

Diarylcation Radicals: Generation and Chemical Reactivity in Solution

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Although the chemistry of neutral carbenes has been extensively studied over the past three decades,¹ little attention has been focused on the oxidized form of these carbenes—carbene cation radicals. Oxidation of carbenes should significantly enhance their electrophilicity and eliminate the chemical ambiguities observed for carbene singlet and triplet spin states. Although recent work has demonstrated that carbene cation radicals can be generated in solution by the unimolecular loss of nitrogen from the corresponding oxidized diazo precursor,² their chemical reactivity has not been well studied. In this context, we recently reported the stereospecific cyclopropanation of diarylcation radicals with alkenes.³ Unfortunately, only relative reactivities could be obtained because of the relatively slow loss of nitrogen from the oxidized diazo precursors. However, recent experiments demonstrated that the diphenylcarbene cation radical could be generated in a matrix by the photolysis of the diphenyldiazomethane cation radical.^{2g,h} We wish to now report the generation of diarylcation radicals in solution by double laser flash photolysis and the measurement of their absolute reactivity with nucleophiles and radicalophiles.

Nanosecond laser photolysis (355 nm) of *N*-(*p*-*tert*-butylbenzyl)quinolinium hexafluorophosphate (NTBBQ, OD = 1.5) in dry, argon-purged 1,2-dichloroethane with added bis(*p*-methylphenyl)diazomethane (**1**, 0.4 mM) yields the transient absorption spectrum shown in Figure 1 (solid line), obtained 1 μ s after the laser pulse. Photolysis by a delayed second laser pulse (645 nm, 930 ns delay) results in a new transient spectrum, Figure 1 (dashed line). Subtraction of these two spectra indicates the spectral change effected by the second laser pulse (inset A). Clearly, a new transient, $\lambda_{\text{max}} \approx 410$ nm, is generated within the second laser pulse (inset C), concomitant with the diminution of the initial transient, $\lambda_{\text{max}} = 680$ nm (inset B). Under these photochemical reaction conditions, the lifetime of the new transient is ≈ 500 ns.

These results are consistent with the photochemical reactions given in Scheme 1. Photoinduced electron transfer from **1** to NTBBQ following the initial 355-nm pulse yields the bis(*p*-

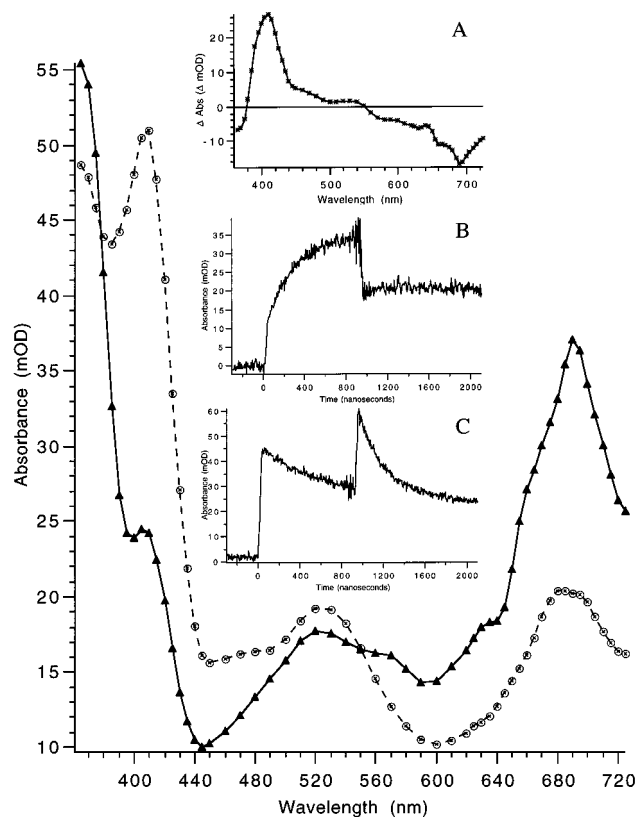


Figure 1. Nanosecond absorption spectra obtained following 355-nm excitation of NTBBQ in degassed 1,2-dichloroethane with added **1** (solid line) and subsequent delayed (945 ns) 645-nm excitation (dashed line). Inset: (A) Difference absorption spectrum from solid and dashed lines. (B) Kinetics monitored at 680 nm. (C) Kinetics monitored at 410 nm.

methylphenyl)diazomethane cation radical, $1^{+\bullet}$ ($\lambda_{\text{max}} = 680$ nm) and NTBBQ \cdot ($\lambda_{\text{max}} = 520$ nm).^{2,4,6,7} Irradiation of $1^{+\bullet}$ with the delayed second pulse results in rapid, < 10 ns, photoinduced unimolecular loss of nitrogen to form the bis(*p*-methylphenyl)carbene cation radical, $2^{+\bullet}$ ($\lambda_{\text{max}} = 410$ nm).⁸ The spectrum of $2^{+\bullet}$ is similar to that reported for the diphenylcarbene cation radical in a frozen matrix.^{2g,h,6} Under similar experimental conditions, photolyses of bis(*p*-chlorophenyl)- and bis(*p*-methoxyphenyl)diazomethane cation radicals, $\lambda_{\text{max}} = 675$ and 725 nm, respectively, yield bis(*p*-chlorophenyl)- and bis(*p*-methoxyphenyl)carbene cation radicals, $\lambda_{\text{max}} = 415$ and 435 nm, respectively.

(5) The absorption spectra of the NTBBQ radical is similar to that of the *N*-methylquinolinium radical, see: Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876.

(6) Under these reaction conditions, the reported spectra of diphenyl diazo cation radical,^{2g,h} $\lambda_{\text{max}} = 650$ nm, can be obtained. Methyl aromatic substitution results in a red shift of λ_{max} for $1^{+\bullet}$ and $2^{+\bullet}$, as has been observed for diarylmethyl cation, radical, and carbene.

(7) It has been suggested that there are two different types of diazo cation radicals formed upon ionization, a π state observed by optical spectroscopy, and a bent σ state observed by EPR.² The effect of solvent and temperature on the interconversion of these two states is not clear at present. On the basis of previous studies, the transient which absorbs at 680 nm maybe the π state of $1^{+\bullet}$.^{2g} It is possible that both states could be formed by photoinduced electron transfer, and that the σ state escapes detection in the near-UV–vis range. However, if the σ state is formed, it would not influence the observed kinetics for $2^{+\bullet}$, and the conclusions herein.

(8) The shoulder at 410 nm observed in Figure 1 (solid line) is most probably due to $1^{+\bullet}$ rather than $2^{+\bullet}$. The decay of the species at 410 nm following 355-nm excitation is significantly slower than that observed at 410 nm following subsequent 645-nm excitation, i.e. the kinetics of the 410-nm shoulder does not match that observed for $2^{+\bullet}$. Previous studies show that the diphenyldiazomethane cation radical has similar fine structure as observed here for $1^{+\bullet}$.^{2g,h} The initial absorbance at 410 nm (inset C, Figure 1) is due to the NTBBQ triplet state.

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(4) Under our experimental conditions, **1** is oxidized by the triplet state of NTBBQ. Identical spectra are obtained by using NTBBQ with toluene as a co-sensitizer.⁵

Scheme 1

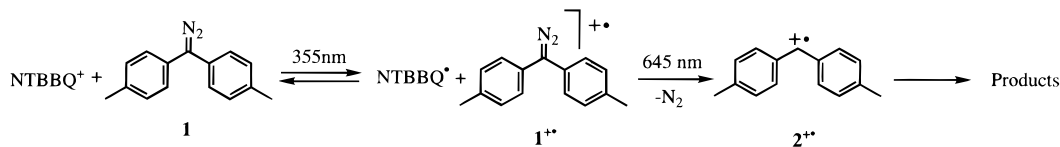


Table 1. Bimolecular Rate Constants for Reaction of $2^{+\bullet}$ with Nucleophiles and Radicalophiles

Reagent	Bimolecular rate constant (M ⁻¹ sec ⁻¹)	Reagent	Bimolecular rate constant (M ⁻¹ sec ⁻¹)
	1.1 e+09 (1.23 e+7) ^c	MeOH	6.4 e+08
	1.8 e+08 (3.68 e+3) ^a	EtOH	6.2 e+08 (1.67 e+7) ^c
	1.5 e+08 (6.8 e+04) ^b	i-PrOH	3.2 e+08
	8.2 e+07	t-BuOH	1.2 e+08
	3.2 e+07 (9.84 e-02) ^a	1	2.1 e+09
	1.7 e+07		2.6 e+09
	4.3 e+07		3.7 e+08
	5.1 e+06	((CH ₃) ₃ Si) ₃ Si-H	1.9 e+08
		O ₂	5.0 e+08

^a Reference 13a, values are calculated from activation parameters.

^b Rate constant for 2-methyl-2-butene. ^c Reference 13b, values are calculated from rates in CH₃CN, assuming $k(\text{CH}_3\text{CN}):k(\text{CH}_2\text{Cl}_2) = 3:1$.

The addition of nucleophiles and radicalophiles results in a decrease in the lifetime of $2^{+\bullet}$, but not $1^{+\bullet}$. Plots of the observed pseudo-first-order rate constant for the decay of $2^{+\bullet}$ vs concentration of reactant are linear. The slopes yield the bimolecular rate constants for the reaction of $2^{+\bullet}$ with the reactant, Table 1. For comparison, the rate constants for the reaction of bis(*p*-methylphenyl)carbenium ion with several substrates are given in parentheses.

It is observed that the ratios of the absolute rate constants for the reaction of $2^{+\bullet}$ with 2,3-dimethyl-2-butene:cyclohexene:1-hexene, 2.23:1:0.39, are quite similar to those of cyclopropane cycloadducts from the reaction of $2^{+\bullet}$ with the same alkenes, 2.05:1:0.47, observed from competition studies. This strongly suggests that $2^{+\bullet}$ is directly involved in the product-determining step for the formation of the corresponding cyclopropanes.

The highly electrophilic nature of $2^{+\bullet}$ is evidenced by its reactivity with nucleophiles (alcohols, pyridine, diazo **1**, and presumably alkenes). Although $2^{+\bullet}$ reacts rapidly with all the alkenes investigated, its reactivity correlates well with the nucleophilicity of the alkene. In comparing the reactivities of $2^{+\bullet}$ and bis(*p*-methylphenyl)carbenium ion, it is clear that $2^{+\bullet}$ is significantly more reactive, albeit less selective, with alkenes. This is further evidenced by the observation that bis(*p*-methylphenyl)carbenium ion does not react appreciably with

(9) With toluene, we observe the growth of a new transient, $\lambda_{\text{max}} = 580$ nm, concomitant with the decay of $2^{+\bullet}$, which we assign to the tris(*p*-methylphenyl)methyl radical, presumably formed by electrophilic attack of $2^{+\bullet}$ followed by proton loss.

either benzene or toluene, whereas $2^{+\bullet}$ does so rapidly, presumably by electrophilic addition.⁹

In addition to the apparent electrophilic behavior of $2^{+\bullet}$, it also has significant radical character. It reacts rapidly with O₂ and ((CH₃)₃Si)₃SiH, an excellent hydrogen atom donor, Table 1.¹⁰ The high radical reactivity of $2^{+\bullet}$, which is unusual for many cation radicals, may be rationalized by its structure. Experiments and calculations on diarylcarbene cation radicals suggest that the ground state electronic structure is $\sigma^+\pi^+$, in which the odd electron is in a σ orbital with an empty π orbital.^{2g,11} This spatial separation of spin and charge for $2^{+\bullet}$ apparently results in high radical reactivity, whereas for many cation radicals, in particular π -cation radicals, the lack of separation renders them inert toward O₂ and hydrogen atom donors.

Although $2^{+\bullet}$ exhibits high radical reactivity, it is often overshadowed by its powerful electrophilicity. For example, in reactions of $2^{+\bullet}$ with alkenes, C–H insertion products, which can be formed from initial hydrogen abstraction, are not observed, presumably because electrophilic addition occurs more rapidly. This reactivity contrasts with that of diarylcarbenes in which reactions with alkenes often yield only C–H insertion products via hydrogen abstraction.^{1,12}

It seems apparent that $2^{+\bullet}$ and probably other diarylcarbene cation radicals will exhibit both electrophilic and radicalophilic behavior. Although their overall reactivity may be simply viewed as a hybrid of that of the carbenium ion and radical, their absolute reactivity and selectivity will probably be quite complicated. In addition, their chemistry may be unique relative to that of carbenes and other cation radicals. In conclusion, we have reported on a two-laser method for the generation of diarylcarbene cation radicals in solution which allows for their spectral observation and the determination of their absolute reactivity with nucleophiles and radicalophiles. Further studies will probe the role of electronic and steric effects on diarylcarbene cation radicals as well as investigate the chemistry and reactivity of other carbene cation radicals.

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