Tunnel Effect

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# Hydroxycarbene: Watching a Molecular Mole at Work

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Imagine you are standing in front of a large pile of earth. On the other side you see your partner. To get to her/him, you have to spend energy walking around the pile of earth or even climbing it to some degree. You would not, however, try to dig a tunnel through the pile of earth. But there are small furry animals, called moles, which have a special preference for doing exactly that.

Let us shift focus from the biology of moles to chemistry: in chemistry, atoms and molecules will also normally search for the path around the pile of earth, and react classically by thermal activation. Quantum mechanics, however, provides for an exception: particularly light particles (electrons, but also hydrogen atoms) can tunnel through a barrier. In other words: their wave function dictates a nonzero probability distribution on the other side of the barrier.

The title molecule, hydroxycarbene, is a singlet carbene. It is a small, highly reactive molecule, which has recently been characterized for the first time. And it shows a remarkable reactivity even at temperatures just above absolute zero, for which the tunnel effect is responsible.

Singlet carbenes are closed-shell compounds of bivalent carbon. Because of the two missing valences, there are two nonbonding orbitals at the carbene carbon atom which determine their reactivity. A nonbonding σ orbital lies in the plane of the carbene carbon atom and its two substituents, and is doubly occupied. Another empty π orbital is orthogonal to the lone pair. Electronegative substituents bearing lone pairs, such as a hydroxy group, are thus doubly stabilizing. The energy of the carbene lone pair is lowered by the σ-electron withdrawing effect of the oxygen atom, whereas the oxygen lone pair is lowered energetically by π-interaction with the *p*-AO at the carbon atom (Figure 1).

All characteristics of singlet carbenes, such as their pronounced electrophilicity, but also their nucleophilic properties, can be derived from the presence of these two orbitals. The reactivity scale of singlet carbenes encompasses exceedingly reactive molecules, such as vinylidene ($H_2C{=}C{:}$),[1] as well as the well-known stable Arduengo (Wanzlick) carbenes,[2] or the recently published stable cyclopropenylidene.[3] Typical reactive singlet carbenes, such as phenoxychlorocarbene, PhO–C–Cl, are frequently investigated workhorse molecules of physical organic chemistry[4,5] and usually

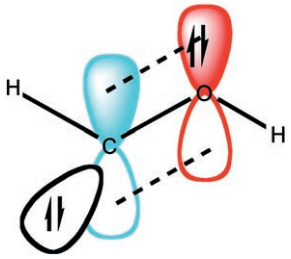
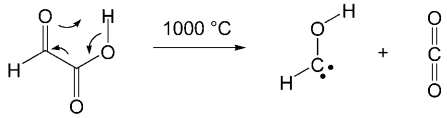



***Figure 1.*** Electronic structure of hydroxycarbene.

have lifetimes in the microsecond range. They are generally easily prepared by thermolysis or photolysis of the corresponding diazirines (or diazo compounds). If, however, these precursors are not accessible owing to a lack of stability, the synthesis of the corresponding singlet carbenes poses a great challenge. One of the problem cases is hydroxycarbene **1**, H–C–OH, which has been discussed as a possible component in interstellar matter and for its role in the high-temperature chemistry of its stable isomer formaldehyde. In a recent publication, hydroxycarbene has now been characterized by matrix isolation spectroscopy and with the help of quantum chemistry.[6,7] The unconventional starting material for the synthesis of **1** was anhydrous glyoxylic acid **2**. Flash vacuum pyrolysis of **2** at $T = 1000\,^{\circ}C$ followed by trapping of the pyrolysis products in solid argon at 10 K led to compound **1** in moderate yield. Formaldehyde and carbon monoxide are also formed in the reaction (Scheme 1).




***Scheme 1.*** Generation of hydroxycarbene by flash vacuum pyrolysis of glyoxylic acid.

Carbene **1** is remarkably unstable at 10 K. In principle, the potential well protecting **1** should be deep enough to render it completely stable under conditions of matrix isolation spectroscopy. Nevertheless, it rearranges into formaldehyde with a half life of 2 h, even in argon at 10 K. The rearrangement into formaldehyde or cleavage into carbon monoxide and dihydrogen can also be induced photochemically. Further experimental findings are that the rate constant of the

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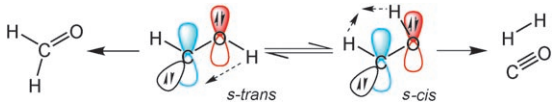
rearrangement is independent of temperature between 11 K and 20 K, and the choice of matrix material (argon, krypton, or xenon) has no impact on the kinetics. These results all indicate that the low-temperature reactivity of **1** is due to hydrogen atom tunneling. Schreiner and co-workers were able to prove this point beyond doubt by pyrolyzing glyoxylic acid deuterated at the carboxy group. This reaction yielded hydroxycarbene deuterated at the hydroxy group (H–C–OD), which was completely stable at 10 K. To support the experimental data, chemical calculations were carried out, as is the case with every physical–organic publication today. Calculations at the highest level of theory (AE-CCSD(T)/cc-pVQZ, including anharmonic potential) allowed the assignment of both the fundamental and the combination modes in the vibrational spectrum of **1** with very high accuracy ($\pm 2\ cm^{-1}$). A comparison between the experimental and calculated infrared spectra indicates that **1** is present as the *s-trans* conformer, which is also more stable according to the calculations. The *s-trans* conformer is predicted to rearrange to formaldehyde, whereas the *s-cis* conformer is prone to cleavage into carbon monoxide and dihydrogen (Scheme 2).




***Scheme 2.*** Decay pathways for hydroxycarbene.

It is not the tunneling of a hydrogen atom as such that is remarkable (unlike heavy atom tunneling, hydrogen atom tunneling is not an exceedingly rare event), it is the fact that the activation enthalpy is relatively high for such a reaction ($\Delta H^{\neq} = 29.7\ kcal\,mol^{-1}$). The height of the barrier and its width are decisive parameters for the tunneling probability, and tunneling processes through a high barrier generally have a low probability. The rate constant of hydrogen atom tunneling was also calculated. For the rearrangement of **1** into formaldehyde, the calculation yielded a half-life $t_{1/2}$ of 122 min, whereas the deuterated isotopomer H–C–OD was predicted to be essentially stable with $t_{1/2} \approx 1200$ years. Both predictions are in perfect agreement with the experimental observations.

Which conclusions can we draw from the work of Schreiner and co-workers? Firstly, it now appears highly unlikely that **1** is a component of interstellar matter, as it will disappear within very short time even at very low temperatures. Secondly, it is worthwhile looking for unconventional precursors to interesting reactive intermediates. And thirdly, physical organic chemistry is alive and well, and we can look forward to learning about many new and surprising discoveries in the years to come. For example, not every animal that looks like a mole is a mole: Dihydroxycarbene, generated by flash vacuum pyrolysis of anhydrous oxalic acid, does not rearrange via hydrogen tunneling. It is stable under conditions of matrix isolation spectroscopy, probably because the second hydroxy group sufficiently stabilizes the carbene center through the additional π interaction.[8]

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