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The Channeling of Hot H Atoms in the Radiolysis and Photolysis of Crystalline Alkane

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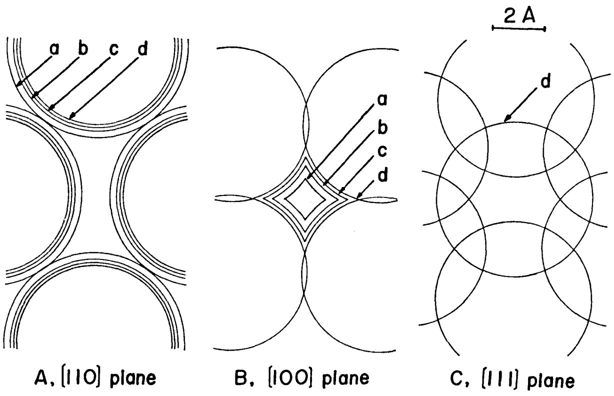
Synopsis. The possibility of a long migration of hot H atoms through crystalline alkane is discussed in terms of a simple channeling theory. The potential energy surface for an H atom in crystalline neopentane shows that the channeling directions are perpendicular to the [110] and [100] planes. The energy dependence of the channeling of hot H atoms is discussed.

Recently Miyazaki *et al.* found that H atoms, which are produced by the radiolysis of solvent neopentane or by the photolysis of hydrogen halide, react selectively with a small amount of solute alkane in a neopentane matrix at 77 K.[1)] A similar phenomenon has also been observed in isobutane, 2,2,3,3-tetramethylbutane and cyclopropane matrices at 77 K.[1)] At present, we cannot give a clear answer to the question whether the reactive H atoms are thermal or hot.

The following observations, however, favor the hypothesis of the hot H atoms: (1) The competitive reaction between *c*-C_6H_{12} and HI for H atoms was studied in the radiolysis and photolysis of a *neo*-C_5H_{12}–*c*-C_6H_{12}–HI mixture at 77 K. The rate constants of these reactions in the neopentane matrix are quite different from those of the thermal H atom reaction.[1)] (2) When a H atom is produced by the photolysis of HBr with a 185 nm light, the hot H atom has initially a kinetic energy of 67 kcal/mol. When C_3H_8 is present in the *i*-C_4H_{10} matrix, the hot H atom reacts selectively with solute C_3H_8 to form the C_3H_7 radical.[1)] (3) The selective hydrogen atom abstraction by H atoms occurs even at 4 K in *neo*-C_5H_{12} matrix and the H atoms cannot be detected at all by ESR spectroscopy.[2)]

There is, however, a dogmatic conception that a long migration of a hot H atom through solid alkane is quite improbable. In this report the author will discuss the possibility of a long migration of the hot H atom by means of the channeling phenomenon.[3)]



A, [110] plane B, [100] plane C, [111] plane

Fig. 1. Projections of potential energy distribution in neopentane crystal.
Contour lines are : a, 1.0 kcal/mol; b, 3.0 kcal/mol; c, 5.0 kcal/mol; d, 9.3 kcal/mol. Position of the contour map represents the position of mass center of H atom.

Potential Energy Surface for H Atoms in Crystalline Neopentane. The occurrence of the channeling in the crystal depends on the existence of the channeling region, which is decided by the potential energy distribution in the crystal. Since the calculation of the potential energy between *neo*-C_5H_{12} and an H atom is quite difficult, the potential energy between an H atom and CH_4, which is a very similar compound to *neo*-C_5H_{12}, is applied here to the neopentane crystal as an approximation. Recently Raff has calculated the potential energy surface between CH_4 and a T atom.[4)] He considered the energy for an angular displacement of C–H bonds in addition to the energy calculated by London-Eyring-Polanyi-Sato's method. The potential energy, $V(R_i, \theta_i)$, is given by:

$$V(R_i, \theta_i) = T(R_1, R_5, R_6) + T(R_2, R_5, R_7) + T(R_3, R_5, R_8) + T(R_4, R_5, R_7) + \frac{1}{2}\sum_{j=1}^{6} k_j(\theta_j - \theta_j^0)^2 \qquad (1)$$

where R_i represents the interparticle distance between C, H, and T atoms. The θ_i are the six H–C–H angles of CH_4. The bending-force constant for the θ_j angle is k_j, with θ_j^0 representing the equilibrium angle. The four terms $(T(R_i, R_j, R_k))$ in Eq. 1 represent the energies of three-body interaction among C, H, and T atoms.

Raff calculated the potential energy surface of the CH_4–T system by means of the above procedure. Here the potential energy surface calculated by him is applied to the crystalline *neo*-C_5H_{12}–H atom system. The crystalline structure of neopentane at 77 K consists of face-centered cubic unit cells with a lattice constant of 11.4 A.[5)] Since the chemical structure of neopentane is symmetrical, the structure is depicted as a sphere. Since an overall rotation of the neopentane molecule occurs even at 77 K,[6)] the positions of the H atoms of the methyl group are not fixed in the lattice. Therefore, the depiction of the neopentane molecule as a sphere is reasonable. The energy of the abstraction saddle point on the potential energy surface is normalized to 9.3 kcal/mol,[7)] which is the observed activation energy for an H atom-abstraction reaction from neopentane by an H atom. Projections of the potential energy distributions of the three principal planes of the f.c.c. lattice of neopentane are shown in Fig. 1. The potential energy surface in Fig. 1 is based on the energy of the H and CH_4 pair, and the distance between the reactive H atom and the H atom of the methyl group is 1.08 Å at the saddle point of the potential energy surface. The distances between the reactive H atom and the nearest H atoms of the other methyl groups are 1.9 Å for the other methyl group of the same neopentane molecule and 2.9 Å for the methyl group of the neighboring neopentane molecule. Therefore, the interaction energies of the reactive H atom and these nearest H atoms may be negligible as compared with the energy at the saddle point.

It is clear that the layers of the [110] and [100] orientations exhibit low potential regions to the incident H atoms, which are produced by the radiolysis of neopentane or by the photolysis of hydrogen halide. If the energy in the transverse motion of a hot H atom is larger than the 9.3 kcal/mol shown in Fig. 1A and B, the H atom reacts with neopentane. If, on the other hand, the energy in the transverse motion is smaller than 9.3 kcal/mol, the hot H atom travels a long distance by a succession of glancing collisions with the channel walls of neopentane molecules and then reacts with a solute alkane, which may exist as a defect in the neopentane crystal. When hot H atoms are incident upon the [111] plane, however, they react with neopentane molecules in the first collision (Fig. 1C).

The selective hydrogen atom abstraction reaction by H atoms in neopentane-alkane mixtures is not observed in the liquid phase.[1] This phenomenon can be explained by the channeling hypothesis. Since a random arrangement of molecules in the liquid phase does not contain channels, the hot H atom collides head-on with a solvent molecule in the liquid phase and loses its energy by chemical reaction or deactivation.

Energy Dependence of the Channeling of Hot H Atoms. When the channeling of H atoms takes place, the intervals of glancing collisions of H atoms with the channel wall are much longer than in the lattice period. It is a good approximation[3] to assume that the potential distribution of Fig. 1A or B continues in a direction perpendicular to the [110] or [100] plane. The collision in the channeling is depicted in Fig. 2A, where E is the kinetic energy of an H atom. If the energy of an H atom in its x-direction motion is smaller than 9.3 kcal/mol, then:

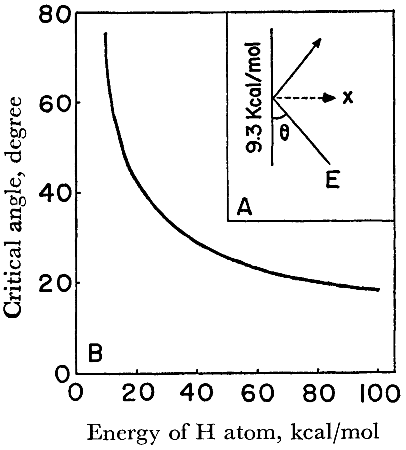


Fig. 2. Critical angle of channeling of hot H atom. A, Glancing collision of hot H atom with channel wall of 9.3 kcal/mol. B, Dependence of critical angle of channeling upon kinetic energy of H atom.

$$E\sin^2\theta < 9.3\ \text{kcal/mol} \tag{2}$$

where θ is the angle between the H-atom motion and the channel direction.

Though the thermalization process of the hot H atom may be important, only the hydrogen-atom-abstraction reaction is considered in this model for the following two reasons: (1) The cross section of the H atom abstraction reaction by hot H atoms in the 3-methylpentane matrix at 77 K is three times as large as that of the thermalization.[8] (2) Though the H atom abstraction reaction by hot H atoms takes place in the neopentane matrix at 4 K, trapped H atoms are not observed at 4 K by ESR spectroscopy.[2]

The substitution reaction of hot H atoms is neglected also in this treatment for the following reasons. The activation energy for the substitution reaction is about 35 kcal/mol,[9] which is much higher than that for the H-atom-abstraction reaction. The cross section for the abstraction from methane by a 65 kcal/mol tritium atom is 3.7 times as large as that for the substitution reaction.[9]

The critical angle for the channeling of the hot H atoms can be calculated by means of Eq. 2; it is shown in Fig. 2B. The H atoms easily undergo a channeling with a decrease in the kinetic energies, when they converse upon the crystal from all directions.

When hot H atoms are produced by the photolysis of hydrogen halide or by the radiolysis of the solvent alkane, the direction of the initial motion of the H atoms is also important. If hydrogen halide is dissolved in a void space of the lattice, as is shown in Fig. 1A, the H atoms easily converse upon the channeling region.

It can be concluded that the channeling phenomenon of hot H atoms can take place in the organic crystal if the conditions are optimum. We cannot reject *a priori* the possibility of long migrations of hot H atoms in the organic crystal.

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