

fumarate produced the cyclopropane in only 2% yield but of a sufficient quantity to determine that no asymmetric induction resulted.

The asymmetric ratios produced from both diazoalkanes are reminiscent of our results on photochemical 2 + 2 cycloadditions.<sup>3b</sup> That is, the asymmetric induction observed is almost entirely due to the first chiral group. Since cooperativity is not observed, a synchronous mechanism cannot be operative. Moreover, the order of effects is also inconsistent with an asynchronous but concerted mechanism, which is operationally equivalent to rate-limiting single-bond formation followed by rapid collapse of the 1,3-biradical. Since the presence of asymmetric induction minimally requires a discrimination between the two ends of a molecule, such single-bond formation would be expected to occur preferentially at the less-hindered methyl end of the monochiral fumarate to yield diradical D (Figure 1), with asymmetric induction increasing when the bischiral fumarate forces first-bond formation at a chiral end. That the asymmetric ratio does *not* increase suggests that the second bond-forming step is rate limiting and that the first step is reversible.<sup>5</sup> This first step could either be intermediate complex formation, which has been invoked for singlet carbenes,<sup>2</sup> or bond formation to a trimethylene diradical. A minimal condition for such reversibility is that the heat of reaction have a positive or small negative value. A Benson calculation on addition of triplet diphenylcarbene<sup>9</sup> to dimethyl fumarate to yield the diradical provides a reaction enthalpy of ca. -4 kcal/mol, a figure permissible for, though not requiring, reversible diphenylcarbene addition.

A final question concerns the identity of the reactive intermediate produced upon irradiation. Recent experimental evidence by Schuster and co-workers<sup>6</sup> and by Scaiano, Griller, and co-workers<sup>7</sup> suggests that singlet fluorenylidene undergoes rapid intersystem crossing to the ground-state triplet. Our fumarate concentrations are such that less than 10% of the singlet can be intercepted even at diffusion control. Scaiano and Griller have observed<sup>7</sup> that triplet fluorenylidene adds to acetonitrile to form a nitrile ylide. Using their activation parameters, we calculate a rate for this process at 0 °C of  $2.3 \times 10^7 \text{ s}^{-1}$ , a rate that is approximately half the pseudo-first-order rate constant of direct addition to 0.031 M diethyl fumarate calculated in a similar fashion, namely,  $(1.37 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})(0.031 \text{ M}) = 4.2 \times 10^7 \text{ s}^{-1}$ . However, the nitrile ylide would form photostable pyrrolines,<sup>10</sup> which are presumably the unidentified additional products of the reaction, rather than cyclopropanes. Finally, the control experiment, which presumably involves 1,3-dipolar addition by the diazofluorene itself, produced no asymmetric induction. We are forced to conclude that the reactive intermediate is triplet fluorenylidene and, by analogy, triplet diphenylmethylene.

That cyclopropanation by triplet diarylcarbenes should prove to be nonconcerted is unsurprising, although we now have direct evidence that this is the case. We also have demonstrated that in our case first bond formation appears to be reversible. This is consistent with, and supportive of, the observation that certain 1,3-biradicals of type D can undergo bond cleavage to form carbenes.<sup>5</sup> Perhaps more important, we have an additional reaction that has proved susceptible to our cooperativity criterion.<sup>11</sup>

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**Supplementary Material Available:** A calculation of the second bond dissociation energy of diphenylmethane (2 pages). Ordering information is given on any current masthead page.

## Large Tunneling Effects in the Migration of Chemisorbed Hydrogen on a Metal

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"The migration of atoms or molecules along the surface is one of the most important steps in surface reactions....Nevertheless only a few experiments provide information about this surface process."<sup>1</sup> Therefore theoretical calculations can play a valuable role. DiFoggio and Gomer have measured surface diffusion coefficients for H and D on a close-packed plane of tungsten and found strong evidence for tunneling at  $T \leq 140\text{--}160 \text{ K}$ .<sup>2,3</sup> Although most theoretical work has been based on classical methods,<sup>4</sup> Valone et al. (VVD),<sup>5</sup> in a Monte Carlo transition-state-theory study of H diffusing on the (100) plane of fcc Cu in the low-coverage limit, included quantal effects by replacing the original pair potential by a temperature-dependent, Gaussian-averaged effective potential derived semiclassically.<sup>6,7</sup> They found non-Arrhenius  $T$  dependences and large differences at low  $T$  from an Arrhenius expression with the activation energy set equal to the classical barrier height. These results are very exciting, but the effective-potential method, which, if valid, could have widespread usefulness for molecular dynamics calculations, has not been tested against a dynamical method of known reliability. We have now calculated the same surface diffusion coefficients using a reaction-path formulation of variational transition-state theory (VTST) with semiclassical adiabatic ground-state (SAG) transmission coefficients,<sup>8-10</sup> a combination that has been tested extensively for gas-phase reactions involving hydrogen.<sup>11-13</sup> This method also has the advantage that it allows us to distinguish quantal effects on bound degrees of freedom from tunneling effects (these effects are not separable in the VVD calculations). This is the first application of reaction-path methods,<sup>14</sup> VTST, or SAG methods to a condensed-phase process, and it extends these powerful tools to the simplest possible elementary step in surface reactions and one that is often<sup>1</sup> rate limiting at low pressure.

We consider the diffusion of a single H atom on a rigid single terrace of Cu. The lattice parameters and interaction potential are the same as used by VVD. The former are based on bulk Cu without surface reconstruction; the latter is based on the pair

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**Table I.** Unimolecular Rate Constants ( $s^{-1}$ ) for Hopping

| T, K | H                    |                      |                      | D                    |                      |                      |
|------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
|      | CHO                  | VVD                  | present              | CHO                  | VVD                  | present              |
| 120  | $9.0 \times 10^{-8}$ | $3.5 \times 10^{-5}$ | $2.5 \times 10^{-5}$ | $6.3 \times 10^{-8}$ | $1.5 \times 10^{-6}$ | $7.8 \times 10^{-7}$ |
| 140  | $9.2 \times 10^{-5}$ | $7.1 \times 10^{-3}$ | $4.4 \times 10^{-3}$ | $6.5 \times 10^{-5}$ | $6.4 \times 10^{-4}$ | $4.2 \times 10^{-4}$ |
| 160  | $1.7 \times 10^{-2}$ | $4.6 \times 10^{-1}$ | $3.2 \times 10^{-1}$ | $1.2 \times 10^{-2}$ | $6.6 \times 10^{-2}$ | $5.0 \times 10^{-2}$ |
| 200  | $2.4 \times 10^1$    | $1.9 \times 10^2$    | $1.7 \times 10^2$    | $1.7 \times 10^1$    | $5.0 \times 10^1$    | $4.4 \times 10^1$    |
| 400  | $5.2 \times 10^7$    | $8.0 \times 10^7$    | $8.6 \times 10^7$    | $3.7 \times 10^7$    | $4.4 \times 10^7$    | $4.6 \times 10^7$    |
| 600  | $6.7 \times 10^9$    | $7.6 \times 10^9$    | $8.4 \times 10^9$    | $4.7 \times 10^9$    | $4.8 \times 10^9$    | $5.2 \times 10^9$    |
| 1000 | $3.3 \times 10^{11}$ | $3.2 \times 10^{11}$ | $3.6 \times 10^{11}$ | $2.3 \times 10^{11}$ | $2.2 \times 10^{11}$ | $2.5 \times 10^{11}$ |

**Table II.** Factors Contributing to the Ratio of the Present Hopping Rate Constant to the CHO Results for H

| T, K | anharmonicity | bound-mode quantization | tunneling | total |
|------|---------------|-------------------------|-----------|-------|
| 120  | 0.83          | 22.1                    | 15.3      | 280.  |
| 140  | 0.85          | 11.7                    | 4.8       | 47.9  |
| 160  | 0.87          | 7.4                     | 2.9       | 19.0  |
| 200  | 0.89          | 4.1                     | 1.88      | 6.8   |
| 400  | 0.95          | 1.52                    | 1.15      | 1.65  |

potential of Gregory et al.<sup>15</sup> The activated diffusion process consists of hopping between fourfold coordination sites (binding energy BE = 40.2 kcal/mol; distance from surface plane  $z = 1.14$  Å). The saddlepoint is a two-fold bridge site (BE = 28.6 kcal/mol,  $z = 1.68$  Å). The polyatomic version of the reaction-path Hamiltonian,<sup>10,14,16</sup> canonical variational transition-state theory,<sup>8-10,17</sup> and the small-curvature-approximation SAG transmission coefficient<sup>9,10,18</sup> are generalized to the case of an adsorbate on a surface and are used to calculate a unimolecular site-to-nearest-site hopping rate constant  $k$ ; anharmonicity is included by the independent-normal-mode<sup>10,17</sup> and WKB<sup>13</sup> approximations, and the small-curvature approximation accounts for the nonrectilinear multidimensional nature of the tunneling path, involving motion both parallel and perpendicular to the surface. The hopping rate constant can be converted to a two-dimensional diffusion coefficient under the assumption of uncorrelated hops<sup>19</sup> by multiplying by  $l^2/4$ , where  $l$  is the hop length (2.624 Å).

The calculated hopping rate constants (including a factor of 4 for the number of equivalent hopping directions) are given in Table I, where they are compared to the results of VVD and to another set of calculations performed by us in which we neglected anharmonicity, quantization of bound vibrational modes, and tunneling. The latter calculation is abbreviated CHO (classical harmonic oscillator). Table I shows excellent agreement among the various methods at high  $T$ , but the two semiclassical rate constants are appreciably higher than the CHO result at low temperature. Considering the large deviations of these two sets of results from the CHO ones and also the fact that the three responsible effects (anharmonicity, bound-mode quantal effects, and tunneling) are implicit in the VVD work only through the effective potential, but are treated explicitly and separately by quite different methods in our work, the agreement of the two sets of semiclassical results within a factor of 1.6 for  $T \geq 140$  K and 1.9 for  $T = 120$  K is quite encouraging.

Table II shows the three separate effects for surface diffusion of H. The last column is the ratio of the present rate constants to the CHO ones, and this ratio is a product of the first three factors. This table shows that the two quantal effects are more important than anharmonicity. Furthermore tunneling increases the rate by factors of 3-15 at 160-120 K and therefore greatly dominates the over-the-barrier contributions at these temperatures.

Primarily because of the tunneling contribution the present calculations show two of the same qualitative features present in

the low-temperature experiments of DiFoggio and Gomer.<sup>2,3</sup> First, the kinetic isotope effects greatly exceed the classical value of 1.4. Second, the Arrhenius plots become quite nonlinear at low temperature, with the deviation from the extrapolation of the high-temperature Arrhenius fit roughly comparable to the tunneling factor. An Arrhenius fit at 1000 K yields activation energies of 11.4 and 11.6 kcal/mol and preexponential factors of  $1.12 \times 10^{14}$  and  $8.31 \times 10^{13} s^{-1}$  for H and D, respectively. However, the activation energies decrease to 7.6 and 10.4 kcal/mol at 120 K.

We draw three significant conclusions from the present study: (i) The Gaussian-averaged effective potential method<sup>5-7</sup> appears to be a reasonably accurate way to incorporate quantal effects into many-body molecular dynamics simulations. (ii) The reaction-path formulation of variational transition-state theory with semiclassical transmission coefficients appears to be a practical and accurate method for calculating surface diffusion coefficients and, as a corollary, probably also for calculating bulk diffusion coefficients,<sup>20</sup> even for hydrogen atoms when quantal effects are very large. (iii) Tunneling does appear to provide the dominant mechanism for low-temperature surface diffusion of H on metals.

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**Registry No.** H<sub>2</sub>, 1333-74-0; Cu, 7440-50-8; D<sub>2</sub>, 7782-39-0.

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## Facile Oxidation of Methoxide to Formaldehyde by a Heterocyclic Quinone

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The oxidation of conjugated alcohols to the corresponding carbonyl derivatives by high redox potential quinones is well documented.<sup>1,2</sup> The postulated mechanism involves hydride transfer from the neutral alcohol to the quinone providing an oxocarbenium ion stabilized by conjugation and the hydroquinone anion.<sup>1,2a</sup> Rapid proton loss from the former species then provides the carbonyl product. Thus, the high-energy oxocarbenium ion which would arise from methanol precludes its oxidation by

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