6H_{13} signal (produced by hydrogen abstraction by hot H) would give interference. Degassed samples were photolyzed in 3-mm i.d. Suprasil tubes in a Varian V-4531 esr cavity using a quartz-jacketed AH4 medium-pressure mercury lamp (with and without a Vycor filter) focused on the sample by a quartz lens. The techniques of purification, measurement, and temperature control by cold helium gas are discussed elsewhere.[2,3,5,6]

Photolysis of the 3MP-d_{14}–HI–iB mixture for 2.5 min at temperatures below 77°K produced both C_6D_{13} and t-C_4H_9 radicals. We therefore photolyzed 3MP-d_{14} containing 0.1 mole % HI without iB. Pronounced lines of the H doublet appeared after 60 sec of photolysis, or less, at all temperatures tested from 20 to 50°K. On further photolysis the two outer lines of the ^{2}H triplet appeared, the central line being obscured by the C_6D_{13} signal (Figure 1). We attribute the ^{1}H doublet to the trapping of thermal H atoms produced from HI photolysis and the ^{2}H lines to trapping of thermal D atoms produced by displacement of D atoms from C_6D_{14} by hot H atoms or by photolysis of DI formed by disproportionation between an I atom and a radical with which it is caged ($C_6D_{13} + I \rightarrow C_6D_{12} + DI$). The radical is formed by attack by the hot H partner split off from the I by photolysis of HI. Decay kinetics of radicals offer strong evidence for such caging.[2]

At 30°K the lines of the ^{1}H doublet grew continuously during a 10-min photolysis, but at a decreasing rate. Initial decay of the ^{1}H signal in a sample which received a 30-sec photolysis was about 50% in 1 min, becoming progressively slower thereafter. Initial decay following longer illuminations was slower, indicating a higher fraction of more strongly trapped atoms. When a sample photolyzed at 30°K was raised to successively higher temperatures, a relatively rapid initial decay followed by much slower decay occurred at each temperature.

Photolysis of HI in 3MP-h_{14}, under conditions identical with those used with the 3MP-d_{14} matrix, shows no evidence of the ^{1}H doublet. This indicates either that 3MP-h_{14} is incapable of trapping ^{1}H, in contrast to the ability of 3MP-d_{14} to trap both ^{1}H and ^{2}H, or that the protiated matrix reduces the escape of thermal H atoms formed from the primary photolytic process more than does the deuterated matrix (by increasing the probability of the hot reaction or of geminate recombination). There is an analogy for such an effect in the slow decay of trapped free radicals in deuterated as compared to protiated matrices at 77°K.[2] Both experimental observations and activation energy considerations exclude the possibility that the latter decay occurs by hydrogen abstraction from the matrix.[2]

Despite the above evidence that D atoms can be trapped and observed in 3MP-d_{14}, no D atom signal appears during the growth of C_6D_{13} radicals produced by the self-radiolysis of tritiated 3MP-d_{14}[7] at 30–50°K in the esr cavity, or during γ radiolysis at 4°K.[5] Likewise no H atoms are produced during γ radiolysis of a variety of other hydrocarbons at 4°K, except CH_4.[8]

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(1) This work has been supported in part by U. S. Atomic Energy Commission Contract AT(11-1)-1715 and by the W. F. Vilas Trust of the University of Wisconsin.

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(6) D. Timm and J. E. Willard, *Rev. Sci. Instr.*, in press.

(7) Prepared by Dr. Mervyn Long of our laboratory.

(8) Trapped H atoms produced in CH_4 at 4°K by radiolysis have previously been observed by (a) B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958); (b) D. W. Brown, R. E. Florin, and L. A. Wahl, *J. Phys., Chem.*, **66**, 2602 (1962); (c) W. Gordy and R. Morehouse, *Phys. Rev.*, **151**, 207 (1966).

The results indicate strongly that the trapped radicals formed in the radiolysis of solid hydrocarbons other than methane are not produced by elimination of thermal H atoms.

When isobutene was present during photolysis of HI in 3MP-d_{14}, the yield of t-C_4H_9 radicals was less than the reduction in yield of trapped H, and the yield of radicals formed by hot abstraction processes was reduced. These effects, which may be due to complexing of HI by iB, are under further investigation.

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Book Reviews

Polyhedral Boranes. By Earl L. Muetterties and Walter H. Knoth, Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 1968. vii + 197 pp. 15.5 × 23 cm. $13.50.

This monograph gives a lucid appraisal of the present state of the bonding theory and chemistry of polyhedral boranes. In the preface the authors express the hope that this book will stimulate further research activity in the field. I believe the book will achieve this end but mainly among the present specialists of the art, not the neophytes. Chapter two starts off by considering some of the most complex boron hydride structures known (*e.g.*, $B_{20}H_{16}$, $B_{20}H_{16}(\text{ligand})_2$, and $B_{20}H_{18}^{2-}$). This most likely will frighten rather than interest the lay reader. It would have been more helpful to suggest that the reader obtain a few stick models to aid in understanding the symmetry and polyhedral transformations of these cage compounds. Inexpensive models can be purchased from Geodestix, P.O. Box 5179, Spokane, Washington. Jargon occurs in several places in the text, and this reduces communication with the lay reader [*e.g.*, $(B_{9,10,11}C^-)$ on page 23, line 20]. The book is written in a very condensed form. This is best illustrated by the 21 equations which appear on page 96. Fine points and interrelationships are easily lost in this taxonomic approach.

There are over a dozen references to unpublished work from the Delaware group cited in the text. Most of these are rather minor points, but a few are significant new results. One item of interest is the reported synthesis of $B_{10}H_7[S(CH_3)_2]_3^+$, a rare positive boron hydride ion. Another is the apparent formation of $B_{10}H_{10}CH \cdot \text{base}^-$ species. This type of result should be initially presented in a critical journal article and not briefly mentioned in a review without experimental detail.

The text appears to have only a few typographical errors (as on pp 2, 42, 75, 123, and 143). Thus I believe this book will be a useful addition to chemistry libraries. But due to the cost and style of presentation, it will be found most frequently in the personal libraries of specialists in the field.

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