On the basis of these observations, it seems likely that the same type of Diels–Alder donor–acceptor complex (**11**) is involved in both trapping modes (Scheme III). For the more powerful acceptors, the degree of electron transfer might become sufficiently high to favor complex collapse via proton transfer and radical coupling (**12**) rather than the more conventional [4 + 2] cycloaddition pathway (**11**). The exact timing of these steps is not certain, but the radical coupling step would either have to occur first or very rapidly following proton transfer in order to afford the regiochemistry observed for **10**.[12]

In summary, this work has not only served to demonstrate the feasibility of the laser-jet delayed trapping technique for intercepting long-lived photochemical intermediates but also has provided evidence which indicates that photoenols function in the previously unrecognized capacity of effective electron donors.

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(12) In the case of **10**, the methyl substituent blocks tautomerization to the hydroquinone which apparently occurs in the trapping with benzoquinone itself. This hydroquinone in turn could be oxidized by the excess benzoquinone trapping agent to form the isolated trapping product **4**.

Formation of Intramolecular Radical Cations with an Iodine–Iodine $2\sigma/1\sigma^*$ Three-Electron Bond in the Oxidation of 1,*n*-Diiodoalkanes

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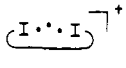
Radical cations of the general type



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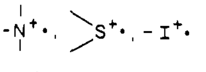
have been identified as transients in the •OH-induced oxidation of 1,*n*-diiodoalkanes in aqueous solutions. They are the first examples for an *intra*molecular cationic $2\sigma/1\sigma^*$ three-electron bond between two monovalent hetero atoms.

Radical cations derived from organic compounds and containing $2\sigma/1\sigma^*$ three-electron bonds have been subject to many experimental and theoretical investigations in recent years.[1,2] Generally such bonds can be formed via interaction of an unpaired (usually p-electron of an oxidized tri-, di-, or monovalent hetero atom, e.g.,



with the free electron pair of a second (identical or different) hetero atom. Alternatively such bonds may result from addition of an electron to an already existing σ-bond. The electronic structure of these three-electron bonds is characterized by the combined effect of two bonding σ-electrons and one antibonding, i.e., bond-weakening σ*-electron.

Three-electron bond formation, in principle, is possible *inter*molecularly between hetero atoms located in different molecules or *intra*molecularly if both interacting hetero atoms belong to the same molecule. The latter generally requires a favorable conformation for sufficient orbital overlap. *Intra*molecular three-electron bonds of high stability are particularly found between multibridged tri- and divalent hetero atoms, e.g., upon reduction of tricyclic hydrazonium dications[3] or oxidation of bicyclic dithia compounds.[1,4] Despite all these many examples it was not until recently that we could report on the first three-electron bonded radical cations in liquid phase which involve monovalent hetero atoms, namely

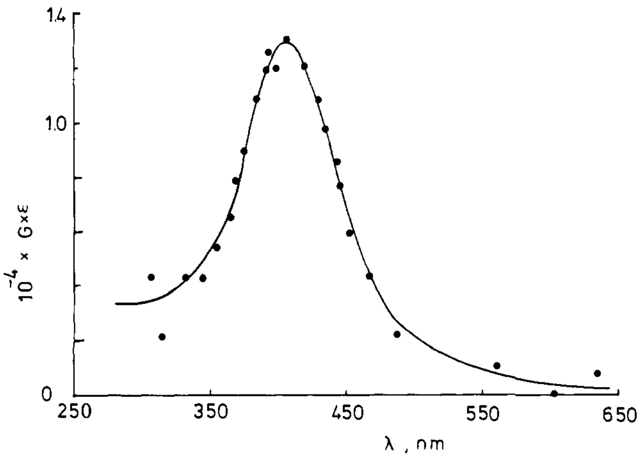
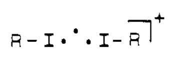


Figure 1. Optical absorption spectrum of **1a**, measured immediately after a 1–2 μs pulse given to an N_2O saturated, pH 3, aqueous solution of 2 × 10^{-5} M 1,3-diiodopropane.



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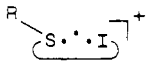

3

The *inter*molecular radical cations **2** were generated in the •OH radical induced oxidation of alkyl iodides in acidic (pH < 4) aqueous solution[5] and exist in the equilibrium

$$RI^{\bullet+} + RI \rightleftharpoons (RI\therefore IR)^+ \qquad (1)$$

The *intra*molecular species **3** results from a corresponding oxidation of 1-iodo-*n*-alkylthioalkanes provided that sulfur–iodine p-orbital overlap is sufficiently facilitated by a suitable steric arrangement.[6]

The only group of three-electron bonded radical cations which has so far evaded experimental verification in liquid environment is that with *intra*molecular interaction of two monovalent halogen atoms. Even low temperature, solid matrix ESR experiments with neat 1,2-diiodo- and 1,2-dibromoethane could not provide unambiguous identification of such species.[7] In the present study we now report on the first observation of *intra*molecular radical cations of type **1** on the basis of their optical absorptions.

Figure 1 exhibits the transient optical absorption spectrum recorded upon pulse radiolysis of an N_2O saturated, pH 3, aqueous solution containing 2 × 10^{-5} M 1,3-diiodopropane. It shows a broad band with a maximum at 405 nm. The absorption decays exponentially with $t_{1/2}$ = 150 μs. Simultaneous time-resolved conductivity experiments revealed the formation of a positively charged transient with corresponding kinetic characteristics.[8] It can thus be concluded that our intermediate is a radical cation. Its yield amounts to G = 2.9 or ca. 50% of the initial •OH radicals as calculated from the conductivity data. The pH dependence of the yield shows essentially the same characteristics as for the

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(8) In acid solution the generation of a radical cation plus an associated OH^- ion, followed by $OH^- + H^+$ neutralization leads to a decrease in conductance. For analysis of such experimental data see, for example, ref 5.

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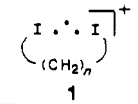
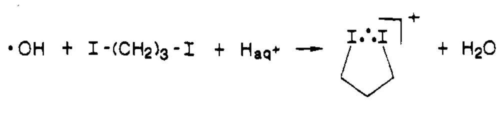
Table I. Properties of *Intra*molecular Radical Cations of Type **1**[a]

 **1**	λ_{max}, nm	$t_{1/2}$, μs	*G*, per 100 eV	ε, M^{-1} cm^{-1}
n = 6	455	75	0.6	5500
n = 5	445	85	1.7	4500
n = 4	435	120	2.1	4700
n = 3 (**1a**)	405	150	2.9	4400
n = 2	(550)		(<0.3)	

[a] Experimental conditions: pulse radiolysis of N_2O saturated, pH 3, aqueous solutions of 2 × 10^{-5} M 1,*n*-diiodoalkanes. Error limits: ±5 nm for λ_{max}, ±50 nm for $n \approx 2$; ±10% for $t_{1/2}$, *G*, and ε, ±20% for *n* = 6.

$^{\bullet}$OH-induced oxidation of monoiodoalkanes, i.e., the radical cations are only formed at low pH (<5). The extinction coefficient of the transient is calculated to 4400 M^{-1} cm^{-1}.

The absorption is assigned to the *intra*molecular radical cation **1a** formed in the overall process



1a (2)

The alternative possibilities, namely a molecular radical cation without iodine–iodine interaction, $I(CH_2)_3{-}I^{\bullet+}$, or a bimolecular complex of type **2**, can be excluded. The former is unlikely because all other $RI^{\bullet+}$ in aqueous solution have been found to absorb around 315 nm.[5] The dimer species, on the other hand, showed a pronounced dependence on the solute concentration with hardly any detectable yield (*G* < 0.2) at the concentration of 2 × 10^{-5} M used in our present experiment.[5] Low solubilities (≲ 5 × 10^{-5} M) unfortunately precluded the study of such a concentration dependence for the diiodo alkanes. A most important argument in support of **1a** is its lifetime which exceeds that of $RI^{\bullet+}$ and $(RI{\therefore}IR)^+$ by almost one order of magnitude. The high stability of **1a** can, of course, be rationalized by its sterically most favorable five-membered ring structure.

Compatible results have been obtained in the oxidation of a number of other 1,*n*-diiodoalkanes. The measured data are summarized in Table I. It can be seen that an increasing chain length between the two iodine atoms and thus an increasing ring size of **1** is accompanied by a red-shift in λ_{max} and a decrease in lifetime and yield. All this matches with corresponding observations for numerous *intra*molecular S∴S-bonded radical cations generated in the oxidation of organic dithia compounds.[1] The underlying rationale is a lower degree of hetero atom p-orbital overlap in the larger ring system.

A geometry situation which is even less favorable would exist in strained three- or four-membered ring structures as has been demonstrated in the oxidation of various sulfur compounds.[1,9] In our present case the oxidation of 1,2-diiodoethane would represent such an example. In fact, only a very small yield of radical cations seems to be formed (*G* < 0.3 according to conductivity measurements) besides a larger yield of neutral, as yet unidentified radicals. The observable UV-absorption in a pulsed aqueous 1,2-diiodoethane solution shows, however, a long tailing with a shoulder around 500 ± 50 nm. Assignment of such a red-shifted band to an *intra*molecular radical cation would be reasonable since the optical transition energies for $2\sigma/1\sigma^*$ species are a direct function of orbital overlap.[1,2] It needs to be mentioned that a relatively fast hydrolysis of the 1,2-diiodoethane leaves, however, some ambiguity about this last result.

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The Photosensitized Production of Singlet Molecular Oxygen ($^1\Delta_gO_2$) in a Solid Organic Polymer Glass: A Direct Time-Resolved Study

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The photosensitized production of singlet molecular oxygen ($^1\Delta_gO_2$) has long been a subject of scientific study.[1–6] Recently, direct evidence for the presence of $^1\Delta_gO_2$ in thin (10–30 μm) polymer films was obtained by Byteva et al.[7,8] who detected $^1\Delta_gO_2$ phosphorescence ($^3\Sigma_g^-O_2 \leftarrow {}^1\Delta_gO_2$: 1270 nm) in a steady-state photosensitized experiment. In a time-resolved study, $^1\Delta_gO_2$ has also been observed in a heterogeneous ionomer system (Nafion powders) in which the $^1\Delta_gO_2$ sensitizer was apparently located at the surface of solvent filled or dessicated cavities.[9] We now report that $^1\Delta_gO_2$ phosphorescence can be detected in a time-resolved photosensitized experiment from a homogeneous, solid polymethylmethacrylate (PMMA) glass. As in the solution phase,[10–26] we expect this technique will become an indispensable

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*Authors to whom correspondence should be addressed.

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