Interpretation of the Excimer Kinetics of Poly(*N*-vinylcarbazole) and 1,3-Dicarbazolylpropane in Dilute Solutions

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ABSTRACT: The fluorescence decay of poly(*N*-vinylcarbazole) and 1,3-dicarbazolylpropane in dilute benzene solution has been reexamined. For poly(*N*-vinylcarbazole)–benzene solution, the decay curves were found to be fitted by a linear combination of three exponentials. The decay times (lifetimes) of the two excimers at room temperature were estimated to be ca. 2.9 and 12.8 ns, respectively. In the case of 1,3-dicarbazolylpropane, the requirement for triple-exponential fitting is evidence for the inadequacy of the conventional Birks scheme for excimer formation and dissociation in bichromophoric molecules.

Introduction

The photophysics of excimer emission from polymers containing pendant aromatic groups is a topic of much current interest. It is well-known that polymers such as polystyrene (PS), poly(vinylnaphthalene) (PVN), and poly(vinylcarbazole) (PVCz) exhibit intramolecular excimers[1] as is evident from the fact that excimer emission is observed, even in very dilute solutions. In many cases, insights about the mechanism and kinetics of intramolecular excimer formation in polymers may be obtained from detailed studies of their corresponding model compounds.

The conventional model used to describe the kinetics of excimer emission was proposed by Birks[2] and is shown in Scheme I, where k_{FM} and k_{DM} are rate constants for the radiative emission from a monomer pendant group and the intrachain excimer state, respectively; k_{IM} and k_{ID} are rate constants for the sum of all nonradiative pathways for deactivation of monomer and excimer excited states, excluding those for excimer formation, k_{DM}, and dissociation to give the excited monomer state, k_{MD}. According to Scheme I, the excimer intensity relaxes with time as a difference of two relaxing exponentials with rates λ_1 and λ_2 given by

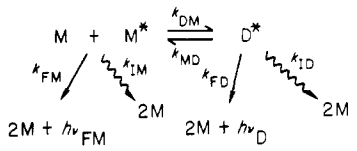
$$\lambda_{1,2} = \tfrac{1}{2}\{(X + Y) \pm [(X - Y)^2 + 4k_{MD}k_{DM}]^{1/2}\} \quad (1)$$

where $X = k_{FM} + k_{IM} + k_{DM}$ and $Y = k_{FD} + k_{ID} + k_{MD}$. Although this scheme has been used extensively to describe intermolecular excimer kinetics for many small aromatic compounds in liquid solutions, there are cases where it is found to be inadequate to account for the experimental decays observed with intramolecular excimers in some polymeric systems.[3,7]

Johnson invoked a kinetic scheme for intramolecular excimer kinetics of PVCz in dilute solution using the model of three interconvertible excited species.[3] Many simplifications on the scheme were proposed involving steady-state measurements over a wide range of temperatures. The same mechanism was expounded by Ishii et al.[4] in their studies of the kinetics of excimer quenching for PVCz. The analysis assumed at the outset that the direct formation of a sandwich excimer from the excited monomer was negligible. Ghiggino et al.[5] also studied the kinetics and relaxation times of fluorescence decay. The analysis was a simplified version of Johnson's scheme in that the emission resulting from excimer–monomer dissociation was ignored, based on a time scale argument. Pulsed radiolysis studies by Tagawa et al.[6] gave evidence for the presence of an additional excited dimer. Time-resolved fluorescence studies by Roberts et al. also invoked a similar interpretation.[7]

Although Scheme I has been found useful in interpreting kinetics of intramolecular excimer formation in many small

Scheme I



dichromophoric compounds, Goldenberg et al.[8] suggested that it was important to take into account more than one rotational conformer for the excited monomer state. Failing to do so results in underestimating the rate constant for excimer formation. However, no dynamic analysis was attempted. In this paper, we propose a three-state scheme in an attempt to improve the kinetic treatment for intramolecular excimer formation in dilute PVCz solutions. Furthermore, it is shown that an analogous scheme may also be applied to the small-molecule model compound 1,3-dicarbazolylpropane (DCzP), in accord with the suggestions of Goldenberg et al.[8]

Experimental Section

The PVCz was purified by precipitation into methanol several times, followed by chromatography on silica gel. DCzP was purified by preparative thin-layer chromatography.[9] Benzene (ACS spectral grade) was distilled over P_2O_5 before use. The solutions were degassed by purging with dry nitrogen and the concentrations were kept at 5×10^{-4} M.

Steady-state emission spectra were recorded with a Hitachi MPF-2A spectrofluorometer with phototube response corrected. The fluorescence decay curves were measured with a single-photon-counting apparatus of standard design.[10] Two 2-mm slits were used at both the entrance and the exit of the monochromator to reduce scattered light. The samples were excited at 313 nm and the lamp profiles were recorded at the same time setting by scattering off a Ludox scattering solution.

In our decay curve measurements, the nonlinear iterative deconvolution technique[11] was extended to simultaneously fit a decay curve with a linear combination of three exponentials. The reliability of the modified computer program was tested against artificially generated decay curves over the regions of relaxation rates of immediate interest.

The simulated curves were constructed by convoluting a decay curve of the desired combination of exponentials with an experimental lamp profile of the appropriate time scale. Subsequently, Poisson noise was added to each channel. For channels with counts higher than 160, Gaussian noise with appropriate standard deviation was added instead. For some curves, a component due to lamp scattering of varying strength was also introduced. Hence, a simulated curve I_{sc} would represent the expression

$$I_{sc}(t) = \int_0^t L(\tau)G_{sc}(t - \tau)\, d\tau + \alpha L(t)$$

where $L(t)$ represents the time dependence of the lamp profile and $G_{sc}(t)$ is the desired decay law whereas α measures the strength of the lamp scatter.

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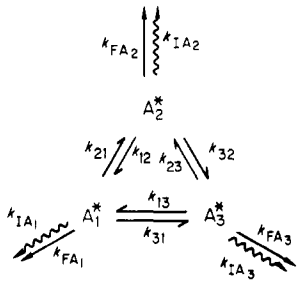
Table I
Two-Exponential Fits of Fluorescence Decay Curves of PVCz in Benzene Solution[a]

λ_{em}, nm	time scale, ns/channel	channel of lamp max	fitting channels	A_1	τ_1, ns	A_2	τ_2, ns	χ^2
420	2.957	13	14 → 128	0.12	4.69	0.22	22.78	1.78
380	2.957	13	14 → 128	0.17	3.35	0.07	19.81	4.07
420	0.451[b]	30	36 → 128	0.005	3.47	0.016	17.88	1.05
420	0.451[b]	30	31 → 128	0.005	4.20	0.016	18.05	1.48
420	0.451[b]	30	1 → 128	0.005	7.96	0.014	19.21	6.54
380	0.451	30	31 → 128	0.016	2.56	0.007	16.57	1.58

[a] λ_{ex} = 313 nm, T = 24 °C. λ_{em} = 380 nm (high-energy excimer), λ_{em} = 420 nm (sandwich excimer). [b] Same experimental curve.

Scheme II



The methods to measure the quality of fit include χ^2, autocorrelation of the residual, and stability of the relaxation rates while varying the starting channel of fit.[11]

Results and Discussion

Steady-state emission spectra for both PVCz and 1,3-DCzP were identical with those reported earlier.[3,12] The decay curves for emission from both PVCz and 1,3-DCzP in benzene solution were found to agree qualitatively with those reported by Johnson.[3] In the case of PVCz in benzene, results of fitting the curves with the sum of two exponentials are listed in Table I. In general, it was found that the results agreed fairly well with those reported by Ghiggino et al.[5] However, it is obvious that the inclusion of channels 1–36 (i.e., before lamp peak) makes a significant difference in the value of τ_1. The same measurements at a somewhat lower temperature (T = 16.0 ± 0.1 °C) show similar effects. The autocorrelation function of the residual with these two exponential fits also shows persistent slow oscillations. Comparison of bi- and triexponential fits is shown in Figure 1 on a typical measurement.

The proposed three excited species scheme proposed by Johnson has actually received some support from related studies.[4,5] However, these studies seem to oversimplify some of the predictions of the theory. To reexamine this scheme, we start the analysis with a somewhat more general context (Scheme II). This scheme involves three excited species (A_1^*, A_2^*, and A_3^*) capable of (1) interconverting from one to another (processes k_{ij}, i, j = 1, 2, 3), (2) undergoing fluorescence (k_{FA_i}, i = 1, 2, 3), and (3) undergoing radiationless relaxations (k_{IA_i}, i = 1, 2, 3) during their excited lifetimes. With first-order kinetics assumed, the rates of change of the excited species concentrations after a δ-pulse external excitation can be represented by the following set of equations:

$$(d/dt)\mathbf{A} = -\mathbf{M}\cdot\mathbf{A} \tag{2}$$

Here, $\mathbf{A}$ is a three-dimensional column vector with elements $[A_1^*]$, $[A_2^*]$, and $[A_3^*]$; $\mathbf{M}$ is a 3 × 3 matrix with

$$\begin{aligned} \mathbf{M}_{11} &= k_{FA_1} + k_{IA_1} + k_{21} + k_{31} \\ \mathbf{M}_{22} &= k_{FA_2} + k_{IA_2} + k_{12} + k_{32} \\ \mathbf{M}_{33} &= k_{FA_3} + k_{IA_3} + k_{13} + k_{23} \end{aligned} \tag{3}$$

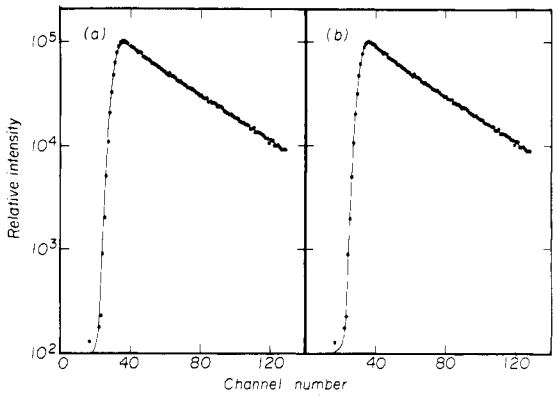


Figure 1. Fluorescence decays of PVCz in deoxygenated benzene at 24 °C, λ_{ex} = 313 nm, λ_{em} = 420 nm: (a) (···) experimental curve; (—) best-fit two-exponential curve; (b) (···) experimental curve; (—) best-fit three-exponential curve.

and $\mathbf{M}_{ij} = -k_{ij}$ for $i \neq j$. In principle, eq 2 can be solved exactly for the time dependence of $\mathbf{A}$ and each $[A_i^*]$ has the form

$$[A_i^*](t) = a_{i1}e^{-t/\tau_1} + a_{i2}e^{-t/\tau_2} + a_{i3}e^{-t/\tau_3} \tag{4}$$

where the preexponential factors are functions of the rate constants and the relaxation times τ_1, τ_2, and τ_3 are inverses of the eigenvalues of the matrix $\mathbf{M}$. Subsequently, the fluorescence intensity of the ith species is seen to be a linear combination of three relaxing exponentials with rates $1/\tau_1$, $1/\tau_2$, and $1/\tau_3$. Johnson's scheme for PVCz can now be recognized easily as one identifies M* with A_1^*, D_1^* (high-energy excimer) with A_2^*, and D_2^* (sandwich excimer) with A_3^*. At room temperature, the monomer emission is nonobservable and leads to the assumption of no significant dissociation of either type of excimer; i.e., $\mathbf{M}_{12} = \mathbf{M}_{13} = 0$. Consequently, this scheme suggests that

$$[A_1^*](t) = [A_1^*](0)e^{-\mathbf{M}_{11}t} \tag{5}$$

Then, eq 2 simplifies to

$$\frac{d}{dt}\begin{pmatrix}[A_2^*]\\ [A_3^*]\end{pmatrix} = -\begin{pmatrix}\mathbf{M}_{22} & \mathbf{M}_{23}\\ \mathbf{M}_{32} & \mathbf{M}_{33}\end{pmatrix}\begin{pmatrix}[A_2^*]\\ [A_3^*]\end{pmatrix} + \begin{pmatrix}\mathbf{M}_{12}\\ \\ \mathbf{M}_{13}\end{pmatrix}[A_1^*](0)e^{-\mathbf{M}_{11}t} \tag{6}$$

Failure to observe emission from the excited monomer may permit one to ignore the contribution of the time dependence of the monomer concentration in eq 6. By dropping the second term of eq 6 one would obtain a scheme in

Table II
Three-Exponential Fits of Fluorescence Decay Curves of PVCz in Benzene Solution[a]

channel of lamp max	fitting channels	A_1	τ_1, ns	A_2	τ_2, ns	A_3	τ_3, ns	χ^2
30	31 → 128	−0.019	0.06	0.007	2.78	0.016	17.75	1.18
30	1 → 128	−0.028	0.06	0.008	2.38	0.017	17.65	1.33
30	31 → 128	0.018	0.05	0.013	2.97	0.007	16.95	1.37

[a] Time scale 0.451 ns/channel.

Table III
Tests on the Three-Exponential Fitting Program with Simulated Two- and Three-Exponential Decay Laws of the Form $G(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$

		best-fit parameters						
	α	A_1	τ_1	A_2	τ_2	A_3	τ_3	χ^2
A. $A_1 = 0.0700, \tau_1 = 0.0700$ ns; $A_2 = 0.0055, \tau_2 = 9.7788$ ns; $A_3 = 0.0135, \tau_3 = 10.5354$ ns; time scale 0.451 ns/channel								
(a)	0.0	0.017	0.068	0.011	9.424	0.016	10.858	1.05
(b)	0.0031	0.021	0.068	0.011	9.422	0.016	10.859	1.04
(c)	0.0313	0.060	0.062	0.010	9.395	0.016	10.860	1.07
(d)	1.565	0.808	0.061	0.001	8.410	0.008	10.546	1.09
B. $A_1 = -0.0480, \tau_1 = 0.0620$ ns; $A_2 = 0.0120, \tau_2 = 4.2320$ ns; $A_3 = 0.0380, \tau_3 = 12.4545$ ns; time scale 0.451 ns/channel								
(a)	0.0	−0.016	0.061	0.004	4.639	0.012	12.579	1.06
(b)	0.08	0.009	0.111	0.004	4.619	0.012	12.576	1.07
(c)	0.80	0.179	0.081	0.003	4.586	0.008	12.545	1.10
C. $A_1 = 0.0123, \tau_1 = 3.5000$ ns; $A_2 = 0.0075, \tau_2 = 4.800$ ns; time scale 0.252 ns/channel								
(a)	0.0	0.0186	3.55	0.0074	5.06			1.07
(b)	0.323	0.448	0.04	0.021	3.49	0.0075	5.00	1.06
D. $A_1 = 0.0079, \tau_1 = 2.3793$ ns; $A_2 = 0.0166, \tau_2 = 17.6540$ ns; time scale 0.451 ns/channel								
(a)	0.0025	0.001	0.004	0.0081	2.31	0.0162	17.65	1.07
E. $A_1 = 0.0123, \tau_1 = 0.0700$ ns; $A_2 = 0.0055, \tau_2 = 9.7788$ ns; $A_3 = 0.0135, \tau_3 = 10.5354$ ns; time scale 0.451 ns/channel								
(a)	0.0	0.0073	7.86	0.0207	10.92			1.49[a]
F. $A_1 = -0.0480, \tau_1 = 0.0620$ ns; $A_2 = 0.0120, \tau_2 = 4.2320$ ns; $A_3 = 0.0380, \tau_3 = 12.4545$ ns; time scale 0.451 ns/channel								
(a)	0.0	0.0084	8.67	0.0066	14.51			1.67[b]
(b)	0.0	0.0045	5.77	0.0011	12.85			1.05[c]

[a] Channels of fit from 32 to 128. [b] Channels of fit from 27 to 128. [c] Channels of fit from 31 to 128.

which the fluorescence decay curves of each excimer follow a sum of only two decaying exponentials. In fact, reasonably good fits with the sum of two expontentials seem to support this procedure. However, the preexponential factors have been found to be all positive. This is incompatible with the findings of Ghiggino et al.[5] and Hoyle et al.,[9] which show that the sandwich excimer fluorescence builds up much more slowly than that from the high-energy excimer. Furthermore, it has been common practice to identify the two relaxation times resolved from the decay curve with the lifetimes of the two excimers.[5,12] It should be noted that this is true only if the rate of dissociation of the sandwich excimer back to the second excimer is negligible (i.e., $k_{23} \ll k_{32}$) and the two-exponential scheme is adequate. Once again, this dissociation process, although small, cannot be ignored.[4]

If the analysis is carried out including the second term on the right-hand side of eq 6, the fluorescence decay curves of either excimer obey a linear combination of three exponentials with relaxation rates

$$1/\tau_1 = \mathbf{M}_{11} \tag{7}$$

and

$$1/\tau_{2,3} = \frac{1}{2}\left\{(k_{A_2} + k_{32}) + (k_{A_3} + k_{23}) \pm \sqrt{[(k_{A_2} + k_{32}) - (k_{A_3} + k_{23})]^2 + 4k_{23}k_{32}}\right\} \tag{8}$$

where $k_{A_i} = k_{FA_i} + k_{IA_i}$ for $i = 2, 3$. It is clear from eq 8 that the lifetimes (defined as total depopulation rate of the excited species) of the excimers τ_{A_2} and τ_{A_3} are related to the measured rates τ_2 and τ_3 by

$$1/\tau_{2,3} = \frac{1}{2}\left\{(1/\tau_{A_2}) + (1/\tau_{A_3}) \pm \sqrt{[(1/\tau_{A_2}) - (1/\tau_{A_3})]^2 + 4k_{23}k_{32}}\right\}$$

$$\equiv \frac{1}{2}\left[[(1/\tau_{A_2}^0) + k_{32}] + [(1/\tau_{A_3}^0) + k_{23}] \pm \sqrt{\{[(1/\tau_{A_2}^0) + k_{32}] - [(1/\tau_{A_3}^0) + k_{23}]\}^2 + 4k_{23}k_{32}}\right] \tag{9}$$

with $\tau_{A_i}^0 = (k_{FA_i} + k_{IA_i})^{-1}$. We have the identities

$$1/\tau_2 = 1/\tau_{A_2} \qquad 1/\tau_3 = 1/\tau_{A_3} \tag{10}$$

if $k_{23}k_{32} = 0$. Furthermore, fitting a three-exponential curve by only two exponential components gives inaccurate values of the true lifetimes. One alternative would be to determine the three relaxation times simultaneously, provided that the fitting procedure has reliable accuracy.

In Table II, results are shown for fitting the same experimental curves by the three-exponential fit and the iterative deconvolution method. In Table III, results using the three-exponential fits on simulated curves are listed: the interpretation of these results is given in the Appendix. It is found that the best-fit relaxation times τ_i's are almost identical for the decay curves of both excimers. The best-fit τ_i's for the sandwich excimer curves are no longer sensitive to the starting channel of fit and the autocorrelation of the excimer decay curves demonstrates significant improvement (autocorrelation completely randomized). The resolution of the decay curves into three components

Table IV
Two- and Three-Exponential Fits of Fluorescence Decay Curves of 1,3-DCzP in Benzene Solution[a]

T, °C	λ_{em}	A_1	τ_1	A_2	τ_2	A_3	τ_3	χ^2
				Two-Exponential Fits				
10	365	0.050	6.51	0.005	35.77			9.25
10	420	*b*						
25	365	0.025	4.92	0.004	30.38			3.14
25	420	*b*						
40	365	0.023	4.05	0.008	27.35			6.23
40	420	−0.05	0.07	0.06	23.99			11.18
				Three-Exponential Fits				
		−0.09	0.015	0.06	5.71	0.006	30.15	1.14
		−0.007	0.015	−0.0001	7.08	0.006	30.67	1.13
		−0.04	0.016	0.03	4.30	0.005	28.34	0.95
		−0.01	0.015	−0.001	3.70	0.009	28.18	1.13
		−0.09	0.015	0.03	3.01	0.009	26.10	1.09
		−0.06	0.019	0.003	5.13	0.06	23.91	1.68

[a] λ_{ex} = 313 nm, λ_{em} = 365 nm (monomer), λ_{em} = 420 nm (excimer). Time scale = 0.451 ns/channel. [b] No convergence is obtained.

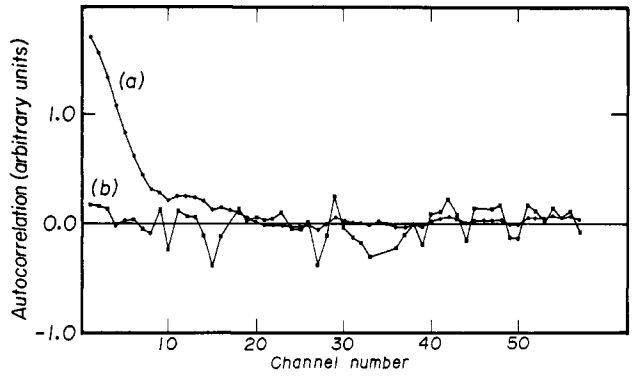
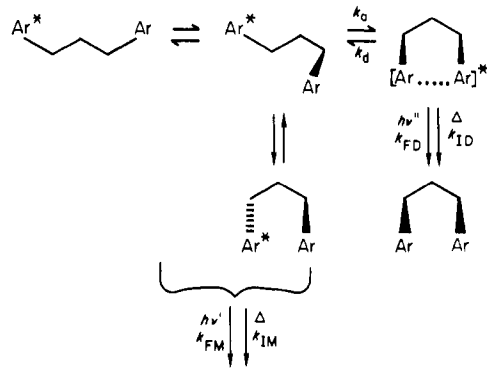


Figure 2. Autocorrelation curves of the residuals obtained on fitting the 420-nm fluorescence decay curve of PVCz in benzene with the decay laws (a) $G(t) = 0.005 \times e^{-t/3.47ns} + 0.016 \times e^{-t/17.88ns}$ and (b) $G(t) = -0.027 \times e^{-t/0.06ns} + 0.008 \times e^{-t/2.38ns} + 0.017 \times e^{-t/17.65ns}$.

is substantiated by the similar improvement on the measurements at T = 16 °C. It is to be noted that the preexponential factor of the τ_1 component in the sandwich excimer curve is negative. This fits in well with the slow growth of the sandwich excimer curve suggested by the time-resolved measurements mentioned earlier.[5,9] Furthermore, it can be shown that the negative exponential factor in the sandwich excimer curve is a natural outcome of adopting Scheme II. Meanwhile, one can see that Johnson's scheme[3] would be identical with Ishii's scheme[4] in the limit of zero quencher concentration if an additional assumption of $k_{31} = 0$ were made. The results in this study suggest that previous treatments of the excimer decay curves, assuming biexponential decay, are incompatible with the adopted scheme.

Once the measured relaxation times τ_1, τ_2, and τ_3 are obtained and interpreted by using eq 7 and 9, one can, in principle, estimate the excimer lifetimes τ_{A_2} and τ_{A_3} from eq 9. Although one may expect that the choice of values for τ_2 and τ_3 in Ishii's studies affects the accuracy of the k_{23} and k_{32} values which they reported, studies in these laboratories found that the value of $\tau_{A_3}^0$ is insensitive to a large range of values for k_{23} and k_{32}. By using Scheme II, adopting the approximate values of k_{32} and k_{23} reported by Ishii,[4] and taking τ_2 = 2.5 ns and τ_3 = 17.0 ns, one finds that $\tau_{A_3}^0$ = 19.5 ns. Although $\tau_{A_2}^0$ is somewhat more sensitive to the accuracy of k_{23} and k_{32}, it is estimated to be $\simeq$8.0 ± 1 ns. Subsequently $\tau_{A_2} \simeq$ 2.9 ns and $\tau_{A_3} \simeq$ 12.8 ns. It is clear that the two excimer lifetimes τ_{A_2} and τ_{A_3} are in fact very different from the measured relaxation

Scheme III



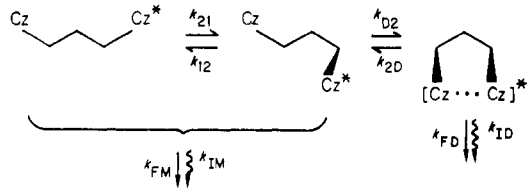
times τ_2 and τ_3. The differences are expected to be more severe in the other temperature ranges where k_{23} can no longer be assumed to be small.

Experimental verification of the monomer fluorescence decay predicted by this scheme is not possible because of the strong spectral overlap at 350 nm. It is, however, reasonable to expect that monomer fluorescence is quenched at rates of the order of 10^{11} s^{-1}. It is precisely this fast quenching process that makes it impossible to observe the monomer emission in PVCz.

In the case of 1,3-DCzP in dilute benzene solution, the fluorescence decay curves of both the monomer (365 nm) and excimer (420 nm) emissions were measured at 10, 25, and 40 °C. The difference in quality of fit by two- and three-exponential fits is shown in Table IV. The longest relaxation times were found to agree well with those reported by Johnson,[3] although a different solvent was used. The two-exponential fits were found to be very poor and in some cases failed to converge. Furthermore, the deviation in τ_1's obtained for the monomer and excimer curves is too large to be explained by experimental error. At each temperature, the set of τ_i's obtained by three-exponential fits for both the monomer and excimer was found to give good agreement. It is therefore evident that the Birks scheme is no longer appropriate.

In their studies of intramolecular excimer formations of diaryl double molecules, Goldenberg et al.[8] proposed a mechanism suggesting that the molecule can form excimer only via the trans–gauche conformer, as shown in Scheme III. For 1,3-DCzP there are two distinguishable conformers in which only one can form excimer via a single hindered C–C bond rotation[13] and the kinetic scheme is shown in Scheme IV.

Scheme IV



Steady-state measurements indicated that 10–40 °C is the onset of the "high-temperature region" of the system, in agreement with that found by Johnson.[3] In this temperature region, dynamic equilibrium between various conformations is established and the decay rates k_M ($=k_{FM} + k_{IM}$) and k_D are small compared to the internal processes (k_{12}, k_{21}, k_{D2}, and k_{2D}). Hence the measured $1/\tau_3$ represents approximately some average of k_M and k_D. The other two measured rates $1/\tau_1$ and $1/\tau_2$ therefore measure internal relaxation processes. In other words, while the molecule was in rotational equilibrium prior to excitation, the equilibrium shifts to a new position due to the increased stability of the sandwich ("excimer") conformation. This internal relaxation, already decoupled from the much slower radiative and nonradiative decays k_M and k_D, can, in principle, be described by two relaxation times τ_1 and τ_2, each of which is a function of the rate constants k_{12}, k_{21}, k_{D2}, and k_{2D}.[14] In the special case where $k_{12} + k_{21} \gg k_{D2}$ and k_{2D}, the relaxation times simplify to $\tau_1 = 1/k_{12} + k_{21}$ and $\tau_2 = 1/k_{D2} + k_{2D}$. Therefore, in our three-exponential analysis, $k_{12} + k_{21} = 1/\tau_1 - 1/\tau_3$ and $k_{D2} + k_{2D} = 1/\tau_2 - 1/\tau_3$. Although the accuracy of the τ_1 values is limited by the nanosecond time resolution of the single-photon apparatus in these laboratories, the values are of the correct order of magnitude. These results demonstrate that the equilibrium between the two monomer conformers is an order of magnitude faster than the equilibrium between the trans–gauche conformer and the excimer.

Conclusions

For PVCz in benzene solution, the biexponential analysis was found to be incompatible with the scheme proposed by Johnson,[3] and the lifetimes of the two excimers, $\tau_{A_2}^0$ and $\tau_{A_3}^0$, differ significantly from the reported lifetimes from previous biexponential analyses. The presence of the rapid-rising component accounts for the slow growing-in of the sandwich excimer emission band observed in previous time-resolved spectra. The studies of 1,3-DCzP in benzene show the inadequacies of the simple Birks scheme in the high-temperature region. The alternative scheme proposed by Goldenberg et al.[8] was found to be appropriate and attainment of monomer–monomer conformer equilibrium was demonstrated to be an order of magnitude faster than that between the monomer and the excimer configuration.

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Appendix

The artificial curves fitted with two- and three-exponential decay laws are listed in Table III. From sets A(a), A(b), and B(a), accuracies of the best-fit relaxation rates are generally within 4% with only one exception in set B(a). But notice that this discrepancy is rather consistent within set B. From sets C and D, while the decay laws are two-exponential and the curves are "contaminated" with lamp scatter, the three-exponential fitting program "sees" the lamp scatter component as an extra exponential with a rate 0.04 ns. This value seems to be insensitive to the time scale and the scattering strength over the range studied here. In set A, even when the shortest rate is of the same order of magnitude as the lamp profile (lamp scatter), the scattering only affects the preexponential factors of the fastest component in a correlated fashion. The drift in the values of the shortest rate seems to suggest that the value from the fit is some average of the real decay time and the "decay time" of the lamp. The two longer decay times practically remain stable.

Set B reflects the effect of lamp scatter on a very fast-rising component (with decay time of comparable magnitude). It is seen that for increasing scattering strength, the rising component gradually turns into "relaxing" components as "seen" by the program. Also, the shortest decay time drifts as the scattering strength becomes very strong. The effect of scattering on the second decay time remains small and on the longest decay time is negligible.

Sets E and F show the effect of an additional fast component in a three-exponential decay curve on the accuracy of fitting the curve using a biexponential decay law (see A(a) and B(a)). Even a fast component (0.06 ns) has a strong influence on the statistics of the biexponential fit. Set F demonstrates a large sensitivity to "starting channel" if one uses a biexponential law to fit a three-exponential decay curve. Also, F(b) shows that if one uses a biexponential fitting program to fit a three-exponential curve, only the longest decay time would bear accuracy while the shortest decay time would not.

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