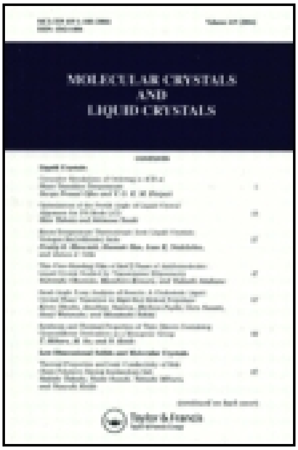

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MECHANISM OF THE PHOTOCHEMICAL HYDROGEN TRANSFER REACTION IN DOPED FLUORENE CRYSTALS

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Abstract New kinetic data from time resolved ONP-data are presented for the solid state photoreaction of a hydrogen transfer from fluorene to photoexcited acridine in doped fluorene single crystals. They remove existing uncertainties about the reaction pathway which proceeds via the lowest excited triplet state of the acceptor. In contrast to general belief, this $^3(\pi\pi^*)$ abstraction shows comparable kinetic parameters to $^3(n\pi^*)$ abstractions observed in solid glass matrix.

INTRODUCTION

Complete determination of a photchemical reaction mechanism is considered to be achieved[1] with the knowledge of (a) all significant transition structures along the reaction pathway (b) the rate constants of conversion from one intermediate structure to its successor structure and (c) the forces responsible for the observed structures. In the general situation of photoreactions in gases and liquids, it will remain unclear for some time how such complete knowledge can be achieved except for molecular beam experiments which can be performed only for the very smallest molecules. In contrast, for photoreactions in ordered systems precise data concerning the above mentioned information can be obtained in principle as will be shown in this contribution for a solid state photochemical model reaction. The main disadvantage is the small number of reactive systems known in solid matrixes so far.

PHOTOCHEMICAL MODEL REACTION IN CRYSTALLINE MATRIX

One such model reaction is the intermolecular photochemical hydrogen transfer observed in fluorene crystals doped with acceptor molecules like acridine, phenazine and anthracene[2]. Following selective light excitation of the acceptor a thermally activated hydrogen transfer takes place and a hydrogen atom is transferred from the donor fluorene to the acceptor guest leading to a radical pair (RP) product in its triplet state. Structural data for both the acceptor and RP triplet state are virtually complete as summarized earlier in [3]. The hydrogen transfer affects atomic coordinates only in the "reaction plane" which is parallel to the crystalline a,b-plane and runs through the molecular centers of both reactants. As shown in Fig. 1 this plane is perpendicular to the aromatic planes of the reactants and parallel to the crystalline a,b-plane. It constitutes a symmetry plane for both, the precursor reactants as well as the final product and it is reasonable to assume that it will be preserved along the whole reaction pathway.

The reaction is fully reversible. The radical pair product reacts back to the original reactant molecules in their ground state from which a new reaction cycle can be started.

THEORETICAL CONSIDERATIONS FOR A REACTION SCHEME

Given this structurally well characterized model reaction available theoretical predictions for the reaction scheme can be subject to a rather rigorous test. Considering the complexity of the reacting molecules quantitative theoretical treatments are so far out of the question. In the first place some crude general rules have been formulated concerning the geometrical requirements for reactivity in the solid state[4] and have been tested for intramolecular hydrogen abstraction reactions. According to the main rule stated the distance between the abstracted hydrogen H' and the abstracting nitrogen N in Fig. 1 ($r_{NH'} = 2.55$ Å) should be and indeed is here smaller than the sum of the van der Waals radii[5], i.e. $r_{H'} + r_N = 1.2$ Å + 1.5 Å = 2.7 Å.

A more substantial theoretical prediction is associated with the specific advantage of photoreactions in ordered systems, that symmetry considerations can be applied rigorously. Salem[6] has treated mainly the case of "coplanar" hydrogen abstraction and concludes otherwise (i.e. for a noncoplanar abstraction, in fact in our case perpendicular to the molecular planes) that a triplet RP-product can be formed only by adiabatic conversion from the lowest triplet precursor state. A thorough treatment of Salem's symmetry considerations allowing for various symmetry planes to be conserved will be published separately[7].

DETERMINATION OF THE REACTION KINETICS

The photoreaction in the acridine-fluorene system can be initiated by a selective light absorption of the acceptor acridine. Given the very fast relaxation of any vibrationally unrelaxed states[8] only the lowest excited singlet S_{1A} $^1(n\pi^*)$ or triplet T_{1A} $^3(\pi\pi^*)$ state are possible precursors. Although it appears to be an easy problem the determination of the correct precursor required considerable experimental effort. Standard techniques like a selective direct T_{1A}-excitation or the use of a T_{1A}-selective sensitizer molecule are either too insensitive or ineffective in the solid lat-

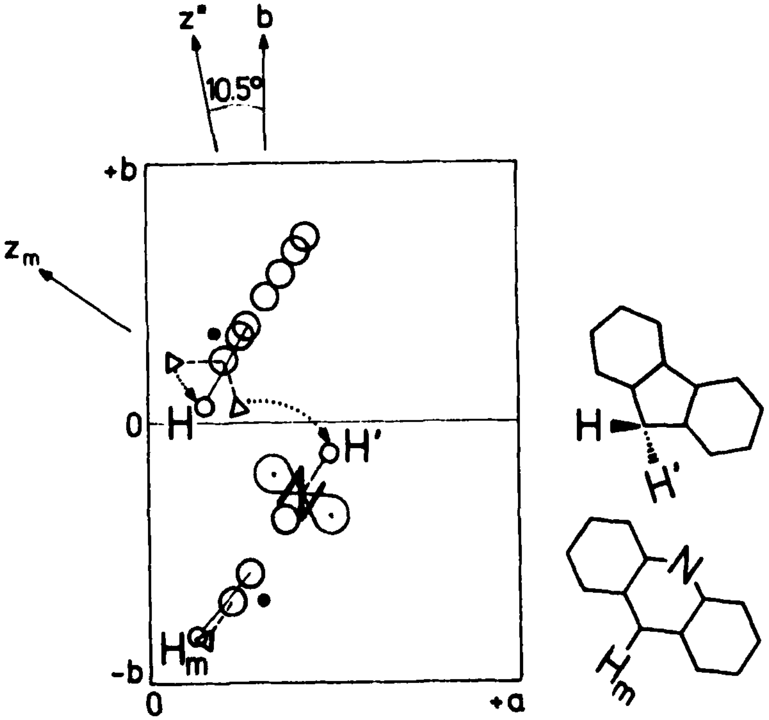

FIGURE 1. right: Molecular structure of the donor (fluorene) and acceptor (acridine) when rotated around the short in-plane axes into the aromatic plane.

left: Change of atomic positions from reactants (Δ) to product (o) as seen in the projection along the long molecular in-plane axes into the "reaction plane" parallel to the crystalline a,b-plane. The reactant molecules occupy translationally equivalent sites in adjacent unit cells. Distances are to scale with the unit cell dimensions a = 8.49 Å, b = 5.72 Å. z_m denotes the direction of the molecular out of plane axis of fluorene. z^* is the main principal axis of the zero field splitting tensor of the RP product and represents roughly the direction between the spin density centers on each of the radicals contributing to the RP-product[3].

tice. Another standard technique is the investigation of the temperature dependence of the reaction kinetics. The decay rate of T_{1A}, one possible precursor state, and the production rate of the RP product are experimentally accessible via the following observables which are still available at high temperatures:

(1) secondary triplet absorption and

(2) the magnetic resonance signals of ESR and ONP[2]. The temperature dependence of the T_{1A} life time[9] requires postulation of an additional high temperature decay channel which originates from a thermally activated process, is fluorene specific and shows a considerable ^{2}D-isotope effect with respect to the transferred hydrogen atom. Therefore it shows essential characteristics expected for the H-transfer reaction. On the other hand, the temperature dependence of the steady state ONP[10] identifies another apparently unique thermally activated process for the RP-formation which at first has to be interpreted as a different process if compared with the one found in the T_{1A}-decay[9]. On this basis, T_{1A} cannot be the precursor[11]. Time dependent ESR[12] also turned out to be unable to decide the question about the precursor state. Hence independent experimental data are needed to determine whether the observed T_{1A}-decay and RP-formation are due to different processes or whether both processes are nevertheless based on a common H-transfer reaction scheme. In this case, the incompatability of the temperature dependencies discussed in [11] must be accounted for by an accidental convolution of various temperature dependent processes. We will see now that the second possibility has to apply here.

TIME RESOLVED ONP-EXPERIMENTS

Optical Nuclear Polarization (ONP) in acridine doped fluorene crystals is known to result from contact of the electron and nuclear spin reservoirs by hyperfine coupling in the RP product triplet state T_{RP}[2b]. We describe now how the rate limiting step of the optical pumping cycle passing through the T_{RP} state can be measured in a time resolved ONP-experiment. Following pulsed light excitation contact between the electron and nuclear reservoir can be allowed to take place in a gated fashion. This may be realized in two ways:

(a) the polarizing field B_p can be switched in and out of level crossing areas in which strong electron nuclear hyperfine coupling occurs[13,14] and

(b) the electron and nuclear spin reservoirs can be coupled by resonant radio frequency irradiation[13].

Typical data with the first technique are presented in Fig. 2. Since distinct ONP signals due to both excited triplet states, T_{1A} of the unreacted acceptor and T_{RP} of the RP-product, can be observed, the time resolved experiment can be performed for each triplet state separately. The obtained nuclear polarizations are plotted in Fig. 2 as a function of the delay time τ after the light pulse when the contact between electron and nuclear spins is turned off by applying a field switch of amplitude ΔB out of the level crossing region. In order to compare the data for the two triplet states they are normalized to an equal ONP-level when no field switch is applied, i.e. B_p is kept constant. Distinctly different results are observed depending on whether the ONP-active pumping cycle through the T_{1A} or T_{RP} triplet state is considered. They are explained most easily

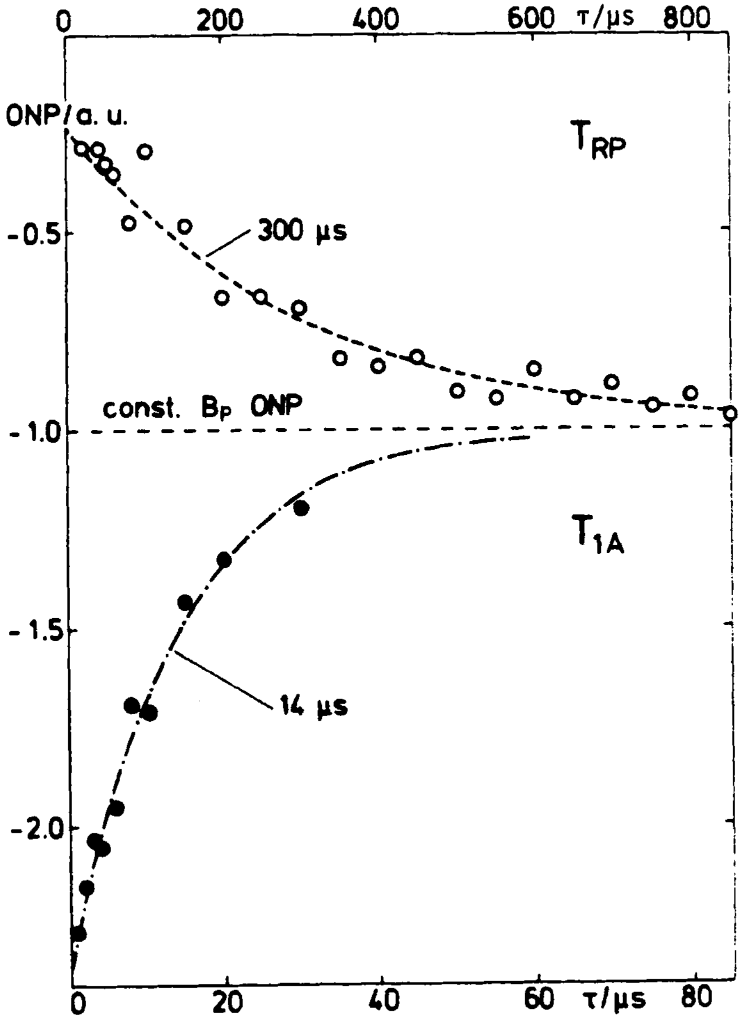

FIGURE 2. Normalized ONP-signals are plotted as a function of the delay time τ between laser pulse and applied field switch of ΔB which cuts off the contact between the electron and nuclear spin reservoirs. The data are taken with the following parameters:

T_{RP}: $B_p || z^*$ (see Fig. 1), B_p = 180 G, ΔB = +55 G.

T_{1A}: $B_p || x$ (long in plane axis), B_p = 410 G, ΔB = +100 G.

Note the different time scale for the two curves!

if we assume right away, as actually justified by the results, two extreme models of triplet kinetics: T_{1A} with highly spin selective population but no decay selectivity and T_{RP} with non selective population but high decay selectivity.

The result for T_{1A} is described in more detail elsewhere[13]. Initially enhanced ONP is consistent with the known high initial electron spin polarization of the T_{1A}-state which is, however, subject to fast electron spin relaxation. The enhanced ONP can be saved only when the electron nuclear contact is turned off in times short or comparable to the electron spin relaxation time, in agreement with the fast time constant of 14 μs observed for T_{1A} in Fig. 2.

For T_{RP} the ONP is exclusively due to the decay selectivity. The maximum ONP level is reached only when all ONP active T_{RP} states had a chance to decay while the contact between electron and nuclear spins remains established. Note that the ONP doesn't start from zero for short delay times. Such a background ONP is expected if the field switch by ΔB is not sufficiently large as was the case here.

The important result here is that an ONP-rate of 300 μs is evaluated from Fig. 2 top, which is identical to the T_{1A}-life time at room temperature obtained from the transient triplet absorption experiment[9]. Identical rates have also been confirmed over a wider temperature range[13]. The most straightforward conclusion is that the rate limiting step in the optical pumping cycle of T_{RP} is the RP formation rate which is then identical to the T_{1A} decay time. Consequently, T_{1A} is shown to be the precursor for the hydrogen transfer reaction. Furthermore we have to conclude that the radical pair decay rate k_{RP} must be large compared to the T_{1A} decay rate. Otherwise the latter could not be the rate limiting step in the optical pumping cycle of T_{RP}.

SUMMARY OF THE REACTION KINETICS

With the identification of the T_{1A}-precursor a quite complete kinetic scheme emerges for the reaction kinetics from the available time resolved experiments[9,12,13]. It is summarized best with reference to Fig. 3.

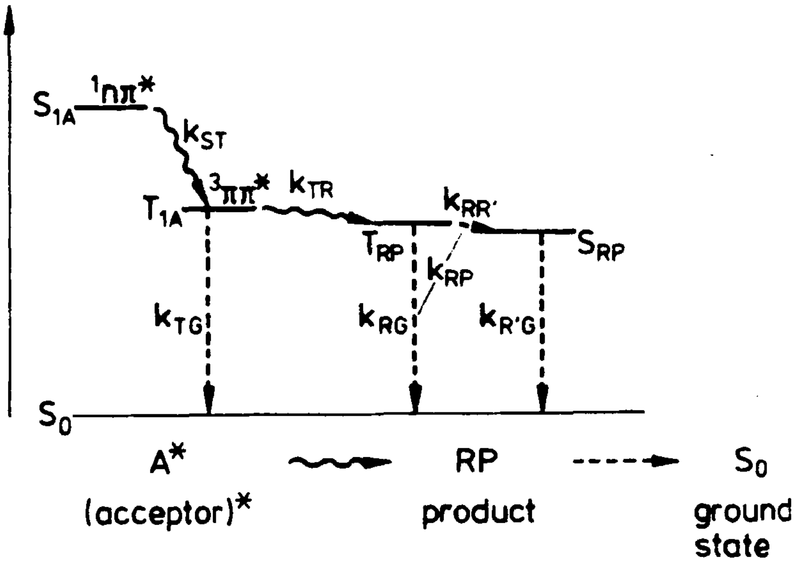

FIGURE 3. Kinetic scheme for the hydrogen transfer reactions starting from the acceptor-donor reactants A*+H-D, reacting to the product RP and back to the ground state.

Light absorption into the singlet acceptor bands is followed by very fast vibrational relaxation and efficient intersystem crossing to T_{1A} $^3\pi\pi^*$ with a rate constant $k_{ST} \sim 30$ ps[8]. The weakly temperature dependent intramolecular decay of T_{1A} is dominated at high temperatures (> 200 K) by a decay rate[9,13] which is now also the reaction rate and can be expressed by

$$k_{TR} = k_o \exp\{-\frac{E_A}{kT}\} \qquad (1)$$

with an activation energy of $E_A = 1600\ \mathrm{cm}^{-1} \hat{=} 4.6$ kJ/Mol. The room temperature rate k_{TR} (300 K) = $3 \times 10^3\ s^{-1}$ corresponds to the preexponential factor $k_o = 6 \times 10^6\ s^{-1}$. The T_{RP} decay rate k_{RP} must be fast compared to the formation rate $k_{TR} \ll k_{RP}$. A room temperature rate k_{RP} (300 K) = $1.5 \times 10^5\ s^{-1}$ evaluated from time resolved ESR data[12] would satisfy this requirement. A more detailed evaluation of the temperature dependence of the T_{1A} decay rate k_{TR} and the steady state ONP-signals will be published elsewhere[15,10]. It is not obvious how the observed photochemical reaction rate can follow the experimentally well verified Arrhenius equation (1). In a most simple fashion the exponential factor gives the average population of a thermally accessible low energy state of energy E_A above the lowest excited triplet state T_{1A}. The preexponential then represents the reaction probability from this state.

In this context it is most surprising that the kinetic parameters in the reaction rate k_{TR} studied in this work are very similar to data known for completely different reactions in ordered systems. Most closely related are hydrogen abstraction reactions by excited acceptors like benzophenone[16] and pyrazine[17] in frozen ethanol glass solution which give both preexponentials and activation energies in the same range as observed here. This is quite unexpected as the remaining mobility in the glass matrix allows for an optimal, at least angular configuration between acceptor and donor on the time scale of the reaction rate. Furthermore, general chemical considerations[1] tend to generalize that H-abstractions from $n\pi^*$ states are preferred to those from $\pi\pi^*$ states. *In contrast, the* H-*abstraction by the* $^3\pi\pi^*$ state of acridine from a fluorene donor studied in this work renders nearly the same kinetic parameters as the abstraction reaction of the $^3n\pi^*$ states of benzophenone[16] and pyrazine[17] in frozen ethanol. A further discussion of this surprising result is found elsewhere[7].

REFERENCES

1. N. J. Turro, Modern Molecular Photochemistry, Benjamin, Cumming, Menlo Park (1978)
2. a) R. Furrer, M. Heinrich, D. Stehlik, H. Zimmermann, Chem. Phys. 36, 27-40 (1979)
   b) V. Macho, J. P. Colpa, D. Stehlik, Chem. Phys. 44, 113-129 (1979)
3. D. Stehlik, R. Furrer, V. Macho, J. Phys. Chem. 83, 3340 (1979)
4. see e.g. John Scheffer's contribution to this conference
5. Handbook of Chem. and Phys. (CRC Press, 59th Ed.) p.D178
6. L. Salem, J. Am. Chem. Soc. 96, 3486 (1974)
7. J. P. Colpa, D. Stehlik, submitted to Chem. Phys.
8. B. I. Greene, R. M. Hochstrasser, R. B. Weisman, J. Chem. Phys. 70, 1247 (1979)
9. B. Prass, F. Fujara, F. Seiff, D. Stehlik, J. Lumin. 24/25, 483 (1981)
10. D. Hoffmann, diploma thesis, FU Berlin (1982), and D. Hoffmann, D. Stehlik, H. M. Vieth, Chem. Phys., to be published
11. J. P. Colpa, D. Stehlik, Chem. Phys. 65, 97 (1982)
12. R. Furrer, F. Fujara, C. Lange, D. Stehlik and W. Vollmann, Chem. Phys. Lett. 76, 383 (1980)
13. H. M. Vieth, submitted to Chem. Phys. Lett.
14. R. Tycko, A. Pines, D. Stehlik, submitted to Chem. Phys. Lett.
15. B. Prass, D. Stehlik, Chem. Phys., to be published
16. H. Murai, M. Jinguji, K. Obi, J. Phys. Chem. 82, 38 (1978)
17. M. Jinguji, Y. Hosako, K. Obi, J. Phys. Chem. 83, 2551 (1979)