Short Communication

Photophysics of 1-phenyl-2-butene

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The photochemistry of 1-phenyl-2-butene has been studied in both the liquid [1 - 3] and gas [4, 5] phases, and quantum yields of fluorescence and product formation have been measured as a function of excitation energy and concentration of both the substrate and various quenchers. Rate constants for radiative and non-radiative decay of *trans*-1-phenyl-2-butene(I) promoted to its first excited state in the gas phase at low pressure have been reported by Comtet [5]. However, the latter data were obtained indirectly by assuming that I has the same S_1 radiative lifetime in the gas phase at low pressure as does toluene in cyclohexane solution [6].

We have previously reported the results of studies of the photophysics of styrene and several of its derivatives [7 - 9]. A number of these molecules are amenable to nanosecond time resolved spectroscopic investigation and exhibit an unusual double exponential fluorescence decay, the slower component of which has been attributed to a twisted second excited singlet state. It was therefore of interest to compare the photophysics of the styrenes with that of I in which the olefinic double bond is one methylene removed from conjugation with the aromatic ring.

Experimental

Singlet excited state lifetimes of I were measured in the gas phase at pressures between 0.10 and 0.25 Torr using equipment and techniques previously described [7, 8]. The accuracy of the lifetimes obtained with this apparatus was checked periodically by measuring the fluorescence lifetime of 0.1 Torr of toluene vapour, for which a value of 56 ns has been previously reported [10].

Nanosecond time resolved emission measurements were carried out using a frequency-doubled cavity-dumped argon ion laser (λ_{ex} = 257.25 nm) and the detection system previously described [11]. A time gate of 2 ns and an

emission spectral bandwidth of 0.4 nm were employed in the present experiments.

The samples of I, available from commercial sources, were purified by preparative gas chromatography and contained minute amounts of the *cis* isomer as the only detectable impurity. The samples were stored, degassed and distilled in a vacuum line free of grease and mercury. All experiments were carried out at room temperature.

Results and discussion

Time resolved fluorescence spectra obtained by exciting 0.10 Torr of I at 257.25 nm exhibited no significant temporal variations up to 127 ns after excitation. The time resolved spectra are similar to the time unresolved low resolution fluorescence spectrum previously reported by Comtet [5]. The temporal invariance of the fluorescence spectrum was confirmed by measuring fluorescence decay rates at several emission wavelengths. When excited at 257.25 nm I exhibits single exponential fluorescence decay with a lifetime of 36.2 ns, independent of emission wavelength.

In contrast, the styrenes do exhibit both a temporal variation in their fluorescence spectra and a variation of their fluorescence decay rates with emission wavelength. In the styrenes absorption at 257.25 nm excites both higher vibrational levels of S_1 (^1L_b) and the lower vibrational levels of S_2 (^1L_a). Excitation of "isolated" *trans*-1-phenylpropene, for example, produces two radiative states. The shorter lived state ($\tau = 2$ ns) has been attributed to vibrationally excited S_1 and the longer lived state ($\tau = 45$ ns) has been attributed to a non-Franck–Condon S_2 state [8, 9]. Excitation to S_2 in the styrenes is thought to involve essentially a one electron promotion in the delocalized π system [12] and there is evidence that this state can be stabilized by twisting about the olefinic double bond [8, 13].

Illumination of I at 257.25 nm, however, initially populates only vibronic levels in S_1. The second excited singlet of this molecule lies much higher in energy, and the absence of two-component fluorescence decay may be taken as evidence in support of both the involvement of S_2 in the radiative decay of the styrenes and the previous proposal [2, 5] that the ring π electrons and the olefinic π electrons are not in communication in either the ground or the first excited singlet states of I.

The fluorescence lifetimes of low pressures of I as a function of excitation wavelength, obtained by conventional time correlated single photon counting techniques, are given in Table 1. These lifetimes were measured at pressures at which less than 8% of the excited species will suffer collision in one lifetime, assuming a collision cross section of 36×10^{-16} cm^2 [14]. Excitation wavelengths correspond to prominent bands in the absorption spectrum. True single vibronic level excitation was not achieved at the excitation bandwidth employed (0.8 nm), however, because the absorption spectrum of I is relatively congested [5]. Nevertheless, because the excited molecules are reasonably "isolated" at the pressures employed and because their measured radiative and non-radiative decay rates vary smoothly and

TABLE 1

λ_{ex} (nm)	τ (ns)	ϕ_f^a	k_r (s^{-1})	k_{nr} (s^{-1})	E_{vib} (cm^{-1})
266.8	45.9	0.25	5.4×10^6	1.6×10^7	0
263.0	43.2	0.23	5.3×10^6	1.8×10^7	540
260.1	43.4	0.22	5.1×10^6	1.8×10^7	970
257.25[b]	36.2	0.19	5.2×10^6	2.2×10^7	1400
256.7	34.8	0.18	5.2×10^6	2.4×10^7	1480
253.9	28.0	0.14	5.0×10^6	3.1×10^7	1900
251.9	25.9	0.11	4.3×10^6	3.4×10^7	2220

[a]Values taken from ref. 5.
[b]Laser excitation.

slowly with excess energy (see later), single exponential fluorescence decay can still occur despite the fact that several overlapping or closely adjacent transitions will be pumped. Single exponential decay was in fact observed except for small deviations at times longer than two lifetimes after excitation, attributable to collisional relaxation.

Combining the lifetime data with the low pressure fluorescence quantum yields previously measured by Comtet [5] and employing the relationships $k_r = \phi_f/\tau_f$ and $k_{nr} = (1 - \phi_f)/\tau_f$, one can calculate the rate constants for the excited singlet radiative and non-radiative decay processes as a function of excitation energy. These data are also presented in Table 1.

The radiative rate constant has a value of 5.4×10^6 s^{-1} for excitation of I into its zero point level. This may be compared with an identical value of 5.4×10^6 s^{-1} for toluene excited into its vibrationless level at low pressures [10], and a value of 5.8×10^6 s^{-1} used by Comtet to obtain approximate values of the rate constants of non-radiative unimolecular and intermolecular quenching processes.

The diminution in fluorescence and product quantum yields with increasing excitation energy is due entirely to a concomitant increase in the rate of a competing non-radiative decay process which does not yield detectable photoproducts. The variation of both k_r and k_{nr} with S_1 vibrational energy exhibited by I is similar to that of other substituted benzenes* [14]. Thus the non-linear increase in k_{nr} with increasing excitation energy is probably due to a "channel III" process, the nature of which has been the subject of prolonged investigation and discussion.

Acknowledgments

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*The value of 36×10^{-16} cm^2 is an upper limit of the measured cross sections for quenching of the S_1 state of toluene. These data are tabulated in ref. 15.

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