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Photocyclisation of phenylbenzoquinone: A time resolved photoacoustic calorimetric and flash photolytic study

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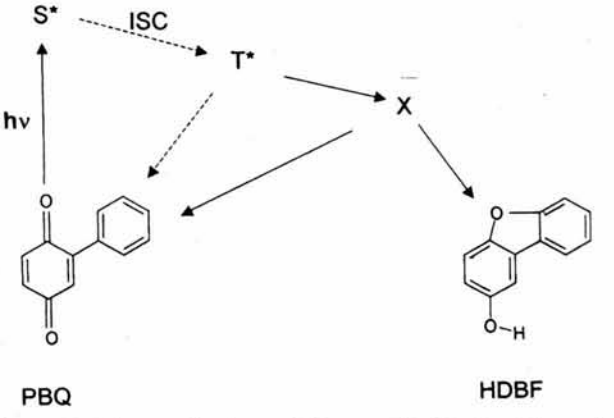
Energetics of formation of the intermediate during the photocyclisation of phenylbenzoquinone (PBQ) to 2-hydroxydibenzofuran (HDBF) in methanol solvent has been investigated by employing the time-resolved photoacoustic calorimetric (TRPAC) technique. The study, in conjugation with the nanosecond/microsecond flash photolytic observations, confirms the formation of a long lived intermediate during the photocyclisation reaction. TRPAC result and semi-empirical (AM1 and PM3) calculations suggest that the intermediate is a biradical.

Phenylbenzoquinones undergo efficient photocyclisation reaction to give dibenzofuran derivatives. Since the first report of such a photoreaction by Hageman and Huysmans[1], several groups have been trying to establish the complete mechanism of the multistep cyclisation process[2-8]. Kuznets *et al.* studied the photocyclisation of 2,6-diphenylbenzoquinone (DPBQ) in ethanol by microsecond flash photolysis and CIDNP, and concluded that the reaction goes through the triplet state of DPBQ involving abstraction of hydrogen or electron from the solvent[2,3]. Sarakha *et al.* proposed that the mechanism involves an intramolecular electron transfer which leads to the formation of a zwitterionic species. The zwitterionic intermediate then undergoes a cyclisation followed by a solvent assisted proton transfer[4]. Later on, Bonneau *et al.* proposed that the photoreaction proceeds through the triplet state of the benzoquinones with the subsequent formation of an intermediate of a biradical nature[5,6]. Scheme 1 presents the suggested mechanism of photocyclisation of PBQ to HDBF[6]. They have further commented that the mechanistic study of the photocyclisation of benzoquinones requires combination of time-resolved spectroscopy and measurements of the quantum yields of reaction under continuous irradiation[7].

Thus, although it is known that the photocyclisation reaction goes through the triplet state of the benzoquinones, the complete mechanism is yet to be confirmed. In spite of the fact that Bonneau *et al.* Proposed the intermediate to be of biradical nature[5], it is yet to be confirmed experimentally. Furthermore, the energetics of the formation of the intermediate has never been studied.



Scheme 1—Photocyclisation of PBQ to HDBF. S*, T* are the lowest excited singlet and triplet states and X is the intermediate.

Since time-resolved photoacoustic calorimetry (TRPAC) detects the time-dependent heat released through radiationless deactivation processes from different metastable species, this technique allows us to acquire information regarding the energetics of a multi-step photoreaction. Recently, we have exploited this technique to study the multi-step photocyclisation reaction of aryl amines[9,10]. Combination of this technique and semi-empirical calculations allowed us to establish the complex reaction mechanism and assign the nature of the intermediate.

In the present work, we have investigated the photocyclisation reaction of phenylbenzoquinone (PBQ) in methanol solvent through TRPAC and nanosecond/microsecond flash photolysis to get the energetics of the formation of the intermediate. TRPAC result combined with semi-empirical (AM1 and PM3) calculations suggests that the intermediate is of biradical nature.

Materials and Methods

PBQ (Aldrich) was purified through vacuum sublimation followed by recrystallisation from ethanol. Spectroscopic grade methanol (Merck) was used as solvent without further purification. 2-Hydroxybenzophenone (HBP, Aldrich) was used as a reference for the TRPAC measurements. Although reported elsewhere[9], we would like to reproduce the main features of the instrumentation used for TRPAC and flash photolytic studies. All the measurements were performed at ambient temperature (22°C).

The flash photolysis set-up comprises a Spectra Physics Quanta-Ray GCR-130 Nd-YAG laser, an Applied Photophysics LKS 60 laser flash photolysis spectrometer and a Hewlett-Packard Infinium Oscilloscope (500 MHz, 1 Gsa/s). The samples were excited with the third harmonic (355 nm, 8 ns FWHM) of the laser. The monitoring light was produced by a 150 W pulsed Xe lamp. The detection of the transient species in the range of 280 - 650 nm was made with a Hamamatsu photomultiplier (model 1P-28). The sample solutions were made with absorbance around 0.2 at the excitation wavelength (355 nm) and were degassed for 20 min with argon prior to their use in the flash experiments. The concentrations of PBQ in the solutions were $\leq 1\times10^{-4}$ *M* to avoid the formation of the dimer[7,8].

The photoacoustic calorimetry apparatus follows the front-face irradiation design described elsewhere[11]. The solutions were pumped through a 0.11 mm thick cell at a flow rate of 1 mL min^{-1} with an SSI chromatography pump (model 300) and irradiated with an unfocussed (area of the laser beam at the cell surface being ≈ 0.5 cm^2) N_2 laser (PL 2300 from PTI) working at a frequency of 2 Hz. The laser energy was a little less than 1 millijoule per pulse. The acoustic waves generated by the non radiative processes following light absorption in the cell were detected with a high frequency transducer (Panametrics, 2.25 MHz), preamplified with a ultrasonic preamplifier (Panametrics, model 5676), captured by the transient recorder (Tektronix DSA 601) and transferred to a PC for data analysis. For each of the sample, reference and pure solvent average of 100 acoustic waves were collected. Four sets of averaged waves for each of the sample, reference and solvent were used for data analysis at a given laser intensity, and four laser intensities were employed in each experiment. The different laser intensities used in the experiment were obtained by interposing filters with transmissions in the range of 30 to 100%. As the photoreaction involves triplet state of PBQ, the experiments were performed under an atmosphere of constant purging of solvent-saturated N_2. Before going through the TRPAC we confirmed that the PAC signal was linear with the concentration of the sample at least up to a concentration of the solution with absorbance = 0.3 (correlation coefficient $\geq$ 0.99). However, for the TRPAC experiments we used sample solutions with absorbance $\cong$ 0.2. The absorbances of the reference solutions were the same as that of the sample solutions within the limit of the experimental error.

Previous studies indicate that semi-empirical methods provide acceptable approximations to give results, quite close to the experimental findings[9,10,12-18]. In the present calculations, we have used the commercial package, Hyperchem 5.01 (Hypercube Inc., Canada). The energies of various electronic states of different species (PBQ, HDBF and different possible intermediates, X) have been calculated for the optimized structures using AM1 and PM3 methods.

Results and Discussion

Flash photolysis

The transient spectrum of PBQ in methanol solvent was presented by Bonneau *et al.*[5]. The spectrum has a reasonably intense band at around 540 nm that is assigned to the T-T absorption from the lowest triplet state of PBQ. Our flash photolysis experiment with a degassed solution of PBQ in methanol gives a single exponential decay of the 540 nm absorption band, with a decay time of 650 ± 50 ns. The concomitant growth of the 290 nm band, with the same rise time as that of the decay time of the 540 nm absorption reveals that the species absorbing at 290 nm originates directly from the triplet state of PBQ (Fig.1). The growth time of the intermediate (at 290 nm) corresponds the decay time of PBQ triplet (at 540 nm). In carefully degassed methanol solution we determined both these times to be 650 ± 50 ns. The value is however more than that reported by Bonneau *et al.*[5],

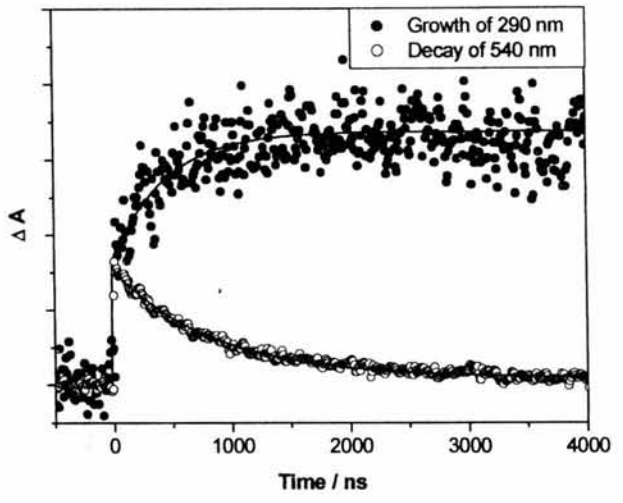


Fig. 1—Kinetic behaviour of the transient absorption from a calc. 1×10^{-4} *M* PBQ solution in degassed methanol at 540 nm (solid circles) and 290 nm (open circles). The traces are analysed with single exponential fits with the same kinetics. Excitation wavelength: 355 nm.

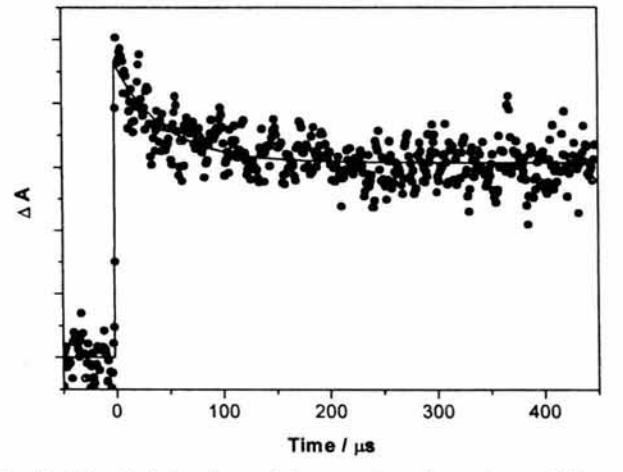


Fig. 2—Kinetic behaviour of the transient absorption at 290 nm from a calc. 1×10^{-4} *M* PBQ solution in degassed methanol. The formation of the permanent product HDBF is responsible for the raising of the baseline. The solid line gives a single exponential fit. Excitation wavelength: 355 nm.

where they reported this time to be around 400 ns. Our TRPAC experiment provides an independent determination of the PBQ triplet lifetime (*vide supra*). The lifetime obtained for the decay of the triplet was 630 ± 50 ns, and confirms the flash photolysis result. That the final photoproduct (HDBF) also absorbs in the same region (Fig.1 of ref. 5) is evidenced from a simultaneous rise in the baseline while monitoring at 290 nm decay. This complicates the assignment of the 290 nm absorption band. A clear decay of the 290 nm absorption band with a very long decay time (Fig. 2), however, confirms that it is not only the ultimate photoproduct (HDBF) that absorbs at 290 nm, but there is some transient intermediate as well. Had the absorption been only due to the permanent product (HDBF), it would not show a decay within the experimental time window. Existence of the intermediate, thus, rules out the possibility that HDBF is directly formed from PBQ triplet state. Although it is obvious from Fig. 2 that the intermediate, absorbing at 290 nm, is long lived (~ 40 μs), the exact determination of the decay time of the species is difficult because of the concomitant formation of the permanent photoproduct (HDBF) absorbing at the same region. For the same complicacy we could not even take the transient spectra of the intermediate which is supposed to be very informative. Anyway, the flash experiments confirm the formation of an intermediate directly from PBQ triplet with a time constant of 650 ± 50 ns. It further establishes that in addition to the absorption of the final photoproduct, there is also a T-T absorption of an intermediate at around 290 nm. The intermediate has a long decay time (around 40 microseconds). Thus, the photoconversion reaction seems to complete in tens of microseconds.

Time-resolved photoacoustic calorimetry (TRPAC)

Time-resolved photoacoustic calorimetry is based on the measurement of the acoustic wave generated by the heat released in the non-radiative processes following electronic excitation. The experimental wave (E-wave) of the sample is compared with that of the pressure transducer (T-wave). The T-wave is obtained with the calorimetric reference, HBP in the same solvent absorbing the same fraction of light as the sample and releasing it as thermal energy in a time much shorter than the transducer oscillation frequency. The phase and amplitude differences between the T- and E-wave allow for the simultaneous determination of the thermal energy (E) released by the transients and their lifetimes (τ). Typical background-corrected reference and sample signals are shown in Fig. 3.

As seen from the flash photolysis experiment, decay time of the intermediate is too long for the transducer to be able to collect the dissipated energy within this time window and the intermediate was considered as the dump for TRPAC experiments. So we restrict ourselves to the formation of the intermediate (X). The waves of the N_2 saturated samples are interpreted with two sequential exponents, as proposed by Bon-

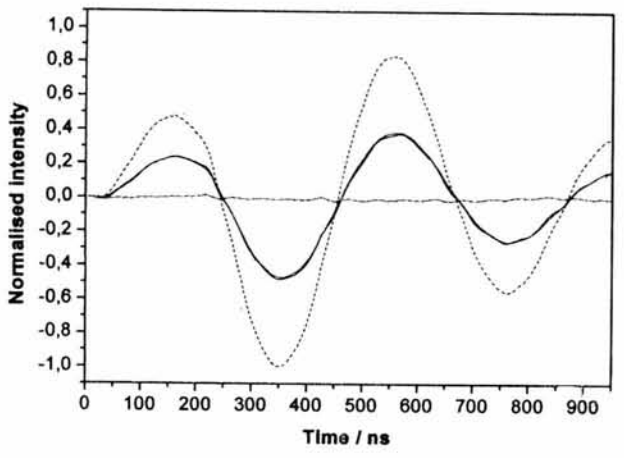
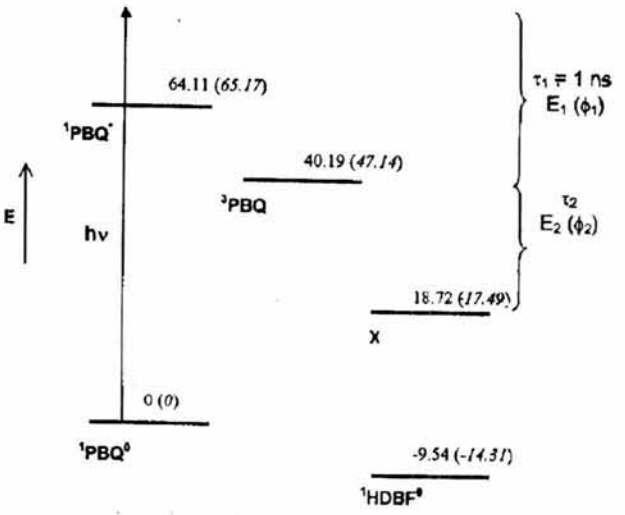


Fig. 3—Typical photoacoustic waves for a calc. 1×10^{-4} *M* PBQ solution in methanol (background corrected and normalised); reference (T-wave, dash), sample (E-wave, solid), calculated wave (C-wave, dot) and the residuals (dash-dot). Residual= (C-wave)-(E-wave). The calculated wave was obtained with two sequential decays with the first lifetime fixed at 1 ns (see text for details). Reference: HBP; experimental conditions: irradiation at 337 nm of N_2 saturated solutions; absorbance of 0.2 for sample and reference; solutions flow rate of 1 ml min^{-1}.



Scheme 2—Schematic energy diagram of the PBQ photocyclisation reaction. ^{1}PBQ°, ^{1}PBQ*, ^{3}PBQ* represent the ground, lowest excited singlet and triplet states of PBQ. ^{1}HDBF° is the final photoproduct in its ground state. X is the intermediate. The energy values (in kcal mol^{-1}) are calculated using AM1 (solid) and PM3 (italic in brackets). The given energies for X have been calculated considering X to be a triplet biradical. E_1 and E_2 are the amount of energies involved in *steps I* and *II* with time windows τ_1 (=1 ns) and τ_2 respectively. ϕ_1 and ϕ_2 are the amount of heat energy released in the two successive steps as measured from the TRPAC experiment.

neau *et al.*[5], the first one for the formation of the triplet state of PBQ (*step I*), and the second one corresponding to the formation of the intermediate (X) (*step II*) (Scheme 2).

Each decay step is described by two parameters: the lifetime of the transient (τ) and the fraction of thermal energy released (ϕ) within that time window. The convolution of the reference waves with parameters of the kinetic model for the decay of the transient species gives the calculated E-wave. The appropriateness of the kinetic model and its parameters to describe the observed E-wave can be evaluated by the difference (termed as residual) between the amplitudes and phases of the observed (E-) and calculated (C-) waves at each decay time (Fig. 3). The formation of ^{3}PBQ* is faster than the time resolution of our experimental set-up, and we arbitrarily set the lifetime of the first exponential decay to τ_1 = 1 ns. Smaller values of τ_1 do not change the other parameters in the deconvolution. We only fix τ_1 (= 1 ns) and let τ_2, ϕ_1 and ϕ_2 to be adjusted by the Marquardt's algorithm employed in the deconvolution. Good fit is obtained only to the E-wave with $\tau_2 = 630 \pm 50$ ns. This is an independent verification of the time constant for the formation of the intermediate, X, from PBQ triplet. There is a very good agreement between the value of τ_2 obtained from the TRPAC experiments and either of the decay time of the PBQ triplet or the growth time of the intermediate (X) obtained from the flash experiments.

The fractions of laser energy released by the system were measured at four laser intensities. The first fraction was found to vary with laser intensity. This fraction was plotted as a function of laser intensity and obtained linear correlation coefficients greater than 0.96 were obtained. The difference was assigned to transient-transient absorption and was corrected by extrapolating the fraction of energy released to zero laser intensity. From this laser intensity corrected value of the first fraction of the released heat, the energy of the PBQ triplet was determined considering the energy of excitation at 337 nm. The formation of the triplet state was considered from the lowest excited singlet state (S_1) to be quantitative (quantum yield of triplet formation, ϕ_T = 1). From the TRPAC experiment, the triplet energy (E_T) of PBQ in methanol was estimated as 48 ± 2 kcal/mol. The estimated E_T agrees well with the value 48.7 kcal/mol reported in the literature from the phosphorescence study[7]. The energy, E_2, involved during the process of formation of X from PBQ triplet (*step II*) was estimated from the other fraction of the heat released in the other exponent ($E_2 = \phi_2 E_{h\nu}$). This energy was estimated to be

21 ± 2 kcal/mol considering *step II* to be quantitative as suggested by Bonneau *et al.*[5].

The energies of the relevant electronic states of different species involved in the photocyclisation process like, the reagent (PBQ), the intermediate (X) and the final photoproduct (HDBF) were calculated using semi-empirical AM1 and PM3 methods. Using single configuration interactions (considering around 250 configurations) energy difference between the S_0 and S_1 states of PBQ was calculated as 64.11 and 65.17 kcal/mole from AM1 and PM3 respectively (see Scheme 2). This corresponds to 446 and 438 nm respectively for a vertical (0-0) transition from S_0 to S_1 state of the molecular system. These values agree well with the absorption spectra of PBQ presented in ref. 5, although it does not correspond to the other work[7] of the same group where the S_1 state of PBQ has been reported to be 56 kcal/mol above the ground state. Depending on the available instrumentation, the sample was excited at 355 nm for flash photolysis and 337 nm for TRPAC experiments respectively. Both the excitations are higher in energy than the S_0-S_1 gap.

The energies of the lowest triplet state of PBQ which are calculated from AM1 and PM3 methods are 40.19 and 47.14 kcal/mol respectively. The determined experimental PBQ triplet energy, 48 ± 2 kcal/mol in methanol (from the present TRPAC experiment) and 48.7 kcal/mol in non-polar solvent (from phosphorescence measurements[7]), agrees well with the triplet energy obtained from PM3 calculation, although the AM1 calculation gives a lower value.

The energies of the intermediate were calculated with different possible structures. The one that gives the best agreement with the experimental energy of the intermediate (obtained from TRPAC) is a biradical of triplet character. The calculated energy of a triplet biradical intermediate is 18.72 and 17.49 kcal/mol (relative to the ground state of PBQ) from AM1 and PM3 respectively. This gives a calculated energy of 21.47 and 29.65 kcal/mol for the *step II* in the TRPAC experiment respectively from the two methods. As mentioned above, the experimental value for this energy is 21 ± 2 kcal/mol in methanol solvent. The general agreement between the calculated and the experimental values strongly suggests a triplet biradical character of the intermediate.

The calculation further suggests that the total photocyclisation reaction from PBQ to HDBF is exothermic to an extent of 9.54 or 14.31 kcal/mol (from AM1 and PM3 respectively). As discussed above, the very long lifetime of the intermediate (X) does not allow us to estimate the energy involved in the step of formation of the final product from X.

Conclusion

The flash photolytic experiment establishes that the 290 nm absorption comprises a transient intermediate (X) along with the permanent photoproduct. Both flash and TRPAC experiments determine the formation time of X to be around 650 ns in methanol solvent. TRPAC experiment gives a measure of the PBQ triplet energy as 48 ± 2 kcal/mol in methanol. The same experiment further estimates the energy involved in the process of formation of the intermediate (X) from PBQ triplet to be 21 ± 2 kcal/mol in the same solvent. A comparison of the experimental energy values with the calculated ones strongly suggests that the intermediate has a triplet biradical character.

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