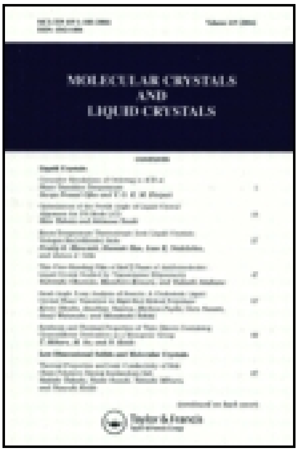

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Solution Chemistry of Dialkoxyanthracene Radical Cations

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SOLUTION CHEMISTRY OF DIALKOXYANTHRACENE RADICAL CATIONS[a].

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Abstract Previous studies on photooxidation of 9,10-diethoxyanthracene (DEA) with diphenyliodonium cation revealed dealkylation of DEA radical cation. Fluorescence, dealkylation quantum yield, and laser-flash transient absorption spectroscopic studies on DEA and its dimethoxy (DMA) and diisopropoxy (DIPA) analogs, probed solvent and substituent effects on this reaction. We reconsider our original inferences as to relative rates of dealkylation and back electron transfer; the results pose new questions, e.g., as to the role of orbital symmetry in controlling rate of back electron transfer.

Keywords: Electron-transfer, picosecond, iodonium, anthracene, spectroscopy

INTRODUCTION

Previous studies on the photooxidation of anthracene[1] and 9,10-diethoxyanthracene[2] (DEA) with diphenyliodonium cation in acetonitrile (AN) solution were carried out in our Laboratories. In the case of DEA, 9-ethoxy-9-phenyl-10-anthrone was a major photoproduct.

A salient feature of the mechanism previously proposed[1] for formation of this product is loss of the ethyl group from DEA radical cation, competitive with back electron transfer to diphenyliodo radical. Possible pathways for this apparently unprecedented, rapid cleavage of a carbon-oxygen bond involve (a) an S_E1 reaction with deprotonation at methyl followed by elimination of ethylene, (b) an 8-membered cyclic transtion state analogous to that

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[a] Contribution no. 1708 from the 3M Corporate Research Laboratories.

proposed by Tolbert[3] for loss of ethyl from 9-ethylanthracene radical cation, and (c) nucleophilic attack of solvent at methylene, i.e. an S_N2 pathway[4]. The present studies were undertaken to clarify this point.

EXPERIMENTAL

Commercial diphenyliodonium PF_6, m.p. 136°, was purified by recrystallization from isopropanol; 2-ethyl-9,10-dimethoxyanthracene (DMA), m.p. 112-4°, DEA, m.p. 146-9°, and 9,10-diisopropoxyanthracene (DIPA), m.p. 119-21°, were prepared by standard procedure[5]. All yielded good 400 MHz nmr spectra and were pure to tlc. Solvents were glass distilled, spectral quality.

Fluorescence spectroscopy was carried out on solutions 1 x 10^{-4} M in the anthracene with excitation at 380 nm. Fluorescence quantum yields were estimated by comparison of integrated emission intensities with those of anthracene[1] and of DEA[2] in AN. Spectrophotometric quantum yields were determined on undegassed solutions 2 x 10^{-4} M in dialkoxyanthracene and 0.005 M in diphenyliodonium cation with ca 10 % conversion under irradiation at 385 nm isolated by a monochromator from the output of a 1 kW Xe lamp. Transient absorption spectra were recorded using instrumentation previously described[6], after excitation with a 355 nm laser pulse (30 ps, FWHM) of solutions 2 x 10^{-4} M in the anthracene and 0.010 M in iodonium salt.

RESULTS AND DISCUSSION

Relative quantum yields for disappearance of dialkoxyanthracenes in the presence of diphenyliodonium cation are reported in Table I as 10^6 x k_o where k_o (M min^{-1}) is the observed zero order rate constant for disappearance of the anthracene chromophore at 385 nm. With 10 % conversion of DEA, 9-ethoxy-9-phenyl-10-anthrone had been shown[2] to be the exclusive photoproduct; reactions of DMA and DIPA were similarly clean to glc.

The photoreaction was followed in four solvents of varying polarity and nucleophilicity: methylene chloride, acetonitrile (AN), methanol, and pyridine (Py). Variation in k_o with alkoxy substituent is small, but significant variation with solvent is observed; values of k_{avg}, equal to 10^6 x k_o averaged over the three anthracenes in each solvent are also reported in Table I.

TABLE I Relative rates of photobleaching of dialkoxyanthracenes

10^6 x k_o in $(M\ min^{-1})$	CH_2Cl_2	AN	CH_3OH	Py
DMA	2.05 ± .09	1.40 ± .03	1.00 ± .06	0.62
DEA	1.73 ± .06	1.40 ± .02	0.65 ± .04	0.36
DIPA	3.34 ± .04	1.7 ± .10	1.00 ± .07	0.67
k_{avg}	2.4 ± .7	1.5 ± .14	0.9 ± .15	0.6 ± .14

Fluorescence quenching data for the three compounds (1 x 10^{-4} M with diphenyliodonium cation 0.4 - 4 x 10^{-3} M) in the four solvents were fit to Stern-Volmer form; quenching constants K_{SV}, and quenching rate constants, k_q, where $K_{SV} = k_q \tau$, and τ is the fluorescence lifetime, equal to $\phi_f \tau_{nat}$, for DMA in each solvent are reported in Table II. Fluorescence quantum yields, ϕ_f, were determined relative to that of DEA in AN[2]; τ_{nat} was calculated in the usual manner[7] from absorption spectra.

Although values of k_q are less than predicted from the Smoluchowski equation by a factor of ca. 4, they scale inversely with solvent viscosity, η, (correlation coefficient, r = 0.979) indicating that electron transfer quenching is diffusion limited, but that every encounter is not necessarily effective. In addition, both k_o for DMA disappearance and k_{avg} scale with K_{SV} (r = 0.989 and 0.993, respectively). The solvent effect on efficiency of photoreaction thus depends primarily on probability of the initial electron transfer event. Branching between dealkylation and back electron transfer is independent of solvent or the nature of the alkyl group!

TABLE II Stern-Volmer Quenching Parameters for DMA.

in...	CH_2Cl_2	AN	CH_3OH	Py
K_{SV}	140	103	53	41 M^{-1}
r	0.995	0.998	0.999	0.998
τ	30	21	21	27 ns
k_q (x 10^{-9} M^{-1} s^{-1})	4.7	5.0	2.5	1.5
ϕ_f	1.0	0.7	0.7	0.9
η (cP)	0.42	0.35	0.55	1.0

This result is accomodated by a mechanism in which the radical cation maintains its integrity for the ca. 250 ps lifetime[1] ($1/k_d$) of the diphenyliodo radical; on decomposition of the latter, the product phenyl radical couples with the radical cation, primarily at the 9-position. A 9,10-dialkoxy-9-phenylanthracenium cation can dealkylate by an S_N1, S_N2, or S_E1 mechanism, depending on conditions, in a subsequent slow step. This proposal is inconsistent with our previous[2] mechanistic interpretation.

The previous assignment of a 475 nm transient, observed on photolysis of DEA under similar conditions, is particularly problematical insofar as the DMA radical cation has been reported as absorbing ca. 100 nm to the red[8]. The laser flash photolysis experiment was repeated in the solvents studied above, substituting DMA for DEA. Transients recorded 1 ns after pump excitation at 355 nm are shown in Fig. 1. No evidence of a 475 nm transient is observed. We infer that the previous observation was either artifactual or associated with some other intermediate in the electron transfer photochemistry.

Quantum yields, ϕ_o, for sensitized photolysis of diphenyliodonium cation (extrapolated to infinite iodonium concentration) are 0.10 and 0.75 for anthracene[1] and DEA[2] respectively, where $\phi_o = k_d/(k_d + k_{-et})$, and $k_d = 4 \times 10^9 s^{-1}$ in AN[1]; the rate constant for back electron transfer, k_{-et}, must be approximately an order of magnitude

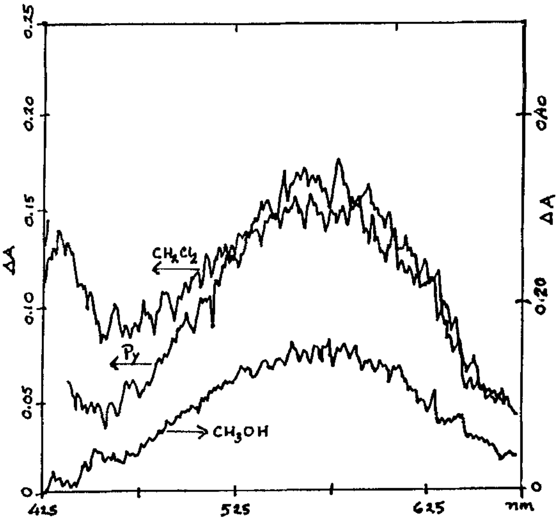

FIGURE 1 Transient absorption spectra for DMA in the presence of 0.01 M diphenyliodonium cation in methylene chloride, methanol, and pyridine, recorded 1 ns after 355 nm excitation.

greater for anthracene than for DEA (5×10^{10} s^{-1} and 5×10^9 s^{-1}, respectively).

In Fig. 2a we propose a schematic of the radical pair formed by electron transfer quenching of a 9,10-substituted anthracene by diphenyliodonium. The trigonal bipyramidal geometry of the diphenyliodo radical is in accord with VSEPR principles, and spin density is localized at the 9- and 10-positions of the anthracene where it can be stabilized by the α-substituents. Given this configuration of the radical pair, conservation of orbital symmetry requires that adiabatic back electron transfer correlates with the first singlet excited state of the anthracene, i.e. in the Marcus model the reorganization energy, λ, derives from the singlet excitation energy of the anthracene (ca. 3.1 eV), as shown in Fig. 2b. The free energy change, ca. −2.0 eV for anthracene itself, is calculated from electrochemical data with respect to the anthracene ground state. The ordering of the k_{-et}'s is apparently in accord with usual linear free energy relationships.

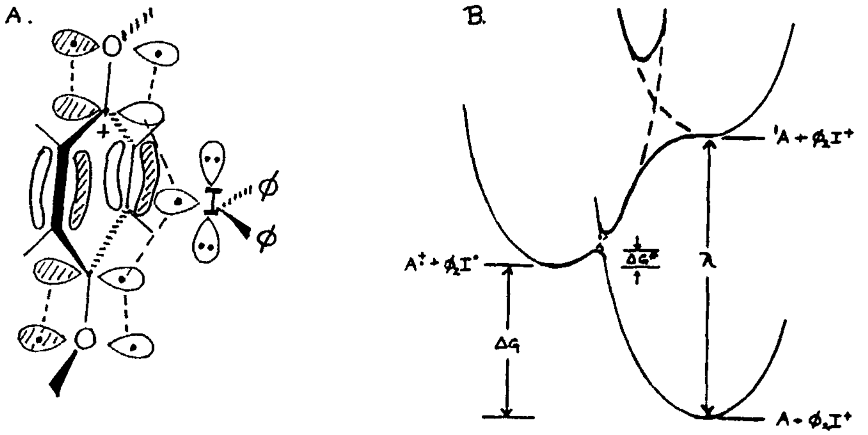

FIGURE 2 (a) Schematic representation of the anthracene radical cation-diphenyliodo radical pair; (b) potential energy surface for back electron transfer in this pair.

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