Photoinduced Chain Reactions of Alcohols in the Presence of Diphenyliodonium Ion Pairs with Cyanometallates—Steady State UV/Visible Spectroscopic and Pulse Radiolysis Studies

Horst Hennig,*[a] Ortwin Brede,[b] Roland Billing,[a] and Jens Schönewerk[a]

Dedicated to Prof. Dr. Dick Stufkens on the occasion of his 65th birthday

Abstract: Diphenyliodonium ions (Ph_2I^+) form donor–acceptor ion pairs with suitable cyanometallates such as $[Mo(CN)_8]^{4-}$, $[W(CN)_8]^{4-}$, $[Ru(CN)_6]^{4-}$ and $[Os(CN)_6]^{4-}$. Such ion pairs are characterized by new spectroscopic transitions due to second-sphere interactions between donor ($[M(CN)_x]^{4-}$, $x=6$, 8) and acceptor (Ph_2I^+) ions. Photochemical excitation of these ion-pair charge-transfer (IPCT) states leads to efficient electron transfer reactions that yield short-lived diphenyliodyl radicals ($Ph_2I^\bullet$) and oxidized cyanometallates ($[M(CN)_x]^{3-}$). Diphenyliodyl radicals decay to iodobenzene and phenyl radicals. This very convenient source for generating phenyl radicals was applied to the photoinduced chain oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, respectively. However, unexpected side reactions led to undesired chain-terminating reactions. Adduct formation of diphenyliodonium ions with α-hydroxyalkyl radicals was verified by pulse radiolysis studies. These relatively long-lived adducts give rise to chain-terminating reactions because of interactions with $[M(CN)_x]^{4-}$ complexes that lead to oxidized cyanometallates $[M(CN)_x]^{3-}$ upon regeneration of the starting alcohols.

Keywords: cyanometallates · radical ions · ion pairs · photolysis · pulse radiolysis

Introduction

Diaryliodonium salts are widely used as photo initiators in both radical and cationic polymerization.[1–8]

Because of the relatively high light sensitivity of these compounds, it is reasonable to search for further photoinduced chain reactions initiated by photochemical excitation of diaryliodonium compounds, for example the photoinduced chain oxidation of alcohols to the corresponding aldehydes or ketones.

The photolysis of diphenyliodonium salts such as $(Ph_2I)Cl$ in primary and secondary alcohols yields primarily iodobenzene, benzene, protons and the corresponding aldehydes and ketones. Prolonged irradiation leads to secondary photolysis of the initially formed products, particularly when iodobenzene is considered. Photolysis of iodobenzene ends in I_3^-, which, with residual Ph_2I^+ ions, forms the corresponding diphenyliodonium salt $(Ph_2I)I_3$. $(Ph_2I)I_3$ itself photodecomposes exclusively to iodobenzene and iodine. As a result, a rather complex product mixture forms, accompanied by increasing filter effects, which diminish the quantum yield of the photolysis of $(Ph_2I)Cl$, and carbonyl compounds are no longer formed. Owing to such side reactions and to the spectroscopic behaviour of single diphenyliodonium salts with a main absorption area <350 nm, the photolysis of these compounds is unsuitable for the initiation of photoinduced chain reactions for the selective oxidation of alcohols. Particularly troublesome is the inevitable photolysis of photochemically generated iodobenzene. These disadvantages can be avoided when aryliodonium ions are used as acceptor components in ion pairs with electron-donating anions.

Diphenyliodonium ions form donor–acceptor ion pairs with suitable cyanometallates.[9–11] Such ion pairs as $[(Ph_2I)_4][Mo(CN)_8]$ (**1**), $[(Ph_2I)_4][W(CN)_8]$ (**2**), $[(Ph_2I)_4][Ru(CN)_6]$ (**3**), and $[(Ph_2I)_4][Os(CN)_6]$ (**4**) are characterized in UV/Vis spectroscopy by low-energy charge-transfer bands (ion-pair charge transfer, IPCT) as shown in Figure 1. Photochemical excitation of these IPCT states leads to very efficient electron transfer (see Figure 2, below) yielding oxidized cyanometallates and diphenyliodyl radicals. Diphenyliodyl radicals decay

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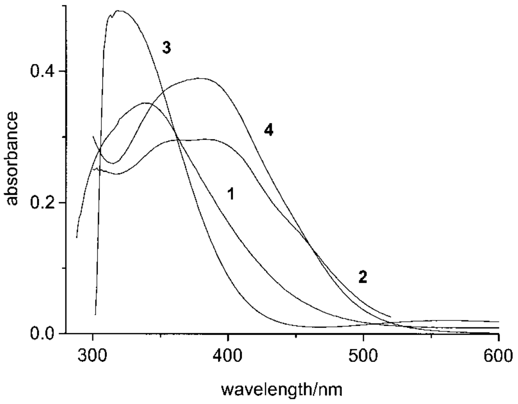
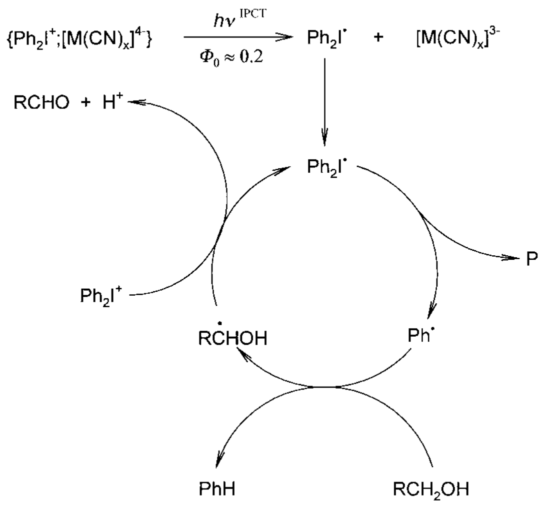


Figure 1. IPCT transitions of **1**, **2**, **3** and **4** shown as difference spectra of the appropriate ion pairs and their components.

very quickly to iodobenzene and phenyl radicals. This reaction path represents a novel and very convenient source for generating phenyl radicals, particularly when reaction (room temperature, or even lower) and irradiation (excitation in the visible) conditions are considered. An attempt was therefore made to use that reaction pathway for photoinduced chain reactions. Oxidation of alcohols to the corresponding aldehydes and ketones was selected (see Scheme 1) because



Scheme 1. Photoinduced chain oxidation of primary alcohols to the corresponding aldehydes in the presence of diphenyliodonium ion pairs with cyanometallates.

selective oxidation of primary alcohols to aldehydes is of considerable synthetic interest.[12] The photochemical generation of phenyl radicals and its application to the chain oxidation of alcohols represents an alternative pathway to thermal or electrochemical generation of differently substituted phenyl radicals in the presence of alcohols.[13–15]

Methanol, ethanol, propan-2-ol and benzyl alcohol were used as substrates to study the efficiency of photoinduced chain oxidations and to search for causes of the subsequently occurring chain-terminating reactions.

Results and Discussion

Spectroscopy and photochemistry of the ion pairs 1–4 in the presence of alcohols: The UV/Vis spectra of solutions of the ion pairs **1–4** in alcohol/water mixtures show new spectroscopic transitions due to second-sphere interactions between diphenyliodonium ions as acceptors and cyanometallates as donors, as shown in Figure 1.[16]

Ion-pair charge-transfer bands are low in intensity and energy, and depend on the standard electrode potentials of the cyanometallates used. IPCT bands appear in the UV/Vis spectra if $[M(CN)_n]^{4-}$ complexes interact with Ph_2I^+ ions in a 1:1 ratio. The formula $\{Ph_2I^+;[M(CN)_n]^{4-}\}$ means, therefore, that at least one diphenyliodonium ion interacts with one complex unit.

Photochemical excitation of the IPCT states of **1–4** leads to an efficient photo oxidation of the corresponding cyanometallates ($\Phi \approx 0.2$) with concomitant formation of diphenyliodyl radicals. Figure 2 shows the spectroscopic changes during the photolysis of **1** on excitation of the IPCT state. The wavelength used ($\lambda_{irr} = 436$ nm) allows selective excitation of the IPCT state of **1** and excludes light-induced reactions of both Mo(IV) and photochemically formed Mo(V) cyanide complexes.

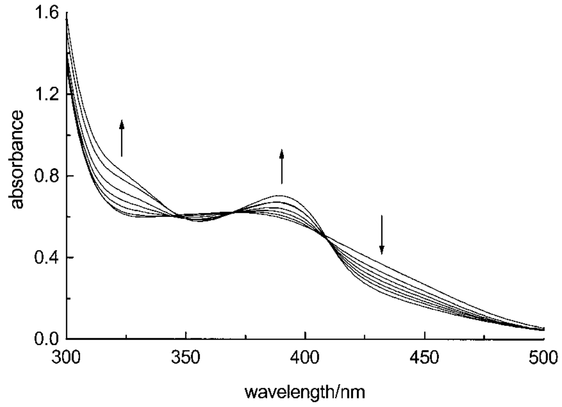


Figure 2. UV/Vis-spectroscopic control of the photolysis of **1** in methanol, depending on the irradiation time, t_{irr}, = 0, 3, 10, 20, 35, 50 or 80 min, with increasing or decreasing absorbance as shown by the arrows. (5×10^{-4} M **1**, 7.6×10^{-2} M Ph_2ICl; $\lambda_{irr} = 475$ nm, $I_0 = 2.7 \times 10^{-9}$ E s^{-1}, $\Phi = 0.21$ for $I_a = 5.35 \times 10^{-10}$ E s^{-1}).

The relatively high product quantum yields of **1–4** (see Table 1) are caused by suppression of back electron transfer. That is due to the fast decay of the diphenyliodyl radicals. The lifetime of these radicals only runs to $\tau \approx 200$ ps.[3, 17, 18] Because there is almost no influence of the solvent viscosity on the quantum yield, as shown with the photolysis of **1**, it can be assumed that photochemically formed $Ph_2I^{\bullet} \cdots [M(CN)_x]^{3-}$

Table 1. Product quantum yield Φ_{IPCT} of the photolysis of **1–4** in *tert*-butanol/water 1:1 (v/v).[a]

	1	**2**	**3**	**4**
Φ_{IPCT}	0.13	0.16	0.17	0.22

[a] $\lambda_{irr} = 436$ nm, $I_A = 1.5 \times 10^{-7}$ E min^{-1}, $t_{irr} = 5$ min, $[Ph_2I^+] = 6 \times 10^{-2}$ M, $[[M(CN)_x]^{4-}] = 3.5 \times 10^{-4}$ M.

successor pairs decay within the solvent cage and not after separation to free $Ph_2I^•$ radicals and $[M(CN)_x]^{3-}$ complexes (see Table 2). In the other case, a considerable decrease of Φ_{IPCT} would be expected, because the quantum yield would then be strongly influenced by the solvent viscosity ($\Phi_{IPCT} \sim 1/\eta_{Solv}$). The extremely fast decay of $Ph_2I^•$ radicals has been explained by population of antibonding σ*(C–I)-orbitals.[19]

Table 2. Product quantum yields of the photolysis of **2** obtained at 25 °C in alcohols of different viscosity.[a]

Alcohol	η_{Solv} (in cP)[b]	Φ_{IPCT}
methanol	0.544	0.25
ethanol	1.07	0.21
propan-1-ol/water 1:1 (v/v)	2.65	0.14
propan-2-ol/water 1:1 (v/v)	2.97	0.17
tert-butanol/water 1:1 (v/v)	5.48	0.16
benzyl alcohol	6.75	0.20
butane-1,2-diol	10.4	0.14
pentane-1,2-diol	11.2	0.15
ethane-1,2-diol	16.79	0.15

[a] $\lambda_{irr} = 436$ nm, $I_A = 2.5 \times 10^{-9}$ E s^{-1}, $t_{irr} = 5$ min, $[Ph_2I^+] = 6 \times 10^{-2}$ M, $[[W(CN)_8]^{4-}] = 3.5 \times 10^{-4}$ M. [b] Data taken from ref. [37].

The course of the photolysis of **1**–**4** strongly depends on the light intensity. With moderate light intensity, photoreactions develop as shown in the upper part of Scheme 1. Higher intensity ($I_0 > 5 \times 10^{-9}$) leads to a decrease in the quantum yield, and the photoreaction is accompanied by undesired side reactions due to increasing stationary radical concentration. Thus, at higher light intensity, the concentration of photochemically formed octacyanomolybdate(v) no longer corresponds to the consumption of **1** as shown by absorbance difference diagrams (see Figure 3). The same results were obtained with the ion pairs **2**–**4**.

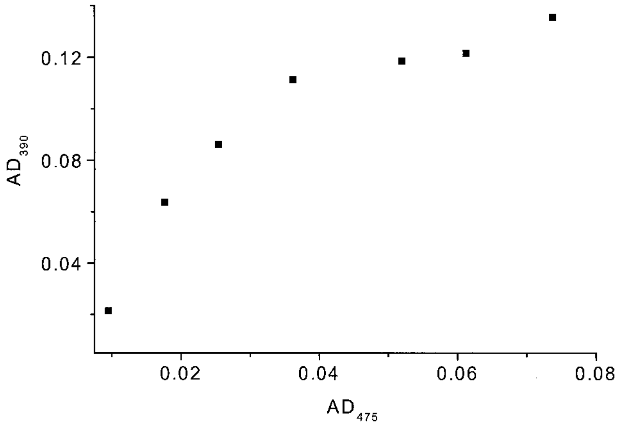


Figure 3. Absorbance difference diagram recorded at 475 nm (AD_{475}) and 390 nm (AD_{390}) for the photolysis of **1** in methanol ($I_A = 6.5 \times 10^{-9}$ E s^{-1}, $t_{irr} = 7$ min, $\lambda_{irr} = 475$ nm, $[Ph_2I^+] = 7.6 \times 10^{-3}$ M, $[[Mo(CN)_8]^{4-}] = 5 \times 10^{-4}$ M).

Further side reactions have to be considered with increasing water content, which is used to improve the solubility of the ion pairs **1**–**4**. Due to decreased ion-pair formation with increasing water content, photo reactions of $[M(CN)_x]^{4-}$ complexes themselves may occur. With decreased ion-pair formation, ligand field (LF) transitions become increasingly dominant and photochemical reactions take place, which are usually observed upon exciting LF states.[20]

The generation of oxidized cyanometallates upon IPCT excitation has been detected by UV/Vis (see Figure 2 for **1**) and ESR spectroscopy.[21] Phenyl radicals, the decay product of $Ph_2I^•$ radicals, were identified by ESR spectroscopy with nitrosodurene as spin trap.[21] Upon H-abstraction in the presence of H-donors such as primary and secondary alcohols, phenyl radicals yield benzene. Photochemically induced H-abstraction is the essential stage for the photoinduced chain oxidation of alcohols as shown in Scheme 1.

When investigating photoinduced chain reactions with **1**–**4** in the presence of alcohols, the oxidized cyanometallates formed in the course of photochemical IPCT excitation are of particular significance. Because these species absorb in the region of $\lambda \geq 350$ nm, the irradiation wavelength has to be selected depending on both the absorption maximum of the IPCT transition and the spectroscopic behaviour of the oxidized cyanometallates, in order to exclude photoreactions of these species.[22]

The UV/Vis spectroscopic control of the course of photoinduced chain reactions should result in a decrease in the IPCT band, accompanied by a stoichiometrically equivalent increase in absorption in the region of the oxidized cyanometallates. It is a certain indication of the occurrence of side reactions if there is no simultaneous change in the disappearing and appearing of these absorption bands. Figure 2 shows UV/Vis spectroscopic changes in the photolysis of **1** in methanol. The consumption of **1** is equivalent to the formation of octacyanomolybdate(v). This means the photoreaction proceeds as described in Scheme 1.

The course of photoinduced chain reactions of 1–4 with alcohols: The photochemical primary step that results from electron transfer between cyanometallates and diphenyliodonium ions proceeds with relatively high efficiency.[9] Diphenyliodyl radicals decay to iodobenzene and phenyl radicals, the actual chain carriers. Benzene, iodobenzene, oxidized cyanometallates and aldehydes or ketones form as stable final products, as shown in Scheme 1. The products should form in the same ratio, provided that a chain reaction takes place and no competitive side reactions occur.

The efficiency of the photoinduced chain oxidation of alcohols to the corresponding carbonyl compounds was proved with ethanol and benzyl alcohol. Ion pairs **1**–**4** were used preferably in solutions of these alcohols. As small a water content as possible was used to obtain sufficient solubility of the ion pairs and high ion-pair formation. The main reaction products were analyzed by gas chromatography, because the stoichiometry of the product formation clearly indicates whether undesired chain termination has taken place.

Photochemical reactions of **1**–**4** in ethanol yield acetaldehyde, which is completely converted to the corresponding diethylacetal. Protons formed during the photoinduced chain process (see Scheme 1) catalyze this reaction. Results of photoinduced chain reactions in the presence of **1** in ethanol are displayed in Figure 4.

Quantum yields of 0.1 were estimated for the consumption of **1**, but only extremely low chain lengths (up to ten cycles)

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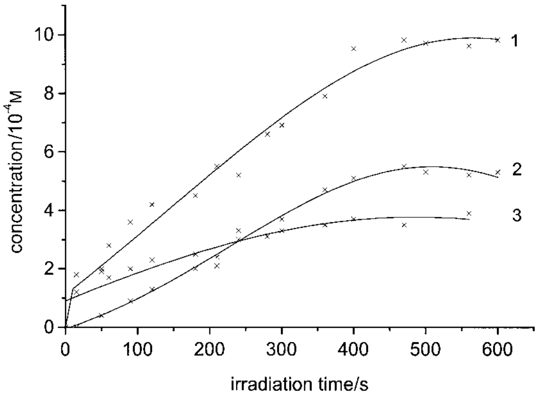


Figure 4. Product distribution of the photolysis of **1** in ethanol: 1) iodobenzene, 2) benzene, 3) diethylacetal. (5×10^{-4}M **1**, 7×10^{-3}M Ph_2IHSO_4, $\lambda_{irr} \geq 470$ nm, HBO lamp.)

could be observed. Furthermore, only half of the benzene, or even less, is formed when compared with the yield of iodobenzene (see Figure 4). These results indicate a fast termination of the chain growth.

To obtain insight into reasons for the chain-terminating reactions, possible side reactions of photochemically formed intermediates and the influence of oxygen were investigated. To begin with, the influence of oxygen as a chain quencher could be excluded, because no side reactions due to the generation of peroxy radicals could be detected. Furthermore, no difference in the product contribution could be observed in the photolysis under oxygen compared with irradiation under a nitrogen atmosphere. Nevertheless, all photolysis experiments were performed under nitrogen and with nitrogen-saturated solutions.

Secondly, the influence of the cyanometallate complexes on intermediately formed α-hydroxyalkyl and phenyl radicals was investigated. Side reactions of α-hydroxyalkyl radicals may lead to electron transfer processes with $[M(CN)_x]^{3-}$ complexes. However, the permanent stoichiometric formation of $[M(CN)_x]^{3-}$ complexes, as shown by UV/Vis spectroscopy, excludes electron transfer reactions of these species. Detailed investigation of the strongest oxidants, $[Os(CN)_6]^{3-}$ and $[Mo(CN)_8]^{3-}$, in ethanol showed no electron transfer with α-hydroxyethyl radicals. In addition to ethanol, benzyl alcohol was used because photochemically formed hydroxybenzyl radicals are stronger reductants than α-hydroxyalkyl radicals.[23] Depending on the redox potentials of the oxidized cyanometallates,[24] these radicals can be consumed, and photoinduced chain reactions may therefore be terminated. Thus, the photolysis of **2** permanently yields $[W(CN)_8]^{3-}$, whereas no generation of $[Mo(CN)_8]^{3-}$ occurs upon the photolysis of **1** (see Figure 5). This is due to the higher oxidation potential of $[Mo(CN)_8]^{3-}$ compared with $[W(CN)_8]^{3-}$. Photo reactions of $[Mo(CN)_8]^{3-}$ itself, and thermal reactions of that species with benzyl alcohol, have been excluded by appropriate control experiments. This means that side reactions can only be observed with the strongly reducing hydroxybenzyl radicals and strongly oxidizing $[M(CN)_n]^{3-}$ complexes such as $[Os(CN)_6]^{3-}$ and $[Mo(CN)_8]^{3-}$. Therefore this reaction pathway can also be excluded as a general reason for the chain-terminating reactions observed.

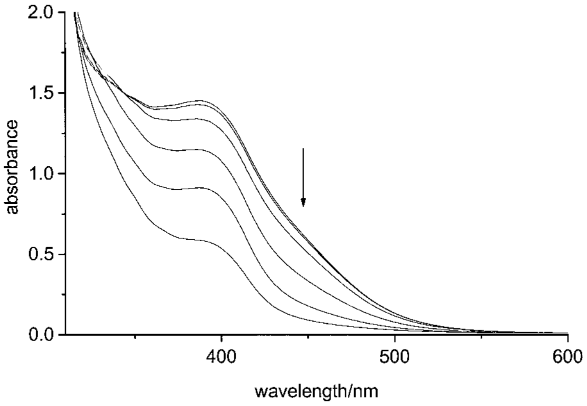


Figure 5. UV/Vis spectroscopic control of the photolysis of **1** in benzyl alcohol; t_{irr}: 0, 10, 20, 120 or 600 s, decreasing absorbance as shown by the arrow (9.5×10^{-4}M **1**, 6×10^{-2}M Ph_2ICl, $\lambda_{irr} = 475$ nm).

Phenylation reactions that yield phenyl ethers or phenyl alcohols could be excluded because only traces of these species form. Furthermore, the UV/Vis spectra of the photolysis products of **1**–**4** showed no formation of the corresponding phenyl isocyanide complexes, and phenyl isocyanide could only be detected in traces.

Biphenyl forms in traces, but only upon polychromatic, long-time irradiation. Biphenyl generation under such extreme irradiation conditions is due to phenylation of diphenyliodonium salts, which, additionally, should yield differently substituted iodobiphenyls. However, isomeric iodobiphenyls could not be detected. These results certainly indicate that this reaction pathway plays no role in the chain-terminating reactions.

Side reactions of α-hydroxyalkyl radicals may further consist of radical-combination reactions;[25] however, radical combination leading to glycol derivatives could not be observed.

Summarizing these results, it can be concluded that the radical-scavenging reactions usually expected could not be identified as a reason for the low efficiency of photoinduced chain reactions according to Scheme 1. Pulse radiolysis studies were therefore performed for an independent and clean generation of chain carriers derived from Ph_2I^+ ions and alcohols.

Pulse radiolysis studies: In aqueous solution, radiolysis generates primarily solvated electrons and hydroxyl radicals in comparable amounts, while the small hydrogen yield can usually be neglected [Eq. (1)].

$$H_2O \rightsquigarrow e^-_{aq} + OH^\bullet + (H^\bullet) \quad (1)$$

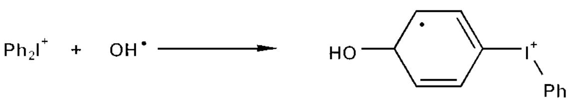
Hydroxyl radicals and solvated electrons can be separated by rapid scavenging of the undesired species by conversion into a nonreactive and, therefore, nondisturbing one [Eq. (2)] or by transformation into the intermediate of interest [Eq. (3)].[26, 27]

$$OH^\bullet + (H_3C)_3C{-}OH \rightarrow H_2O + (H_3C)_2(H_2C^\bullet)C{-}OH \quad (2)$$

$$e^-_{aq} + N_2O \rightarrow OH^\bullet + OH^- + N_2 \quad (3)$$

Solvated electrons and hydroxyl radicals generated by pulse radiolysis are particularly interesting with respect to a selective generation of such intermediates that control the photoinduced chain reactions under discussion.

Pulse radiolysis experiments with aqueous solutions of diphenyliodonium salts were performed to control the competition between the addition of OH radicals to phenyl residues of Ph_2I^+, Scheme 2, (which generates intermediate cyclohexadienyl-type radicals[28]) and H-abstraction reactions from the alcohols used.[27] In aqueous solution, hydroxycyclohexadienyl(phenyl)iodonium radicals form due to the addition of OH radicals to phenyl residues of Ph_2I^+ (Scheme 2), as to be seen from the fast part of the time profile 1 in Figure 6.



Scheme 2. Intermediate cyclohexadiene-like radicals generated in aqueous solution.

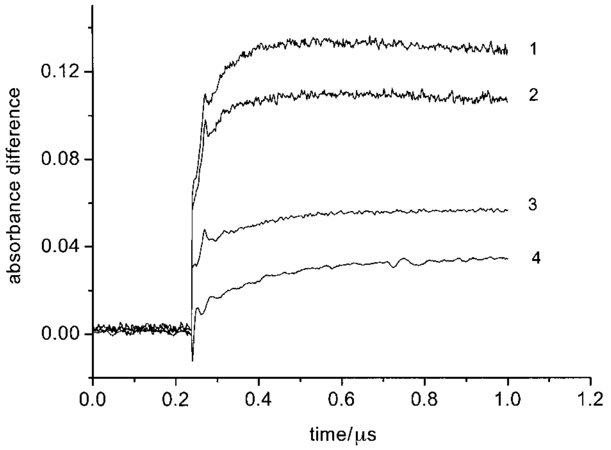


Figure 6. Quenching of the pulse radiolytic generation of hydroxycyclohexadienyl-(phenyl)iodonium radicals in aqueous solutions of Ph_2IBF_4 by addition of *tert*-butanol monitored at 340 nm. 1) aqueous solution, 2) 10^{-2}M *tert*-butanol added, 3) 10^{-1}M *tert*-butanol added, 4) 1M *tert*-butanol added. (4×10^{-3}M Ph_2IBF_4 in H_2O, N_2, 18 krad.)

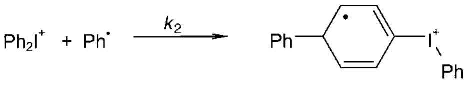
Addition of *tert*-butanol (or other alcohols) suppresses the generation of hydroxycyclohexadienyl(phenyl)iodonium radicals because H-abstraction from *tert*-butanol by OH radicals becomes increasingly dominant [cf. Eq. (2)] as seen from the diminishing of the fast part of the time profiles in Figure 6. In the presence of 0.1M *tert*-butanol, the reaction path according to Scheme 2 is suppressed to less than 40%. It can be neglected at concentrations higher than 1M. The constant growth of the time-dependent absorption after complete OH-radical scavenging is due to cyclohexadienyl-type radical generation, caused by adding phenyl radicals to the aromatic moiety of Ph_2I^+ ions. That reaction proceeds as a subsequent step in the interaction with solvated electrons (see below).

Considering the results of these pulse radiolysis experiments, it can be concluded that hydroxycyclohexadienyl-(phenyl)iodonium radicals do not have to be considered in further mechanistic discussions because all studies were performed in solutions containing a high excess of alcohols.

To study reactions with solvated electrons (Scheme 3), diphenyliodonium salts dissolved in *tert*-butanol/water were treated with high-energy electron pulses. For this reaction, a diffusion-controlled rate constant $k_1 = 3.5 \times 10^{10}\,\mathrm{M^{-1}\,s^{-1}}$ was determined from the decay of the transient absorption of solvated electrons ($\lambda = 600$ nm). Diphenyliodyl radicals, the primary product of this reaction, could not be detected. Instead, the generation of a secondary product was observed, characterized by a growing absorption at 340 nm. Its formation followed a pseudo-first-order time law depending on the diphenyliodonium salt concentration ($k_2 = 1.8 \times 10^8\,\mathrm{M^{-1}\,s^{-1}}$). By analogy with other cyclohexadienyl-type radicals,[28] this transient was assigned to phenylcyclohexadienyl(phenyl)iodonium radicals formed by the addition of intermediate phenyl radicals to Ph_2I^+ ions (Scheme 4); this explains the constant time-resolved part of the time profiles given in Figure 6.

$$\mathrm{Ph_2I^+} + e^-_{aq} \xrightarrow{k_1} \mathrm{Ph_2I^\bullet} \longrightarrow \mathrm{Ph^\bullet} + \mathrm{PhI}$$

Scheme 3. Effect of solvated electrons on the reaction of PhI^+.



Scheme 4. Transient radical formation from the phenyl intermediate.

Figure 7 shows the growth of the transient depending on the concentration of Ph_2I^+ ions. In Figure 7, curve 1 shows the absorption of solvated electrons in the pure solvent, which disappears with increasing Ph_2I^+ concentration (curves 2–5). It is quite evident that a time gap between reduction (Scheme 3) and product formation (Scheme 4) appears because phenyl radicals form intermediately by the fast decay of diphenyliodyl radicals (Scheme 3). Under the experimental conditions used, the lifetime for phenyl radicals was estimated approximately to 1 µs.

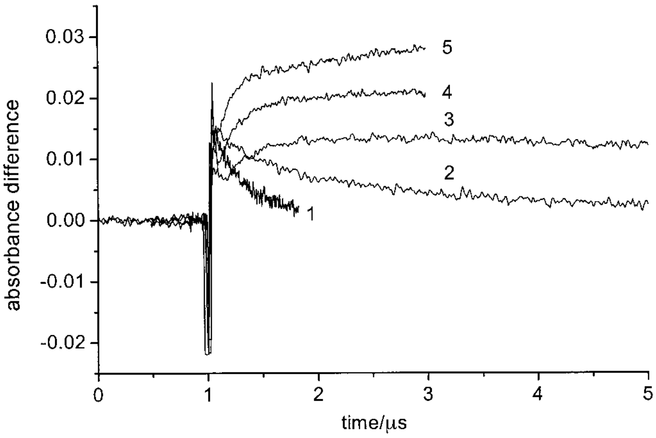
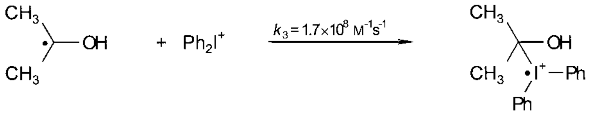


Figure 7. Formation of a new transient at 340 nm on pulse radiolysis of Ph_2IBF_4 in *tert*-butanol/water mixtures dependent on the concentration: 1) no Ph_2IBF_4, 2) 10^{-4}M, 3) 10^{-3}M, 4) 2×10^{-3}M, 5) 4×10^{-3}M. (18 krad, N_2 atmosphere.)

Converting solvated electrons into OH radicals by using N_2O [Eq. (3)] allows scavenging of hydroxyl radicals by propan-2-ol; this results in 2-hydroxypropyl radicals [Eq. (4)].[29]

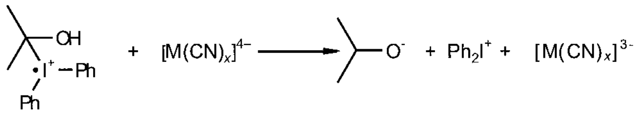
$$OH^{\bullet} + (H_3C)_2CH{-}OH \rightarrow H_2O + (H_3C)_2C^{\bullet}{-}OH \qquad (4)$$

Surprisingly, these radicals do not spontaneously react with Ph_2I^+ ions to form acetone, phenyl radicals and iodobenzene as expected. Instead, relatively long-lived adducts form ($\tau \approx 100\,\mu s$), see Scheme 5, as shown by a growing absorption at 360 nm.



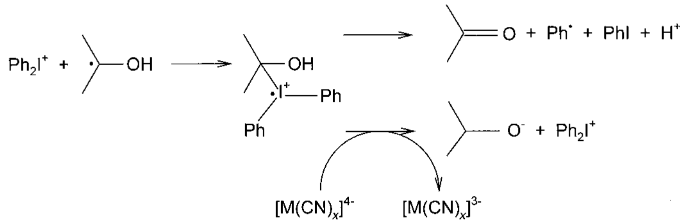
Scheme 5. Formation of long-lived 2-hydroxypropyl-based radicals.

Of significance with respect to the chain-terminating processes is the finding that the adduct formed from 2-hydroxypropyl radicals and Ph_2I^+ ions is reduced by cyanometallates ($[M(CN)_x]^{4-}$) with regeneration of diphenyliodonium ions and transformation of the chain carrier into alkoxides (Scheme 6).



Scheme 6. Chain terminating reduction of 2-hydroxypropyl-based radicals by cyanometallates.

This finding is strongly supported by the UV/Vis spectroscopic detection of oxidized cyanometallates ($[M(CN)_x]^{3-}$). Furthermore, in the absence of PH_2I^+ ions, no oxidation of $[M(CN)_x]^{4-}$ complexes by hydroxyl radicals occurs. Scheme 7 shows the observed reaction pathway in the presence and absence of cyanometallates.



Scheme 7. Influence of $[M(CN)_x]^{4-}$ complexes on the reaction pathway of 2-hydroxypropyl/Ph_2I^+ radical adducts.

Figure 8, which shows spectra taken at different time after the electron pulse, indicates the reduction of 2-hydroxypropyl/Ph_2I^+ radical adducts with $[Os(CN)_6]^{4-}$ as seen by the decay of its absorption at 360 nm. Because **4** absorbs in the same region, the decreasing of the absorption is due to the decay of 2-hydroxypropyl/Ph_2I^+ radical adducts (dominating at 360 nm) and to the consumption of $\{Ph_2I^+;[Os(CN)_6]^{4-}\}$ as shown by an absorption minimum at 410 nm. To reduce this disturbing depletion effect, an excess of NaCl was added to suppress the ion-pair formation. The presence of NaCl is very helpful in avoiding most of the depletion, that is, reducing the base line drift to negative absorption.

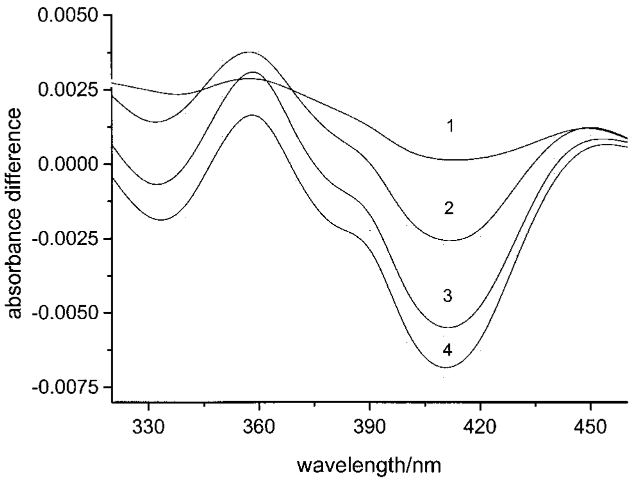


Figure 8. Bleaching of 2-hydroxypropyl/Ph_2I^+ radical adducts in the presence of $[Os(CN)_6]^{4-}$: 1) 2 µs, 2) 8 µs, 3) 25 µs, 4) 50 µs. (5×10^{-5} M $K_4[Os(CN)_6]$, 2×10^{-3} M Ph_2IBF_4, 1 M propan-2-ol, N_2O, 5 krad.)

The addition of NaCl has only negligible influence on the reaction mechanism as shown in Figure 9. For high NaCl concentration, the small difference in the time profiles can be understood in terms of a possible conversion of OH radicals into Cl radicals.[30] It is assumed that these radicals, generated only in small yields, react quite similarly to OH radicals.

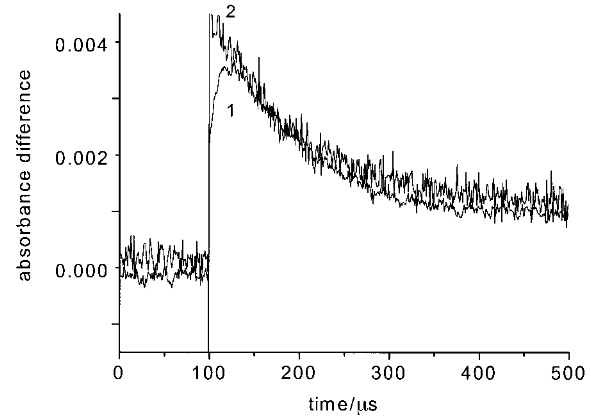


Figure 9. Influence of the NaCl concentration on the decay of the 2-hydroxypropyl/Ph_2I^+ radical adduct: 1) 0.1 M NaCl, 2) 0.5 M NaCl. (2×10^{-3} M Ph_2IBF_4, 1 M propan-2-ol, N_2O, 5 krad, detection wavelength 360 nm.)

The decay of the 2-hydroxypropyl/Ph_2I^+ radical adduct to phenyl radicals, iodobenzene and acetone should be favoured by increased pH, as shown in Scheme 7, whilst the competitive reaction, the reduction of that radical adduct by $[M(CN)_x]^{4-}$ complexes, is preferred at low pH values. The influence of the pH value is shown in Figure 10. At pH 7, the 2-hydroxypropyl/Ph_2I^+ adduct is relatively long-lived. Increasing the pH value

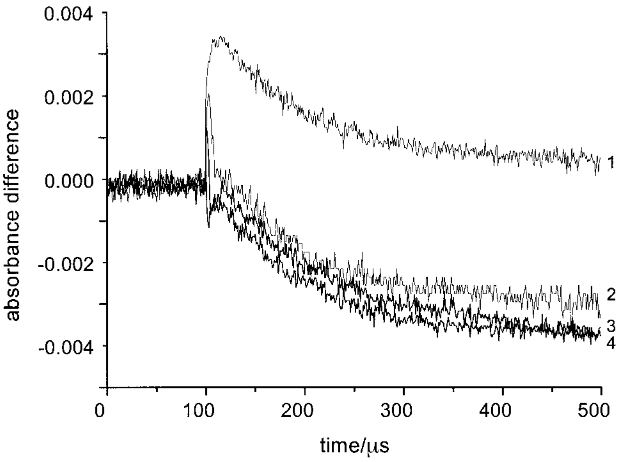


Figure 10. Dependence of the lifetime of the 2-hydroxypropyl/Ph_2I^+ radical adduct on pH, KOH added up to: 1) pH 7, 2) pH 10, 3) pH 10.3, 4) pH 10.5. (1.8×10^{-3} M Ph_2IBF_4, 1 M propan-2-ol, N_2O, 5 krad, detection wavelength 360 nm.)

up to ten substantially shortens the lifetime of this radical. Because the chain reaction proceeds accompanied by increasing proton concentration, chain-terminating reactions become favoured when $[M(CN)_x]^{4-}$ complexes are present.

Summarizing the results of pulse radiolysis studies, it follows that rather uncommon radical reactions, such as the adduct formation of α-hydroxyalkyl radicals with Ph_2I^+ ions and their reduction by $[M(CN)_x]^{4-}$ complexes, give rise to consumption of the chain carriers required for efficient photoinduced chain reactions according to Scheme 1.

Conclusion

The results presented herein demonstrate that photochemical excitation of IPCT states of $\{Ph_2I^+;[M(CN)_x]^{4-}\}$ ion pairs represents a novel source for the convenient generation of phenyl radicals. Utilization of that source for photoinduced chain oxidations of alcohols is considerably restricted, however, because chain carriers are consumed by unexpected and uncommon side reactions.

The findings of pulse radiolysis studies show that a hitherto uninvestigated formation of relatively long-lived addition products between 2-hydroxypropyl radicals and Ph_2I^+ ions occurs. The reduction of these radical adducts by $[M(CN)_n]^{4-}$ complexes leads to rather uncommon side reactions which finally result in the termination of photoinduced chain oxidations of primary and secondary alcohols. Recently we were able to show that in the presence of suitable sensitizers, like α-diketones, such chain-terminating reactions can be efficiently quenched. In this way it is possible to considerably improve the efficiency of photoinduced chain reactions based on the ion pairs **1**–**4**.[31, 32]

Experimental Section

Methods: Pulse radiolytic experiments were performed by means of an electron accelerator (Elit 1 M, Institute of Nuclear Physics, Novosibirsk). The absorbed dose of electron impulses (pulse width 10–15 ns, energy 1 MeV) amounts to 5–20 krad (50–200 Gy) and yields 5×10^{-6} to 2×10^{-5} mol L^{-1} radicals (G-value = 1). Sample solutions were pumped through the cuvette upon concomitant gassing with argon and N_2O. Time-resolved UV/Vis absorption spectroscopy with a pulsed xenon lamp (XB = 900, Osram), a Spectra Pro-500 monochromator (Acton Research Corporation), a photomultiplier (1P28, RCA) and 500 MHz digitizing oscilloscope (TDS 640, Tektronics) was used as detection system. Further details of the equipment and the data analysis are described elsewhere.[33]

The gas chromatograph used (HP 5890 II A) was equipped with a flame ionization detector (HP 19231) and columns of higher (HP-5) and medium polarity (CP-Sil-19-CB). Photolysis products up to 10^{-4} M benzene, iodobenzene and benzaldehyde could be analyzed after extraction with *n*-pentane.

Water-free samples with low Ph_2I^+ concentrations were analyzed directly. In most cases, however, they were extracted with *n*-pentane. Hexafluorobenzene, *n*-decane and *n*-tetradecane were used as internal standards.

UV/Vis spectra were recorded with a Lambda 900 (Perkin-Elmer) or Cary 3 (Varian) spectrometer.

Irradiation experiments were performed with AMKO apparatus with a grid monochromator (LTi 01-001). Mercury/xenon lamps (XBO 150, Osram) or mercury lamps (HBO 100, Osram) were used as light sources. 3 mL quartz cuvettes with an optical path length of 10 mm were used. Spectrograde solvents were used as obtained commercially (Uvasol, Merck), while methanol was dried with magnesium and purified by distillation.

Preparative photoreactions were performed in 30 mL quartz cuvettes or by means of a 300 mL water-cooled quartz photo reactor (Normag). The reactor was equipped with a mercury medium-pressure lamp (TQ 150). Usual filter solutions were partially used to cut off wavelengths lower than 350 nm.

Quantum yields were estimated by actinometry with $[Fe(ox)_3]^{3-}$. Fe^{2+} formed photochemically was analyzed spectrophotometrically by using phenanthroline as chelate former.[34] Actinochrome was used as an actinometric standard for quantum yield estimation at lower energy ($\lambda_{irr} > 460$ nm).

Syntheses: Diphenyliodonium chloride was prepared according to Beringer.[35] Tetrakis-(diphenyliodonium)octacyanomolybdate(IV) (**1**), tetrakis(diphenyliodonium)octacyanotungstate(IV) (**2**), tetrakis(diphenyliodonium)-hexacyanoruthenate(II) (**3**) and tetrakis(diphenyliodonium)hexacyanoosmate(II) (**4**) were synthesized as described elsewhere.[36]

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