MECHANISM OF THE PHOTOISOMERIZATION OF 1,3-DIPHENYLALLYL CARBANION

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Summary

The fluorescence of 1,3-diphenylallyl lithium (DPA$^-$Li$^+$) in 2-methyltetrahydrofuran (MTHF) is due to the presence of the loose ion pair having the trans,trans conformation: no fluorescence from the cis,trans conformer could be detected. Conformational photoisomerization accompanies fluorescence. The lifetime and the quantum yield of fluorescence increase with decreasing temperature and reach limiting values by about -100 °C. A mechanism in which the excited state is deactivated by fluorescence and non-radiative decay in competition with activated twisting about the allylic skeleton is proposed and shown to be compatible with the observed temperature dependences. Alternative mechanisms involving the corresponding allylic radical are discussed.

1. Introduction

1,3-Diphenylallyl lithium (DPA$^-$Li$^+$) exists in 2-methyltetrahydrofuran (MTHF) almost entirely as the loose ion pair at temperatures below -40 °C; at higher temperatures a small fraction of tight ion pairs is also present, in the form of aggregates. The ^{1}H nuclear magnetic resonance spectrum shows that the trans,trans and cis,trans conformers are present in the ratio 9:1 [1]. Exposure of such solutions to light causes photochemical interconversion of the conformers; the position of the ensuing photostationary state is strongly temperature dependent [2]. Solutions of DPA$^-$Li$^+$ in MTHF fluoresce [3]. The close match of the absorption spectrum of the trans,trans conformer with the excitation spectrum together with the occurrence of a normal Stokes shift shows that the emitting species is the trans,trans loose ion pair; no emission attributable to the cis,trans form was detected. The observed strong temperature dependence of the fluorescence intensity was satisfactorily interpreted in terms of the deactivation of the excited state by fluorescence accompanied by a non-radiative activated process, namely isomerization by twisting about the allylic skeleton [2]. We now report measurement of fluorescence lifetimes and quantum yields of fluorescence.

2. Experimental details

The solutions of DPA–Li$^+$ in MTHF were prepared under high vacuum as previously described [2].

The fluorescence lifetimes were determined using light from the discharge of an Edinburgh Instruments lamp with a 2 ns pulsewidth in conjunction with the time-resolved single-photon-counting technique. Quantum yields were determined by reference to Rhodamine B for which the quantum yield was taken [4] as 0.69.

3. Results and discussion

The values obtained for the fluorescence lifetimes and the quantum yields are given in Table 1.

TABLE 1

Fluorescence of DPA–Li$^+$ in 2-methyltetrahydrofuran

Temperature (°C)	Lifetime (ns)	Quantum yield	Lifetime/quantum yield
20	0.195	0.057	3.42
0	—	0.135	—
−20	1.05	0.314	3.38
−20	1.7	0.423	4.01
−60	2.6	0.684	3.8
−80	3.5	0.75	4.66
−100	—	0.81	—

Figure 1 summarizes the situation where only internal conversion and twisting compete with fluorescence to deactivate the excited state. Using the rate constants indicated, the fluorescence lifetime is given by $1/(k_1 + k_2 + k_3)$ and the quantum yield by $k_1/(k_1 + k_2 + k_3)$. The ratio of the lifetime to the quantum yield ought to be constant if the scheme is appropriate to the system. The scatter observed in not unreasonable for these kinds of measurement; the value deduced for k_1 is 2.6×10^8 s^{-1}.

Cooling the sample below −100 °C did not cause any further increase in the intensity of the fluorescence and it may be concluded that skeletal twisting was effectively stopped. The quantum yield may be expressed as $\phi_F = k_1/\{k_1 + k_2 + A \exp(-E/RT)\}$ down to this limiting condition whereafter it may be written $\phi_F^0 = k_1/(k_1 + k_2)$. On this basis, a plot of $\ln(1/\phi - 1/\phi^0)$ vs. $1/T$ should be linear; Fig. 2 shows that this is true within reasonable experimental error. The gradient is $-E/R$ and the intercept $\ln(A/k_1)$. Least-mean-squares analysis gives the activation energy of skeletal twisting as 24.1 kJ mol^{-1} and the pre-exponential factor as 6.6×10^{13} s^{-1} employing the value deduced for k_1. As expected, the activation energy for
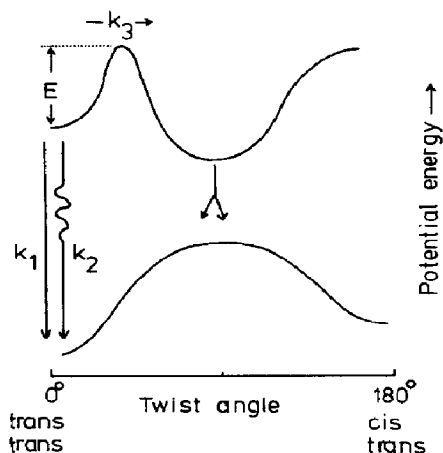
Fig. 1. Potential energy diagram showing the competition between internal conversion, twisting and fluorescence to deactivate the excited state.
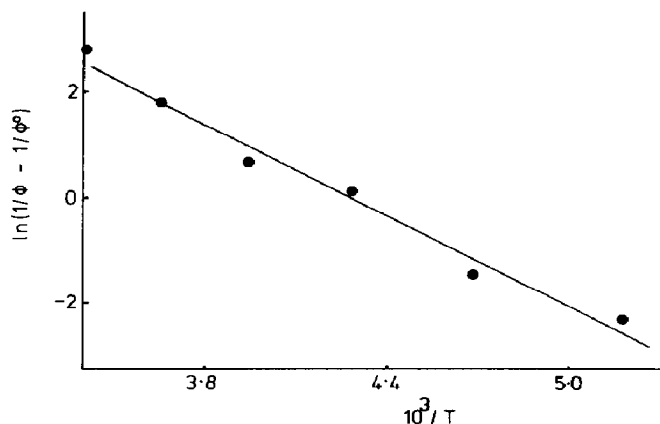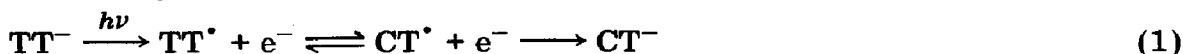
Fig. 2. Plot of $\ln(1/\phi - 1/\phi^0)$ vs. $1/T$.

skeletal twisting in the ground state is much higher — values of 79 kJ mol^{-1} [5] and 74 kJ mol^{-1} [1] have been reported.

Recently Bushby and Tykto reported [6] that the ground state relaxation of the cis,trans conformer into the trans,trans in tetrahydrofuran is catalysed by aromatic hydrocarbons and concluded that an electron is transferred from the anion to the hydrocarbon, thereby forming the allylic radical which is conformationally more labile than the hydrocarbon. Since loss of an electron from the excited state carbanion must be much easier than from the ground state, it is necessary to consider two other mechanisms:

$$TT^- \xrightarrow{h\nu} TT^{\bullet} + e^- \rightleftharpoons CT^{\bullet} + e^- \longrightarrow CT^- \tag{1}$$

$$TT^- \xrightarrow{h\nu} (TT^-)^* \longrightarrow TT^{\bullet} + e^- \rightleftharpoons CT^{\bullet} + e^- \longrightarrow CT^- \tag{2}$$

In mechanism (1) immediate photoejection of an electron results in the formation of the *trans,trans*-diphenylallyl radical. The same products are formed in mechanism (2) but by an activated process from the excited carbanion. Isomerization of the radical followed by electron recapture completes mechanisms (1) and (2). The radical is known to be conformationally labile and the rate constant for the process $CT^{\bullet} \longrightarrow TT^{\bullet}$ has been estimated [7] as 5×10^8 s^{-1} at -65 °C. If a pre-exponential factor of 10^{13} s^{-1} is assumed the activation energy is about 18 kJ mol^{-1}. Mechanism (1) can be discarded on the grounds that photoejection of an electron would not be expected to be temperature dependent. Mechanism (2) cannot be so readily dismissed. Application of the steady state approximation leads to an expression for the photostationary state in terms of 12 rate constants; trials with a computer failed to mimic the simple temperature dependence observed experimentally. No such difficulty was found with the mechanism of Fig. 1 and it is the favoured mechanism on the basis of Occam's razor.

Acknowledgment

References

1 G. Boche and D. R. Schneider, *Tetrahedron Lett.*, (1976) 3657.
2 R. N. Young, H. M. Parkes and B. Brocklehurst, *Makromol. Chem. Rap. Commun., 1* (1980) 65.
3 J. W. Burley and R. N. Young, *J. Chem. Soc., Chem. Commun.*, (1970) 1649.
4 J. N. Demas and G. A. Crosby, *J. Phys. Chem., 75* (1971) 991.
5 H. M. Parkes and R. N. Young, *J. Chem. Soc., Perkin Trans. II*, (1980) 1419.
6 R. J. Bushby and M. P. Tytko, *J. Chem. Soc., Chem. Commun.*, (1986) 23.
7 G. Boche and D. R. Schneider, *Angew. Chem. Int. Ed. Engl., 16* (1977) 869.