Fluorescence Quenching of Naphthalene by Conjugated Dienes. Steric, Solvent, and Conformational Effects

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Abstract: Small solvent effects on the rates of quenching of naphthalene fluorescence by the piperylenes (1,3-pentadienes) are consistent with the view that solvents modify charge-transfer interactions between quencher and quenchee. Since deuteration of the solvent leads to a small decrease in reactivity, vibrational modes in the medium may also be implicated. The outstandingly high quenching reactivity of 2-*tert*-butyl-1,3-butadiene is attributed to the fact that the bulky substituent forces the diene into the s-cis conformation.

The general background of the nonclassical fluorescence quenching problem and a simplified, mechanistic overview have been presented in an accompanying paper.[3] In this paper we present results of quenching studies designed to investigate medium effects and steric influences on the reactivity of acyclic dienes as quenchers.

Results and Discussion

Solvent Effects. Charge-transfer and molecular-exciton contributions to exciplex stability can be described by eq 1. Normalization requires that $\Sigma_i C_i^2 =$

$$\Psi = C_1\Psi_1(A^-Q^+) + C_2\Psi_2(A^+Q^-) + C_3\Psi_3(A^*\cdot Q) + C_4\Psi_4(A\cdot Q^*) \quad (1)$$

1 so that for a case of pure charge transfer C_1 or C_2 is unity and the remainder of the coefficients is zero. This case is at least approached in the fluorescence quenching of aromatic hydrocarbons by amines.[4,5] Rate enhancements by factors of 10–100 are observed for such quenching processes upon changing from nonpolar (methylcyclohexane) to polar (acetonitrile, methanol) solvents, and in polar media separated ion radicals are produced as decay products.[6] However, variations also arise in nonpolar solvents which can be associated with changes in the polarizability of the media.[5]

Excimers of aromatic hydrocarbons are believed to have considerably attenuated charge-resonance properties.[7] However, calculations emphasize that such contributions may be significant[8] although symmetry requires that there be no permanent charge separation. The few available data[9] indicate that solvent polarizability may make a contribution to the stabilization of symmetrical excimers.[10] Thus the observation of large rate enhancements in more polar solvents for naphthalene fluorescence quenching by dienes would be indicative of large charge-transfer interactions, but small effects must be interpreted with caution.

The results of solvent studies using *cis*- and *trans*-piperylene as quenchers of naphthalene fluorescence are summarized in Table I and are consistent with some charge-transfer involvement. The quenching rate constants were obtained from least-squares Stern–Volmer plots using either fluorescence intensity or fluorescence lifetime measurements. Rate constants obtained by the two methods agreed to within ±2%. Values of τ_0 were obtained directly or from the intercept of the Stern–Volmer plot of eq 2. Agreement to within ±3%

$$1/\tau = 1/\tau_0 + k_q[Q] \quad (2)$$

was observed for these methods. τ_0 = fluorescence intensity and lifetime in the absence of quencher [Q].

Table I. Solvent Effects on Naphthalene Fluorescence Quenching by *cis*- and *trans*-Piperylene at Room Temperature[a]

Solvent	η_D	ϵ	Quencher	τ_0[b]	$k_q \times 10^{-8}$ M^{-1} sec^{-1}
Hexane	1.3754	1.9	Cis	106 ± 2	1.11 ± 0.03
			Trans		1.29 ± 0.03
Methanol	1.3288	32.6	Cis	91 ± 3	1.85 ± 0.05
			Trans		2.58 ± 0.07
Acetonitrile	1.3460	38.8	Cis	90 ± 3	1.52 ± 0.03
			Trans		2.24 ± 0.06
Cyclohexane	1.4266	2.0	Cis	116 ± 3	1.31 ± 0.03
			Trans		1.98 ± 0.04
Cyclohexane-d_{12}			Trans	119 ± 4	1.86 ± 0.05

[a] All samples were degassed at $<5 \times 10^{-4}$ Torr using three freeze–pump–thaw cycles with the exception of four such cycles in the case of methanol. [b] Lifetime in nanoseconds; value determined from the average of two or more runs.

The significance of k_q as a composite of rate constants has been discussed elsewhere.[3]

Small but significant solvent effects are observed and are of such a nature as to be qualitatively attributable to control of reactivity by charge-transfer interactions. According to the Onsager model,[11] which ignores localized interaction between solvent and solute, the energy of a dipole immersed in a continuous medium

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should be a function of both the polarizability and dielectric constant of the medium. Thus the rate enhancements in methanol and acetonitrile might be expected since they are classically polar solvents and the increase in rate on passing from *n*-hexane to cyclohexane may be attributed to the higher polarizability of the latter solvent, indicated by its higher refractive index. However, the effects are a couple of orders of magnitude smaller than those observed in quenching by amines,[5,6] indicating that kinetic effects associated with charge transfer are relatively small in quenching by dienes. It is also significant that medium effects on the energy of the emission from exciplexes formed from 1-cyanonaphthalene and alkenes[12] are intermediate in magnitude between the kinetic effects observed in this work and those observed in amine quenching. By extrapolation we see two possible inferences: (1) quenching of naphthalene by piperylene may involve irreversible formation of an exciplex with charge transfer only beginning to develop in the transition state for complex formation, or (2) the coefficient C_1, in eq 1, is considerably smaller for the naphthalene–piperylene exciplex than is the case with the exciplexes from cyanonaphthalene. The result is clearly consistent with results reported in a companion paper.

The τ_0 values in Table I are consistent and the differences are real under the degassing conditions employed. However, larger numbers of freeze–pump–thaw cycles did afford increased values of τ_0 in hexane thus indicating the presence of some impurity quenching under standard degassing conditions. It is not certain whether the variation of τ_0 with solvent is caused by alterations in the various decay processes or by differing amounts or types of impurities present in each of the solvents.

The solvent effects may also reflect participation of the solvent in the vibronic relaxation process. The effect of isotopic substitution in the solvent shown by cyclohexane-d_{12} is small but probably significant. If so, the result indicates that some intimate role of the solvent is indeed involved. Similar results have been obtained for the phosphorescent lifetimes of naphthalene and naphthalene-d_8 in crystalline durene[13] and in ethanol.[14] In both instances the lifetimes were longer in the deuterated medium. The present results may also implicate solvent vibrational modes in radiationless decay processes. Eisinger and Navon[15] and Heller[16] have recently presented interesting theoretical interpretations.

Steric and Conformational Effects. Since previous studies indicated that bulky substituents on the aromatic sensitizer hindered the quenching process,[17] we investigated similar effects in the quencher. The results of our study using *trans*-5,5-dimethyl-1,3-hexadiene and 2-*tert*-butyl-1,3-butadiene and suitable model compounds are summarized in Table II. In general, the results parallel those with the substituted naphthalenes in that bulky *tert*-butyl substituents retard the quenching rate, again implying that intimate contact between the sensitizer and quencher is required during the quenching process.

Table II. Fluorescence Quenching of Naphthalene by Selected Conjugated Dienes in *n*-Hexane at Room Temperature

Quencher	$k_q \times 10^{-7}$ M^{-1} sec^{-1}	k_{rel}	λ_{max}	ϵ_{max}
trans-Piperylene (**1**)	12.9 ± 0.3	1.000	215^a	27,500^a
trans-5,5-Dimethyl-1,3-hexadiene (**2**)	3.88 ± 0.20	0.301	224	26,900
Isoprene (**3**)	1.84 ± 0.06	0.143	216^a	19,800^a
2-*tert*-Butyl-1,3-butadiene (**4**)	5.03 ± 0.30	0.390	236	6,800

^{a} Reference 23.

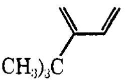
Even more striking is the fact that a *tert*-butyl group in the 2 position leads to more effective fluorescence quenching than the *trans*-piperylene although substitution at secondary positions generally does not produce such trends.[17] If the steric hindrance of the *tert*-butyl group is taken into account by comparing **1** and **2** in which the diene conformations are predominantly s-trans, then the actual rate enhancement observed for **4** relative to the isoprene model **3** is approximately an order of magnitude. This result can be explained by a conformational effect in the diene.

Little quantitative data are available in the literature concerning equilibria between the s-trans and s-cis forms of 1,3-dienes.

(3)

For butadiene all of the available data indicate that the s-trans conformation is favored by more than 2 kcal/mol at room temperature.[18] Similar results have also been obtained for isoprene with a lower limit of 2 kcal/mol being proposed.[19] To date no other dienes have been studied.

There is, however, other indirect evidence from Diels–Alder reactions[20] which gives a clear indication of the cisoid and transoid character of dienes. The striking effect of the *tert*-butyl group is nicely illustrated by the fact that **4** readily enters into Diels–Alder reactions while **5** does not, even under forcing conditions.



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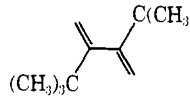

5

On the basis of conformational enthalpies in the cyclohexane series[21] one could argue that the preferred conformation for **4** might be s-cis. This is supported by the spectroscopic data in Table II. The absorption maxima of cisoid dienes are red shifted and have lower extinction coefficients than the corresponding transoid conformers.[22] Thus the trends in Table II uphold the contention that 2-*tert*-butyl-1,3-butadiene exists predominantly in the s-cis form.

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The order of magnitude difference between s-cis and s-trans species is also evident in the literature.[17] Thus, 1,3-cyclohexadiene quenches naphthalene fluorescence 11 times as fast as does *cis,cis*-2,4-hexadiene, which exists in the s-cis form in only trace amounts.[20] Many of the remaining data[17] follow similar patterns but do not fit quantitatively with rates predicted on the basis of given percentages of s-cis and s-trans conformers and the respective s-cis and s-trans rate constants for dienes having a fixed number of alkyl substituents. Obviously, a number of other factors are involved as well.

Conclusions

Small solvent effects on quenching rates are consistent with the belief that charge transfer may make a significant contribution to the free energy of formation of exciplexes. The unique effect of attachment of a bulky *tert*-butyl group to an internal position on the diene unit is a clear indication that especially high reactivity is associated with dienes having the s-cis conformation.

Experimental Section

Materials. Phillips commercial grade hexane was heated to reflux over sulfuric acid for several days and then distilled. Then it was heated to reflux over potassium permanganate for 2 days and distilled. Finally it was distilled from phosphorus pentoxide through a 60-cm column packed with glass helices, the fraction boiling at 68–69° being collected. Hexane purified in this manner showed no absorption in a 10-mm quartz cell at wavelengths greater than 230 nm. Cyclohexane was purified in a similar fashion and exhibited no absorption in a 10-mm quartz cell at wavelengths greater than 240 nm. Cyclohexane-d_{12} was obtained from Stohler Isotope Chemicals and was purified by distillation from lithium aluminum deuteride followed by redistillation. Its absorption characteristics were nearly identical with those of cyclohexane, the difference consisting of some end absorption between 240 and 260 nm. Matheson Coleman and Bell Spectroquality acetonitrile was distilled twice from phosphorus pentoxide, once from potassium carbonate, and finally two more times with the fraction used being that collected at 81–82°. Naphthalene, reagent grade, was purified by two recrystallizations from ethanol followed by two sublimations at atmospheric pressure.

***trans*-5,5-Dimethyl-1,3-hexadiene** was prepared according to the method of Bohlmann.[23] The material obtained in this manner showed only one peak on either a 20% Carbowax 20M column, a 5% poly-*m*-phenyl ether column, or a 25% saturated silver nitrate–tetraethylene glycol column. It is assumed to be the trans isomer. The olefinic region in the nmr and the ultraviolet absorption spectra are in accord with such an assignment. Prior to use in the quenching experiments the material was bulb-to-bulb distilled from lithium aluminum hydride at aspirator pressure.

2-*tert*-Butyl-1,3-butadiene was prepared by the dehydration of 3,4,-4-trimethyl-1-penten-3-ol over basic alumina at 250–300° by a method similar to that developed by Marvel and coworkers.[24] The allylic alcohol was obtained using a procedure reported by Russian workers.[25] Glpc analysis showed that the diene purity was greater than 92%. The purity was improved to better than 99.5% by preparative glpc using a 15 ft × 3/8 in. 25% β,β'-oxydipropionitrile–5% silver nitrate column at 35° and 72 ml/min. Prior to the quenching experiments the diene was bulb-to-bulb distilled from lithium aluminum hydride.

***cis*- and *trans*-piperylene** were distilled from lithium aluminum hydride prior to use in the quenching experiments. Analysis by glpc using the β,β'-oxydipropionitrile–silver nitrate column described above revealed isomeric purities in excess of 98% for both piperylenes. Isoprene was distilled from lithium aluminum hydride prior to use in the quenching experiments.

Procedures. Fluorescence intensities were measured with an Aminco-Bowman spectrophotofluorometer, using an excitation wavelength of 320 nm. Fluorescence lifetimes were measured with a TRW Model 31A nanosecond spectral source coupled to a Tektronix Model 556 dual-beam oscilloscope. Emitted light was filtered using a 340-nm interference filter.

Samples (3 ml) containing 0.01 *M* naphthalene and varying concentrations of diene quencher were placed in either 13-mm Pyrex test tubes or 12-mm quartz tubes. The samples were degassed at $<5 \times 10^{-4}$ Torr using three freeze–pump–thaw cycles. The intensities and/or lifetimes were measured 5–10 times for each tube and an average value for each sample was recorded. Runs employing 0.10 *M* naphthalene afforded rate constants identical with those obtained with the above samples. The fluorescence lifetime of naphthalene in hexane in the absence of quencher remained constant for the two concentrations of naphthalene employed.

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