moved from the plates with methanol. The tyrosine derivative was further purified by HPLC with use of a reverse phase ODS column (30 cm × 4 mm) and by eluting (2 mL/min) at room temperature with 35% methanol in water. *N*-Acetyl-L-tyrosine ethyl ester was identified by comparing its TLC R_f, HPLC retention time, IR, and mass-spectral data with those of the authentic material. The product had mp 77–78 °C (lit.[71] mp 79–80 °C. The yield was determined by injecting known amounts into the liquid chromatograph followed by integration (cut and weigh method of the resulting peaks. The yield of *N*-acetyl-L-tyrosine ethyl ester was 1%.

In separate experiments it was shown that no tyrosine derivative was produced in the absence of diphenyldiazomethane, or when the procedure is carried out without irradiation, or when 0.95 g (5.2 mmol) of benzophenone is substituted for diphenyldiazomethane.

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Intramolecular Excimer Formation with 1,3-Di(1-pyrenyl)propane. Decay Parameters and Influence of Viscosity

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Abstract: The fluorescence decays, studied as a function of temperature, of 1,3-di(1-pyrenyl)propane undergoing intramolecular excimer formation in toluene and other solvents can be fitted to a sum of three exponentials. The decay times have similar values for the monomer and the excimer at temperatures above 20 °C. Data showing that the decay parameters and the excimer-to-monomer fluorescence intensity ratio are strongly influenced by solvent viscosity are presented.

Introduction

Recently Thistlethwaite et al.[1] reported on the kinetics of intramolecular excimer formation with 1,3-di(1-pyrenyl)propane (Py(3)Py) and 1,10-di(1-pyrenyl)decane (Py(10)Py) in a number of solvents, based on time-correlated single-photon counting measurements at one temperature (20 °C). They concluded from their data that for Py(3)Py the excimer formation rate does not show a marked dependence on solvent bulk viscosity. This conclusion is in conflict with results obtained before using Py(3)Py and similar bichromophoric systems.[2-5] With these probe molecules, for example, the viscosity-dependent main-phase transition and the pretransition in phosphatidylcholine bilayers could readily be detected. In other studies the fluidity of micelles and biological membranes was investigated as a function of temperature. As the impression could have been made[1] that fluorescence studies with Py(3)Py do not give meaningful results on the fluidity of media such as biological membranes, we present here experimental data confirming that the kinetic parameters of Py(3)Py indeed strongly depend on solvent viscosity. Further, the kinetic model and the data published by Thistlethwaite[1] will be discussed in some detail and it will be shown that an accurate determination of the triple-exponential fluorescence decay parameters is difficult at 20 °C for Py(3)Py in solvents such as toluene, due to the small values of the amplitude ratios of the three exponentials.

Experimental Section

The 1,*n*-di(1-pyrenyl)alkanes Py(*n*)Py with $n = 3$ and 10 were synthesized as described before[6] and were purified by high-pressure liquid chromatography (HPLC). The alkane solvents (Merck) hexane, dodecane, hexadecane, and cyclohexane were purified by chromatography over SiO_2/Al_2O_3. Tetrahydrofuran (Merck, Uvasol) was refluxed over potassium in a nitrogen atmosphere. Toluene (Merck, for fluorescence spectroscopy) and the alcohols (Merck, Uvasol or the best commercially available quality) were used as received. The solutions, lower than 10^{-5} M, were degassed by the freeze-pump-thaw technique (5 cycles). The fluorescence decays were measured employing time-correlated single-photon counting.[7] As an excitation source a nitrogen-filled (1 atm) flash lamp (Edinburgh Instruments, 199 F) was used, operating at 100 kHz. The half-width of the pulse had a value between 3 and 4 ns. Under these conditions the lamp proved to be stable over periods up to 100 h. Single exponential decay times down to 500 ps can be accurately determined with this apparatus.[8] The scatter solution (Ludox, Du Pont) and the sample were alternatively positioned in the light path until 1000 counts

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Table I. Reciprocal Decay Times (λ in 10^6 s^{-1}) Obtained from Fitting the Monomer and Excimer Fluorescence Decay Curves of 1,3-Di(1-pyrenyl)propane to the Sum of Three (III) or Two (II) Exponentials ($e^{-\lambda t}$) in a Number of Solvents at 21 °C[a]

	monomer			excimer		
solvent	λ_1	λ_2	λ_3 (error, χ^2)[b]	λ_1	λ_2	λ_3 (error, χ^2)[b]
toluene (III)	5.5	16.7	112 (1.12)	7.6	16.6	112 (1.44)
(II)		11.5	109 (1.92)		11.0	152 (22.0)
ethanol (III)	4.6	14.2	127 (1.14)	6.5	14.8	124 (1.83)
(II)		7.6	125 (1.81)		9.8	166 (20.0)
cyclohexane (III)	5.1	17.3	131 (1.24)	6.6	14.8	127 (1.69)
(II)		9.0	127 (2.71)		12.0	165 (22.0)

[a] The fits with two exponentials lead to considerably larger errors than the triple exponential fits. See text. [b] The mean of the squares of the weighted deviations between the experimental curve and the sum of exponentials. The expected error for a perfect fit and experiment is unity. See ref 10 and 12.

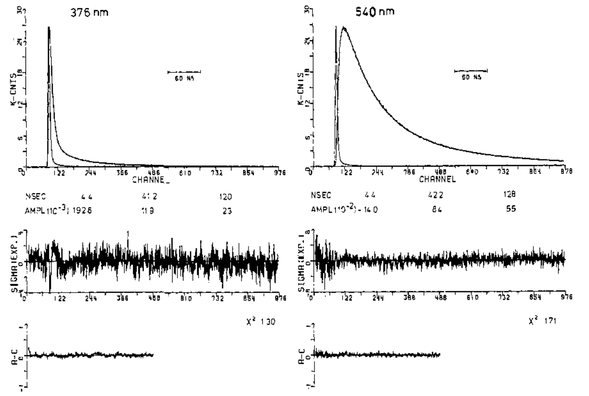

Figure 1. Rise and decay curves of the monomer (376 nm) and intramolecular excimer (540 nm) fluorescence of 1,3-di(1-pyrenyl)propane in toluene at 51 °C fitted to three exponentials. The excitation pulse (316 nm) is also depicted in each case. The values for the decay parameters λ^{-1} (in ns) and their amplitudes are given (see text). The weighted deviations in units of σ (expected deviation), the autocorrelation function A–C, and the value for χ^2 are also indicated.

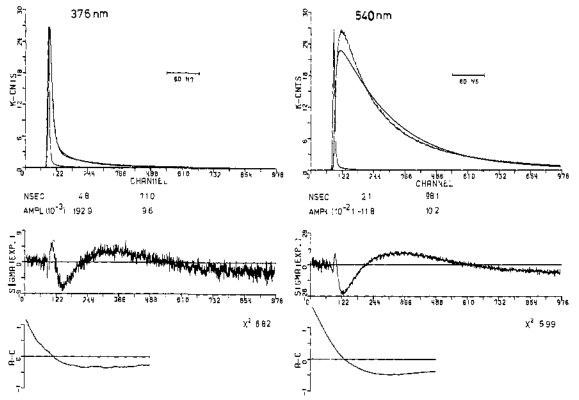

Figure 2. Rise and decay curves of the monomer and excimer fluorescence of 1,3-di(1-pyrenyl)propane in toluene at 51 °C (same experimental curves as in Figure 1) fitted to two exponentials. The values for the decay parameters λ^{-1} (in ns) and their amplitudes are given (see text). The weighted deviations, in units of σ (expected deviation), the autocorrelation function A–C, and the value for χ^2 are also indicated. Normalization of the autocorrelation to the total χ^2 can lead to A–C values greater than unity. See ref 12.

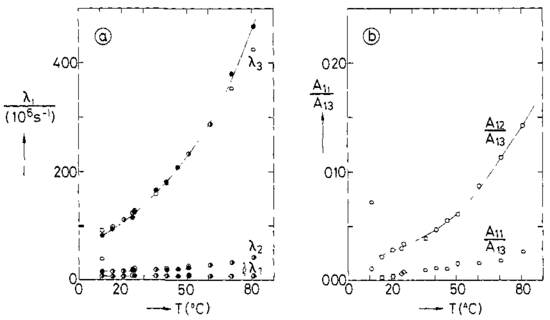

Figure 3. (a) Decay parameters λ_1, λ_2, and λ_3 (see text) for the monomer (○) and excimer (●) fluorescence decay of 1,3-di(1-pyrenyl)propane in toluene as a function of temperature. The half-filled symbols indicate that the monomer and excimer data coincide. (b) The corresponding amplitude ratios A_{12}/A_{13} and A_{11}/A_{13} for the monomer fluorescence increase with temperature. See text.

in one of the channels (Canberra 8100 multichannel analyzer) were collected in each case. Typically, the number of counts in the maximum channel was between 20 000 and 30 000 (see Figures 1,2,4,5). The excitation light (316 nm) and the fluorescence of the monomer (376 nm) and the excimer (540 nm) were passed through monochromators (Jobin-Yvon H.20 UV). The monomer and excimer decays were determined simultaneously at each temperature. Further details will be published elsewhere.[9] The decay curves were deconvoluted employing the method of modulating functions[10,11] on a Univac 1100 computer using the weighted deviations (Sigma (Exp.)) and the autocorrelation function A–C (see Figures 1, 2, 4, 5) as an indication of the quality of the fit.[12] The fluorescence spectra (uncorrected) were measured on a Hitachi-Perkin-Elmer MPF-2 fluorimeter.

Results and Discussion

The fluorescence response functions $i_M(t)$ (monomer) and $i_D(t)$ (excimer) of Py(3)Py have been fitted to sums of exponentials giving in the case of three components

$$i_M(t) = A_{11}e^{-\lambda_1 t} + A_{12}e^{-\lambda_2 t} + A_{13}e^{-\lambda_3 t} \quad (1)$$

and

$$i_D(t) = A_{21}e^{-\lambda_1 t} + A_{22}e^{-\lambda_2 t} + A_{23}e^{-\lambda_3 t} \quad (2)$$

As an example of multiexponential decay curves and their analysis, the monomer and the excimer decay functions of Py(3)Py in toluene at 51 °C have been depicted in Figure 1, showing good fits with three exponentials, as seen from the quality of the error function and the autocorrelation function (A–C), see Table I.[10] It is important to note that the decay constants $1/\lambda$ have similar values for the monomer and excimer decays. Fits of the fluorescence response functions with two decay parameters λ lead to considerably larger errors (Figure 2), underlining the fact that the monomer and excimer fluorescence decay curves can only be fitted with three exponentials. These results clearly indicate that three kinetically coupled excited-state species operate in the intramolecular excimer formation with Py(3)Py in toluene (see below). It should be noted here already that Thistlethwaite reported that attempts to fit $i_M(t)$ at 20 °C to a triple-exponential function were unsuccessful and yielded two identical values,[1] in

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(9) Busse, R.; Zachariasse, K. A., to be published.

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(12) The autocorrelation of a finite set of data can only treat one half of the set (see Figures 1, 2, 4, and 5), using the second half to permit the offset.[11] If the χ^2 of the entire set is used to normalize the autocorrelation, then the scale will in fact be magnified, leading in some cases (Figures 2 and 5) to autocorrelations greater than unity. Normalizing the A–C value at offset zero would rectify this, but then the correlation shown would be slightly smaller than when calculated relative to the total χ^2.

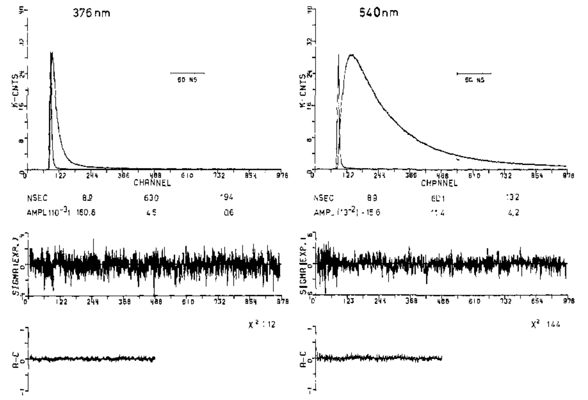

Figure 4. Rise and decay curves of the monomer (376 nm) and intramolecular excimer (540 nm) fluorescence of 1,3-di(1-pyrenyl)propane in toluene at 21 °C fitted to three exponentials. The excitation pulse (316 nm) is also depicted in each case. The values for the decay parameters λ^{-1} (in ns) and their amplitudes are given (see text). The weighted deviations, in units of σ (expected deviation), the autocorrelation function A-C, and the value for χ^2 are also indicated.

conflict with our findings (see below, Figures 4 and 5). Such a discrepancy is not only observed in the case of Py(3)Py, but also with Py(10)Py,[1,13] for which likewise three exponentials are required to fit the decay curves for the monomer and the excimer, double exponential fits leading to substantially larger errors.[14]

In Figure 3a,b the decay parameter λ_1, λ_2, and λ_3 for the monomer and excimer fluorescence decay of Py(3)Py in toluene have been plotted as a function of temperature (a). Simultaneously, the corresponding amplitude ratios for the monomer decay are given (b). It is seen that already at 21 °C (cf. Figure 4 and Table I) similar values for the three reciprocal λ's of the monomer and excimer decay are obtained. Especially at this temperature (Figure 3b), the two longest components λ_1 and λ_2 in the monomer decay have small amplitudes as compared to λ_3 (Figure 1). As these amplitude ratios become still smaller with decreasing temperature (Figure 3b), it is clear that for 21 °C and lower temperatures an accurate determination of the values of λ_2 and, especially, of the weakest component λ_1 and of their relative amplitudes, will become more and more difficult. This is illustrated (Figure 4) by the fact that at 21 °C the values for the longest decay times $1/\lambda_1$ do not have exactly the same values for the monomer (184 ns) and the excimer (132 ns) decay and by the anomalous amplitude ratios observed for the monomer decay at 11 °C (Figure 3b). However, even at this latter temperature, the decay curves can only be fitted accurately with three exponentials, double exponential fits still having relatively large errors ($\chi^2 = 1.53$ as compared to 1.29 for the triple exponential fit; cf. Table I). For the excimer decay, in contrast, the amplitude ratios have considerably larger values: $A_{21}/A_{23} = -0.272$ and $A_{22}/A_{23} = -0.732$ at 21 °C (see Figure 3). This makes it understandable that it is experimentally much simpler to determine the three decay time parameters λ from the excimer than from the monomer decay curves, a situation that for unfavorable amplitude ratios (as with Py(3)Py in toluene at 20 °C) easily can lead to the simultaneous observation[1] of two components in the monomer decay and three components in the excimer decay.

An inspection of the λ's obtained for Py(3)Py in toluene at 21 °C as a result of fitting the monomer fluorescence decay curve with either three or two exponentials (Table I) supports this conclusion. The following values (in 10^6 s^{-1}) are found: In the case of three exponentials (Figure 4) $\lambda_1 = 5.5$, $\lambda_2 = 16.7$, and $\lambda_3 = 112$, with the amplitude ratios $A_{11}/A_{13} = 0.004$ and $A_{12}/A_{13} = 0.028$. For the fit with two exponentials (having a clearly larger error, see Figure 5) $\lambda_1 = 11.5$ and $\lambda_2 = 109$, with $A_1/A_2 = 0.024$. It is seen that the value for the predominant fastest decay channel (λ_3) is practically the same for both fits, whereas the λ_2 of the double exponential fit apparently results from a mixing of the values of λ_1 and λ_2 of the fit with three exponentials. The data presented in Table I for ethanol and cyclohexane lead to the same conclusion. It is to be expected that under these conditions an analysis of λ_1, λ_2 and A_1/A_2 derived from the fit with two exponentials will tend to give unreliable values for the rate constants involved in any kinetic scheme.

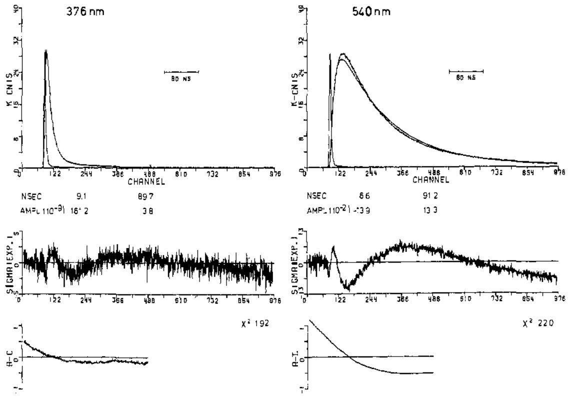

Figure 5. Rise and decay curves of the monomer and excimer fluorescence of 1,3-di(1-pyrenyl)propane in toluene at 21 °C (same experimental curves as in Figure 4) fitted to two exponentials. The values for the decay parameters λ^{-1} (in ns) and their amplitudes are given (see text). The weighted deviations, in units of σ (expected deviation), the autocorrelation function A-C, and the value for χ^2 are also indicated. Normalization of the autocorrelation to the total χ^2 can lead to A-C values greater than unity. See ref 12.

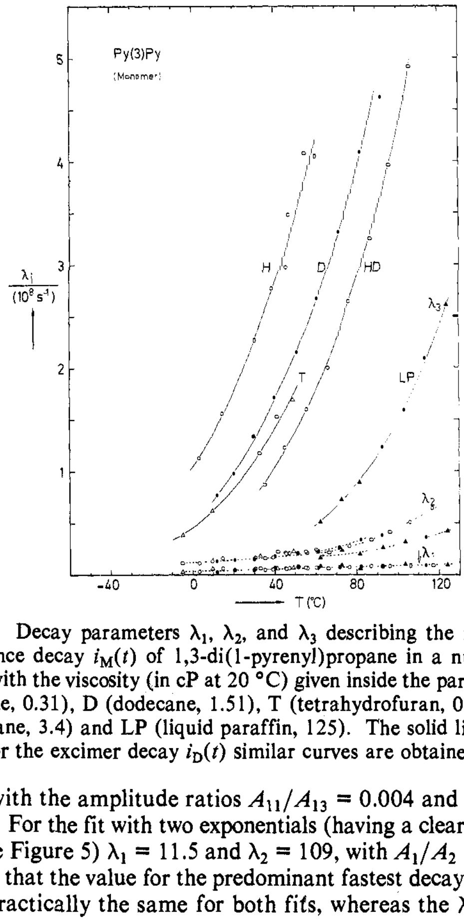

Figure 6. Decay parameters λ_1, λ_2, and λ_3 describing the monomer fluorescence decay $i_M(t)$ of 1,3-di(1-pyrenyl)propane in a number of solvents with the viscosity (in cP at 20 °C) given inside the parentheses: H (hexane, 0.31), D (dodecane, 1.51), T (tetrahydrofuran, 0.55), HD (hexadecane, 3.4) and LP (liquid paraffin, 125). The solid lines refer to λ_3. For the excimer decay $i_D(t)$ similar curves are obtained.

The fact that the monomer and excimer fluorescence decay curves of Py(3)Py can only be fitted with three exponentials has been observed in a variety of solvents over a broad temperature range, such as for tetrahydrofuran and for a number of alkanes having viscosities (at 20 °C) between 0.31 and 125 cP (Figure 6). Of the decay parameters λ of Py(3)Py, presented in Figure 6 for the monomer as a function of temperature, especially λ_3

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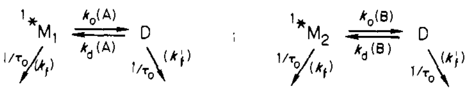
(13) The fact that $\lambda_1 > \lambda_2$ for Py(10)Py in benzene at 20 °C[1] is probably due to a typographical error, as only by interchanging λ_1 and λ_2 (giving $\lambda_1 = 1.9 \times 10^7$ s^{-1} and $\lambda_2 = 4.4 \times 10^7$ s^{-1}) and with A (as defined in ref 1) equal to 1.67 are the rate constants as given in Table II of ref 1 obtained. Also, in the excimer decay λ_2 invariably has the negative amplitude. The interchange of λ_1 and λ_2 has not been carried over to the discussion of the data for Py(3)Py.

(14) Zachariasse, K. A.; Duveneck, G.; Busse, R.; Kühnle, W.; Striker, G., to be submitted.

Scheme I



strongly depends on the viscosity of the solvent. This observation contradicts the conclusion of Thistlethwaite that the kinetic behavior of Py(3)Py is virtually independent of the solvent.[1]

For Py(3)Py in tetrahydrofuran (monomer and excimer decay curves at 33 °C quoted in ref 10), for example, triple exponential decay is observed down to −15 °C, the decay parameters λ becoming identical above 10 °C (Figure 6).[14] It should be noted, however, that in all cases, even when the three decay parameters λ of the excimer differ from those of the monomer at the lower temperatures, nevertheless fits with two exponentials lead to larger errors in the appropriate temperature ranges for the solvents investigated (cf. Figure 4).

It can be concluded from the data presented that identical λ's for the monomer and excimer decay are only observed when the amplitude ratios are not too unfavorable and when the λ values are not too close (better than a factor of two, see Figures 3 and 6), otherwise the decay times cannot be correctly separated in the data analysis. For this reason, measurements at 20 °C in solvents such as toluene, cyclohexane, and ethanol[1] are not in the optimal temperature range to obtain accurate values for the rate constants describing intramolecular excimer formation. This makes it difficult to use these rate constants to differentiate between the various kinetic schemes which are in principle possible for Py(3)Py.

Kinetic Schemes

Thistlethwaite et al.[1] described the intramolecular excimer formation with Py(3)Py by using a kinetic model consisting essentially of two simultaneously operating but noninteracting subschemes that are each identical with the schemes that describe intermolecular excimer formation[15] (here completed by addition of the excimer dissociation rate constants (k_d(A) and k_d(B)). In Scheme I, k_a is the rate constant of excimer formation, whereas k_f and k_f' are the radiative rate constants of the monomer and the excimer, respectively. The decay times τ_0 (monomer) and τ_0' (excimer) are assumed to be identical in both subschemes. This model will be discussed in some detail, using mainly the kinetic data reported in ref 1. Expressions for the time dependence of the monomer fluorescence $i_M(t)$ and excimer fluorescence $i_D(t)$ after pulse excitation are then obtained by simple addition of the equations describing the fluorescence response functions in each of the two subschemes IA and IB:[15]

$$\begin{aligned} i_M(t) = {} & \frac{\alpha k_f[\lambda_2(A) - X(A)]}{[\lambda_2(A) - \lambda_1(A)]} e^{-\lambda_1(A)t} + \\ & \frac{(1-\alpha)k_f[\lambda_2(B) - X(B)]}{[\lambda_2(B) - \lambda_1(B)]} e^{-\lambda_1(B)t} + \\ & \frac{\alpha k_f[\lambda_2(A) - X(A)][X(A) - \lambda_1(A)]}{[\lambda_2(A) - X(A)]} e^{-\lambda_2(A)t} + \\ & \frac{(1-\alpha)k_f[\lambda_2(B) - X(B)][X(B) - \lambda_1(B)]}{[\lambda_2(B) - X(B)]} e^{-\lambda_2(B)t} \end{aligned} \quad (3)$$

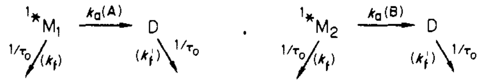
and

$$\begin{aligned} i_D(t) = {} & \frac{\alpha k_f' k_a(A)}{[\lambda_2(A) - \lambda_1(A)]} e^{-\lambda_1(A)t} + \frac{(1-\alpha)\, k_f' k_a(B)}{[\lambda_2(B) - \lambda_1(B)]} e^{-\lambda_1(B)t} - \\ & \frac{\alpha k_f' k_a(A)}{[\lambda_2(A) - \lambda_1(A)]} e^{-\lambda_2(A)t} - \frac{(1-\alpha)k_f' k_a(B)}{[\lambda_2(B) - \lambda_1(B)]} e^{-\lambda_2(B)t} \end{aligned} \quad (4)$$

In these expressions $\alpha = M_1/(M_1 + M_2)$, where M_1 and M_2 are the concentrations of the two monomers present upon excitation and

$$\lambda_{1,2} = 1/2\{(X + Y) \mp [(Y - X)^2 + 4k_a k_d]^{1/2}\} \quad (5)$$

Scheme II



with $X = k_a + 1/\tau_0$ and $Y = 1/\tau_0' + k_d$. Generally, Scheme I will give rise to four exponentials (λ_1(A), λ_2(A), λ_1(B), and λ_2(B))[16] in the monomer as well as the excimer decay. It is only when k_d(A) and k_d(B) are neglected[1] (i.e., $k_d << 1/\tau_0'$)[5] that the equations as given by Thistlethwaite (Scheme II) result, featuring two λ's for the monomer, i.e., λ_1(A) and λ_1(B) (the last two of the original amplitudes in eq 3 becoming zero), and three λ's for the excimer, i.e., λ_1(A), λ_1(B), and λ_2(A,B) (λ_2(A) and λ_2(B) becoming degenerate). Within these limits one obtains:[1,16,17] $\lambda_1(A) = 1/\tau_0 + k_a(A)$; $\lambda_1(B) = 1/\tau_0 + k_a(B)$ and $\lambda_2(A,B) = 1/\tau_0'$. This then necessarily leads, within the limits of Scheme II, to the inequality $\lambda_1(A),\lambda_1(B) \leq \lambda_2(A,B) = 1/\tau_0'$, as under all conditions $\lambda_1 \leq \lambda_2$ (eq 5). Whether $\lambda_1(A) > \lambda_1(B)$ or vice versa, depends, of course, on k_a(A) and k_a(B).

When the above equations (Scheme II) are used, the following values (in 10^6 s^{-1}, taken from Table III in ref 1) for the λ's are obtained in toluene at 20 °C: $\lambda_1(A) = 107.7$, $\lambda_1(B) = 8.7$, and $\lambda_2(A,B) = 1/\tau_0' = 17$; i.e., $\lambda_1(B) < \lambda_2(A,B) < \lambda_1(A)$, in contradiction with the condition for the relative magnitude of the λ's dictated by Scheme II (see above). For the other solvents (Table III of ref 1) similar relations hold. The discrepancy as to the relative values of λ_1 and λ_2 reported for dipyrenyldecane (see Figure 1 in ref 1) is probably due to typographical error.[1,13] The considerations presented here already indicate that the values of the rate constants derived from the experimental data are in conflict with the special conditions of Scheme II, which are a consequence of the neglect of k_d.

The most conspicuous aspect of Scheme II is in fact this absence of the rate constant k_d,[18] for which a value of 2.5×10^6 s^{-1} ($k_d\tau_0' = 0.24$) has been reported[5] for Py(3)Py in methylcyclohexane at 20 °C, employing a combination of decay times and photostationary data. Further experimental evidence concerning this assumption $k_d << 1/\tau_0'$ can be derived from the temperature dependence of the excimer-to-monomer fluorescence intensity ratio I'/I. We will remain for this discussion within the conditions of Schemes I and II. As the major part[1] of the excimers is formed via the subscheme IA (or IIA), we can use as a first approximation (for Scheme IA) the expression[14]

$$\frac{I'}{I} \approx \frac{\phi'}{\phi} = \frac{k_f' k_a(A)}{k_f(k_d(A) + 1/\tau_0')} \quad (6)$$

instead of the more general expression for the complete Scheme I.[19] For Scheme IIA, the low-temperature or high-viscosity region,[4] one obtains[5]

$$\frac{I'}{I} \approx \frac{\phi'}{\phi} = \frac{k_f'}{k_f} k_a(A)\tau_0' \quad (7)$$

In eq 6 and 7, ϕ' and ϕ are the fluorescence quantum yields for the excimer and the monomer, respectively. It should be noted that eq 7 (derived from Scheme II) does not predict that I'/I goes through a maximum with increasing temperature, as is observed for Py(3)Py in toluene (Figure 7) and for other diarylalkanes.[2-5] This signifies already that the condition $k_d << 1/\tau_0'$ does not

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(15) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970; Chapter 7.

(16) The notation λ_1 and λ_2 is retained for both subschemes to indicate the origin of the λ's in the composite Schemes I and II.

(17) In the notation of ref 1: $\lambda_1(A) = \lambda_1' = 1/\tau_0 + k_a(A)$; $\lambda_1(B) = \lambda_2' = 1/\tau_0 + k_a(B)$; $\lambda_2(A,B) = \lambda_3' = 1/\tau_0'$.

(18) This condition $k_d << 1/\tau_0'$ holds, e.g., for pyrene only at relatively low temperatures (below −46 °C in cyclohexane, for example).[15]

(19) For the total Scheme I

$$\frac{\phi'}{\phi} = \frac{k_f'\tau_0'}{k_f}\left[\frac{\alpha k_a(A)X(B) + (1-\alpha)k_a(B)X(A)}{\alpha X(B) + (1-\alpha)X(A)}\right]$$

with $\alpha = W/(1 + W)$ and W (ref 1) equals the relative concentration of the two monomers M_1 and M_2.

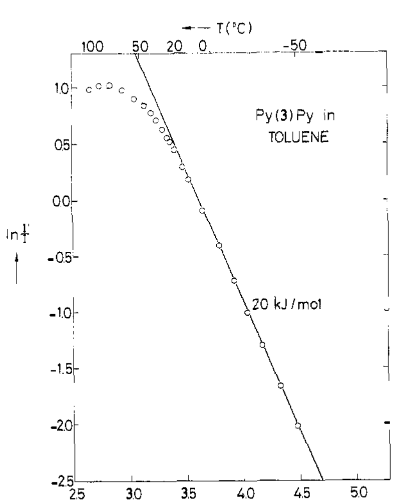


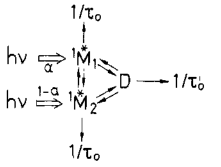
Figure 7. Arrhenius plot of the excimer-to-monomer fluorescence intensity ratio I'/I of 1,3-di(1-pyrenyl)propane in toluene. The value of the slope of the straight line going through the data points in the low temperature region is indicated in the figure.

generally hold (except for the low-temperature or high-viscosity region) for intramolecular excimer formation with Py(3)Py, which then cannot be described by Scheme II.

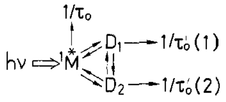
In Figure 7 the Arrhenius plot of the ratio I'/I for Py(3)Py in toluene has been presented. It is seen that the linear low-temperature region, where $k_d << 1/\tau_0'$ (eq 7), extends up to approximately 0 °C. For higher temperatures the data points start to deviate from the straight line (slope = 20 kJ/mol) of the low-temperature domain. As the distance between the straight line (eq 7) and the experimental curve (eq 6) is equal to ln $(1 + k_d\tau_0')$,[5] within the conditions of Scheme IA, the deviation from the linear plot signifies that, for example, at 20 °C in toluene[20] (and also in methylcyclohexane)[5] the condition $k_d\tau_0' << 1$ (Scheme II) is not fulfilled. It is seen (Figure 7), that for temperatures above 20 °C the distance between the low-temperature line and the experimental curve increases due to the entropy-assisted increase of k_d (large preexponential factor, see below), which rate constant will become predominant at sufficiently high temperatures.[4] At around 80 °C the ln I'/I curve goes through a maximum, indicating that the values of k_d and $1/\tau_0'$ have become equal.[5]

From these photostationary data it can be concluded that Scheme II cannot correctly describe intramolecular excimer formation with Py(3)Py in toluene even at 20 °C, as it neglects k_d. Also Scheme I is unlikely to be correct, as it leads to four exponentials in the monomer and excimer decay, as discussed above, whereas three are observed with identical values for the monomer and the excimer. It is not to be expected that with four λ's identical values for the excimer and monomer decay times $1/\lambda$ will be obtained in a fit with three exponentials over a broad temperature range (cf. Figures 3 and 6). A further argument to support the fact that k_d cannot be neglected for Py(3)Py in solvents such as toluene at 20 °C comes from a calculation of its value on the basis of the data given in ref 1, via the preexponential factor k_d^0 and the activation energy E_d. The value of k_d^0 for Py(3)Py in toluene can be obtained from $k_a^0 = 5.6 \times 10^{11}$ s^{-1} (derived from k_a and E_a)[1] and the expression $e^{\Delta S/R} = k_a^0/k_d^0$, where ΔS is the change in entropy upon excimer formation. E_d can be calculated from E_a and the value for the excimer stabilization energy ($-\Delta H$ = 21.8 kJ/mol)[5], giving with E_a = 21 kJ/mol,[1] ΔS = −40 JK^{-1} mol^{-1},[5] and $E_d = E_a - \Delta H$ a value of $k_d = 1.6 \times 10^6$ s^{-1} at 20 °C, similar to the value observed in methylcyclohexane.[5] This result again contradicts the basic assumption $k_d\tau_0' << 1$ of Scheme II.

Scheme III



Scheme IV



Three Excited-State Species

The solution of the differential equations describing intermolecular excimer formation, involving a single molecule ^{1}M* and one excimer D, results in expressions consisting of the sum (monomer) or the difference (excimer) of two exponentials for the time dependence of fluorescence intensity.[5,15] In general, the number of exponentials is equal to the number of kinetically distinguishable species that are coupled in the excited state. In our data analysis program the decay curves can be fitted with up to three exponentials. When the decays contain more than three exponentials, although the results will still be expressed as sums or differences of three exponentials, it is not to be expected that then the same values for the decay parameters λ will be found in a large number of solvents and over a broad temperature range, as has been observed to be the case for Py(3)Py. This leads to the conclusion that three excited state species are operating in the intramolecular excimer formation with dipyrenylpropane.

It is not possible, however, to indicate a priori the molecular nature of these kinetically identified species. Two possibilities have to be envisaged: (1) two kinetically different monomeric species, $^1M_1$* and $^1M_2$*, and one excimer, D, or (2) one monomer, ^{1}M*, and two kinetically distinguishable excimers, D_1 and D_2. The first possibility has been discussed (in a restricted sense, see below) by Morawetz[21] and by Guillet,[22] describing the two monomers as different conformers with the two end groups not in the excimer configuration. The second alternative has been shown to operate in the excimer kinetics of poly(*N*-vinylcarbazole).[23] Somewhat different kinetic schemes have also been discussed.[24]

This situation leads in its most general form to the two kinetic diagrams in Scheme III and IV. The arrows between the various M's and D's in the schemes indicate the rate constants, which will not be elaborated here. The difference between the Schemes III and IV rests, from the kinetic point of view, primarily in the fact that in Scheme III two species ($^1M_1$* and $^1M_2$*) can be directly excited by light, i.e., $^1M_1$* and $^1M_2$* are present at time zero, whereas in Scheme IV only one species (^{1}M*) is present immediately after excitation. In other words, kinetically the only difference between a "monomer" and an "excimer" is the question whether the state can be populated by the exciting light, i.e., whether or not in setting up the differential equations describing the kinetics, the initial concentration (at $t = 0$) of the particular excited-state species can be equated to zero.

Scheme III contains eight unknowns: six rate constants, $1/\tau_0'$, and α (with $\alpha = M_1/(M_1 + M_2)$, see above). Similarly, also Scheme IV involves eight unknowns: six rate constants, $1/\tau_0'(1)$,

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[20] For Py(3)Py in toluene at 20 °C the excimer-to-monomer fluorescence quantum yield ratio ϕ'/ϕ (cf. eq 6) has the value 12.1, whereas I'/I = 1.56 on our equipment (see Experimental Section). This obvious difference between ϕ'/ϕ and I'/I, caused by the difference in spectral shape of the excimer and monomer emissions, is the basis for the discrepancy noted[1] between the ratio in ref 4 (ϕ'/ϕ) and the ratio I'/I in ref 1.

(21) Goldenberg, M.; Emert, J.; Morawetz, J. *J. Am. Chem. Soc.* **1978**, *100*, 7171.

(22) Ng, D.; Guillet, J. E. *Macromolecules* **1981**, *14*, 405.

(23) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697. Ghiggino, K. P.; Wright, R. D.; Phillips, D. *Eur. Polym. J.* **1978**, *14*, 567. DeSchryver, F. C.; Vandendriessche, J.; Toppet, S.; Demeyer, K.; Boens, N. *Macromolecules* **1982**, *15*, 406.

(24) Todesco, R.; Gelan, J.; Martens, H.; Put, J.; DeSchryver, F. C. *J. Am. Chem. Soc.* **1981**, *103*, 7304. Wang, Y.; Crawford, M. C.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 5874.

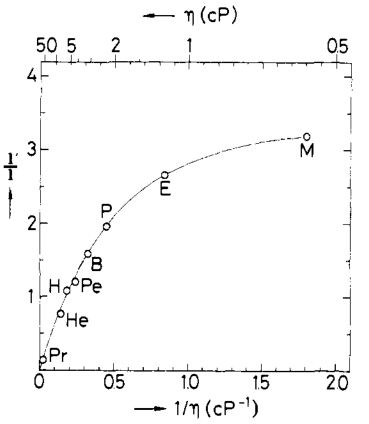

Figure 8. The excimer-to-monomer fluorescence intensity ratio I'/I of 1,3-di(1-pyrenyl)propane at 20 °C as a function of the reciprocal solvent viscosity in a number of alcohols: M (methanol), E (ethanol), P (1-propanol), B (1-butanol), Pe (1-pentanol), H (1-heptanol), He (1-hexanol), and P_r (1,3-propanediol).

and $1/\tau_0'(2)$. As from an analysis of the monomer and excimer fluorescence decay curves six independent kinetic data (three λ's and three amplitude ratios, two for the monomer and one for the excimer) can be obtained, the two general schemes III and IV cannot be completely determined, from an analysis of fluorescence decay data.

Therefore, several simplifying assumptions have been made in the literature,[21,25] leading to the following subschemes:

$$^1M_2{}^* \rightleftarrows {}^1M_1{}^* \rightleftarrows D \qquad \text{(IIIA)}$$

Here it is assumed[21] that the direct transformation of $^1M_2{}^*$ into D, and vice versa, can be neglected. This assumption is based on the identification of $^1M_2{}^*$ with a conformer having the end groups in the trans-trans configuration,[25] arguing that the two simultaneous bond rotations that are necessary in the transition $^1M_2{}^* \rightleftarrows D$, are associated with a considerably higher energy barrier than the single bond rotations involved in the transitions $^1M_2{}^* \rightleftarrows {}^1M_1{}^*$ and $^1M_1{}^* \rightleftarrows D$.

$$^1M_2{}^* \rightleftarrows D \rightleftarrows {}^1M_1{}^* \qquad \text{(IIIB)}$$

In this subscheme two different monomer conformers both form the same excimer with, in principle, different rate constants. The interconversion between the two monomer conformers in the excited state, $^1M_1{}^*$ and $^1M_2{}^*$, is assumed to be negligibly slow. See also ref 24.

In Scheme IVA,B it is assumed that only one monomer excited

$$D_2 \rightleftarrows {}^1M^* \rightleftarrows D_1 \qquad \text{(IVA)}$$

$$^1M^* \rightleftarrows D_1 \rightleftarrows D_2 \qquad \text{(IVB)}$$

state species is kinetically distinguishable, being able to form either two different excimers that do not interconvert (IVA) or forming one excimer D_1 that can give rise to a second excimer D_2.

Schemes IIIA,B and IVA,B lead to different expressions for the decay parameters λ and for their amplitude ratios.[14] In order to determine the correct scheme, our kinetic data on intramolecular excimer formation with 1,3-di(1-pyrenyl)propane, i.e., the monomer and excimer decay times (1/λ) together with the corresponding amplitudes, will be inspected and analyzed on the basis of these various a priori possible kinetic models.[14]

Influence of Viscosity

Finally, in Figure 8 the excimer-to-monomer fluorescence intensity ratio I'/I of Py(3)Py in a series of alcohols at 20 °C, is plotted as a function of viscosity. It is seen that I'/I decreases with increasing viscosity, a behavior similar to that observed with Py(3)Py in a number of other solvents and heterogeneous media.[2-5]

Even for solvents of different molecular nature still a clear viscosity dependence, as expressed by I'/I, is observed when the values of the macroscopic viscosity of the solvents are not too close (see below). This has been found to be the case not only for Py(3)Py but also for other dipyrenylalkanes such as, e.g., Py(10)Py and Py(13)Py.[14] It is therefore surprising that Thistlethwaite et al.[1] conclude to the absence of an influence of solvent viscosity in the low-viscosity region. They furthermore state that "with use of the earlier calibration curve[2] and their steady-state result the viscosity of ethanol would be determined as 50 cP". Already an inspection of the I'/I data given in Table III of ref 1 shows that this statement is questionable as the I'/I value of Py(3)Py in ethanol at 20 °C given there falls between those of benzene and cyclohexane, leading to a viscosity of the order of 1 cP as should be the case. The reason for this misconception[1] apparently comes from the fact that the calibration curve employed (taken from ref 2) can only be used in conjunction with the particular spectrofluorimeter on which the curve has been determined. This is the case as the spectral shape of uncorrected fluorescence spectra depend on the nature of the equipment and also (I'/I) on the slit width utilized. In fact, our I'/I data for Py(3)Py in ethanol ($I'/I = 2.3$ at 20 °C) lead to an apparent viscosity of the order of 1 cP. This I'/I value is considerably larger than that observed for instance in hexadecane ($I'/I = 1.36$ at 20 °C),[4] which has a viscosity of 3.4 cP at that temperature. It should be noted that hexadecane is the solvent having the lowest viscosity in the cited calibration curve.

Conclusion

It has been shown that the response functions of the monomer and excimer fluorescence of 1,3-di(1-pyrenyl)propane in toluene and a number of other solvents can be fitted to the sum of three exponentials, with identical values for the decay parameters λ at not too low temperatures. In addition, it has been concluded that the thermal dissociation (k_d) of the excimer has to be taken into account in discussions of intramolecular excimer formation with Py(3)Py, for which, more specifically, the condition $k_d\tau_0' << 1$ does not hold at 20 °C in, for example, toluene. As the kinetic Scheme II, with $k_d\tau_0' << 1$, leads to two exponentials in the monomer and three exponentials in the excimer decay, the observations given above indicate that this scheme[1] is unlikely to be the correct one for Py(3)Py.

Further, the negative conclusions derived by Thistlethwaite et al.[1] as to the applicability of Py(3)Py and other dipyrenylalkanes as viscosity probes have been shown to be unfounded. The usefulness of these probe molecules had, in fact, already been extensively demonstrated in the literature.[2-4] On the other hand, one has to consider the intrinsic limits inherent in the use of all probe molecules.[2-4] The viscosity values determined with a probe molecule such as Py(3)Py have to be viewed in an operational manner, as discussed before.[2-4] In addition, in solvents of similar macroscopic viscosity, such as, for example, toluene, cyclohexane, and ethanol (±0.3 cP),[1,14] the intrinsic influences on, e.g., the rate constant k_a caused by the differences in the molecular nature of the solvents can interfere with the effect of relatively small differences in viscosity. This will be the case even when accurate values for the rate constants can be obtained. The specific effect of the solvent can be expressed in terms of the differences in the values of the Hildebrand solvent parameter δ, for which the interrelation with the effects of the macroscopic viscosity has been discussed.[26,27] The difference in the δ values for the solvent, the chain, and the end groups in the dipyrenylalkanes determines the coupling between the solvent and the constituent groups of Py(n)Py, each influencing intramolecular excimer formation. It is then to be expected that, for example, a solvent with a large δ value, such as ethanol (δ = 12.7), will interact with Py(n)Py in a different manner than a solvent such as cyclohexane (δ = 8.2), having properties similar to that of the chain, or than toluene (δ

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(25) Ito, S.; Yamamoto, M.; Nishijima, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 363.

(26) Hildebrand, J. H.; Scott, R. L. "The Solubility of Non-electrolytes", 3rd ed.; Reinhold: New York, 1949. Burrell, H. In "Polymer Handbook"; Brandup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; Vol IV, p 337.

(27) Winnik, M. A.; Li X.-B.; Guillet, J. E. *J. Polym. Sci*, in press.

= 8.9), which is similar to the pyrenyl end groups.[14] This is an expression of the old adagium of the alchemists: similia similibus solvuntur.

Acknowledgment. Many thanks are due to George Striker for stimulating discussions on the various aspects of data analysis and for making his deconvolution program available to us. The use of the excellent facilities of the Gesellschaft für wissenschaftliche Datenverarbeitung GmbH Göttingen (GWDG) are gratefully acknowledged.

Registry No. 1,3-Di(1-pyrenyl)propane, 61549-24-4.

Ring-Closure Reactions. 22.[1] Kinetics of Cyclization of Diethyl (ω-Bromoalkyl)malonates in the Range of 4- to 21-Membered Rings. Role of Ring Strain

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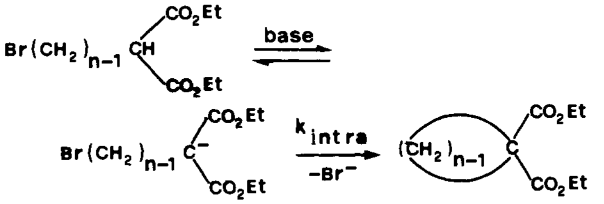
Abstract: The kinetics of closure of 1,1-bis(ethoxycarbonyl)cycloalkanes from the anions derived from diethyl (ω-bromoalkyl)malonates have been investigated in Me$_2$SO at 25 °C. Rate constants and effective molarities (EM) have been obtained for the ring sizes 4–13, 17, and 21. This is the first quantitative study on the kinetics of S$_N$2 closure of all-carbon rings, which includes small, common, medium, and large rings. The reactivity data span over nine powers of ten, which is the widest reactivity range recorded so far in a cyclization series. Due to the extremely low EM for the 9-, 10-, and 11-membered rings, a special competition technique was developed for these rings. Comparison of the present results with literature data on S$_N$2 ring-closure reactions reveals structure-dependent reactivity patterns showing varying features, which are qualitatively accounted for on the basis of structure effects on transition-state strain energies. A dissection of the EM data for the malonate cyclization into strain and probability factors was attempted. Perhaps the most interesting result is a definite tendency for transition-state strain energies to parallel cycloalkane strain energies for the 7-membered and larger rings but not for the smaller rings. In the latter cases the ring product no longer appears to be a proper model for comprehending the transition state.

As a continuation of our studies on reactivity in ring-closure reactions[2] and with particular reference to the role of strain on medium-ring formation, we now report on the kinetics of the base-promoted cyclization of diethyl (ω-bromoalkyl)malonates to 1,1-bis(ethoxycarbonyl)cycloalkanes in Me$_2$SO.



(1)

The existence of a very pronounced medium-ring effect was already apparent from the yield data in a recent work[3] on the synthetic applicability of reaction 1 to the preparation of cyclic compounds over a wide range of ring sizes. In addition to the medium rings (8- to 11-membered) the present kinetic investigation includes the 4-membered small ring, the common rings (5- to 7-membered), and the 12-, 13-, 17-, and 21-membered large rings. In comparison with previous studies in this series,[2] the novel features of the present investigation are (i) cyclization via C–C bond formation by intramolecular alkylation of a carbon nucleophile and (ii) formation of wholly saturated carbocyclic rings.

Methods and Results

The kinetics were carried out in Me$_2$SO at 25.0 °C by monitoring the disappearance of the strong absorption of the tetramethylammonium salts of the (ω-bromoalkyl)malonic esters at 288 nm (ϵ = 17 100 cm^{-1} M^{-1}). This was carried out by stopped-flow spectrophotometry in the case of the 4-, 5-, and 6-membered rings and by conventional spectrophotometry in all the other cases.

The tetramethylammonium salts were generated in situ by adding the calculated amount of Me$_4$NOH stock solution to a solution of the malonic ester. The acid–base reaction is virtually quantitative even in the very dilute solutions used in the kinetic runs (ca. (1–2) × 10^{-4} M), so that only the stoichiometric amount of base was required in addition to the amount used up to neutralize the free acidity of the solvent (see Experimental Section). Under the given conditions carbanion production is much faster than cyclization,[4] with the sole exception of the extremely fast reaction leading to the 5-membered ring (vide infra).

As to the small amount of water accompanying the added base, we note that the present reactions, involving highly delocalized carbanionic species, proved to be particularly insensitive to the water content of the medium. We found negligible effects on reactivity on going from neat to 99% Me$_2$SO in typical cases. A similar insensitiveness to added water has been reported for the rate of methylation with methyl iodide of the potassium salt of dibenzoylmethane in Me$_2$SO.[5]

The counterion effect has been checked both by replacing K$^+$ for Me$_4$N$^+$ and by adding a large excess of Me$_4$NBr. In both cases no significant effect on rates was observed,[6] indicating that ion

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(1) Part 21: Dalla Cort, A.; Mandolini, L.; Masci, B. *J. Org. Chem.* **1983**, *48*, 3979.

(2) Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95.

(3) Casadei, M. A.; Galli, C.; Mandolini, L. *J. Org. Chem.* **1981**, *46*, 3127.

(4) In connection with related studies we find that the second-order rate constant for proton abstraction by Me$_4$NOH from Cl(CH$_2$)$_5$CH(CO$_2$Et)$_2$ in Me$_2$SO at 25 °C is 2 × 10^6 M^{-1} s^{-1}.

(5) De Palma, V. M.; Arnett, E. M. *J. Am. Chem. Soc.* **1978**, *100*, 3514.

(6) These observations are a part of a detailed study on the effect on ion pairing on reaction 1, which has been reported in a preliminary form at the Sixth IUPAC Conference on Physical Organic Chemistry, Louvain-La-Neuve, Belgium, July 11-16, 1982. See: Galli, C.; Mandolini, L. *Bull. Soc. Chim. Belg.* **1982**, *91*, 432.

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