

Letters to the Editor

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Communications

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 59, NUMBER 4

15 AUGUST 1973

Measurements of the rate of the excited charge-transfer complex formation using picosecond laser pulses

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(Received 26 April 1973)

In this communication we report the first time-resolved measurements of the formation of an excited state molecular complex arising from the transfer of an electron from a donor molecule to an excited singlet state acceptor molecule, ${}^1A + D \xrightarrow{h\nu} {}^1A^* + D \xrightarrow{CT} (A^-D^+)$. Since the discovery of these charge-transfer complexes,¹ which are stable in the excited state but unstable in the ground state, much effort has been devoted to understanding the primary physical and chemical processes involved in their formation and decay. Although the rate of electron transfer has been determined to be diffusion controlled at long times using fluorescence quenching methods,² the kinetics of electron transfer in the time region where the transfer may not be diffusion controlled are not known. Furthermore, the important questions regarding the critical intermolecular distance and relative orientational requirements for reactions,³ the generation of locally excited triplet states,⁴ and the very nature of translational and rotational motions in these systems are yet to be clearly answered. In this first report, we have used picosecond methods^{5,6} to answer some of these crucial questions on reaction dynamics. Anthracene in its lowest excited singlet state served as the acceptor and *N,N'*-diethylaniline as the donor component in forming the complex. The solvent is *n*-hexane and the solution is saturated with nitrogen to avoid oxygen quenching processes. The experimental arrangement is shown in Fig. 1. A single picosecond pulse at 6943 Å was extracted from the output train of a mode-locked ruby laser by an electrooptical shutter triggered by the breakdown of a spark gap. The single pulse, having a

width of about 7 psec measured by TPF method,⁷ is amplified in passing through a flash lamp pumped ruby rod and is then frequency doubled to 3472 Å using an appropriately cut KDP crystal. The second harmonic pulse at 3472 Å excites anthracene to the 1L_a state. On transfer of an electron from D to A^* a new absorption can be detected at 6943 Å corresponding to the $(A^-D^+) \rightarrow (A^{*-}D^+)$ transition.⁸ In this way the transfer of an electron leading to the formation of the complex is monitored by measuring the absorption of the 6943 Å probe pulse at times equal and subsequent to the 3472 Å excitation pulse. Since an anisotropy is generated by the excitation, it is necessary to separate the change in absorption due to orientational relaxation from that due to the formation of the charge-transfer com-

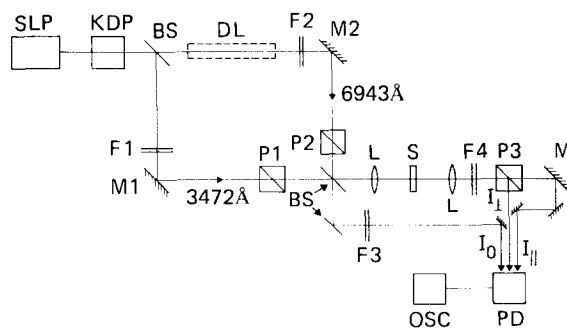


FIG. 1. Experimental arrangements. SLP-Ruby oscillator, single pulse selector and amplifier; BS-beam splitter; F-filter; DL-optical delay; M-mirror; P-polarizer; L-lens; S-sample cell; PD-photodiode; OSC-oscilloscope.

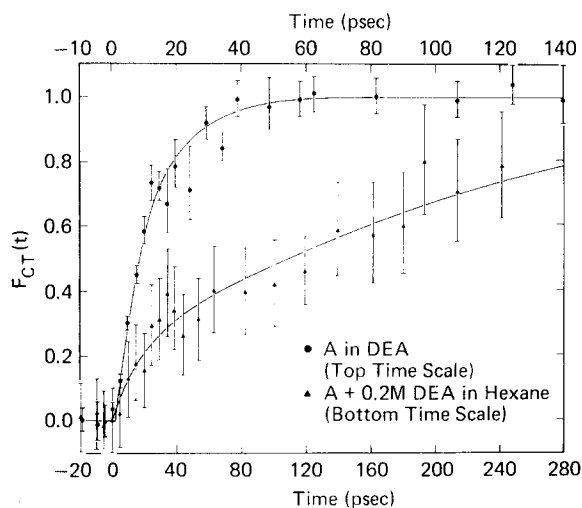


FIG. 2. Experimental results.

plexes. This is readily done by taking the sum of the absorbances for probe light polarized parallel and polarized in the two orthogonal directions (which are equal by symmetry). This sum is independent of the orientational motions of the complex and depends only on the population of complexes at the time of measurement. To this end polarizers are used before and after the sample to measure the transmitted intensities $I_{\parallel}(t)$ and $I_{\perp}(t)$ as well as I_0 . These intensities are measured by a fast response photodiode and Tektronix 519 oscilloscope. The result at each point is an average of five laser shots with a precision indicated by the error bars in Fig. 2.

In the present work the concentration of anthracene was fixed at $2.5 \times 10^{-3} M$ and *n*-hexane was added to vary the diethylaniline (DEA) concentration from 0.1M to 6M (pure liquid). Figure 2 shows the formation curves of the charge-transfer complexes. We observed that the lowest concentration of DEA, the longer time (≥ 300 psec) behavior yields a value of k_{CT} close to the steady-state diffusion rate constant.² However, at earliest and intermediate times the existence of transient terms found in the Smoluchowski diffusion model or the Noyes molecular pair model⁹ are evident in our data. As the concentration of DEA is increased, the transient

effect becomes even more important. Computer analysis indicates that formation curves calculated from the solution of diffusion model, including all transient terms, seem to fit reasonably well for all experimental data except those in the highest concentration regions. Detailed comparison of these two models with experimental results will be published later. It should be pointed out that this is the first direct experimental observation of the complete transient behavior predicted by models of reaction kinetics. The analysis yields an encounter distance of 8 Å. For the 3M and 6M DEA the growth curves are the same, which suggests that there is a static quenching sphere of about 8 Å, calculated from the average intermolecular distance at 3M. This value agrees with those obtained in lower concentrations. Apparently, at these concentrations, no translational diffusion is involved in the electron transfer reaction.

We wish to thank Dr. Rehm for his contribution to this work, and R. M. Bolding for his assistance.

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