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Photoreduction of Azoalkane Triplet States by Hydrogen Atom and Charge Transfer

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In contrast to the classical n,π* carbonyl chromophore, little is known on the *intermolecular* photoreactivity of the n,π*-excited azo group. While some intermolecular photoreactions have been substantiated for the n,π* singlet-excited 2,3-diazabicyclo[2.2.2]oct-2-ene,[1] there is only one mention of an n,π* azoalkane *triplet* state.[2] Thus, no comparison of the *intermolecular* triplet photoreactivity of the two isoelectronic carbonyl and azo n,π* chromophores has been possible.

We have recently discovered that the triplet state of azoalkane **1** undergoes spontaneous intersystem crossing and displays a remarkably long lifetime of 630 ns[3,4] and distinct chemical reactivity.[5] While the singlet state produces exclusively the housane **2** as photoproduct, the triplet state yields also the characteristic azirane **3** (Scheme 1). We have now initiated a mechanistic study of the intermolecular photoreactivity of this n,π* triplet-excited azoalkane, for which the long-lived transient absorption and the fraction of azirane photoproduct serve as spectroscopic and chemical probes through time-resolved absorption spectroscopy and product studies. Our results demonstrate efficient photoreduction of the triplet azoalkane **1** by hydrogen atom abstraction or charge transfer. In all cases, the hydrazine **4** was obtained as photoreduction product, which provides experimental evidence for an intermolecular photoreaction in competition with the unimolecular formation of the housane **2** and azirane **3**. Comparison between the azo and carbonyl chromophores allows a generalization of the chemical reactivity of their n,π* states.

Photolysis of azoalkane **1** in the presence of 1,4-cyclohexadiene, tributyltin hydride, and benzhydrol, which are known to photoreduce triplet-excited ketones,[6] yields significant amounts of the hydrazine **4** as photoreduction product (Table 1). The photoreduction of azoalkane **1** was also found to be quite general for a variety of primary, secondary, and tertiary amines and afforded high yields (ca. 50−90%) of the hydrazine **4**; however, α C−H bonds are required since for *tert*-butylamine no photoreduction takes place. In the presence of the photoreducing agents, a decrease or even complete absence of the azirane **3** product is noted in the photolysates, which confirms that the triplet state is involved in this photoreduction. The participation of the triplet state is further supported by the observation that other azoalkanes with long-lived triplet states ($^3\tau > 200$ ns),[4] e.g., the bridgehead diphenyl-substituted derivative of azoalkane **1**, are also photochemically reduced in the presence of the examined hydrogen donors.

Scheme 1

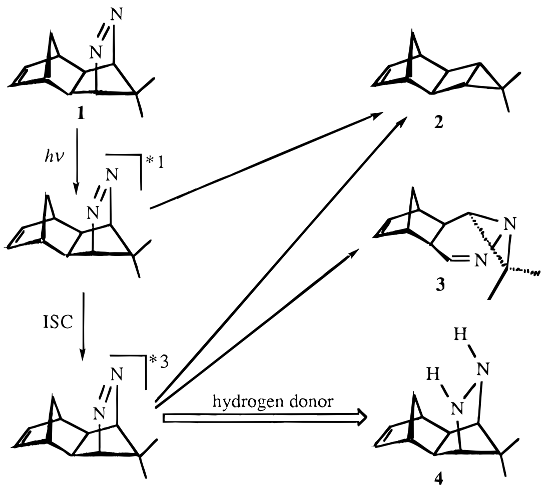

Table 1. Rate Constants and Product Studies for the Photoreduction of the n,π* Triplet-Excited Azoalkane 1 and for Triplet Benzophenone

	k_r[a] (10^7 M^{-1} s^{-1})		yield[b] (%)		
hydrogen donor	azoalkane **1**	Ph_2CO	**2**	**3**	**4**
none			54	46	
1,4-cyclohexadiene	2.4[c,d]	31	23	3	74
tributyltin hydride	3.5[c,d]	30	<34[c]		>66[c,e]
benzhydrol	1.9	0.90[f]	5		95
n-butylamine			20	9	71
diethylamine			20		80
triethylamine	15[c]	300[g]	40		60
diphenylamine	130[c]	400			
triphenylamine	66	76[h]			

[a] Values (±15%) determined by laser flash spectroscopy ($\lambda_{exc} = 355$ nm). [b] Relative yields (± 3%), normalized to 100%, were determined from the methyl or olefinic ^1H NMR signals. [c] Measured for the derivative with hydrogenated C=C double bond; for benzhydrol and triphenylamine, both derivatives gave the same k_r values within experimental error. [d] Reference 11. [e] Lower limit refers to yield of isolated photoproduct, trapped by ethyl chloroformate (*cf.* ref 2). [f] Reference 6. [g] Reference 16. [h] Reference 19.

In laser flash photolysis experiments, the hydrogen donors caused a shortening of the lifetime of the n,π* triplet-excited azoalkane **1**. Kinetic analysis of the triplet lifetime dependence on additive concentration provides the reaction rate constants k_r, which are given in Table 1 along with the corresponding rate constants for triplet benzophenone as prototypal ketone. In the case of tributyltin hydride and benzhydrol, the concomitant formation of tributyltin and hydroxydiphenylmethyl radicals was observed by means of their time-resolved transient absorption at 400 and 540 nm,[7−9] which indicates that hydrogen atom abstraction leads to the formation of the primary radical pairs in eq 1.

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(9) Independent flash photolysis experiments carried out with azoalkane **1** or 2,3-diazabicyclo[2.2.2]oct-2-ene in tetrahydrofuran as hydrogen donor (k_r = 0.9 and 4.7 × 10^6 M^{-1} s^{-1}) indicate that the transient absorption of the hydrazinyl radical lies at 290−310 nm.

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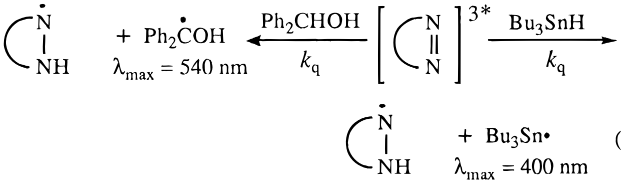


(1)

To corroborate quantitatively the interception of the azo triplet state, the preparative yields of the hydrazine **4** were determined at different hydrogen donor concentrations. From the competition kinetics of the azo triplet state, i.e., photoreduction *versus* unimolecular reactions (Scheme 1), and the assumption that one molecule of hydrazine is formed per reactive encounter,[10] it follows that the ratio of the yield of the hydrazine derived from the azo triplet state, $^{T}[\mathbf{4}]$, and the combined yields of the intramolecular triplet photoproducts housane and azirane derived from the triplet state, $^{T}[\mathbf{2} + \mathbf{3}]$, should increase linearly with concentration of the hydrogen donor [HD] according to eq 2a. By neglecting photoreduction of the

$$^{T}[\mathbf{4}]/^{T}[\mathbf{2} + \mathbf{3}] = k_r{}^3\tau[\mathrm{HD}] \qquad (2a)$$

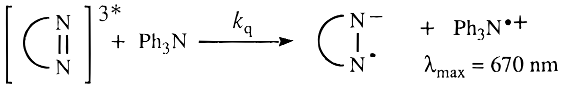
$$[\mathbf{4}\%]/([\mathbf{2}\% + \mathbf{3}\%] - {}^{S}[\mathbf{2}]) = k_r{}^3\tau[\mathrm{HD}] \qquad (2b)$$

singlet-excited azoalkane **1**, the overall yield of hydrazine, [**4**%], coincides with the yield from the triplet state, $^{T}[\mathbf{4}]$. The triplet-derived yield $^{T}[\mathbf{2} + \mathbf{3}]$ is then obtained by subtracting the fraction of singlet-derived housane, $^{S}[\mathbf{2}]$, from the measured overall yield [**2**% + **3**%] (eq 2b). Since $^{S}[\mathbf{2}]$ is known from earlier studies in the absence of chemical quenchers (ca. 9%)[3,4] and should be independent of the hydrogen donor concentration (subject to the assumed absence of singlet photoreduction), eq 2b contains only the known product yields and additive concentrations as experimental parameters.

Indeed, when the yield of hydrazine **4** is plotted against concentrations of benzhydrol and cyclohexadiene up to 0.65 M according to eq 2b, linear correlations with slopes ($k_r{}^3\tau$) of 9 ± 2 M^{-1} (four data points, $r = 0.97$) and 14 ± 3 M^{-1} (six data points, $r = 0.97$) were obtained. Since the values for k_r are known from independent laser-flash measurements (Table 1), excited state lifetimes of 480 ± 100 and 580 ± 130 ns are estimated, which agree reasonably well with the known triplet lifetime[3,4] of azoalkane **1** (630 ± 20 ns). This result renders also any efficient photoreduction through a chain reaction unlikely, since too long lifetimes would results.[13] Although it is known that n,π* singlet-excited states are more reactive toward hydrogen donors,[11] the singlet lifetime of azoalkane **1** (2.4 ns)[4] is too short to account for the observed high product yields. Thus, the photoreduction of azoalkane **1** by 1,4-cyclohexadiene, benzhydrol, and tributyltin hydride is rationalized mechanistically as a triplet reaction, analogous to benzophenone.[12]

For a more detailed comparison of the reactivity in the photoreduction of azoalkanes and ketones, the quantum yield of hydroxymethyl radical formation was quantified through its transient absorption ($\epsilon^{550} = 3300\ M^{-1}\ cm^{-1}$)[14] produced in nanosecond time-resolved laser flash experiments in benzene; triplet benzophenone was employed as actinometer ($\epsilon^{525} = 7800\ M^{-1}\ cm^{-1}$).[15] The measured quantum yield of hydroxymethyl radicals was only 0.12 ± 0.04 in the case of azoalkane **1**. In contrast, the reaction of triplet benzophenone with benzhydrol produces the radicals with unit efficiency ($\phi = 2$).[6,16] The reduced quantum yield for hydroxymethyl radical formation indicates a change in mechanism compared to the reaction of triplet benzophenone.

The rate constants for azoalkane **1** and benzophenone in Table 1 allow us to compare quantitatively the reactivity of the n,π*-excited triplet states of the carbonyl and azo chromophores. Since the triplet energy of azoalkane **1** (62 kcal/mol)[4] lies 7 kcal/mol below benzophenone (69 kcal/mol), one would expect, to a first approximation, a lower reactivity for the azoalkane. This expectation is met for all additives except benzhydrol, for which a slight enhancement of reactivity is noted compared to triplet benzophenone. However, the quenching rate constants for the amines are 1 order of magnitude higher than for tributyltin hydride and cyclohexadiene, although the α C−H bonds of the former are ca. 10 kcal/mol stronger than the Sn−H and C−H bonds in the latter.[17] Hence, another mechanism than direct hydrogen atom transfer must apply in the photoreduction of azoalkane **1** by amines. Since it has been demonstrated for triplet-excited ketones that charge transfer interactions dominate their reactions with amines,[18] this photomechanistic possibility was also probed for azoalkane **1**. Indeed, we have succeeded in establishing the intermediacy of amine radical cations in the case of triphenylamine (eq 3), which constitutes a limiting case where full electron transfer is feasible. Thus, flash photolysis of azoalkane **1** in the presence of triphenylamine, which contains no abstractable hydrogen atoms, produced a growth in transient absorption at ca. 670 nm with the kinetics as the decay at 450 nm, and its spectrum was virtually superimposable with that reported for the photoreaction of benzophenone by triphenylamine.[19]



(3)

The comprehensive exploration of the intermolecular photochemistry of azoalkanes and comparison with n,π*-excited ketones is warranted to generalize further or differentiate in detail the intermolecular photochemical reactivity of n,π* states.

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(10) Benzhydrol and 1,4-cyclohexadiene are capable of the stepwise transfer of two hydrogen atoms and may produce one molecule of hydrazine and benzophenone or benzene per reactive encounter.

(11) Hydroxydiphenylmethyl radicals are capable of reducing azoalkanes, *cf.* Engel, P. S.; Wu, W.-X. *J. Am. Chem. Soc.* **1989**, *111*, 1830. Such a process, along with the hydrogen abstraction by hydrazinyl radicals from the hydrogen donors, could initiate a chain reaction.

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