

Quasiclassical Trajectory Study of Hot-Atom Reactions of C(¹D) with HI*

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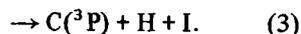
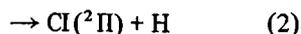
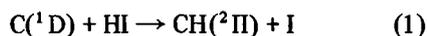
Hot atom chemistry / ¹C-recoil / HI / Trajectory calculations

Abstract

Extensive quasiclassical trajectory calculations using a valence bond diatomics-in-molecules potential energy surface indicate that in reactions of C(¹D) with HI the products CI + H should be slightly favoured over CH + I, the more exothermic products, at center-of-mass collision energies below ~ 2.5 eV. Above that energy, CH is the only diatomic product formed, but this high-energy CH product may dissociate upon subsequent collisions in a hot-atom experiment with a neon moderator. At the lower energies, nearly all the reactive collisions proceed *via* an insertion/decomposition mechanism. At higher energies, direct abstraction processes increase in importance.

Introduction

Recent experimental work [1] on the reactions of energetic carbon atoms in gas phase hydrogen halide systems has led us to carry out a quasiclassical trajectory study on such a system. Using a valence bond diatomics-in-molecules (VB-DIM) potential energy surface [2], we have analyzed the attributes of reactions (1), (2), and (3) at several relative collision energies between 0.1 and 10.0 electron volts:



In formulating our set of valence bond basis functions for the C–H–I system, the carbon atom (with electronic configuration $1s^2 2s^2 2p^2$) is treated as a two electron (p^2) atom, not allowing for any hybridization of the atomic orbitals. We also have chosen to ignore the directional character of the p-orbitals on iodine and to treat it, as far as electronic configuration is concerned, in precisely the same manner as the hydrogen atom. As we are only interested in the qualitative features of the reaction dynamics, we do not believe this to be an unreasonable approximation to make.

There is, in fact, a dual motivation for the present study. The first is to investigate the qualitative features of the reaction dynamics of the C(¹D) + HI system for comparison with the results of experimental studies. It should be noted, however, that the experimental work to date [1] has dealt with an uncharacterized mixture of C(¹D) and C(³P), and perhaps even C(¹S) reactions. Here we consider only those of C(¹D). The second is to elucidate

the *detailed* dynamical behaviour of a model system with novel chemical properties. Previous quasiclassical trajectory studies of O(¹D) and C(¹D) reactions with isotopic hydrogen molecules [3, 4, 5], which also employed VB-DIM potential energy surfaces, showed that at low collision energies the reaction proceeds primarily by “insertion” of the ¹D atom into the H–H bond to form an intermediate H₂O or CH₂ ¹A' complex, which subsequently decomposes to products. At higher energies the importance of a direct “abstraction” process to form the same OH + H or CH + H, products increases. In the case of O(¹D) + HD, at a relative collision energy of 2.0 kcal mole⁻¹, it was found [5] that of the products formed *via* the intermediate HDO complex, OD is favoured over OH by a factor of 5.6. Since classically the OH and OD bond energies are equal, this strong preference for the OD molecular product must reflect only a mass effect. In the present study, the mass difference between the two possible “leaving groups” (H and I compared to H and D) is greatly exaggerated. The bond strength effect, however, would be expected to oppose the mass effect, favouring the formation of the most exothermic set of products (CH + I). It is of considerable interest to ascertain the relative importance of these opposing factors in the “unimolecular” decomposition of collision complexes.

The electronic Hamiltonian for the present study is constructed from the diatomic and atomic potentials according to the formula

$$H = \sum_c \sum_{d>c} H_{cd} - \sum_c H_c, \quad (4)$$

where H_{cd} is the Hamiltonian matrix for the cd diatomic molecule and H_c is the Hamiltonian matrix of atom c. Once the appropriate diatomic and atomic data have been obtained, the potential energy surface is calculated by solution of the secular equation

$$|H - ES| = 0 \quad (5)$$

where E is the potential energy (here we consider only the lowest-energy ¹A' electronic state) and S is the overlap matrix.

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