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LASER FLASH STUDIES OF THE PHOTOCHEMISTRY OF ANTHRONE

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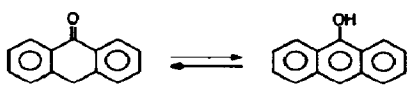
Summary

The tautomeric equilibrium between anthrone and anthranol has been shown to play an important role in the photochemistry of this system. The triplet–triplet spectrum of anthranol shows a maximum at 430 nm, while the triplet state of anthrone resembles typical aromatic ketones with $\lambda_{max} \approx 580$ nm. Anthrone undergoes apparent self-quenching which results from the transfer of triplet energy from excited anthrone to anthranol. Triplet anthrone can be quenched efficiently by typical triplet quenchers such as oxygen, di-*tert*-butylnitroxide and conjugated dienes, *e.g.* for 1,3-octadiene $k_q = 6.8 \times 10^9\ M^{-1}\ s^{-1}$ in benzene at 27 °C. The behaviour and spectral properties of triplet anthranol resemble those of anthracenes.

1. Introduction

While the solution photochemistry of carbonyl compounds has been the subject of numerous studies, anthrone has received only very limited attention. Given the structural resemblance between anthrone and benzophenone and the similarity of their triplet energies [1] (E_T for anthrone is 72 kcal mol^{-1}), very similar photochemical behaviour could be expected. Unfortunately, the photochemistry of anthrone is complicated by the keto–enol equilibrium of the reaction



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Reaction (1) has been recognized for over 70 years [2], but its role in photochemistry has been the subject of only a few studies [3 - 6], even though the thermodynamics and kinetics of the keto–enol interconversion are now well understood [7 - 12]. A few recent studies of the photochemistry of anthrone have been concerned only with the behaviour of the keto form in very short time scales, mostly using picosecond techniques [13 - 15]. In this time domain intersystem crossing is the main process taking place.

In this study we have examined the photochemistry of anthrone in polar and non-polar solvents using nanosecond laser flash photolysis techniques. Our results clearly show that the photochemistry of anthrone is far more complicated than that of other more "typical" carbonyl compounds such as benzophenone and acetophenone. These complications arise not only from the equilibrium of reaction (1) but also from the fact that II is an excellent quencher of the triplet state of I.

2. Experimental section

2.1. Materials

Anthrone (Aldrich) was recrystallized from ethanol and sublimed twice. Benzene (Aldrich, Gold Label) was purified as indicated in earlier reports [16]. Acetonitrile (Fischer, HPLC grade) was refluxed and distilled over CaH_2. Methanol (Aldrich, Gold Label) was used as received. Dienes and $Cu(acac)_2$ were obtained from Aldrich; $Cu(acac)_2$ was recrystallized from methanol. Di-*tert*-butylnitroxide (P and B) was used as received.

2.2. Spectra

UV–visible spectra were recorded using a Cary 219 instrument.

2.3. Laser photolysis

Our instruments use the pulses (337.1 nm, about 8 ns, up to 10 mJ) from a Molectron UV-24 nitrogen laser for excitation. The transient signals are initially captured by a Tektronix R7912 transient digitizer which is fully interfaced with a PDP-11/03L computer that also controls the experiment and provides suitable storage, processing and hard copy facilities. Further details are given elsewhere [17].

All the errors quoted correspond to 95% confidence limits.

3. Results and discussion

3.1. Spectra of the samples

The UV–visible spectra of solutions of anthrone in organic solvents vary with the polarity and in particular the hydrogen bonding ability of the media. This effect is the result of the tautomeric equilibrium of reaction (1)

[7 - 9]. At 400 nm I has virtually no absorption, while for II $\epsilon_{400} \approx 4000$ $M^{-1} cm^{-1}$ [7, 8]. It is thus possible to estimate the concentration of anthranol (II) from the UV–visible spectra of anthrone solutions.

We find that I is the predominant form in benzene and carbon tetrachloride. The concentration of II is relatively minor but unfortunately is not entirely reproducible because the equilibrium is established quite slowly [7 - 9]. The reaction (leading to the equilibrium) can be catalysed by bases such as triethylamine [7, 8], but these cannot be used in photochemical experiments because they are known to be excellent triplet quenchers [18] and would probably add more complications to an already complex problem. In acetonitrile, even when carefully dried, we find that 2% - 5% of II is usually present; this concentration is enough for II to absorb around 50% of the light at 337.1 nm (the nitrogen laser wavelength) where the ratio of the extinction coefficients is around 40 [7]. In methanol and other alcohols the enol form II is present in sufficient abundance (10% - 20% according to the reported equilibrium constants) to be regarded as the species responsible for over 80% of the light absorption at 337.1 nm.

In a few experiments we dissolved anthrone in methanol, and then evaporated the solvent under vacuum and redissolved the residue in benzene. The changes in UV absorption at each stage confirmed the reversibility of the equilibrium of eqn. (1). The concentrations of these solutions in benzene initially contained slightly more II than when prepared from sublimed anthrone, as would be expected when the equilibrium is approached from the enol form.

3.2. Transient spectra

Laser excitation of a deaerated solution of anthrone in methanol leads to the transient spectrum of Fig. 1. The peak at 430 nm is produced in all systems containing (or generating (see below)) significant concentrations of enol and is assigned to triplet–triplet (T–T) absorptions due to the triplet state (denoted II* hereafter) of II. The lifetimes of II* are usually in the 4 - 7 μs range and incorporate some second-order processes, probably including T–T annihilation. After about 10 μs most of the triplet decay is usually complete and the transient spectrum reveals the presence of substantially

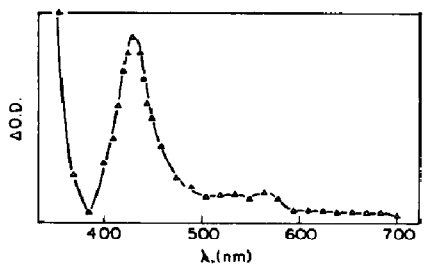
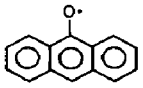


Fig. 1. Transient spectrum obtained on laser excitation of a 0.010 M solution of anthrone in methanol at 27 °C.

weaker signals in the 380 - 500 nm region; these have not been characterized, but may be partially due to III:



III

In non-polar solvents such as benzene the spectrum observable at times longer than 500 ns following laser excitation is virtually identical with that observed in methanol. At shorter times it becomes evident that a different transient is present in the system; its signals are generally weaker than those due to II*, but in the 395 and 630 nm regions they are stronger and thus can be monitored directly. Figure 2 shows spectra obtained at two different

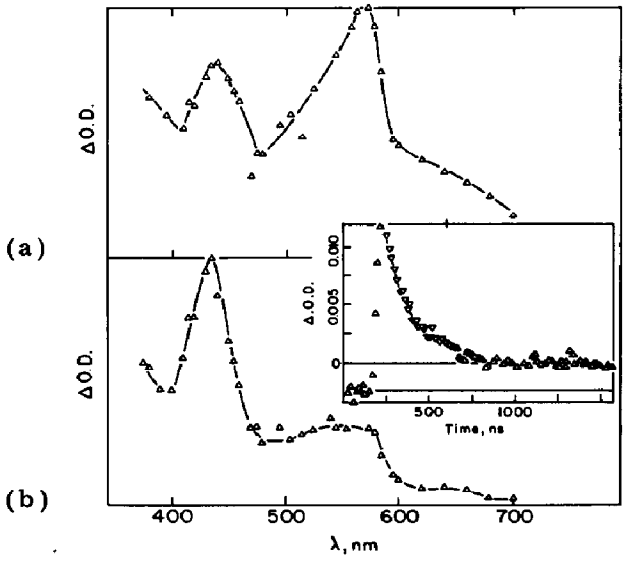


Fig. 2. Transient spectrum obtained following excitation of a 0.005 M solution of anthrone in dry benzene: (a) immediately after excitation; (b) average of data taken from 200 to 300 ns after excitation. The inset shows the decay trace monitored at 630 nm.

times following excitation and illustrates the evolution of the signal; the inset in Fig. 2 shows a decay trace obtained at 630 nm. The spectrum at short times must be mostly due to the ketone triplet I*.

The transient spectrum observed in acetonitrile is virtually the same as that observed in methanol, although a delayed build-up ($\tau \approx 200$ ns) can be detected at 430 nm where II* absorbs. A similar build-up was detected in carbon tetrachloride.

3.3. The anthrone triplet (I) in benzene*

We have observed that the lifetimes of I* monitored at either 395 or 630 nm are concentration dependent, *i.e.* self-quenching is an important

TABLE 1

Rates of quenching of anthrone triplets (keto form) in benzene at 27 °C

Quencher	k_q (M^{-1} s^{-1})
Oxygen	2×10^9
t-$Bu_2NO^{\bullet}$	5.2×10^9
$Cu(acac)_2$	5.0×10^9
1,3-octadiene	6.8×10^9
Anthrone[a]	1.63×10^8

[a]See text.

mode of decay for the keto triplet. From a plot of the pseudo-first-order rate of decay as a function of total anthrone concentration we obtain a self-quenching rate constant k_{SQ} of $(1.63 \pm 0.10) \times 10^8$ M^{-1} s^{-1}. Since we also observe a delayed build-up of II* at 430 nm that occurs concurrently with the decay of I*, we believe that "self-quenching" is largely the transfer of triplet energy between I* and II

$$\mathrm{I}^* + \mathrm{II} \xrightarrow{k_2} \mathrm{I} + \mathrm{II}^* \tag{2}$$

although some excited state isomerization

$$\mathrm{I}^* + \mathrm{I} \xrightarrow{k_3} \mathrm{II}^* + \mathrm{II}\ (\text{or I}) \tag{3}$$

is possible [3].

Naturally II is expected to have a very low triplet energy, presumably comparable with that of anthracene ($E_T \approx 42$ kcal mol^{-1}), and therefore reaction (2) will probably be almost diffusion controlled. Thus, k_{SQ} would reflect $k_2 + k_3$ as well as the abundance of II; freshly prepared solutions in benzene contain relatively low concentrations of II owing to the fact that the equilibrium is established quite slowly under these conditions. We find that I* can be quenched by typical triplet quenchers such as dienes, oxygen and di-*tert*-butylnitroxide. Table 1 summarizes the rate constants.

We note that the self-quenching plot leads to an intercept corresponding to $\tau_T \approx 790$ ns in an infinitely dilute solution. Short lifetimes of this magnitude are not uncommon for ketone triplets in aromatic solvents [19] and are presumably the result of quenching by the aromatic ring, which may involve an exciplex mechanism [20], addition to the aromatic ring [21] or both.

3.4. Quenching of the generation of triplet enol

In those systems where the formation of II* results largely from the decay of I* (regardless of the decay mechanism) it is possible to measure the Stern–Volmer slope $k_q\tau_T$ corresponding to I* from a study of the transient yield of II* as a function of quencher concentration. One system where this

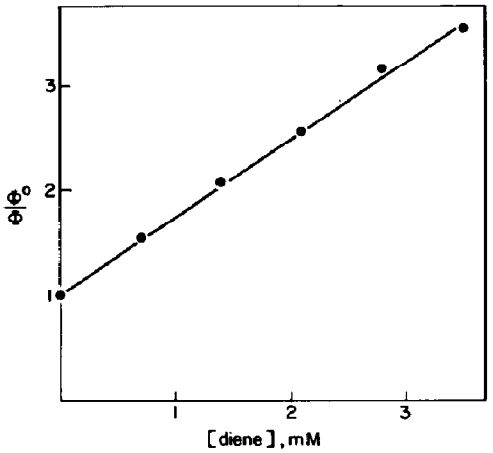


Fig. 3. Stern–Volmer plot for the quenching of I* (as monitored from the absorption due to II*) by 2,5-dimethyl-2,4-hexadiene in acetonitrile. Conditions: anthrone, 0.01 M; 27 °C; monitored at 430 nm.

condition is fulfilled is in the case of fresh solutions in acetonitrile. Figure 3 shows a Stern–Volmer plot given by

$$\Phi^0/\Phi = 1 + k_q\tau_T[\text{diene}] \quad (4)$$

for the formation of II* as a function of the concentration of 2,5-dimethyl-2,4-hexadiene which is a typical triplet quencher. The ratio Φ^0/Φ corresponds to II*, as measured by its transient absorption monitored at 430 nm, and can be approximated by the ratio of transient optical densities at that wavelength. The value of the Stern–Volmer slope $k_q\tau_T$ in acetonitrile was $731 \pm 34\ M^{-1}$, from which we estimate $\tau_T \approx 73$ ns for a 0.01 M anthrone concentration, in good agreement with the values obtained in other solvents (assuming that self-quenching also takes place in acetonitrile).

A similar study in benzene (27 °C; 0.01 M anthrone) led to $k_q\tau_T$ ($565 \pm 70\ M^{-1}$), which seems consistent with the short lifetimes observed in this solvent.

*3.5. Attempts to quench the triplet enol II**

II* was not quenchable by conjugated dienes, as would be expected if its triplet energy were similar to or smaller than that for anthracene. Attempts to quench II* (in methanol) with $Cu(acac)_2$ [22], oxygen or di-*tert*-butylnitroxide indicated very inefficient quenching, if any at all. This observation is in agreement with several reports that have indicated that quenching of triplet states by paramagnetic substrates is dependent on the triplet energy of the sensitizer and shows a minimum efficiency for triplet energies around that for anthracene [23 - 26]. Consistent with this, we observe that the sensitized photodecomposition of $Cu(acac)_2$ [22], which occurs efficiently at shorter wavelengths ($\lambda < 350$ nm), does not occur at $\lambda > 400$ nm where only II is subject to photoexcitation.

3.6. Sensitization by 2-acetonaphthone

According to reaction (2), anthrone behaves as a triplet sensitizer for its own enol, anthranol. If this mechanism is correct, we would expect a wide variety of molecules to be able to play a similar role as sensitizers. Testing this simple idea is rather more difficult than is initially anticipated. This is due to the fact that, whatever the choice of sensitizer, we are always dealing with a system of three chromophores (I, II and the sensitizer S) which absorb at 337.1 nm and where multiple energy transfer processes are possible (*i.e.* I* → II, S* → II, I* → S). Eventually we found that 2-acetonaphthone, with a triplet energy of 56.5 kcal mol^{-1} [1], was a viable choice. The spectrum of triplet 2-acetonaphthone shows a maximum very close to the 430 nm band for II*; however, at around 480 nm the extinction coefficient for the triplet sensitizer is, while small, considerably larger than that for II* and can be monitored with reasonable accuracy. These experiments were carried out in methanol to minimize the role of I as a light absorber and sensitizer. We found that triplet sensitization takes place with $k_q = (1.8 \pm 0.7) \times 10^9\ M^{-1}\ s^{-1}$ at 27 °C. As in earlier examples, the value of k_q is a composite that incorporates the fraction of anthrone present as II under a given set of experimental conditions. The true rate constant for pure anthranol would naturally be higher.

4. Conclusion

Our results clearly show that, while the equilibrium constant for reaction (1) [7, 8] will favour the keto form in non-hydroxylic solvents, the enol form II plays a most important role in the photochemistry of anthrone. This is due to the higher extinction coefficient for II at the excitation wavelength as well as to the fact that quenching of I* by II leads to II* quite efficiently. In addition, the extinction coefficient for T–T absorptions by II* seems greatly to exceed that for I*, thus making the former the more easily detectable transient.

An examination of Fig. 2 indicates that the ketone triplet spectrum is very similar to that for the benzophenone triplet that presents a maximum at 525 nm [27]. It seems reasonable to expect this triplet to show excited state chemistry similar to that of benzophenone and other carbonyl compounds [28], and in fact some evidence for hydrogen abstraction has been reported [5]. The triplet state of II seems to show anthracene-like behaviour, and even the position of its maximum (430 nm) is quite close to that of the anthracene triplet (425 nm) [29].

Anthrone, that *a priori* would have been expected to be a useful triplet sensitizer, is with hindsight a rather poor choice. In fact, the involvement of two triplets with very different energies, the transfer of energy between the two species and the fact that even the thermal equilibrium is approached rather slowly are overwhelming reasons for *not* choosing anthrone as a sensitizer.

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