Photochemistry

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Rich Athermal Ground-State Chemistry Triggered by Dynamics through a Conical Intersection

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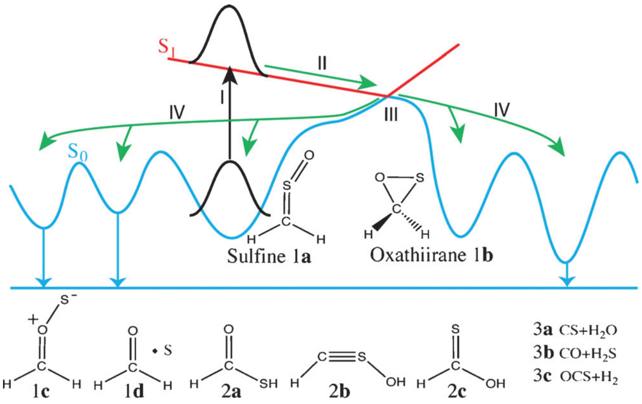
Abstract: *A fundamental tenet of statistical rate theories (such as transition state theory and RRKM) is the rapidity of vibrational relaxation. Excited-state reactions happen quite quickly (sub-picosecond) and thus can exhibit nonstatistical behavior. However, it is often thought that any diversity of photoproducts results from different conical intersections connecting the excited and ground electronic states. It is also conceivable that the large energy of the photon, which is converted to vibrational energy after electronic transitions could lead to athermal hot ground state reactions and that these might be responsible for the diversity of photoproducts. Here we show that this is the case for sulfines, where a single conical intersection is implicated in the electronic transition but the excited state reaction leads to nine different products within less than a picosecond.*

Most theoretical studies on photochemical reactions involving conical intersections focus on radiationless decay from the excited electronic state to the ground state and do not examine the resulting ground state dynamics. This is largely because vibrational relaxation on the ground state is assumed to be fast. In this case, venerable statistical rate theories would be sufficient to determine the fate of the ground state products.[1] However, the kinetic energy released upon reaching the ground electronic state can be substantial. Vibrational relaxation could compete with reactive events in the "hot ground state" molecule, and this might lead to rich and unexpected chemistry. Schreiner and co-workers recently reported a startling example of the diversity of possible photoproducts starting with the H_2CSO sulfine. Despite the small size of this molecule, nine photoproducts were observed including acids, dissociated molecules and exotic species such as the previously unobserved three-membered C−S−O ring oxathiirane[2] and HC≡S−OH containing a rare carbon–sulfur triple bond[3] (Scheme 1). Unfortunately, the detailed mechanisms giving rise to these products were unclear. Here, we show that the excited state dynamics proceeds by a single mechanism and that hot ground state dynamics is responsible for eight of the nine observed products.



Scheme 1. Schematic representation of the sulfine photochemistry. Upon photoexcitation to its first excited electronic state S_1 (step I), the sulfine **1a** starts evolving in this electronic state (step II) until it eventually reaches a conical intersection, which will either take the sulfine back to its original ground-state geometry or trigger the formation of oxathiirane (step III). Either molecule reaches its ground electronic state with a large kinetic energy that can be used to overcome reaction barriers and to form other species (step IV).

We shed light on the dynamics following 313 nm photoexcitation in an argon matrix of thioformaldehyde S-oxide sulfine (**1a**) to its first excited state (S_1), which exhibits $n\pi^*$ character,[4] by in silico reproduction of Schreiner's experiment[2a] using state-of-the-art theoretical techniques. The non-radiative decay to the ground state is described in gas phase using the ab initio multiple spawning[5] (AIMS) method carried out at the MS-CASPT2[6] level, while the subsequent dynamics occurring in the ground electronic state is described with Born–Oppenheimer molecular dynamics (BOMD) carried out at the DFT/PBE0 level (see the Supporting Information (SI) for further information on the methods and electronic structure calculations used in the simulations).

The nuclear wavepacket formed in S_1 upon photoexcitation (step I in Scheme 1) evolves (step II) in the excited state until it eventually reaches a conical intersection[7] (step III), transferring it to the ground state. The excited-state dynamics indicates that the non-radiative decay occurs in two steps: a large transfer of population from S_1 to S_0 happens first after ≈70 fs and is then followed by a slower population decay (Figure 1 a). The vast majority of the population is transferred at configurations where the S_1–S_0 energy gap is below 0.15 eV, i.e., near a conical intersection. However, the population transfer takes place mostly at energies significantly above the minimum energy conical intersection (MECI) (Figure 1 b,c).[7d,8] This observation implies that the nuclear wave-

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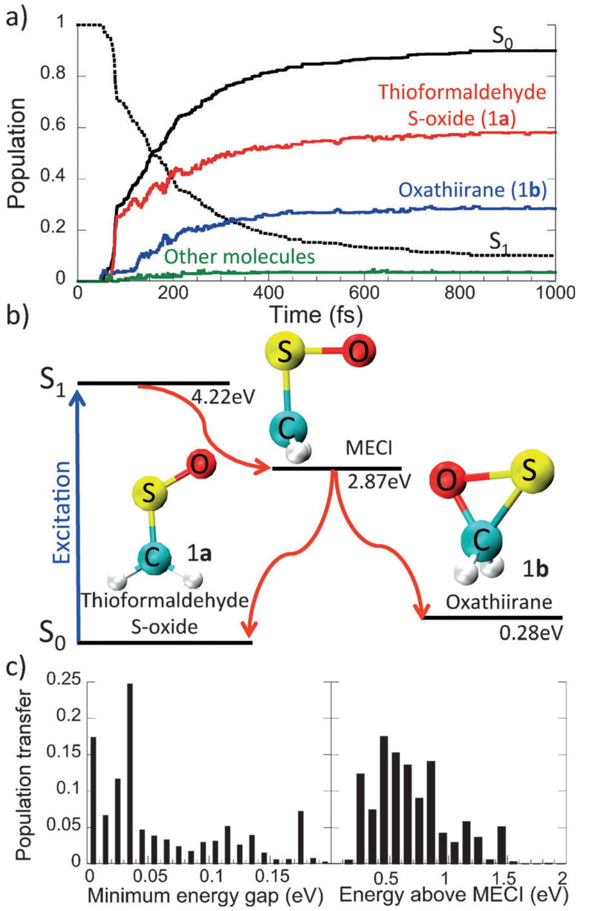

Figure 1. a) Population trace of the S_0 and S_1 states following the photoexcitation of the sulfine in S_1 at time $t=0$. The fraction of **1a**, **1b**, and other molecules in the ground state is also shown. (The geometric criteria selected to define the molecules are given in the SI.) b) Energy diagram of the critical points on the S_1 and S_0 potential energy surfaces for sulfine and oxathiirane. c) Histograms of the population transferred from S_1 to S_0 as a function of the minimum energy gap and of the energy above the MECI.

packet in S_1 never crosses the MECI, but instead usually encounters higher energy CIs along the intersection seam.[7d] Analysis of the AIMS dynamics shows strong correlation between the way the wavepacket approaches the conical intersection and the ground state product.[9] For instance, short SO and CO bond lengths, along with a long CS bond length and a small CSO angle, are correlated with the formation of oxathiirane and correspond to the closing of the CSO ring (further information is available in the SI). Relaxation of the nuclear wavepacket on the ground state results solely in formation of oxathiirane (31 %) and regeneration of the sulfine photoreactant (65 %). This is surprising given the diversity of products observed by Schreiner (Scheme 1).

When the molecule reaches the ground state after nonadiabatic processes, much of the photon energy is converted to kinetic energy that can be used to overcome reaction barriers and to form a variety of molecules that could not be otherwise reached (step IV in Scheme 1). In this sense, the molecule can be considered as being in a "hot ground state". Despite the high temperature of the molecule when it reaches the ground state (around 5000 K, see SI), the prompt formation of photoproducts cannot be described by statistical methods such as RRKM[10] (see SI) or TST.[11] Indeed, the timescale of the dynamics—few picoseconds—is faster than the time for the molecule to vibrationally relax and form a quasi-equilibrium state with the transition state, the cornerstone of standard transition state theories. Nonstatistical behavior has been previously reported in thermal reactions[1,12] and also in excited state reactions mediated by decay through different conical intersections.[13] The present case extends this to ultrafast reactions beginning in the excited state and decaying through the same conical intersection. In order to model the subsequent ground-state dynamics on a picosecond timescale, we switch from nonadiabatic dynamics to adiabatic BOMD at the PBE0 level.

All photoproducts are formed within a picosecond, even though the reactions exhibit barriers as large as hundreds of kJ mol^{-1} (see SI for further information). In the first 100 fs of dynamics following deexcitation to S_0, we only observe a conversion from the sulfine (**1a**) or the oxathiirane (**1b**) to thioformaldehyde O-sulfide (**1c**) and formaldehyde + S(^{1}P) (**1d**) (Figure 2b,c). Experimentally, the product formaldehyde + S implies that the sulfur is in its triplet state as a result of spin–orbit coupling. We indeed computed an important spin–orbit coupling for the molecules **1b, 1c** and **1d**, which will likely lead to the formation of the carbonyl and sulfur in its triplet state (see SI for more details).

After an additional 100 fs of BOMD, a build up of methylidyne-λ^4-sulfanol (**2b**) is observed, along with a transient population of methanethioic *S*- and *O*-acid (**2a** and **2c**), whose population oscillates between 1 and 5 % (Figure 2b,d). These transient acids are potential intermediates in the formation of $CO + H_2S$. Experimentally three dissociation products are detected, $CS + H_2O$ (**3a**), $CO + H_2S$ (**3b**) and $OCS + H_2$ (**3c**). All of these dissociation products are observed in the simulations, but the second one represents the main dissociation channel (see SI for details). Interestingly, a significant correlation can be observed between the immediate result of nonadiabatic dynamics (sulfine or oxathiirane) and the ultimate dissociation products. For example, at the end of a BOMD trajectory initiated from oxathiirane the fraction of $CO + H_2S$ is 2.5 × larger than when the dynamics starts from sulfine (see SI for further information). The oxathiirane appears therefore to be less stable than the sulfine following the deexcitation, and will likely dissociate either into $CO + H_2S$ or formaldehyde + S(^{3}P). It is worth pointing out that, experimentally, a strong IR signal of fragmented molecules is recorded, as the system is pumped for one hour until the complete disappearance of the sulfine signal.[2a] Given the ultrafast electronic quenching, sulfine may thus be subject to repeated excitation on the nanosecond or longer time scale, driving the production of fragmented molecules. Finally, none of the simulations showed the formation of the potentially interesting carbene $HO{-}\ddot{C}{-}SH$, which was expected experimentally but disappointingly not observed.[2a]

As the experiment was performed in an argon matrix, we investigated the role played by confinement on the molecules

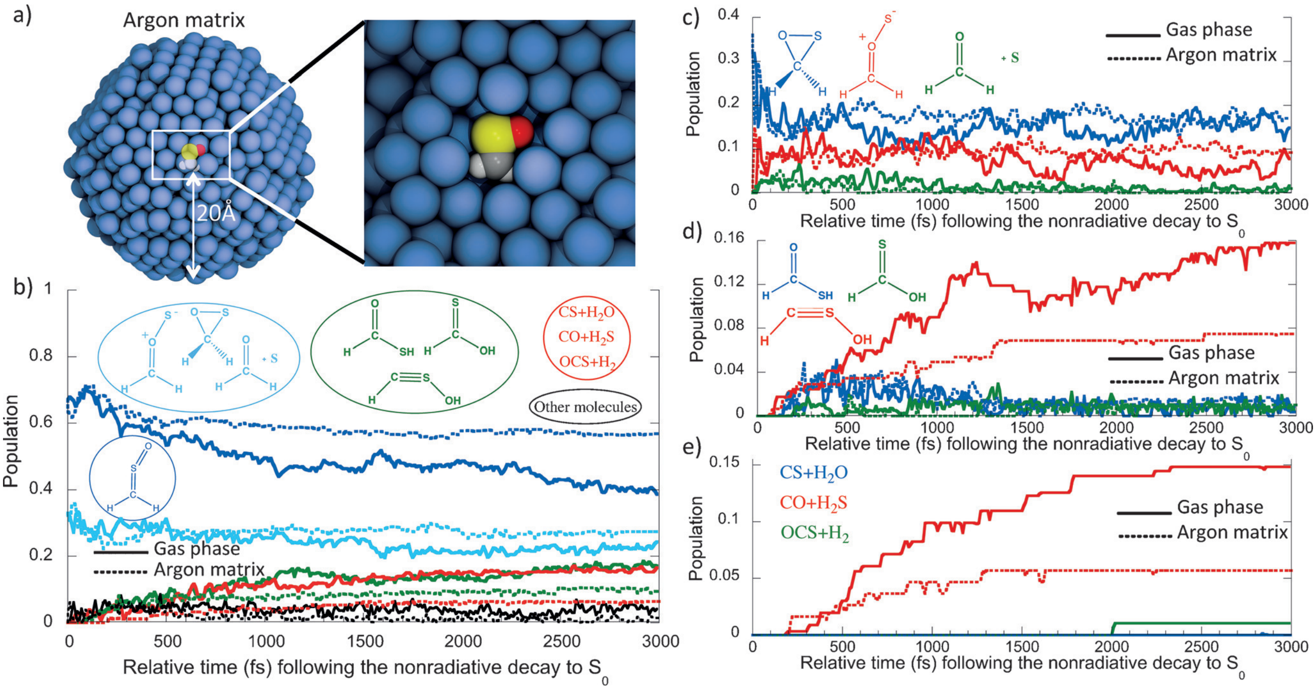

Figure 2. a) Argon matrix used in the QM/MM dynamics. b) Population of the species formed during the BOMD. The full lines represent the population of molecules formed in gas phase and the dotted lines the same population but in the argon matrix. As the BOMD dynamics is initiated from the AIMS trajectories, which are stopped whenever they reach S_0, the time $t=0$ corresponds to the beginning of the BOMD and is not an absolute time. c) Population of **1b**–**d** molecules during the BOMD. d,e) Same as (c) for the acids (**2a**–**c**) molecules and dissociated species (**3a**–**c**).

formed using the QM/MM formalism for adiabatic BOMD. Interestingly, the dynamics carried out in the argon matrix—based on the same initial conditions as those of the QM part—give a very similar picture to the pure gas phase dynamics, although the $CO+H_2S$ and bulky acid **2b** yields are decreased by more than 50% (Figure 2a and e). The argon matrix appears to significantly decrease the yield of hot ground state products and to stabilize the populations more quickly by cooling the molecule (see SI), as expected from previous work.[14] Furthermore in the gas phase, the fragments are free to move away from each other during the dissociation process, whereas confinement effects of the argon matrix disfavor the formation of dissociated species.

The chemistry following the photoexcitation of the sulfine **1a** is unusually rich, leading to the creation of nine new molecules. Surprisingly though, the ultrafast excited-state dynamics of sulfine only accounts for the formation of oxathiirane directly. The experimentally observed molecules instead result from chemical transformations taking place after relaxation in the ground state of the sulfine or the oxathiirane. Due to the large amount of kinetic energy released after nonradiative quenching, these reactions are much faster and more efficient than one would expect from transition state theory, and an explicit treatment of the dynamics is needed to represent them properly. It is this "hot ground state" which results in the unusual reactivity of this otherwise simple 5-atom molecule. Our study also attests to the accuracy and efficiency of current theoretical methods, both for excited-state dynamics—AIMS/MS-CASPT2—and for adiabatic ground-state dynamics—GPU-accelerated (QM/MM) BOMD/DFT.

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