The Man Behind 'Femtochemistry'

Ahmed Zewail Wins the 1999 Nobel Prize in Chemistry

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He hails from the land of the Pharaohs; he came to the United States, like many, to seek higher education and today he is at the top of his achievements. He is Ahmed H Zewail, Linus Pauling Chair of Chemical Physics at the California Institute of Technology. He has just been honoured with the Nobel Prize in Chemistry by the Royal Swedish Academy of Sciences on October 12, 1999, '*for his studies of the transition state of chemical reactions using femtosecond spectroscopy*'. Bond formation and bond breaking are the two most fundamental concepts that make chemistry. Zewail studied these two processes using ultrashort techniques on the time scale on which they actually occur.

The Man

Born February 26, 1946 in Egypt, Ahmed H Zewail (*Figure* 1) received his BS and MS degrees from Alexandria University which was, perhaps, once the greatest place for learning on earth. He then moved to the University of Pennsylvania, Philadelphia in USA and obtained a PhD degree in 1974 working with R M Hochstrasser.

Figure 1. A stamp size portrait (truly) of Zewail. In fact, this stamp was issued by Egypt, his native country, in 1998 honoring him even before he was made famous by the chemistry Nobel Prize!

Following his postdoctoral work with Charles Harris at the University of California at Berkeley, he joined the chemistry department of Caltech in 1976. He was tenured in two years and became a full professor in 1982. He is currently the Linus Pauling Chair Professor of Chemistry and Professor of Physics at Caltech. His wife Dema Zewail is a physician and they have four children. His scientific family over the past twenty years at Caltech is much bigger though, and it consists of approximately 150 postdoctoral fellows, graduate students and visiting scholars.

His Work

In 1872, an English photographer Eadward Muybridge was trying to capture on film a horse flying through the air. It was challenging enough for him in those days since the eye could not follow such a motion and he was given a handsome grant by a businessman to do that. After many attempts, Muybridge developed a camera shutter, which opened and closed for only two thousandths of a second. To do the experiment Muybridge spaced 12 of these cameras half a meter apart alongside the horse track. A string was stretched across the track to a mechanism that would trigger the camera when the horse broke through the string. This shutter speed allowed him to attain a resolution of about 2 centimeters in each picture for a horse that was galloping at 10 meters per second (resolution is defined as the speed of the horse multiplied by the exposure time). The speed divided by the spacing between the cameras equals the number of frames per second, which is 20 in this example. The motion within a picture becomes sharper as the shutter speed becomes faster. The resolution of the motion improves as the spacing between the cameras is reduced. Two aspects of high-speed photography described above are relevant to femtosecond molecular spectroscopy pioneered by Zewail and his coworkers at Caltech. First a continuous motion is broken up into a series of snapshots or frames. In this way a fast motion is slowed down so that the eye can see it. Second, both methods must produce enough snapshots in rapid succession in such a way that the frames can be arranged to produce an illusion of a continuous motion. In fact, approximately 30 frames are necessary to provide one second of animation.

> A series of snapshots of a moving object taken in rapid succession can be arranged to produce an illusion of continuous motion.

Molecular Photography

The time resolution or shutter speed needed to capture bond making and bond breaking processes is beyond any conventional scale. When a molecule dissociates into fragments or

A femtosecond (10^{-15} second) is to a second what a second is to 32 million years!

when it combines with another molecule to form a new molecule, it passes through transition states which last less than a trillionth of a second, or one picosecond (10^{-12} second). At a molecular level a reaction starts when two molecules, A and B come close to each other and begin to interact. Finally, through an event of trans-substantiation, a new molecule C which is chemically distinct from A or B is formed. This simple reaction can be depicted as:

$$A + B \rightarrow [A\cdots B]^{\#} \rightarrow C$$

where the species $[A\cdots B]^{\#}$ conceptualize the full family of configurations through which the reaction evolves en route from reagents to products and what Henry Eyring in 1931 called the ‘transition state’ of the reaction. Conversely, a molecule of C can be excited with light from a source (say a laser) and A and B can be produced. The whole trip from reagents to products involves changes in internuclear separation of the order of 10 Angstroms or 1 nanometer. If the typical velocity of the reagents at room temperature were 1000 meters per second, then the entire trip through the transition state would take about 1 picosecond. Therefore, molecular photography as described above would demand a time resolution (shutter speed) which is less than a picosecond or a few femtoseconds. A femtosecond (10^{-15} second) is to a second what a second is to 32 million years! In one femtosecond light travels 0.3 micrometer – about the diameter of a bacterium.

The Apparatus

Although the idea behind these femtosecond experiments is simple, the experimental set-up to carry out the experiments is not at all trivial. In brief, it consists of a pulsed laser source capable of generating two femtosecond pulses of various duration (at the moment the world’s shortest pulse is 6 femtosecond), a high vacuum chamber where a beam of molecules is flowing, and a sophisticated detector. A start laser flash called the ‘pump’ pulse intercepts an ‘isolated’ molecule in a molecular jet (see

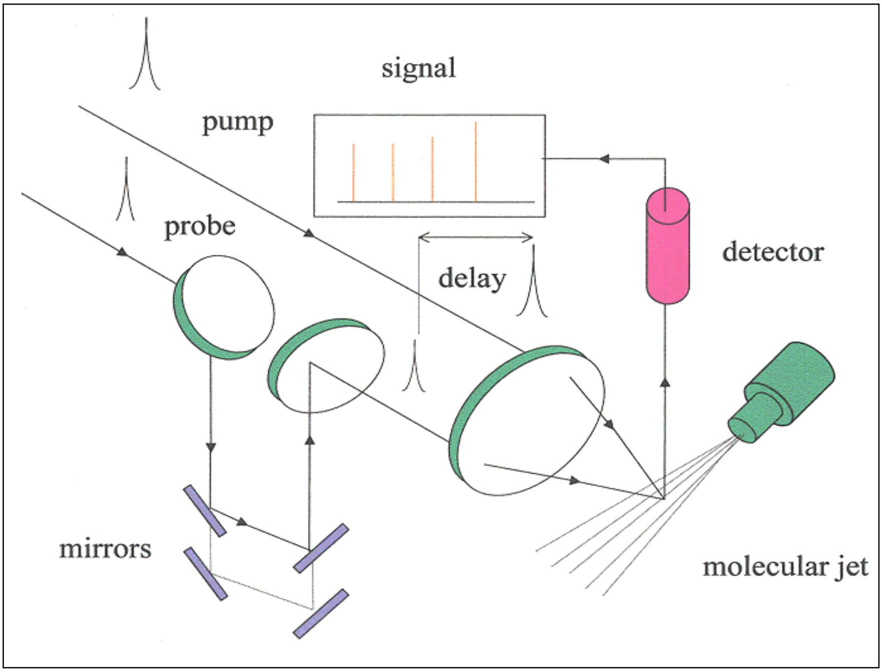


Figure 2) and sets the experimental clock at zero. A second flash called the 'probe' pulse suitably delayed with respect to the 'pump' pulse hits the 'same molecule' and captures a photograph of the reaction in progress at that particular instant. Like the cameras in Muybridge's experiment, a femtosecond camera takes snapshots at different delay times to record the progress of the entire reaction from reagents (zero time) to products (long time).

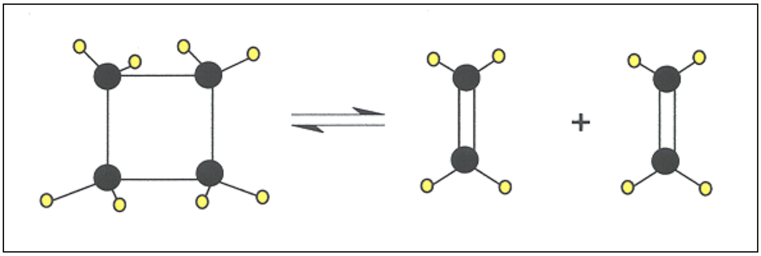
Figure 2. Schematic diagram of the femtosecond apparatus used by Zewail and his co-workers in Caltech. The femtosecond pump and probe pulses delayed suitably in time with respect to each other are combined and focussed on a molecular jet inside a high vacuum chamber. The signal from the interaction region is detected in another direction, which can distinguish between events starting at different times.

Two Examples

For more than a century, one of the most well studied addition/ elimination reactions is the addition of two ethylene molecules to form cyclobutane or the reverse reaction involving the ring opening of cyclobutane to produce two ethylene molecules. This is a classic example of a concerted reaction, which is photochemically allowed by Woodward–Hoffman rules [3]. The chemical transformation is shown in *Scheme* 1.

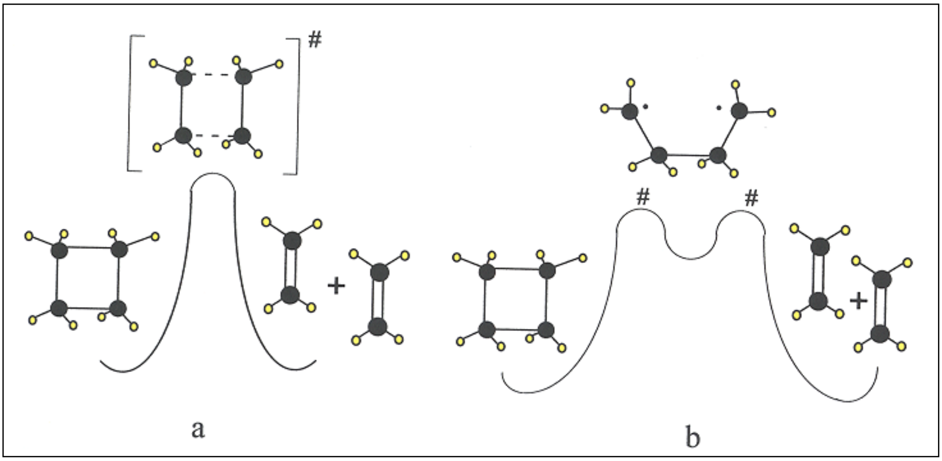
This reaction, however, may proceed directly through a transition state (see *Figure* 3a) or it could proceed through a diradical

Scheme 1.



intermediate (see *Figure* 3b), beginning with the rupture of one σ-bond in cyclobutane to yield tetramethylene, which in turn goes through a transition state to give ethylene. Thus the stability of the diradical as an intermediate is crucial to our understanding of the mechanism of this simple reaction: a concerted single-step process vs a two-step process with an intermediate. Zewail and his coworkers addressed this question in their laboratory and studied the stability of the tetramethylene diradical generated from various precursors (see *Figure* 4) in real time. Using cyclopentanone as the precursor they have shown that with two photons at 310 nm (pump) carbon monoxide is eliminated through an α-cleavage. The tetramethylene diradical intermediate has been clearly identified by mass spectrometry as a stable species having a lifetime of 700 femtoseconds. By varying the 'pump' wavelength (total energy) and using different substitutions on the ring, they have concluded that this cycloaddition reaction, contrary to the current belief, proceeds in a nonconcerted fashion through an intermediate via a two-

Figure 3. a) Single transition state mechanism, and b) diradical intermediate mechanism.



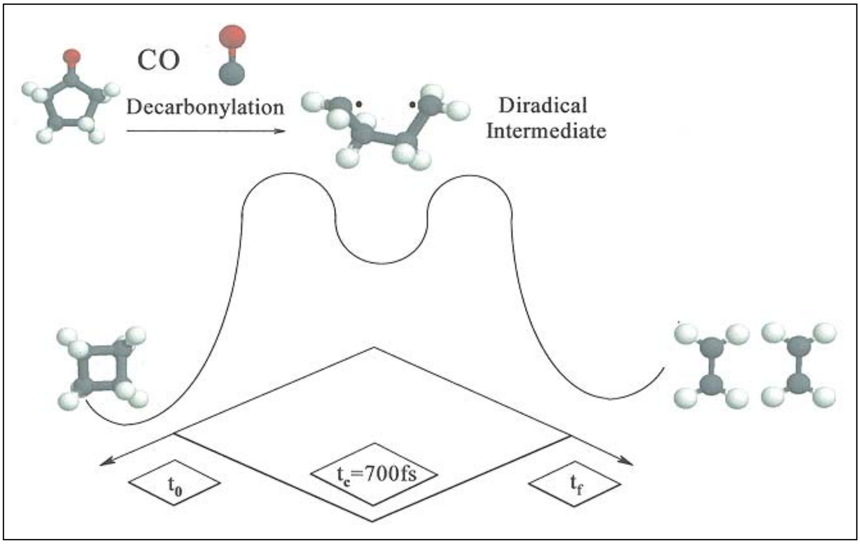


***Figure* 4. The diradical reaction shown schematically in an energy diagram. After elimination of carbon monoxide from the parent cyclopentanone photochemically, the tetramethylene diradical is created; this can undergo ring closure to yield cyclobutane or can produce two ethylenes.**

step process. This approach is general for the study of other reaction intermediates.

Another example where the femtosecond dynamics of bond breaking and bond making was examined is a simple exchange reaction between bromine atom and iodine molecule which goes through a collision complex (intermediate) as follows:

$$Br + I_2 \rightarrow [\,Br–I–I]^{\#} \rightarrow BrI + I.$$

The time evolution of this reaction was followed by detecting the product BrI with probe-pulse induced fluorescence. The reaction is found to go through a stable collision complex $[Br–I–I]^{\#}$ (*Figure* 5). The complex lasts for about 50 picoseconds. Quantum chemical calculations along with the experimental data predicts that the $[Br–I–I]^{\#}$ complex is bent and the Br–I–I angle is ca. 150°. The energy (depth) of the potential well in which Br–I–I is trapped, as well as the activation energy barrier to go to the final products, have also been determined.

Epilogue

Femtochemistry following Zewail's work has become a 'buzz word' in experimental physical chemistry research today. It has changed our view of chemical reactions and we can ask detailed

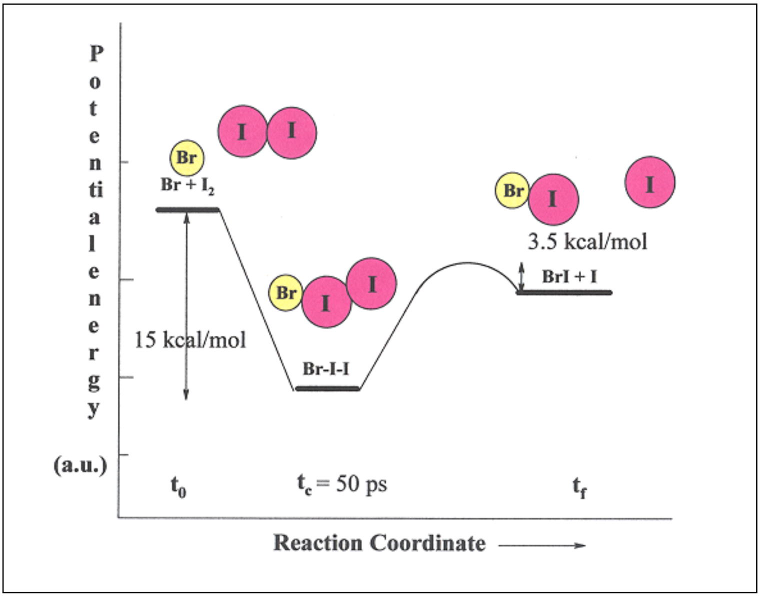


Figure 5. The femtosecond dynamics of the iodine atom abstraction reaction. The corresponding structures are shown with emphasis on three 'molecular photographs' at t_0, t_c and t_f as the reaction proceeds to completion. The calculated well-depth and barrier height are also noted.

questions which could not be asked before. We can now follow the individual atoms and molecules as they react to produce new molecules or atoms. They are no longer elusive! A variety of processes and their mechanisms are now being 'clocked' using femtosecond 'pump' and 'probe' experiments. It includes catalysis (to probe mechanism and improve catalysts), liquid phase reactions (to understand reactions in solution), polymers (to improve physical properties of polymers), and biological processes (e.g., to understand the primary photochemical step in vision). With the development of the world's fastest camera, Zewail has let loose a stream of dreams where only imagination can limit new problems to be explored.

Suggested Reading

[1] A H Zewail, The birth of molecules, *Scientific American*, p.40, December 1990.

[2] J C Polanyi and A H Zewail, Direct observation of the transition state, *Accounts of Chemical Research* (Holy-Grail special issue), Vol.28, p.119, 1998.

[3] S Ranganathan, A tale of two topologies: Woodward–Hoffman rules at your fingertips, *Resonance*, Vol.2, No.2, 1997.

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