Transient Carbocations and Carbanions Generated by Laser Flash Photolysis and Pulse Radiolysis

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Contents

A native of the part of Indian subcontinent now called Bangladesh, P. K. Das obtained his undergraduate education at Dacca University, Dacca. In 1977, he received his Ph.D. in Physical Chemistry from the University of Houston under supervision of Prof. Ralph S. Becker. He spent about 10 years (1978–1987) on the research faculty of the University of Notre Dame and, while employed at the Radiation Laboratory there, worked mostly in various areas of time-resolved photochemistry (laser flash photolysis and pulse radiolysis). An author or coauthor of more than 140 research publications, he is presently a Research Chemist-Specialist at the Phillips Research Center, Bartlesville, OK. Current research interests include polymer photodegradation/stabilization, carbocationic photochemistry and photophysics, and computational chemistry of organometallic catalysts.

I. Introduction

Closed-shell carbocations and carbanions have long been implicated as well-defined intermediates in ionic reaction mechanisms involving organic compounds.[1–12] There is plentiful spectroscopic and other evidence for formation of stable or metastable carbocations in acidic media. Similarly, stabilized carbanions formed as a result of deprotonation mediated by a strong base in deaerated nonprotic solvents are easily recognized by their color and absorption spectra. Depending on the electronic makeup of a molecule as well as its environment (solvent), the heterolysis of an appropriate bond leading to carbocations or carbanions can be as important as homolysis producing radicals. An understanding of the structure and reactivity of carbon-centered ions is of pivotal importance to kinetics and mechanisms of organic reactions, including ionic polymerization.

Resonance-stabilized carbocations and carbanions are responsible for certain photochromic phenomena (e.g., photodissociation of triphenylmethane leuco derivatives into colored ion pairs and UV-induced color changes of nitrotoluenes).[13,14] Furthermore, as the present review will provide many examples, these species often constitute spectrally observable, relatively long-lived intermediates in the course of radiation–chemical charge separation.

Although a large body of information[1–20] on carbon-centered ionic intermediates is available based on conventional studies at subambient temperatures, under extremal conditions (e.g., in the presence of strong acids or bases), and via indirect kinetic methods, the range and volume of this information have been further expanded by results recently obtained via relatively fast techniques based on electron and laser pulses. This review will deal with kinetic data, generated mostly on carbocations in the past two decades, by application of laser flash photolysis (LFP) and pulse radiolysis (PR) in fluid solutions at room temperature. In most of the studies under review, the precursors of the ions are energy-rich photoexcited states and radical ions. Properties of photoexcited carbocations and electron transfer involving them in both excited and ground states have drawn some attention in recent times and will also be considered. However, the primary focus of this review will be on absolute rates, related to nucleophilic interactions, on a relatively fast time scale (submillisecond).

Absolute rate constants for reactions of some very stable carbenium ions have been obtained by direct kinetic studies based on rapid mixing techniques.[21–29]

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The cations in these studies were characterized by half-lives longer than 100 ms (in water). Although the kinetic data of these stable systems formed the foundation of models and schemes for solvolysis and nucleophilic reactivity,[15] these will not be covered in this review. Also, in view of the fact that the amount of recently obtained kinetic–spectral information on transient ions is voluminous, restraint has sometimes been exercised in quoting data from the literature in this area.

II. Generation of Carbocations and Carbanions by Laser Flash Photolysis and Pulse Radiolysis

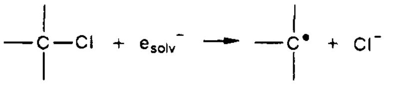
A variety of photochemical and radiation-based methods have been conceived and used for facile production of carbocations and carbanions. Many of these methods have been conveniently utilized for studying these intermediates by time-resolved techniques. The latter include emission lifetime measurements, laser flash photolysis (LFP), and pulse radiolysis (PR). For lifetime measurements, photon pulses (micro- to nanojoules) of short duration (pico- to nanoseconds) are used to excite molecules and produce emission to be monitored directly by fast detectors, namely, photomultiplier tubes (PMT) and optical multichannel analyzers (OMA). In LFP, laser pulses (pico- to nanoseconds) of higher energy (usually microjoules) are used to produce photoexcited states at micromolar concentrations. Photoejection of an electron and singlet or triplet state mediated bond cleavages lead to intermediates that are observed via absorbance changes on pico- to microsecond time scales. In PR,[30-33] the interaction of a high-energy pulse of electrons (usually of nanosecond duration) with a solution gives rise to solvated electron and solvent-derived cations (hole) (eq 1). In many solvents (e.g., alcohols, ethers),

$$S + e^-_{\text{fast}} \rightarrow S^{\bullet +} + 2e_{\text{solv}}^- \quad (1)$$

$$\mathrm{RR'CHOH^{\bullet +}} + \mathrm{RR'CHOH} \rightarrow \mathrm{RR'C^{\bullet}OH} + \mathrm{RR'CHOH_2^+} \quad (2a)$$

$$\rightarrow \mathrm{RR'CHO^{\bullet}} + \mathrm{RR'CHOH_2^+} \quad (2b)$$

the solvated electron is a well-defined, spectrally recognizable, reducing species, which easily attaches itself to a substrate, producing a radical anion. In alcohols, the solvent-derived positive ions disappear quickly, producing ketyl (reducing) and alkoxy (oxidizing) radicals (eqs 2a,b). In aliphatic chlorinated hydrocarbons, e.g., 1,2-dichloroethane (DCE), the solvated electron does not persist because of its dissociative capture by the solvent molecules (eq 3). The solvent-

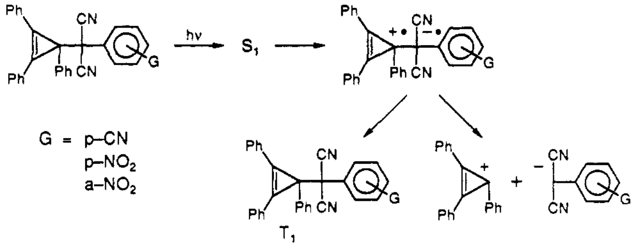


$$-\overset{|}{\underset{|}{C}}-Cl + e_{\text{solv}}^- \rightarrow -\overset{|}{\underset{|}{C}}^{\bullet} + Cl^- \quad (3)$$

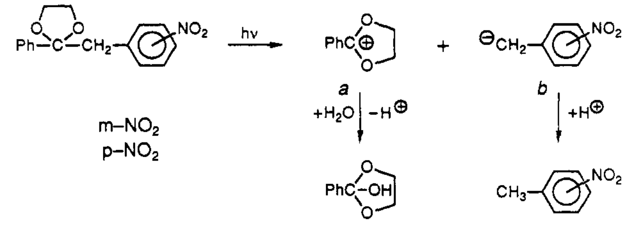
derived cations remain available for diffusional charge transfer to an added solute, leading to cationic species. Under certain conditions, e.g., in the course of PR in 2-propanol containing 0.2–0.5 M concentrations of acetone and carbon tetrachloride, a high concentration of protons may be generated via fast reactions on a submicrosecond time scale; this is convenient for studying kinetics of protonation reactions (eq 4).[34]

$$3(CH_3)_2CHOH + 2CCl_4 \xrightarrow{e} 2(CH_3)_2CHOH_2^+ + 2Cl^- + 2^{\bullet}CCl_3 + (CH_3)_2CO \quad (4)$$

Scheme I

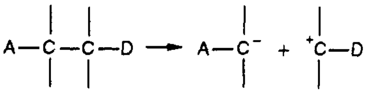


Scheme II



Examples and important features of photolytic and electron-pulse based methods of carbocation and carbanion generation are described below.

A. Direct Photoheterolysis of a C–C Bond Linking Acceptor- and Donor-Type Moieties[35-38]



$$A-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-D \rightarrow A-\overset{|}{\underset{|}{C}}^- + {}^+\overset{|}{\underset{|}{C}}-D \quad (5)$$

Pienta et al.[35] employed picosecond and nanosecond LFP techniques to study the photolysis mechanism of a series of molecules, each containing a pair of stable carbanion and carbocation covalently attached to each other. A typical example is [3-(1,2,3-triphenylcyclopropenyl)](4′-cyanophenyl)malonitrile (Scheme I). The picosecond results suggest that the singlet states in these molecules initiate intramolecular electron transfer leading to linked radical ion pairs which in turn undergo either back electron transfer to form triplet excited states localized on the triphenylcyclopropenyl moiety, or cleavage of the central bond leading to carbocations and carbanions.

In a steady-state photochemical study of several appropriately substituted nitroaromatic derivatives, Wan and Muralidharan[36,37] proposed triplet state mediated photoheterolytic cleavage of the benzylic bond as the primary photochemical step to produce a nitrobenzyl carbanion and a carbocationic fragment. At pH <12, the nitrobenzyl carbanions are efficiently trapped by molecular oxygen to give hydroperoxides.

Steenken and McClelland[38] carried out 248-nm LFP of two nitrobenzyl acetals (Scheme II) for which C–C bond photoheterolysis had been suggested by Wan and Muralidharan.[36,37] The transient spectra (Figure 1) showed the formation of 2-phenyl-1,3-dioxolan-2-ylium ion (λ_{max}, 260 nm) and nitrobenzyl anions (λ_{max}, 355 nm

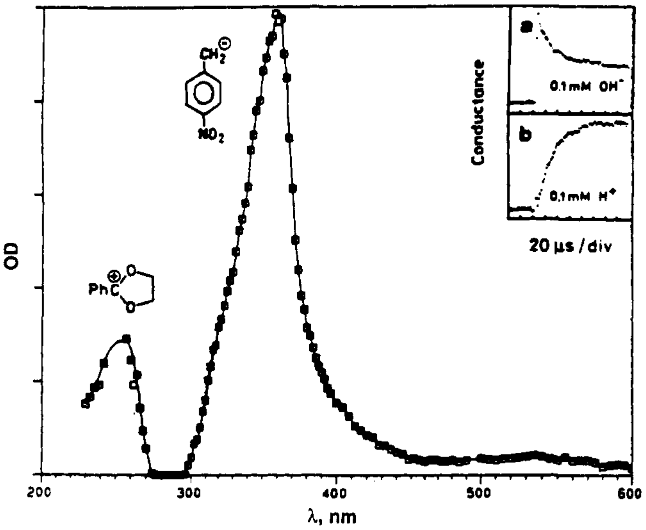


Figure 1. Transient absorption spectrum (not corrected for depletion of parent) at 4–6 μs following 248-nm LFP of 2-(*p*-nitrobenzyl)-2-phenyl-1,3-dioxolane in argon-saturated 1:2 acetonitrile–water. The insets show traces obtained with conductivity detection in solutions containing (a) 0.1 mM OH^- and (b) 0.1 mM H^+. Reproduced with permission from ref 38. Copyright 1989 American Chemical Society.

for *p*-nitrobenzyl anion). The *p*-nitrobenzyl anion decayed very slowly ($\tau_{1/2} > 1$ s) in 1:2 acetonitrile–water. In contrast, the *m*-nitrobenzyl anion from the second substrate was not observed, presumably due to fast protonation (reaction b in Scheme II) within the 20-ns laser pulse. Supporting experiments based on conductivity detection showed characteristic increases in conductance in acid and decreases in basic solution (due to reaction a in Scheme II) with kinetics identical to those measured from absorbance changes associated with the oxocarbocation at 260 nm.

Photolytic C–C bond cleavage in carboxylates resulting in decarboxylation to carbanions is discussed in a later section.

B. Direct Photoheterolysis of a Carbon–Heteroatom Bond[39–84]

$$-\overset{|}{\underset{|}{C}}-X \longrightarrow -\overset{|}{\underset{|}{C^+}} + X^- \tag{6}$$

The photodissociation represented by eq 6 is a key step in photosolvolysis reactions.[39–50] It also constitutes by far the most commonly used method for photogenerating carbocations. In most cases, the photoexcitation is initially localized in a π-system (aromatic or polyenyl group) proximal to the leaving, potential anion; in a few cases, the leaving group (e.g., *p*-cyanophenoxide) is the chromophore. A large variety of systems with leaving groups (X) such as hydroxide, halide, cyanide, acetate, tosylate, *p*-cyanophenoxide, and phosphonium chloride have been explored. The photoheterolysis is usually accompanied by homolysis leading to radicals. Occasionally, in polar/protic solvents, electron ejection (often biphotonic) leading to radical cations is also observed. Depending on the structure of the substrates, the radical cations may undergo intramolecular C–C bond cleavage leading to carbocationic fragments (see later). The heterolytic photocleavage is favored in solvents of high polarity and in substrates (RX), the cations (R^+) from which have low pK_{R^+} and the leaving groups (X^-) in which have conjugate acids of low pK_a. The observation of reactive cations is facilitated[57] by rendering them longer-lived in weakly nucleophilic polar solvents, e.g., 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP).

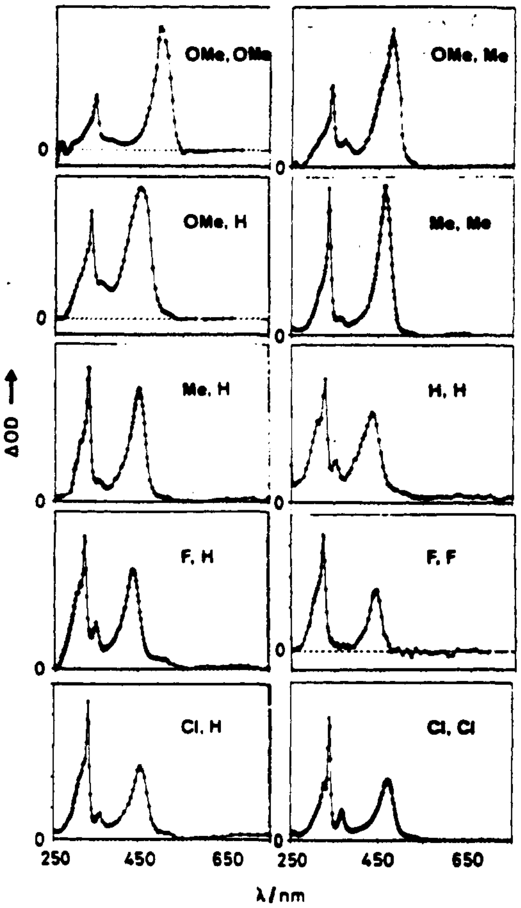


Figure 2. Absorption spectra of transients observed at ~70 ns following LFP (248 nm, 20–60 mJ/pulse) of ~0.1 mM solutions of para-substituted diphenylmethyl chlorides in acetonitrile. The para substituents are indicated in the panels. Reproduced with permission from ref 55. Copyright 1990 American Chemical Society.

An interesting example where the ease of photoheterolysis does not follow the ground-state stability of cations or leaving groups is furnished by Zimmerman's "meta electron transmission" effect.[43,44] On the basis of photosolvolysis reactivity, *m*-methoxybenzyl derivatives are found[43] to produce cations more easily than their *p*-methoxy counterparts. Similarly, for nitro- and cyanophenyl trityl ether isomers, the photosolvolysis is more efficient for meta isomers than for para isomers.[44]

McClelland, Steenken, and co-workers[55,58] have studied in detail the quantum efficiencies of photohomolysis and -heterolysis in the course of 248-nm LFP of various triarylmethyl and diarylmethyl derivatives in acetonitrile and aqueous acetonitrile. The transient absorption spectra from LFP of several substituted diphenylmethyl halides are shown in Figure 2. In each case, three distinct band systems have been identified. These are due to cations (λ_{max} = 430–500 nm, strong and broad), radicals ($\lambda_{max} \approx$ 325–350 nm, narrow), and excited radicals (λ_{max} = 325–350 nm, weak). Repre-

Table I. Cation and Radical Yields from Photoheterolysis and Photohomolysis of Diarylmethyl Chlorides (ArAr′CHCl) in Acetonitrile[55] (λ_{ex} = 248 nm)

para substituents					
Ar	Ar′	$\Sigma\sigma^+$(R,R′)	pK_{R^+}	ϕ(C^+)	ϕ($C^\bullet$)
4-methoxyphenyl	4-methoxyphenyl	−1.56	−5.71, −5.56	0.31	0.24
4-methoxyphenyl	4-phenoxyphenyl	−1.28		0.16	0.22
4-methoxyphenyl	4-methylphenyl	−1.09	−8.32, −7.36	0.22	0.27
4-methoxyphenyl	phenyl	−0.78	−7.9, −8.12	0.32	0.26
4-methylphenyl	4-methylphenyl	−0.62	−10.4, −9.53	0.18	0.27
4-methylphenyl	phenyl	−0.31	−11.6, −12.29, −10.59	0.11	0.18
phenyl	phenyl	0	−13.3, −13.56, −11.77	0.13	0.23
4-fluorophenyl	phenyl	−0.07	−11.55	0.09	0.26
4-fluorophenyl	4-fluorophenyl	−0.14	−13.03	0.085	0.29
4-chlorophenyl	phenyl	0.114	−12.08, −13.7	0.15	0.27
4-chlorophenyl	4-chlorophenyl	0.23	−13.96	0.052	0.20
4-(trifluoromethyl)phenyl	phenyl	0.61		<0.07	0.39
mesityl	mesityl	−0.82	−6.6	0.11	0.12

Table II. Dependence of Cation and Radical Yields on the Nucleofugal Leaving Group X and Thermodynamic Parameters for C–X Bond Dissociation in the System Ph_2CH–X (R = R–X) in Acetonitrile[55] (λ_{ex} = 248 nm)

X	[C^+]/[$C^\bullet$]	ϕ(C^+)	ϕ($C^\bullet$)	EA($X^\bullet$)	pK_a(HX) in H_2O	pK_a(HX) in DMSO	ΔH°_f (R–X)	ΔH°_{hom} (R–X)	ΔH°_{het} (R–X)	ΔG_{sol} v for X^-	ΔG_{het} (solv)
Br	0.63	0.12	0.19	3.36	−8	0.9	44.8	51	142	−69	7
Cl	0.59	0.13	0.23	3.61	−7	1.8	32.6	64	150	−73	11
F	0.26	0.05	0.20	3.40	3.16	15	−1.8	89	179	−96	17
CF_3CO_2	0.14	0.04	0.31		0.52	3.45					
CH_3CO_2	<0.08			3.26	4.76	12.3	−54.7	76	170	−62	42
4-NO_2PhO	<0.1			3.55	7.16	10.8					
4-CNPhO	0.22	0.02	0.09	3.33	7.97						
HO	<0.03		0.04	1.83	15.7	32	0.9	77	204	<−84	54
H	<0.02		<0.1	0.756			40.3	81	232		
PhO				2.37	10	18					

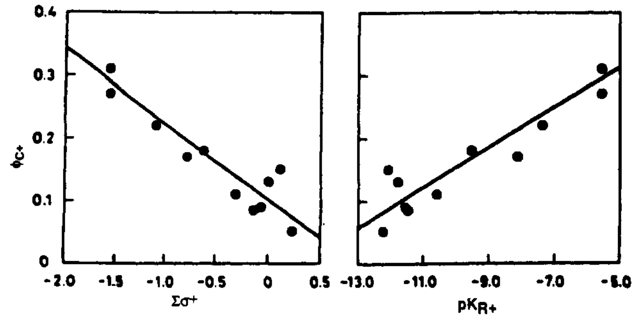


Figure 3. Dependence of photoheterolysis quantum yield on the electrofugal leaving group properties of the para-substituted benzhydryl cations as expressed by $\Sigma\sigma^+$ and pK_{R^+}. Reproduced with permission from ref 38. Copyright 1989 American Chemical Society.

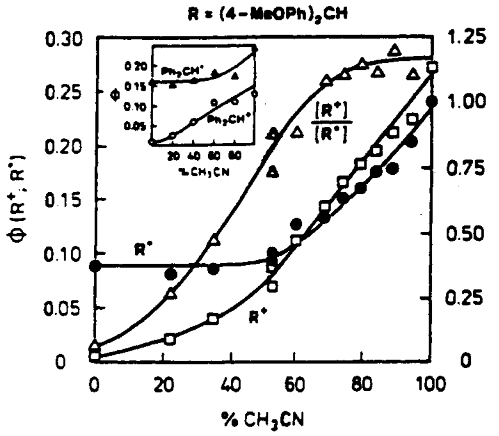


Figure 4. Dependence of photoheterolysis and photohomolysis quantum yields of (p-MeO-Ph)$_2$CHCl on the composition of the binary solvent mixture acetonitrile–dichloromethane. (Inset) Dependence for Ph_2CHCl. Reproduced with permission from ref 38. Copyright 1989 American Chemical Society.

sentative data regarding yields are given in Tables I and II. In acetonitrile, the quantum yields for homolysis (0.2–0.4) are found to be essentially independent of the nature of the substituent on the benzene ring, while those for heterolysis increase with increasing electron-donating strength (from <0.07 for CF_3 to 0.3 for OMe, Table I). The dependence of cation yield on the σ^+ of para substituents and on the pK_{R^+} value (i.e., a measure of cation stability in solution) is illustrated in Figure 3. The cation yields (Table II) also depend on the nucleofugal properties of X; for the halides, the observed heterolysis to homolysis ratio correlates with the pK_a value of the conjugate acid HX and not with the electron affinity of $X^\bullet$.

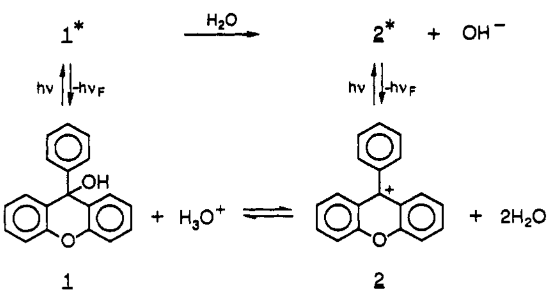
The effect of solvent on radical and cation yields is amply demonstrated by the data for (p-MeOPh)$_2$CHCl in acetonitrile–dichloromethane mixtures.[55] As Figure 4 shows, both cation and radical yields increase with increasing acetonitrile content. The inset in Figure 4 shows a similar, though less pronounced, behavior for Ph_2CHCl. Apparently, for these two substrates, both homolysis and heterolysis benefit from the increasing polarity of the solvent, although the reason for decrease in bond cleavage yields at increasing dichloromethane content could be in part due to the singlet excited state being quenched by dichloromethane.[55] The dominance of homolytic cleavage in relatively nonpolar solvents (e.g., n-heptane and benzene) and that of heterolysis in polar/hydroxylic solvents, particularly, aqueous mixtures, have also been noted by Minto and Das[65] in the course of 248-nm LFP of 9-phenyl-9-xanthenol.

An interesting observation made by Bartl et al.[55] is that the bond cleavage in several substituted diphenylmethyl halides can be induced indirectly by sensitization with triplet acetophenone (produced by 308-nm excitation). That the lowest triplet state of acetophenone is involved is established on the kinetic ground that the relatively slow decay of acetophenone triplet and the similar formation of radicals and cations are observed at the same time scale. On the basis of a triplet energy of 74 kcal/mol for acetophenone compared to 64 kcal/mol for the chlorides (estimated from the phosphorescence maximum of 450 ± 10 nm in 2-methyltetrahydrofuran glass at 77 K), it has been argued[55] that exothermic energy transfer occurs from acetophenone triplet to diphenylmethyl halides and, hence, the bond cleavage from the triplet states of the latter becomes feasible. It may, however, be noted that the observed half-band widths of 100 nm in the phosphorescence spectra[55] suggest the onsets (0–0 band) of the emission to be at <400 nm and, hence, the triplet energies (calculated from onsets) at above 71 kcal/mol. An alternative explanation for sensitization of photocleavage by acetophenone would be in terms of charge-transfer interactions proposed by Slocum and Schuster[85] and by Arnold et al.[86] Also worth mentioning in this connection is the involvement of upper triplet excited states in sensitized photosolvolysis of benzyl halides, as proposed by Cristol and Bindel.[48]

The identification of fluorenyl cation as a result of photodissociation of 9-fluorenol has been a subject of controversy. The fluorenyl cation forms an example of benzannelated 4*n* anti-Huckel cyclic system which may possess an aromatic character in the excited state and hence would be a favored product as a result of adiabatic photodehydroxylation of 9-fluorenol.[71-74] A 640-nm species with lifetimes in microseconds was observed by Gaillard et al.[63] upon 266-nm laser pulse (10 ns) excitation of 9-fluorenol in aqueous methanol. This was erroneously assigned to the carbocation. Later, Meclenburg and Hilinski[64] carried out a picosecond LFP study of 9-fluorenol in a 9:1 (v/v) mixture of water and methanol and observed a transient species with λ_{max} at 515 nm and a lifetime of <20 ps. They assigned this extremely short-lived species to the 9-fluorenyl cation and, furthermore, characterized the 640-nm species as 9-fluorenol radical cation by generating it via photoinduced electron transfer from 9-fluorenol to chloranil. More recently, McClelland et al.[57] observed the 515-nm transient as a relatively long-lived species (30 μs) upon 248-nm LFP of 9-fluorenol in HFIP. On the basis of lack of quenching by oxygen and high reactivity toward nucleophiles such as water and 2,2,2-trifluoroethanol (TFE), they confirmed the identification of this species as the carbocation. In aqueous TFE and aqueous acetonitrile, McClelland et al.[57] observed the 640-nm transient as the product of oxidation of 9-fluorenol by $SO_4^{\bullet-}$ (generated by 248-nm laser photolysis of $S_2O_8^{2-}$ ion) and also as the product of a biphotonic photoprocess under direct laser excitation of 9-fluorenol. These observations led to the reliable assignment of the 640-nm species as the 9-fluorenol radical cation produced as a result of electron photoejection under direct laser photolysis.

In contrast to fluorenyl cation, dibenzosuberenyl cation constitutes a $4n+2$ π-system and should not attain stabilization from aromaticity in the excited state. In support of this contention, several dibenzosuberenyl systems have been shown to have lower photochemical yields in photosolvolysis reactions under conditions where 9-hydroxyfluorene and its derivatives react relatively efficiently.[72-74] However, Johnston et al.[70] easily observed dibenzosuberenyl cation (λ_{max} = 525 and 390 nm) as a long-lived species (>100 μs) in the course of 308-nm LFP of the parent alcohol in TFE. It has also been noted[70] that minor changes in solvent composition (e.g., 5% water in TFE) make the observation of the cation difficult, probably because of a combination of reduction in both yield and lifetime.

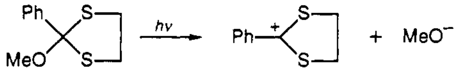
Scheme III



The observation of fluorescence of xanthenyl cations upon photoexcitation of their parent alcohol substrates under conditions where ground-state ionization of the alcohols could not occur led to the conclusion that the photodissociation in these systems is adiabatic[84,87] (Scheme III). Adiabaticity is postulated[88] to be common in photoprotonation and photodehydroxylation reactions leading to carbocations. Recent LFP studies[59,65] of 9-xanthenol and its 9-phenyl analog have shown that only a small fraction of the photoheterolysis occurs through the adiabatic route (about 1% for 9-phenyl-9-xanthenol in 1:1 water–acetonitrile).[65]

An interesting class of carbon-centered cations comprises vinyl cations,[66-69] which can also be viewed as intermediates from protonation of acetylenes.[88] Several recent time-resolved studies by Schnabel and co-workers[66-68] and by VanGinkel et al.[69] have shown that these cations can be easily generated via photodissociation of substituted vinyl halides in acetonitrile.

Okuyama et al.[83] have studied 2-phenyl-1,3-dithiolanylium ion generated as a very long-lived transient intermediate by lamp flash photolysis of aqueous ethanol and acetonitrile solutions of 2-methoxy and other dithiolane derivatives (eq 7). The dithioanylium cation shows maximum absorption at 342 nm and decays with pseudo-first-order rate constants of 3.83 and 0.56 s^{-1} in 1:1 H_2O–ethanol and 1:1 H_2O–acetonitrile, respectively.



(7)

Spears et al.[76] have studied in detail the ultrafast ionic photodissociation dynamics of malachite green leucocyanide (MGCN) using picosecond spectroscopic techniques. The ionic dissociation lifetimes of MGCN from its lowest excited singlet state are 0.1–5 ns and are controlled by solvation of an ionic transition state. In aprotic solvents, the solvent dielectric constant determines the stabilization of the ionic transient state and hence the ionization rate. Modeling the ionization rate using classical solvation energies of a dipole in a dielectric gives a partial charge formation of 0.54–0.70

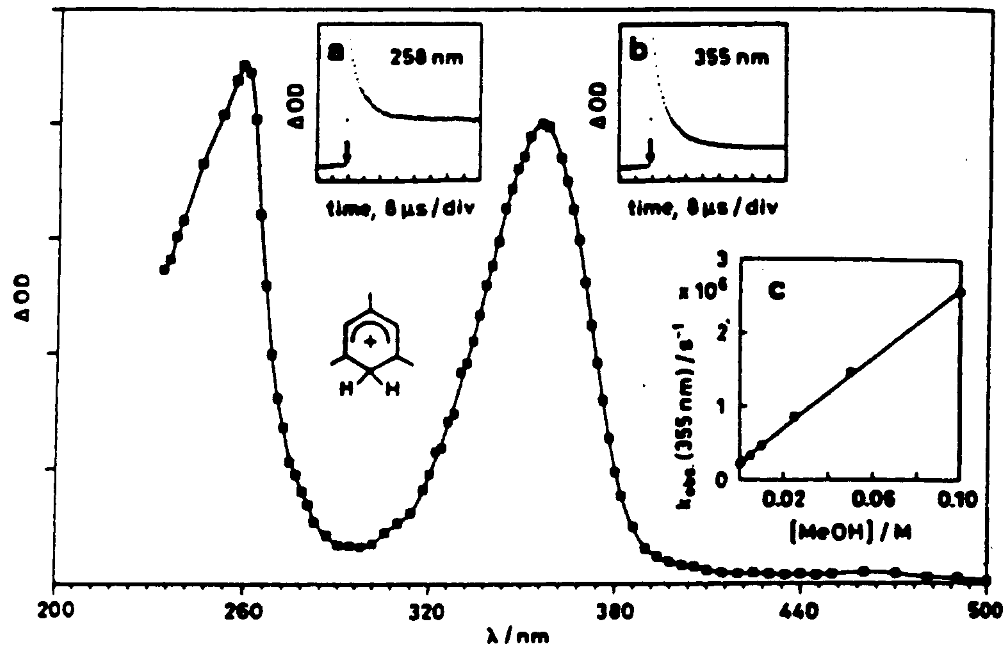


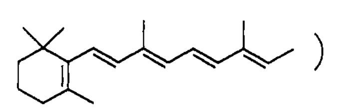
Figure 5. Transient absorption spectrum of MESH$^+$ monitored at 100 ns following 248-nm LFP of 10 mM mesitylene in HFIP at 20 °C. (Insets a and b) Decay of MESH$^+$ transient at 258 and 355 nm, respectively. (Inset c) Dependence on [MeOH] of k_{obsd} for decay monitored at 355 nm. Reproduced with permission from ref 98. Copyright 1990 American Chemical Society.

for the transition-state dipole moment. A higher energy excited state of MGCN, apparently accessible by absorption of a second photon from the lowest excited singlet, rapidly dissociates into ions after radiationless conversion. The recombination yields of the vibrationally excited contact ion pair depend on the dielectric constant and are related to vibrational relaxation and longitudinal dielectric relaxation. The cation (MG$^+$, monitored at 600 nm) in the initial contact ion pair has a tetrahedral geometry, which subsequently reorganizes to a charge-delocalized, planar form. The times of this conversion in aprotic solvents increase from 6 to 13 ps with increasing dielectric constant and are explainable in terms of solvent energetics. However, large reorganization rates in alcohol solvents are determined by alcohol monomer orientation times (that is, specific solvent motion controls the transition-state barrier crossing in this case).

Recently, picosecond absorption spectroscopy has also been applied by Pienta and Kessler[77] to study photodissociation dynamics of *all-trans*-retinol acetate (eq 8). This work gave evidence for formation of contact

$$ROCOCH_3 \longrightarrow R^+ + CH_3CO_2^- \qquad (8)$$

R =



ion pairs over a picosecond time scale following the formation of the pentaenyl cation and before the appearance of free ions observed over nanoseconds. Partly because of their biological implication, the photodissociation of retinyl derivatives (particularly, *all-trans*-retinol and *all-trans*-retinol acetate) has received considerable attention.[77-82] Between *all-trans*-retinol acetate and *all-trans*-retinol, the photodissociation (in polar solvents and aqueous micellar solutions) is monophotonic and more efficient in the case of the former, while it is predominantly biphotonic in the case of the polyene alcohol.[80,81] The higher propensity of photodissociation in the case of the acetate is probably a reflection of the higher nucleofugal character of the leaving group (acetate). Another finding, subject to a similar interpretation, is that in hydroxylic solvents the pulse-radiolytically produced radical anions of *all-trans*-retinol acetate and palmitate undergo immediate elimination of carboxylate ions forming the retinyl methyl radical (λ_{max} = 395 nm, $\tau_{1/2} > 100$ μs), while those of *all-trans*-retinol and retinyl methyl ether undergo fast protonation, giving rise to radicals of shorter chain lengths (λ_{max} = 370–375 nm, $\tau_{1/2} > 100$ μs). In nonprotic solvents (e.g., tetrahydrofuran), the radical anions (λ_{max} = 575–590 nm, τ = 0.5–7 μs) of the alcohol and the ether are easily observed as products of e_{solv}^- attachment.[82,89,90]

C. Photoprotonation of Aromatics and π-Systems (Alkenes, Alkynes, and Allenes)[52,88,91-99]

Both intra- and intermolecular proton transfer in the excited states of allenes, alkenes, and alkynes and intermediacy of resultant cations have been recognized in the steady-state photochemistry of systems containing these moieties.[88,91-99] The fluorescence quenching of some benzenes and naphthalenes by protons has been explained in terms of electrophilic attack of the aromatic ring in the excited state by the proton; this results in overall proton exchange.[91,92,97] The acid-catalyzed ipso photosubstitution of alkoxy-substituted benzenes by solvent water is believed to occur by a mechanism in which the benzene ring becomes photoprotonated in the singlet excited state. Recently, Steenken and McClelland[98] observed cyclohexadienyl cations (Figure 5) as a result of 248-nm laser excitation of mesitylene, hexamethylbenzene, and 1,3,5-trimethoxybenzene in HFIP (quantum yields, 0.04–0.08).

LFP[99] (248 nm) of *p*-methoxyphenylacetylene in TFE gives the 1-*p*-methoxyvinyl cation (λ_{max} = 335 nm; decay rate constant, 1.3 × 10^6 s^{-1}). The latter is spectrally and kinetically similar to the 1-*p*-methoxyphenethyl cation (λ_{max} = 340 nm; decay rate constant, 3.9×10^5 s^{-1}) produced by laser-pulse photoprotonation of *p*-methoxystyrene. The similarity of the spectra, and probably the reactivity, arises from a structure of the vinyl cation in which the π-systems of the benzene and alkene are orthogonal to each other and the formally empty p orbital is conjugated with the benzene ring in a manner similar to that in a benzyl cation.

D. Reaction of Carbocations with Aromatics[100]

9-Fluorenyl cation, generated by LFP (309 nm) of 9-fluorenol in HFIP, has been shown[100] to be readily quenched by arenes, giving rise to cyclohexadienyl cations. For example, with mesitylene, the product transient is identified as the 1-(9′-fluorenyl)-2,4,6-trimethylbenzenium ion (λ_{max} = 365 nm, τ = 20 μs in HFIP). These cyclohexadienyl cations may be recognized as the σ-complexes in Friedel–Crafts alkylation and are shown to be highly electrophilic (for example, the complex from mesitylene reacts with Br^- and methanol with rate constants 2.8×10^9 and 3.3×10^6 M^{-1} s^{-1}, respectively).

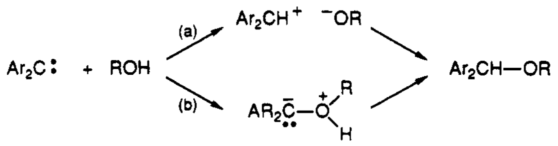
E. Protonation–Elimination[34]

With pulse-radiolytically released hydrogen ion in 1,2-dichloromethane,[34] *all-trans*-retinol and its acetate ester in the ground state form H^+ adducts that lead to retinyl cation (λ_{max} = 585 nm; τ, 14 ± 4 μs) through elimination of water and acetic acid, respectively. The spectrum agrees with those (λ_{max} = 598 ± 14 nm, ϵ_{max} = 44 000–113 000 M^{-1} cm^{-1}) observed from reaction with retinol and retinol acetate with trichloroacetic acid and H_2SO_4 in various solvents at subambient temperatures.[101] The apparent rate constants for protonation, measured[34] from the linear dependence of observed first-order formation rate constant of cation on substrate concentrations, are 2.7×10^7 and 2.2×10^7 M^{-1} s^{-1} for *all-trans*-retinol acetate and *all-trans*-retinol, respectively.

F. Protonation of Photogenerated Carbenes[102–104]

In keeping with their name, several carbenium ions have been identified as short-lived intermediates as a result of proton addition to carbenes photogenerated by LFP of diazo precursors in hydroxylic solvents. Kirmse et al.[102] have shown that the 248-nm LFP of various substituted diphenyldiazomethanes in aqueous acetonitrile and in acetonitrile–TFE mixtures gives transient absorptions spectrally and kinetically identical to those attributed to corresponding diaryl carbenium ions produced by photoheterolysis in Ar_2CHX substrates (X = Cl, OAc, and OC_6H_4-CN-*p*). Also, with tetraphenyl oxirane and Ph_2CN_2 as carbene precursors in TFE and 1:1.6 acetonitrile–TFE mixture, respectively, the unsubstituted diphenyl carbenium ion could be observed (τ = 313 ns and λ_{max} = 435 nm in TFE; τ = 152 ns and λ_{max} = 430 nm in 1:1.6 acetonitrile–TFE). These results provide evidence for the fact that diarylcarbene singlets interact with hydroxylic molecules by abstracting a proton from them, rather than by electrophilic attack on the oxygen atom (Scheme IV). More recently, Chateauneuf[103] detected shorter-lived diphenyl carbenium ion in the course of picosecond LFP of diphenyldiazomethane in various hydroxylic solvents; the lifetimes of the carbenium ion in 1:1 water–acetonitrile, propan-2-ol, ethanol, and methanol are 750, 85, 70, and 40 ps, respectively. Reversible carbene protonation to a carbocation has also been implicated by Boate and co-workers[104] to explain the intermolecular reactivity of an oxacarbene photogenerated from benzocyclobutenedione.

Scheme IV



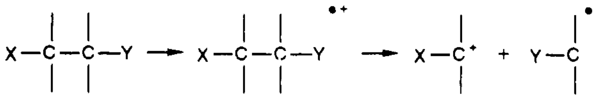
G. One-Electron Oxidation and Photoionization of C-Centered Radicals[105–108]

Inorganic oxidants such as $[Fe(CN)_6]^{3-}$ and $[IrCl_6]^{2-}$ have been utilized to generate carbocations via one-electron oxidation of alkoxymethyl radicals produced in aqueous solution via H abstraction from alkoxymethanes by pulse-radiolytic OH radical and H atom.[105,106] Electrochemical one-electron oxidation–reduction occurs in photomodulation voltammetric experiments,[108] generating carbanions and carbocations from corresponding radicals.

Recently, Faria and Steenken[107] reported dual-laser-pulse experiments regarding the monophotonic photoejection of an electron from trityl radical to give trityl cation and solvated electron. In their experiments, first the $Ph_3C^\bullet$ transient was produced from triphenylacetic acid in aqueous solution at pH 7–10 via decarboxylation of the corresponding radical cation (a product of biphotonic electron photoejection under laser excitation at 248 nm). A few microseconds following its formation, the radical was subjected to 248- or 308-nm LFP, showing the formation of both the trityl cation and hydrated electron, each recognized by characteristic transient spectra (Figure 6). In addition, as a result of photolysis by the second laser pulse, depletion was noted in the region where the trityl radical absorbed. This result is also interesting in view of the fact that the trityl radical is recognized for intramolecular photochemistry, namely, electrocyclic ring closure to a dihydrofluorenyl-type radical, rendering its doublet–doublet fluorescence lifetimes short in fluid solvents (compared to long fluorescence lifetimes of the diphenylmethyl radical under similar conditions).[109–111]

H. Heterolytic Fragmentation, Including C–C Bond Cleavage in Radical Cations[38,106,112–122]

Certain radical cations, e.g., those containing relatively weak C–C bonds, undergo intramolecular fragmentation, leading to radicals and carbocations (eq 9).



$$\mathrm{X{-}C{-}C{-}Y} \longrightarrow \mathrm{X{-}C{-}C{-}Y}^{\bullet+} \longrightarrow \mathrm{X{-}C^{+}} + \mathrm{Y{-}C^{\bullet}} \qquad (9)$$

The radical cation precursors can be produced photochemically, namely, via photoejection (often biphotonic) of an electron, excited-state mediated electron transfer from a substrate to an acceptor, or one-electron

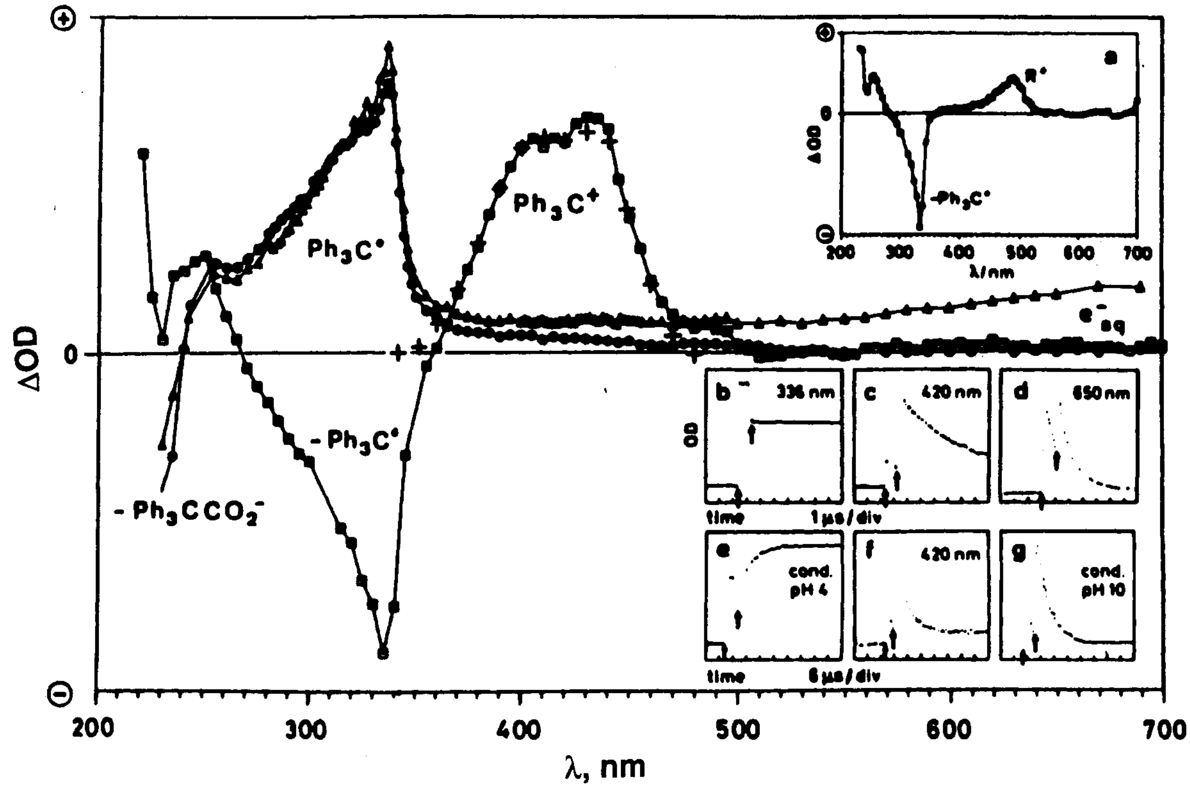


Figure 6. Transient absorption spectra observed upon LFP of a deaerated 0.4 mM solution of triphenylacetic acid at pH 7.5. The arrows indicate the pulse positions. (Triangles) ΔOD recorded 560 ns after the first laser pulse (248 nm, 20 ns). (Circles) 0.12 M $HOCH_2CH_2Cl$ added to scavenge e_{aq}^-. (Squares) Spectrum recorded 320 ns after the second laser pulse (308 nm, 20 ns), delayed 1 μs from the first pulse. (Crosses) Absorption spectrum of Ph_3C^+ in 60% H_2SO_4 obtained by dissolving 0.04 mM Ph_3COH. (Inset a) Spectrum recorded 530 ns after the second pulse in the presence of 1 mM NaN_3, added to scavenge Ph_3C^+. (Insets b–d) (b) Depletion of $Ph_3C^\bullet$ at 336 nm; (c) formation of Ph_3C^+ at 420 nm; (d) formation of e_{aq}^- at 650 nm. (Insets e–g) Decay of Ph_3C^+ by reaction with H_2O in solutions containing 0.3 mM Ph_3CH in 2:1 H_2O–CH_3CN at pH 4 (e) and 0.4 mM $Ph_3CCO_2^-$ in H_2O at pH 10 (f and g). Reproduced with permission from ref 107. Copyright 1990 American Chemical Society.

oxidation by a photolytically generated oxidant (e.g., $SO_4^{\bullet-}$ from $S_2O_8^{2-}$). The oxidizing species can also be generated radiation chemically (e.g., hydrogen abstracting agents, OH and H in water, solvent-derived radical cations in chlorinated hydrocarbons, and $SO_4^{\bullet-}$ produced by the reaction $S_2O_8^{2-} + e_{solv}^- \rightarrow SO_4^{\bullet-} + SO_4^{2-}$).

Steenken and McClelland[38] generated α-dialkoxymethyl carbocations $RC^+(OR')^2$ in aqueous solution by 248-nm LFP of peroxydisulfate $S_2O_8^{2-}$ (leading to $SO_4^{\bullet-}$) in the presence of acetals $PhCH_2CR(OR')_2$. The radical cations of the latter, formed as a result of one-electron oxidation by $SO_4^{\bullet-}$, underwent intramolecular fragmentation to benzyl radical and the carbocations in question. The initial radical cations were also produced by direct two-photon photoionization in benzyl acetals.

The extensive amount of data on carbocations generated by Dorfman and co-workers using PR[30–33,115–120] deserves special mention. These authors generated the carbocations in chlorocarbon solvents (particularly DCE) via interaction of solvent radical cations (or other cationic species)[30–33] with substrates such as arylmethyl halides and dibenzylmercury.

$$S^{\bullet+} + Ph_nCH_{(3-n)}X \rightarrow PhCH_{(3-n)}^{\ \ +} + X^\bullet + S \quad (10)$$

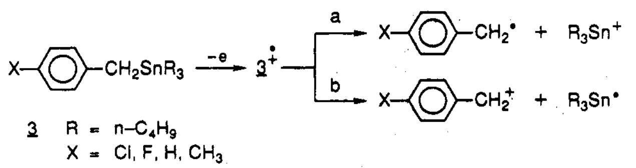
$$S^{\bullet+} + (PhCH_2)_2Hg \rightarrow PhCH_2^{\ +} + PhCH_2Hg^\bullet + S \quad (11)$$

Recently, McClelland et al.[52] reported on the transient-spectral behavior of several benzyl, phenethyl, and cumyl cations in TFE and HFIP. These cations were produced via excited-state photoprotonation of styrenes and by photoheterolysis of arylmethyl halides or trimethylammonium fluoroborates (both groups of substrates subjected to 248-nm LFP). The observed trends in λ_{max} (310–360 nm) with respect to para substituents were 4-MeO > 4-Me > H for a given type of cation and cumyl > phenethyl > benzyl for a given para substituent. The observed locations and trends in the spectral maxima of these well-identified benzyl-type cations led McClelland et al.[52] to suggest that Dorfman et al.[116] were probably incorrect in their benzyl-cation assignment of a pulse-radiolytic transient with a single broad peak at 363 nm and weak absorbances at 320 and 420 nm.

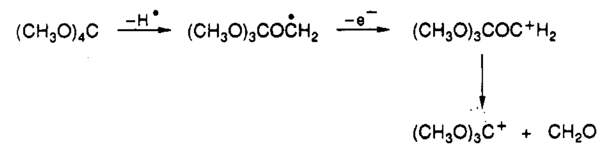
Bobrowski et al.[121] observed the formation of malachite green cation (MG^+, λ_{max} = 620 nm) in the course of PR of malachite green leucocyanide (MGCN) in various solvents, particularly chlorohydrocarbons, DMSO, dimethylformamide, alcohols, and acetonitrile. They attributed the cation formation, at least in part, to the intermediacy of MGCN radical cation.

Eaton[122] has shown that benzyltrialkylstannanes in the presence of tetracyanoethylene (electron acceptor) give rise to photochemistry explainable in terms of competition between two modes of cleavage of the stannane radical cation. These are shown in Scheme V. With R = n-C_4H_9, the benzyl cation mediated photochemistry (mode b) becomes pronounced in the order of X: CH_3 > F > H > Cl, that is, in the expected order of stability of the benzyl cation.

Scheme V



Scheme VI



I. Bond Heterolysis in a Cation[105]

The α-(β-trialkoxy)methoxyalkyl cations (Scheme VI), produced via H abstraction from tetraalkoxymethanes followed by one-electron oxidation, have been shown[105] to undergo β-fragmentation of the C–O bond, producing trialkoxymethyl cations. These cations were detected by conductivity changes.

J. Heterolytic Fragmentation of Radical Anions[123–136]

Anions and radicals are known to form readily as a result of intramolecular heterolysis of a bond in radical anions (eq 12).[123–136]

$$Ar{-}X{-}Y \rightarrow Ar{-}X{-}Y^{•-} \rightarrow Ar{-}X^• + Y^- \text{ or } A{-}X^- + Y^• \quad (12)$$

$$R_2Hg \rightarrow [R_2Hg]^{•-} \rightarrow R^- + RHg^• \quad (13)$$

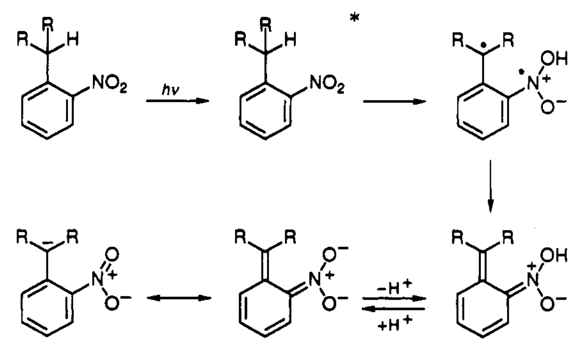
The carbanion formation mediated by pulse-radiolytic radical anions has been utilized by Beletskaya et al.[131,132] and Dorfman and co-workers[133–135] for fast kinetics studies. In their work, arylmethyl anions have been generated from dissociative solvated electron attachment to organomercury compounds in tetrahydrofuran (eq 13).

Recently, Maslak et al.[136] applied pulse radiolysis to investigate the intramolecular fragmentation behavior of radical anions of a series of electron-poor substrates, p-X–$C_6H_4C(CN)(Y)C(CH_3)_2C_6H_4CN$-$p$ (X = H, OMe, CF_3, X and Y = Me, CN). In acetonitrile at 3×10^{-4} M substrate concentration, the fragments [anions, p-X–$C_6H_4C(CN)(Y)^-$, and radical, p-$CNC_6H_4C^•(CH_3)_2$] evolve over 10^{-6}–10^{-7} s and are monitored in terms of transient absorptions (~295 nm for the radical and 300–370 nm for the anions).

K. Photoelimination Leading to Carbanions[137–145]

The elimination of CO_2, HCHO, PO_3^-, etc. from the excited states of suitable substrates leads to carbanions.[137–145] In particular, steady-state photochemical studies point to facile photodecarboxylation to carbanions in the case of benzannelated carboxylic acids.[137,139] The photoinduced loss of monomeric metaphosphate anion (PO_3^-) from nitrosubstituted benzyl phosphonates and formation of nitrobenzyl anion derived products have been established by Okamoto et al.[141,142]

Scheme VII



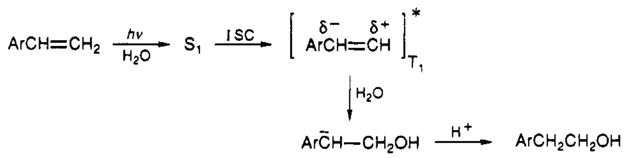
Employing lamp flash photolysis, Margerum and Petrusis[143] obtained for the first time the transient absorption spectra of carbanions derived from nitrophenyl acetates in aqueous solution. More recently, Craig et al.[144] carried out detailed pico- and nanosecond LFP studies of p-nitrophenyl acetate in aqueous solutions and showed the photodecarboxylation to occur from the lowest triplet n,π* state. Interestingly, their results strongly suggest a photoadiabatic nature of the decarboxylation process. That is, it occurs through the intermediacy of p-nitrobenzyl anion triplet (λ_{max} ~ 290 nm, τ = 90 ns at pH 5.0).

Craig and Atherton[145] reported in detail on the transient-spectral properties of p-nitrobenzyl anion by generating it via photodecarboxylation of p-nitrophenyl acetate. At pH >6, this species in aqueous solution decays by mixed kinetics, comprising first-order solvent protonation ($k_1 = 1.3 \times 10^{-2}$ s^{-1}) and second-order dimerization ($2k_2 = 1.7 \times 10^3$ M^{-1} s^{-1}). The anion is reluctantly quenched by O_2 with a rate constant of 7.8 M^{-1} s^{-1}.

L. Excited-State Mediated Heterolysis of C–H[146–154]

For substrates such as dibenzosuberenol, 5H-dibenzo[a,c]cycloheptene, and related substrates, C–H bond heterolysis in S_1 leading to carbanions has been proposed as a key step in the mechanism of steady-state photochemical transformations and deuterium incorporation in these substrates.[146–148] In these cases, the stabilization of the carbanion in the excited state has been suggested in terms of attainment of 8π electron arrangement in the cyclic array. No direct evidence for it has yet been obtained by time-resolved studies.

The mechanism of the overall C–H bond heterolysis in nitrotoluenes containing a nitro group ortho to the methyl group is now well-understood. For 2,6-dinitrotoluene in various solvents, Atherton and Craig[149] observed the formation of the aciquinoid isomer (λ_{max} = 400–420 nm, pH <1.0, nonpolar media) formed via intramolecular hydrogen transfer (Scheme VII). The latter then undergoes deprotonation to 2,4-nitrobenzyl anion (λ_{max} = 490–550 nm, pH >2.0, polar solvents). This result has been corroborated by McClelland and Steenken,[150] who, on the basis of conductivity measurements, established the initial formation of the aciquinoid species as a nonconductive transient. The intramolecular hydrogen atom transfer is a very fast process ($k = 0.5 \times 10^9$ and 0.6×10^9 s^{-1} for 2,6-dinitrotoluene and 2,4-dinitrotoluene in methanol, Scheme VIII



respectively) occurring from the lowest n,π* triplet state.[151]

M. Nucleophilic Attack on Olefin Excited States[152-154]

Wan and co-workers[152-154] have shown that anti-Markovnikov photoaddition of water and alcohols to several 3-nitrostyrenes takes place via their triplet excited states. The proposed mechanism involves initial nucleophilic addition of water or alcohols to the β-carbon of the alkene moiety to generate *m*-nitrobenzyl anion intermediates (Scheme VIII).

III. Time-Resolved Detection: Spectroscopic Properties

Conjugated carbocations and carbanions absorb strongly in the UV–visible region and are conveniently monitored and identified in terms of their transient absorption spectra in fluid solution. For many carbocations, spectral data are available from earlier work based on steady-state measurements in strongly acidic media; these often prove valuable for comparison purposes in assigning transient carbocations produced in nonacidic media. Care should be exercised in applying this method of assignment because, in strongly acidic media, radical cations are sometimes formed through one-electron oxidation and may easily be confused with a carbocation. The identification of a carbocation based on spectral comparison should be corroborated by its generation by multiple routes, insensitivity to oxygen, and electrophilic reactivity (one should, however, keep in mind that the last two properties are also exhibited by radical cations). Similarly, the spectral identification of carbanions should be supported by their characteristic kinetic behavior, such as nucleophilic reactivity (protonation), sensitivity to oxygen, and role as a donor in single-electron transfer.

Electrical conductivity is another property that has been used by many groups to detect the formation of transient ionic species as well as their decay via reactions leading to new ionic species or undissociated products. For example, as supporting evidence for photoformation of vinyl cations in fluid solutions, both Schnabel et al.[66-68] and VanGinkel et al.[69] presented data in terms of photoinduced changes in electrical conductivity. Similarly, in much of their work concerning transient carbocations, McClelland, Steenken, and co-workers[51-61,105,106] provided evidence from conductivity measurements (parallel to optical detection) in support of photoinduced ion separation. As a matter of fact, in the case of some aliphatic systems such as tri- and dialkoxymethyl cations for which a convenient spectral region for optical measurement is not available, kinetics data have been obtained by taking recourse to time-resolved conductance.[105,106]

The emission spectral properties of several carbocations and carbanions have been utilized to shed light on their excited-state and, sometimes, ground-state, interactions. Xanthenyl and several other cations exhibit fluorescence characterized by high quantum yields (>0.1) and relatively long lifetimes (20–30 ns) in acid solutions at room temperature.[65,70,87,155,156] The quenching of fluorescence of xanthenyl carbocations has yielded information on electrophilic and electron-transfer reactivity in their singlet excited states.[65,87,155,156] Many resonance-stabilized carbanions are also known to emit. A study of Fox and Voynick[157] of alkali metal salts of acyclic carbanions led to the observation that the picosecond fluorescence lifetimes of these ion-paired, acyclic anions are affected more by the associated cation than by the type of ion pairing.

A. Absorption Spectra

In connection with a study of quantum yields of photohomolysis and photoheterolysis of substituted diphenylmethyl derivatives in acetonitrile, Bartl et al.[55] compiled the absorption spectral data of corresponding diphenylmethyl radicals and cations. These data are reproduced in Table III. Traditionally, the spectral data for cations are obtained by steady-state spectrophotometry on stabilized species in strongly acidic solutions. Those for the radicals are from measurements on transient species generated by applying time-resolved techniques based on electron or laser pulses; the latter data are subject to higher uncertainties. The spectral maxima of cations in strongly acidic media are only slightly red-shifted compared to those observed by LFP in neutral solvents. On the basis of emission location with respect to absorption (and other evidence), while the λ_{max} values for cations in Table III correspond to the lowest-energy electronic transition in these systems, this is not the case with radicals. The radicals are characterized by additional weak absorptions corresponding to lower-energy transitions in the visible; these are revealed by better-resolved spectra and detailed photophysical considerations. Interestingly, for the cations, para substitutions by both electron-withdrawing and electron-releasing groups cause red shifts in absorption spectral maxima and increases in molar extinction coefficients (relative to unsubstituted diphenylmethyl cation). Pronounced red shifts in the absorption maxima upon substitution by electron-donating groups (methyl and methoxy) at the para position have also been observed for cumyl, phenethyl, and benzyl cations.[52]

The absorption spectral maxima of a number of other cations and several carbanions as obtained by time-resolved studies in neutral solvents are compiled in Table IV. Usually, the absorption spectra of anionic systems are very sensitive to environmental effects or specific interactions with cations. For example, McClelland and Steenken[150] found that for 2,4-dinitrobenzyl anion λ_{max} varied from 400 and 640 nm in acetonitrile to 350 and 500 nm in water. In aqueous acetonitrile, the two spectrally distinct forms of the anion coexist. Similarly, for *p*-nitrobenzyl anion in aqueous DMSO, Craig and Atherton[145] showed the presence of two forms of the anion corresponding to λ_{max} = 356 and 440 nm, respectively. Large red shifts (100–130 nm) in λ_{max} have been noted for *all-trans-*

Table III. Absorption Spectral Data[a] for Diarylmethyl and Trityl Cations and Radicals[55]

para substituents		radical C$^\bullet$		cation C$^+$	
Ar	Ar′	λ, nm	log (ε in M^{-1} cm^{-1})	λ, nm	log (ε in M^{-1} cm^{-1})
4-methoxyphenyl	4-methoxyphenyl	348		500	
		~350 (CH_2Cl_2)		~512 (CH_2Cl_2)	
		352 (THF)	4.67	507 (H_2SO_4)^{d}	5.04
				503 (H_2SO_4)^{e}	5.10
				501	
4-methoxyphenyl	4-phenoxyphenyl	350		500	
		354 (THF)	4.63	516 (CH_2Cl_2)	5.20
4-methoxyphenyl	4-methylphenyl	344		478	
		346 (THF)	4.63	482 (H_2SO_4)^{f}	4.92
				476	
4-methoxyphenyl	phenyl	340		455	
		344 (THF)	4.53	466 (H_2SO_4)^{g}	4.52
				463 (H_2SO_4)	4.79
				457	
4-methylphenyl	4-methylphenyl	338		464	
		340 (THF)	4.72	472 (H_2SO_4)^{d}	4.87
				462	
4-methylphenyl	phenyl	336		450	
		338 (THF)	4.65	456 (H_2SO_4)^{g}	4.43
				456 (H_2SO_4)^{f}	4.87
				455 (H_2SO_4)	4.86
				449	
phenyl	phenyl	330		435	
		331^{b}	4.64	453 (nitromethane)^{h}	
		332 (THF)	4.64	440 (H_2SO_4)^{d}	4.64
		330 (H_2O)	4.64	442 (H_2SO_4)^{f}	4.74
				449 (DCE)^{i}	4.58
				435	
4-fluorophenyl	phenyl	326		436	
		330 (THF)	4.61	445 (H_2SO_4)	
				439	4.72
4-fluorophenyl	4-fluorophenyl	324		444	
		327 (THF)	4.65	452 (H_2SO_4)^{j}	4.87
				448 (H_2SO_4)	4.86
				453 (CH_2Cl_2)^{k}	
				442	
4-chlorophenyl	phenyl	336		456	
		336 (THF)	4.76	463 (H_2SO_4)	4.73
				467 (CH_2Cl_2)^{k}	
4-chlorophenyl	4-chlorophenyl	340		472	
		344 (THF)	4.76	485 (H_2SO_4)^{d}	5.14
				483 (H_2SO_4)	5.00
				489 (CH_2Cl_2)^{k}	
4-(trifluoromethyl)phenyl	phenyl	334		425	
		336 (THF)	4.50	430 (H_2SO_4)	4.5
mesityl	mesityl	350		524	
		354 (THF)	4.34	527 (H_2SO_4)	4.50
				522 (nitromethane)^{h}	
				528 (H_2SO_4)^{d}	
Ph_3C^+		338		410	
		334 (EtOH)^{c}	4.56	404/431 (H_2SO_4)^{d}	4.60
		339 (H_2O)	4.61	404/432 (H_2SO_4)^{l}	4.58
				432 (H_2SO_4)^{e}	

[a] These data, obtained by PR or LFP or steady-state measurements, are either measured or compiled in ref 58, wherein more details are given. Unless otherwise mentioned in parentheses, the solvent is acetonitrile. The ε data are from the same source and in the same solvent as indicated for the corresponding λ_{max}. [b] From ref 110. [c] Taub, I. A.; Harter, D. A.; Sauer, M. C.; Dorfman, L. M. *J. Chem. Phys.* **1964**, *41*, 979. [d] Deno, N. C.; Jaruzelski, J. J.; Schriesheim, A. J. *J. Am. Chem. Soc.* **1955**, *77*, 3044. [e] Arnett, E. M.; Bushick, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1564. [f] White, W. M.; Stout, C. D. *J. Org. Chem.* **1962**, *27*, 2915. [g] Deno, M. C.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3051. [h] Volz, H.; Schnell, H. W. *Angew. Chem.* **1965**, *19*, 864. [i] Reference 33. [j] Deno, M. C.; Evans, W. L. *J. Am. Chem. Soc.* **1957**, *79*, 5804. [k] Volz, H.; Mayer, W. P. *Leibigs Ann. Chem.* **1975**, 835. [l] Harmon, K. M.; Hesse, L.; Kleeman, L. P.; Kocher, C. W.; McKinley, S. V.; Young, A. E. *Inorg. Chem.* **1969**, *8*, 1054.

retinal radical anion upon going from nonpolar and/or nonprotic solvents (*n*-hexane, acetonitrile)[158] to polar/H-bonding solvents (alcohols) as well as upon cation pairing.[159] The effect of ion pairing on carbanion spectra is also illustrated by the data on free vs ion-paired benzyl anion, observed[134] by PR in THF (Table IV).

In Tables V and VI are presented photophysical data of several carbocations and ion-paired carbanions, respectively.

B. Fluorescence

In the absence of electrophilic or another type of quenching, xanthenium and thioxanthenium cations display relatively intense fluorescence characterized by long lifetimes (Table V). Under the conditions (e.g., in acetonitrile acidified with H_2SO_4 or trifluoroacetic acid) where these cations exhibit moderately strong fluorescence, the emission from trityl cation is very weak;

Table IV. Absorption Spectral Data for Carbocations and Carbanions in Solutions at Room Temperature (Data Obtained by LFP or PR)

cation or anion	solvent[a]	λ_{max}, nm	ref
carbocations			
$PhCH_2^+$	DCE	363	32
Ph_2CH^+	DCE	445	32
	TFE	440	60
Ph_3C^+	DCE	415, 439	32
$Ph(c\text{-}C_3H_5)CH^+$	DCE	343	32
$Ph(c\text{-}C_3H_5)_2C^+$	DCE	296, 353	32
$(4\text{-MeO-Ph})_2CH^+$	1:4 ACN-H_2O	500	60
$(4\text{-MeO-Ph})(4\text{-Me-Ph})CH^+$	1:4 ACN-H_2O	475	60
$(4\text{-MeO-Ph})(Ph)CH^+$	1:4 ACN-H_2O	455	60
$(4\text{-Me-Ph})_2CH^+$	1:4 ACN-H_2O	460	60
$(3\text{-MeO-Ph})(4\text{-MeO-Ph})CH^+$	1:4 ACN-H_2O	440	60
$(4\text{-MeO-Ph})(4\text{-}CF_3\text{-Ph})CH^+$	1:4 ACN-H_2O	440	60
$(4\text{-Me-Ph})(Ph)CH^+$	TFE	450	60
$Ph_2C(CH_3)^+$	TFE	425	60
9-xanthenyl	H_2O	365	60
9-phenylxanthenyl	1:1 H_2O-MeOH	375	65
cumyl	HFIP	325, ~410	52
4-methylcumyl	HFIP	340, ~380	52
4-methoxycumyl	HFIP	360	52
phenethyl	HFIP	315, ~430	52
4-methylphenethyl	HFIP	325, ~390	52
4-methoxyphenethyl	HFIP	340	52
4-methylbenzyl	HFIP	310	52
4-methoxybenzyl	HFIP	320	52
9-fluorenyl	HFIP	515	57
$(4\text{-MeO-Ph})_2C{=}C^+(Ph\text{-}4\text{-MeO})$	ACN	~350	67
$(Ph)_2C{=}C^+(Ph\text{-}4\text{-MeO})$	ACN	~345	67
	ACN	350	69
$(Me)_2C{=}C^+(Ph\text{-}4\text{-MeO})$	ACN	~340	67
$H_2C{=}C^+(Ph\text{-}4\text{-MeO})$	TFE	335	99
dibenzosuberenyl	TFE	390, 525	70
(4-MeO-1-naphthyl)phenylmethyl	TFE	~360, 500	75
2-phenyl-1,3-dithiolanylium	1:1 ACN-H_2O	342	83
$MESH^+$	HFIP	260, 355	98
$HMBH^+$	HFIP	275, 390	98
$TMBH^+$	HFIP	250, 345	98
4,4′-bis(dimethylamino)triphenylmethyl	chlorohydrocarbons	630	121
all-trans-retinyl	2-propanol	585	34
carbanions			
$PhCH_2^-$	THF	362	106
$PhCH_2^-Na^+$	THF	355	106
$PhCH_2^-NBu^+$	THF	342	106
$PhCH_2^-Li^+$	THF	330	106
4-nitrophenylmethyl	1:2 ACN-H_2O	355	38
2,4-dinitrophenylmethyl	ACN	400, 640	150
	H_2O	350, 500	150

[a] DCE, 1,2-dichloroethane; ACN, acetonitrile; THF, 2,2,2-trifluoroethanol; HFIP, 1,1,1,3,3,3-hexafluoro-2-propanol; THF, tetrahydrofuran.

this is in spite of the fact that the Strickler–Berg radiative rate constant[155] calculated for trityl cation from its lowest-lying, intense absorption band system is higher, by an order of magnitude, than those of xanthenium cations. Ivanov et al.[160] attributed the mild nature of trityl cation fluorescence in weakly acid solutions to quenching via electron transfer from solvents (water or acetic acid). Enhanced electrophilic interaction with the singlet may also be a plausible reason for the fluorescence quenching.[155] Bis(4-methoxyphenyl)methyl cation, like trityl cation, is also weakly emitting in TFE acidified with trifluoroacetic acid ($\phi_F < 0.01$).[156]

The oxygen quenching of xanthenyl and thioxanthenyl carbocationic fluorescence is inefficient (k_{q,O_2} ~10^9 M^{-1} s^{-1})[155] when compared with the usually observed, diffusion-controlled quenching of singlet excited states by oxygen ($k_{q,O_2} > 10^{10}$ M^{-1} s^{-1}).[161–163] A possible explanation[155] for this behavior is that the charge-transfer interaction with the electron-poor carbocation (acting as a donor in this case) is not favorable. According to a recent paper by Berger and Weir,[164] the fluorescence of 9-phenylxanthenium cation on silica gel surface has a lifetime of 37 ns and is quenched by oxygen with a Smoluchowski-type rate constant of 1.5×10^4 $Torr^{-1}$ s^{-1}.

In contrast to the oxygen quenching, the quenching of carbocationic fluorescence by a stable nitroxy radical occurs[155] with rates, 3–6 × 10^9 M^{-1} s^{-1}, comparable to those observed in the case of singlet excited states of aromatics and polyenes.[165–169] From the kinetic data, if a charge-transfer mechanism[165] is operative in nitroxy radical quenching, the role of the carbocation as a facile acceptor is not particularly manifested.

The UV–visible absorption spectra of ion-paired carbanions make it possible to assign the ion-pairing type, namely, contact, solvent-separated, and free. The effect of ion pairing on excited states, as manifested in fluorescence efficiencies, has long been of interest.[157,170–174] For example, the cyclooctatetraenyl

Table V. Photophysical Data of Carbocations in Solutions at Room Temperature

cation	solvent[a]	λ_{max}^{abs}, nm	ϵ_{max}, (10^3 M^{-1} cm^{-1})	λ_{max}^{F}, nm	ϕ_F	τ_F	ref
9-xanthenyl	1:1 TFA-ACN	254	35.1	533	0.16	17.5	155
		372	32.7				
		434	1.75				
	TFE[b]	372		500	0.12	31	156
	aq H_2SO_4[c]					19.4	87
9-phenylxanthenyl	1:1 TFA-ACN	260	33.1	535	0.48	28.5	155
		375	28.7				
		450	4.75				
	TFE[b]	372		500		36	156
		450					
	aq H_2SO_4[c]					26.6	87
9-methylxanthenyl	TFE[b]	372		495		41	156
	aq H_2SO_4[c]					35.0	87
9-isopropylxanthenyl	aq H_2SO_4[c]					35.4	87
9-cyclopropylxanthenyl	aq H_2SO_4[c]					32.6	87
9-*tert*-butylxanthenyl						10.9	87
9-thioxanthenyl	1:1 TFA-ACN	277	30.2	580	0.24	22.8	155
		380	9.05				
		477	1.02				
9-phenylthioxanthenyl	1:1 TFA-ACN	280	60.7	590	0.025	1.0	155
		384	16.1				
		495	5.20				
trityl	1:1 TFA-ACN	248	5.01	~530	<0.001	<1.0	155
		292	1.52				
		405	37.6				
		430	36.7				
	TFE[b]	400		475		<1	156
		425					
dibenzosuberenyl	TFE[b]	370		550	0.087	40	156
		395					
		495					
		550					
11-phenyldibenzosuberenyl	TFE[b]	382		580		<1	156
		410					
		520					
		556					
$(4\text{-MeO-Ph})_2C(CH_3)^+$	TFE[b]	475		535		6	156
$(4\text{-MeO-Ph})_2CH^+$	TFE[b]	500		600		3	156

[a] TFE, 2,2,2-trifluoroethanol; TFA, trifluoroacetic acid; ACN, acetonitrile. [b] Acidified with trifluoroacetic acid. [c] 76.9% H_2SO_4.

Table VI. Photophysical Data of 1,3-Diphenylpropenyl and 1,5-Diphenylpentadienyl Anions[157]

anion	M^+	solvent[a]	type of ion pairing[b]	λ_{max}^{abs}, nm	λ_{max}^{F}, nm	τ, ps
diphenylpropenyl	Li^+	THF	SS	528 (*c,t*)		
				560 (*t,t*)	582	185
	Li^+	THF-DME	SS	515 (*c,t*)		
				565 (*c,t*)	583	188
	Li^+	THF-Hex	C	510 (*c,t*)		
				520 (*t,t*)	560	178
	K^+	THF	C	515 (*c,t*)		
				530 (*t,t*)	525	85
diphenylpentadienyl	Li^+	THF	SS	596	617	107
	Li^+	THF-DMF	SS	593	626	98
	Li^+	THF-Hex	C	560	617	108
	K^+	THF	C, SS	570	595	73
	K^+	THF-DME	SS	590	612	84

[a] THF, tetrahydrofuran; Hex, hexane; DME, diglyme. [b] C, contact; SS, solvent separated.

anion (COT^-) associated with cations ($M^+COT^-M^+$) fluoresces strongly with $M^+ = Cs^+, Rb^+$, or K^+, but no emission is observed with $M^+ = Li^+$ or Na^+ or with ion pairs of the type M^+COT^-.[170] Similarly, the fluorescence yields of 1,3-diphenylpropenyl anions depend on temperature (ion pairing)[171] and on geometry.[172] These behaviors have been explained[174] in terms of decreased rigidity or nonplanarity in some ion-pair forms, effect of ion pairing on relative locations of excited states of different multiplicity, and energy ordering of charge-transfer states. Recently, Fox and Voynick[157] studied the fluorescence yields and lifetimes of two acyclic anions, namely, 1,3-diphenylpropenyl and 1,5-diphenylpentadienyl (Table VI). The trends in absorption–emission spectral maxima of these carbanions run parallel to those observed with cyclic, aromatic carbanions.[173,174] For example, the contact ion pairing shifts the absorption maxima to shorter wavelengths, the shifts being higher for pairing with cations of smaller radius. The separations of absorption and emission maxima in the contact ion pairs are somewhat larger than those in analogous solvent-separated pairs. Finally, the ion pairing has a smaller effect on fluorescence lifetimes than the identity of the associated cation (Li^+ vs K^+, Table VI). Electron transfer from carbanions to metal ions in the excited states of ion pairs has been proposed as a possible cause for the short lifetimes (picoseconds).

The photophysical properties of 9-arylfluorenyl anions have been reported[175] recently. For a series of anions containing para-substituted phenyl groups as 9-substituents, picosecond transient absorption and fluorescence single-photon counting measurements gave lifetimes in the range 26–45 ns (in DMSO). The nonradiative component, $1.7\text{–}3.1 \times 10^7$ s^{-1}, of the excited-state decay has been shown to follow the energy gap law in its relation to the energy difference between the first excited singlet state and the ground state.

Table VII. Rate Constants (*k*) for Reactions of Nucleophiles with Trityl Cation in 1:2 Acetonitrile–H_2O at 20 °C[61]

	nucleophile	k, M^{-1} s^{-1}
sol	H_2O	1.50×10^5 [d]
a	OH^-	5.2×10^6
b	$CF_3CH_2O^-$	6.5×10^6
c	N_3^-	4.1×10^9
d	SO_3^{2-}	2.4×10^8
e	CN^-	5.5×10^6
f	$CH_3CO_2^-$	4×10^5
g	F^-	8.6×10^5
h	Cl^-	2.2×10^6
i	Br^- [a]	5×10^6
j	$^-SCH_3CO_2^-$	2.2×10^8
k	$NH_2CH_2CH_2S^-$	3.0×10^8
l	$CH_3CH_2CH_2NH_2$	1.3×10^7
m	$CH_3OCH_2CH_2NH_2$	9.6×10^6
n	$CF_3CH_2NH_2$ [b]	2.7×10^6
o	NH_2NH_2 [c]	2.1×10^7
p	NH_2OH	1.3×10^7
q	$NH_2CH_2CO_2^-$	1.9×10^7
r	morpholine	9.0×10^6
s	piperidine	1.04×10^7
t	imidazole	2.8×10^6
u	Dabco	7.7×10^5

[a] 0.1–0.3 M KBr. [b] 0.05 M NaCl. [c] In 0.02 M Na_2SO_4. [d] In s^{-1}.

IV. Ground-State Electrophilic Reactivity of Carbocations

The bulk of the fast kinetics data regarding electrophilic reactivity of carbocations in the ground state was obtained earlier by Dorfman's group[30–32,115–120] using PR and more recently by McClelland, Steenken, and co-workers[51–61] using LFP. The comprehensive work by the latter group in this area has been focused on structure–reactivity correlations, steric effects, and reactivity–selectivity aspects. Kinetic spectrophotometry has been the primary method employed for monitoring the transients.

A. Arylmethyl Cations

The rate constants (Table VII) for reactions of various ionic and neutral nucleophiles with triphenylmethyl cation have been measured[61] in aqueous acetonitrile and discussed from the viewpoint of reactivity–selectivity. On the basis of the decay rate constant in the solvent (1.5×10^5 s^{-1}) and the bimolecular rate constant (4.1×10^9 M^{-1} s^{-1}) for reaction with azide ion, the azide:water rate ratio is calculated to be 1.0×10^6. The discrepancy of this value from some of those (4×10^2 to 3×10^5) measured[15,21,22] by the competition method in acetone:water mixtures has been attributed to poor mixing during Ph_3CX solvolysis in the experiments for indirect measurements (a local depletion of azide ion led to artificially low experimental numbers for the rate constants). The difference in solvent mixtures used is another reason for the discrepancy.

Interestingly, Br^- undergoes equilibrium–addition to the triphenylmethyl cation (eq 14). An analysis of the

$$Ph_3C^+ + Br^- \rightleftarrows Ph_3CBr \qquad (14)$$

decay rate in the initial stage of the equilibration gave 5.1×10^6 M^{-1} s^{-1} for k_{comb} and 7.6×10^5 s^{-1} for k_{ion}. From these data, the K_{eq} is calculated to 6.6 M^{-1}, a value in good agreement with that (5.5 M^{-1}) obtained by analysis of absorbances (due to Ph_3C^+) before and after equilibration.

The correlation of the rate constant for electrophilic reactivity of Ph_3C^+ with the N_+ nucleophilicity parameter is shown in Figure 7. The line drawn (excluding points corresponding to azide, Dabco, and solvent) has a slope of 0.33. If the cation behaved like its more stable, properly substituted triarylmethyl analogs [e.g., tris(methoxyphenyl)methyl cation],[28] this plot would have a slope of unity and would rise, with a sharp break, to the encounter-controlled limit (shown by the dashed line drawn arbitrarily through the point corresponding to CN^-). One explanation for the deviation from the simple predicted behavior in the case of Ph_3C^+ is that the rate constants for better nucleophiles do level, but at a value considerably below the 10^{10} limit. Alternatively, the less than unity slope reflects a selectivity in the reactivity exhibited by the relatively reactive cation (Ph_3C^+).

An LFP-based kinetic method used by Mathivanan et al.[56] to measure the pK_{R^+} value of trityl cation (eq 15) deserves mention. The rate constant (k_f) for the

$$Ph_3C^+ + H_2O \underset{k_r}{\overset{k_f}{\rightleftarrows}} Ph_3COH + H^+$$

$$K_{R^+} = [ROH][H^+]/[R^+] = k_f/k_r \qquad (15)$$

forward reaction was measured directly from the decay of photogenerated Ph_3C^+ in water while that (k_r) for the backward reaction was obtained by following oxygen exchange in a labeled alcohol in a weakly acidic (0.005 M HCl) solution. At 25 °C in water, $k_f = (1.68 \pm 0.06) \times 10^5$ s^{-1} and $k_r = (5.79 \pm 0.29) \times 10^{-2}$ M^{-1} s^{-1}, giving a value -6.46 ± 0.03 for pK_{R^+}. This value falls in the range of those measured by equilibrium methods in strong acids (−5.89 to −6.89).

The decay rate constant (k_s) for substituted triphenylmethyl cations in 1:2 acetonitrile–H_2O at 20 °C range from 10^1 [for 4,4,′,4″-$(MeO)_3$-substituted ion] to 9×10^6 s^{-1} [for 4,4′-$(CF_3)_2$-][58] (Table VIII). A plot of log k_s vs σ^+ (Figure 8A) shows a significant deviation from linearity for the points for the π-donors; the direction of this deviation suggests that σ^+ underestimates the stabilizing effect of these substituents for a fully formed cation. A plot vs σ^{C^+}, a parameter obtained from the analysis of NMR spectra of carbocation solutions, is reasonably linear (Figure 8B). A rate–equilibrium linear plot (log k_s vs pK_R, Figure 9) based on combined data on diarylmethyl and triarylmethyl cations has a slope of 0.64. This plot, after extrapolation, leads to value of 3.16×10^{10} s^{-1} for k_s or *tert*-butyl cation.

Assumed diffusion control for the nucleophilic reaction of reactive azide ion has served as a basis for its use as a "clock" for converting relative rates of electrophilic reactions of carbocations into absolute values. McClelland et al.[54] carried out a comprehensive study of reactions of 18 triarylmethyl and 10 diarylmethyl cations with azide ion in acetonitrile–water mixtures of varying composition. For the more stable ions, k_{az} increases with decreased electron-donating power of substituents and with increasing acetonitrile content. For less stable cations, k_{az} is independent of the substituent. The limiting rate constants, in the vicinity

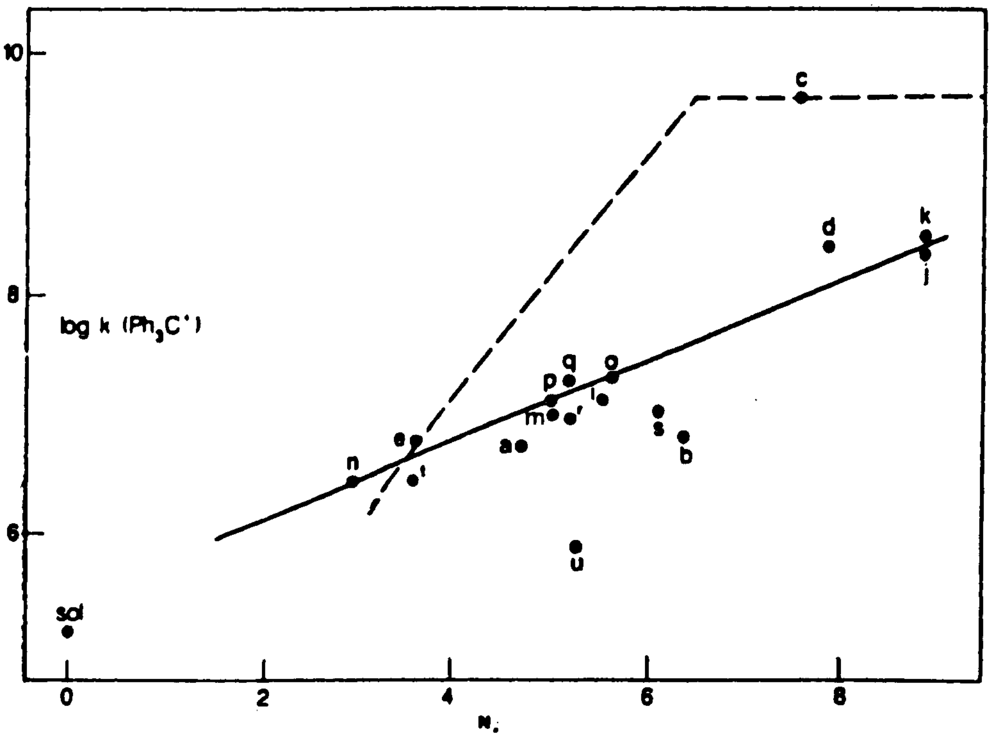


Figure 7. Correlation with N_+ for reaction of Ph_3C^+ with nucleophiles. Nucleophiles are identified in Table VII. N_+ values were taken from Ritchie (*J. Am. Chem. Soc.* **1975**, *97*, 1170). For RS-, a value[29] of 8.8 for N_+ was used. The solid line (slope 0.33) drawn by linear regression fit excluded points c, u, and sol. The slanted part of the dashed line was drawn through e with a slope of unity. Reproduced with permission from ref 61. Copyright 1986 American Chemical Society.

Table VIII. First-Order Rate Constants for Decay of Diphenylmethyl (D) and Triphenylmethyl (T) Cations in 1:2 Acetonitrile–H_2O at 20 °C[58]

cation	$-pK_{R^+}$	k_s, s^{-1}
4,4′,4″-$(MeO)_3T^+$	−0.82	1.0×10^1
4,4′-$(MeO)_2T^+$	1.24	8.6×10^1
4-Me, 4′-$MeOT^+$		5.7×10^2
3-Me,4′-$MeOT^+$		1.1×10^3
4-$MeOT^+$	3.40	1.4×10^3
3,4′-$(MeO)_2T^+$		1.8×10^3
4,4′,4″-Me_3T^+	3.56	3.6×10^3
4,4′-Me_2T^+	4.71	1.1×10^4
4-MeT^+	5.41	3.7×10^4
T^+	6.63	1.5×10^5
3-$MeOT^+$		1.7×10^5
4-ClT^+		1.8×10^5
3-ClT^+		5.1×10^5
3-CF_3T^+		6.8×10^5
4-CF_3T^+		1.1×10^6
3,3′-Cl_2T^+		1.6×10^6
3,3′,3″-Cl_3T^+	11.03	4.6×10^6
4,4′-$(CF_3)_3T^+$		8.8×10^6
4,4′-$(Me_2N)_2D^+$	−5.61	2.6×10^{-2}
4,4′-$(MeO)_2D^+$	5.71	1.3×10^5
4-Me,4′-$MeOD^+$	8.32	9.1×10^5
4-F,4′-$MeOD^+$		1.7×10^6
4-$MeOD^+$	7.90	2.1×10^6
4-Cl,4′-$MeOD^+$		2.3×10^6
3,4′-$(MeO)_2D^+$		2.4×10^6
3-Cl,4′-$MeOD^+$		3.6×10^6
3-CF_3,4′-$MeOD^+$		4.6×10^6
4-CF_3,4′-$MeOD^+$		5.8×10^6
4,4′-Me_2D^+	10.4	3.2×10^7
4-MeD^+	11.6	$\sim 1.2 \times 10^8$
D^+	13.3	$\sim 9 \times 10^8$

of 10^{10} M^{-1} s^{-1}, depend on solvent and type of cation; diarylmethyl cations react at the limit 1.6 ± 0.2 times faster than triarylmethyl (Figure 10). The fact that the observed diffusion-limited values are smaller than those calculated from the Debye–Smoluchowski equation has been explained in terms of a steric effect, that is, nonproductive encounters ensuing from the anion approaching the cation in the plane of one of the rings and thus not being able to attain a proper reactive configuration. The difference between diarylmethyl and triarylmethyl cation arises from the greater difficulty of achieving this configuration in the case of more sterically congested triarylmethyl systems.

The reactivities of primary amines of varying basicity toward diarylmethyl and triarylmethyl cations have also been studied in detail by McClelland et al.[53] In pure acetonitrile, for diarylmethyl cations, the reaction rates approach the diffusion limit (5×10^9 M^{-1} s^{-1}). For a given cation, they increase with increasing amine basicity, and for a given amine, they increase with decreased electron-donating character of substituents. In mixed water–acetonitrile solvents, the rate constants decrease systematically with increasing water content (on the order of 10–100 on going from pure acetonitrile to pure water). Plots of log $k(RNH_2)$ vs $pK_a(RNH_3^+)$ are curved and show a change in the sign of their slope on progressing from weakly basic amines (positive β_{nuc}) to strongly basic ones (negative β_{nuc}) (Figure 11). Analyses based on a mechanism in which an unreactive hydrated amine undergoes equilibrium desolvation to a "free" reactive form led to equilibrium constants (e.g., 1.19 ± 0.20 M for $CH_3CH_2NH_2$ in 91% acetonitrile) for the desolvation, with the expected $\beta = -0.2$ dependency on amine basicity. In 33% acetonitrile, for a series of triarylmethyl cations [ranging from 4,4′-$(Me_2N)_2$-substituted to 4,4′-$(CF_3)_2$-], the β_{nuc} values (though all positive) are found to decrease with increasing cation reactivity. It is concluded that amine nucleophiles do not obey the N_+ constant selectivity relation for both series of relatively stable and unstable cations.

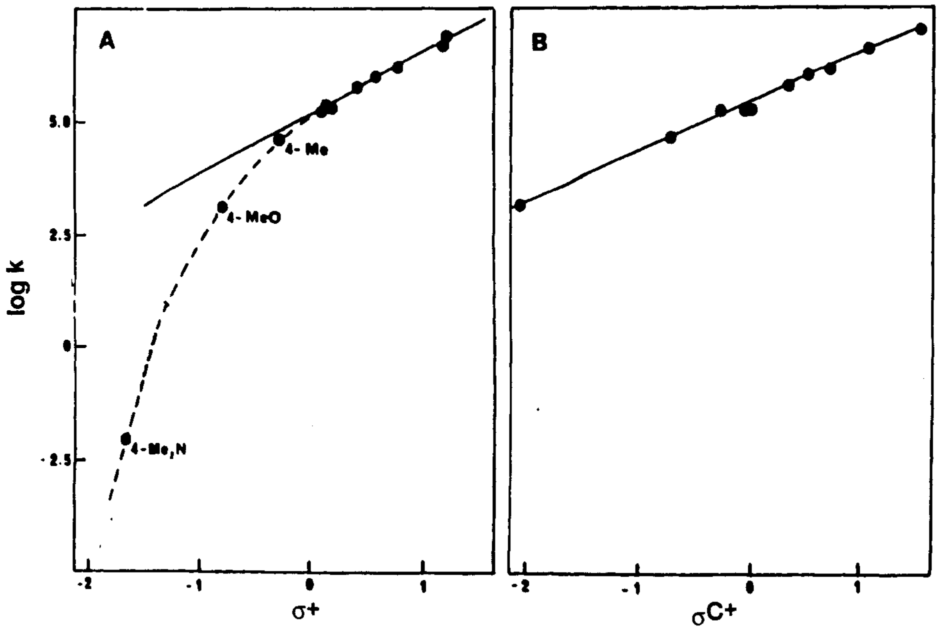


Figure 8. Correlations of rate constants (k_s) with σ^+ and σ^{C+}. Reproduced in part with permission from ref 61. Copyright 1986 American Chemical Society.

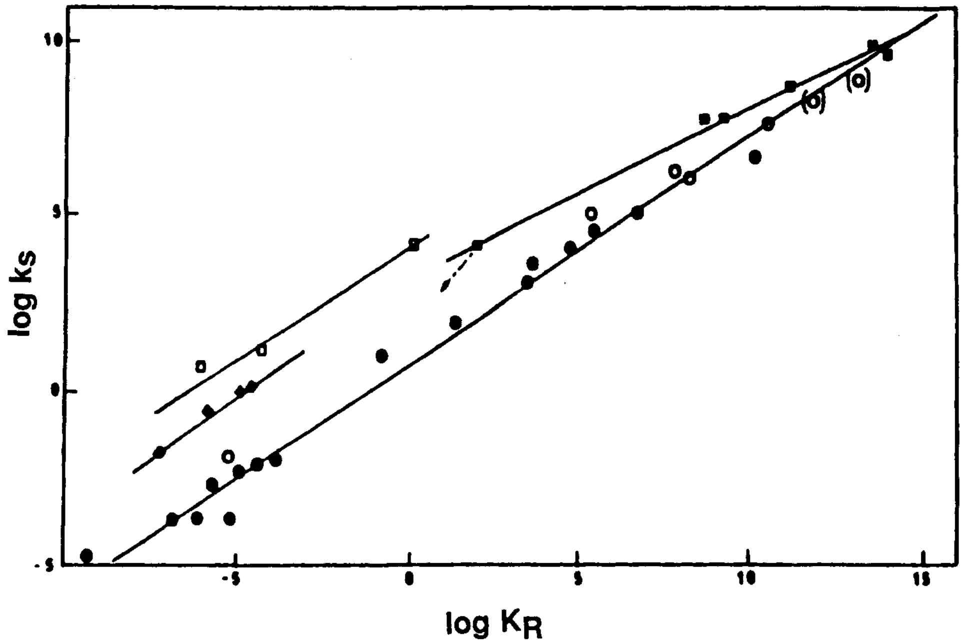


Figure 9. Rate–equilibrium correlations for addition of water to carbocations. Cation types and linear regression slopes of the solid lines are as follows: triarylmethyl (solid circles) and diarylmethyl (open circles), 0.64; phenyltropylium (solid diamonds), 0.58; xanthenium ions unsubstituted at 9-position (open squares); 1-arylmethyl (solid squares), 0.48. The open circles within parentheses represent the parent diphenylmethyl ion and its 4-methyl derivative, for which k_s values are estimated. Reproduced with permission from ref 58. Copyright 1989 American Chemical Society.

Recently, Bartl et al.[51] reported on and discussed the reactivity of several diarylcarbenium ions toward a host of n- and π-nucleophiles (anions, alcohols, water, alkenes, allylsilanes, alkyl and silyl enol ethers). In acetonitrile at 20 °C, the largest observed values for bimolecular reaction rates (k_2) are ~2×10^{10} for reaction with anions (Table IX) and 1–2×10^9 M^{-1} s^{-1} for reaction with hydroxylic nucleophiles (Table X). Alkyl-substituted ethylenes are 300–10^5 times more sluggish that their alkoxy-substituted counterparts. The reactivities of structurally similar alkyl and silyl enol ethers differ from each other by less than 1 order of magnitude. The nucleophilic reactivities of enol ethers correlate with their ionization potentials (Figure 12) and not with the stabilities of the carbenium ions produced in the rate-determining step. The results with various alkenes led to a nucleophilicity scale shown in Chart I.

From the positive trend in electrophilic reactivity on going from triphenylmethyl to diphenylmethyl cations, it is indicated that the benzyl cations would be the most reactive. Shown in Table XI are some data in TFE and HFIP recently reported by McClelland et al.[52] Evidently, for a given para substituent in the cation, the rate constants for reaction with a given nucleophile decrease in the order benzyl > phenethyl > cumyl. This trend is probably a reflection of

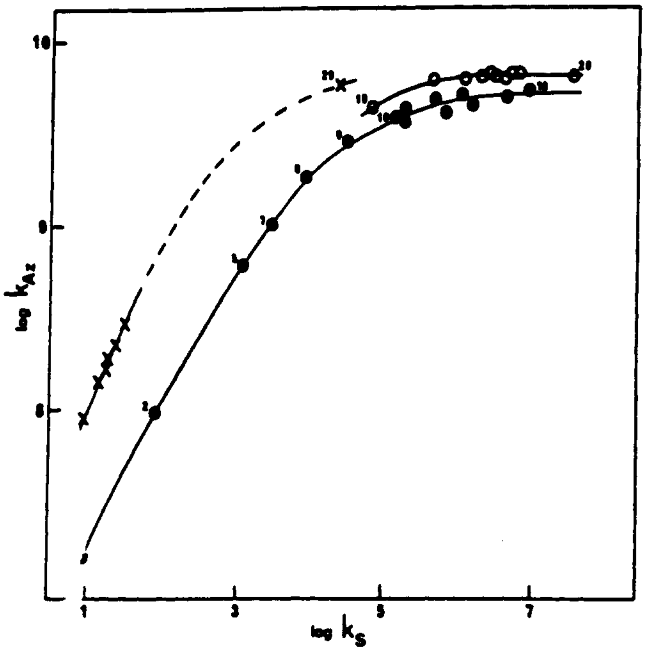


Figure 10. Variation of k_{az} (in M^{-1} s^{-1}) as a function of k_s (in s^{-1}) in 1:2 acetonitrile–water at 20 °C. (Solid circles) Triarylmethyl cations. (Open circles) Diarylmethyl cations. (Crosses) 9-Xanthenium and its 9-aryl derivatives. Reproduced with permission from ref 54. Copyright 1991 American Chemical Society.

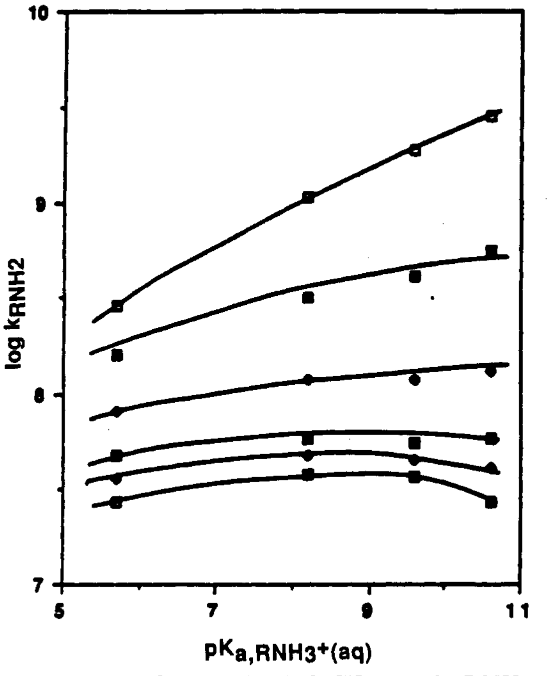


Figure 11. Dependence of log $k(RNH_2)$ on $pk_a(RNH_{3+})$ for the reactions of amines with diarylmethyl cation, 3,4′-$(MeO)_2D^+$, in aqueous acetonitrile solutions. Percent volumes of acetonitrile from the top of the figure are 100 (open squares), 91 (solid squares), 67 (solid diamonds), 33 (solid squares), 20 (solid diamonds), and 0 (open squares). Reproduced with permission from ref 53. Copyright 1992 American Chemical Society.

combined steric and electronic effects at the cation center.

Table IX. Second-Order Rate Constants (k_2) for Reactions of Benzhydryl Cations with Anionic Nucleophiles in Acetonitrile at 20 °C[81]

	10^{10} M^{-1} s^{-1}	
nucleophile	Ph_2CH^+	$(p\text{-MeO-Ph})_2CH^+$
F^-	2.0	1.4
Cl^-	2.0	1.5
Br^-	2.1	1.6
I^-	1.9	1.6
SCN^-	2.7	1.4
SH^-	2.4	
$H_2PO_4^-$	2.1	1.3
NO_2^-	2.2	
NO_3^-	2.1	0.25

Nearly all of the PR-based data generated by Dorfman's group[30–32,115–120] for electrophilic reactivity of $Ph_nCH_{(3-n)}$ cations (n = 1–3) are in chlorohydrocarbon solvents, namely, 1,2-dichloroethane (DCE), dichloromethane, and 1,1,2-trichloroethane. In DCE, the rate constants (k_2) for the reaction of these cations with halide ions are in the diffusion-controlled limiting range, 3.6–8.0 × 10^{10} M^{-1} s^{-1}.[115] Smaller k_2 values (7.0 × 10^6 to 2.0 × 10^9 M^{-1} s^{-1}) are observed[115] with tertiary alkylamines as nucleophiles. For a given trialkylamine[115] as well as ammonia,[31] k_2 values increase in the order $PhCH_2^+$ > Ph_2CH^+ > Ph_3C^+, the trityl cation being the most discriminating. Similarly, for a given cation, k_2 values increase in the order triethylamine > tri-*n*-propylamine > tri-*n*-butylamine, tri-*n*-butylamine being the most differentiating. Another interesting series of nucleophiles is triethylamine, triethylphosphine, and triethylarsine, for which the reported k_2 values for reaction with $PhCH_2^+$ are (in 10^9 M^{-1} s^{-1}) 2.0, 8.1, and 2.2, respectively. For this series, no correlation is observed with respect to the size of the central atom (N < P < As), k_2 for triethylphosphine being the largest.

With alcohols and water as nucleophiles in DCE, Dorfman and co-workers[30–32,119] noted that the plots of observed pseudo-first-order rate constants against [nucleophile] were supralinear (i.e., curved upward). They explained this behavior in terms of intermolecular dimer formation by water or alcohol molecules at increasing concentrations. The dimer in a given case is more reactive than the corresponding monomer. For example, with Ph_2CH^+ as the reacting cation, the rate constants for water monomer (H_2O) and dimer [$(H_2O)_2$] are estimated[32] to be 1.3 × 10^6 and 1 × 10^8 M^{-1} s^{-1}, respectively.

Kundu and Dorfman[118] examined the effect of solvents (chlorohydrocarbons and hydrocarbons) on the reactivity of Ph_2CH^+ toward halides and tertiary alkylamines. For both type of reactions, namely, cation–anion and cation–neutral molecule, in a given type of solvent (chlorohydrocarbon or hydrocarbon), they noted reasonable constancy in $k_2\epsilon\eta$, where k_2 is the measured rate constant, ϵ is the dielectric constant, and η is the viscosity.

The rate constants (<10^5 to 1.0 × 10^9 M^{-1} s^{-1}) for reactions of benzyl and benzhydryl cations with alkenes and conjugated dienes in DCE vary over 4 orders of magnitude.[119] With benzyl cation, the variation in the rate constants (in M^{-1} s^{-1}) in the series ethylene (<10^5) < propylene (1.9 × 10^6) < cyclohexene (9.4 × 10^6) < isobutylene (1.0 × 10^7) follows the increasing stability of the product carbenium ion (primary < secondary < tertiary). The product ion stability also seems critical in the order of reactivity of benzhydryl cation with conjugated dienes (rate constants in M^{-1} s^{-1}): 1,3-butadiene (<10^5) < 2-methyl-1,3-butadiene (7.1 × 10^6)

Table X. Second-Order Rate Constants (k_2) for Reactions of Benzhydryl Cations with Water and Alcohols in Acetonitrile at 20 °C[51]

	k_2, M^{-1} s^{-1}				
para substituents	H_2O	MeOH	EtOH	*i*-PrOH	*t*-BuOH
Cl, Cl	1.7×10^8	1.1×10^9	1.1×10^9	4.1×10^8	1.4×10^8
Cl, H			8.9×10^8		
H, H	1.2×10^8	1.2×10^9	8.5×10^8	3.1×10^8	6.9×10^7
F, H			5.0×10^8		
F, F			4.4×10^8		
Me, H	1.7×10^7		2.0×10^8		
Me, Me	4.3×10^6		5.0×10^7		

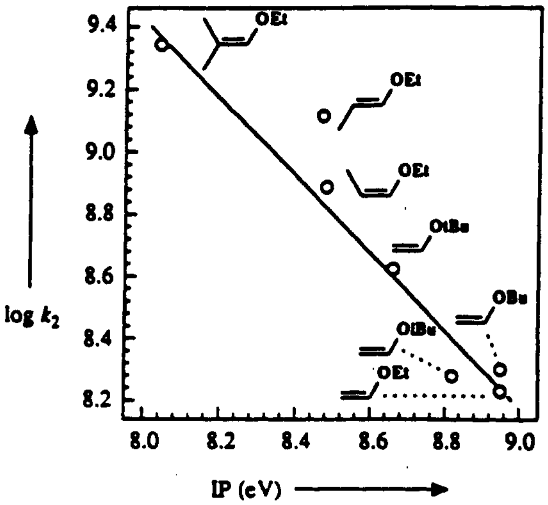


Figure 12. Correlation of the reactivities of various enol ethers toward $(p\text{-}ClC_6H_4)_2CH^+$ at 20 °C in acetonitrile with their ionization potentials. Reproduced with permission from ref 51. Copyright 1991 American Chemical Society.

< 2,3-dimethyl-1,3-butadiene (2.7×10^7) < 4-methyl-1,3-pentadiene (2.5×10^8) < 2,4-dimethyl-1,3-pentadiene (1.0×10^9).

B. Cyclopropylphenyl Carbenium Ions

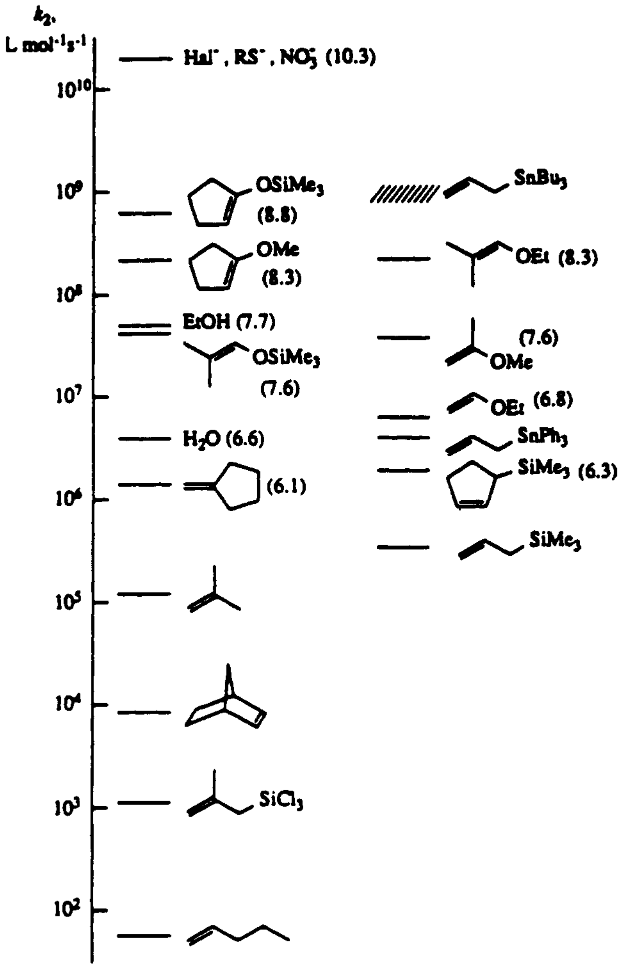
In view of a possible stabilizing effect of cyclopropyl substitution on carbenium ions, Dorfman et al.[32,117] studied the kinetics of reactions of α-cyclopropyl- and α,α-dicyclopropylphenylcarbenium ions with trialkylamines in DCE and dichloromethane. The data are shown in Figure 13. With respect to benzyl and benzhydryl cations, there is no pronounced effect from cyclopropyl substitution on the electrophilic reactivity. For example, for α-cyclopropylphenylcarbenium ion in DCE, the reactivity toward TEA is equal to that of benzyl and twice that of benzhydryl, that toward tri-*n*-propylamine is slightly higher than that of benzhydryl, and that toward tri-*n*-butylamine is somewhat less than that of benzhydryl. In dichloromethane, the effect of cyclopropyl substitution is very small, except at the trisubstituted stage where there is an order of magnitude increase on going from trityl to α,α-dicyclopropylphenyl.

C. Xanthenium Cations

The electrophilic reactivity of xanthenium cation and eight of its 9-aryl analogs (aryl = 4-substituted phenyl) toward a variety of nucleophiles (solvent, anionic, and neutral) has been examined[59] in 1:4 acetonitrile–water. The slopes (ρ) of Hammett plots (log k vs σ substituent constant) for 9-aryl xanthenium cations are relatively small (in the range 0.4–1.1). The relative insensitivity to substituent has been explained in terms of two factors. First, the positive charge in these cations is highly localized on the xanthenium portion and hence is less subject to interaction from the substituent on the 9-phenyl group. Second, steric interactions cause the 9-phenyl ring to be twisted with respect to the plane of the xanthenium moiety, thus diminishing the conjugative interaction of para substituents.

9-Arylxanthenium ions are relatively stable, as evident by their small decay rates (11–34 s^{-1}) in 1:4 acetonitrile–water. For these systems, the plots of log k_{nuc} against nucleophile N_+ parameter are linear, with slopes close to unity (Figure 14); that is, these systems

Chart I. Reactivities of Some Typical Nucleophiles toward $(p\text{-}CH_3C_6H_4)_2CH^+$ in Acetonitrile at 20 °C[a]



[a] Values of log k_2 are in parentheses. Reprinted with permission from ref 51. Copyright 1991 American Chemical Society.

Table XI. Rate Constants for Reactions of Derivatives of Benzyl Cations with Solvents (k_s, s^{-1}) and Nucleophiles (k_2, $M^{-1}\ s^{-1}$) in 2,2,2-Trifluoroethanol (TFE) and 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP)[58]

cation	k_s(TFE)	k_s(HFIP)	k_2(Br)[a]	k_2(MeOH)[a]
cumyl				
4-methoxy	1.6×10^4	$<1 \times 10^2$	1.1×10^8 (TFE)	9.1×10^5 (TFE)
4-methyl	1×10^7	6×10^2	1.3×10^9	3.4×10^5
4-H		9×10^3	6.7×10^9	4.1×10^6
phenethyl				
4-methoxy	3.9×10^5	$<1 \times 10^2$	4.5×10^9 (TFE)	5.6×10^6 (TFE)
4-methyl	$>5 \times 10^7$	5×10^4	7.2×10^9	1.1×10^7
4-H		6×10^5	8.2×10^9	4.3×10^7
benzyl				
4-methoxy	4.3×10^6	3.2×10^2	4.8×10^9	3.8×10^5
4-methyl	$>5 \times 10^7$	2×10^6	1.0×10^{10}	6.5×10^7

[a] In HFIP, unless a solvent is mentioned in parentheses.

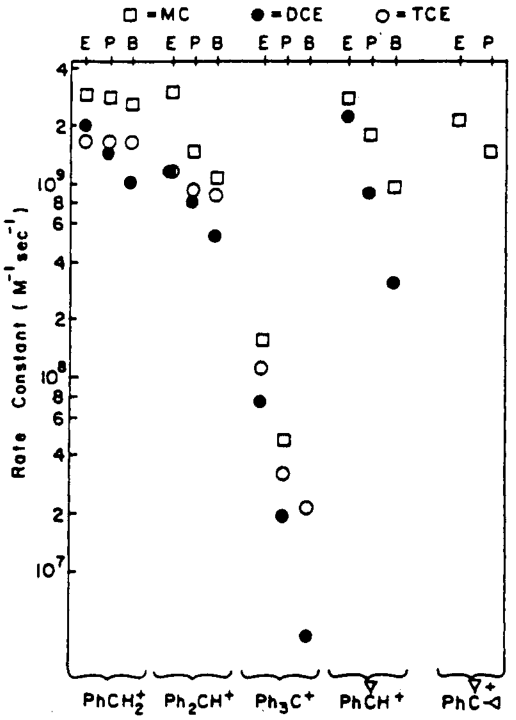


Figure 13. Rate constants ($M^{-1}\ s^{-1}$) for the reactions of five arylcarbenium ions (indicated on the abscissa at bottom). The data for each cation are presented in separate columns. The values for each nucleophile are identified by the column positions E (triethylamine), P (tri-*n*-propylamine), and B (tri-*n*-butylamine). The solvents are identified by open squares (dichloromethane), solid circles (1,2-dichloroethane), and open circles (trichloroethane). Reproduced with permission from ref 117. Copyright 1978 American Chemical Society.

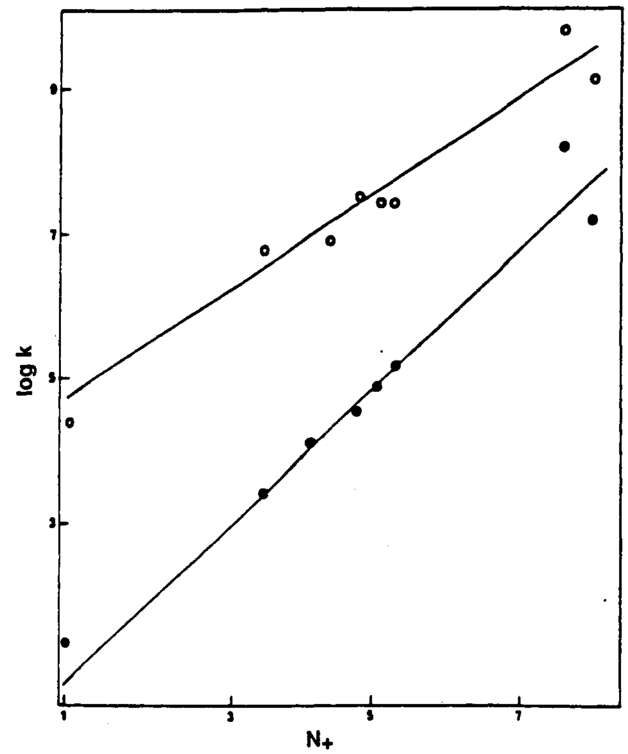


Figure 14. N_+ correlations for reactions of xanthenium ion (open circles) and 9-phenylxanthenium ion (solid circles) with nucleophiles. Linear regression fit lines (excluding the solvent point) have slopes of 0.65 and 0.97, respectively. Reproduced with permission from ref 59. Copyright 1989 American Chemical Society.

obey the Ritchie relationship.[23,25] This is, however, not the case with the more reactive cation, xanthenium, for which poor correlation is noted in log k_{nuc} vs N_+ and a slope <1 is obtained (Figure 14). A similar example of noncompliance with the Ritchie equation by relatively reactive cations is provided by Ph_3C^+ (mentioned earlier).

D. Fluorenyl and Dibenzosuberenyl Cations

Fluorenyl and dibenzosuberenyl cations constitute examples of internal cyclic arrays (ICA) with $4n$ and $4n+2$ electrons, respectively. Because of the possible aromaticity, the latter is expected to be more stable in the ground state. According to the results of Mecklenburg and Hilinsky,[64] the rate constants for decay of fluorenyl cation are $>5 \times 10^{10}\ s^{-1}$ in 9:1 water–methanol and $3 \times 10^{10}\ s^{-1}$ in 9:1 water–TFE. Also, McClelland et al.[57] determined a bimolecular rate constant of $1.5 \times 10^6\ M^{-1}\ s^{-1}$ with water as the nucleophile at low concentrations (up to 0.5 M) in HFIP. All of these results point to the reactive nature of the fluorenyl cation. No comparable data for electrophilic reactivity of dibenzosuberenyl cation are available, except that this cation does not undergo substantial decay in TFE over a 100-μs time scale and that the rate constant for its reaction with azide ion is $1.1 \times 10^9\ M^{-1}\ s^{-1}$ in TFE containing 4% water.[70] In contrast, the lifetime of fluorenyl cation in the less nucleophilic solvent HFIP is 25–30 μs.[57]

The bimolecular reactivity of the fluorenyl cation with arenes and olefins has been shown to be high.[100] The rate constants (in HFIP) with benzene and toluene as reactants are 3.3×10^5 and $1.1 \times 10^7\ M^{-1}\ s^{-1}$, respectively, and reach the limit of diffusion control

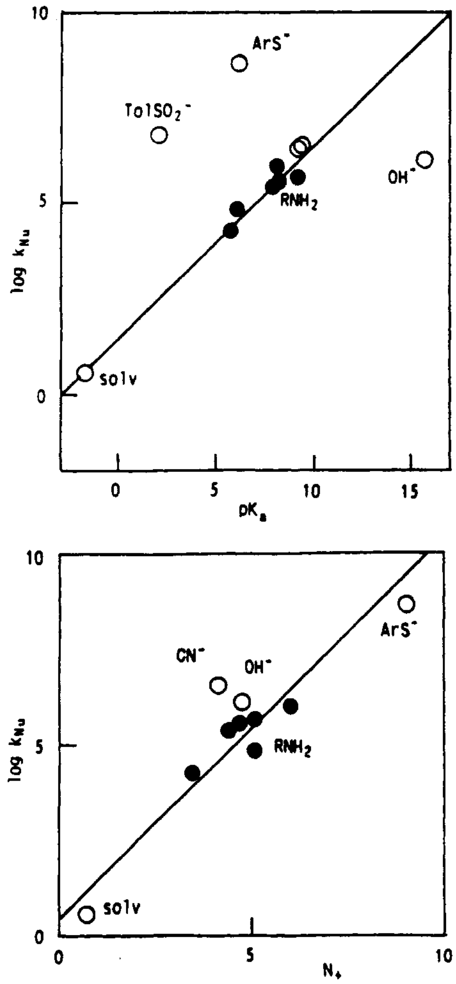


Figure 15. Correlations of rate constants for reactions of 2-phenyl-1,3-dithiolanylium ion with nucleophiles vs pK_a and N_+. Reproduced with permission from ref 83. Copyright 1991 Nippon Kagakkai.

(2–3 × 10^9 M^{-1} s^{-1}) with electron-rich donors (e.g., anisole and mesitylene). The reactivity with olefins, such as styrenes and 1-methylcyclohexane, is also diffusion-limited (k = ~3 × 10^9 M^{-1} s^{-1}).

E. Phenyl-1,3-dithiolanylium Ion

Judged from its long lifetimes in 1:1 H_2O–acetonitrile (0.26 s) and 1:1 H_2O–ethanol (1.8 s),[83] 2-phenyl-1,3-dithiolanylium cation is relatively stable. The rate constants for the reaction of this cation with various nucleophiles correlate well with pK_a of the conjugate acid of nucleophiles (Figure 15A) and with Ritchie's nucleophilicity parameter N_+ (Figure 15B). The slope in the latter case is close to unity, in agreement with the Ritchie equation.

F. Cyclohexadienyl Cations

The electrophilic reactivity of three cyclohexadienyl cations, namely those derived from photoprotonation of mesitylene (MES), hexamethylbenzene (HMB), and 1,3,5-trimethoxybenzene (TMB) in HFIP, has been studied by Steenken and McClelland.[98] The three cations have lifetimes of 10, 140, and >10 000 μs in HFIP. As shown in Table XII, the relative stability of the cations is also duly manifested into the order of reactivity with nucleophiles. Interestingly, with the series of alcohols (Table XII), very little steric effect is observed. Apparently, the basicity, being similar for the alcohols in question, is the controlling factor.

Table XII. Rate Constants (k_2) for Reactions of Cyclohexadienyl Cations with Nucleophiles in 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) at 20 ± 1 °C[98]

	k_2, M^{-1} s^{-1}		
nucleophile	$MESH^+$	$HMBH^+$	$TMBH^+$
H_2O	8.8 × 10^6	2.7 × 10^5	<10
MeOH	2.4 × 10^7	1.5 × 10^6	<1 × 10^2
EtOH	1.7 × 10^7	8.2 × 10^5	<1 × 10^2
i-PrOH	2.0 × 10^7	8.1 × 10^5	<1 × 10^2
t-BuOH	1.2 × 10^7	8.7 × 10^5	<1 × 10^2
tetrahydrofuran	2.0 × 10^7	2.1 × 10^6	34
1,4-dioxane	5.4 × 10^6	1.3 × 10^5	
$C_2H_5OCH{=}CH_2$	~2.2 × 10^6	~1.6 × 10^5	
$CH_2(CH_2)_2CH{=}CHO$	5.6 × 10^6	3.0 × 10^5	
$CH_2(CH_2)_3CH{=}CH(Me)$	~9 × 10^6	~9 × 10^5	
Cl^-	2.4 × 10^9	4.3 × 10^8	≤5 × 10^2
Br^-	3.7 × 10^9	6.3 × 10^8	≤1 × 10^3
I^-	3.8 × 10^9	1.1 × 10^9	
NO_3^-	1.4 × 10^9	1.7 × 10^8	

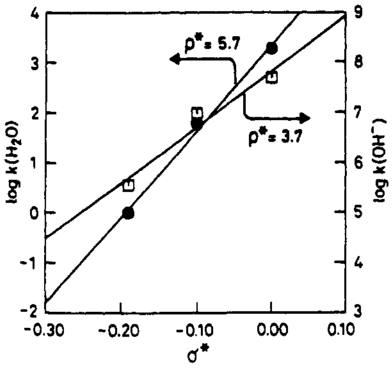


Figure 16. Dependence of log $k(H_2O)$ (circles) and log $k(OH^-)$ (squares) on the σ^* values of the substituents Me, Et, and *i*-Prop. The slopes correspond to Taft ρ^* values of 5.7 and 3.7, respectively. Reproduced with permission from ref 105. Copyright 1986 American Chemical Society.

The cyclohexadienyl cation derived from the reaction of 9-fluorenyl cation with mesitylene has also been shown[100] to be strongly electrophilic. In HFIP, with alcohols (ROH, R = Me, Et, *i*-Pr, and *t*-Bu) as nucleophiles, the rate constants (in 10^6 M^{-1} s^{-1}) are 3.3, 3.0, 1.9, and 1.3, respectively. A small but systematic steric effect is observed in this case.

G. Di- and Trialkoxymethyl Carbocations

The reactivity of trialkoxymethyl cations, $(RO)_3C^+$, with water and OH^- (studied[105] by time-resolved conductance techniques) exhibits a strong dependence on the alkoxy group. On going from methoxy to ethoxy and isopropoxy, a pronounced decrease occurs in the rate constants. The Taft ρ^* values, obtained from the slopes of log k against Taft parameter σ^* (Figure 16), are 5.7 and 3.7 for H_2O and OH^-, respectively. In terms of both lifetime in water and reactivity with OH^-, the cyclic trialkoxymethyl cation bearing a six-membered 1,3-dioxane system is more stable than its five-membered counterpart (derived from 1,3-dioxolane).

Cyclic and acyclic α-dialkoxymethyl carbocations, $RC^+(OR')_2$, have also been investigated[38,106] by time-resolved conductance (R = H, alkyl, Ph) and spectrophotometric (R = Ph) methods. Structure–activity relations[106] have been examined on the basis of the rate

Table XIII. Rate Constants (k_2) for Reactions of Vinyl Cations with Nucleophiles in Acetonitrile at Room Temperature[67,68]

	k_2, M^{-1} s^{-1}		
nucleophile	$An_2C{=}C^+An$	$Ph_2C{=}C^+An$	$Me_2C{=}C^+An$
N-vinyl-2-pyrrolidone	5.2×10^5	6.4×10^5	
styrene	1.9×10^4	1.8×10^4	
n-butyl vinyl ether	7.1×10^4		
α-methylstyrene	2.6×10^4		
methyl methacrylate	1.2×10^4		
vinyl acetate	2.2×10^4		
acrylonitrile	*a*		
N-methyl-2-pyrrolidone	3.4×10^6	4.0×10^6	1.1×10^8
ethylbenzene	*a*	*a*	
tetrahydrofuran	5.7×10^5	5.7×10^5	1.1×10^7
diethyl ether	5.4×10^4	6.5×10^4	2.9×10^6
methanol	3.8×10^5		1.3×10^7
ethanol	3.2×10^5		9.5×10^6
2-propanol	1.2×10^5		3.6×10^6
2-methyl-1-propanol	1.8×10^4		1.0×10^6

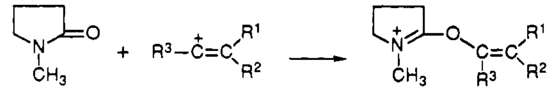
[a] Unreactive ($k_2 < 5 \times 10^3$ M^{-1} s^{-1}).

constants of 30 open-chain and cyclic aliphatic cations. In the aliphatic systems, the substitution in the OR′ group follows a reactivity order OMe > OEt > O-*i*-Pr and a good correlation vs σ^* is noted ($\rho^* = +4.4$). However, the substitution of R does not follow the expected steric/electronic order; for example, *t*-Bu-$C(OEt)_2^+$ reacts with water 2.3 times faster than $MeC(OEt)_2^+$. To explain this, counteracting solvation effects for cation hydration giving rise to negative $\Delta S^\dagger$ in the order Me ~ Et > *i*-Pr ≫ *t*-Bu have been invoked.

The decay rate constants,[38] $k(H_2O)$, of carbocationic systems, $RC(OR')_2^+$, in water vary over a wide range, 8.6×10^2 to 4.6×10^7 s^{-1}. On going from systems with R = H to those with R = CH_3, an increase in $k(H_2O)$ by about 3 orders of magnitude occurs. However, replacing CH_3 by bulkier alkyl groups (e.g., *tert*-butyl) causes no further stabilization of the cation in the case of cyclic systems and leads to destabilization in the case of acyclic systems. Furthermore, in the case of acyclic systems with R = Ph, no increase in kinetic stability is observed with respect to R = CH_3; this is explained by loss of coplanarity at C^+ due to steric interaction between ortho hydrogen atoms of the phenyl ring and the OR′ substituents, and hence inefficient charge delocalization into the phenyl ring. The corresponding cyclic systems are sterically uncongested, and therefore in their cases Ph causes the usual increase in stability relative to R = CH_3.

H. Vinyl Cations

The electrophilic reactivity data obtained by Kobayashi et al.[68] for three vinyl cations in acetonitrile are presented in Table XIII. Among the nucleophiles investigated, *N*-methyl-2-pyrrolidone shows the highest reactivity. This is attributed to the attack by a vinyl cation at the carbonyl oxygen of the pyrrolidone and stabilization of the cationic product through delocalization (eq 16). The reduction in the reaction rate upon



(16)

replacement of the methyl group in the pyrrolidone by the vinyl group is due to the electron-withdrawing nature of the vinyl group, lowering the nucleophilicity of the oxygen. The progressive decrease in the rate constant on going from methanol to 2-methyl-1-propanol has been explained in terms of increasing steric hindrance.

For the intermediate identified by VanGinkel et al.[69] as vinyl cation, $Ph_2C{=}C^+(An)$, the rate constants (in M^{-1} s^{-1}) for quenching by water, methanol, tetraethylammonium bromide, and tetraethylammonium acetate in acetonitrile are 6.0×10^4, 5.0×10^5, 2×10^9, and 3×10^9, respectively. The increase in *k* on going from water to methanol reflects the corresponding increase in N_+ (0.01 for methanol and −0.26 for water). The selectivity of the cation with respect to bromide vs acetate ion is found to be low (about unity).

Table XIV. Second-Order Rate Constants (k_2) for Reactions of *all-trans*-Retinyl Carbocation in Dry and Aqueous Acetonitrile[77]

		k_2, M^{-1} s^{-1}			
nucleophile	n_{MeI}[a]	dry	1 M H_2O	11 M H_2O	36 M H_2O
H_2O	(−1.0)[b]				1.0×10^2
$CF_3SO_3^-$				$<1 \times 10^2$	
CH_3OH	0.0			(1.1×10^3)[c]	(1.1×10^3)[c]
p-$MePhSO_3^-$		1.2×10^8		2.2×10^4	
NO_3^-	1.5	1.8×10^7	1.2×10^8	4.1×10^4	1.4×10^4
F^-	2.7	1.1×10^9	1.4×10^8	6.1×10^4	
OAc^-	4.3	5.1×10^9	1.6×10^8	3.8×10^5	
Cl^-	4.37	2.6×10^9	3.3×10^8	1.9×10^6	
Br^-	5.79	1.4×10^9	1.1×10^8	1.9×10^6	
N_3^-	5.78			1.1×10^7	
SCN^-	6.7			1.9×10^7	
$(CH_3CH_2)_3N$	6.66			3.0×10^7	
Ph_3P	7.0			7.4×10^7	
I^-	7.42	4.0×10^9	7.7×10^8	9.2×10^7	
PhS^-	9.92				

[a] Pearson *n* values (Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* 1968, *90* 319). [b] Estimated value.[82] [c] From high CH_3OH concentration region (16–24.7 M).

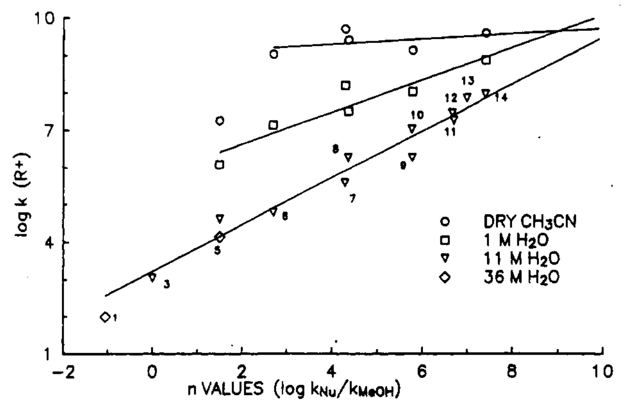


Figure 17. Plots of rate constants of reactions of *all-trans*-retinyl cation with nucleophiles in indicated solvents vs Pearson *n* values. The numbers identify the nucleophiles by their entry in Table XIV. Reproduced with permission from ref 77. Copyright 1992 American Chemical Society.

I. *all-trans*-Retinyl Cation

Recent work by Pienta and Kessler[77] highlights the importance of hydrogen-bonding and salt effects on the reaction of *all-trans*-retinyl cation with nucleophiles. Some kinetic data are listed in Table XIV and plotted in Figure 17 as a function of the water content of acetonitrile solutions. The slope of the lines, a measure of nucleophile selectivity toward the cation, increases with added water. This is interpreted as an

Table XV. Second-Order Rate Constants (k_2) for Protonation of Free and Ion-Paired Benzyl Carbanion in Tetrahydrofuran at Room Temperature[134,135]

	k_2, $M^{-1}\ s^{-1}$			
electrophile	$PhCH_2^-$	$PhCH_2^-Li^+$	$PhCH_2^-Na^+$	$PhCH_2^-NBu_4^+$
H_2O	5.3×10^7		5.5×10^9	
MeOH	2.3×10^8	3.4×10^8	5.8×10^9	6.0×10^8
EtOH	1.4×10^8		3.7×10^9	
EtOD	1.2×10^8		2.1×10^9	
t-BuOH	1.6×10^7	9.7×10^7	1.3×10^9	4.6×10^8

Table XVI. Bimolecular Rate Constants (k_2) for the Quenching of 9-Phenylxanthenium Cation Singlet in Acetonitrile and Stern–Volmer Constants (K_{SV}) for the Quenching of Steady-State Fluorescence of 9-Phenylxanthenium Cation Adiabatically Photogenerated from 9-Phenylxanthen-9-ol in 3:1 H_2O–Acetonitrile at Room Temperature[65]

quencher	k_2, $M^{-1}\ s^{-1}$	K_{SV}, M^{-1}
triethylamine	3.0×10^{10}	24
Cl^{-a}	3.0×10^{10}	19
tetrahydrofuran	6.2×10^8	1.2
2-methyl-1-propanol	6.9×10^7	0.082
2-propanol	1.2×10^8	0.62
methanol	9.7×10^7	0.39
water	3.3×10^7	

[a] Added as tetraethylammonium chloride.

effect of hydrogen bonding between water and a nucleophile, the hydrogen-bonded form being less reactive. Li^+ exerts a similar effect as a result of its strong interaction, as a Lewis acid, with nucleophiles.

V. Ground-State Nucleophilic Reactivity of Carbanions

Nearly all of the absolute kinetics data regarding nucleophilic reactivity of carbanions came from Dorfman's group.[30,133-135] The PR-based work by this group in this area has been confined to benzyl carbanion and its ion pairs. The kinetic data for nucleophilic reactivity (proton transfer) with alcohols are compiled in Table XVI. Evidently, ion pairing augments the rate of protonation. Among the three cations examined, Na^+ has the largest enhancement effect. Na^+ is also the cation that induces the smallest blue shift in absorption spectral maxima relative to free cation (vide supra), suggesting that it forms a loose rather than a contact ion pair. It has been speculated[110] that alcohol molecules might enter the primary solvation shell of the cation in a selective solvation which facilitates the proton transfer. Such a close approach is not possible in the case of NBu_4^+. In the case of benzyllithium, a partial covalent character of the cation–anion bonding reduces the effective charge on Li^+ and hence subdues its enhancement effect on proton transfer.

The trend in reactivity among the alcohols follows that of their acidity. The acid–base nature of the reaction is also inferred from the fact that with ethanol as the electrophile for $PhCH_2^-$ and $PhCH_2^-Na^+$, isotope effects (k_H/k_D) of 1.2 and 1.7 are observed, respectively. This implies the involvement of OH bond breaking in the transition state.

VI. Singlet Excited-State Electrophilic Reactivity of Carbocations

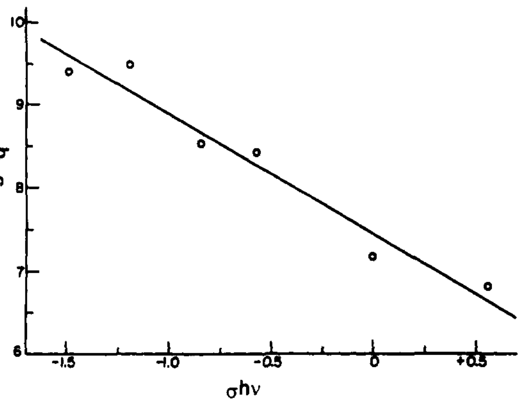


Figure 18. Plot of k_q for the fluorescence quenching of 9-aryl-substituted xanthenium cations by water vs $\sigma^{h\nu}$. Reproduced with permission from ref 87. Copyright 1991 American Chemical Society.

Minto and Das[65] measured bimolecular rate constants for the quenching of 9-phenylxanthenium cation singlet (monitored by fluorescence decay) by various neutral nucleophiles in acetonitrile. The data presented in Table XVI indicate a pronounced enhancement on going from the ground to the singlet excited state. For example, from the reported lifetime (0.04 s)[62] of this cation in the ground state in 1:4 acetonitrile–water, the rate constant for reaction with water is estimated to be 0.5 $M^{-1}\ s^{-1}$. In contrast, the rate constant for reaction of water with the singlet is $3.3 \times 10^7\ M^{-1}\ s^{-1}$. Similarly, among a number of primary amines that have been studied[62] for nucleophilic reactivity with 9-phenylxanthylium ground state, the most reactive is *n*-propylamine, with a rate constant of $1.7 \times 10^5\ M^{-1}\ s^{-1}$ (in 1:4 acetonitrile–water). In comparison, the tertiary amine, triethylamine, reacts with the singlet in acetonitrile with a fully diffusion-controlled rate (observed value, $3.0 \times 10^{10}\ M^{-1}\ s^{-1}$).

Boyd et al.[87] studied changes in fluorescence quantum yields and lifetimes of a series of 9-alkyl- and 9-aryl-substituted xanthenium cations in strongly acidic 1:2 H_2O–acetonitrile as a function of acid concentration (39–78% H_2SO_4). Fluorescence lifetimes vary considerably with acid concentration, from subnanosecond at low acidity to 20–35 ns at high acidity. Stern–Volmer linear plots of the fluorescence quenching against "free" water concentration give k_q values in the range 10^6–10^9 $M^{-1}\ s^{-1}$. For the 9-aryl-substituted systems, a plot of log k_q vs $\sigma^{h\nu}$ (recently determined on the basis of photohydration reactions of substituted styrenes and phenylacetylenes)[176] is reasonably linear (Figure 18). The slope of this plot gives a negative ρ value (−1.5), which is opposite in sign to that ($\rho = 0.5$) obtained[59] for water quenching of the same cations in the ground state. A possible explanation for the excited-state behavior has been found by Huckel MO calculations. The latter suggest that in S_1, after promotion of an electron to the LUMO, there is very little residual cationic charge on C_9 and that the corresponding lobe and MO coefficient become pronounced in systems containing electron-donating substituents.

VII. Electron-Transfer Reactions of Carbocations

It is natural that parallel to electron-pair (Lewis) interactions, the participation of carbocations in single electron transfer would be of interest. Although the occurrence of single electron transfer to carbocations is well-recognized, time-resolved studies in this area have been few and far between. Kochi and coworkers[177,178] carried out picosecond laser spectroscopy studies of electron donor–acceptor (EDA) complexes of tropylium cation with a series of substituted arenes in acetonitrile. The picosecond laser photoexcitation of these EDA complexes leads to observation of the arene radical cations within the 30-ps laser pulse. The decay of the radical cations and concomitant regeneration of the ground-state EDA complex take place quickly with rate constants $>4 \times 10^{10}$ s^{-1}. This is attributed to fast back electron transfer dominating over dissociation of and photochemical transformations in photogenerated ion–radical pairs in the singlet configuration.

For EDA complexes of tropylium cation with such labile partners as dianthracene and hexamethyl Dewar benzene, permanent photochemical changes in terms of cycloreversion and isomerization are observed upon photoactivation of the EDA complexes.[177,178] In these cases, the initial radical cations undergo ultrafast unimolecular chemical processes (namely, cycloreversion to anthracene and anthracene radical cation or conversion to hexamethylbenzene radical cation). The rates of the latter processes are fast enough to compete favorably with back electron transfer (discussed above).

On the basis of steady-state photochemical and flash-photolytic transient spectral evidence, Al-Ekabi et al.[179] suggested that electron transfer occurs between an excited state of protonated 1,1-di-*p*-ansylethylene and the ground state of the parent ethylene. The flash photolysis (xenon lamp) of a solution of 1,1-di-*p*-ansylethylene in benzene containing 0.52 M TFA generated a transient absorption (observed at 100 and 200 μs after the flash) at 340–440 nm that underwent second-order decay ($k/\epsilon \simeq 5.5 \times 10^5$ cm s^{-1} at 360 nm). This was assigned to the radical cation of the ethylene. Supporting evidence for this assignment was obtained from experiments in which the radical cation was produced via photoinduced electron transfer to 9,10-dicyanoanthracene.

A number of xanthenium and thioxanthenium cations in their singlet excited states have been found[155,180] to be efficiently quenched by a wide range of aromatics. The rate constants for 9-phenylxanthenium cation singlet in acetonitrile vary from 4.5×10^9 (for benzene) to 2.6×10^{10} M^{-1} s^{-1} (for anthracene). The electron transfer derived product transients (arene radical cation and xanthenyl radical) have been observed in the course of LFP of the cations in the presence of donor quenchers, but their yields are small (<0.02). In spite of high exothermicity of electron transfer in the case of some of the donors, there is no indication regarding a lowering of k_q.

Azarani et al.[156] noted that the fluorescences of dibenzosuberenyl, xanthenyl, and 9-phenylxanthenyl are efficiently quenched by benzene and substituted benzenes with rate constants in excess of 10^9 M^{-1} s^{-1}. The electron-transfer nature of the quenching has been established by a correlation between the observed rate constant and the oxidation potential of the aromatic quencher. Transient absorption experiments based on LFP failed to show transient products of net electron transfer (except with biphenyl as a donor for which a weak signal at 650 nm due to biphenyl radical cation was noted).

Carbocations are found to be facile electron acceptors when used as triplet quenchers. The quenching of 1-methoxynaphthalene triplet by bis(4-methoxyphenyl)methyl cation occurs with a rate constant of $\sim 1 \times 10^9$ M^{-1} s^{-1} in TFE.[181] The transient absorption spectra resulting from LFP of the naphthalene in the presence of the cation show formation of radical cation (from the naphthalene) and radical (from the cation). The relatively high efficiency of net electron transfer is consistent with the triplet nature of the initial radical/radical cation pair, allowing cage escape to compete favorably with back electron transfer. On the basis of nonnegligible irreversible cation depletion in the course of the quenching, it is also concluded that radical/radical cation coupling within the pair is favorable.

A study[182] of the quenching of a wider range of aromatic triplets by several carbocations has shown that the diffusion-controlled quenching rates as well as high yields of net electron transfer are general characteristics of this quenching. Interestingly, for certain systems, although the energy transfer from aromatic triplets to cations is favorably exothermic, this process does not occur to any significant extent.

VIII. Electron Transfer Involving Carbanions

Many steady-state studies[183–188] established carbanions as facile electron donors in both ground and excited states. However, time-resolved work to support electron transfer from carbanions and to measure related kinetics has been rare. For the quenching of *p*-nitrobenzyl anion by hexachloroiridate ion ($IrClO_6^{2-}$), a rate constant of 2.6×10^8 M^{-1} s^{-1} has been reported by Craig and Atherton.[145]

According to a recent paper by Tolbert et al.,[175] the fluorescence of a series of 9-arylfluorenyl anions is efficiently quenched by biphenyl ($k_q = 3.8$–5.5×10^9 M^{-1} s^{-1} in DMSO) and other polycyclic aromatic hydrocarbon acceptors. In the presence of biphenyl as the quencher, the picosecond excited-state absorption of 9-phenylfluorenyl anion shows increased absorbance at 450- and 600–700-nm regions, attributable to biphenyl radical anion formed in the course of photoinduced electron transfer from the carbanion singlet.

IX. Triplets of Carbocations

The lowest excited triplet states of a few carbenium ions and their isoelectronic boron compounds have been investigated[189,190] at low temperature by optical and ODMR spectroscopic methods. Upon lamp flash photolysis in a mixture of sulfuric and acetic acids at 77 K, Ivanov et al.[160] claimed to have detected the triplet–triplet absorption of trityl cation in the UV-visible region. Also, the lamp flash photolysis of protonated xanthone and benzophenone gives rise to transient absorptions that have been assigned to their triplets.[191,192] All of these results suggest that carbocations may have nonnegligible intersystem crossing yields and their triplets should be easily observable.

In a recent study,[193] Johnston and Wong characterized the triplet excited state of the 9-phenylxanthenium cation by both luminescence and transient absorption. The excitation of the cation in TFE or in ethanol/H$^+$

glasses at 77 K shows weak phosphorescence at 600 nm, giving an estimate of its triplet energy at ~48 kcal/mol. The triplet–triplet absorption, obtained by LFP (355 nm) in TFE, shows $\lambda_{max} \leq 300$ nm and decays over several microseconds. The triplet is efficiently quenched by O_2, cyclohexadiene, and biphenyl with rate constants of $\sim 8 \times 10^9$, 3.5×10^9, and 4.0×10^9 M^{-1} s^{-1}, respectively. That the quenching by biphenyl involves electron transfer is shown by the formation of 9-phenylxanthenyl radical and biphenyl radical cation, observed via transient absorptions in the regions of 340 and 650 nm, respectively.

The above observations regarding the triplet of 9-phenylxanthenium cation agree very well with the results of similar studies[194] on xanthenium and thioxanthenium cations in general in acetonitrile–trifluoroacetic acid mixtures and in Nafion matrices at room temperature. The latter results show the formation of short-lived transients (τ = 4–50 μs) with prominent absorptions in the UV (280–320 nm) and broad weak absorptions in the visible. These transients are easily quenchable by oxygen, nucleophiles, and various aromatics. Attempted energy transfer from the carbocationic triplets to polycyclic aromatics with low triplet energies (e.g., tetracene) revealed only electron transfer in these cases and apparently no formation of aromatic triplets. This behavior is reminiscent of similar dominance of electron transfer in the course of quenching of aromatic triplets by carbocation ground states (vide supra).

X. Summarizing Remarks

The application of nanosecond PR and LFP has made it possible to obtain a wealth of data on absolute kinetics of *reactive* cations in the ground state. These cations are intermediates in common organic reactions such as solvolysis, ionic polymerization, and Friedel–Crafts alkylation. An important characteristic of the data obtained by LFP and PR is that these are in neutral solvents. It has been shown that the structure–reactivity relationships derived from the behavior of relatively stable cations are not generally applicable to their reactive counterparts. Interesting steric effects have been recognized for cations substituted at the cation center. The amine nucleophiles have been shown not to obey the N_+ constant selectivity relation, and the hydration of amines plays a critical role in their nucleophilicity. Hydration and interaction with cations (Li^+) has been shown to be important in the electrophilic behavior of *all-trans*-retinyl cation. Additional kinetic data concerning solvent and temperature effects are expected to give a fuller picture of nucleophilic reactions.

While the kinetic data for photogenerated carbocations and carbanions have brought out newer features of nucleophilic reaction mechanisms, the yield data on cations have given insight into the factors that contribute to charge polarization in photoexcited states of the precursors. For certain *o*-nitrotoluene precursors of nitrobenzyl anions, fast intramolecular hydrogen atom transfer in the triplet state has been shown to be the mechanism leading to carbanions. Also, for *p*-nitrophenyl acetate, photoadiabaticity has been indicated for decarboxylation from the triplet state. Several recent studies have been directed toward characterizing the excited states of the carbocations and carbanions themselves and studying their behaviors in bimolecular electron-pair and electron-transfer interactions.

The relevance of carbocations and carbanions to organic photochemistry is threefold. First, they can be produced as a result of charge separation in photoexcited states or in the course of photoinduced electron (single or in-pair) migration. Subsequent to their formation, they play significant roles as energy-rich intermediates in reaction pathways. Photosolvolysis, photoelimination, and photopolymerization are exemplary of this aspect. Second, the photoexcitation of these labile species under sufficiently stabilizing conditions can give rise to chemistry that is novel or extraordinarily facile relative to that usually seen with common molecules. Spectacular enhancement of electrophilicity of singlets and triplets of carbocations is a case in point. Third, carbanions and carbocations in ground states can participate in bimolecular interactions with usual photoexcited states and photointermediates, and thus form new species that can act as energy or electron carriers. As a matter of fact, certain carbocations and carbanions may be used as probes for photophysical phenomena and photochemical reaction mechanisms.

Subnanosecond techniques appear promising to address details of ultrafast phenomena related to carbocations and carbanions. For example, the mechanism of photoheterolysis of a C–X bond is still open. There is a question as to whether this takes place as a direct process parallel to homolysis or via homolysis followed by electron transfer between so-formed radical pair. The recent work by Hilborn and Pincock[195] points to in-cage electron transfer in radical pairs produced from C–O photohomolysis in 1-naphthyl methyl alkanoates. There is scope for using picosecond techniques to sort out competitions among dissociation, back electron transfer, and various chemical processes (e.g., proton transfer) in photogenerated radical/radical ion pairs. Very reactive cations, namely those not stabilized by delocalization of the charge, are amenable to detection by direct or indirect means in the subnanosecond domain. Finally, there have not been many studies regarding the ultrafast kinetics of solvent relaxation/reorganization in the early stage of photoinduced ion separation.

Compared to carbocations, there have been only a limited number of time-resolved studies on properties of carbanions, including their nucleophilic and electron-transfer reactivity. However, carbanions[196-200] are viable intermediates in many photochemical reactions, intrinsically rich in photochemistry, and potentially useful for energy conversion and storage. They deserve as much attention as their cationic analogs.

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References

(1) Bethell, D.; Gold, V. *Carbonium Ions*; Academic Press: New York, 1967.
(2) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: London, 1969.
(3) Saunders, M.; Jimenez-Vazquez, H. A. *Chem. Rev.* **1991**, *91*, 375.

(4) Olah, G. A.; Schleyer, P. V. R. *Carbonium Ions*; Wiley: New York, 1968–1976; Vols. I–V.
(5) Olah, G. A. *Chem. Ser.* **1981**, *18*, 97.
(6) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173.
(7) Gillespie, R. J. *Acc. Chem. Res.* **1968**, *1*, 202.
(8) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965.
(9) *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1975.
(10) Buncel, E. *Carbanions: Mechanistic and Isotope Aspects*; Elsevier: Amsterdam, 1975.
(11) Tolbert, L. M. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1987; Part C.
(12) Stang, P. G.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. In *Vinyl Cations*; Academic Press: New York, 1979; Chapter 6.
(13) Brown, G. H. *Techniques of Chemistry*; Wiley: New York, 1971; Vol. 3, p 294.
(14) Wettermark, G.; Ricci, R. *J. Chem. Phys.* **1963**, *39*, 1218, and references cited therein.
(15) Ta-Shma, R.; Rappoport, Z. *J. Am. Chem. Soc.* **1983**, *105*, 6082.
(16) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238.
(17) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 4689, 4691; **1984**, *106*, 1373, 1383, 1396.
(18) Richard, J. P.; Rothrenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361.
(19) Ta-Shma, R.; Jencks, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 8040.
(20) Richard, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 6819.
(21) Swain, C. G.; Scott, C. B.; Lohmann, K. H. *J. Am. Chem. Soc.* **1953**, *75*, 136.
(22) Golomb, D. *J. Chem. Soc.* **1959**, 1334.
(23) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348.
(24) Ritchie, C. D. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; Advances in Chemistry Series 215; American Chemical Society: Washington, DC, 1987; p 169.
(25) Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2239.
(26) Ritchie, C. D.; Hofelich, T. C. *J. Am. Chem. Soc.* **1980**, *102*, 7039.
(27) Ritchie, C. D.; Gandler, J. *J. Am. Chem. Soc.* **1979**, *101*, 7318.
(28) Bunton, C. A.; Huang, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 3536; **1973**, *95*, 2701; **1974**, *96*, 515.
(29) Bunton, C. A.; Paik, C. H. *J. Org. Chem.* **1976**, *41*, 40.
(30) Dorfman, L. M.; Sujdak, R. J.; Bockrath, B. *Acc. Chem. Res.* **1976**, *9*, 352.
(31) Dorfman, L. M.; Wang, Y.; H. -Y.; Sujdak, R. J. *Faraday Discuss. Chem. Soc.* **1977**, *63*, 149.
(32) Dorfman, L. M.; DePalma, V. M. *Pure Appl. Chem.* **1979**, *51*, 123.
(33) Wang, Y.; Tria, J. J.; Dorfman, L. M. *J. Phys. Chem.* **1979**, *83*, 1946.
(34) Bobrowski, K.; Das, P. K. *J. Am. Chem. Soc.* **1982**, *104*, 1704.
(35) Pienta, N. J.; Kessler, R. J.; Peters, K. S.; O'Driscall, E. D.; Arnett, E. M.; Molter, K. E. *J. Am. Chem. Soc.* **1991**, *113*, 3773.
(36) Wan, P.; Muralidharan, S. *J. Am. Chem. Soc.* **1988**, *110*, 4336.
(37) Wan, P.; Muralidharan, S. *Can. J. Chem.* **1986**, *64*, 1949.
(38) Steenken, S.; McClelland, R. A. *J. Am. Chem. Soc.* **1989**, *111*, 4967.
(39) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131.
(40) Cristol, S. J.; Bindel, T. H. *Org. Photochem.* **1983**, *6*, 327.
(41) Hoyomaki, J.; Koskikallo, J. *Acta Chem. Scand.* **1977**, *31*, 321.
(42) Jaarinen, S.; Niiranen, J.; Koskikallio, J. *Int. J. Chem. Kinet.* **1985**, *17*, 925.
(43) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915.
(44) Zimmerman, H. E.; Somasekhara, S. *J. Am. Chem. Soc.* **1963**, *85*, 922.
(45) Turro, N. J.; Wan, P. *J. Photochem.* **1985**, *28*, 93.
(46) Cristol, S. J.; Greenwald, B. E. *Tetrahedron Lett.* **1976**, 2105.
(47) Cristol, S. J.; Bindel, T. H. *J. Org. Chem.* **1980**, *45*, 951.
(48) Cristol, S. J.; Bindel, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 7287.
(49) Irie, M. *J. Am. Chem. Soc.* **1983**, *105*, 2078.
(50) Hall, B.; Wan, P. *J. Photochem. Photobiol. A: Chem.* **1989**, *46*, 49.
(51) Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 7710.
(52) McClelland, R. A.; Chan, C.; Cozens, F.; Modro, A.; Steenken, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1337.
(53) McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Stenken, S. *J. Am. Chem. Soc.* **1992**, *114*, 1816.
(54) McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. *J. Am. Chem. Soc.* **1991**, *113*, 1009.
(55) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918.
(56) Mathivanan, N.; McClelland, R. A.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 8454.
(57) McClelland, R. A.; Mathivanan, N.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 4857.
(58) McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 3966.
(59) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929.
(60) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913.
(61) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1986**, *108*, 7023.
(62) Okuyama, T.; Ueno, K.; Morishima, Y.; Kamachi, M.; Fueno, T. *Chem. Lett.* **1990**, 1129.
(63) Gaillard, E.; Fox, M. A.; Wan, P. *J. Am. Chem. Soc.* **1989**, *111*, 2180. See also footnote 11 and related text in ref 57.
(64) Mecklenburg, S. L.; Hilinski, E. F. *J. Am. Chem. Soc.* **1989**, *111*, 5471.
(65) Minto, R. E.; Das, P. K. *J. Am. Chem. Soc.* **1989**, *111*, 5471.
(66) Schnabel, W.; Naito, I.; Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Tetrahedron* **1980**, *36*, 3229.
(67) Kobayashi, S.; Kitamura, T.; Taniguchi, H.; Schnabel, W. *Chem. Lett.* **1983**, 1117.
(68) Kobayashi, S.; Zhu, Q. Q.; Schnabel, W. *Z. Naturforsch.* **1988**, *43B*, 825.
(69) VanGinkel, F. I. M.; Visser, R. J.; Varma, C. A. G. O.; Lodder, G. *J. Photochem.* **1985**, *30*, 453.
(70) Johnston, L. J.; Lobaugh, J.; Wintgens, V. *J. Phys. Chem.* **1989**, *93*, 7370.
(71) Wan, P.; Krogh, E. *J. Am. Chem. Soc.* **1989**, *111*, 4887.
(72) Krogh, E.; Wan, P. *Can. J. Chem.* **1990**, *68*, 1725.
(73) Wan, P.; Krogh, E. *J. Chem. Soc., Chem. Commun.* **1985**, 1207.
(74) Krogh, E.; Wan, P. *Tetrahedron Lett.* **1986**, 823.
(75) Alonso, E. O.; Johnston, L. J.; Scaiano, J. C.; Toscano, V. G. *J. Am. Chem. Soc.* **1990**, *112*, 1270.
(76) Spears, K. G.; Gray, T. H.; Huang, D. *J. Phys. Chem.* **1986**, *90*, 779.
(77) Pienta, N. J.; Kessler, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 2419.
(78) Rosenfeld, T.; Alchalal, A.; Ottolenghi, M. *Chem. Phys. Lett.* **1973**, *20*, 291.
(79) Rosenfeld, T.; Alchalal, A.; Ottolenghi, M. In *Excited States of Biological Molecules*; Birks, J. B.; Ed.; Wiley: New York, 1976; p 540.
(80) Chattopadhyay, S. K.; Bobrowski, K.; Das, P. K. *Chem. Phys. Lett.* **1982**, *91*, 143.
(81) Bhattacharyya, K.; Rajadurai, S.; Das, P. K. *Tetrahedron* **1987**, *43*, 1701.
(82) Lo, K. K. N.; Land, E. J.; Truscott, T. G. *Photochem. Photobiol.* **1982**, *36*, 139.
(83) Okuyama, T.; Haya, N.; Takane, S.; Ueno, K.; Fueno, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2751.
(84) Wan, P.; Yates, K.; Boyd, M. K. *J. Org. Chem.* **1985**, *50*, 2881.
(85) Slocum, G. H.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 2177.
(86) Arnold, B.; Donald, L.; Jurgens, A.; Pincock, J. A. *Can. J. Chem.* **1985**, *63*, 3140.
(87) Boyd, M. K.; Lai, H. Y.; Yates, K. *J. Am. Chem. Soc.* **1991**, *113*, 7294.
(88) Wan, P.; Yates, K. *Rev. Chem. Intermed.* **1984**, *5*, 157.
(89) Bhattacharyya, K.; Bobrowski, K.; Rajadurai, S.; Das, P. K. *Photochem. Photobiol.* **1988**, *47*, 73.
(90) Raghavan, N. V.; Das, P. K.; Bobrowski, K. *J. Am. Chem. Soc.* **1981**, *103*, 4569.
(91) Shizuka, H. *Acc. Chem. Res.* **1985**, *18*, 141.
(92) Shizuka, H.; Tobita, S. *J. Am. Chem. Soc.* **1982**, *104*, 6919.
(93) Isaks, M.; Yates, K.; Kalanderopoulos, P. *J. Am. Chem. Soc.* **1984**, *106*, 2728.
(94) Rafizadeh, K.; Yates, K. *J. Org. Chem.* **1984**, *49*, 1500.
(95) Wan, P.; Yates, K. *J. Org. Chem.* **1983**, *48*, 869.
(96) Wan, P.; Culshaw, S.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 2509.
(97) Wan, P.; Wu, P. *J. Chem. Soc., Chem. Commun.* **1990**, 822.
(98) Steenken, S.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 9648.
(99) McClelland, R. A.; Cozens, F.; Steenken, S. *Tetrahedron Lett.* **1990**, *31*, 2821.
(100) Cozens, F.; Li, J.; McClelland, R. A.; Steenken, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 743.
(101) Blatz, P. E.; Pippert, D. L. *J. Am. Chem. Soc.* **1968**, *90*, 1296.
(102) Kirmse, W.; Kilian, J.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 6399.
(103) Chateauneuf, J. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1437.
(104) Boate, D. R.; Johnston, L. J.; Kwong, P. C.; Lee-Ruff, E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 8858.
(105) Steenken, S.; Buschek, J.; McClelland, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 2808.
(106) McClelland, R. A.; Steenken, S. *J. Am. Chem. Soc.* **1980**, *110*, 5860.
(107) Faria, J. L.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 1277.
(108) Nagaoka, T.; Griller, D.; Wayner, D. D. M. *J. Phys. Chem.* **1991**, *95*, 6264.
(109) Bromberg, A.; Schmidt, K.; Meisel, D. *J. Am. Chem. Soc.* **1984**, *106*, 3056.
(110) Bromberg, A.; Schmidt, K.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83.
(111) Bromberg, A.; Meisel, D. *J. Phys. Chem.* **1985**, *89*, 2507.
(112) Popielarz, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3068.
(113) Davis, H. F.; Das, P. K.; Reichel, L. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 6938.
(114) Reichel, L. W.; Griffin, G. W.; Muller, A. J.; Das, P. K.; Ege, S. *Can. J. Chem.* **1984**, *62*, 424.
(115) Sujdak, R. J.; Jones, R. L.; Dorfman, L. M. *J. Am. Chem. Soc.* **1976**, *98*, 4875.
(116) Jones, R. L.; Dorfman, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 5715.
(117) DePalma, V. M.; Wang, Y.; Dorfman, L. M. *J. Am. Chem. Soc.* **1978**, *100*, 5416.
(118) Kundu, K. P.; Dorfman, L. M. *Radiat. Phys. Chem.* **1982**, *20*, 247.
(119) Reed, D. T.; Dorfman, L. M. *Macromolecules* **1984**, *17*, 32.
(120) Wang, Y.; Dorfman, L. M. *Macromolecules* **1980**, *13*, 63.

(121) Bobrowski, K.; Dzierzkowska, G.; Grodkowski, J.; Stuglik, Z.; Zagorski, Z. P.; McLaughlin, W. L. *J. Phys. Chem.* **1985**, *89*, 4358.
(122) Eaton, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 3278.
(123) Neta, P.; Behar, D. *J. Am. Chem. Soc.* **1980**, *102*, 4798.
(124) Neta, P.; Behar, D. *J. Am. Chem. Soc.* **1981**, *103*, 103.
(125) Bays, J. P.; Blumer, S. T.; Baral-Tosh, S.; Behar, D.; Neta, P. *J. Am. Chem. Soc.* **1983**, *105*, 320.
(126) Behar, D.; Neta, P. *J. Phys. Chem.* **1981**, *85*, 690.
(127) Behar, D.; Neta, P. *J. Am. Chem. Soc.* **1981**, *103*, 2280.
(128) Andrieux, C. P.; Merz, A.; Saveant, J.-M. *J. Am. Chem. Soc.* **1985**, *107*, 6097.
(129) Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2628.
(130) Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2637.
(131) Beletskaya, I. P.; Armankina, G. A.; Pikaev, A. K. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1976**, *25*, 2247.
(132) Pikaev, A. K.; Artamkina, G. A.; Beletskaya, I. P. *Dokl. Phys. Chem.* **1977**, *232*, 112.
(133) Dorfman, L. M.; Bockrath, B. *J. Phys. Chem.* **1974**, *79*, 3040.
(134) Bockrath, B.; Dorfman, L. M. *J. Am. Chem. Soc.* **1975**, *97*, 3307.
(135) Bockrath, B.; Dorfman, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 5708.
(136) Maslak, P.; Kula, J.; Chateauneuf, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 2306.
(137) McAuley, I.; Krogh, E.; Wan, P. *J. Am. Chem. Soc.* **1988**, *110*, 600.
(138) Wan, P.; Xu, X. *Tetrahedron Lett.* **1990**, *31*, 2809.
(139) Krogh, E.; Wan, P. *J. Am. Chem. Soc.* **1992**, *114*, 705.
(140) Wan, P.; Krogh, E.; Chak, B. *J. Am. Chem. Soc.* **1988**, *110*, 4073.
(141) Okamoto, Y.; Iwamoto, N.; Takamuku, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1516.
(142) Okamoto, Y.; Iwamoto, N.; Toki, S.; Takamuku, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 277.
(143) Margerum, J. D.; Petrusis, C. T. *J. Am. Chem. Soc.* **1969**, *91*, 2467.
(144) Craig, B. B.; Weiss, R. G.; Atherton, S. J. *J. Phys. Chem.* **1987**, *91*, 5906.
(145) Craig, B. B.; Atherton, S. J. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1929.
(146) Wan, P.; Budac, D.; Krogh, E. *J. Chem. Soc., Chem. Commun.* **1990**, 255.
(147) Wan, P.; Budac, D.; Earle, M.; Shukla, D. *J. Am. Chem. Soc.* **1990**, *112*, 8048.
(148) Budac, D.; Wan, P. *J. Org. Chem.* **1992**, *57*, 887.
(149) Atherton, S. J.; Craig, B. B. *Chem. Phys. Lett.* **1986**, *127*, 7.
(150) McClelland, R. A.; Steenken, S. *Can. J. Chem.* **1987**, *65*, 353.
(151) Chattopadhyay, S. K.; Craig, B. B. *J. Phys. Chem.* **1987**, *91*, 323.
(152) Wan, P.; Davis, M. *J. Photochem. Photobiol. A Chem.* **1989**, *48*, 387.
(153) Wan, P.; Chak, B.; Krogh, E. *J. Photochem. Photobiol. A Chem.* **1989**, *46*, 49.
(154) Wan, P.; Davis, M. J.; Teo, M.-A. *J. Org. Chem.* **1989**, *54*, 1354.
(155) Samanta, S.; Gopidas, K. R.; Das, P. K. *J. Phys. Chem.* **1993**, in press.
(156) Azarani, A.; Berinstein, A. B.; Johnston, L. J.; Kazanis, S. *J. Photochem. Photobiol. A Chem.* **1991**, *57*, 175.
(157) Fox, M. A.; Voynick, T. A. *Tetrahedron Lett.* **1980**, *21*, 3943.
(158) Bobrowski, K.; Das, P. K. *J. Am. Chem. Soc.* **1985**, *89*, 5733.
(159) Bobrowski, K.; Das, P. K. Unpublished work.
(160) Ivanov, V. L.; Al'-Ainen, S. A.; Kuz'min, M. G. *High Energy Chem.* **1978**, *12*, 39.
(161) Patterson, L. K.; Porter, G.; Topp, M. R. *Chem. Phys. Lett.* **1970**, *7*, 612.
(162) Brown, R. G.; Phillips, D. *Trans. Faraday Soc.* **1974**, *70*, 630.
(163) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *J. Am. Chem. Soc.* **1982**, *104*, 4507.
(164) Berger, R. M.; Weir, D. *Chem. Phys. Lett.* **1990**, *169*, 213.
(165) Green, J. A., II; Singer, L. A.; Parks, J. H. *J. Chem. Phys.* **1973**, *58*, 2690.
(166) Watkins, A. R. *Chem. Phys. Lett.* **1980**, *70*, 262.
(167) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 6205.
(168) Kuzmin, V. A.; Tatikolov, A. S. *Chem. Phys. Lett.* **1977**, *51*, 45.
(169) Watkins, A. R. *Chem. Phys. Lett.* **1974**, *29*, 526.
(170) Dvorak, V.; Michl, J. *J. Am. Chem. Soc.* **1976**, *98*, 1080.
(171) Burley, J. W.; Young, R. N. *J. Chem. Soc., Chem. Commun.* **1970**, 1649.
(172) Parkes, H. M.; Young, R. N. *J. Chem. Soc., Perkin Trans.* **1978**, 249.
(173) Velthorst, N. H. *Pure Appl. Chem.* **1979**, *51*, 85.
(174) Vos, H. W.; Blom, H. H.; Velthorst, N. H.; Maclean, C. *J. Chem. Soc. Perkin Trans.* **1972**, 635.
(175) Tolbert, L. M.; Nesselroth, S. M.; Netzel, T. L.; Raya, N.; Stapleton, M. *J. Phys. Chem.* **1992**, *96*, 4492.
(176) McEwen, J.; Yates, K. *J. Org. Phys. Chem.* **1991**, *4*, 193.
(177) Takahashi, Y.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2954.
(178) Kochi, J. K. *Acta Chem. Scand.* **1990**, *44*, 409.
(179) Al-Ekabi, H.; Kawata, H.; deMayo, P. *J. Org. Chem.* **1988**, *53*, 1471.
(180) Samanta, A.; Gopidas, K. R.; Das, P. K. *Chem. Phys. Lett.* **1990**, *167*, 165.
(181) Johnston, L. J.; Kanigan, T. *J. Am. Chem. Soc.* **1990**, *112*, 1271.
(182) Samanta, A.; Gopidas, K. R.; Das, P. K. *Chem. Phys. Lett.* **1992**, submitted for publication.
(183) Krogh, E.; Wan, P. *Top. Curr. Chem.* **1990**, *156*, 93.
(184) Courtneidge, J. L.; Davies, A. G.; Gregory, P. S.; Yazdi, S. N. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 49.
(185) Yamada, K.; Shigehiro, K.; Tomizawa, T.; Iida, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3306.
(186) Ito, O.; Aruga, T.; Matsuda, M. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2259.
(187) Tolbert, L. M.; Merrick, R. D. *J. Org. Chem.* **1982**, *47*, 2808.
(188) Fox, M. A. *ACS Symp. Ser.* **1981**, *No. 266*, 107.
(189) Slama, H.; Braeuchle, C.; Voitlaender, J.; Vogler, H. *J. Am. Chem. Soc.* **1987**, *109*, 2569.
(190) Slama, H.; Braeuchle, C.; Voitlaender, J. *Chem. Phys. Lett.* **1983**, *102*, 307.
(191) Ireland, J. F.; Wyatt, P. A. H. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1053.
(192) Ireland, J. F.; Wyatt, P. A. H. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 161.
(193) Johnston, L. J.; Wong, D. F. *Can. J. Chem.* **1992**, *70*, 280.
(194) Samanta, A.; Gopidas, K. R.; Das, P. K. Unpublished work.
(195) Hilborn, J. W.; Pincock, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2683.
(196) Toncheva, V. D.; Velichkova, R. S. *Macromol. Chem.* **1983**, *184*, 2231.
(197) Abraham, W.; Dreher, B.; Buck, K.; Kreysig, D. *J. Pract. Chem.* **1982**, *324*, 925.
(198) Abraham, W.; Kupfer, M.; Ruetz, C.; Tietz, U.; Kreysig, D. *Polym. J. Chem.* **1979**, *53*, 737.
(199) Tolbert, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 3531.
(200) Fox, M. A. *Chem. Rev.* **1979**, *79*, 253.