

# Dynamic Solvent Effects on Polar and Nonpolar Isomerizations

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During the past decade an international effort has been made to understand the kinetics of ultrafast reactions, which could roughly be defined as reactions that proceed with a half-life that is in the range of few femtoseconds ( $10^{-15}$  s) to a few nanoseconds ( $10^{-9}$  s). This field has been made possible by a number of important advances in the technology of ultrafast spectroscopy, including picosecond and more recently femtosecond spectroscopy. Much of the research has been concerned with ultrafast photochemical isomerizations. Three types of isomerization have received the greatest attention, namely, cis/trans isomerization,<sup>1-6</sup> intramolecular proton transfer, and intramolecular electron transfer.<sup>10-15</sup> Figure 1 shows isomerization reactions that have been studied in our laboratory. In each case the reaction is initiated by optically exciting the ground-state reactant with an ultrashort (<1 ps) light pulse to prepare the reactant in its lowest excited singlet state. Subsequently, *the excited reactant isomerizes to yield the product in its lowest excited singlet state.* The kinetics of these excited-state reactions have been measured by monitoring the time- and wavelength-resolved fluorescence of both the reactants and products during the reaction.

Ultrafast isomerizations are interesting from many perspectives. They are important prototypes for fast processes in chemistry and biology such as (i) proton transfer in water and alcohols, (ii) proton transfer, electron transfer, and cis/trans isomerization in photosynthesis, vision, and other photobiological reactions, and (iii) numerous ultrafast reactions of short-lived intermediates in slower thermal, photochemical, and electrochemical reactions. Furthermore, ultrafast reactions defy explanation by the conventional picture of chemical reactions in solution, i.e., transition-state theory.<sup>16</sup> Thus ultrafast chemistry is an important area of fundamental research in kinetics.

In the past few years we have studied the kinetics of the reactions in Figure 1 as a function of solvent, temperature, molecular structure, and in a few cases isotopic substitution, in order to gain insight into ultrafast reactions. At the same time, some of these reactions and related reactions have been studied by several other groups as described in review articles and well-refer-

enced papers in the field.<sup>1,4-8,10,16,17</sup> Simultaneously, theorists have made great progress in establishing the special principles that distinguish ultrafast reactions from the more widely studied slower reactions.<sup>18-22</sup> Indeed, theorists and experimentalists have attempted whenever possible to make a comparison between experiment and the predictions of the various theoretical models developed to date.

The remainder of this paper is organized as follows. The following section reviews some of the special theoretical notions and models that have been introduced to describe ultrafast reactions. This is followed by separate sections on each of the reaction types in Figure 1. Finally, the last section offers conclusions and future perspectives on this field.

## Theoretical Issues

Chemical reaction rates in solution are conventionally assumed in most cases to be well predicted by transi-

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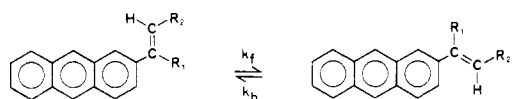
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## EXCITED STATE ISOMERIZATIONS

## 1. Cis/Trans Isomerization of Alkenylanthracenes

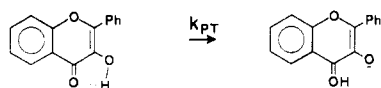


2VA ( $R_1=H, R_2=H$ ), 2PA ( $R_1=Me, R_2=H$ ), 2BA ( $R_1=Me, R_2=Me$ )

## 2. Electron Transfer of Bianthryl



## 3. Proton Transfer of 3-Hydroxyflavone



**Figure 1.** Structure drawings for the ultrafast reactions that have been studied in the authors' laboratory.

tion-state theory.<sup>16</sup> According to this theory isomerization reactions should exhibit first-order kinetics, and the rate constant should be a simple function of the free energy of activation  $\Delta G^\ddagger$ :

$$k_{\text{tst}} = (k_B T/h) \exp(-\Delta G^\ddagger/RT) \quad (1)$$

Here  $k_B$  is Boltzmann's constant,  $T$  is absolute temperature,  $h$  is Planck's constant, and  $R$  is the gas constant.

Experiment and theory have shown that transition-state theory breaks down for ultrafast isomerizations for a variety of reasons, as described in detail in later sections and introduced here. For example, for proton-transfer isomerizations, such as the reaction of 3-hydroxyflavone (3HF) (Figure 1), non-first-order kinetics have been observed.<sup>23-26</sup> This breakdown of transition-state theory is due to a distribution of reactant/solvent complexes. Each type of complex reacts with a different proton-transfer rate that is actually faster than the time scale for interconversion of the complexes.<sup>8,9,22-26</sup> In other cases, such as electron transfer of bianthryl (BA) (Figure 1), the free energy barrier is so small that one of the assumptions of transition-state theory, namely,  $\Delta G^\ddagger \gg k_B T$ , becomes invalid.

Perhaps the most important and most studied breakdown of transition-state theory is the so-called *dynamic solvent effect*. The origin of this effect is subtle and deserves some discussion. One of the assumptions of transition-state theory is that if the reacting system (solute and solvent) is in the configuration of the transition state, it will be converted to product with unit efficiency.<sup>16</sup> But this assumption can be in-

valid if collisions between the solvent and reactant induce recrossings of the barrier at the transition state.<sup>16,20-22</sup> This effect is a function of the dynamics of the solvent. It causes the true reaction rate constant to be less than the rate predicted by eq 1.

Historically, dynamic solvent effects have been discussed in terms of Kramers' theory,<sup>27</sup> in which isomerization in solution is viewed as a thermally activated barrier crossing in a one-dimensional reaction potential. The collisions with the solvent are included as a friction that impedes the progress of the system along the reaction coordinate. The Kramers theory expression for the rate constant is as follows:

$$k = k_{\text{tst}} \{ [\xi/2\omega_b m]^2 + 1 \}^{1/2} - \xi/2\omega_b m \quad (2)$$

Physically,  $m$  represents the effective mass of the reacting molecule as it progresses along the reaction coordinate. The quantity  $\xi$  is a friction coefficient that measures the effect of dynamic solvent interactions on the reaction coordinate motion. As the rate of solvent/solute collisions increases,  $\xi$  increases also. Finally, the variable  $\omega_b$  characterizes the reaction potential near the transition state. It is the barrier vibrational frequency, which depends on the curvature of the potential at the barrier and the mass  $m$ .

Many experimental studies on cis/trans isomerizations have been concerned with the validity of Kramers' theory and more contemporary approaches,<sup>3-6</sup> as discussed below for the s-cis/s-trans isomerization of 2-vinylantracene (2VA), 2-(2-propenyl)anthracene (2PA), and 2-(2-butenyl)anthracene (2BA) (Figure 1).

Dynamic solvent effects are particularly important for intramolecular electron transfer, such as that observed for BA (Figure 1). Theory shows that for electron transfers with small barriers, the progress of the reaction can be limited by the motion of the solvent.<sup>18,19</sup> This is a consequence of strong dielectric coupling that exists between the developing charge separation on the solute and the solvent dipoles. In other words, the dynamics of solvation are rate limiting for ultrafast electron transfers. Experimental studies on electron transfer have been concerned with establishing the kinetic role of solvent dynamics. In addition, a simple model for predicting the solvation times and electron-transfer times has been evaluated.

## Proton Transfer

We and others have measured the excited-state intramolecular proton-transfer kinetics of 3HF by ultrafast emission spectroscopy.<sup>8,23-26</sup> The stable ground-state isomer of 3HF is the normal (N) form. Electronically excited N molecules undergo proton transfer to yield the tautomer (T). Optical excitation of N produces two distinct fluorescence bands centered at 410 and 543 nm, which have been assigned to the N and T isomers, respectively. Time-resolved emission transients at 413 nm give a measure of the time dependence of the concentration of N, while emission transients at 543 nm analogously monitor T, as portrayed in Figure 2.

In non-hydrogen-bonding solvents such as alkanes the proton-transfer rate constant  $k_{\text{PT}}$  is extremely large ( $>10^{11}$ ) at all temperatures<sup>9,9</sup> like many other proton-transfer examples.<sup>7</sup> But, in hydrogen-bonding solvents

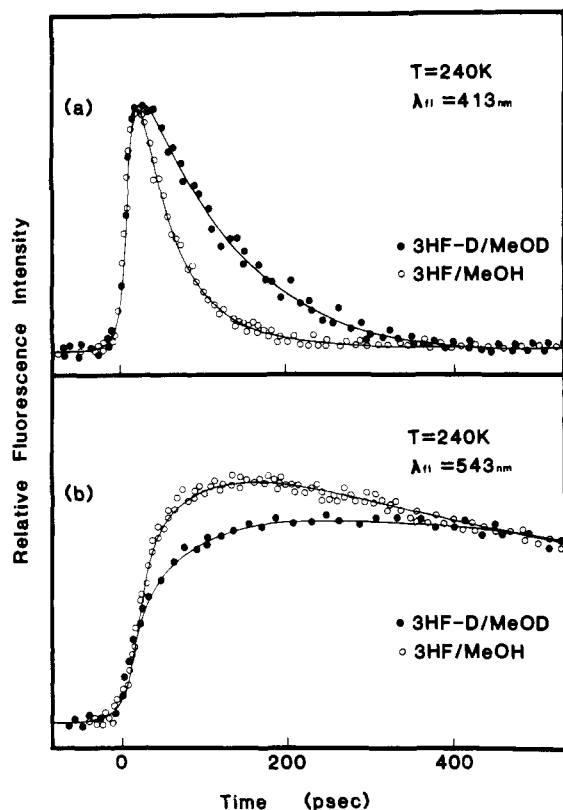
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**Figure 2.** Time-resolved emission traces at 413 (a) and 543 nm (b) for 3-hydroxyflavone (○) and monodeuterated 3-hydroxyflavone (●) induced by 355-nm, 30-ps pulses. The points in the figure (● or ○) represent experimental data. The solid lines are computer fits of the data that take into account the time response of our apparatus and the two kinetic components for proton transfer.

such as alcohol and ethers,  $k_{PT}$  is much smaller. These results demonstrate that the uncomplexed "free" 3HF can rapidly transfer the proton across the existing intramolecular hydrogen bond. In contrast, hydrogen-bonded complexes of 3HF with the solvent apparently have a weakened or broken intramolecular hydrogen bond, which increases the barrier to proton transfer. Examples of possible complexes are as follows:



The hydrogen-bonded complexes have a profound effect on the proton-transfer kinetics of 3HF. For example, specific complexes of 3HF and a varying number of alcohol molecules can be prepared in cryogenic matrices of argon. The different complexes exhibit very different proton-transfer rates.<sup>9</sup> In the solution reaction of 3HF in alcohols the existence of 3HF/solvent complexes causes the proton-transfer kinetics to have a fast and slow component, which is clearly observable in the kinetics of the T emission. This transient shows an apparently instantaneous rise followed by a slower time-resolvable component; see Figure 2.

A variety of evidence on the proton transfer of 3HF and derivatives of this compound suggests that the 3HF proton-transfer kinetics are not modulated by the dynamics of the solvent. Rather the results indicate

that the kinetic variations reflect different rates of quantum mechanical tunneling of the proton in the specific complexes. The solvent and substituent kinetic effects can be rationalized by attributing the effects to modulation of the proton-transfer reaction potential. Ongoing research on 3HF, and proton transfer in general, in our group is concerned with obtaining an accurate, quantitative theory to understand the microscopic proton transfer of the complexes.

### Electron Transfer

Recent theoretical work on small-barrier ( $\Delta G^\ddagger \ll k_B T$ ) electron-transfer isomerizations, for which the reaction coordinate is primarily reorientation of the solvent molecules, shows that the kinetics of these processes should be limited by the time scale for solvent motion. In other words,  $\tau_{et}$  should be equal to  $\tau_s$ , the microscopic relaxation time of the solvent.<sup>10,18,19</sup> This effect comes about because the polar solute/solvent interactions allow the solvent molecules to retard the progress of the reaction, an effect called dielectric friction. Polar dynamic solvent effects like this are far reaching and even play a role in slow thermal electron-transfer reactions.<sup>28</sup>

Theoretical models for dynamic solvent effects on electron transfer usually employ the dielectric continuum model of solvation, in which the solute is represented by a spherical cavity with a point dipole at the center and the solvent is represented by a uniform dielectric continuum. According to this model,  $\tau_s$  should be equal to the longitudinal relaxation time  $\tau_1$  of the solvent. This relaxation time is given by the expression  $\tau_1 = (\epsilon_\infty/\epsilon_s)\tau_D$ , in which  $\epsilon_\infty$  (the infinite-frequency dielectric constant),  $\epsilon_s$  (the static dielectric constant), and  $\tau_D$  (the dielectric relaxation time) can be measured by dielectric dispersion methods on the solvent only. Thus the dielectric continuum model in combination with the electron-transfer theories predicts that  $\tau_{et}$  should be equal to  $\tau_1$ .

Some experimental results on ultrafast electron transfer in *alcohols* seem to support this prediction. In an attempt to test the generality of  $\tau_{et}/\tau_s$  equality we have studied the kinetics of the electron transfer of BA (Figure 1), which is an excellent prototype for electron-transfer reactions. The molecule bianthryl (BA) has two fluorescence bands in polar solvents. One of the bands is due to the nonpolar LE (locally excited) isomer, while the other is due to the highly polar CT (charge transfer) isomer, which is simply an intramolecular ion pair (see Figure 1). The dynamics of the LE emission give a direct measure of the electron-transfer time  $\tau_{et}$  (inverse rate constant) of electronically excited BA.

We have measured  $\tau_{et}$  in various polar aprotic solvents as summarized in Table I. Polar aprotic solvents were studied as opposed to alcohols, because the solute/solvent interaction in polar aprotics is more compatible in principle with the dielectric continuum models of solvation; i.e., specific solvation effects such as hydrogen bonding are less important in aprotics. Our data (Table I) on electron-transfer times of BA in polar aprotic solvents show that  $\tau_{et}$  is *not equal* to  $\tau_1$  in general.<sup>11,13</sup> We have also measured the microscopic sol-

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**Table I**  
A Comparison of  $\tau_{et}$  for 9,9'-Bianthryl with  $\tau_s$  and  $\tau_1$  for Different Solvents

solvent	$\tau_{et}$ , ps	$\tau_1$ , ps	$\tau_s$ , ps
acetonitrile	0.7	0.2	0.4–0.9 <sup>d</sup>
propionitrile	1.2	0.3	1.1–1.5
butyronitrile	2.0	0.5	1.5–2.1
pentanonitrile	4.4	0.7	3.6
PC <sup>a</sup>	3.4	5.1	4.9
triglyme	11.7		25
GTA <sup>b</sup>	750 <sup>c</sup>		820

<sup>a</sup>Propylene carbonate. <sup>b</sup>Glycerol triacetate. <sup>c</sup>The GTA numbers are from Nagarajan et al.<sup>15</sup>  $T = 11.5$  °C. The rest of the values in the table were recorded at ambient temperature.<sup>11,13</sup> <sup>d</sup>These values represent the range of observed  $\tau_s$  values with different probes; see Kahlow et al.<sup>12</sup>

vation times  $\tau_s$  of the solvents in Table I by recording the excited-state solvation times of various polar aromatic molecules that are not capable of electron transfer. It is interesting that the agreement between  $\tau_{et}$  and  $\tau_s$  is fairly good, supporting the notion that the electron-transfer dynamics of BA are indeed controlled by transient solvation.

The lack of agreement between  $\tau_{et}$  and  $\tau_1$  apparently reflects the failure of the dielectric continuum model to describe transient solvation accurately.<sup>12,29–31</sup> Presumably continuum models fail for transient solvation because, while they include the long-range correlations of the solvent motion, they ignore the molecular interactions and structure of the inner solvation shells. Fortunately, theoretical treatments that go beyond continuum theory are actively being developed.

Research is in progress in our laboratory to extend electron-transfer and solvation measurements to the femtosecond time scale. Theory predicts that the structure of the solvent will be especially important on this time scale, which to date remains unexplored. Furthermore, the femtosecond time scale is critically important in the dielectric friction of the ubiquitous thermal (large barrier) electron-transfer reactions.

### Cis/Trans Isomerization

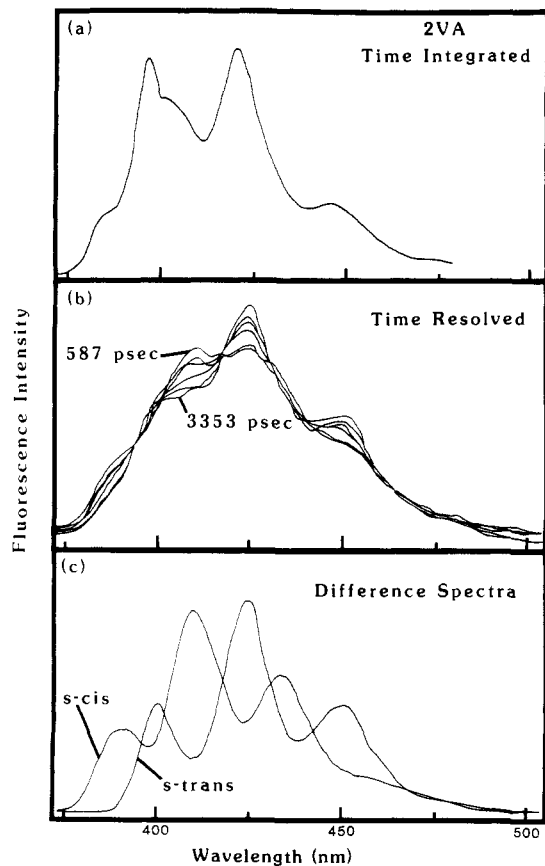
The most widely studied ultrafast isomerization type is the excited-state cis/trans isomerization.<sup>1,6</sup> We recently introduced a new prototypical cis/trans reaction, namely, the s-cis/s-trans interconversion of the alkenylantracenes (Figure 1). This new model reaction has several important advantages for comparison to theory that are not all available with any preexisting model reaction, as discussed in detail elsewhere.<sup>1</sup> In this section we describe kinetic experiments on the solvent dependence of the isomerization kinetics of the alkenylantracenes that have allowed for a deeper insight into the role of dynamic solvent effects in solution reactions. Before describing the results, we review how dynamic spectroscopy can be used to study the kinetics of these compounds.

The isomerization kinetics of the alkenylantracenes can be measured by time-resolved fluorescence spectroscopy, as shown in Figure 3 for the specific example

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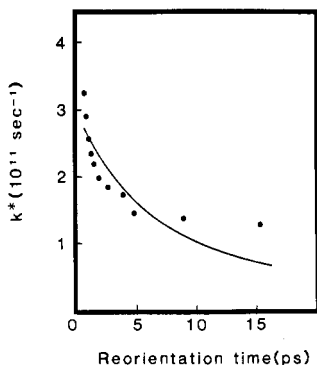
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**Figure 3.** Fluorescence emission spectra of 2-vinylantracene in cyclohexane solution at ambient temperature: (a) time-integrated emission; (b) picosecond time-gated emission, accumulated over 1600 laser shots, at 587, 920, 1587, 2253, 2920, and 3353 ps, respectively; (c) derived emission spectra of the two interconverting isomers. In the spectra in (b), the integrated emission intensities have been normalized.

2VA. Both isomers contribute to the ordinary (time integrated) fluorescence spectrum (Figure 3a) of the compound. Furthermore, if instantaneous time-gated spectra are recorded at specific delay times after laser excitation, the interconversion of two distinct spectra from s-cis and s-trans is clearly evident (Figure 3b). Computer manipulation of the time-gated spectra allows one to calculate distinct spectra for the two isomers, as shown in Figure 3c. The isomerization rate constants are determined by analyzing data of the type shown in Figure 3 in conjunction with emission transients at narrow emission wavelength regions.

We have studied the dependence of the isomerization kinetics of 2VA, 2PA, and 2BA on solvent in the series  $C_4$ – $C_{16}$  linear alkanes. Interestingly, the rate of isomerization of 2VA is independent of solvent in this series, while both 2PA and 2BA isomerize more slowly as longer (more viscous) alkane solvents are substituted. The solvent dependence of 2BA and 2PA is consistent with conventional understanding of nonpolar isomerizations in nonpolar solvents. The important dynamic solvent interactions for reactions of this type, which involve large-amplitude intramolecular motion, are short range, repulsive, intermolecular forces that are associated with solute/solvent "collisions". Crudely speaking (employing a continuum model), the friction ( $\xi$  in eq 2) associated with these collisions is proportional to the solvent viscosity. The decrease of the rate constant of 2PA and 2BA with increasing solvent size



**Figure 4.** Solvent dependence of the rate constant for the *cis/s-trans* excited-state isomerization of 2-(2-propenyl)anthracene (2PA) (experimental points) in linear alkane solvents (hexane through hexadecane) and mixtures of cyclohexane with paraffin oil. Reorientation time signifies an empirical measure of the solvent friction, namely the rotational reorientation time of acetonitrile in the various solvents. The solid line in the figure is the best fit of Kramers' theory to the data using the reorientation times as a measure of the solvent dependence of the friction that impedes the reaction.

(viscosity) is due to a dynamic solvent effect. In contrast, the kinetics of 2VA seem to be well described by transition-state theory, and dynamic solvent effects may play no role for this molecule in these solvents.

The different behavior of the three compounds can be understood in terms of theories of dynamic solvent effects on nonpolar isomerizations. The best known approach is Kramers' theory, which was described above in Theoretical Issues. In Kramers' theory, the solute/solvent dynamic interactions are characterized by a simple friction coefficient  $\xi$  for the pertinent intramolecular motion along the reaction coordinate.<sup>27</sup> The friction coefficient is a function of properties of the solvent as well as the solute, e.g., size of the molecular group. The simplest approach to estimate the friction coefficient is to use hydrodynamic theory, which relies on the solvent viscosity as the only measure of the solvent's properties. Kramers' theory does not agree with experiment for any of the alkenylanthracenes using this simple method of obtaining the solvent friction.<sup>1</sup>

A different approach is to use an empirical measure of the solvent friction. One such measure is the overall molecular reorientation time of molecules with similar size to the isomerizing group in the alkenylanthracenes.<sup>1,2-5</sup> Figure 4 portrays a plot of the isomerization rate of 2PA versus the reorientation time of acetonitrile. Each point represents a different pure alkane solvent or mixtures of alkanes. The agreement

between the experimental points and the theoretical line (Kramers' theory) is not good. A similar comparison for 2VA shows an even a greater deviation between theory and experiment. These results cast doubt on the validity of Kramers' theory for solution-phase reactions. Similar conclusions have been made for the reactions of other molecules such as stilbene, diphenylbutadiene, and related molecules.<sup>3-6</sup>

Research under way in our group presently is concerned with analyzing the isomerization kinetics of the alkenylanthracenes in terms of theories that go beyond Kramers' theory, such as the Grote-Hynes theory<sup>20</sup> and other approaches.<sup>21</sup> From a simple physical perspective the critical difference between Kramers' theory and the more modern treatments is the assumed properties of the solvent friction. For Kramers' theory the inclusion of a simple single parameter for the solvent friction is based on the assumption that solute/solvent interactions (crudely speaking, collisions) are uncorrelated in time, on the time scale of the progress along the reaction coordinate. In contrast, the more modern theories allow for correlated collisions and other non-Kramers' effects.

### Concluding Remarks

The study of the kinetics of ultrafast isomerizations has progressed in recent years as better experimental methods and useful molecular examples have been employed by many scientists working in this field. Progress has been made on three prototypical reactions: proton transfer, electron transfer, and *cis/trans* isomerization. The results have led to a greater insight into the role of the solvent in chemical reactions. In particular, the importance of solvent dynamics in chemical kinetics has been clearly established.

Future progress in this field will take many directions. New theoretical methods that take advantage of modern supercomputers will offer chemists an ever increasingly detailed view of chemical dynamics on a molecular level. The rapidly developing experimental technique femtosecond spectroscopy will offer kineticists a new frontier. At the same time, ultrafast chemical reactions of greater and greater complexity and broader significance will be investigated.

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