Sensitized Photolysis of Iodonium Salts Studied by CIDNP. Solvent Dependence and Influence of Lipophilic Substituents

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The sensitized photoreactions of diphenyliodonium salt and four of its technically relevant derivatives bearing lipophilic substituents were investigated by pseudo-steady-state and time-resolved CIDNP experiments. Singlet (naphthalene, diphenylanthracene, dimethylanthracene) and triplet (xanthone, thioxanthone, Michler's ketone) sensitizers were used in a variety of solvents (acetonitrile, dimethyl sulfoxide, dimethylformamide, methanol, chloroform, tetrahydrofurane, diethylene glycol dimethyl ether, dioxane, toluene). Under all conditions, the primary step leading to CIDNP was found to be electron transfer from the excited sensitizer *Sens to the onium cation On^+. All spin-polarization effects could be explained consistently within the framework of radical pair theory ($S-T_0$-type CIDNP). Pair substitution, i.e., the transformation of the primary radical pairs RP 1 ($\overline{On^\bullet Sens^{\bullet+}}$) into secondary pairs RP 2 ($\overline{Ph^\bullet Sens^{\bullet+}}$, where $Ph^\bullet$ is the phenyl or an aryl radical) plays a key role for the CIDNP effects and even leads to a field dependence of the polarization phases for the system diphenyliodonium cation/naphthalene in dioxane. Decreasing solvent polarity causes an increase of the rate RP 1 → RP 2. The introduction of a long lipophilic side chain into the onium salt has the same effect, presumably owing to self-solvation.

Introduction

Stable iodonium and sulfonium salts possess considerable importance as initiators for both cationic and radical photopolymerizations, especially in polymer-based photoimaging.[1] To overcome their unfavorable absorption properties, sensitization by energy or electron transfer must often be used. This leads to complex mechanisms involving several types of radical intermediates in succession, so that studies of the product distribution do not always yield unambiguous information about the microscopic details of the reaction.

CIDNP[2] spectroscopy (measurements of chemically induced dynamic nuclear polarizations) provides a complementary approach, which appears to be tailored to the investigation of such complex processes. CIDNP effects arise through nuclear spin sorting in the paramagnetic intermediates (radical pairs) and directly reflect the chemical nature of the latter while at the same time allowing one to monitor the pathways and kinetics of radical formation and decay. The observables in a CIDNP experiment are spin polarizations, i.e., populations of the nuclear spin states that deviate from the equilibrium values; these polarizations manifest themselves as anomalous line intensities in NMR spectra recorded during the reaction.

The most valuable assets of CIDNP spectroscopy are as follows. First, the occurrence of polarizations in a product shows that the latter is formed via the radical pair the polarizations stem from; in doubtful cases, more sophisticated experiments can be devised to ensure that this pathway is indeed the main reaction.[3] Second, the absolute polarization phase (absorption or emission) is simultaneously connected with the initial and final electron spin multiplicities of that pair, i.e., the electron spin state of its precursor and that from which the pair decays to the product in question. Third, under usual conditions the polarization of a particular proton i is proportional to its hyperfine coupling constant a_i in the radical. The so-called polarization pattern (the relative CIDNP intensities of the different protons) thus mirrors the spin density distribution in this intermediate;[4] in other words, it is directly related to its EPR spectrum, the correspondence also extending to the sign of the a_i. Fourth, the polarizations are exclusively generated during the life of the radical *pairs* (a few nanoseconds) but persist in the diamagnetic products for seconds. In consequence, even radicals that are much too short-lived to be detectable by EPR can be identified and characterized by CIDNP because they leave their polarization pattern as their characteristic signature.[5] Fifth, owing to this disparity of time scales, one can also measure the rate of appearance of a product by using pulsed light sources (lasers) and pulsed NMR detection;[6] a time resolution in the submicrosecond range can be reached with readily available equipment. Sixth, much faster transformations of the radical pairs can be investigated by using the rate of singlet−triplet mixing of the pairs as an inherent clock.[7] The present work utilizes all these facets of CIDNP spectroscopy.

Only very few CIDNP studies of sensitized photolysis of iodonium[8] and sulfonium[8d,9] salts have been reported so far. In all of them, except for a preliminary communication by us,[8d] electron-transfer sensitization of these initiators was investigated in highly polar solvents, typically acetonitrile. This is in striking contrast to the situation prevailing in technical applications of sensitizer/onium salt combinations: There, the polarity is usually quite low because the monomer ($\epsilon = 4-6$) serves as the reaction medium. To obtain a more complete picture, in this work we therefore cover a much wider range of conditions and also employ more refined CIDNP techniques than were available in the earlier[8a,c,9a,c] studies. First, by experiments with the same iodonium salt and different sensitizers in acetonitrile we elucidate the pathways leading to spin-polarized products in detail. Second, we compare the same sensitizer/onium salt

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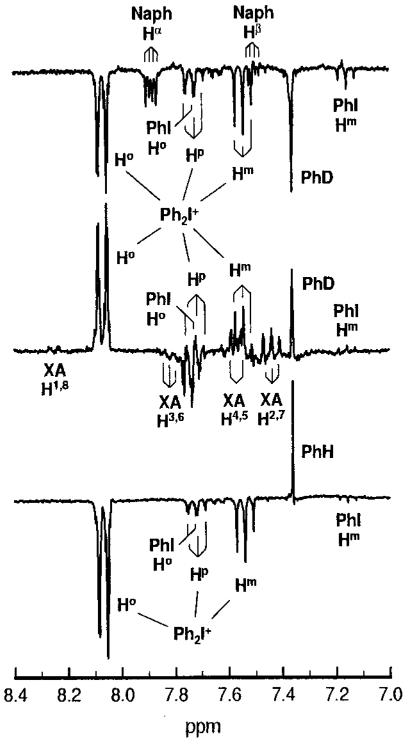


Figure 1. CIDNP spectra of diphenyliodonium hexafluoroantimonate with different sensitizers (top trace, naphthalene; center trace, xanthone; bottom trace, dimethylanthracene) in acetonitrile-d_3. For the assignment of the resonances, see text.

combination in different solvents to get information on the importance of the medium on the mechanism. Third, we investigate onium salts bearing lipophilic substituents—the type of initiators actually used in technically relevant systems—to learn how these substituents influence the reaction.

Results and Discussion

Diphenyliodonium Cation with Different Sensitizers in Acetonitrile. A CIDNP spectrum of the system diphenyliodonium hexafluoroantimonate/naphthalene ($Ph_2I^+SbF_6^-$/Naph) in acetonitrile is shown as the top trace of Figure 1. The polarizations of the products and of the onium salt are identical to those found with the sensitizers anthracene[8a,b] and diphenylanthracene;[8d] however, naphthalene has the advantage that the sensitizer polarizations are much larger, and not obscured by the resonances of the onium salt. In this system, as well as all the others investigated, the strong CIDNP signals exclude the possibility that the polarizations are only generated in a minor side reaction.

In a previous publication,[8d] we accumulated evidence that diphenylanthracene sensitizes onium salt decomposition by electron transfer from the singlet state. In contrast to that system, electron-transfer quenching of the naphthalene triplet ($E_T = 2.64$ eV, $E_{1/2}(\text{Naph}^{\bullet+}/\text{Naph}) = 1.54$ V vs SCE)[10] by our onium salt would probably be exergonic (reduction of Ph_2I^+ is an irreversible process, but from the cyclic voltamogramm of Ph_2I^+ in acetonitrile, $E_{1/2}(Ph_2I^+/Ph_2I^\bullet)$ was calculated to be -0.64 V vs SCE).[11] However, the identical CIDNP signals indicate that the predominant precursor multiplicity is also singlet in the naphthalene-sensitized reaction.

The fact that the protons of regenerated Naph exhibit CIDNP unambiguously shows that the radical pairs giving rise to these polarizations must contain sensitizer-derived radicals. This rules out CIDNP generation via an energy-transfer pathway,[12] which would furthermore appear to be somewhat endergonic (E_T of the onium salt is estimated to be larger than 2.69 eV).[1b] Finally, the polarization pattern of the naphthalene protons (polarization ratio $P(H^\alpha):P(H^\beta) \approx 4:1$) reflects the spin density distribution in the naphthalene radical cation $\text{Naph}^{\bullet+}$ ($a(H^\alpha) = -0.74$ mT, $a(H^\beta) = -0.187$ mT).[13]

All these observations are consistent with CIDNP generation in radical pairs that are formed by electron transfer from the excited sensitizer, i.e., in pairs $Ph_2I^\bullet\text{Naph}^{\bullet+}$. The polarizations can be analyzed with Kaptein's rule[14] of a CIDNP net effect

$$\Gamma_i = \mu\,\epsilon\,\text{sign}(a_i)\,\text{sign}(\Delta g) \qquad (1)$$

which connects the polarization phase Γ_i of nucleus i in a product ($\Gamma_i = +1$, absorption; $\Gamma_i = -1$, emission) with the reaction pathway, i.e., the precursor multiplicity μ ($\mu = +1$, triplet; $\mu = -1$, singlet) and the exit channel ϵ ($\epsilon = +1$, product formation from singlet pairs; $\epsilon = -1$, from triplet pairs), and the magnetic parameters (a_i, hyperfine coupling constant of nucleus i; Δg, difference of the g values when the radical bearing nucleus i is counted first) of the radical pairs.

The precursor multiplicity has been shown to be singlet. For energetic reasons, regeneration of Naph by back electron transfer of $Ph_2I^\bullet\text{Naph}^{\bullet+}$ is not feasible in the triplet state. As the proton hyperfine coupling constants in $\text{Naph}^{\bullet+}$ are negative,[13] the g value of $\text{Naph}^{\bullet+}$ ($g = 2.0025$)[15] must thus be smaller than the (unknown) g value of $Ph_2I^\bullet$. This appears reasonable because the latter radical is expected to bear a significant unpaired spin density on the iodine atom with its high spin−orbit coupling constant. The polarizations of the onium salt Ph_2I^+ can be analyzed in the same way. From the polarization pattern, it is seen that the proton hyperfine coupling constants in $Ph_2I^\bullet$ must all possess the same sign (+) and that their ratio $a(H^o):a(H^m):a(H^p)$ should be about 10:4:1.

The product PhD is formed via cleavage of $Ph_2I^\bullet$ to give iodobenzene PhI and phenyl radicals $Ph^\bullet$,[8a,b] which then abstract deuterium from the solvent. The strong emissive polarization of PhD cannot stem from $Ph_2I^\bullet\text{Naph}^{\bullet+}$ alone: The emissive phase of the PhD signal would demand that the cleavage step is electron-spin selective and occurs for singlet radical pairs only, which is inconceivable on chemical grounds and also contradicted by time-resolved CIDNP experiments, which show that the PhD signal appears gradually on a time scale of several microseconds; furthermore, CIDNP signals of PhD become stronger under conditions where those of the starting onium salt become weaker (see next section). However, the experimental facts are consistent with a pair-substitution[7] effect, i.e., a transformation of the primary radical pairs $Ph_2I^\bullet\text{Naph}^{\bullet+}$ (RP 1) into secondary radical pairs $Ph^\bullet\text{Naph}^{\bullet+}$ (RP 2) on a time scale comparable with the spin-correlated life of RP 1. With such a scenario, the polarizations can be thought of as arising in a hypothetical radical pair with the precursor multiplicity of RP 1, the exit channel of RP 2, and magnetic parameters that are weighted averages of those of RP 1 and RP 2, the weights being functions of the respective pair lifetimes.[7d] Our results at different magnetic fields in dioxane (see below) confirm that pair substitution plays an important role for the polarizations in these systems.

The proton hyperfine coupling constants in the phenyl radical are positive[16] as are those in the onium radical, so averaging will not change the sign of this parameter in eq 1. The g value of $Ph^\bullet$ ($g = 2.002\,27$)[17] is lower than than of $\text{Naph}^{\bullet+}$ while that of $Ph_2I^\bullet$ is much higher. However, simulations (see the discussion of Figure 6) indicate that for a wide range of parameters the averaged g value of $Ph_2I^{\bullet}$ and $Ph^{\bullet}$ is still smaller than that of $Naph^{\bullet+}$. With this premise, eq 1 predicts an emissive phase for the escape product PhD, in accordance with experimental observation. These estimations are corroborated by our results in nonpolar solvents (see below) and with trialkylsulfonium salts,[8d,9d] where pair substitution is so fast as to suppress all polarizations from RP 1, and where the (emissive) CIDNP phase for PhD must be ascribed solely to RP 2.

Geminate reaction of RP 2 in the singlet state followed by deprotonation of the resulting Meisenheimer cation leads to 1-phenylnaphthalene.[9d,18] In acetonitrile, the CIDNP signals of the phenyl moiety of this product are obscured by polarizations of Ph_2I^+ (H^m) and Naph (H^{β}); however, in other solvents they become visible and show the expected phase, i.e., opposite to that of PhD.

$Naph^{\bullet+}$ is not able to oxidize $Ph^{\bullet}$ (the oxidation potential of $Ph^{\bullet}$ in acetonitrile is estimated to be 2.45 V vs SCE),[19] so in contrast to RP 1 electron transfer is not a feasible decay channel for RP 2. Nevertheless, spin-polarized Naph can be formed from RP 2 by an electron-spin-independent pathway (i.e., triplet exit channel), namely by escape of $Naph^{\bullet+}$ from the cage followed by degenerate electron exchange with surplus naphthalene; analogous processes are well known for other radical ions.[20] Pair substitution must influence the polarization phase of Naph qualitatively in the same way as that of PhD because the transformation RP 1 → RP 2 again does not change the sign of the hyperfine coupling constants of the protons considered but inverts the sign of the g-value difference. With a dominance of RP 2 in the superposition, emission is thus predicted also for Naph formed via RP 2.

Owing to the high sensitivity of the pseudo-steady-state CIDNP technique[21] employed in this work, we were further able to detect the polarizations of iodobenzene PhI. The ortho and meta protons of this product appear in emission, while the signal of the para proton is too weak to be visible. Cleavage of $Ph_2I^{\bullet}$ to give PhI is an "escape reaction" of RP 1 because it is not multiplicity-selective. The presence of pair-substitution effects indicates that this cleavage occurs on a time scale comparable to the spin-correlated life of RP 1, so any radicals $Ph_2I^{\bullet}$ that escape from RP 1 in the true sense of the word (i.e., by diffusion) will have transformed into free phenyl radicals and PhI before having had a chance of reacting with other partners. Hence, formation of PhI is most likely the only escape channel of RP 1. At first glance, the polarizations of PhI would, therefore, possess the wrong phase (the opposite phase as for the regenerated onium salt Ph_2I^+, i.e., absorption, would be expected, emission is observed) and also be much too weak (the polarizations in the escape product PhI should have the same magnitude as in the cage product Ph_2I^+, a ratio of about 1:4 is observed), whereas the polarization patterns of PhI and Ph_2I^+ are identical.

Ulrich et al.[8c] suggested a nonplanar geometry of $Ph_2I^{\bullet}$ as the origin of these effects. With such a structure, the π system of one of the phenyl rings would be in conjugation with the orbital at the iodine atom bearing most of the unpaired spin density. For the ortho protons of this benzyl-type moiety, this would give rise to negative hyperfine coupling constants by the $\pi-\sigma$ spin-polarization mechanism.[23] As the ring−iodine bond of this moiety is likely to remain intact in the scission process, these polarizations would appear in PhI, leading to the absolute phase observed for the ortho protons of this product. The out-of-plane motion of the other ring would enable hyperconjugation of the pertinent orbital at iodine with the phenyl protons, resulting in positive hyperfine coupling constants of magnitude decreasing with the distance between iodine and H. Because the hyperconjugation mechanism is more efficient than the $\pi-\sigma$ spin-polarization one,[23] the polarization pattern in the regenerated onium salt would predominantly correspond to the spin density distribution in this phenyl-type moiety, and the absolute polarizations of Ph_2I^+ would be larger than those of PhI.

However, the polarization phase of the meta protons in PhI does not agree with this picture: Emission is observed for them, but absorption would clearly be expected because it is well-known that the hyperfine coupling constant of the meta protons in a benzyl-type radical is positive.[23] A stronger doubt is cast on the inequivalence hypothesis by the fact that, although AM1[22] calculations indeed give a twisting angle between the two phenyl rings in $Ph_2I^{\bullet}$ of about 45°, the computed lengths of the two phenyl−iodine bonds do not differ by more than 0.002 Å, and very similar spin densities and charge distribution are obtained for the two rings.

Instead, we believe that the pair substitution RP 1 → RP 2 is indirectly responsible for the polarizations of PhI because after scission of $Ph_2I^{\bullet}$ the cleavage product PhI is still contained in the same cage with $Ph^{\bullet}$ and $Naph^{\bullet+}$, i.e., in RP 2. Addition of $Ph^{\bullet}$ to the aromatic ring of PhI leads to formation of iodobiphenyls in considerable yields.[19] By this process, PhI is removed from RP 2. Because in the singlet state $Ph^{\bullet}$ can also undergo a cage reaction with $Naph^{\bullet+}$, its multiplicity-independent attack on PhI is an "escape" reaction of the consecutive pairs RP 1 and RP 2. Consequently, the *surviving* PhI is polarized via the singlet exit channel. The lower efficiency compared to Ph_2I^+ is due to the indirect pathway. This mechanism does not only explain that the iodobenzene polarizations have the same absolute phase as the polarizations of the starting onium salt and are weaker but also that they exhibit exactly the same polarization pattern; it is thus consistent with all the experimental facts.

The center trace of Figure 1 shows CIDNP of $Ph_2I^+SbF_6^-$ in acetonitrile with the triplet sensitizer xanthone Xa. From the occurrence of considerable polarizations of the regenerated sensitizer, one can again exclude energy transfer[19] as the pathway to the radical pairs that are responsible for the CIDNP effects in this system; besides, control experiments in acetone-d_3, which exclusively acts as energy-transfer sensitizer,[9b] gave polarizations that were smaller by at least 2 orders of magnitude under the same experimental conditions.

As an $n\pi^*$ triplet, ^3Xa is capable of hydrogen abstraction. Although phenyl hydrogens are not easily abstractable, this process cannot be ruled out a priori as the first photochemical step in this system. However, the polarization pattern of regenerated Xa cannot be reconciled with this pathway. As the figure shows, $H^{1,8}$ are polarized weakly in absorption, $H^{3,6}$ weakly in emission, and $H^{2,7}$ and $H^{4,5}$ strongly in absorption. The radical that must result from such a hydrogen abstraction, the 9-hydroxyanthryl radical, possesses a spin density distribution that is characterized by large and approximately equal hyperfine coupling constants for $H^{1,8}$ and $H^{3,6}$, and small ones for $H^{2,7}$ and $H^{4,5}$;[24] from Hückel arguments it follows that the former two must be negative and the latter two positive. This would lead to large polarizations of one phase for $H^{1,8}$ and $H^{3,6}$, and smaller polarizations of the opposite phase for $H^{2,7}$ and $H^{4,5}$. As this is completely at variance with the experimental spectrum, hydrogen abstraction cannot be the pathway to the radical pair in question. This reasoning does not rely on any assumptions regarding g values, precursor multiplicities, or exit channels.

In contrast, the observed intensity pattern is compatible with the xanthone radical cation $Xa^{•+}$ as the intermediate giving rise to the polarizations, in other words, with radical pair formation by electron transfer from the excited sensitizer to the onium salt, exactly as in the preceding system: Although the magnetic parameters of $Xa^{•+}$ are not known, it is obvious from simple molecular orbital considerations (in fact, even from drawing the Lewis structures) that this species must be regarded as an aryl ether radical cation rather than an aryl ketone radical cation, i.e., that the positive charge and the unpaired spin density must be located more on the aryl ether oxygen than on the carbonyl oxygen. This immediately leads to the prediction of large (and negative) hyperfine coupling constants for $H^{4,5}$ and $H^{2,7}$, a smaller positive one for $H^{3,6}$ and presumably also for $H^{1,8}$. As this is in much better agreement with the observed polarization pattern (except for the weak signal of $H^{1,8}$, for which one would expect the opposite phase), we conclude that RP 1 in this system is $Ph_2I^•Xa^{•+}$. The absolute polarization phase is also consistent with this: Because the *g* value of $Ph_2I^•$ is certainly larger than that of any other radical in this system not containing iodine, absorption is predicted for $H^{2,7}$ and $H^{4,5}$ of the regenerated sensitizer (triplet precursor, back electron transfer in the singlet state, $\Delta g < 0$, $a(H^{2,4,5,7}) < 0$), as observed.

The occurrence of both absorption and emission in the spectrum shows that CIDNP is of the usual $S-T_0$ type and rules out $S-T_\pm$ type CIDNP, a hypothesis that had been proposed[8a,b] to account for the dominance of polarizations of one phase in the CIDNP spectra. Exactly the same polarization phases as in the xanthone case were also observed with the triplet sensitizer thioxanthone. In that system, however, the sensitizer polarizations cannot be used as diagnostic criteria because they are obscured by other signals.

As is evident from Figure 1, naphthalene and xanthone yield opposite CIDNP phases for all relevant species (regenerated Ph_2I^+, reaction products PhI and PhD) but very similar relative intensities. This shows that the same basic mechanism is realized in both systems and, because xanthone must react from the triplet state, provides independent confirmation that the precursor multiplicity in the naphthalene experiment is singlet.

Finally, the bottom trace of Figure 1 displays the CIDNP spectrum with the sensitizer dimethylanthracene Me_2An. The polarizations of Ph_2I^+ and PhI are seen to exhibit the same phases and relative intensities as with naphthalene, which does not come as a surprise because one would predict the same mechanism of radical pair formation in both instances, electron transfer quenching of the excited sensitizer in its singlet state. The striking difference in the dimethylanthracene experiment is the opposite phase of the benzene signal. However, inspection of the line width reveals that the peak in question is not due to monodeuterobenzene PhD as in the naphthalene and xanthone cases, but to benzene PhH. From this, it is immediately obvious that this product is not formed by free phenyl radicals $Ph^•$ abstracting deuterium from the solvent but by a cage reaction between $Ph^•$ and $Me_2An^{•+}$ to give PhH and a carbocation; the opposite exit channel causes the phase inversion. As we recently reported,[9d] exactly the same behavior is realized in the dimethylanthracene-sensitized photolysis of triphenylsulfonium salts.

DeVoe et al. observed the same seeming anomaly for the triplet sensitizer bis(dimethylamino)benzophenone (Michler's ketone).[8a,b] The dimethylamino protons of Michler's ketone are also easily abstractable. Repeating their experiment, we found the broader signal of PhD with the expected phase (absorption as with the triplet sensitizer xanthone) superimposed on the narrow but considerably more intense emission signal of PhH. Most likely, this superposition could not be detected in their study because with their experimental technique (CIDNP with continuous illumination) line broadening is unavoidable; this results in partial cancellation of the opposite signals of PhH and PhD, with that of PhH remaining as the more intense of the two. This problem is practically eliminated by the pseudo-steady-state technique[21] used in the present work.

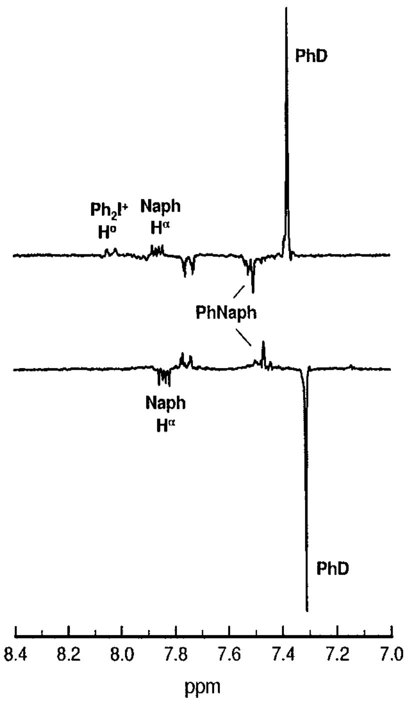


Figure 2. CIDNP spectra of diphenyliodonium hexafluoroantimonate with the sensitizer naphthalene in diethylene glycol dimethyl ether-d_{14} (bottom) and in chloroform-*d* (top).

We point out that DeVoe et al. also report absolute signal phases that are opposite to those we observe in this system, namely emission for the onium salt and absorption for benzene.[8a,b] Given our findings for the system naphthalene/diphenyliodonium in dioxane (see below), this may well be due to a field dependence—their experiments were carried out at 2.4 T (100 MHz), which is not accessible with our equipment—of the polarizations, i.e., be a manifestation of the pair substitution RP 1 → RP 2.

Diphenyliodonium Cation/Naphthalene in Different Solvents. No evidence was obtained for a change of the basic reaction mechanism when the medium was changed. Generally, in solvents other than acetonitrile, lower intensities were found for the signal of the regenerated onium salt with concomitant decrease of the polarization of PhI, and the benzene peak became very intense. These effects are readily explained by a faster rate of pair substitution RP 1 → RP 2 and, therefore, a shift of the source of the polarizations from RP 1 to RP 2. Total CIDNP intensities were not affected very strongly by the solvent.

Figure 2 displays two examples for the system $Ph_2I^+SbF_6^-$/Naph. Owing to the reduction of the polarizations of the onium salt and the increase of those from RP 2, the CIDNP signal of 1-phenylnaphthalene PhNaph, a cage product of RP 2, becomes detectable and shows the expected phase, i.e., opposite to that of PhD. The multiplet with the same phase at lower field must be ascribed to an unstable cage product of RP 2 because its position is sensitizer-dependent and the signal is no longer present in a spectrum without illumination recorded after the CIDNP experiment.

The polarizations of the naphthalene protons are still clearly visible in the CIDNP spectrum with diethylene glycol dimethyl ether as the solvent (bottom trace of the figure); their polarization pattern is the same as in acetonitrile and reveals the intermediacy of radical pairs containing the naphthalene radical cation. The same is found in dioxane (see below, Figure 5). This illustrates that even in these solvents, the least polar ones in which the diphenyliodonium salt was sufficiently soluble, the primary chemical step is electron transfer quenching of the excited sensitizer by the onium cation. The obvious reason why this process is still efficient in a nonpolar solvent is that it does not involve charge separation but only a charge shift. The same feature is also responsible for the fact that polarizations can be generated at all in these electron transfer reactions under nonpolar conditions: The CIDNP effect relies on diffusive separation of the radicals constituting a pair to a distance where the exchange interaction between them becomes negligible, and this would be suppressed for oppositely charged radical ions in a nonpolar solvent.

Interestingly, the phases of all polarizations are inverted when the CIDNP spectrum is recorded in chloroform (top trace of Figure 2); this was observed both at 5.9 T (250 MHz) and 11.7 T (500 MHz). In the light of the results presented in the preceding section, this effect is explained most naturally by a triplet precursor in this case, which must be due to the heavy-atom effect of the solvent on the intersystem crossing rate of the excited sensitizer. Attempts to isolate a possible contribution of singlet precursors in this system by a variation of the onium salt concentration were unsuccessful because for sensitivity reasons (quenching efficiency) the experiments had to be carried out near the solubility limit.

Evaluation of absolute CIDNP intensities is prone to errors, the principal reason being that they are directly proportional to the number of radical pairs formed within the active volume V of the NMR spectrometer; as V is not defined very well, this number is difficult to determine and control. Evaluating relative polarizations is much more reliable because this eliminates all factors influencing the efficiency of radical pair formation (e.g., light intensity, absorption properties, quenching efficiencies) and also the dependence of the enhancement factors on the solvent viscosity.

The signal of the naphthalene α protons was used as internal reference. As a disadvantage, these protons potentially bear polarizations from RP 1 and RP 2 and from different exit channels, which cannot be separated; hence, the reference polarizations also depend in an unknown manner on the rate of pair substitution. However, another reference signal is unavailable, and it is estimated that this procedure is still more accurate than using the absolute CIDNP intensities, not the least because the exact magnetic parameters of the onium radical are inaccessible and most likely will remain so owing to its short life.

Figure 3 displays the relative CIDNP signals $P_{\mathrm{rel}}(\mathrm{Ph_2I^+})$ of the most strongly polarized protons of the substrate (i.e., $\mathrm{H^o}$) in the solvents used. Because the onium salt can only be recovered by back electron transfer of RP 1 whereas there is no pathway to it from RP 2, $P_{\mathrm{rel}}(\mathrm{Ph_2I^+})$ is a measure of how well back electron transfer is able to compete with the other decay pathways of RP 1, escape and pair substitution; in other words, $P_{\mathrm{rel}}(\mathrm{Ph_2I^+})$ indicates where the rate of fragmentation of the onium radical is positioned within the kinetic window of the CIDNP effect. It is seen that $P_{\mathrm{rel}}(\mathrm{Ph_2I^+})$ varies roughly in parallel with the solvent polarity. However, quantitative single-parameter correlations with the relative permittivity, the Dimroth polarization parameter, the acceptor number, the donor number, or the solvent basicity were found to be unsatisfactory. Several of the deviations, such as the position of dimethylformamide and dimethyl sulfoxide relative to methanol and acetonitrile, and that of chloroform relative to the other less polar solvents, can be explained by the different viscosity: a higher viscosity increases the time between reencounters, and must thus decrease the rate of back electron transfer and increase the probability of fragmentation. The polarizations in dioxane, which possesses the lowest polarity and the highest viscosity of all the solvents in Figure 3 are, however, inexplicable by this simple model.

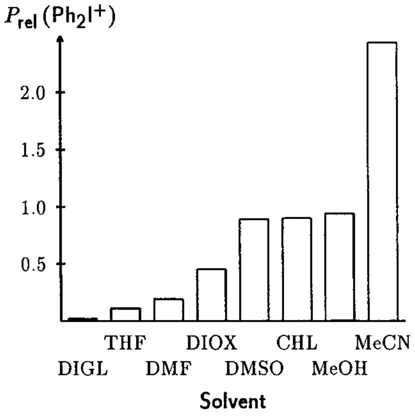


Figure 3. Relative polarizations $P_{\mathrm{rel}}(\mathrm{Ph_2I^+})$ of the ortho protons of diphenyliodonium hexafluoroantimonate (reference signal, α protons of the sensitizer naphthalene) in different solvents. DIGL, diethylene glycol dimethyl ether-d_{14}; THF, tetrahydrofuran-d_8; DMF, dimethylformamide-d_7; DIOX, dioxane-d_8; DMSO, dimethyl sulfoxide-d_6; CHL, chloroform-d; MeOH, methanol-d_4; MeCN, acetonitrile-d_3.

The polarizations of escaping $\mathrm{Ph^\bullet}$ are transferred to diamagnetic products by the subsequent reactions of this free radical with the solvent or with surplus sensitizer. In a recent study[9d] of sensitized photolysis of triphenylsulfonium salt in acetonitrile, where $\mathrm{Ph^\bullet}$ plays the same mechanistic role as in the iodonium case, we have shown that addition products are indeed formed and significantly influence the yield of spin-polarized PhD, although at first glance the latter appears to be the only polarized species from this pathway. Exchange phenomena, distribution of the polarizations among several regioisomers, and the fact that the NMR signals of the addition products are complex multiplets with concomitant low intensity of the individual lines account for the failure to detect their CIDNP signals. As the pseudo-first-order rate constant of deuterium abstraction was found[9d] to be greater than $2 \times 10^5\ \mathrm{s^{-1}}$ even in acetonitrile—thermodynamically the least favorable of our substrates for deuterium abstraction, on a par with dimethyl sulfoxide—whereas the nuclear T_1 in $\mathrm{Ph^\bullet}$ is estimated to be at least 50 μs, the influence of nuclear spin relaxation on the PhD polarization is expected to be negligible.

Hence, the relative CIDNP intensity of PhD should be proportional to the ratio of rate constants of deuterium abstraction and of combination with the sensitizer (as the dominant competing bulk reaction). As our results for the triphenylsulfonium systems indicate,[9d] the latter is activation-controlled and should thus not depend much on the solvent. For the deuterium abstraction by $\mathrm{Ph^\bullet}$ from the solvent, we assume Arrhenius behavior, an identical preexponential factor within our series of solvents, and a linear relationship between driving force of the reaction and activation barrier. This leads to a linear relationship between the logarithm of the relative polarization of monodeuterobenzene ln $P_{\mathrm{rel}}(\mathrm{PhD})$ corrected for the number n of equivalent protons that can be abstracted from the solvent, and the reaction enthalpy ΔH_{abs}

$$\ln P_{\mathrm{rel}}(\mathrm{PhD}) - \ln n = A - \frac{B}{RT}\Delta H_{\mathrm{abs}} \qquad (2)$$

The reaction enthalpy was obtained from the heats of formation of the solvent and its radical, the phenyl radical, and benzene as calculated by PM3. For simplicity, values were computed for the protonated compounds instead of the deuterated ones. ΔH_{abs} for dimethylformamide is a weighted average (one proton at the carbonyl carbon, six less easily abstractable dimethylamino protons). As Figure 4 shows, there is a linear correlation according to eq 2, i.e., the relative intensity of the PhD signal reflects the capability of the solvent to act as a hydrogen atom donor. The slope of the plot, however, would correspond to a value of the Brønsted α much smaller than 0.5. The reason for this might be the strong exergonicity of the reactions.

Dioxane was the only one of our solvents to reveal another intriguing aspect of CIDNP in these complex systems. With this medium, different magnetic fields led to opposite signal phases both for Naph and for PhD (the CIDNP signals of the starting onium salt and of PhI are undetectable in this nonpolar solvent). While the expected phases, emission, are found at 11.7 T (proton resonance frequency 500 MHz), experiments at 5.9 T (250 MHz) gave absorption signals. As can be seen in Figure 5, this phenomenon is clearly not an artifact due to an insufficient signal-to-noise ratio; moreover, the absolute phase of the spectrum was carefully calibrated with a normal NMR spectrum of the same sample recorded with exactly the same acquisition parameters. CIDNP spectra acquired without presaturation also confirmed the observations.

Simulations of this effect for a model system with one proton in one of the radicals are shown in Figure 6. The calculations were performed with a reencounter model[25] based on the Freed–Pedersen formalism.[26] The parameters used for RP 2 were those of the pair $\mathrm{Ph}^{\bullet}\mathrm{Naph}^{\bullet+}$ ($\Delta g = -2.3 \times 10^{-4}$,[15,17] $a = +1.8$ mT for the ortho protons[16] of $\mathrm{Ph}^{\bullet}$). For RP 1 we chose $\Delta g = +2 \times 10^{-3}$ and $a = +4.5$ mT, on the grounds (see above) that the g value difference of RP 1 must be significantly higher than that of RP 2 and positive, that the hyperfine coupling constants in $\mathrm{Ph_2I}^{\bullet}$ must be positive, and that hyperconjugation in $\mathrm{Ph_2I}^{\bullet}$ should be more efficient than in $\mathrm{Ph}^{\bullet}$ because of the better orbital overlap. An interdiffusion coefficient D of 2×10^{-5} cm^2 s^{-1}, an exchange radius d of 7 Å, and a length of 1.5 Å for a diffusional step were assumed, corresponding to a total probability of reencounter of about 0.9. Because in the expressions for the nuclear-spin-dependent reaction probabilities the matrix elements of intersystem crossing and the rate constant k of pair substitution are scaled with d^2/D, a change of the latter quantity would correspond to a proportional change of the magnetic parameters and of k.

As is seen in Figure 6, the experimental effect is reproduced qualitatively by the calculations. The figure also shows that it should occur for a small range of k only, of less than an order of magnitude. Values of k outside this interval do not lead to a sign change, which might explain why the anomaly was only observed in a single solvent. When other magnetic parameters are used for RP 1, the range of anomalous polarization phases moves, but the shift is not a strong function of these parameters. From this, we can infer that the rate constant of cleavage of the onium radical $\mathrm{Ph_2I}^{\bullet}$ should be around 3×10^{8} s^{-1} in dioxane, an order of magnitude lower than that estimated by DeVoe et al. from modeling the results of their laser flash photolysis experiments.[8a,b] An accurate value cannot be obtained because of the uncertainty of g and a of this radical. Still, the phase inversion provides very strong evidence that the CIDNP effects for Naph and PhD in this system indeed arise from consecutive radical pairs, i.e., are due to pair substitution.

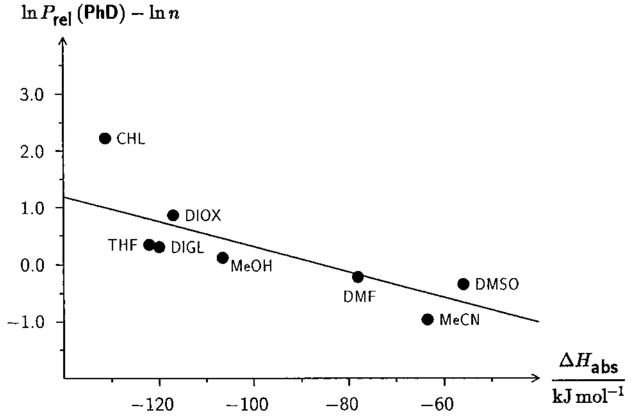


Figure 4. Photoreaction of diphenyliodonium hexafluoroantimonate with naphthalene in different solvents. Shown are the relative polarizations P_{rel}(PhD) of the product monodeuterobenzene (reference signal, α protons of the sensitizer), after correction for the number n of abstractable protons per solvent molecule, as functions of the calculated enthalpy of hydrogen abstraction ΔH_{abs}. Chloroform was not included into the regression because the precursor multiplicity is different in this solvent. The labels are the same as in Figure 3. For further explanation, see text.

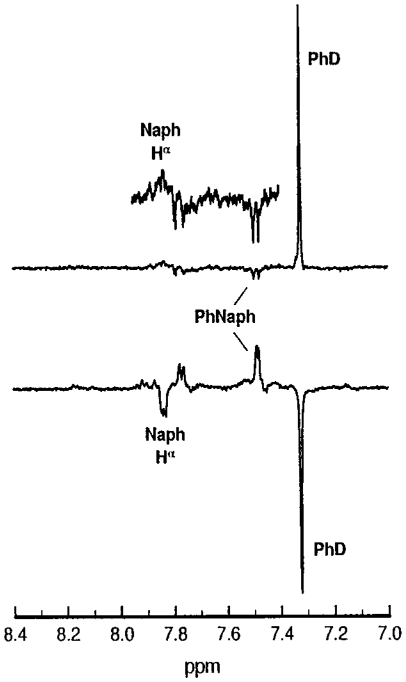


Figure 5. CIDNP spectra of the system diphenyliodonium hexafluoroantimonate/naphthalene in dioxane at two different magnetic fields. Top trace, magnetic field 5.9 T, proton resonance frequency 250 MHz; bottom trace, 11.7 T, i.e., 500 MHz. Absolute intensities in the two spectra are not directly comparable because the optical efficiencies and active volumes of the two probes are different.

Onium Salts with Lipophilic Substituents. The formulas of the technically relevant substrates studied, dicumyliodonium hexafluorophosphate $\mathrm{Cm_2I^+PF_6^-}$, Cm = p-$(\mathrm{Me_2CH})\mathrm{Ph}-$, and the three alkoxy-substituted salts $\mathrm{PhAr_{(a)}I^+SbF_6^-}$, $\mathrm{PhAr_{(b)}I^+SbF_6^-}$, and $\mathrm{PhAr_{(c)}I^+SbF_6^-}$ are displayed in Chart 1.

With the sensitizer naphthalene in acetonitrile, $\mathrm{Cm_2I^+}$ (Figure 7, bottom trace) gave identical sensitizer polarizations as with the unsubstituted compound $\mathrm{Ph_2I^+}$ and polarizations of the onium-derived products that were very similar: The ring protons

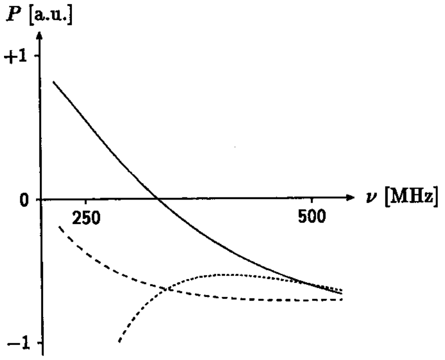
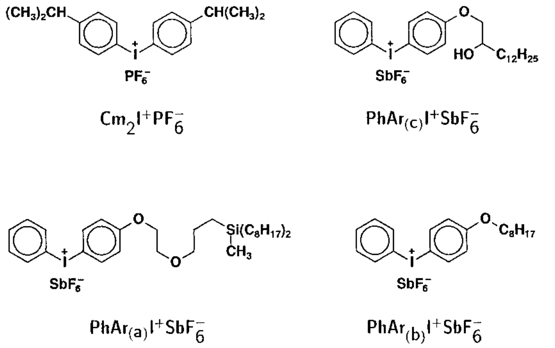


Figure 6. Simulation of the field dependence of the polarization P in a model system (consecutive radical pairs containing one proton, the transformation of the pairs occurring with a rate constant k). The x axis gives the proton resonance frequency ν, 250 MHz corresponding to 5.9 T, and 500 MHz to 11.7 T. Solid line, $k = 3 \times 10^8$ s^{-1}; short dashed line, $k = 2 \times 10^8$ s^{-1}; long dashed line, $k = 1.2 \times 10^9$ s^{-1}. For other parameters and further explanation, see text.

CHART 1



$Cm_2I^+PF_6^-$

$PhAr_{(c)}I^+SbF_6^-$

$PhAr_{(a)}I^+SbF_6^-$

$PhAr_{(b)}I^+SbF_6^-$

of the starting onium salt appear in emission, with the protons ortho to the iodine atom being polarized more strongly than the meta protons, as before. Likewise, the isopropyl-substituted iodobenzene CmI, the analog to PhI, exhibits emissive polarizations of the ring protons that again are about 4 times weaker than those of the starting compound and show the same polarization pattern. The two absorptive signal groups must stem from two combination products of the cumyl radical Cm$^\bullet$ with the sensitizer, because they are found at slightly changed positions also in a spectrum with xanthone. The one at about 7.4 ppm is almost certainly due to 1-cumylnaphthalene, as is inferred from a comparison with the CIDNP spectra of the unsubstituted iodonium salt; the other could not be identified because it does not persist (see preceding section). Deuterocumene CmD is polarized in emission.[27]

A new feature is the sharper emission line of cumene CmH,[27] which is superimposed on the CmD signal but possesses the same phase, as opposed to our observations in the system diphenyliodonium/dimethylanthracene (compare Figure 1, bottom trace). However, the explanation of this discrepancy is straightforward. In the dimethylanthracene case, abstraction of the hydrogen atom is a geminate reaction between the phenyl radical and the sensitizer radical cation, which can only take place in the singlet state of the radical pair. In contrast, the isopropyl protons of dicumyliodonium are abstracted by free cumyl radicals that have escaped from the cage. This pathway, therefore, corresponds to the triplet exit channel. Consistent with this interpretation is that abstraction from the substrate Cm_2I^+ can be suppressed with a solvent that is a better hydrogen-atom donor than is acetonitrile: In diethylene glycol dimethyl ether-d_{14}, only the signal of the deuterated compound CmD is found.

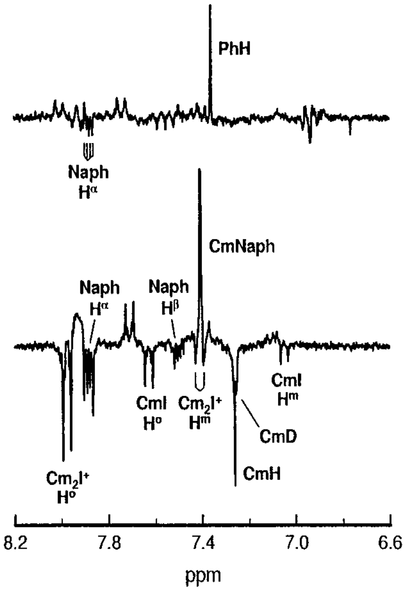


Figure 7. Photoreaction of dicumyliodonium hexafluorophosphate (bottom trace) and of the alkoxy-substituted onium salt $PhAr_{(a)}I^+SbF_6^-$ (top trace) with naphthalene. Shown are the CIDNP spectra in acetonitrile-d_3. For the assignment of the resonances, see text.

The changes of the polarizations when other sensitizers and solvents were used can be explained within the framework discussed in the preceding sections.

Electron-transfer sensitization of the alkoxy-substituted onium salts $PhAr_{(x)}I^+SbF_6^-$ (x = a, b, c) with triplet sensitizers was not feasible, probably because their reduction potentials are more negative than that of Ph_2I^+.[11] As an example, the CIDNP spectrum of $PhAr_{(a)}I^+SbF_6^-$ with naphthalene in acetonitrile-d_3 is displayed in the top trace of Figure 7. Besides the benzene peak, the characteristic multiplet of the naphthalene α protons is clearly discernible. The other polarizations were not assigned; a part of them might also be due to impurities and failure to achieve complete background saturation because these onium salts were technical products. In solvents of lower polarity, even toluene, the general appearance of the CIDNP spectra does not change.

The polarized naphthalene signal with the expected emissive phase again bears out that the mechanism of radical pair formation is electron transfer from the excited sensitizer to the onium cation. The fact that the onium salt is unpolarized shows that clevage of the onium radical is fast compared to the life of the primary radical pair. In the absence of any evidence for a through-bond effect of the alkoxy substituent on the cleavage rate, we take this to indicate that despite the highly polar solvent acetonitrile the local polarity of the medium is low, in other words, that the iodonium radical is solvated by its lipophilic chain. This was also concluded from measurements of the quantum yields of sensitizer decay and proton formation in these systems.[28]

Formation of alkoxybenzene or alkoxydeuterobenzene is not found, so it is evident that cleavage of the iodonium radical preferentially occurs at the bond to the unsubstituted ring, although PM3 calculations predict a negligible difference in ΔH for the two alternatives. As the line width clearly shows, the singlet at 7.35 ppm is indeed benzene, not monodeuterobenzene. Hence, the phenyl radical stabilizes by hydrogen abstraction from the alkoxy chain, not by deuterium abstraction from the solvent. The higher efficiency of the former process even in solvents that are good hydrogen-atom donors must be due to spatial proximity, and thus provides further corroboration of a solvation of the radicals by the alkoxy chain.

Strikingly, the absorptive phase of the benzene signal is opposite to that expected for a reaction of free radicals. No phase inversion was observed within our experimentally accessible range of magnetic fields, which, however, does not completely rule out a pair-substitution effect analogous to that encountered in the system $\mathrm{Ph_2I^+}$/Naph in dioxane (Figure 5) as the reason of the phase anomaly. The only other explanation would appear to be a multiplicity-dependent (singlet) reaction in the complex consisting of the phenyl radical, the alkoxy “solvent”, and the naphthalene radical cation, similar to the one responsible for the iodobenzene polarizations in the system $\mathrm{Ph_2I^+}$/Naph.

Conclusions

These examples demonstrate the power of CIDNP spectroscopy to probe the microscopic details of such complex mechanisms. Interesting and unusual CIDNP effects are encountered in these systems. As has been shown, the solvent and the substituents of the substrate have a significant influence on key steps of the reaction, namely the cleavage of the primarily formed onium radical and the decay of the resulting phenyl (or aryl) radical. Many of the results could be explained within a consistent framework, but further work is clearly warranted to elucidate the solvent dependence and the behavior of iodonium salts bearing lipophilic substituents, especially because of the relevance for technical applications of sensitized onium salt photolysis.

Experimental Section

The lipophilic onium cations $\mathrm{PhAr}_{(x)}\mathrm{I}^+$ (x = a, b, c) were experimental or commercial products ($\mathrm{PhAr}_{(a)}\mathrm{I}^+$, Wacker-Chemie; $\mathrm{PhAr}_{(b)}\mathrm{I}^+$, General Electric; $\mathrm{PhAr}_{(c)}\mathrm{I}^+$, Sartomer); $\mathrm{Cm_2I^+PF_6^-}$ was synthesized according to ref 31. The hexafluoroantimonates were prepared from the chlorides by anion exchange and purified by precipitation from an isopropanol solution by adding heptane (50% v/v). All sensitizers were obtained commercially and purified by sublimation. Deuterated solvents were used as received. Sensitizer and onium salt concentrations were chosen such that the optical density of the samples was about 1.0 at the excitation wavelength and that the quenching quantum yields were at least 90%. The freshly prepared samples were deoxygenated by bubbling purified nitrogen through the solution and then immediately sealed.

The CIDNP experiments were performed on a Bruker WM-250 NMR spectrometer equipped with a home-made data acquisition system and pulser unit, and a Varian Gemini 500 spectrometer. An excimer laser (XeCl, $\lambda = 308$ nm) that was triggered by the pulse generator or the spectrometer was used as the light source. An energy of about 5 mJ per pulse was absorbed in the samples, as determined actinometrically. Optical setup[29] and pulse sequences for the time-resolved[30] and pseudo-steady-state[21] CIDNP experiments have been described previously. Both these techniques completely eliminate the background signals and yield CIDNP signals that are undistorted by nuclear spin relaxation in the diamagnetic reaction products and free from linebroadening.

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