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Hypovalent Radicals. 7.[1] Gas-Phase Generation of Phenylnitrene Anion Radical and Its Reaction with Phenyl Azide

Sir:

In thermal decompositions and photodecompositions of aryl azides to yield the corresponding nitrenes, it was suggested that the nitrene reacts at N_α of the azide to produce the azo product **1** and at N_γ to yield a 1,4-diaryltetrazadiene (**2**) as an unobserved

$$\mathrm{ArN} + \mathrm{ArN_3} \rightarrow \underset{\mathbf{1}}{\mathrm{Ar{-}N{=}N{-}Ar}} + \mathrm{N_2}$$

$$\rightarrow \underset{\mathbf{2}}{\mathrm{Ar{-}N{=}N{-}N{=}N{-}Ar}}$$

reactive intermediate.[2] Intermediates **3** and **4**, which are related

$$\underset{\mathbf{3}}{\mathrm{R_2CH{-}N{=}N{-}\bar{N}{-}Ts}} \quad \underset{\mathbf{4}}{\mathrm{R'NH{-}N{=}\bar{N}{-}Ts}}$$

to **2**, may be produced in diazo transfer processes between carbanions (R_2CH^-) and the conjugate bases of amines ($R'NH^-$) with azides (e.g., tosyl azide), giving diazo compounds (R_2CN_2)[3] and exchanged azides ($R'N_3$),[4] respectively. Our preliminary results of electroreduction of aryl azides suggested that $\mathbf{2}^{-}\cdot$ species were formed as intermediates.[5] We wish to describe the results of the gas-phase ion–molecule reaction of phenylnitrene anion radical with phenyl azide, which establish two primary reaction channels occurring at N_α and N_γ of the azide.

Phenylnitrene anion radical ($PhN^{-}\cdot$) was produced in our flowing afterglow apparatus (1-m flow tube, $\bar{v}$ = 80 m s^{-1}, P_{He} = 0.5 torr, He buffer gas, 298 K) from phenyl azide (PhN_3) by dissociative electron attachment and monitored with a quadrupole mass spectrometer. At relatively low flows of PhN_3 ($\sim 10^{10}$ molecules cm^{-3}), the anion composition of the flow was >99% $C_6H_5N^{-}\cdot$ [*m/z* 91; *m/z* 92 (M + 1); the observed isotope ratio was 1:0.071, theory 1:0.070][6] with a trace of *m/z* 26, probably due to CN^-. When ion–molecule bracketing reactions were used, the following thermochemical properties of $C_6H_5N^{-}\cdot$ were determined: PA = 372 ± 2 kcal mol^{-1};[7] ΔH_f° = 60 ± 2 kcal mol^{-1};[8] and D° ($C_6H_5N^-$–H) ≤ 96 kcal mol^{-1}.

Not only is the multiplicity problem (singlet vs. triplet) of PhN removed in going to the doublet $PhN^{-}\cdot$ but also the possibilities of related intramolecular rearrangements observed with PhN[9,10b] are eliminated in its reduction product, $PhN^{-}\cdot$. Adding an electron to PhN should doubly occupy the out-of-plane $3b_2$ orbital of triplet PhN[10] and effectively shut down the rearrangements of $PhN^{-}\cdot$. Further, the temperature of our experiment (298 K) and method of generation of $PhN^{-}\cdot$[11] would not allow for the endothermic processes required in the interconversion of $PhN^{-}\cdot \rightleftarrows$ 1-aza-1,2,4,6-cycloheptatetraene$^{-}\cdot \rightleftarrows$ 2-pyridylmethylene$^{-}\cdot \rightleftarrows$ etc.[9,12,13]

With the structure of ion *m/z* 91 established as $PhN^{-}\cdot$ with reasonable certainty, the reaction of $PhN^{-}\cdot$ with PhN_3 was investigated. Increasing the flow of PhN_3 past the ionizer or inletting further PhN_3 downstream of the ion preparation–thermalization region in the flow tube produced a slow ($\sim 10^{-12}$ cm^3 molecule^{-1} s^{-1}) reaction between $PhN^{-}\cdot$ and PhN_3. Two new higher mass

$$\underset{(m/z\ 91)}{\mathrm{PhN^{-}\cdot}} + \mathrm{PhN_3} \rightarrow \underset{(m/z\ 210)}{\mathrm{Ph{-}N{=}N{-}N{=}N{-}Ph^{-}\cdot}} \qquad (1)$$

$$\rightarrow \underset{(m/z\ 182)}{\mathrm{Ph{-}N{=}N{-}Ph^{-}\cdot}} \qquad (2)$$

signals were observed at *m/z* 182 [*m/z* 183 (M + 1), observed 1:0.151, theory 1:0.141],[6] $C_{12}H_{10}N_2^{-}\cdot$, and *m/z* 210 [*m/z* 211 (M + 1), observed 1:0.151, theory 1:0.147],[6] $C_{12}H_{10}N_4^{-}\cdot$. Increasing the flow pressure and decreasing the flow velocity (P_{He} = 1.2 torr, $\bar{v}$ = 50 cm s^{-1}) gave proportionate increases in *both* product ion signals and no change in the rate constant. The ratio of the intensities of the *m/z* 182 and 210 signals was 1:4. That the rate constant and the product-branching ratio were independent of changes in the flow velocity or the flow pressure, within the constraints of the experiment, strongly suggests that both product ions were formed in primary reaction channels and that each is a stable, bound structure under these conditions. Alternate structures for the product ions $C_{12}H_{10}N_4^{-}\cdot$ and $C_{12}H_{10}N_2^{-}\cdot$ are difficult to imagine, considering the ground-state reaction by which they are produced.

These two product ions would be formed by reactions analogous to those observed in the reaction of cyclopentadienylidene anion radical ($c\text{-}C_5H_4^{-}\cdot$) with its precursor diazo compound ($c\text{-}C_5H_4N_2$).

$$\underset{(m/z\ 64)}{c\text{-}C_5H_4^{-}\cdot} + c\text{-}C_5H_4N_2 \rightarrow \underset{(m/z\ 156)}{c\text{-}C_5H_4{=}N{-}N{=}c\text{-}C_5H_4^{-}\cdot} \qquad (3)$$

$$\rightarrow \underset{(m/z\ 128)}{c\text{-}C_5H_4{=}c\text{-}C_5H_4^{-}\cdot} \qquad (4)$$

Two principal product ions, *m/z* 156 ($C_{10}H_8N_2^{-}\cdot$) and 128 ($C_{10}H_8^{-}\cdot$), were formed in a ratio of 3:1 under these same flowing afterglow conditions.[14] The formation of both product anion radicals (azine$^{-}\cdot$ and olefin$^{-}\cdot$) by eq 3 and 4 has direct solution analogies.[1,15] The similarities between reactions 1 and 3, and 2 and 4 are striking even in the magnitudes of the two branching ratios. We therefore conclude that $PhN^{-}\cdot$ reacts with PhN_3 by addition to N_γ, producing 1,4-diphenyltetrazadiene anion radical, and to N_α, yielding azobenzene anion radical and nitrogen.

The overall rate constant observed for the reaction of $PhN^{-}\cdot$ and PhN_3 is the same as that given for the gas-phase reaction of PhN + PhN_3 → PhN=NPh ($k \sim 10^{-12}$ cm^3 molecule^{-1} s^{-1}) where azobenzene formation was monitored.[17] We consider the identity of these rate constants to be more than fortuitous, and indicative of related processes and energetics.[18] We hope that the present results will stimulate research designed to observe **1** from the reaction of PhN and PhN_3.

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Richard N. McDonald,* A. Kasem Chowdhury
Department of Chemistry, Kansas State University
Manhattan, Kansas 66506

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Applications of Light-Induced Electron-Transfer and Hydrogen-Abstraction Processes: Photoelectrochemical Production of Hydrogen from Reducing Radicals

Sir:

Several recent studies have focused on the interception of long-lived or transient one-electron oxidants or reductants formed in light-induced electron-transfer processes. A number of heterogeneous or colloidal catalyst systems have been found useful for the coupling of multielectron redox reactions with reactions of the "one-electron" reagents to mediate the oxidation and/or reduction of water to oxygen and hydrogen.[1-9] Other investigations have demonstrated the possibility for obtaining a similar coupling of redox reactions through the use of photoelectrochemical cells.[10,11] In one study, it was found possible to couple the reduction of photogenerated $\mathrm{Ru(bpy)_3^{3+}}$ in one cell with oxidation of $\mathrm{Fe^{2+}}$ in a second nonilluminated compartment.[10] More recently, it has been shown that hydrogen generation from a nonilluminated compartment containing aqueous acid can be coupled with oxidation of the methylviologen radical cation, $\mathrm{MV^{+}}$, formed by irradiation of a compartment containing $\mathrm{Ru(bpy)_3^{2+}}$, $\mathrm{MV^{2+}}$, and triethanolamine.[11] In the present paper, we report a study of several photoprocesses which generate reducing radicals in similar photoelectrochemical cells. We find that coupling of a light-induced reaction to produce a photocurrent concurrent with hydrogen generation in a second compartment can occur for a number of electron transfers and hydrogen abstractions in what appears to be a fairly general process.

Photoelectrochemical cells used in these studies consisted of the following components: a nonirradiated cathode compartment equipped with platinum gauze (2 × 1 cm) or platinized platinum foil (4 × 1 cm) electrodes and filled with 1 M HCl, a photoanode compartment equipped with similar electrodes and filled with various stirred aqueous or nonaqueous solutions (see Table I), and a salt bridge consisting of 5 M KCl and agar for the aqueous system and 2 M tetraethylammonium perchlorate in pyridine–silica gel for the nonaqueous systems. Both compartments were deoxygenated by flushing with oxygen-free nitrogen for ca. 20 min. The photoanode compartment was irradiated with various wavelengths selected by a monochromator from a 1000-W mercury–xenon lamp. The current was measured with a microammeter and recorder; the gas produced in the cathode compartment was analyzed by gas chromatography.[12]

Table I. Substrate–Quencher Combinations Used in the Photoanode Compartment

substrate	quencher (M)	λ, nm	photo-current, μA	efficiency, %[d]
benzophenone	2-propanol (6.5)	366	25	1.7
benzophenone	2-propanol (6.5)[a]	366	320	22.2
benzil	2-propanol (6.5)[a]	366	35	2.5
$\mathrm{TPP{\cdot}SnCl_2}$	diisopropylethylamine (0.6)[b]	420	35	n.d.
$\mathrm{RuL_3^{2+}}$	triethylamine (0.08)[b]	436	70	5.0
$\mathrm{RuL_3^{2+\prime}}$	triethylamine (0.08)[b]	436	12	n.d.

[a] With 10 mmol of $\mathrm{MV^{2+}}$. [b] In acetonitrile; 2 M $\mathrm{Et_4NClO_4}$ in pyridine/silica gel used as salt bridge. [c] L′ = 5,5′-carboxy-2,2′-bipyridine diethyl ester. [d] Observed quantum yield for the electron flow under the experimental conditions described. The concentrations of the substrates are adjusted so that they absorb more than 99% of the light at the irradiation wavelength. Efficiencies are not corrected for the unquenched excited states.

Initial experiments employed the complex $\mathrm{RuL_3^{2+}}$, where L = 4,4′-dicarboxy-2,2′-bipyridinediisopropyl ester, as the light-absorbing substrate together with triethylamine (0.08 M) in acetonitrile. Previous studies have indicated that quenching by electron transfer occurs on irradiation in a sequence indicated by eq 1 and 2.[13-15] Both of the radicals formed in the photolysis are good reductants, having potentials $E_{\mathrm{red/ox}} \simeq$ 0.8–1.0 V.[14] Irradiation of this system in the presence of platinum catalysts and water has been found to lead to fairly efficient hydrogen generation.[12] Consequently, it was not surprising to observe that

$$\mathrm{RuL_3^{2+*} + Et_3N\colon \rightarrow RuL_3^{+} + Et_3N^{+\cdot}} \qquad (1)$$

$$\mathrm{Et_3N^{+\cdot} + Et_3N\colon \rightarrow Et_3NH^{+} + CH_3\dot{C}HNEt_2} \qquad (2)$$

irradiation of the $\mathrm{RuL_3^{2+}/Et_3N}$: photoanode compartment leads to production of a photocurrent (Table I) together with generation of hydrogen at the cathode. The photocurrent observed is a linear function of the square of the absorbed light intensity, indicating that both radicals generated in eq 1 and 2 are reactive in the electrode process, or alternatively that production of a second molecule of $\mathrm{RuL_3^{+}}$ can occur via reaction 3. The quantum

$$\mathrm{RuL_3^{2+} + CH_3\dot{C}HNEt_2 \rightarrow RuL_3^{+} + CH_3CH{=}NEt_2^{+}} \qquad (3)$$

efficiency of the cell in terms of current produced per photon absorbed in this case is 5%, which is comparable to that obtained in other systems involving photoelectrochemical cells.[10,11] Similar results were obtained with other systems previously found to undergo reductive electron-transfer quenching by amines; lower photocurrents were obtained with tetraphenylporphyrintin(IV), and reversible spectral changes occurring during the photolysis suggested a buildup of the tin porphyrin radical.

A rather different type of reaction that also results in formation of two reducing radicals as primary photoproducts is the photoreduction of ketones and N-heteroaromatics by alcohols and other hydrogen atom donors. Irradiation of benzophenone in 2-propanol, for example, gives rise to potentially reducing ketyl radicals as indicated by eq 4.[16-18] Irradiation of benzophenone in partially

$$\mathrm{(C_6H_5)_2C{=}O^* + (CH_3)_2CHOH \rightarrow (C_6H_5)_2\dot{C}{-}OH + (CH_3)_2\dot{C}{-}OH} \qquad (4)$$

aqueous 2-propanol in the photoanode compartment of the cell

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