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Photoinitiation of the Reactions of Quinones

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The primary photochemical reactions of quinones as well as secondary dark or light-induced processes involving either the initial quinones or the products of their primary photochemical reactions are considered and the reaction mechanisms are discussed. The bibliography includes 262 references.

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I. INTRODUCTION

Under the influence of light, quinones are capable of undergoing numerous reactions. Some of the photochemical reactions (for example photochemical reduction) are components of important processes such as photosynthesis in green plants and photochemical degradation of materials coloured by vat dyes. Other photoinitiated reactions of quinones can also be of considerable theoretical and practical interest, since many of them have no analogues among dark chemical reactions.

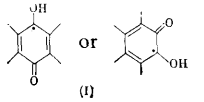
Attempts to survey the light-induced reactions of quinones were made outside the Soviet Union in 1947,[1] 1967,[2] and 1969,[3] the last review dealing with *o*-quinones only. However, since the publication of these reports, a series of new photochemical reactions of quinones have been discovered and those already known have been investigated in greater detail, which has led to the revision of old views and to the appearance of new ones in this field. Bearing in mind these factors and the fact that similar reviews have not been published in the Soviet Union, we attempted to survey the published data (up to 1974 inclusive) and to demonstrate as fully as possible the entire wide variety of the photochemical reactions of quinones. Equal attention has been devoted both to the primary photochemical steps and to the secondary processes leading to the final photolysis products.

II. PHOTOCHEMICAL REDUCTION

1. Primary Photochemical Processes

Photochemical reduction is the simplest photochemical reaction of quinones (Q). It involves the addition of an electron or a hydrogen atom to the oxygen atom of the carbonyl group under conditions where the analogous dark

reactions are impossible. The formation of ketyl radicals (I) (or the corresponding anions), the redistribution of electron density in which leads to semiquinones or their dissociated forms, is assumed under these conditions[4]. Ketyl structures, mesomeric with respect to semiquinones, can also make a definite contribution to their resonance hybrid[5]:

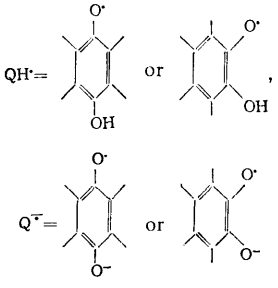


(I)

The products of one-electron reduction of quinones can be obtained in two ways. In one of these, which is less frequently encountered and has therefore been less thoroughly studied, the quinone molecule in the ground state behaves as the electron (or hydrogen) acceptor in relation to the photoexcited molecules of certain pigments (chlorophylls, porphyrins, etc.), usually in the triplet state[6]. The process proceeds as a result of the significant decrease, following electronic excitation, of the ionisation potentials of the pigments or the increase of their capacity to donate a hydrogen atom. Mainly 1,4-benzoquinones[7-14] and in a few instances naphtho- and anthra-quinones[6,15-20] have been studied in such photochemical reactions, unrelated to the excitation of the quinone molecule.

Another, more frequently encountered process used in the photochemical reduction of quinones has been studied in much greater detail. It involves the abstraction of an electron by the excited quinone molecule Q* from a molecule (anion) X with conversion of the latter into a radical-cation (radical) $(X - \bar{e})$ or the abstraction of a hydrogen atom from a molecule AH with formation of a radical A· from the latter[1-3,15]:

$$Q^{\bar{\cdot}} + (X - \bar{e}) \xleftarrow{X} Q^* \xrightarrow{AH} QH^{\cdot} + A^{\cdot},$$



When the side chain of quinones contains substituents which are potential electron (hydrogen) donors, the photochemical reduction of quinones also proceeds via an intramolecular mechanism. On the other hand, when both photochemical reduction pathways are possible, it is frequently difficult to decide whether the process proceeds intramolecularly or intermolecularly or via both mechanisms simultaneously.

One should note that the possibility of subdividing reagents (or substituents in quinone molecules) into electron and hydrogen donors of the kind discussed above, which seemed an obvious approach, has now given rise to doubts. One cannot rule out the possibility that the semiquinones QH· are not formed in a single-stage step involving the abstraction of a hydrogen atom from a neutral reactant molecule but are produced as a result of the abstraction of an electron from such a molecule with subsequent rapid proton transfer from the resulting radical-cation $AH^{\dot{+}}$ to the radical-anion $Q^{\bar{\cdot}}$:[21,22]:

$$Q^* + AH \rightarrow Q^{\bar{\cdot}} + AH^{\dot{+}} \rightarrow QH^{\cdot} + A^{\cdot}.$$

In particular, this mechanism has been suggested for the photochemical oxidation of hydrocarbons[2,23] and alcohols[24,25] by quinones in matrices. In view of the lack in the vast majority of instances of rigorous evidence for one- or two-step abstraction of a hydrogen atom by excited quinone molecules, it appears more correct to regard the process as the transfer of $(\bar{e} + H^+)$ with the possibility of a two-stage mechanism (see, for example, Refs. 2 and 23–25).

The driving force of the photochemical reduction of quinones is the increase in the electron affinity of the quinonoid system on excitation. It is therefore natural that the efficiency of the process should depend primarily on the oxidation–reduction potential of the quinone in the reactive electronically excited state. However, these quantities have so far been determined only in a few instances[15]; attempts to relate the efficiency of photochemical reduction to the polarographic characteristics of quinones in the ground state have been made much more frequently[15]. Because of this, it is at present impossible to resolve adequately the problem of the comparative reactivities of various quinones and of its relation with their structure in photochemical reduction processes; one can only assess their behaviour in photolysis in reducing media, with reference to the nature of the lowest excited states.

It was believed that the reactive excited states of quinones in their photochemical reduction may be both triplet and singlet states; for some quinones (for example duroquinone), the involvement of only the singlet state is postulated[2]. Incidentally, numerous experiments have made it possible to exclude in almost all the known instances the involvement of the S state of quinones (without denying such a possibility in individual cases)[15,26-28] and to give preference in this role to the long-lived biradical[4,29] triplet[15,30,31] state.

Of the two states T_{n,π^*} and T_{π,π^*}, the former should be more active despite its shorter lifetime[4,29], because the delocalisation of π electrons in the T_{π,π^*} state leads to a low unpaired electron density at the reaction centre, while the localisation of excitation in the carbonyl group and the radical-like nature of the oxygen atom are characteristic of the T_{n,π^*} state[4,15,29]. Indeed, this hypothesis has been found to hold and photoexcited quinones with the lowest T_{n,π^*} level are effective oxidants. The transitions to this reactive state from higher energy levels usually proceed with the same probabilities (frequently close to unity), which are manifested by the constancy of the quantum yield of the photochemical reduction of the substrate over the entire wavelength range of its absorption[2,15,25,32]. If the photochemical reduction of quinones of this type is inefficient, which happens rarely, the phenomenon is usually attributed[15] to a low interconversion quantum yield Φ_{ST}—for example, Φ_{ST} for ubiquinone-30, which is difficult to reduce, amounts to approximately 0.04.[30]

A small change in the ratio of the number of n and π orbitals on passing from quinones with a T_{n,π^*} lowest excited state to polyquinones does not lead to significant changes in the ordering of the energy levels and in the photochemical properties[33,34]. However, when the solvent is altered, a specific substituent is introduced, etc., there is a possibility of the inversion of the quinone levels and the relatively unreactive T_{π,π^*} or $T_{c.t.}$ levels can become the lowest†[2,15,22,35]. Anthraquinone (as well as

† The $S_{c.t.}$ or $T_{c.t.}$ levels correspond to the state with charge transfer.

other quinones [33]), with powerful electron-donating groups (OH, NH_2, NR^1R^2) as ring substituents, can serve as a characteristic example of the considerable decrease of photodehydrogenating capacity under the influence of the substituent [2,15,36,37]. The fact that such quinones do not lose completely their capacity for photochemical reduction is explained either by the involvement in the process of their T^2_{n,π^*} state, whose level lies above the T^1_{π,π^*} (or $T_{c.t.}$) [38] level, or by their reduction in the relatively inactive T_{π,π^*} (or $T_{c.t.}$) state [35,37]. Nevertheless even compounds of this kind can be reduced photochemically with a fairly high efficiency. For this purpose, one uses as the light absorbing substrate a hydrogen (electron) donor, i.e. a pigment [6] which interacts with the quinone in the ground state (see above) or the photochemical reaction is carried out with the usual reducing agents but in acid media with excitation of the protonated molecules of the quinones, which have the lowest T_{n,π^*} state [26,39,40].

Quinones can form fairly stable charge-transfer complexes (CTC) with the other reactant (solvent). If T_{n,π^*} remains the lowest state under these conditions, then excitation by light corresponding to their absorption band is accompanied by the reduction of the quinone. The formation of such CTC is assumed for the reaction of 1,4-benzoquinone and its derivatives with ethanol [41], of sulphoanthraquinones with halide anions in aqueous solutions [42], and of quinones with aliphatic amines [2,25] and has been observed for the reactions of 1,4-benzoquinone with certain aliphatic-aromatic hydrocarbons in low-temperature matrices [23] but not solutions [43]. If the CTC energy level is lower than the T_{n,π^*} level of the quinone (which is characteristic of powerful electron donors), then, as in the photolysis of quinones with the lowest T_{π,π^*} (or $T_{c.t.}$) levels (see above), the photochemical reduction of the quinonoid structure is inhibited [23].

Water [15,16,18,19,44] and virtually all organic compounds (hydrocarbons [6,45], alcohols [2,5,15,45-51], aldehydes [1], ketones [52,53], ethers [52], amines [46,54], and amides [55]), which are usually regarded as hydrogen donors, can serve as reductants in the intermolecular photochemical reduction of quinones. Organic anions (for example alkoxide anions [15,32,39,42,56], CH_3COO^-, and CCl_3COO^- [15]), inorganic anions (OH^-, SO_4^{2-}, SO_3^{2-}, SeO_3^{2-}, SCN^-, CO_3^{2-}, PO_4^{3-}, NC_3^-, [15,57,58] and Hal^- [15,59]), and sometimes alcohols [24-26,60], and amines [2,46] are believed to be electron donors. Quinones with side-chain substituents, resembling the above reductants in their capacity to donate an electron (hydrogen), undergo intramolecular photochemical reduction.

The properties of the reductants as well as those of the quinones determine the efficiency of the photochemical reduction. This applies in the first place to the capacity of the reductant to give up an electron or hydrogen. The latter is clearly illustrated by the reactivity series of alcohols in their photochemical dehydrogenation by quinones: t-BuOH $\ll$ MeOH $<$ EtOH $<$ i-PrOH; [47] this series has been explained [2,15] by the increased mobility of hydrogen atoms at the carbinol carbon atoms as a result of the increased positive inductive effect of the alkyl group in the alcohol molecule. The conclusion that a hydrogen atom is abstracted from this position was reached on the basis of the analysis of the products of the photochemical oxidation of alcohols [2,15,47,48]. One must also take into account the steric characteristics of the reacting molecules: in particular, it has been suggested that the bulk and mass of the substituents in the quinone molecule can influence significantly its photodehydrogenating capacity in intermolecular photochemical reduction [2]. The steric factors in the reductant molecules are important in their turn; for example, in ethers the hydrogen atom is abstracted from the carbon atom involved in the ether linkage and an increase in the length and branching of the alkyl groups reduces the reactivity of the ether by shielding [2,15,47]. Steric factors play an even greater role in the intramolecular photochemical reduction of quinones, where the feasibility of the process is determined, apart from other requirements, by the possibility of achieving a cyclic transition state [2].

The photochemical reduction of quinones has been investigated in greatest detail in alcohol matrices [24,25]. It has been shown recently by electronic spectroscopy and ESR that the hydroxy-group of the alcohol R^1R^2CHOH serves in this case as the donor of hydrogen (an electron and then a proton); the $R^1R^2\dot{C}OH$ radicals are formed from the radicals $R^1R^2CHO^\cdot$ in secondary reactions (cf. the interaction of photoionised quinone molecules with alcohols in the gas phase [61]):

$$(R^1R^2CHOH)^{\cdot+} + Q^{\cdot-} \leftarrow Q^* + R^1R^2CHOH \xrightarrow{R^1R^2CHOH} R^1R^2CHOH + R^1R^2\dot{C}OH \qquad Q^{\cdot-} + R^1R^2\overset{+}{C}HOH_2 + R^1R^2CHO^\cdot,$$

$$R^1R^2CHO^\cdot \rightarrow R^1R^2\dot{C}OH \quad \text{or}$$

$$R^1R^2CHO^\cdot + R^1R^2CHOH \rightarrow R^1R^2CHOH + R^1R^2\dot{C}OH,$$

$$Q^{\cdot-} + R^1R^2\overset{+}{C}HOH_2 \rightarrow QH^\cdot + R^1R^2CHOH,$$

$$QH^\cdot + R^1R^2CHOH \rightarrow QH_2 + R^1R^2CHO^\cdot, \quad \text{or}$$

$$QH^\cdot + R^1R^2CHOH \rightarrow QH_2 + R^1R^2\dot{C}OH.$$

The above mechanism agrees with the hypothesis that the hydrogen bond between the alcoholic hydroxyl and the carbonyl group of the quinone in the ground state should facilitate the abstraction of a hydrogen atom ($e + H^+$) from the OH group [62-64]. Possibly the above mechanism is also applicable to the photochemical dehydrogenation of alcohols by quinones in solution (see, for example, the studies on the photochemical reduction of tetrachloro-1,4-benzoquinone in alcohols [26,60]); this process is still being discussed [24,25,47]. On the other hand, in the photochemical reduction of certain quinones in solution by acetone and aromatic [65] and acetylenic ($RC \equiv CH$) [25] hydrocarbons, the primary electron transfer in the abstraction of a hydrogen atom from their molecules is believed to have been experimentally demonstrated.

The photochemical reduction of anthraquinone and its derivatives on cellulose [66] and the hydrated surface of silica gel [67] is evidently closely related to the photochemical dehydrogenation of alcohols in matrices as regards mechanism (in the sense that a hydrogen atom is abstracted from the hydroxy-group). On the other hand, in solutions the abstraction of a hydrogen atom by excited quinone molecules from the hydroxy-group of the reductant (other than water) has been observed for certain oximes ($R^1R^2C=NOH$) with formation of iminoxy-radicals ($R^1R^2C=NO^\cdot$) from the latter [68] and for t-butylphenols with formation of the corresponding phenoxy-radicals [69]. In the latter case, the radicals produced from the substrate and the reductant have the same spin polarisations (which has been demonstrated by chemically induced dynamic electron polarisation), in agreement with the theoretical model propoced by the authors [69]. The spin states of the radicals formed in the photochemical reduction of quinones were also considered in other studies [23,70].

Finally, we shall consider the possibility of a type of intermolecular photochemical reduction of quinones where the reductant is the quinone molecule in the ground state. It is suggested, for example, that at fairly high concentrations of 2-sulphoanthraquinone, its excited molecules

react with the unexcited molecules and form the corresponding radical-anion ($Q^{\cdot-}$) and radical-cation ($Q^{\cdot+}$). Their interaction with H^+ and OH^- ions (from water) leads to anthrasemiquinonesulphonate ($QH^{\cdot}$) and the $^{\cdot}OH$ radical [71-74]:

$$Q^* + Q \longrightarrow [Q^{\cdot-}\ Q^{\cdot+}] \longrightarrow Q^{\cdot+} + Q^{\cdot-}$$
$$[Q^{\cdot-}\ Q^{\cdot+}] \xrightarrow{H_2O/-OH} Q + {}^{\cdot}OH,$$
$$Q^{\cdot-} + H^+ \rightarrow QH^{\cdot}.$$

It is suggested that this mechanism be regarded as a pathway competing with other pathways to the photochemical reduction of 2-sulphoanthraquinone (as well as quinones of other types) under any conditions [72], although its feasibility has frequently aroused doubts [73-76] or has been rejected on energetic grounds [15], the photochemical reduction of 2-sulphoanthraquinone being attributed solely to the interaction of the excited substrate (Q^*) and the reductant ($^-OH/H_2O$).

It is assumed that the excited quinone molecule may also be reduced by a quinone molecule in the ground state as a result of the oxidation of a substituent and not the quinonoid ring—for example, such a pathway is possible (but has not been demonstrated rigorously), in the photochemical reduction of alkoxymethyl-1,4-benzoquinones [2].

2. Secondary Intermolecular Photochemical Reduction Reactions

Intermolecular photochemical reduction involves numerous secondary reactions in which quinones and their reduced forms, the reductants, and their oxidation products participate in various combinations.

Apart from its formation in the photochemical process, the product of the one-electron reduction of the quinone can be obtained also in a secondary dark reaction of the quinone with the radical (radical-anion) produced from the reductant, as happens, for example, in alcoholic media [2,77]:

$$Q + R\dot{C}HOH \rightarrow QH^{\cdot} + RCHO.$$

The interaction of the product of the one-electron reduction of the quinone and the oxidised substance can lead to the regeneration of the initial compounds. Thus, this type of reaction is fairly rapid in the photochemical reduction of sulphoanthraquinones by the CO_3^{2-} ion [6,15,78]:

$$Q^* + CO_3^{2-} \rightarrow Q^{\cdot-} + CO_3^{\cdot-}, \qquad Q^{\cdot-} + CO_3^{\cdot-} \rightarrow Q + CO_3^{2-}.$$

photochemical (forward) reaction — dark (reverse) reaction

The reverse reaction is frequently comparatively slow and there is then sufficient time for the product of the one-electron reduction of the quinone to undergo other reactions. In particular, regardless of which of the species ($QH^{\cdot}$ or $Q^{\cdot-}$) arises in the primary photochemical step, an equilibrium is established among the photolysis products:

$$QH^{\cdot} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} Q^{\cdot-}.$$

Its position is determined by the acid–base properties of these species and the medium [2,15,21,79-81].

In the ground or a high vibrationally excited state, the semiquinone can abstract a hydrogen atom from the reductant, forming the hydroquinone (QH_2): [2,82]

$$QH^{\cdot} + AH \rightarrow QH_2 + A^{\cdot}.$$

The study of the photochemical reduction of anthraquinone in alcohols with added alkali led the author to the conclusion that there is also a possibility of the photochemical reaction of the products of the one-electron and two-electron reduction of the quinone [83,84]:

$$(QH^{\cdot})^* \xrightarrow{AH} QH_2 + A^{\cdot}$$
or
$$(Q^{\cdot-})^* \xrightarrow{X} Q^{2-} + (X - \bar{e}).$$

However, hydroquinones are not formed solely in the processes enumerated above. It is believed that the main pathways to their formation is the disproportionation of the semiquinones $QH^{\cdot}$ and the radical-anions $Q^{\cdot-}$ in the reversible process [2,15,72,77,79,82,85-87]; the semiquinones then disproportionate approximately 10 and more times as efficiently as the radical-anions [2,15,79]. All these substances are at the same time involved in an acid–base equilibrium:

$$2\,Q^{\cdot-} \rightleftarrows Q^{2-} + Q \qquad 2\,QH^{\cdot} \rightleftarrows QH_2 + Q$$
$$Q^{\cdot-} \xrightarrow{+H^+} QH^- \xrightarrow{+H^+} QH^{\cdot}$$
$$QH^{\cdot} \xrightarrow{-H^+} QH^- \xrightarrow{-H^+} Q^{2-}$$

where QH^- and Q^{2-} are the hydroquinone mono- and di-anions.

In certain cases (see Refs. 88–90), the hydroquinones thus produced can retard the photochemical reduction of the quinone, deactivating its excited state (chemical quenching) via the reaction

$$Q^* + QH_2 \rightarrow 2QH^{\cdot} \rightarrow Q + QH_2$$

or can undergo further photochemical reduction. Thus it has been established that prolonged irradiation of anthrahydroquinone and its derivatives produced photochemically in hydrocarbons [91] and alcohols as well as aqueous alcoholic media [31,40,92-94] leads to the corresponding anthrols, anthrones, and anthracene.

Taking into account the above formation reactions and subsequent transformations of the reduced forms of quinones, a mathematical model has been devised for the intermolecular photochemical reduction of quinones, which describes satisfactorily the process as a whole [95,96].

Semiquinones as well as radical-anions, hydroquinones, and their dissociated forms are produced in deaerated media, since they are all readily oxidised by oxygen (and are capable of being oxidised by other reagents [2,15,97]) with regeneration of the initial quinone [15,47,72]:

$$QH^{\cdot} + O_2 \rightarrow Q + HO_2^{\cdot}; \quad Q^{\cdot-} + O_2 \rightarrow Q + O_2^{\cdot-};$$
$$QH_2 + O_2 \rightarrow Q + H_2O_2.$$

Under aerobic conditions, the overall process appears to involve the photochemical oxidation of the reductant and there is good reason for the term "photochemical oxidation sensitised by quinones" frequently given to it [15]. When the reductant is an alcohol, the overall mechanism is as follows [72]:

$$Q^* + RCH_2OH \rightarrow QH^{\cdot} + R\dot{C}HOH,$$
$$Q + R\dot{C}HOH \rightarrow QH^{\cdot} + RCHO,$$
$$QH^{\cdot} + O_2 \rightarrow Q + HO_2^{\cdot},$$
$$R\dot{C}HOH + O_2 \rightarrow RCH(O_2^{\cdot})OH,$$
$$RCH(O_2^{\cdot})OH + HO_2^{\cdot} \rightarrow RCHO + H_2O_2 + O_2,$$
$$2\,RCH(O_2^{\cdot})OH \rightarrow 2\,RCO_2H + H_2O_2,$$
$$RCH(O_2^{\cdot})OH \rightarrow RCHO + HO_2^{\cdot},$$
$$2\,HO_2^{\cdot} \rightarrow H_2O_2 + O_2.$$

The mechanism does not include hydroquinones QH_2, since there is insufficient time for their formation from

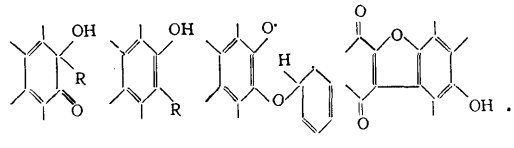
the semiquinones QH· owing to the rapid oxidation of the latter[15]‡. Naturally, such photochemical oxidation of the reductant can be achieved only in those cases where oxygen does not quench or only slightly quenches the reactive state of the quinone. In particular, this happens for anthraquinone and its derivatives owing to the short lifetime of their T states[6,15,75,76,100].

In the light of the foregoing considerations, the photochemical reduction of anthraquinone dyes in matrices in the presence of air as a result of the transfer of a hydrogen atom (or electron) appears fairly probable and is believed to be the main primary process in the theory of the photochemical degradation of materials coloured by such dyes which is most widely held at the present time[15,38,39,100-105].

The secondary intermolecular photochemical reduction processes, described above in the most general form, are the most typical examples; the specific products of similar and other secondary reactions as well as the pathways leading to their formation are discussed below.

Hydrocarbons. The hydrocarbon radicals arising in the photochemical oxidation of hydrocarbons by *p*-quinones under anaerobic conditions alkylate the quinone (semiquinone) ring and add to the oxygen atom, forming ultimately a hydroquinone ether, or are dehydrogenated by the quinone (semiquinone) to alkenes[1,2]. In the photochemical reduction of *o*-quinones by hydrocarbons, 1,2-addition [compounds (II)] and 1,4-addition [compounds (III)] products are obtained[1-3]. Thus the cyclohexyl radicals generated in the photolysis of 1,4-benzoquinone in cyclohexane give rise to cyclohexyl-1,4-benzoquinone and cyclohexene in the corresponding reactions[2]. By irradiating quinizarin in aliphatic hydrocarbons, alkyl derivatives of its leuco-form were obtained, but the positions of the alkyl groups were not established[106].

Mainly cycloaddition products are formed in the photochemical reactions of *o*-quinones with olefins, but the photolysis of phenanthrenequinone in the presence of isobutene, *cis*- and *trans*-but-2-enes, and tri- and tetramethylethylenes also results in the formation of the compounds (II, $R=CH_2CR^1=CR^2R^3$, $CR^2R^3CR^1=CH_2$) as a result of the capture of the allyl radical by the semiquinone[3]:



(II) (III) (IV) (V)

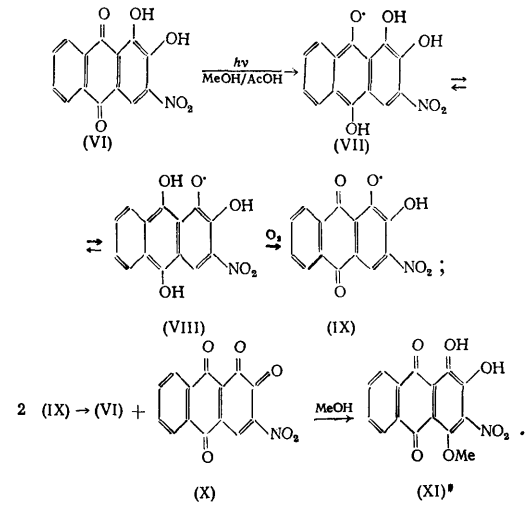
The nature of the secondary products of the photochemical reduction of quinones by alkylbenzenes as a function of the nature of the quinone and the radical formed from the reductant has been more thoroughly investigated than for aliphatic hydrocarbons. The photochemical reduction of *p*-quinones with a relatively high oxidation-reduction potential yields products of the addition of radicals of the type $Ar\dot{C}H_2$ to the oxygen atom and of the dehydrogenation of radicals of the type $Ar\dot{C}H-CH$. Thus irradiation of tetrachloro-1,4-benzoquinone (but not of 1,4-benzo- and naphthoquinones) in the presence of *p*-xylene, cumene, or tetralin leads respectively to the mono-*p*-methylbenzyl ether of 1,4-dihydroxybenzene, methylstyrene, and 1,2-dihydronaphthalene[2].

The radicals obtained by the abstraction of a benzyl hydrogen atom in the photolysis of the corresponding compounds in the presence of *o*-quinones are sometimes dehydrogenated[107], but 1,2- and 1,4-addition products are normally formed[1,2,5]. The ratio of the products of the 1,2- and 1,4-addition of the p-$RC_6H_4\dot{C}H_2$ radicals has been shown[2] to be determined by the nature of the substituent R—the fraction of the 1,2-addition product increase with increase of its electron-donating capacity owing to the electron deficiency at the carbon atom and the electron excess at the oxygen atom of the semiquinone.

By irradiating phenanthrenequinone[3,108] and tetrachloro-1,2-benzoquinone[3] in benzene, the monophenyl ethers of the hydroquinones (III, R = Ph) were obtained together with the corresponding hydroquinones and biphenyl. In the case of phenanthrenequinone, the formation of a 1,4-adduct is assumed to result from the intramolecular abstraction of a hydrogen atom from the biradical (IV) produced photochemically; incidentally, the usual pathway involving the recombination of the semiquinone and phenyl radicals, but without their emergence from the solvent cage, is not excluded either.

One should bear in mind that, apart from the above pathways leading to the stabilisation of hydrocarbon radicals, another pathway, which is not discussed here, frequently occurs, namely their recombination[2,109].

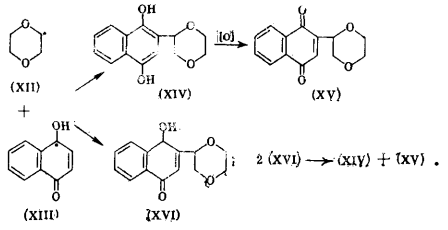
Alcohols. In contrast to hydrocarbon radicals, the $R^1R^2\dot{C}OH$ radicals obtained in the photochemical oxidation of alcohols by quinones do not form adducts with the latter or with their reduced forms. They are stabilised by disproportionation or are dehydrogenated by the quinone or the semiquinone. Semiquinones are stabilised in alcoholic solutions by an intramolecular mechanism or interact (sometimes after conversion into other intermediates) with the solvent. An example of the first pathway is the formation of the cyclic products (V) when 2,2'-biphenyl- and 2,2'-binaphthyl-1,4,1',4'-diquinones are irradiated in alcohols[2]. The second pathway is illustrated by the conversion of 1,2-dihydroxy-3-nitroanthraquinone (VI) into 1,2-dihydroxy-4-methoxy-3-nitroanthraquinone (XI):[2]



(VI) (VII) (VIII) (IX) (X) (XI)

‡ All the secondary reactions of semiquinones or the corresponding radical-anions discussed above can be suppressed by combining the reactive species into complexes and micelles[98,99].

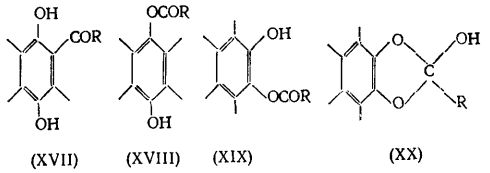
Ethers and related compounds. The radicals generated in the photochemical oxidation of ethers (thioethers) by quinones alkylate *p*-semiquinones in the ring form 1,2- and 1,4-addition products with *o*-semiquinones. For example, the dioxanyl radical (XII) was found to react with the radical (XIII) (obtained from 1,4-naphthoquinone), compound (XV) being the final product [110]. The dioxanyl derivative of 1,4-benzoquinone may be present among the unidentified products of the photolysis of 1,4-benzoquinone in dioxan [2]. Phenoxymethyl-1,4-benzoquinone is obtained similarly by the irradiation of 1,4-benzoquinone in aqueous anisole [2]:



1,4-Addition products are formed by the recombination of radicals generated from *o*-quinones and ethers (thioethers), i.e. by the reactions of tetrachloro-1,2-benzoquinone with dioxan [2] and of phenanthrenequinone with di-isopropyl, dibutyl [110], benzyl phenyl, and dibenzyl ethers as well as the dibenzyl ethers of ethyleneglycol and 1,4-dihydroxybenzene [111], ethyl acetate and propionate, dithian [2], and ethyl vinyl sulphide [3]. In most cases the products are unstable and readily decompose in air, for example as a result of hydrolysis, while on irradiation they can rearrange to 1,2-addition products, as shown for the adducts of phenanthrenequinone with anisole and dioxan [2].

The formation of the 1,2-addition product in the photolysis of acenaphthenequinone in tetrahydrofuran [112] and of 1,4-dihydro-2-hydroxy-1-oxo-4-xanthylnaphthalene on irradiation of 1,2-naphthoquinone or its 3-chloro, 3-bromo-, and 6-bromo-derivatives in the presence of xanthene are rarer examples [113,114].

Aldehydes. The products of the secondary reactions in the photochemical reduction of *p*-quinones by aldehydes are compounds of type (XVII) and (or) (XVIII):

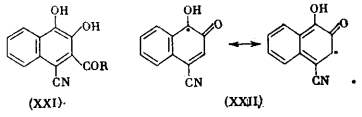


Ring acetylation by the $CH_3\dot{C}O$ radical occurs in the photolysis of 1,4-benzoquinone and its mono-, di-, and tri-methyl, acetyl, and 2,3-dichloro-derivatives, 1,4-naphthoquinone, 2-methylnaphthoquinone [2], 1,4,9,10-anthradiquinone, 1,4,5,8-naphthodiquinone, the anhydride of 1,4-benzoquinone-2,3-dicarboxylic acid, and 2,3-dicyano-1,4-benzoquinone [115,116] in acetaldehyde; the products of the photolysis of anthraquinone in acetaldehyde were not identified [2]. Acyl derivatives of type (XVII) have also been obtained in the photolysis of 1,4-benzoquinone in the presence of trimethylacetaldehyde and acrylaldehyde [2,115]. Diacylhydroquinones are sometimes formed in these processes [2].

The final products of the reactions of tetrasubstituted 1,4-benzoquinones (dichlorodicyano- and tetrachloro-derivatives) are hydroquinone monoethers, which are formed also in the photolysis of quinizarin in the presence of the aldehydes *p*-XC_6H_4CHO (X = H, NO_2, or MeO). [2] Irradiation of 1,4-benzoquinone in the presence of cinnamaldehyde yielded only the hydroquinone monoether [3], irradiation of cortonaldehyde gave both possible substances of types (XVII) and (XVIII), [115] and irradiation of the benzaldehydes *p*-XC_6H_4CHO resulted in the formation of benzoylhydroquinones (X = Me, t-Bu, or MeO) and monobenzoates (X = NO_2, CHO, CN, or CF_3). [115]

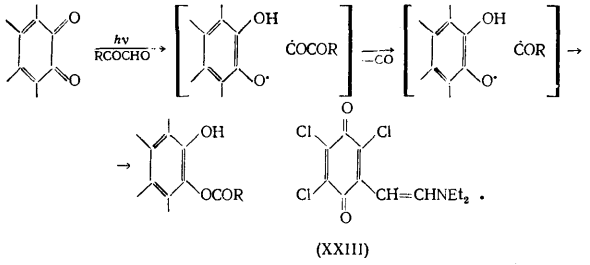
Together with the view that the $R\dot{C}O$ radicals and the semiquinone are involved in the formation of compounds (XVII) and (XVIII), there exists another hypothesis, namely that the $R\dot{C}O$ radical reacts with the quinone [2,115]. It is believed that the nature of the reaction product [(XVII) or (XVIII)] depends on the nucleophilic properties of the $R\dot{C}O$ radical: the more nucleophilic the radical, the greater the probability of attack on the ring (if not all its positions are occupied) and, conversely, a decrease of nucleophilicity leads to an increased yield of the ether. The oxidation-reduction potential of the quinone plays a significant role. Thus, it is assumed that a competitive mechanism involving electron transfer from the $R\dot{C}O$ radical to the quinone Q and the formation of the radical-ion pair $[Q^-R\dot{C}O^+]$, in which the acylium ion should be localised near one of the oxygen atoms, operates in the case of quinones with high oxidation-reduction potentials (1,4,9,10-anthradiquinone, 1,4,5,8-naphthodiquinone, the anhydride of 1,4-benzoquinone-2,3-dicarboxylic acid, and 2,3-dicyano-1,4-benzoquinone). This also explains the interaction of acyl radicals with the above quinones at the oxygen atom.

The photolysis of *o*-quinones in the presence of aldehydes yields mainly 1,4-addition products—the monoethers of 1,2-enediols (XIX) and (or) the cyclic acetals (XX): [2,3,117]



By irradiating 1,2-naphthoquinone and many of its derivatives in aliphatic (but not aromatic [2]) aldehydes, it was possible to obtain ring-acylation products (XXI) [evidently by the recombination of the radicals (XXII) and $R\dot{C}O$ [2,3,109]], in addition to enediol ethers of type (XIX), and to substitute the halogen atom (if present) in the 3-position in the acyl group.

Compounds of type (XIX) are formed on recombination of the radicals $RCO\dot{C}O$ obtained from glyoxals and semiquinones as a consequence of decarbonylation in the solvent cage [118]:



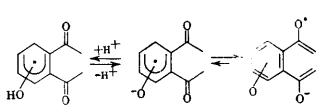
Amines. The excitation of [amine$^+$ quinone$^-$] CTC or the [(amine − H)$^\cdot$ (quinone + H)$^\cdot$] radical pair in quinone

(2,5-dichloro-3,6-dimethoxy- and tetrachloro-1,4-benzoquinones)–tertiary amine (triethylamine and 2-methylpiperidine) systems leads to the hydroquinone monoanion (QH^-) and an ion of the type $Et_2\overset{+}{N}=CHCH_3$. When they interact, the chlorine atom is substituted with formation of aminovinylquinones, for example (XXIII).[2]

Water, H^+ and OH^- ions, and ammonia. The photolysis of tetramethyl-1,4-benzoquinone in water yields only the corresponding hydroquinone[2,119], while 1,2,4-trihydroxybenzene and (or) 2-hydroxy-1,4-benzoquinone have been obtained from 1,4-benzoquinone in addition to 1,4-dihydroxybenzene[2,119–122]. The formation of these substances has been explained[121] by the interaction of the photochemically generated ·OH radical with the quinone (or semiquinone). The 1,2,4-trihydroxybenzene thus produced reacts with the initial quinone to form 2-hydroxy-1,4-benzoquinone and 1,4-dihydroxybenzene. This oxidation is faster in acid and alkaline solutions and is slow in solutions close to neutrality; consequently the pH of the medium determines the composition of the final products. The alternative mechanism involving the abstraction of the ·OH radical from water by the excited quinone followed by attack by a hydrogen atom on the quinone molecule in the ground state[2] appears much less probable.

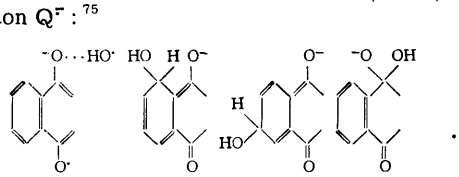
The efficiency of the single-photon process involving the disappearance of 1,4-benzoquinone is independent of its concentration in solution and of the wavelength of the exciting light, remaining constant in the pH range between 0.4 and 8; according to some data, the quantum yield is smaller than unity[2,119–121], while according to others[122] it is greater than unity. The variation of the quantum yield in the photolysis of 1,4-benzoquinone in micellar systems (increased and decreased respectively in the presence of anionic and cationic surfactants) can indicate, according to some workers[119], the involvement of cationic intermediates in the process.

The weakly electrophilic ·OH radicals generated in the photolysis of 2-sulphoanthraquinone in neutral, aqueous alkaline[15,75,123–127], and aqueous alcoholic[2,48,124,128] media hydroxylate sulphoanthraquinone in the range without the sulpho-group[15]. The adduct (XXIV) formed is oxidised by the initial quinone or oxygen to hydroxysulphoanthraquinone[15,123,129,130]:



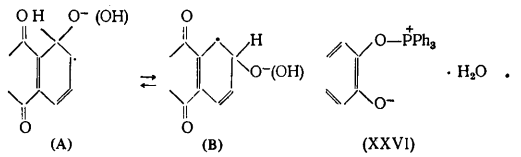
(XXIVa) (XXIVb) (XXIVc)

A hydrogen-bonded complex (XXVa) or an adduct of type (XXVb)–(XXVd) may precede the intermediate (XXIV) and only their interaction with an unexcited sulphoanthraquinone molecule leads to the adduct (XXIV) and the radical-anion $Q^{\cdot-}$:[75]



(XXVa) (XXVb) (XXVc) (XXVd)

The composition of the products of the hydroxylation of 2-sulphoanthraquinone as well as 1,4-benzoquinone depends on the pH of the medium: in highly alkaline solutions (pH ≥ 12), the main products are 6- or 7-hydroxyanthraquinone-2-sulphonates, while in neutral and weakly alkaline solutions (pH ≤ 12), the main products are 6-, 7-, 5-, and 8-hydroxy-derivatives[15,130], this is attributed either to the different natures of the hydroxylating agents (·OH or $O^{\cdot-}$ formed as a result of the $\cdot OH \rightleftharpoons O^{\cdot-} + H^+$ equilibrium)[15,126] or to the reversible interconversion of forms A and B, which depends on the pH of the medium[75]:



(A) (B) (XXVI)

1-Sulphoanthraquinone, which is photochemically reduced with greater difficulty and has therefore been less thoroughly investigated in photochemical hydroxylation reactions, evidently yields hydroxy-1-sulphoanthraquinones by a similar mechanism.

Photochemical hydroxylation yields dihydroxy-derivatives of sulphoanthraquinones in addition to the monohydroxy-derivatives; their formation is promoted by the decrease in the concentration of the substrate and when the photolysis is carried out under aerobic conditions[130]. The selectivity of the hydroxylation reaction and the possibility of introducing the OH group into other aromatic compounds present in the reaction mixture, particularly in a cyclic process using oxidants, can make it useful for the synthesis of aromatic hydroxy-derivatives[15].

Amination of 2-sulphoanthraquinone in its photolysis in aqueous ammonia, hydrazine, and methylamine solutions, resulting in the preferential formation of 6(7)-amino-(methylamino)-2-sulphoanthraquinones[15], is tentatively assumed to involve a mechanism similar to that of photochemical hydroxylation.

In the instances described above, the oxidised form of the reductant interacts with the quinone, but processes are also known where the reduced forms of the quinones interact with the reductants (solvents). For example, the displacement of methoxy-group by the OH^- ion (dark process) on irradiation of 1- and 2-methoxyanthraquinones in alkaline aqueous alcoholic solutions occurs precisely in the way described—in the photochemically generated dissociated methoxyanthrasemiquinones[131]. The semiquinone obtained by the photochemical reduction of phenanthrenequinone in water reacts similarly with triphenylphosphine and then either with water or with the ·CH radical, forming the dipolar hydrate (XXVI), which is unstable in air[132].

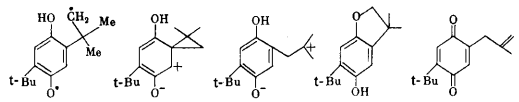
The functional groups in quinones reduced by the two-electron mechanism are also capable of reacting under the influence of the reductant. In particular, it has been established that anthrahydroquinonesulphonic acids dissociated at the alcoholic hydroxyl—the products of the reaction of photochemically generated anthrasemiquinonesulphonates—eliminate the sulpho-group on photoexcitation[15,94,133,134]. The quantum yield of this single-photon process has been shown in the case of 1-sulphoanthrahydroquinone to be higher for the dianion than for the monoanion and to be independent of the concentration of OH^- ions in the region corresponding to the existence of both forms. It is assumed that the highest electronically excited state of the substrate is reactive, since desulphonation proceeds effectively only on excitation with light corresponding to the absorption band at the shortest wavelength. The sulpho-group in the β-position is eliminated with greater difficulty than that in the α-position; halogenoanthrahydroquinonesulphonic acids undergo photochemical dehalogenation together with photochemical

desulphonation[15,94]. The photochemical desulphonation of undissociated anthrahydroquinonesulphonic acids, obtained by the photolysis of sulphoanthraquinones in aqueous alcoholic solutions of inorganic acids proceeds via a different (hydrolytic) mechanism; in this case, light is photochemically active over the entire region corresponding to absorption by sulphoanthrahydroquinones[135,136].

3. Secondary Intramolecular Photochemical Reduction Reactions

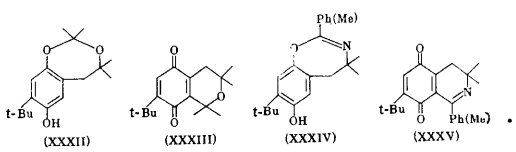
Intramolecular photochemical reduction of quinones almost always involves the abstraction of a hydrogen atom from the 2'-position of the side chain via a readily achieved six-membered cyclic transition state. This determines both the structure of the biradicals generated and the nature of the products formed on their stabilisation (intramolecular or intermolecular) with participation of the solvent.

Quinones with a hydrocarbon side chain. The radicals (XXVII), obtained from t-butyl-1,4-benzoquinones on photolysis of the latter in benzene, dioxan[137], acetone, acetonitrile, and benzonitrile[138], are converted into a zwitter-ionic spirocyclopropane structure (XXVIII), which exhibits a strong tendency towards aromatisation. Because of this, the three-numbered ring is cleaved and converted into the structure (XXIX):



(XXVII) (XXVIII) (XXIX) (XXX) (XXXI)

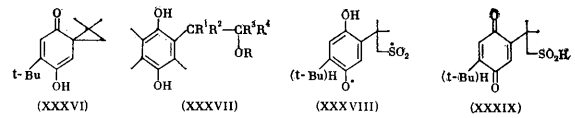
When the latter is subjected to nucleophilic attack, it can give rise to dihydrobenzofuran (XXX), the products of the rearrangement of the side chain (XXXI), and the products (XXXII)–(XXXV) resulting from the 1,4- and 1,5-cycloaddition of solvents (acetone, nitriles)[138,139]:



(XXXII) (XXXIII) (XXXIV) (XXXV)

Incidentally, one cannot rule out the possibility that the spiroketone (XXXVI) is an intermediate, the anomalous Claisen rearrangements of which yields compound (XXXI), while the remaining substances, (XXX) and (XXXII)–(XXXV), are formed as a result of the opening of the cyclopropane ring[138,139]. It is noteworthy that other compounds, in addition to those described, are formed, but their yields are insignificant[140].

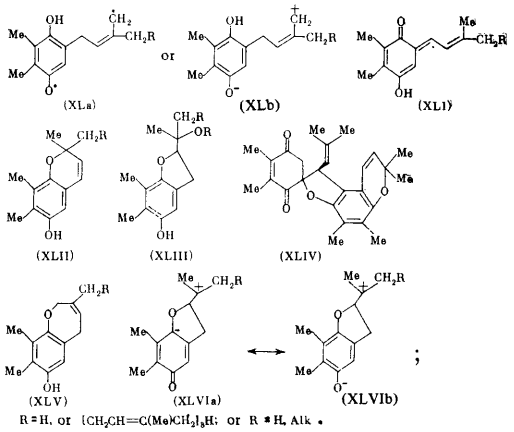
The exclusive formation of dihydrobenzofuran derivatives of type (XXX) was noted in the photolysis of 2-(2-phenylethyl)- and 2-(2,2-diphenylethyl)-1,4-benzoquinones in benzene[141]. Apart from similar substances, products resulting from the introduction of an alkoxy-group in the 2'-position [compounds (XXXVII)] are formed preferentially from 2-ethyl-, 2-isobutyl-, 2,5-dipropyl-,[139] 2-t-butyl-,[2,137] 2,5-di-t-butyl-, and 2,6-di-t-butyl-1,4-benzoquinones[2,137,142], probably via the interaction of the ROH alcohol molecule with a structure of type (XXVII) or (XXIX). *O*-Alkylation of the hydroquinones thus produced is possible[2], but data concerning the insertion of an alkoxy-group in the hydroquinone rings[143] are erroneous[2]:



(XXXVI) (XXXVII) (XXXVIII) (XXXIX)

The interaction of biradicals of type (XXVII), generated in the photolysis of t-butyl- and 2,5-di-t-butyl-1,4-benzoquinones with SO_2, leads to structures (XXXVIII), and the migration of hydrogen in the latter results in the formation of unstable sulphinic acids (XXXIX).[144]

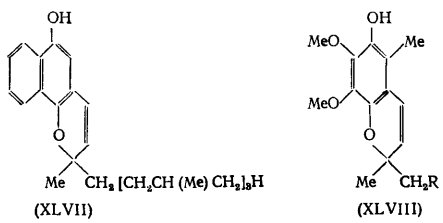
Structures (XL), formed by the intramolecular photochemical reduction of plastoquinones 1 [145,146] and plastoquinones 9 [146,147] on photolysis in benzenes, alcohols R'OH, and aqueous organic mixtures, are believed[145–147] to be stabilised by conversion into intermediate hydroxy-derivatives of *o*-methylenequinones (XLI) or into the corresponding anions. Their intramolecular cyclisation leads to compounds (XLII) and the reactions of the latter with addition of alcohol or water result in the formation of dihydrobenzofuran derivatives (XLIII); attack by a plastoquinone molecule yields the spiro-compound (XLIV). Compound (XLV) can be obtained from the intermediate structure (XL). The previously assumed[145] formation of dihydrobenzofurans (XLIII) in the interaction of alcohols (water) with the zwitter-ions (XLVI) and the involvement in this process of the radicals obtained by the intermolecular abstraction of a hydrogen atom are less likely:



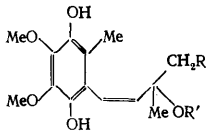
(XLa) (XLb) (XLI) (XLII) (XLIII) (XLIV) (XLV) (XLVIa) (XLVIb)

R = H, or $[CH_2CH{=}C(Me)CH_2]_3H$; or R = H, Alk.

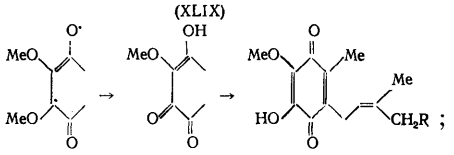
Irradiation of vitamin K_1 in benzene, ethanol, and water[148–151] and of certain coenzyme quinonoid structures in alcohols (R'OH)[2,152] leads in a similar manner—via the intermediate hydroxy-*o*-methylenequinones—to naphthopyranol (XLVII) and chromenols (XLVIII). The formation of the latter is accompanied by hydroquinones (XLIX), which are converted on oxidation into the corresponding quinones and the series of transformations (L) → (LI) → (LII) leads to demethylation products (LII):



(XLVII) (XLVIII)



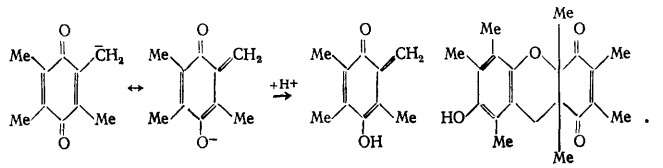
(XLIX)



(L) (LI) (LII)

R=[CH_2CH=C(Me)CH_2]$_n$H, n=3,6,9.

The formation of the adduct (LV) is also explained by the photochemical generation of hydroxy-*o*-methylenequinone (LIV) from tetramethyl-1,4-benzoquinone and its interaction with the unexcited substrate. The deprotonation of tetramethyl-1,4-benzoquinone in the T state and the subsequent protonation of structure (LIII) at the oxygen atom is considered to be a possible reaction pathway [27,64,153]:

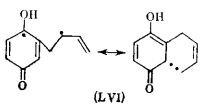


(LIII) (LIV) (LV)

The possibility that hydroxy-*o*-methylenequinones can indeed serve as intermediates in the processes discussed has been demonstrated by the detection of long-lived compounds of type (XLI) and their anions in the flash photolysis of 1-tocoquinone and vitamin K_1 in alcohols and hydrocarbons [154,155].

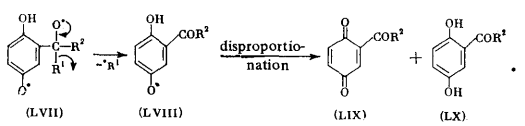
If there is a multiple bond in the 1-position in the side chain, as in 2-(1-methylvinyl)- and 2-(2,2-diphenylvinyl)-1,4-benzoquinones, then photolysis yields benzofuran structures exclusively [2].

The formation of 1,4-dihydro-5,8-dihydroxynaphthalene on irradiation of 2-(3-but-1-enyl)-1,4-benzoquinone under the same conditions is explained by the stabilisation of the biradical (LVI) [2]:



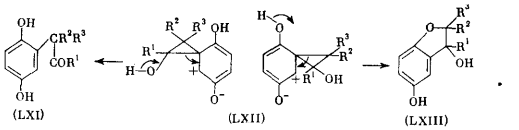
(LVI)

Quinones with oxygen-containing groups. A hydrogen atom may be abstracted during the intramolecular photochemical reduction of hydroxyalkylquinones both from the hydroxy-group and from a carbon atom in the side chain. The former mechanism operates with (1-hydroxyalkyl)quinones in the absence of a hydrogen atom in the 2′-position (hydroxymethyl-1,4-benzoquinone [2] etc.). The biradicals (LVII) formed from these quinones are stabilised either by the addition of a solvent molecule to the radical oxygen atom in the side chain or by the elimination of the alkyl substituent (hydrogen atom) with conversion into radicals (LVIII); disproportionation of the latter leads to the quinones (LIX) and hydroquinones (LX) with an oxidised side chain [2,156]:



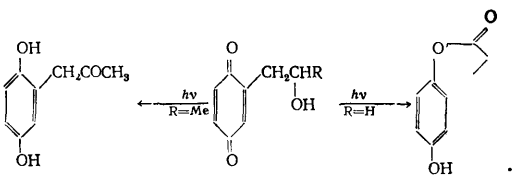
(LVII) (LVIII) (LIX) (LX)

The presence of a hydrogen atom in the 2′-position of (1-hydroxyalkyl)quinones, permits photochemical reduction via two pathways, the second of which gives rise to structures (LXII) analogous to those obtained from alkylquinones (see above). Subsequent reactions of these spirocyclopropane dipolar ions can lead to dihydrobenzofurans (LVIII); owing to the presence of the hydroxy-group, rearrangement to compounds (LXI) becomes possible at the same time [156]:



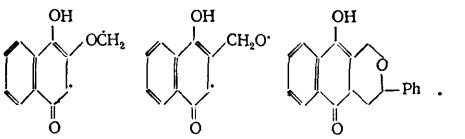
(LXI) (LXII) (LXIII)

The reactions of the biradicals formed as a result of the abstraction of a hydrogen atom exclusively from the 2′-position on photolysis of (2-hydroxyalkyl)-1,4-benzoquinones (LXV) leads to similar products [(LXIV) and (LXVI)]: [2]



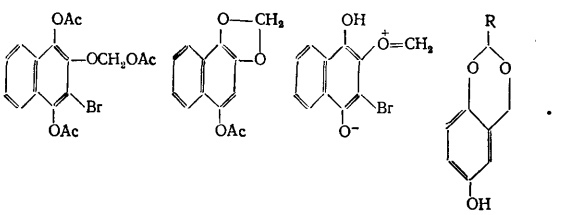
(LXIV) (LXV) (LXVI)

The biradical (LXVII), generated in the photolysis of 2-methoxy-1,4-naphthoquinone in benzene solution, apparently rearranges to the more stable biradical (LXVIII), to which styrene adds, forming compound (LXIX); [157] at the same time, there is sufficient time for the biradical (LXVII) obtained in acetic anhydride to react with the solvent, forming 1,4-diacetoxy-2-methoxynaphthalene [158]:



(LXVII) (LXVIII) (LXIX)

The photolysis in acetic anhydride of the same quinone but with a bromine substituent in the 3-position leads to compounds (LXX) and (LXXI), tentatively via the intermediate dipolar structure (LXXII): [158]

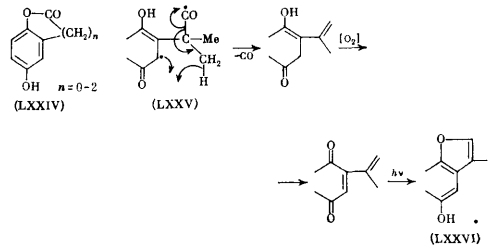


(LXX) (LXXI) (LXXII) (LXXIII)

On photolysis, alkoxymethyl-1,4-benzoquinones yield polymeric phenolic acetals as a result of the intermolecular interaction of the substrate which has undergone intramolecular reduction. Benzo-1,3-dioxans (LXXIII) are sometimes formed, which may indicate the possible involvement of radicals generated by intermolecular photochemical reduction [2].

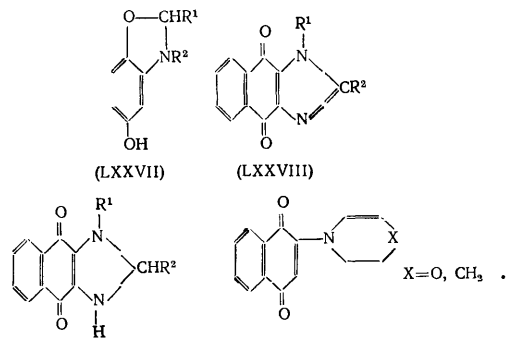
The presence of an ester group in the 2′-position of 1,4-benzoquinone does not lead to unexpected results following its photolysis: the corresponding benzofuran

derivative was obtained from 2-(2-ethoxycarbonylethyl)-1,4-benzoquinone in benzene[2]. If the side chain contains a terminal formyl group, the photochemical reaction products are lactones (LXXIV) or the corresponding hydroquinonecarboxylic acids[159]. The stabilisation of the biradicals (LXXV), obtained photochemically from 2-(1-formyl-1-methylethyl)-1,4-benzoquinone and the corresponding naphthoquinone, proceeds in a different way (with decarbonylation) and leads to benzo- and naphtho-furans of type (LXXVI) as a result of subsequent reactions[159]:



(LXXIV) (LXXV) (LXXVI)

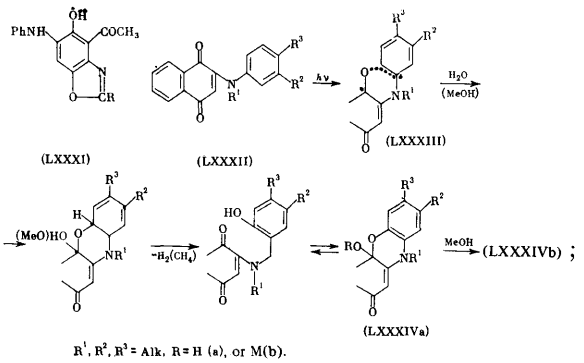
Aminoquinones. Amino-1,4-benzoquinones, containing the fragment $\rangle N-CH\langle$, give rise on photolysis to cyclisation products—derivatives of dihydro-oxazole (LXXVII).[2,160,161] Similar products were obtained from *NN*-dialkyl- or *N*-alkyl-2-amino-*N*-aryl-1,4-naphthoquinones when there was no amino-group in the 3-position[2,162,163]. Compounds (LXXVII) are unstable and undergo oxidative hydrolysis particularly readily, forming products resulting from the dealkylation of the initial quinones[2,161-163]:



(LXXVII) (LXXVIII) (LXXIX) (LXXX)

Naphthimidazoles (LXXVIII) and their dihydro-derivatives (LXXIX) have been obtained by the photolysis of 3-amino-2-dimethylamino(piperidino, morpholino)-1,4-naphthoquinones[164]. 2-Piperidino- and 2-morpholino-1,4-naphthoquinones do not cyclise but are dehydrogenated, forming compounds (LXXX).[165,166]. Although the mechanism of the formation of compounds (LXXVII)–(LXXX) has not been discussed, one cannot rule out intramolecular photochemical reduction as the first stage in such cases also.

The biradicals formed by the photochemical reduction of 2-acetyl-3-alkylamino-6-phenylamino-1,4-benzoquinones are converted, as a result of hydrogen transfer followed by ring closure and aromatisation (there is also a possibility of the formation of intermediate spiro-aziridines or imines) into the benzoxazole (LXXXI):[167,168]

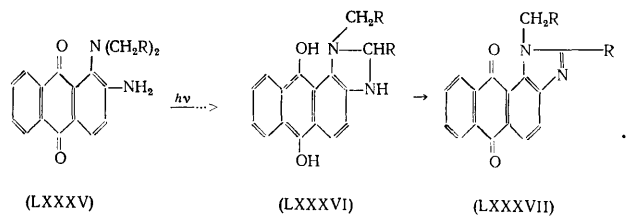


(LXXXI) (LXXXII) (LXXXIII) (LXXXIVa) (LXXXIVb)

R^1, R^2, R^3 = Alk, R = H (a), or M(b).

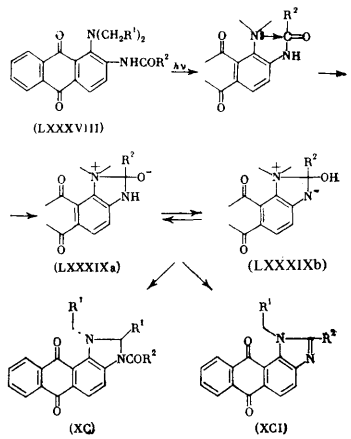
In the photolysis of *N*-substituted 2-phenylamino-1,4-naphthoquinones (LXXXII) in aqueous methanol solution, there is insufficient time for the intramolecular and intermolecular abstraction of a hydrogen atom by the biradical (LXXXIII) formed and the latter is stabilised by combining with a solvent molecule; the cyclisation products (LXXXIV) are formed ultimately[169].

The intramolecular photochemical reduction of the aminoanthraquinones (LXXXV) stabilises the intermediate biradicals by their conversion into anthrahydroquinones (LXXXVI), which are in turn converted into imidazoles (LXXXVII):[164]



(LXXXV) (LXXXVI) (LXXXVII)

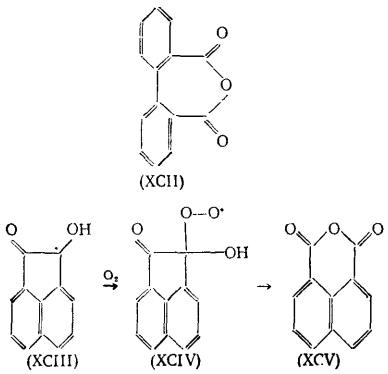
On the other hand, when an acylamino-group is present in the 2-position instead of the amino-group, it is reduced photochemically instead of the quinonoid moiety; the resulting dipolar structures (LXXXIX) are converted into imidazolines (XC) and imidazoles (XCI);[170,171] thus data[165,166] concerning the photochemical conversion of the acylamino-group of compounds (LXXXVIII) into the oxaziridine group were not confirmed:



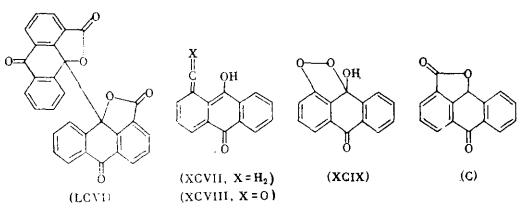
(LXXXVIII) (LXXXIXa) (LXXXIXb) (XC) (XCI)

III. PHOTOCHEMICAL OXIDATION

The photochemical oxidation of quinones reduces either to the oxidation of the side chain, which is characteristic of *p*-quinones or to the oxidative cleavage of the quinonoid fragment, which is characteristic of *o*-quinones. The primary step in the process is usually believed to be the photochemical reduction of the carbonyl group in one form or another. Thus the formation of the anhydrides (XCII) and (XCV) when aerobic solutions of phenanthrenequinone [3] and acenaphthenequinone [3,112] in acetonitrile, benzene, tetrahydrofuran, etc. are irradiated is attributed to the photochemical generation of a radical of type (XCII). The latter interacts with oxygen and gives rise to the peroxy-radical (XCIV), which is then converted into the anhydride (XCV):



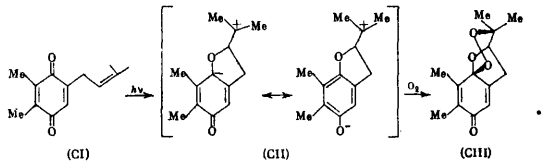
The photolysis of 1-methylanthraquinone in benzene saturated with oxygen yields compound (XCVI), while in the presence of air anthraquinone and anthraquinone-1-carboxylic acid are also formed [172,173]. In this case, the formation in the primary step of a photochemically enolised form of the quinone (XCVII) is postulated, the latter being converted by reaction with oxygen into the peroxide (XCIX) and then into 1-formylanthraquinone. The photochemical enolisation of the latter to the keten (XCVIII) and intramolecular attack by the hydroxyl on the keten group lead to the lactone (C) or its ketone tautomer. These compounds can be readily oxidised to the dilactone (XCVI). Anthraquinone is probably formed on photochemical decarbonylation of 1-formylanthraquinone:



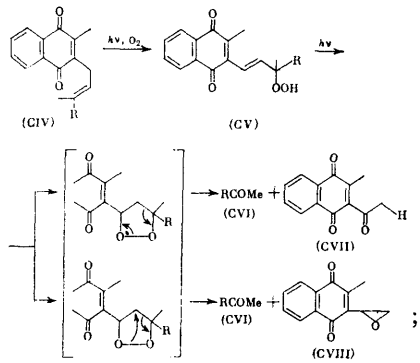
Products with a related structure have also been obtained from methyl-1,4-naphthoquinone [173].

1-Acetylanthraquinone was obtained by the photochemical oxidation of 1-ethylanthraquinone. The photochemical oxidation of the less reactive isomer (2-methyl- and 2-ethyl-anthraquinones) leads to anthraquinone-2-carboxylic acid and 2-acetylanthraquinone respectively [172,173], but the mechanism involving photochemical enolisation is apparently not applicable to these reactions.

The presence of a multiple bond (a π-electron donor) in the side chain of the quinone can lead to intramolecular cyclisation on excitation of the molecule. It has been suggested [145,174,175] that plastoquinone 1 (CI) is in fact converted in this way into the zwitter-ion (CII), which reacts with oxygen to form the peroxide (CIII). Oxygen is apparently involved in the process in its ground state, since the peroxide (CIII) is not formed when singlet oxygen generated with the aid of sensitisers acts upon compound (CI):

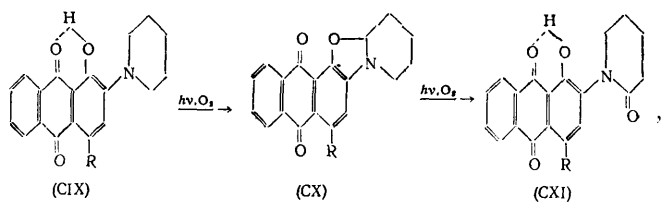


Other isoprenoid *p*-quinones (CIV) which have been investigated participate in the photochemical oxidation reaction in a different way: on reaction with singlet oxygen (generated in control experiments by means of dyes), they form hydroperoxides (CV). On irradiation, these substances are then converted into ketones (CVI) and compounds (CVII) and (CVIII); the latter were not isolated owing to their instability [176]:



R = Me, $CH_2CH_2CH{=}CHMe$, $(CH_2)_4Me$, $(CH_2CH{=}CMeCH_2)_2H$, or $(CH_2CH_2CHMeCH_2)_3H$.

The specific influence of the quinonoid fragment appears unlikely in the oxidative cyclisation of 2-dialkylamino-1-hydroxyanthraquinones (CIX) (but not the 1-amino-derivatives), leading to anthraoxazolines (CX), and in the photochemical oxidative cleavage of the heterocycle of the latter [177], as in the previous reaction:

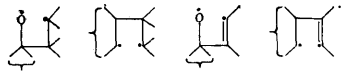


R=H,OH, or $NHCOCH_3$.

IV. PHOTOCHEMICAL ADDITION

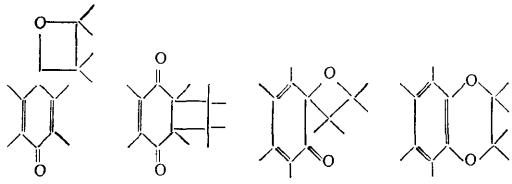
In almost all the processes examined, the reductant, a neutral molecule or an anion, behaves as a hydrogen atom or electron donor in relation to the excited quinone. We believe that one should not combine in a special group of reductants substances with multiple carbon–carbon bonds, differing from those described above by the nature of their interaction with quinones, since they are potential donors of π electrons. Presumably the transfer of π electrons from these substances to the oxygen or carbon

atom of the quinone leads to the formation of C–O and C–C bonds respectively in the photochemical step. The biradical structures (CXIIa) and (CXIIb) generated (by the addition of alkenes) or (CXIIIa) and (CXIIIb) (by the addition of alkynes) are subsequently stabilised by ring closure:



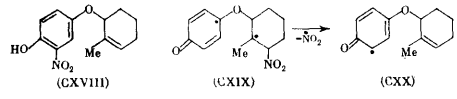
(CXIIa) (CXIIb) (CXIIIa) (CXIIIb)

As a result of photochemical addition to the C=C bond of such substances, *p*-quinones are converted into oxetans (CXIV) and cyclobutane derivatives (CXV), while *o*-quinones give rise to oxetans (CXVI) and 1,4-dioxens (CXVII); the photochemical addition of quinones to the C≡C bond of the reductant leads to the corresponding oxeten, cyclobutene, and 1,4-dioxin derivatives:



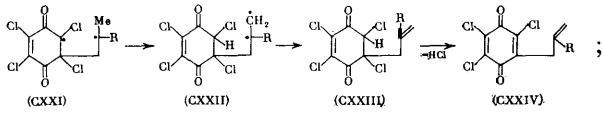
(CXIV) (CXV) (CXVI) (CXVII)

Substances with a different structure are formed much more rarely. Their generation is usually associated with the fact that there is insufficient time for the biradicals produced on addition of unsaturated hydrocarbons to undergo ring closure and they are stabilised in a different way. For example, the photochemical reaction of 1,4-benzoquinone with 1-methyl-6-nitro-1-cyclohexene gave compound (CXVIII), probably as a result of the elimination of the NO_2 group from the biradical (CXIX) with its subsequent addition to the radical (CXX):[178]



(CXVIII) (CXIX) (CXX)

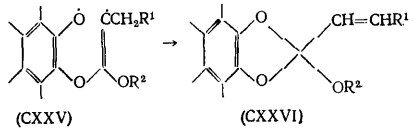
In another instance, the photolysis of tetrachloro-1,4-benzoquinone in the presence of 2-methylpropene or 2,3-dimethylbuta-1,3-diene produces biradicals (CXXI) which are converted as a result of hydrogen migration into (CXXII), after which pairing of electrons leads to (CXXIII); the latter compound is unstable, splits off HCl, and thus gives rise to compound (CXXIV):[179]



(CXXI) (CXXII) (CXXIII) (CXXIV)

R = Me or CMe = CH_2 .

The formation of dioxoles (CXXVI) on photolysis of phenanthrenequinone in the presence of alkyl- or alkoxyacetylenes has been explained[3,180,181] by a 1,2-hydrogen shift in the biradicals (CXXV) formed, which leads to allyl biradicals, stabilised by closure to a dioxole ring:



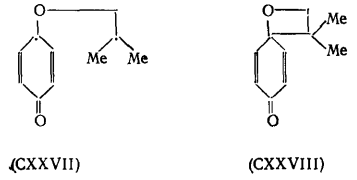
(CXXV) (CXXVI)

The quinone always participates in photochemical addition reactions in the excited state. In most but not all instances the triplet state of the substrate is then reactive and it is therefore desirable to explain the nature of the reactive excited state in each specific instance. The photochemical reaction of tetramethyl-1,4-benzoquinone with cyclo-octene is interesting from this point of view: in the presence of an excess of the quinone, the product is an oxetan and in the presence of an excess of cyclo-octene, it is a 1:2 adduct formed via the C=C bonds of the quinone[2]. It has been established that the oxetan is formed with participation of the *T* state of the quinone, while an increase in the concentration of the olefin should favour (in the absence of other complicating factors) the reactions of the quinone in the singlet state. If this interpretation is correct, significant differences between the photochemical reactions of quinones in the *S* and *T* states should naturally be expected.

Photochemical addition occurs successfully only when E_T for the hydrocarbon (olefin, acetylene) is comparable or greater than E_T for the quinone, so that there is no transfer of the energy of the triplet state. In particular, this factor is associated with the observation that simple ketones (for which usually $E_T > 60$ kcal mole^{-1}) rarely react with dienes and conjugated polyenes ($E_T < 60$ kcal mole^{-1}), whereas quinones ($E_T \leq 60$ kcal mole^{-1}) frequently enter into this reaction.

The following view appears to predominate at the present time concerning the n,π^* or π,π^* nature of the reactive state of quinones: quinones react via their C=C bonds in the π,π^* state and via their C=O bonds in the n,π^* state[2,179]. The distribution of the corresponding energy levels should be, from this standpoint, one of the principal characteristics determining the type of addition. The capacity of quinones for the simultaneous formation of different products can be accounted for either by the competition of processes involving energetically similar n,π^* or π,π^* states or by the fact that the excitation energy (n,π^*) is not fully localised in the carbonyl group, but is partly transmitted also to the C=C bonds of the quinone.

The photochemical addition of olefins to the carbonyl group of quinones is a specific instance of such a photochemical reaction in the series of ketones. It has been shown for the simplest ketones that the cryptoradical mechanism of such a process permits the correct prediction of the structure of the principal isomer among the oxetans formed: the oxetan corresponding to the most stable biradical with the largest number of alkyl or aryl groups at radical centres always predominates. This rule proved to be valid also in the photochemical reactions of certain *p*-quinones with olefins[2,179]: for example, the isomer (CXXVIII), formed from the biradical (CXXVII), predominates among the oxetans in the photolysis of 1,4-benzoquinone in the presence of 2-methylpropene:

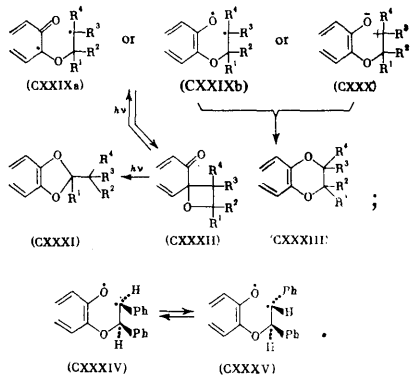


(CXXVII) (CXXVIII)

Predictions of this kind can probably be made for the photochemical reactions of both *p*- and *o*-quinones when the addition is to the carbonyl group; one cannot rule out the applicability of this rule also to photochemical addition to the C=C bonds of the quinone.

In the photochemical reactions of olefins with *o*-quinones, the biradical (CXXIX), obtained by the addition of the olefin to the quinone, gives rise to a dioxen (CXXXIII) and

(or) an oxo-oxetan (CXXXII), which, being unstable, is converted photochemically into the starting materials and (to a slight extent) into the dioxole (CXXXI):

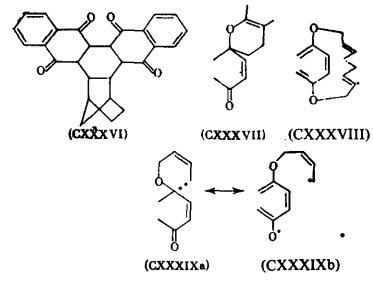


If the olefin contains the appropriate substituents, the above products [for example (CXXXIII)] can be obtained in the form of a mixture of stereoisomers. Thus the photochemical addition of phenanthrenequinone to simple *cis*- or *trans*-alkenes (but-2-ene, oct-4-ene, etc.) leads to a mixture of *cis*- or *trans*-dioxens [2,3]. Evidently the intermediate triplet biradical (CXXIX) is sufficiently long-lived for the establishment of conformational equilibrium, which in fact determines the proportions of the *cis*- and *trans*-adducts formed on pairing of the electrons. The observed stereospecificity in the photochemical reactions of tetramethyl-1,2-benzoquinone with *trans*-stilbenes and a certain selectivity in the photochemical addition of phenanthrenequinone to stilbenes [3] have been explained by the considerable contribution in such cases of the ionic structure (CXXX) to the resonance hybrid of the intermediate biradical; the interaction between the charges to a large extent limits the free rotation about the C–C bond, which should ensure steric control.

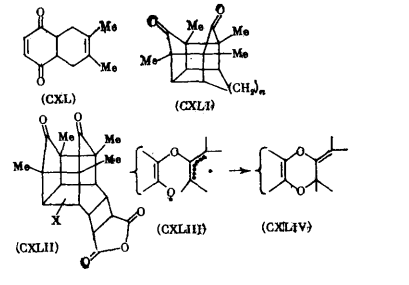
The above assumptions are in good agreement with the finding that the ratio of the *cis*- and *trans*-adducts formed from simple olefins does not depend on temperature, while the addition of phenanthrenequinone to stilbenes exhibits a decrease of selectivity with increase of temperature [3]. In the latter case, the interconversion of the radicals (CXXXIV) and (CXXXV) probable begins to compete with ring closure, since there is only a small energy barrier to rotation.

The simplest of the *p*-quinones (1,4-benzoquinone) forms only oxetans in photochemical reactions with non-conjugated acyclic and cyclic alkenes [2,179]. 2,3-Dimethyl- and tetramethyl-1,4-benzoquinones combine with alkenes only via the C=C bond [2,179,182]; tetrachloro-1,4-benzoquinone gives rise to both cyclobutanes and oxetans [2,179]; in the presence of an excess of the olefin, biscyclobutane structures may be obtained.

1,4-Naphthoquinone combines with alkenes to form oxetans and cyclobutanes [2,183,184]; its characteristic feature is the ability to form 2 : 1 quinone–olefin adducts [for example, the reaction with norbornene results in the formation of the adduct (CXXXVI) [185]]. The photolysis of anthraquinone in the presence of cyclo-octene and cyclo-octa-1,5-diene leads exclusively to oxetans [186]. All *o*-quinones give rise to oxetans or dioxens in reactions with alkenes; the addition to the C= C bond of the quinone has not been observed [1-3,187-193]:



Spirodihydropyrans (CXXXVII) are the products of the photochemical reactions of *p*-quinones (1,4-benzo- [2,282] and naphtho-quinones [179]) and certain conjugated olefins, while the macrocyclic adduct (CXXXVIII) is also formed in the reaction of buta-1,3-diene and 1,4-benzoquinone. The macrocyclic adduct is believed to be produced as a result of the addition of a second buta-1,3-diene molecule to the biradical (CXXXIXb), while compound (CXXXVII) is formed as a result of the intramolecular stabilisation of the mesomeric form (CXXXIXa) of the biradical. Depending on the photolysis conditions, compounds (CXXXVII) or (CXL) can be obtained for 2,3-dimethylbuta-1,3-diene. The reactions of tetramethyl-1,4-benzoquinone with certain conjugated dienes (cyclopentadiene, cyclohexa-1,3-diene) result in the formation of cage structures (CXLI), [194] while 1 : 1 : 1 adducts have been obtained in the photolysis of the benzoquinone in benzene derivatives (C_6H_5X, X = H, CH_3, or a halogen) in the presence of maleic anhydride [2]:



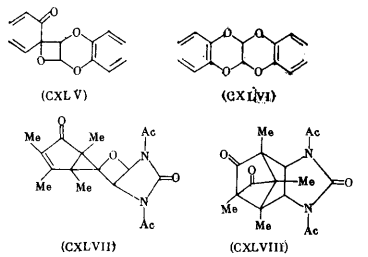
It is believed [195-197] that, in the photochemical reactions of allenes with *o*-quinones (phenanthrenequinone, tetrachloro-1,2-benzoquinone), the central carbon atom of the allene system is attacked with formation of the biradicals (CXLIII), whose stabilisation leads to dioxens (CXLIV).

Cyclobutene structures have been obtained in the photochemical addition of mono- and di-substituted acetylenes to 1,4-naphthoquinone and its methyl and acetoxy-derivatives [198,199]. The exclusive addition of acetylenes to the C=C bond of methoxy-1,4-naphthoquinones [2,200-203] has been explained [202] by the fact that the OCH_3 group localises the excitation at this bond and stabilises the intermediate biradical, promoting the formation of cyclobutene derivatives.

Phenanthrenequinone and tetrachloro-1,2-benzoquinone add to alkenynes with conjugated multiple bonds only at the C=C bond with formation of the corresponding oxetans and dioxens [204].

The primary products of the photochemical addition of unsaturated hydrocarbons to the C=C and C=O bonds of

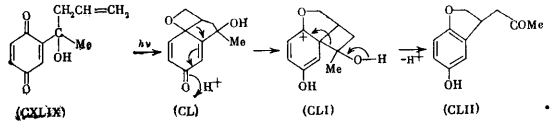
quinones are frequently unstable and cannot be isolated, since they undergo further dark or photochemical reactions. For example, the photo-adducts of phenanthrenequinone with chloro-olefins split off HCl and the compound thus produced adds to the excited phenanthrenequinone, forming adducts with 2 : 1 quinone : olefin ratios [compounds (CXLV) and (CXLVI)]: [2,205]



(CXLV) (CXLVI) (CXLVII) (CXLVIII)

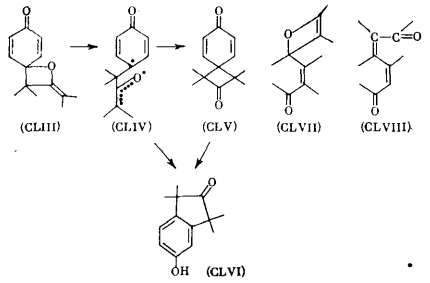
The oxetan obtained by irradiating tetramethyl-1,4-benzoquinone in the presence of 1,3-diacetyl-Δ^4-imidazolin-2-one is converted photochemically into compound (CXLVII), from which compound (CXLVIII) is formed via a dark process [2].

The spiro-oxetan (CL) produced by the photolysis of compound (CXLIX) in benzene ultimately gives rise to dihydrobenzofuran (CLII); it is noteworthy that the conversion of (CXLIX) into (CL) is the only known example of the intramolecular formation of an oxetan from quinones with an unsaturated side chain [156]:



(CXLIX) (CL) (CLI) (CLII)

As in the examples quoted above, it is assumed that the photochemical reactions of *p*-quinones (1,4-benzo- and naphtho-quinones) with allenes result in the formation of an oxetan (CLIII), which rearranges to the phenolic derivative (CLVI) either directly or via an intermediate spirocyclobutanone (CLV): [206]



(CLIII) (CLIV) (CLV) (CLVII) (CLVIII) (CLVI)

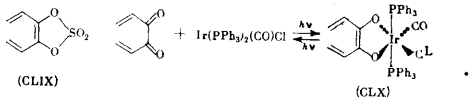
Mono- and di-substituted acetylenes undergo photochemical addition to the carbonyl groups of 1,4-benzoquinone, tetramethyl-1,4-benzoquinone, anthraquinone [2,179,186], 1,4-naphthoquinone, and its methyl and acetoxy-derivatives [198] with formation of quinonemethines (CLVIII) via the intermediate oxetens (CLVII). Phenanthrenequinone and tetrachloro-1,2-benzoquinone form 1 : 2 adducts of type (CXLVI) with individual acetylenes, since the initial dioxyns subsequently undergo a further photochemical addition reaction [3,180,181].

Apart from the instances described above, in photochemical addition processes the excited *p*-quinone molecule frequently reacts with another molecule of the same quinone but in its ground state; such examples are unknown for *o*-quinones. This type of photochemical dimerisation of the simplest *p*-quinones (1,4-benzo- and naphthoquinones and their derivatives) [2,207-211] and more complex natural products [2,212] takes place in solutions and in the solid state, resulting in the formation of spiro-oxetan, cyclobutane, and cage structures similar to those discussed above.

The ability to undergo photochemical dimerisation is determined to a large extent by the stabilisation energy of the exciplexes of quinones: those which are converted into stable adducts (for example, the species formed from 2,3-, 2,5-, and 2,6-dimethyl-1,4-benzoquinones) have a significantly greater stabilisation energy than those which do not form dimers (for example, the species formed from tetramethyl-1,4-benzoquinone) [213].

In contrast to solutions [2,214-216], the crystal structure, which determines the feasibility and direction of the reaction (the type of the product and its stereochemical characteristics), plays an important role in solid-phase photochemical dimerisation. Thus the process occurs when the reaction centres are separated by not more than 4 Å; on the other hand, the structure of the dimer is determined by the relative orientations of the monomers (the geometrical disposition of the parallel C=C and C=O bonds) in the crystal. The formation of polymeric materials in the photolysis of certain *p*-benzoquinones (1,4-benzoquinone, tetramethyl-1,4-benzoquinone) in the solid phase is attributed to the fact that the crystal structures of these compounds are characterised by an infinite chain of close C...C contacts between non-parallel C=C chains; their interaction leads to dimeric biradicals, which initiate polymerisation [2].

Whereas a characteristic feature of *p*-quinones is their capacity for photochemical dimerisation, a specific feature of *o*-quinones is their ability to combine on photochemical excitation with inorganic substances and organic derivatives of the elements with formation of O—element (element ≠ carbon) bonds. A reaction of this type, which has been known for a long time, is the so called "cyclosulphate synthesis" [2,3]—the addition of sulphur dioxide to the oxygen atoms of *o*-quinones (tetramethyl-1,2-benzoquinone, 1,2-naphthoquinone, its 3-nitro-derivative, phenanthrenequinone, its 2-, 3-, and 4-nitro-derivatives, chrysenequinone) with formation of compounds (CLIX):



(CLIX) (CLX)

The oxidative photochemical addition of $Ir(PPh_3)_2(CO)Cl$ to *o*-quinones (tetramethyl-1,2-benzoquinone, phenanthrenequinone, 1,2-naphthoquinone) [217] may be a convenient method for the synthesis of complexes of type (CLX). The process is reversible and takes place until the attainment of a specific equilibrium. Although both components are excited, the authors believe that the triplet state of quinones is reactive, by analogy with the cyclosulphate synthesis.

V. PHOTOCHEMICAL SUBSTITUTION

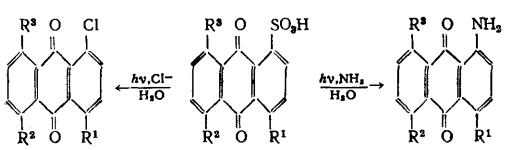
It is clear from the foregoing data, that the structure of the final photolysis products cannot in all cases constitute a sufficient criterion for the assignment of the photochemical reactions of quinones to a particular type. This is due to the formal nature of this feature, since the final products which can be isolated from the photolysed mixture do not always arise as a result of the photochemical

reaction of the excited quinone molecule with a given reactant. They are frequently formed in secondary dark or photochemical reactions, while the primary photochemical processes generate only the reactive species necessary for their occurrence. It is not even an obligatory condition that the quinone should participate in the secondary processes; the species produced by its primary reaction may be involved. All the foregoing considerations apply fully also to the photochemical reactions in which products resulting from substitution in the quinone ring or in its side chain are formed. For example, the photochemical process in the light-induced hydroxylation of sulphoanthraquinones, the elimination of their sulpho-group in reducing media, and the substitution of the OCH_3 group in methoxyanthraquinones by a hydroxy-group is the reduction of the quinone (see above), while the substitution of chlorine in tetrachloro-1,4-benzoquinone by an unsaturated hydrocarbon takes place as a result of the photochemical addition of hydrocarbons to the quinone (see section IV). One must therefore investigate in detail the mechanisms of such photochemical reactions before concluding that they are photochemical substitution reactions.

This section is concerned with the photochemical reactions of quinones which have been assigned on the basis of available data to photochemical substitution processes, and with reactions whose mechanism still has to be refined.

In concentrated aqueous solutions of inorganic acids, the sulpho-group is eliminated photochemically from 1-sulphoanthraquinone (but not the 2-derivative) via a hydrolytic mechanism with simultaneous formation of 1-hydroxyanthraquinone. The quantum yield of the photochemical hydrolysis is independent of the wavelength of the exciting light and its limiting value (approximately 10^{-3}) is low, probably owing to the quenching of the excited substrate molecules by H^+ ions [15,135,136].

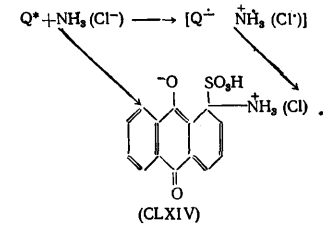
The irradiation of α-sulphoanthraquinones (CLXII) in aqueous solutions containing chloride ions or ammonia results in the substitution of the sulpho-group by a chlorine atom or an amino-group respectively [15] (see also Eckert [218]). The yields of chlorination products are higher than those of the amination products, since the side products formed in the latter case (water-soluble hydroxy- and amino-sulphoanthraquinones) filter out photochemically active light. In contrast to electron-accepting substituents (SO_3H, NO_2, halogens), electron-donating substituents (OH, NH_2) inhibit the photochemical process; contrary to one report [54], the substitution of β-sulpho-groups always takes place with a very low efficiency. The photochemical substitution of α- and β-sulpho-groups by alkyl- or aryl-amino-groups does not take place; traces of 1-methylaminoanthraquinone have been detected only when 1-sulphoanthraquinone was irradiated in aqueous methylamine solution with long-wavelength light ($\lambda_{exc} > 300$ nm): [15]



(CLXI) (CLXII) (CLXIII)

R^1, R^2, R^3 = H, Cl, SO_3H, or NO_2.

The available data suggest that the mechanisms of the photochemical chlorination and amination are the same and that the same excited state of the substrate (probably n,π^*) is reactive [15,136,219]. Two hypotheses have been put forward concerning the reaction pathways in the above processes. The first involves the nucleophilic substitution (in the classical sense, via an intermediate σ-complex) of the sulpho-group. The structure (CLXIV) can then be formed also as a result of the interaction of the radical (radical-ion) pairs generated by electron transfer in the solvent cage [15,54]:

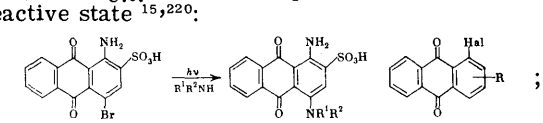


(CLXIV)

The second, alternative pathway involves the radical substitution of the sulpho-group. For example, the photochemical stage in the chlorination process may involve the generation of a Cl· atom by electron transfer from the Cl^- ion to the excited substrate molecule; in the subsequent dark process, the sulpho-group is substituted by chlorine:

$$Q^* + Cl^- \rightarrow Q^{\cdot-} + Cl^\cdot; \; Q + Cl^\cdot \rightarrow QCl.$$

Apart from the sulpho-group, it is also possible to substitute photochemically the halogen atom in the anthraquinone ring by an amino-group. Thus the bromine atom is readily substituted by amino-, alkylamino-, and dialkylamino-groups in the photolysis of 1-amino-4-bromo-2-sulphoanthraquinone (CLXV) in aqueous aerated solutions of the corresponding amines. The increased rate of the process following the introduction of additives (MeCN > PrOH > dioxan > H_2O) is treated as evidence of the formation of a polar intermediate. The cleavage of the carbon–halogen bond under the influence of light is believed to be unlikely; the $S^1_{c.t.}$ state of compound (CLXV) is treated as the reactive state [15,220]:



(CLXV) (CLXVI) (CLXVII)

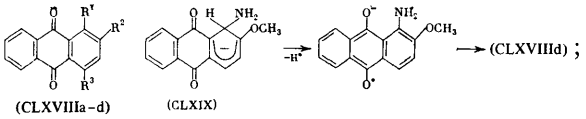
R = 4-OH, 2-NH_2, or 4-NH_2; Hal = Cl, or Br; R^1, R^2 = H, or Alk.

The capacity for the photochemical substitution of the halogen by an amino-group in aerobic alcoholic solutions of ammonia is characteristic of 1-halogenoanthraquinones when there are powerful electron-donating substituents in the 2- or (and) 4-positions, i.e. is characteristic of compounds of type (CLXVII). The process does not occur in the absence of substitutions, in the presence of only electron-accepting or weak electron-donating (methyl) groups, and also when strong electron-donating substituents are located in positions other than those indicated [221–224]. It has been possible to show that the $T^1_{c.t.}$ (or π,π^*) state is reactive in the case of 1-amino-4-chloroanthraquinone and 1-amino-4-bromoanthraquinone [223].

The role of oxygen is not merely oxidative, since the corresponding anthrasemiquinones and anthrahydroquinones are not involved in photoamination, while in deaerated media in the presence of other oxidising agents the halogen is not substituted (in polar solvents) [15,220,224]. The interaction of the substrate with singlet oxygen (obtained as a result of energy transfer from a triplet halogenoanthraquinone molecule) or attack by the amine (ammonia) on the exciplex of the excited substrate and oxygen is believed to be possible [220]. It has been shown for 1-amino-2,4-dibromoanthraquinone that the substrate

interacts in the $S^1_{c.t.}$ state in a polar solvent (MeCN), while in a non-polar solvent (C_6H_6) the compound in the $T^1_{c.t.}$ state is attacked by the amine and there is no necessity for oxygen. This change in the nature of the reactive excited state is attributed to a change in the disposition of the energy levels of the substrate when the nature of the solvent is altered [225].

The amino-group can substitute photochemically both the hydrogen atom and the OCH_3 group in the anthraquinone ring [226,227]. Thus compounds (CLXVIII, a–d) were obtained from 1- and 2-methoxyanthraquinones on irradiation in an acetonitrile–water mixture containing ammonia. Since the addition of radical acceptors does not decrease the rate of reaction, it is concluded that it is heterolytic. Whereas the formation of aminoanthraquinones is believed to proceed in the usual way, it is assumed that the σ-complex (CLXIX) is stabilised on formation of compound (CLXVIIId) by the abstraction of atomic hydrogen and not a hydride ion; accordingly, the rate of formation of compound (CLXVIIId) is reduced in the absence of oxygen. The $S^1_{n,\pi^*(\pi,\pi^*)}$ state of the substrate is assumed to be reactive:



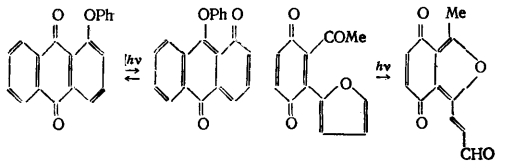
(CLXVIIIa–d) (CLXIX)

(a) $R^1 = NH_2$, $R^2 = R^3 = H$; (b) $R^1 = OCH_3$, $R^2 = H$, $R^3 = NH_2$; (c) $R^1 = R^3 = H$, $R^2 = NH_2$; (d) $R^1 = NH_2$, $R^2 = OCH_3$, $R^3 = H$

When 1-phenoxyanthraquinone is irradiated with ultraviolet light in benzene solution, it is converted into a coloured form. If irradiation is not interrupted, the product is 1-hydroxyanthraquinone, which is also formed on contact between the light-induced coloured form of 1-phenoxyanthraquinone and Al_2O_3. The mechanism of the process has not been discussed [228,229].

VI. UNIMOLECULAR PHOTOCHEMICAL REACTIONS OF QUINONES UNRELATED TO THEIR PHOTOCHEMICAL REDUCTION

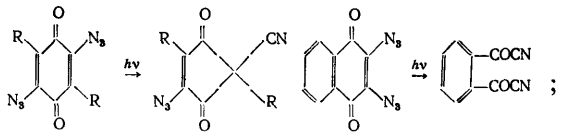
Reactions of the above type are few and are characterised by the fact that electronic excitation is localised in side chains; the primary photochemical reactions of the latter can be accompanied by secondary processes involving the quinonoid fragment. An exception is probably the formation, already mentioned, of the light-induced coloured forms of 1-phenoxy-, 1,5-diphenoxy-, and 1,8-diphenoxyanthraquinones and 10-phenoxynaphthacenequinone on their irradiation in non-polar solvents [228–230]. The spectra of the starting materials are restored when the irradiated solutions are kept in the dark or are irradiated with light corresponding to the new absorption band ($\lambda_{max} > 440$ nm). There are no exact data available for the mechanism of the photochromic transformations, but the authors assume that the colour of the light-induced form is associated with the polarisation of the carbonyl groups [229] or with the photoisomerisation of the *p*-quinone to an isomer with a higher oxidation-reduction potential—anaquinone [for example, (CLXX) → (CLXXI)]: [230]



(CLXX) (CLXXI) (CLXXII) (CLXXIII)

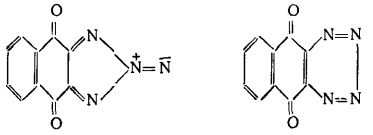
The photochemical rearrangement of the quinone (CLXXII) to compound (CLXXIII) is explained by the local excitation of the acetyl group [2].

Photolysis of 2,5-diazido-1,4-benzoquinones (CLXXIV) [231] and 2,3-diazido-1,4-naphthoquinone (CLXXVI) [232] leads to the elimination of one and two nitrogen molecules respectively; the resulting nitrenes are stabilised by conversion into compounds (CLXXV) and (CLXXVII). In the latter case, structures (CLXXVIII) and (CLXXIX) are postulated as intermediates which split off nitrogen:



(CLXXIV) (CLXXV) (CLXXVI) (CLXXVII)

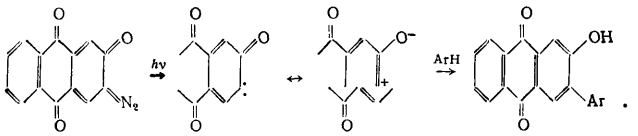
R=Me, Me_3C



(CLXXVIII) (CLXXIX)

The esters of 1,2-naphthoquinonediazosulphonic acids and di(tri)hydroxyanthraquinones, containing 1–2 free hydroxy-groups, also eliminate a nitrogen molecule on irradiation and the ketocarbenes formed rearrange to ketens [233]; a similar process is characteristic of *o*-quinone diazides, used as the main component in various light-sensitive layers [234]. The sensitisation of the photochemical decomposition by the anthraquinone residue is postulated in this case [233].

The electrophilic ketocarbenes (CLXXXI), formed by the photolysis of compound (CLXXX), interact with a solvent of type ArH and give rise to 2-hydroxy-3-arylanthraquinones (CLXXXII): [235]



(CLXXX) (CLXXXI) (CLXXXII)

VII. THE INITATION AND INHIBITION OF PHOTOCHEMICAL REACTIONS BY QUINONES

One of the possible mechanisms of the initiation of photochemical reactions by quinones involves the transfer of the triplet state energy by the latter to various reactants. This sensitisation pathway§ is facilitated by the wide range of values of E_T for different quinones (see Table) and the fairly high values of Φ_{ST} (as shown by the quantum yields of the photochemical reduction of many quinones, which are close to unity); for example, $\Phi_{ST} \simeq 0.9$ for anthraquinone [236].

The decomposition of 1-iodonaphthalene [242], the *cis-trans*-isomerisation of stilbenes, 2-, 3-, and 4-styrylpyridines, and 1- and 2-styrylnaphthalenes [243,244], and the

§ The term "sensitisation" is used here in a wide sense and implies the initiation of the photochemical process in the presence of an additive, regardless of the method by which initiation is achieved.

The energetic characteristics of the excited states of certain quinones.

Compound	E, kcal mole^{-1}	Compound	E, kcal mole^{-1}
1,4-Benzoquinone	59 (S^1)[237]; 53.5 (T^1)[239]; 53 (T^1)[237]; 50 (T^1)[238]	2,7-Disulphoanthraquinone (disodium salt)	60 (T^1)
1,4-Benzoquinone-d_4	53.5 (T^1)[239]	1-Chloroanthraquinone	60.5 (T^1)
1-Methyl-1,4-benzoquinone	54.7 (T^1)[239]	1,5-Dichloroanthraquinone	59.4 (T^1)
2,5-Dichloro-1,4-benzoquinone	55 (T^1)[239]	1,8-Dichloroanthraquinone	59.7 (T^1)
Tetramethyl-1,4-benzoquinone	52 (T^1)[238]	2-Chloroanthraquinone	60 (T^1)
1,4-Naphthoquinone	62.8 (S^1)[239]; 58 (T^1)[237]; 53,7 (T^1)[239]	1-Aminoanthraquinone	52.2 (S^1)
2-Methyl-1,4,-naphthoquinone	63.3 (S^1)[239]; 53.8 (T^1)[239]	2-Aminoanthraquinone	54.1 (S^1)
9,10-Phenanthrenequinone	49 (T^1)[240]	1-Amino-2-methylanthraquinone	53 (S^1)
Anthraquinone	67.8 (S^1)[239]; 62 (T^1)[238]; 60,5 (T^1)[241]	1-Amino-5-chloroanthraquinone	51.3 (S^1)
2-Methyl-anthraquinone	68 (T^1)[239]; 60,2 (T^1)[241]	1-Amino-4-hydroxyanthraquinone	48.9 (S^1)
2-Sulphoanthraquinone (sodium salt)	60 (T^1) *	1,4-Dihydroxyanthraquinone	53.8 (S^1)
2,6-Disulphoanthraquinone (disodium salt)	60 (T^1) *	1,4-Di(methylamino)anthraquinone	39.8 (S^1)
		1-Methylamino-4-*p*-toluidinoanthraquinone	38 (S^1)

*Data taken from Dearman and Chan [241].

reaction of anthracene with CCl_4 [245] may be quoted as examples of this type of sensitisation. In all cases, the systems were irradiated with light corresponding to the absorption band of the triplet energy donor (anthraquinone) and the occurrence of sensitisation confirmed the triplet nature of the excited states of the reactants.

Together with the solution of theoretical problems, energy transfer from quinone molecules has been used also for practical purposes. Thus the graft-copolymerisation of natural rubber with various monomers (styrene, methyl methacrylate) can be achieved in an emulsion under the influence of ultraviolet and visible light if 1-chloroanthraquinone is added to the mixture [246]. Various polycyclic quinones are used to initiate the photopolymerisation of acrylic or α-alkylacrylic esters [247]. In order to "sensitise" layers based on organic azides towards light with wavelengths > 300 nm, anthraquinone is added to cyclorubber based on 4,4′-bisazidodiphenylmethane [248], while 1,4-benzoquinone and 1,2-benzanthraquinone are added to the polymer $[-CH_2CH.(O_2CC_6H_4N_3\text{-}p)-]_n$. [249]

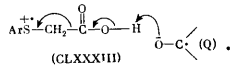
The photochemical oxidation of isopropylbenzene, tetralin, and benzaldehyde is sensitised by anthraquinone, 2-chloroanthraquinone, and 2-aminoanthraquinone [250-252]. It is believed that the biradical $^{\cdot}QO_2^{\cdot}$, formed on interaction between the excited quinone molecule and oxygen, is the initiator in this radical process; it is noteworthy that the yield of triplet quinone (Q) molecules increase under the influence of oxygen [253]. The intermediate form $^{\cdot}QO_2^{\cdot}$ either has a sufficiently large energy store to convert the substance being oxidised into a biradical (triplet) state or, if this condition is not fulfilled, it initiates the chain, dehydrogenating the substance AH undergoing oxidation:

$$Q\,(S^1) + O_2 \rightarrow {}^{\cdot}Q^{\cdot}\,(T^1),$$
$$Q\,(T^1) + O_2 \rightarrow {}^{\cdot}QO_2^{\cdot},$$
$$^{\cdot}QO_2^{\cdot} + AH \rightarrow QO_2 + {}^{\cdot}AH^{\cdot}\,(T^1) \xrightarrow{} \text{chain},$$
$$\text{or } {}^{\cdot}QO_2^{\cdot} + AH \rightarrow {}^{\cdot}QO_2H + A^{\cdot} \xrightarrow{} \text{chain}.$$

Apart from the photochemical oxidation of alcohols sensitised by quinones, which was examined previously (see Section II), other photochemical reactions are known, whose initiation by quinones involves the photochemical reduction of the latter. This applies particularly to the decarboxylation of acids of the type $RXCH_2CO_2H$ (R = alkyl or aryl; X = O, S, or NH) in the presence of quinones (1,4-benzoquinone, tetrachloro-1,4-benzoquinone, anthraquinone). The process mechanism can be represented as follows [254]:

$$Q^{\cdot} + RXCH_2CO_2H \longrightarrow QH^{\cdot} + RX\dot{C}H_2 + CO_2,$$

$$QH^{\cdot} + RX\dot{C}H_2 \longrightarrow Q + RXCH_3,$$



(CLXXXIII)

One cannot rule out the possibility of decarboxylation in a cage formed by the charge-transfer complex (CLXXXIII) of the acid and the quinone, where the most mobile hydrogen atom of the carboxy-group approaches the oxygen atom of the carbonyl group of the quinone.

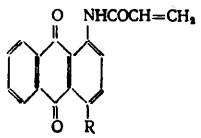
Anthraquinone-β-sulphonates which have been reduced photochemically in aqueous or aqueous alcoholic solutions (to sulphoanthrahydroquinone in neutral media or a radical anion at pH > 11) can serve as electron donors in relation to many compounds The process may involve only electron transfer (to stable radicals, quinones, and Fe^{3+} ions) or the simultaneous initiation of a chain of chemical reactions (the reduction of nitro-compounds, certain decomposition reactions, etc.). β-Sulphoanthraquinones thus behave as sensitisers of the reduction of electron acceptors, which are themselves relatively inactive photochemically [255].

The introduction of anthraquinone during the irradiation of toluene increases the yield of 1,2-diphenylethane [256]. Since there is no energy transfer under these conditions [E_T(toluene) $> E_T$(anthraquinone)], the increase in process efficiency is probably caused by the greater number of benzyl radicals due to the photochemical dehydrogenation of toluene by anthraquinone.

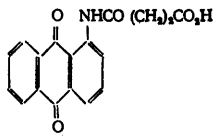
The photochemical degradation of *cis*-1,4-polyisoprenes in solutions is believed [257] to be caused by radicals formed from additives—quinones (1,4-naphthoquinone, anthraquinone, 1,2-benzanthraquinone, phenanthrenequinone).

Anthraquinone is used as the sensitising additive to photochemically polymerisable materials for photographic films [258] and to phototropic thermoplastic resins [259], while 1,5-diphenoxy-, 1,6-diphenoxy-, and 1,5-di-(*p*-methoxyphenoxy)-anthraquinones are also added to thermoplastic resins. The purpose of the addition of quinones to certain polymers is exactly the opposite; for example, 1,2- and 1,4-naphthoquinones, anthraquinones, and 1,2-benzanthraquinones are added to polystyrene in order to decompose it by photochemical oxidation [260].

It has been suggested that quinones can be used for this purpose also in compositions with other polymers in order to solve the problem of the degradation of packing materials. In this and many other examples enumerated above, it has not been established exactly how the photochemical reactions are initiated—by energy transfer from quinone molecules or by the reactive semiquinones formed on their photochemical reduction. Both initiation mechanisms may operate simultaneously:



(CLXXXIV)
R=H,OH



(CLXXXV)

Cases are known where quinones do not sensitise but actually inhibit photochemical processes: thus 1,4-naphthoquinone and anthraquinone diminish the extent of the photochemical degradation of vinyl polymers [261], while dyes of the anthraquinone series (CLXXXIV) and (CLXXXV) stabilise poly(methyl methacrylate) [262]. Such phenomena have so far been attributed only to the light filtration effect, but this explanation is probably not the only one possible.

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It has been found that excited quinones almost always behave as electron (hydrogen) acceptors in the primary photochemical step; on the other hand, the secondary processes reduce to intermolecular interaction with the reductant (solvent) or to the intramolecular stabilisation of the radical or biradical intermediates formed. We have endeavoured to demonstrate this in a logical manner in the description of the entire relevant data. This approach may not be entirely rigorous, since in many instances the formation of intermediates and the reaction mechanism as a whole have not been fully demonstrated and are tentative or have been assumed by analogy. Nevertheless, we believe that it can serve as a basis for a systematic treatment of the photochemical reactions of quinones.

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