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Photoreduction of 2,6-dichloroquinone in aqueous solution Use of a diode array spectrophotometer concurrently to drive and detect a photochemical reaction

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Abstract

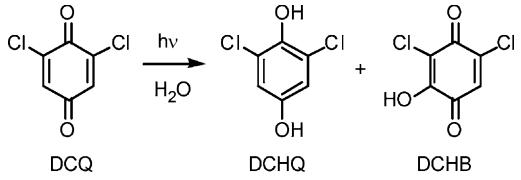
The aqueous photoreaction of 2,6-dichloro-1,4-benzoquinone produces 2,6-dichlorohydroquinone, 2,6-dichloro-3-hydroxy-1,4-benzoquinone and dioxygen. This reaction was used to demonstrate that a commercial diode-array spectrophotometer is a useful tool for the study of photochemical reactions. The white light going through the sample cell concurrently drives and detects photoreactions. It is shown how quantum yields can be determined. A method for interpreting the full time course of the photoreaction is also presented.

Keywords: Diode-array spectrophotometer; Photoreactions; Quinones

1. Introduction

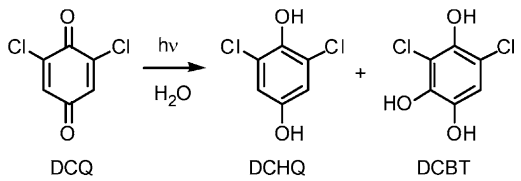
Quinones are known to undergo a large variety of photoinduced reactions which are dependent on the solvent [1–3]. Simple quinone derivatives show $n \rightarrow \pi^*$ transitions usually in the near UV [4,5]; intersystem crossing to the triplet state is very efficient, and the lifetime of the triplet state is long enough for successful trapping [1,6,7].

In our ongoing experiments designed to study the mechanism of the destructive aqueous oxidation of 2,4,6-trichlorophenol, a compound regarded as priority pollutant because of its toxicity and persistency, we noted that the reaction rates were influenced by light, even the fluorescent room lights of the laboratory [8]. The aqueous photoreaction of 2,6-dichloro-1,4-benzoquinone (DCQ), a known intermediate during the oxidation process, was identified as a possible source of light sensitivity in the system [8]. Earlier data available on aqueous photochemical reactions of 1,4-benzoquinone and its substituted derivatives [1,6,9–23] showed that the product should be a mixture of 2,6-dichlorohydroquinone (DCHQ) and 2,6-dichloro-3-hydroxy-1,4-benzoquinone (DCHB) as shown in Eq. (1).



DCQ DCHQ DCHB (1)

In early (but not in more recent) reports [16,18–20], it was suggested that the actual photochemical process produces a mixture of substituted hydroquinone and 1,2,4-benzenetriol as shown in Eq. (2), and hydroxyquinones are formed only in secondary chemical processes. This implies the formation 3,5-dichloro-1,2,4-benzentriol (DCBT) as an intermediate in the DCQ-system.



DCQ DCHQ DCBT (2)

The formation of DCBT is formally an addition of water to the quinone; the product DCHQ derives from reduction, whereas DCHB is from oxidation. Reaction (1) cannot be water-assisted disproportionation because the two products are not formed in equimolar amounts. The triplet excited

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states of 1,4-benzoquinones are known to be strong oxidizing agents [6,13], thus the direct formation of the oxidized product DCHB in the photochemical process seems to be unlikely. The only available reagent is water, and in earlier work [6,11,12,16] it was postulated that water is oxidized, but the oxidation product was not identified. In the introduction of two closely connected papers it is stated that H_2O_2 is produced, but neither references nor experimental data are offered to support this statement [11,12].

In this paper, we report our results on the aqueous photoreaction of 2,6-dichloroquinone. Using this reaction as an example, we intend to prove that a commercial diode-array spectrophotometer can be used as a tool to study photochemical reactions. In a diode array spectrophotometer intense polychromatic light goes through the sample, which can be used to drive the photochemical reaction. The same beam can also be used to detect the process as well. Quantitative interpretation of the data obtained with the polychromatic light beam is possible considering the emission characteristics of the light source and the absorption properties of the photoactive substance. As photochemical reactions necessarily involve spectral changes, the method presented here is general and could in principle be used for every photochemical process.

2. Experimental section

2.1. Materials

DCHQ was prepared by reducing DCQ with diethylhydroxylamine [24,25]. ^{1}H NMR in $CDCl_3$: 6.82 (s, 2H), 5.45 (s, broad, 1H); in D_2O: 6.86 ppm (s); ^{13}C NMR in CD_3CN: 151.2, 143.0, 122.8, 116.4 ppm. The peculiar feature of this compound is that only one of the two non-equivalent OH hydrogen atoms is detectable in the ^{1}H NMR spectrum in $CDCl_3$. This signal disappears after the addition of a drop of D_2O. The EI mass spectrum of the prepared solid was in very good agreement with a published spectrum [26]. 2,2′,6,6′-Tetrachlorodiphenoquinone was prepared by dry microwave oxidation of 2,6-dichlorophenol by $FeCl_3{\cdot}6H_20$ [27]. ^{1}H NMR,($CDCl_3$): 7.41 (s); (D_2O) 7.40 (s).

A stock solution of DCBT was prepared by illuminating a 2 mM aqueous solution of DCQ for about 2 h and then reducing the DCHB with aqueous $NaBH_4$. The reducing agent had to be used in deficiency, because using it in excess resulted in further unidentified reactions.

2,4,6-Trichlorophenol-3-5-d_2 was synthesized by a modification of a literature method reported for the preparation of undeuterated 2,4,6-trichlorophenol [28]. Five hundred sixty milligram of phenol-d_6 and 1.28 g $MgCl_2{\cdot}6H_2O$ were dissolved in 8.5 ml of concentrated hydrochloric acid. Then 2.0 ml of 30% H_2O_2 was added dropwise to the ice cooled mixture, which was kept at 50 °C for 4 h. Light yellow crystals formed (1.07 g, 96%), which were filtered and purified by vacuum sublimation. NMR ^{1}H ($CDCl_3$): 5.8 ppm (s, broad); ^{2}H (H_2O); 7.00 ppm; ^{13}C ($CDCl_3$): 147.1, 128.0 (t, $J = 27$ Hz), 125.4, 121.7 ppm; m.p. 66–67 °C.

DCQ-d_2 was prepared by oxidizing 2,4,6-trichlorophenol-d_2 with CrO_3 in glacial acetic acid using a procedure published earlier for the synthesis of undeuterated product [29]. The raw product was purified by vacuum sublimation. NMR ^{2}H ($CHCl_3$): 6.64 ppm; ^{13}C ($CDCl_3$) 182.6, 172.9, 143.4, 133.6 (t, $J = 27$ Hz); mp. 117–118 °C.

Other reagents, including 1,4-benzoquinone, DCQ, and 1,2,4-benzentriol were purchased and used without further purification. Ion exchanged and ultrafiltered water from a Millipore MILLI-Q purification system was used to prepare solutions.

2.2. Instruments and software

NMR spectra were calibrated using the residual signal of the deuterated solvent. ^{2}H NMR spectra were recorded in non-deuterated solvents and referenced for the signal of CD_3CN ($\delta = 1.55$ ppm) [30]. GC/MS experiments were performed on a Finnigan Magnum ion trap mass spectrometer equipped with a 30 m DB-5 column using He carrier gas. Electron impact and electrospray ionization mass spectra were recorded on a Finnigan TSQ700 triple quadrupole mass spectrometer fitted with a Finnigan AI/CI ion source or Finnigan ESI interface, respectively.

A combination chloride ion selective and pH electrode was used with a precision pH-meter. The electrodes were calibrated daily using standard NaCl solutions and standard buffers. An oxygen monitor was used to measure the concentration of dissolved oxygen.

A Shimadzu MultiSpec-1500 single-beam diode-array spectrophotometer equipped with a temperature controller unit was used to study the photoreaction. The halogen and deuterium lamps can be independently switched on and off in this instrument, and their focused polychromatic light beam is directly led to the sample. In addition to the usual absorbance and transmission measurements, it is also possible to measure the energy of light with this instrument. The instrument has 512 elements in the diode array in a wavelength range of 190–800 nm, affording an independent experimental reading every 1.2 nm. The operating software can collect data with optional wavelength steps of 2, 1, 0.5, 0.2, 0.1 nm using an appropriate interpolating algorithm. As the independent readings are 1.2 nm apart, using a lower wavelength step does not result in more measured data, and the 2 nm wavelength step was used throughout this work. An attenuating filter lies in the light beam between the sample cell and the detector in the wavelength range of 634–684 nm, to prevent the saturation of the detector at the strong 656 nm resonant line of the deuterium lamp. This filter could in principle cause complications because it is after the sample but before the detector. However, in our photoreaction light is not absorbed above 500 nm and the presence of the filter was not a problem. A standard 1 cm quartz cell was used in all experiments. The solution in the

cell was stirred by a 12 mm × 12 mm × 7 mm stirrer that fits beneath the cell. Ferrioxalate actinometry was performed following published protocols [31–36].

Some measurements were also carried out where the photoreaction was followed off-line and driven by a commercially available 500 W halogen lamp. The spectral properties of this lamp were recorded by directing its light beam to the detector of a diode-array spectrophotometer used in the energy-sensitive mode. These experiments were done using Pyrex glassware.

Although absorbance is unitless, the notation absorbance unit (AU) will be used whenever it is important to emphasize the origin of the data. The pK_a values were determined by a combined pH-metric and UV-Vis spectrophotometric technique. The software Scientist was used to carry out least-squares fitting [37]. Differential equations were solved numerically on a Microsoft Excel worksheet with Euler's method.

3. Results and discussion

3.1. General chemical observations

When an aqueous solution of DCQ is subjected to the intense light of a halogen lamp, substantial changes can be detected by UV-Vis spectrophotometry (Fig. 1). A solution kept in the dark does not change for hours, but fluorescent room light also drives the photochemical reaction.

In earlier reports, it was clear that water is oxidized during the reaction [6,11,12], but the oxidation product was not identified. Two possible oxidation products are H_2O_2 and O_2, and we carried out experiments to decide which of these is formed. The presence of H_2O_2 was tested by adding KI in a somewhat acidic medium to observe the strong absorption of I_3^- formed. This method could be used only when DCQ was absent because it also oxidizes iodide ion. Molecular oxygen does not react with iodide ions under these conditions. A test carried out with a fully photolyzed solution was negative showing that H_2O_2 and DCQ were not present in the final solution. Experiments with an O_2-measuring system showed that the concentration of dissolved oxygen started to increase as soon as the illumination began (Fig. 2), and after about 15 min it was not possible to continue the measurement because bubbles at the surface of the electrode corrupted the results. It is thus concluded that dioxygen is formed in the process.

Further experiments with a pH electrode showed that an unbuffered and originally neutral sample of DCQ turns acidic during the photoreaction. The pH reached a value about three in 2 h. Measurements with a chloride ion selective electrode showed that Cl^- was not a product or intermediate of the reaction.

To determine the final organic product distribution, a 2 mM solution of DCQ was illuminated for 5 h and then water was carefully evaporated at ca. 10 °C under high

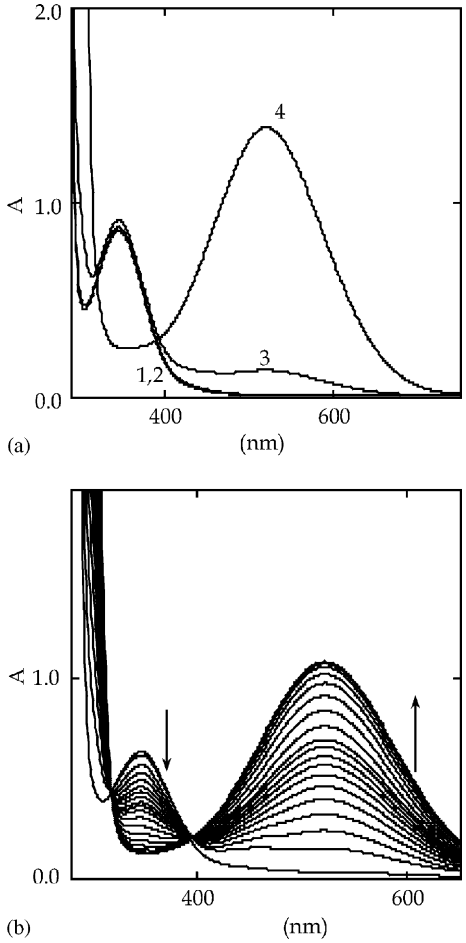


Fig. 1. UV-Vis spectral changes in the aqueous photoreaction of 2,6-dichloro-1,4-benzoquinone. (a) **1**: freshly prepared solution, **2**: after 70 min in the dark, **3**: after 65 min in room light; **4**: after 61 min of illumination. (b) Spectral changes in an illuminated sample as a function of time; individual spectra at 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 19, 24, 30, 39, 51, 66, 73 min. [DCQ] = 2.2 mM; T = 25.0 °C; path length: 1 cm.

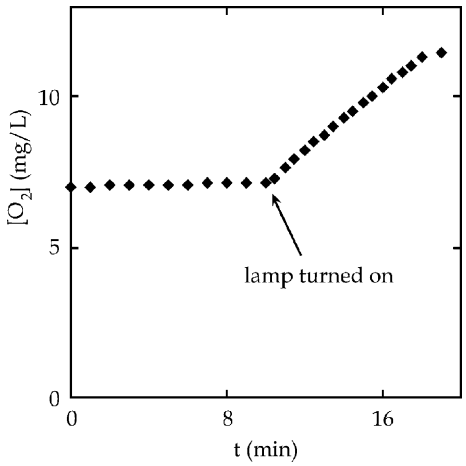


Fig. 2. Dissolved oxygen concentration as a function of time in the dark and under illumination in an aqueous solution of 2,6-dichloro-1,4-benzoquinone. [DCQ] = 2.0 mM; T = 25.0 °C.

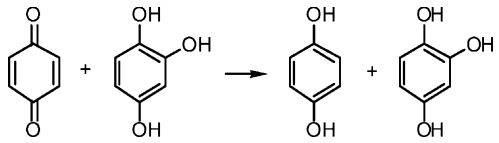
vacuum. The remaining solid was analyzed by various methods. In the NMR, DCHQ was the major product and a large number of small peaks were also detected. A GC–MS run (solvent: CH_2Cl_2) gave evidence for the presence of more than 30 compounds at low concentration levels with molecular weights about or higher than 300. When the photoreaction was carried out in D_2O and analyzed with NMR directly (without isolating any solid), the only detectable products were DCHQ and DCHB and their concentration ratio was constant throughout the course of the reaction ([DCHQ]:[DCHB] = 1:0.52). These results suggest that the chemical composition of the sample changes considerably during the workup necessary for GC–MS analysis. To confirm this conclusion, water was gradually evaporated from a fully photolyzed DCQ solution and samples were taken from time to time. UV-Vis and ESI mass spectrometric analysis of these samples gave evidence for substantial chemical changes during concentration and the appearance of compounds with high (>300) molecular weights were confirmed by ESI MS. Similar phenomena were observed when the photolyzed solution was heated (40–50 °C). It is clear that workup before any analysis could result in chemical changes. Based on earlier observations, these chemical reactions are likely to be oligomerization processes involving DCHB ('humic acid formation') [16]. It should also be noted that a fully photolyzed, dilute solution was stable at room temperature for at least 10 h even under illumination.

Spectroscopic methods not requiring sample treatment were used to search for further products or intermediates. 2,2′,6,6′-Tetrachlorodiphenoquinone, in principle a possible intermediate [38], is not formed during the reaction. This was confirmed by comparing NMR and UV-Vis observations with those obtained using an authentic sample of 2,2′,6,6′-tetrachlorodiphenoquinone prepared independently. The possibility of the formation of a quinhydrone, i.e. a highly colored molecular complex of DCQ and DCHQ, was also rejected experimentally: mixing a 1 mM solution of DCQ with a 3 mM solution of DCHQ did not result in any UV-Vis spectral changes.

It was concluded that the photoreaction produces only DCHQ and DCHB in a molar ratio of 1.89. Spectrophotometry and pH determinations gave $pK_a = 1.57 \pm 0.02$ for DCHB and showed that the anionic form has the strong band with the peak at 524 nm dominating the spectra shown in Fig. 1. The acid dissociation of DCHB clearly explains why the solution turns acidic during the photoreaction. The molar absorbance of the dissociated anionic form of DCHB ($\varepsilon = 2530 \pm 60\,M^{-1}\,cm^{-1}$) was determined by measuring the UV-Vis and the NMR spectra of a photolyzed solution in the presence of a standard substance in known concentration. These values compare well with 2-hydroxy-1,4-benzoquinone: it has a pK_a of 3.5, the dissociated form has UV-Vis peak at 485 nm and a molar absorbance of $2500\,M^{-1}\,cm^{-1}$ [18]. To further confirm the identity of the DCHB, DCQ was oxidized with H_2O_2 in slightly basic solution, conditions under which 1,4-benzoquinone is known to be oxidized to 2-hydroxy-1,4-benzoquinone [39]. The UV-Vis and the NMR spectrum of the product matched the ones observation made in the photolytic reaction.

3.2. Reaction of benzoquinones with benzenetriols

If one accepts the hypothesis that DCBT is the direct photoproduct, then DCHB is formed in a secondary chemical reaction. Reliable thermodynamic data were only available for the unsubstituted 1,4-benzoquinone system. Electrode potentials indicate that ΔE° = ca. +0.1 V [40] for Eq. (3).



(3)

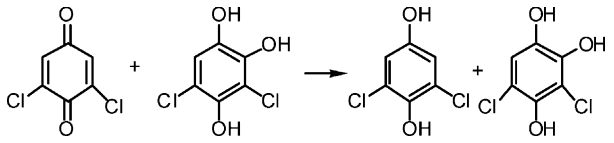
The product, 2-hydroxy-1,4-benzoquinone, is a relatively strong acid ($pK_a \sim 3.5$) [18] and its dissociation should significantly contribute to the driving force and make the reaction practically complete. We postulated that a secondary chemical reaction like this between the primary photoproduct DCBT and reagent DCQ could be responsible for the formation of DCHB in our reaction. Experiments confirmed that this reaction in fact occurs and its kinetics was also studied.

Detailed kinetic measurements were carried out with unsubstituted 1,4-benzoquinone (Q) and 1,2,4-benzenetriol (BT) because the solubility of these offered a much larger working concentration range than that available in the DCQ system. At pH 6.55 in phosphate buffer the reaction could be followed by the stopped-flow method. The absorbance of the dissociated 2-hydroxy-1,4-benzoquinone at 485 nm was monitored ($\varepsilon = 2500\,M^{-1}\,cm^{-1}$) and 1,4-benzoquinone was used in large excess. Single exponential curves were detected and the pseudo first-order rate constants were directly proportional to the concentration of the excess reagent 1,4-benzoquinone proving that the reaction is first-order with respect to both reagents. At pH 4.40 in acetate buffer the reaction was slower. A pH-dependent study showed that the rate was inversely proportional to the hydrogen ion concentration in the studied range, pH = 4–7. The overall experimental rate law is

$$v = k\frac{[Q][BT]}{[H^+]} \tag{4}$$

The value $k = (1.69 \pm 0.07) \times 10^{-3}\,s^{-1}$ was determined with least-squares fitting. This rate equation was also confirmed in experiments without buffer, where the pH change was also taken into account. The detected kinetic curves gave an excellent fit to the integrated form of rate Eq. (4). The inverse dependence on the hydrogen ion concentration is readily interpreted by assuming that the reactive form of benzenetriol is the anion obtained after an acid dissociation step. The known pK_a of this process is about 9.1 [41].

Similar measurements were carried out using DCQ and a stock solution of DCBT, although the concentration range was somewhat limited by the relatively low solubility of DCQ. Because of the preparation method of the DCBT stock solution, these experiments were carried out in the presence of DCHQ and boric acid (about 0.1 and 0.02 mM, respectively), but adding more of these compounds did not influence the rate. This reaction was faster than the one with unsubstituted reagents, the typical reaction time being about 1 s even at pH 3. The rate law shown in Eq. (4) was found to be valid for reaction (5) with $k = 4.8 \pm 1.0\,s^{-1}$ (measured pH-range: 2.5–3.5). The larger value for the rate constant is in agreement with the expectations that DCBT should have a lower pK_{a1} than 1,2,4-benzenetriol.



(5)

In summary. we have shown that reaction (5) may be responsible for the observed formation of DCHB in our system. This conclusion is most likely true for the photoreactions of other substituted benzoquinones as well. We also note that on the time scale of a laser flash photolysis experiment (which is usually shorter than 1 ms), a benzenetriol could reasonably be considered as a product.

3.3. Photochemical studies with a diode-array spectrophotometer

When a stirred solution of DCQ is placed into the diode array spectrophotometer, the photoreaction can be driven and monitored conveniently at the same time. Absorbance–time traces are shown in Fig. 3. This figure shows that the reaction proceeds with the same rate at 10.0 and 25.0 °C as expected for photoreactions. In other experiments, the reaction was shown to be temperature-independent from 10.0 to 50.0 °C. The figure also shows that the absence of stirring results in irreproducible traces. The reaction can still be detected when the deuterium lamp of the instrument is turned off and only the W lamp is used, but the rate is much lower. The experimental observations were the same in air-saturated and oxygen-free solutions, so dissolved oxygen does not seem to influence the overall photoreaction. It is also notable that the presence of some oxygen is inevitable even in experiments started with degassed solutions because O_2 is produced during the process.

The initial rate measured at 524 nm was used for kinetic purposes, to monitor the formation of DCHB ($\varepsilon = 2530\,M^{-1}\,cm^{-1}$). First it should be noted that the initial rate was inversely proportional to the volume of the solution used in the cell. This phenomenon was not unexpected and the reason is also clear: the light source provides a constant number of photons, which cause a constant number of molecules

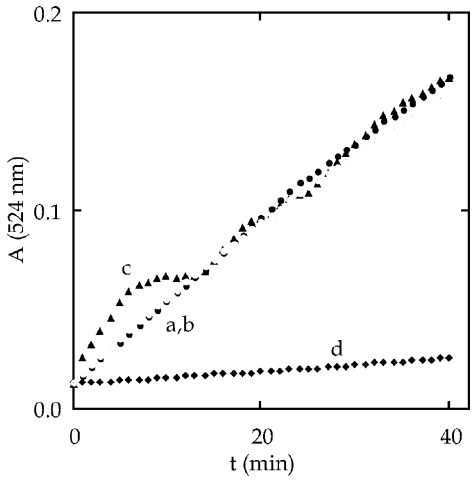


Fig. 3. Kinetic traces measured by a diode-array spectrophotometer in the aqueous photoreaction of 2,6-dichloro-1,4,-benzoquinone. [DCQ] = 1.08 mM, (●) = 524 nm and path length = 1 cm for all curves. $T = 25.0\,°C$ (trace a, c and d); $T = 10.0\,°C$ (trace b); no stirring for trace c; only the visible lamp was used for trace d.

to photolyze. A constant number of photolyzed molecules is equivalent to a smaller concentration change when the volume is larger. All later experiments were done using a fixed volume (3.00 cm^3). Fig. 4a shows how the initial rate depends on the concentration of DCQ. The saturation in this curve is not unexpected because the rate should be proportional to the number of absorbed photons rather than to the concentration. Addition of $NaNO_3$ slows down the process as shown in Fig. 4b. In the UV, nitrate ion absorbs some of the light driving the reaction. Similarly, dimethyl sulfoxide (DMSO) also slows down the reaction, but the reason must be different because DMSO does not have significant absorption. Quantitative analysis of the data showed that the effect of DMSO is competitive inhibition and the initial rate at constant DCQ concentration is expressed by Eq. (6). The dependence of the initial rate on these three concentrations will be interpreted quantitatively in later sections.

$$v = \frac{k_a}{1 + k_b[\mathrm{DMSO}]} \tag{6}$$

With the diode array spectrophotometer used in this study, it is possible to measure the relative energy of the light at each wavelength. This was a key factor in the quantitative interpretation of the photoreaction driven by polychromatic light. The part of the *photon flow* [42] of the light beam absorbed by the solution, which we term *photon count* for brevity, can be calculated for monochromatic light as follows:

$$N = C \times \lambda \times E_{\mathrm{beam}} \times (1 - 10^{-A}) \tag{7}$$

where A is the absorbance of the solution, E_{beam} the energy of the light beam, C the constant incorporating Planck's constant, the speed of light and a conversion factor which is needed because energy is measured on a relative scale.

When polychromatic light is used, the photon counts of all wavelengths are summed, Eq. (8). Here the 'λ' superscripts

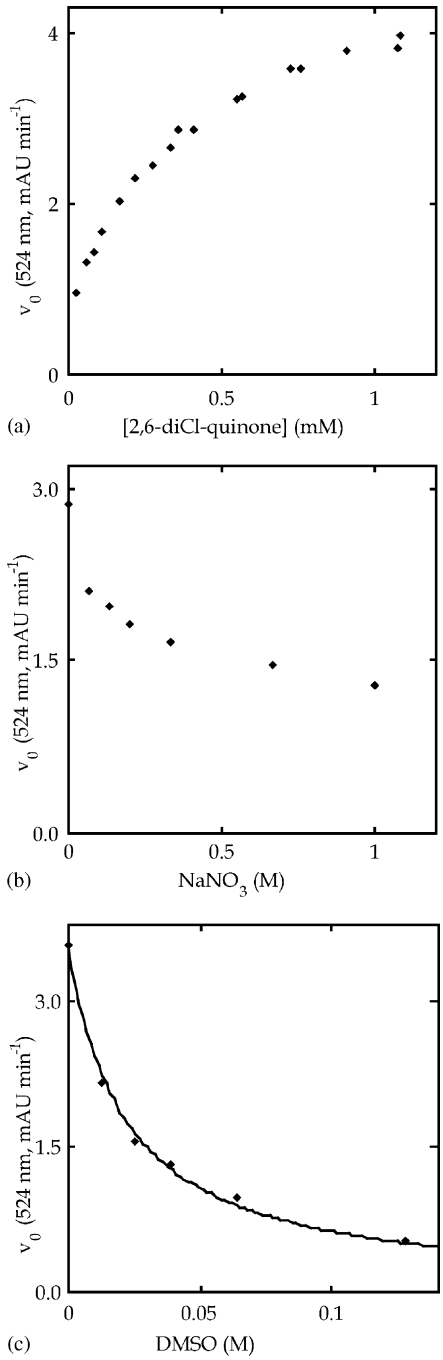


Fig. 4. Initial rate at 524 nm in the aqueous photoreaction of 2,6-dichloro-1,4-benzoquinone as a function of the concentration of 2,6-dichloro-1,4-benzoquinone (a), added $NaNO_3$(b), added dimethyl sulfoxide (c). Path length = 1 cm and $T = 25.0\,^{\circ}C$ for all figures; [DCQ] = 0.36 mM (b), 0.72 mM (c).

are used to emphasize that the absorbances and energies are functions of the wavelength.

$$N = C \times \sum_{\lambda} \{\lambda \times E^{\lambda}_{\text{beam}} \times (1 - 10^{-A^{\lambda}})\} \tag{8}$$

When the photoactive component is not the only absorbing species in solution, the appropriate proportion absorbed by the photoactive component can be calculated if the molar absorbances and concentrations are known:

$$N = C \times \sum_{\lambda} \left\{ \frac{c_{\text{act}}\varepsilon^{\lambda}_{\text{act}}}{\sum_i (c_i \varepsilon^{\lambda}_i)} \times \lambda \times E^{\lambda}_{\text{beam}} \times (1 - 10^{-A^{\lambda}}) \right\} \tag{9}$$

where c_{act} is the concentration of the photoactive species, ε_{act} its molar absorption, and the summation in the denominator is done for all the absorbing species present in solution.

Ferrioxalate actinometry was used to determine the constant C [33]. A standard 0.006 M ferrioxalate solution was studied in the diode-array instrument. The amount of Fe(II) formed after different illumination times was determined by taking samples through its ferroin complex following accepted protocols [33]. From these data, the formation rate of Fe(II) was calculated. The quantum yield of the process is known and it shows some minor wavelength dependence [31]. Constant C was calculated by dividing the formation rate of Fe(II) with the photon count of the solution also taking the quantum yield into account. During the actinometric calibration we also noticed that the spectral changes in the ferrioxalate solution are small but measurable, and after careful validation it may be possible to do ferrioxalate actinometry without the need for iron(II) determination in separate analysis steps.

Fig. 5 shows the initial rate measured at 524 nm as a function of the photon count. The data define a straight line with some scatter. Most of the points appearing in this figure were measured at different DCQ concentrations, hence the different photon counts. Points measured in the presence of nitrate ion, a point measured with DCQ dissolved in D_2O, and points measured using the driving force of the with visible lamp only are also on the line. These observations

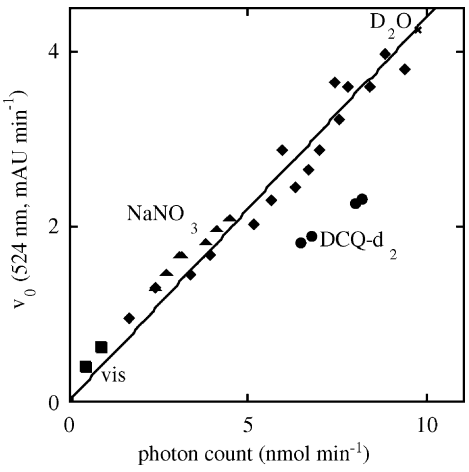


Fig. 5. Initial rate at 524 nm in the aqueous photoreaction of 2,6-dichloro-1,4-benzoquinone as a function of photon counts. Path length = 1 cm; $T = 25.0\,^{\circ}C$. Vis (squares): using the visible lamp only as a driving force. D_2O (cross): experiment done in D_2O. $NaNO_3$ (triangles): experiments done in the presence of $NaNO_3$. DCQ-d_2 (circles): experiments done using 2,6-dichloro-1,4-benzoquinone-d_2 dissolved in H_2O.

prove that nitrate ion does not exert a specific effect on the photoreaction, it simply acts as an internal filter, and this is already taken into account in the definition of photon count, Eq. (9). The rate is the same in D_2O and H_2O showing that there is no solvent isotope effect. A solvent isotope effect would have been unexpected in the photoreaction because the rate is proportional to the number of photons absorbed by the photoactive species. Points measured using a solution of DCQ-d_2 in H_2O deviate from the line significantly. The comparison of rates measured with DCQ and DCQ-d_2, gives an overall kinetic isotope effect of 1.49 ± 0.05. It should be noted that the UV-Vis spectral properties of these two compounds are the same within experimental error.

This isotope effect will be interpreted later.

From the slope of the line in Fig. 5, $(4.39 \pm 0.08) \times 10^{-4}$ AU/nmol, the known molar absorbance of DCHB, and the volume of the solution the quantum yield of the photochemical process can be determined:

$$\Phi = \frac{\alpha V}{\varepsilon} \tag{10}$$

The quantum yield $\Phi_{DCHB} = 0.52 \pm 0.01$ was calculated for DCHB formation. Based on the constant concentration ratio of DCHQ and DCBT, the quantum yield of DCHQ formation is $\Phi_{DCHQ} = 0.98 \pm 0.02$. Because the formation of either one DCHQ or DCHB necessary involves the loss of one DCQ, the quantum yield of DCQ loss is $\Phi_{DCQ} = \Phi_{DCHB} + \Phi_{DCHQ} = 1.50 \pm 0.02$. This is larger than unity, in agreement with the assumption the DCQ is lost in secondary chemical reactions in addition to the photoreaction.

The spectral dependence of photon count for several different solutions is shown in Fig. 6. The spectral properties of the light used to drive the reaction varies considerably from experiment to experiment. Despite the different spectral distribution of driving photons in different experiments, the initial rates correlate with the photon counts quite well (see Fig. 5). This shows that the quantum yield does not depend significantly on wavelength.

Fig. 1b illustrates that the photoreaction is accompanied by an absorbance decrease in the region around 350 nm. Thus 346 nm, the peak of DCQ, was also used to study the photoreaction. At this wavelength several components have absorptions as also indicated by the non-zero final absorbance reading shown in Fig. 1b. The dominating absorbing species is DCQ. Fig. 7a shows that the kinetic curves detected at 524 nm were not dependent on whether the reaction was started in neutral solution, or with previous addition of some acid. The same is not true for 346 nm (Fig. 7b). Experiments started in neutral solution showed a small absorbance increase first followed by an almost steady decrease. Experiments started with the addition of some acid always gave a steady decrease in absorbance. When the photoreaction was carried out in phosphate buffer at about pH 7, a very slow and steady increase was seen in absorbance. The reason for this phenomenon was found to be

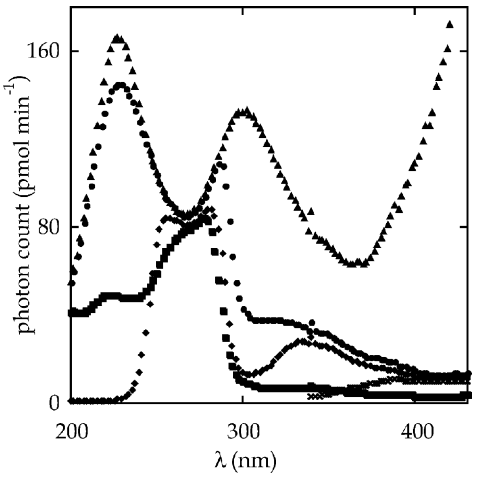


Fig. 6. Spectral dependence of photon count for different starting solutions in the aqueous photoreaction of 2,6-dichloro-1,4-benzoquinone. (▲): light beam only, cell filled with water; circles, 0.62 mM DCQ; (■): 0.092 mM DCQ; diamonds, 0.36 mM DCQ, 0.133 M [$NaNO_3$]; hatched squares, 1.13 mM DCQ with the visible lamp only; path length = 1 cm; $T = 25.0\,^{\circ}C$.

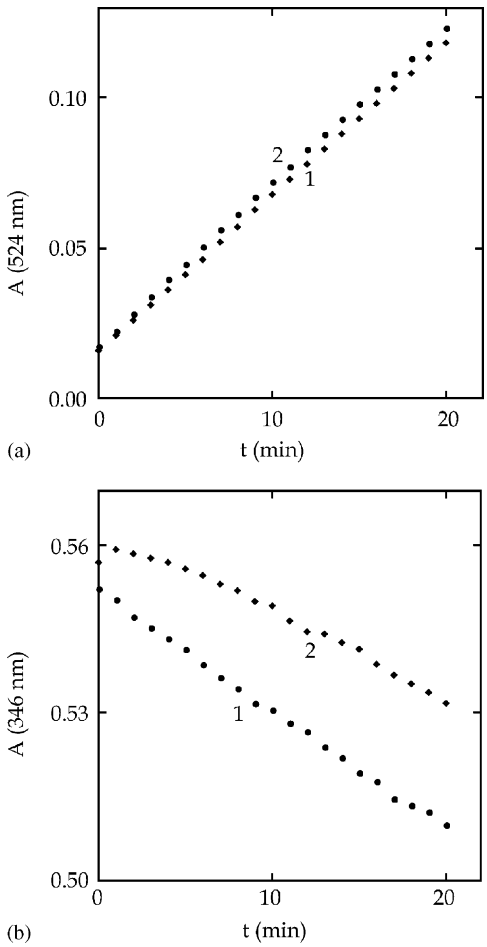


Fig. 7. Absorbance traces at 524 (a) and 346 nm (b) in the aqueous photoreaction of 2,6-dichloro-1,4-benzoquinone started with (1) and without (2) the addition of acid. [DCQ] = 1.17 mM; $[H^+] = 0$ (curves), 32 mM (curves), path length = 1 cm; $T = 25.0\,^{\circ}C$.

the acid dissociation of DCHQ; it has pK_{a1} 7.44 ± 0.03 and its deprotonated form has $\varepsilon_{346nm} = 970 \pm 50\,M^{-1}\,cm^{-1}$. Fully protonated DCHQ does not have significant absorption at this wavelength. The molar absorbance of DCQ is $484 \pm 5\,M^{-1}\,cm^{-1}$ at 346 nm. Thus the small increasing part in the experiments started with unbuffered neutral solution can be explained. At the beginning of the reaction the pH is close to neutral and a good portion of DCHQ is deprotonated giving a significant contribution to the absorbance. The reaction produces acid and after some time the pH becomes because deprotonated DCHQ is no longer present.

With this in mind, initial rates were determined at 346 nm in experiments where about 20 μM nitric acid was added to the solution before the experiment. The correlation between the initial rates measured at 524 and 346 nm is shown in Fig. 8. The points define a straight line going through the origin proving that the same process is being monitored at the two wavelengths. It is important to note that the points measured in the presence of DMSO are also on the line in Fig. 8. This means that DMSO inhibits not only the formation of DCHB (monitored at 524 nm), but also the loss of DCQ (the largest part of the signal monitored at 346 nm); it does not change the ratio of these two rates. This finding is important when the effect of DMSO is interpreted.

The slope of the line shown in Fig. 8 is −0.377 ± 0.004. This slope can also be calculated from the molar absorbances and quantum yields as given in Eq. (11).

$$\beta = \frac{\Delta\varepsilon_{346\,nm} \times \Phi_{DCQ}}{\varepsilon_{524\,nm} \times \Phi_{DCHB}} \tag{11}$$

The notation $\Delta\varepsilon_{346nm}$ is used here because DCQ is not the only absorbing species at 346 nm. The molar absorbance of DCQ is $484\,M^{-1}\,cm^{-1}$ at 346 nm. In the experiment shown in Fig. 1b, the initial absorbance at 346 nm was

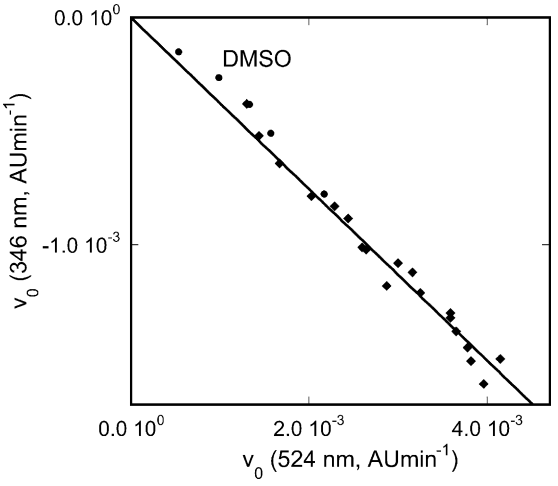
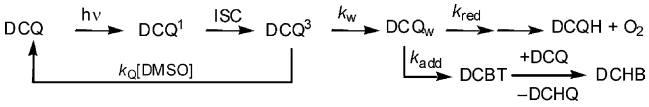


Fig. 8. Initial rate measured at 346 nm as a function of the initial rate measured at 524 nm in the aqueous photoreaction of 2,6-dichloro-1,4-benzoquinone. Path length = 1 cm; T = 25.0 °C. DMSO (●) points measured in the presence of varying amounts of dimethyl sulfoxide.



Scheme 1. Photochemical and thermal reactions.

0.633, the final absorbance was 0.128. The reaction was driven to completion in that experiments, thus $\Delta\varepsilon_{346nm}$ can be calculated as $484\,M^{-1}\,cm^{-1} \times (0.128–0.633)/0.633 = -386\,M^{-1}\,cm^{-1}$. With this value $\beta = -0.440$ can be obtained, and the agreement with the experimental value is not unreasonable. This serves as an internal test of the consistency of our interpretation.

3.4. Proposed scheme

Based on all the information presented, we propose Scheme 1 to interpret the experimental observations.

In this scheme, the triplet state of DCQ formed after light absorption and intersystem crossing reacts with water to give an adduct DCQ_w, which is not necessarily an intermediate; it may be a common transition state for the k_{red} and k_{add} pathways. Two possible processes compete: the k_{red} pathway leads to the eventual formation of DCHQ and oxygen through a series of steps, and the k_{add} pathway leads to the formation of DCBT, which is oxidized to DCHB by the DCQ present in the reaction. The k_{red} pathway leaves the hydrogens on DCQ intact and only a very small deuterium isotope effect is expected. However, the k_{add} pathway leads to breaking one of the C–H bonds and a primary kinetic isotope effect is expected. From the constant ratio of DCHQ and DCQ formed $k_{red}/k_{add} = (1 - 0.53)/0.53 = 0.89$. The kinetic isotope effect 1.49 was measured for the formation rate of DCHB, which is proportional to $k_{add}/(k_{red} + k_{add})$. Assuming the k_{red} is the same for deuterated and non-deuterated DCQ, $k_{red}/k^{D}_{add} = 1.82$ can be calculated and $k_{add}/k^{D}_{add} = 2.04$ can be obtained; this is not an unreasonable primary kinetic isotope effect.

An alternative scheme involving some kind of hydroxylating agent, thus avoiding the formation of the intermediate DCBT, had been proposed earlier [12]. However, evidence has already been reported against the involvement of free hydroxyl radicals in the photoreaction using 2-methyl-1,4-benzoquinone [6]. Further, it is unlikely that a reaction with a hydroxylating agent would not result in substitution of the chlorine atoms in DCQ in our system.

To interpret the inhibiting effect of DMSO it should be kept in mind that the presence of DMSO does not change the rate of DCQ loss relative to that of DCHB production (Fig. 8). This observation strongly suggests that the reaction pathway involving DMSO does not lead to net loss of DCQ. The only plausible simple explanation we can propose is that DMSO quenches the triplet excited state of DCQ, as shown in Scheme 1.

It should be noted that our experiments do not define how oxygen is formed after step k_{red}. This is almost sure to happen in several steps, but these occur after the rate determining step and no kinetic and mechanistic information can be deduced from our data.

3.5. Full time course curve fitting

The conclusions presented in the previous sections were based on initial rates as a quantitative measure of the progress of the photoreaction. We also noted that the concept of photon counts with Eq. (12) may be used to characterize the full time course of photochemical reactions for which the stoichiometry and the spectra of all absorbing species are known.

$$\frac{d[DCQ]}{dt} = -\kappa N \tag{12}$$

We could not use the diode array experiments for this purpose because the molar absorbances of DCHB were unknown in the UV region and using only the visible lamp of the instrument resulted in an inconveniently slow reaction rate. However, the experiment shown in Fig. 1b, in which a very intense halogen lamp was used with offline spectrophotometric detection, was suitable for such data treatment. Only DCQ and DCHB have absorptions in the emission region of the lamp, and the spectrum of DCHB could be calculated from the final spectrum in this region.

Differential Eq. (12) was solved with numerical methods and the value of giving the best fit for the absorbance values measured at 524 nm was found by least-squares minimization. The measured curve and the best fit are shown in Fig. 9. The fit is reasonably good and suggests that our model is sufficient to interpret the photoreaction even when it is driven to completion.

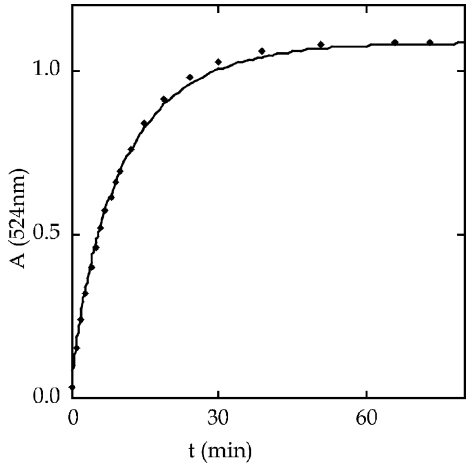


Fig. 9. Full time course kinetic trace in the aqueous photoreaction of 2,6-dichloro-1,4-benzoquinone. [DCQ] = 2.2 mM; T = 25.0 °C; path length = 1 cm, (●) = 524 nm. Markers: measured points; line: best fit to Eq. (12).

4. Conclusions

A commercial diode array spectrophotometer can be used to study photochemical reactions and to determine quantum yields. The quantitative evaluation of experiments where a photoreaction is driven to completion also seems to be feasible using numerical integration of differential equations.

Acknowledgements

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References

[1] J.M. Bruce, in: S. Patay (Ed.), The Chemistry of the Quinonoid Compounds, vol. 1, Wiley, London, 1974, Chapter 8.
[2] H.J. Hageman, W.G.B. Huysmans, Chem. Commun. (1969) 837–838.
[3] K. Maruyama, T. Otsuki, A. Takuwa, S. Arakawa, Bull. Chem. Soc. Jpn. 46 (1973) 2470–2474.
[4] G. Cilento, D.L. Sanioto, K. Zinner, Spectrochim. Acta A 24 (1968) 785–786.
[5] H.P. Trommsdorff, J. Kahane-Paillous, Spectrochim. Acta A 23 (1967) 1661–1670.
[6] A. Pochon, P.P. Vaughan, D. Gan, P. Vath, N.V. Blough, D.E. Falvey, J. Phys. Chem. A 106 (2002) 2889–2894.
[7] T. Azumi, K. Maeda, T. Aizawa, Y. Yamakage, K. Shindo, S.S. Ali, Y. Araki, Proc. Ind. Acad. Sci. (Chem. Sci.) 107 (1995) 831–840.
[8] G. Lente, J.H. Espenson, Chem. Commun. (2003) 1162–1163.
[9] J.M. Bruce, E. Cutts, J. Chem. Soc. C (1966) 449–458.
[10] A.D. Broadbent, Chem. Commun. (1967) 382–383.
[11] A.E. Alegría, A. Ferrer, E. Sepúlveda, Photochem. Photobiol. 66 (1997) 436–442.
[12] A.E. Alegría, A. Ferrer, G. Santiago, E. Sepúlveda, W. Flores, J. Photochem. Photobiol. A 127 (1999) 57–65.
[13] A.D. Broadbent, R.P. Newton, Can. J. Chem. 50 (1972) 381–387.
[14] T. Foster, A.J. Elliot, B.B. Adeleke, J.K.S. Wan, Can. J. Chem. 56 (1978) 869–877.
[15] D.R. Kemp, G. Poerter, Proc. Royal Soc. A 326 (1971) 117–130.
[16] K.C. Kurien, P.A. Robins, J. Chem. Soc. B (1970) 855–859.
[17] G.O. Phillips, N.W. Worthington, Chem. Commun. (1967) 835.
[18] A. Rossi, G. Guyot, P. Boule, Comptes Rendus 303 (1986) 1179–1182.
[19] M. Shirai, T. Awatsuji, M. Tanaka, Bull. Chem. Soc. Jpn. 48 (1975) 1329–1330.
[20] G. Perbet, P. Boule, J. Lemaire, J. Chim. Phys. Phys. Chim. Biol. 79 (1982) 95–100.
[21] A.I. Ononye, A.R. McIntosh, J.R. Bolton, J. Phys. Chem. 86 (1986) 6266–6270.
[22] A.I. Ononye, J.R. Bolton, J. Phys. Chem. 86 (1986) 6270–6274.
[23] S. Hashimoto, K. Kano, H. Okamoto, Bull. Chem. Soc. Jpn. 45 (1972) 966.
[24] S. Fujita, K. Sano, Tetrahedron Lett. 16 (1975) 1695–1696.
[25] S. Fujita, K. Sano, J. Org. Chem. 44 (1979) 2647–2651.

[26] R.P. Ferrari, E. Laurenti, F. Trotta, J. Biol. Inorg. Chem. 4 (1999) 232–237.
[27] D. Villemin, F. Sauvaget, Synlett (1994) 435–436.
[28] H. Lübbecke, P. Boldt, Angew. Chem. Int. Ed. 15 (1976) 608.
[29] W.H. Hunter, M. Morse, J. Am. Chem. Soc. 48 (1926) 1615–1624.
[30] A. Durazzo, M.M. Abu-Omar, Chem. Commun. (2002) 66–67.
[31] N.J. Bunce, in: J.C. Scaiano (Ed.), CRC Handbook of Organic Photochemistry, vol. 1, CRC Press, Boca Raton, Florida, 1989, pp. 241–259.
[32] C.A. Parker, Proc. Royal Soc. A 220 (1953) 104–116.
[33] C.G. Hatchard, C.A. Parker, Proc. Royal Soc. A 235 (1956) 518–536.
[34] A.D. Kirk, C. Namasivayam, Anal. Chem. 55 (1983) 2428–2429.
[35] W.D. Bowman, J.N. Demas, J. Phys. Chem. 80 (1976) 2434–2435.
[36] K.C. Kurien, J. Chem. Soc. B (1971) 2081–2082.
[37] Scientist 2.01, Micromath Software, Salt Lake City, UT, 1995.
[38] O.B. Lantratova, A.I. Prokof'ev, I.V. Khudyakov, V.A. Kuzmin, I.E. Pokrovskaya, Nouv. J. Chim. 6 (1982) 365–371.
[39] A. Brunmark, E. Cadenas, Free Rad. Biol. Med. 3 (1987) 169–180.
[40] C.A. Reynolds, J. Am. Chem. Soc. 112 (1990) 7545–7551.
[41] A.R. Forrester, J.L. Wardell, Nuclear Hydroxy Derivatives of Benzene and its Homologues, in: S. Coffey (Ed.), Rodd's Chemistry of Carbon Compounds, vol. III A, Elsevier, Amsterdam, 1971.
[42] J.W. Verhoeven, Pure Appl. Chem. 68 (1996) 2223, this article gives the IUPAC definition of *photon flow*.