CHEMICAL PHYSICS

A Quick Look at Hydrogen Bonds

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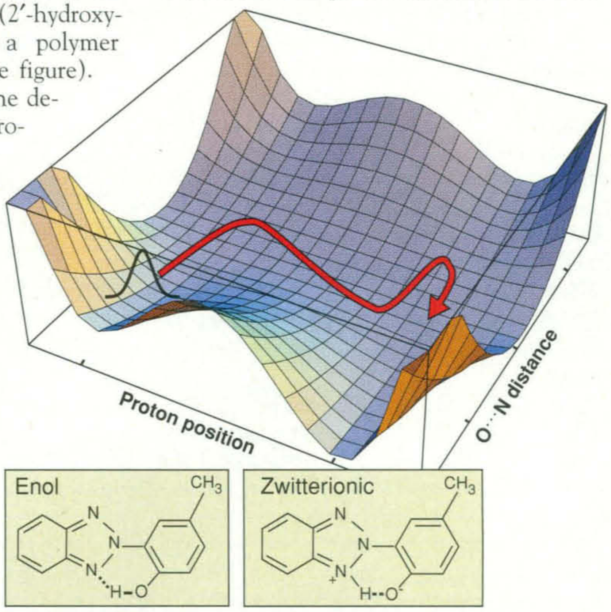
In photochemical reactions involving proton transfer, the driving force comes from drastic and simultaneous changes in the acidity and basicity of the involved groups. These swings in pH arise from a fast electronic redistribution after photoexcitation (1). Elsaesser and colleagues now report an important observation: using an optical pump-probe method with 20-fs resolution, they have observed coherent vibrational motion in the excited state that modulates and controls a proton transfer reaction (2).

One of the questions in proton-transfer dynamics is whether the proton motion is decoupled from other geometry coordinate changes, so that the reaction can be described in terms of a localized coordinate along the hydrogen bond, or whether more complex motions of the molecular frame are involved in the reactive pathway (1). The time required to move from the reactant well to the photoproduct well may be on the time scale of low-frequency motions (1–4). The dynamics of any chemical reaction is determined by the shape of the potential energy surfaces and can be visualized by ultrafast pump-probe experiments (5, 6) and by vibronic width analysis of the absorption of isolated and cooled molecules in a supersonic expansion (7).

In chemical or biological systems, the elementary vibrations of the whole reaction might be in phase, with oscillations on a picosecond time scale. In the condensed phase, because of collisions with solvent molecules, the time and energy barrier of the reaction (if it exists) may change with respect to those in free conditions, and the nascent vibrational coherence is lost at the earliest stage of the reaction. Contrary to this expectation, coherent nuclear motions in the retinal chromophore of rhodopsin (8) and in a membrane protein (9), both in the condensed phase, have been observed.

In a photoinduced proton-transfer reaction, the situation is even more complex: the nuclear and electronic redistribution must destroy the phase coherence of the elementary vibrational motions on a time scale shorter than that required (about 60 fs) to move the proton from the initial well to the final one. In addition, a very fast spreading of the wave packet along several modes must help to suppress the vibrational coherence. Chudoba, Riedle, Pfeiffer, and Elsaesser (2) showed a surviving phase coherence of two vibrational modes during and after the proton motion, despite the involvement of these internal (and external) modes in this reaction.

Chudoba *et al.* used a pump-probe technique with a time resolution of 20 fs to observe phototautomerization in 2-(2′-hydroxy-5′-methylphenyl)benzotriazole, a polymer photostabilizer, in solution (see figure). The highly anharmonic in-plane deformation mode (470 cm^{-1}) provides the most important contribution in the reaction by modulating and moving the reactive wave packet along a barrierless pathway in the potential energy surface (figure). Phase memory is retained because the density of the vibrational energy mostly involves low-frequency modes, similar to those of other simple molecules where coherent wave packet motion has been established (5, 6). Thus, both the structure and dynamics of a hydrogen bond are caught in the act. Now, we can redefine the driving force of proton motion as a fast electronic redistribution induced by light, and a vibrational coherence of the elementary modes that modulate the H-bond coordinates. Spectrally resolved experiments with a jet-cooled molecular beam (1, 7) and recent ab initio calculations (10) on a similar molecule support these findings and lead to a proton-transfer model in which the dynamics of the wave packet is determined first by the reduction in the distance between the directly implicated groups in the reaction, which allows a barrierless channel to open.



Light-induced proton transfer dynamics of 2-(2′-hydroxy-5′-methylphenyl)benzotriazole along the potential energy surface. The created wave packet evolves along the N...O coordinate, reducing the width and energy of the barrier to the transfer and leading to movement along the O...H coordinate from the enol (left) to the zwitterionic (right) wells.

Because of the existence of an energy barrier at zero time, one may expect two competitive mechanisms (7). One moves the system along the heteroatomic distance until it reaches a region where the barrier vanishes (figure), and the other involves quantum tunneling dynamics. This latter process might occur while the wave packet spreads according to the former mechanism. Both channels might together bring the system from the reactant to the product well. A direct way to discriminate between these different dynamics is to study the H/D isotope effect in the rate of the transfer (1, 3, 7). If the system goes through quantum tunneling, a change in the mass from hydrogen (1 atomic mass unit) to deuterium (2 amu) leads to an increase in the width and energy of the barrier to the transfer. Thus, the deuteron motion has a slower dynamics.

Several ways for controlling the reaction with femtosecond-pulse timing, pulse shaping, and pulse sequencing have been developed (5, 6). An attractive way to control the hydrogen bond structure, spectroscopy, and dynamics is to reduce the degrees of freedom available to the proton motion coordinate (along the hydrogen bond) by caging the system. In this way, out-of-plane rotational motions are prevented. Upon ultrafast electronic excitation, the nascent wave packet is trapped in a small region of the energy surface, and its evolution will mainly depend on quantum tunneling and relaxation processes to the ground state. On the theoretical side, to correctly model the energy surfaces and related dynamics in a multidimensional way, one has to take into account the coupling between the hydrogen bond mode and the in-plane and out-of-plane motions of the implicated moieties. This kind of modeling in biologically and chemically important systems is time consuming and will require more

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sophisticated treatments with more powerful computers (*10*). So, perhaps the ball (proton) is now in the theoretical court.

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PREBIOTIC CHEMISTRY

Where Smokers Rule

Robert H. Crabtree

Deducing the mechanism of the origin of life on Earth (*1*, *2*) has always remained a fascinating but unsolved puzzle. Some have even considered it too difficult for scientific study, because the direct evidence is long gone and we can only work by plausible inference. Although this is indeed a very difficult problem to approach experimentally, a number of striking observations over the years have allowed the formulation of plausible scenarios for the prebiotic synthesis of various important biomolecules. The report by Huber and Wächtershäuser on page 245 of this issue (*3*) directs our attention to the possibilities (*4*) afforded by the unusual chemistry (*5*) of deep sea vents.

Huber and Wächtershäuser reaction

$2CH_3SH + CO \xrightarrow{\text{NiS/FeS}} CH_3CO(SCH_3) + H_2S$

Acetyl-CoA synthase reaction

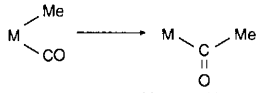
$CH_3\text{-corrin} + CO + HSCoA \xrightarrow{\text{Acetyl-CoA synthase}} CH_3CO(SCoA)$

(HSCoA = coenzyme A)

Monsanto process

$CH_3OH + CO \xrightarrow{\text{Catalyst}} CH_3COOH$

Key step in Monsanto process



(M = metal in Monsanto catalyst)

In a celebrated experiment (*1*) by Miller, a mixture of hydrogen, methane, ammonia, and water, a then-plausible imitation of the early Earth atmosphere and ocean, was exposed to electric discharges, much as this early chemical mixture might have been exposed to lightning, to produce several amino acids in significant amounts. Purines and pyrimidines were obtained from hydrogen cyanide and cyanoacetylene under similar conditions. Organic molecules formed in this or other ways are considered to give rise to a "primordial soup" that may have provided favorable conditions for the origin and development of life. Subsequent revisions of the probable composition of the early Earth atmosphere (hydrogen, for instance, may not have been an important constituent) have clouded the interpretation of the experiment.

In the deep ocean, hydrothermal vents can discharge a cocktail of chemicals, including hydrogen sulfide and related species and a dark "smoke" of metal sulfides—hence, the term "black smokers." Today, these locations shelter a group of unusual biota that depend on these volcanic discharges for their energy supply.

Most scenarios for the origin of life involve processes that might occur in surface waters or in shallow seas. Huber and Wächtershäuser have instead favored the possibility (*4*) that the exotic environment of the deep-sea vents might be favorable for the origin of life. They have shown that mixed iron nickel sulfides act as a catalyst for the conversion of methyl thiol and carbon monoxide, present in vent gases, to methyl thioacetate, $CH_3CO(SCH_3)$, a compound with a C-C bond and containing an activated acetyl group (see figure). This compound resembles acetyl–coenzyme A (acetyl-CoA), or $CH_3CO(SCoA)$, a central intermediate in the biosynthesis of a variety of important biomolecules. The abiological C-C bond–forming reaction of Huber and Wächtershäuser can therefore be seen as a plausible preliminary step in the building up of more complex organic molecules in or near the early Earth vents.

The hypothesis that metal sulfides could play a prebiotic catalytic role is attractive because nature uses Fe_4S_4 and Fe_2S_2 groups, essentially fragments of the iron sulfide lattice, as the catalytic sites in many enzymes found in all types of organisms today (*6*). Nickel-iron-sulfur sites, though much rarer, most notably occur (*7*) in acetyl-CoA synthase and other enzymes present in a group of evolutionarily primitive organisms, the archaebacteria (*8*), which show a number of biochemical peculiarities that distinguish them from other organisms. In particular, acetyl-CoA synthesis occurs in some of these organisms from CoASH, methylcorrin, and CO (figure), a reaction catalyzed by a Ni-Fe-S cluster of still undetermined structure in the Ni-Fe-S enzyme acetyl-CoA synthase (*9*).

The mechanism of the reactions discussed above is uncertain, but a clue is afforded by an important industrial process, first developed by Monsanto Company, for which the mechanism is well known (*10*). In this metal-catalyzed process, CH_3OH reacts with CO to give CH_3COOH via the intermediates shown in the figure. The key C-C bond–forming step, a migration of a methyl group to a coordinated CO, is the most likely pathway for the newly proposed reaction.

The results raise interesting questions. Could the acetyl-CoA synthase pathway be a biochemical fossil, not only from the first organisms, but also from the prebiotic pathway that produced activated acetyl fragments, the prebiotic equivalents of acetyl-CoA? Is the presence of life in subsurface water deposits a possibility even when a planet has an inhospitable surface?

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