migration distance exceeds that for the back reaction, the redox products are stable.[10]

The weak absorbance at 510 nm (Figure 1) is attributed to $[Ru(bpy)_2(bpy^-)]^+$ that arises from the photoinduced disproportionation of the complex.[10,18] Since the oxidation potential of $[Ru(bpy)_2(bpy^-)]^+$, 1.3 V, exceeds the reduction potential of MV^{2+}, −0.44 V, MV^+ formation may also arise from the secondary reaction

$$[Ru(bpy)_2(bpy^-)]^+ + MV^{2+} \rightarrow Ru(bpy)_3{}^{2+} + MV^+ \quad (1)$$

when the reactants are within the thermal-electron-transfer distance. Electron transfer between $*Ru(bpy)_3{}^{2+}$ and MV^{2+}, which has a driving force of 0.4 eV, occurs in cellulose when the separation is ≤14 Å.[22] Reaction 1 is not burdened by an exergonic thermal back reaction, and its occurrence promotes product stability by reducing the driving force for the back reaction from 2.5 eV for the disproportionation products to 1.6 eV for the $Ru(bpy)_3{}^{3+}$–MV^+ reaction.

In both reaction sequences, product stability occurs provided the mean separation between the immobilized redox products exceeds that for the thermal back reaction.[10] Our experiments indicate that this spatial separation occurs within the boundary region between these partitioned reagents. Further experiments are in progress, but the current data illustrate that a net formation of MV^+ occurs in PVG in the absence of an external electron donor.

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Supplementary Material Available: A plot of the optical densities of adsorbed $Ru(bpy)_3{}^{2+}$ at 450 nm and chemically generated MV^+ at 610 nm as a function of relative thickness of an impregnated 25- × 25- × 4-mm PVG sample (1 page). Ordering information is given on any current masthead page.

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Mechanistic Investigation of the Photoinitiated Autocatalytic Chain Decomposition (PACD) Reaction of Phenyl Azide and Derivatives

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Investigations of the photochemistry of phenyl azide[1-7] have led to documentation of an autocatalytic (branching[8]) chain reaction. This molecular explosion in solution is characterized by quantum yields for the disappearance of phenyl azide that greatly exceed unity[1,5,7] and which increase exponentially with increasing concentration.[5,7] Cryogenic[4] and transient absorption[3,6] spectral methods have been used in attempts to identify the branching chain propagator. Tetraaza species, i.e., 1,4-diphenyl tetraazadiene, have been eliminated since irradiation of phenyl azide and of phenyl isocyanate afforded essentially identical cryogenic and transient absorption spectra. Thus, a C_6H_5N species is thought to be the chain propagator. Four species are possibilities:[9] singlet phenylnitrene, triplet phenylnitrene, and the singlet species benzazirine[12-16] and azacycloheptatetraene.[10,11,16,17] We report here the use of substituted phenyl azides[18] and triplet-sensitized photochemical methods to identify which C_6H_5N species is the branching chain propagator.

Table I. Quantum Yields of Disappearance of Phenyl Azide and Derivatives[a]

	Φ			
[azide], M[b]	phenyl azide[c]	4-bromo phenyl azide[c]	2,4,6-tribromo phenyl azide[c]	4-nitrophenyl azide[d]
10^{-4}	0.56	0.80	0.16	0.54
10^{-3}	4.7	1.6	0.46	1.7
10^{-2}	93	6.6	15	6.4
10^{-1}	1800	81	143[e]	434

[a] Acetonitrile solutions deoxygenated by bubbling with nitrogen gas for 3 min at 0 °C. [b] Concentrations range was (0.868–2.06) × 10^{-Y}, Y = 1–4. [c] 254-nm excitation. [d] 313-nm excitation. [e] Concentration = 5.05 × 10^{-2} M.

Table II. Triplet-Sensitized Quantum Yields of Disappearance of 4-Nitrophenyl Azide[a]

sensitizer	λ, nm[b]	[azide], M	[sensitizer], M	Φ
none	313[c]	0.10	0	319
benzophenone	254[d]	0.10	0.073	677
biphenyl	254[d]	0.10	0.093	593
none	313[c]	0.20	0	846
benzophenone	254[e]	0.19	0.15	2500
biphenyl	254[e]	0.19	0.19	937

[a] Acetonitrile solution deoxygenated by nitrogen bubbling. [b] Wavelength of excitation. [c] *I*(313 nm) = 1.0 × 10^{14} photons/s. [d] *I*(254 nm) = 2.98 × 10^{13} photons/s. [e] *I*(254 nm) = 3.26 × 10^{13} photons/s.

Quantum yields of disappearance (Φ) were measured[1,5,7] for phenyl azide, 4-bromophenyl azide, 2,4,6-tribromophenyl azide, and 4-nitrophenyl azide as a function of concentration: values greatly exceed unity, Table I.[21] On the basis of absorption spectral

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Table III. Quantum Yields of Disappearance of 4-Nitrophenyl Azide in the Presence of *n*-Butylamine[a]

set	λ, nm[b]	[*n*-butylamine], M	[biphenyl], M	Φ
I	313	0	0	514
	313	0.12	0	113
	254	0.12	0.096	228
II	254	0	0.092	74
	254	0.10	0.092	124
	254	0.045	0.092	109

[a] 0.1 M 4-nitrophenyl azide in acetonitrile deoxygenated by nitrogen bubbling. [b] Wavelength of excitation, I(254 nm) = 2.7 × 10^{13} photons/s. I(313 nm) = 9.27 × 10^{13} photons/s.

changes at low conversions, corresponding azobenzenes are the photoproducts. Plots of Φ vs. azide concentration show an exponential increase in Φ with increasing concentration for all four azides. Thus, a photoinitiated autocatalytic chain decomposition (PACD) reaction occurs for each substituted phenyl azide, as has been reported for phenyl azide.[1,5,7]

Since Φ values for 4-bromophenyl azide and 2,4,6-tribromophenyl azide greatly exceed unity, a triplet species is suggested as the PACD reaction chain propagator: an accelerated intersystem crossing due to an internal heavy atom effect is expected to promote formation of the triplet states of these species. 2,4,6-Tribromophenyl azide cleanly affords the triplet nitrene.[23] 4-Nitrophenyl azide also affords the triplet nitrene,[24,25] further suggesting this intermediate as the PACD reaction chain propagator.

Triplet-sensitized Φ values of 4-nitrophenyl azide were measured with benzophenone and biphenyl as sensitizers, adjusting concentration ratios such that >90% of the exciting light (254 nm) was absorbed by the sensitizer and that >90% of the monitoring light (313 nm) was absorbed by 4-nitrophenyl azide.[26] All Φ values measured greatly exceed unity, Table II. Triplet-sensitized Φ values exceed values measured upon direct excitation; however, this probably results from the lower lamp intensities in the sensitized experiments, since lower light intensities result in greater Φ values.[7] Thus, triplet 4-nitrophenylnitrene is thought to be the PACD reaction chain propagator.

Finally, Φ was determined upon direct excitation and biphenyl triplet sensitization of 4-nitrophenyl azide in the presence and absence of *n*-butylamine, since such nucleophilic species have been used to chemically trap singlet reaction intermediates.[12-15] Φ values greatly exceed unity whether or not *n*-butylamine is present, Table III. *n*-Butylamine reduces Φ values only upon direct excitation; it does not affect Φ values measured upon triplet sensitization. This can be understood if triplet 4-nitrophenylnitrene reacts with 4-nitrophenyl azide to produce *two* triplet nitrenes, the PACD reaction. Since added *n*-butylamine reduces measured Φ values upon direct excitation but not upon triplet sensitization, Table III, a singlet species is thought to be trapped: singlet nitrene precursor[25] to the PACD reaction triplet propagator and/or the singlet species thought responsible for polymer formation[13,27] since polymer is not formed upon triplet sensitization of phenyl azide.[1,27]

Thus, results of quantum yield measurements of 4-bromo-, 2,4,6-tribromo-, and 4-nitrophenyl azide and of triplet-sensitized studies of 4-nitrophenyl azide in the presence and absence of *n*-butylamine all indicate that triplet phenylnitrene intermediates act as the propagator of the photoinitiated autocatalytic chain decomposition (PACD) reaction.

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[21] Φ values were measured for room temperature acetonitrile solutions by exciting with monochromatic light from a 450-W Hg lamp and Schoeffel GM-252 1/4-m monochromator, using ferrioxalate actinometry[22] to determine the photon flux and using absorption spectral changes to determine changes in concentration;[1,5,7] volumetric dilutions were necessary to determine absorption spectral changes for concentrated (>10^{-3} M) solutions.

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Nitrite-Induced Carbyne to Acyl Conversion. Unprecedented Formation of an Arylglyoxyl Ligand via Coupling of an Oxidized Carbyne with a Coordinated Carbon Monoxide

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Carbene complexes react with suitable oxygen donors to release the carbene ligand in the form of a free ester, amide, or ketone,[1] and this is usually the method of choice for removing a modified carbene from a metal in a complex organic synthesis.[2] Surprisingly, analogous oxidation reactions of carbyne complexes have not been reported. To explore this aspect of carbyne chemistry, we have examined the reactions of the carbyne complexes $[\mathrm{Cp(CO)_2M{\equiv}CR}]^+$ (M = Re (**1**)[3], Mn(**2**)[4]) with $\mathrm{NO_2^-}$, a potential oxygen atom donor, and as described herein have observed the smooth conversion of the carbyne into an acyl ligand. Remarkably, this reaction with **2** gives a product containing an arylglyoxyl ligand that has been formed from the oxidized carbyne and a coordinated carbonyl ligand. Glyoxyl ligands have never before been assembled from coordinated ligands, and previous studies of glyoxyl complexes have led to the general conclusion that such ligands are not likely to form by migration of an acyl ligand to a coordinated CO.[5]

Our initial studies with the carbyne complex I showed that addition of 1 equiv of $[\mathrm{PPN}][\mathrm{NO_2}]$ {PPN = $(\mathrm{Ph_3P})_2\mathrm{N}$} to this species gave smooth, immediate conversion to the acyl complex **3**,[6] eq 1. Formally, this reaction involves addition of $\mathrm{O^-}$ to the

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