Pergamon

Tetrahedron, Vol. 52, No. 20, pp. 6823-6858, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00020-8

TETRAHEDRON REPORT NUMBER 400

Flash Photolysis Generation and Reactivities of Carbenium Ions and Nitrenium Ions

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1. Introduction

The technique of flash photolysis provides for the direct observation of a short-lived species, often under conditions that closely resemble those of a thermal reaction where that species has been proposed as a reactive intermediate. This technique not only establishes that the intermediate does exist under such conditions, but also, and more importantly, provides direct information about kinetics of its further reactions. Such direct information cannot be obtained when the intermediate is generated only in small, undetectable, stationary state amounts. Since flash photolysis employs light to produce the reactive entity, any species that can be generated photochemically can, in principle, be studied by this technique. A list of intermediates extensively investigated in this regard would now include free radicals, biradicals, carbenes, nitrenes, ketenes, enols, as well as various excited states. These of course are all neutral species. More recent studies have focussed on cationic intermediates, especially carbenium ions, and very recently on nitrenium ions. That research is the subject of this report.

Carbenium ions of course have been extensively examined under superacid (or stable ion) conditions. These investigations have furnished detailed information about the structure of the cations, but studies of reactivities have been generally limited to internal rearrangements and fragmentations, where they occur. The weakly nucleophilic solvents and counterions required for such studies are however very different from those encountered in reactions such as solvolysis and alkene additions. The strongly acid character of these conditions also precludes the addition of potential nucleophiles. Thus superacid studies cannot address questions relating to the reactivity of a cationic intermediate with a second reagent, either with a strongly nucleophilic solvent such as water or with some added nucleophile.

Such reactivities have been directly measured for highly stabilized cations, principally by Ritchie and his co-workers.[1,2] However, for cations of the type more commonly encountered in organic reactions, the standard approach has been to measure selectivities, i.e., ratios of rate constants.[3] This was done through the competition kinetics method, in which a cationic intermediate is allowed to partition between two nucleophiles to produce different products, or through the kinetic analysis of common ion inhibition. Absolute rate constants have been estimated from such selectivities with the assumption that one of the competing nucleophiles reacts at the diffusion limit.[4]

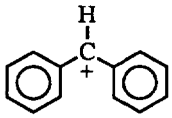
Flash photolysis obviously offers a way of directly measuring reactivity of cations, and over the last ten years, we have been involved in a number of such studies. This report summarizes that research.[5] The requirements for the study of cationic intermediates by this technique are first presented, followed by the types of photoreactions that have been employed. The main body of the text then discusses aspects of the directly measured reactivities.

2. Requirements for Study of Cations by Flash Photolysis

There are three requirements for this method to be successful for the study of a cationic intermediate, or indeed of any transient species. (A) Some photochemical reaction must generate the desired cation. (B) The cation must be 'observable' with the monitoring method. (C) The cation must have a sufficient lifetime to be detected. The next two subsections elaborate on points B and C; section 3 considers point A.

2.1 Detection Methods

By far the most common detection method in flash photolysis is absorption spectroscopy, which requires that the cation being generated absorb in the UV-visible. This requirement has meant that the majority of cations successfully studied by flash photolysis have had conjugated π systems. In most cases these cations have been "benzylic-like" systems where aryl groups are attached to the formal C^+ center (e.g. **1**,**2**,**3**), or "cyclohexadienyl-like" systems involving protonated or alkylated aromatic systems (e.g. **4**, **5**). Alkyl carbenium ions, such as the tert-butyl cation, do not absorb above 220 nm,[6] and, in consequence, are not directly detectable with this method.



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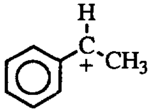

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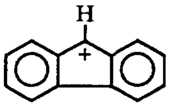

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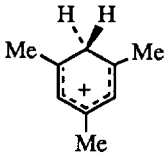

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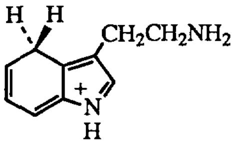

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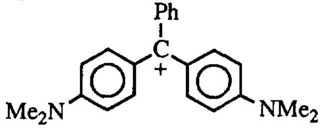
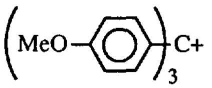
Conductivity detection can also be employed. This method takes advantage of the relatively large changes in conductivity that accompany the generation of H^+ when an organic cation reacts with protic solvent (or the consumption of OH^- if the reaction occurs in basic aqueous solution).[7] An absorbing intermediate is not required, as shown by the successful application to alkyldialkoxycarbenium ions.[8] A chromophore in the precursor is obviously needed for the photochemical generation of the cation.

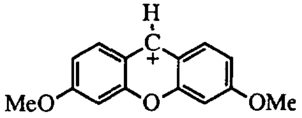
2.2 Lifetime Limits

The lifetime of a cation in a solvent with which it reacts is defined as $1/k_S$, where k_S is the first-order rate constant for decay in that solvent. The obvious requirement for that cation to be observed is that its lifetime must be at least of the same order of magnitude as the width of the 'flash' or 'pulse' of light employed for its generation.

<u>(a) Highly Stabilized Cations — Mixing Experiments</u>. These cations include triarylmethyl cations bearing highly stabilizing substituents such as **6** and **7**, tropylium ions (e.g. the parent **8**), and xanthylium ions (e.g. **9**). As mentioned in the Introduction, these had seen previous direct study, since their lifetimes in water were such that kinetics could be followed by conventional or stopped-flow spectroscopy. This approach involved adding one solution containing the pre-formed cation to a second solution. The time required to mix these solutions was the important factor and limited measurements to cations with lifetimes longer than several milliseconds.







	6	**7**	**8**	**9**
Lifetime in water	5000 s	0.07 s	0.4 s	0.07 s

(b) Conventional Lamp Photolysis. Flash photolysis experiments reported in the early seventies involved the observation of some triarylmethyl cations in aqueous solution following excitation with a flash lamp.[9] The width of the flash in such experiments is of the order of 100 µs. Consequently these studies were limited to cations not that much less stable than the highly stabilized ones, namely triarylmethyl cations with at least one para- or ortho-methoxy substituent. A less stable cation, the parent triphenylmethyl cation, was observed in one of these studies. This cation has a lifetime of 6 µs in 100% aqueous solution[10,11] but was observed with the longer flash lamp through the use of very high concentrations of sodium perchlorate. The added salt ties up water molecules and has the effect of significantly reducing rate constants for reactions with cations.

(c) Nanosecond Laser Flash Photolysis (ns LFP). This is the most common current experimental set-up and employs a laser as the excitation source, with a pulse width of 5-20 ns. This technique decreases the requisite lifetime of cations by a further 3-4 orders of magnitude over the flash lamp and by 6-7 orders of magnitude over the highly stabilized examples. Even so, there are restrictions on the structure of cations that can be observed. For example, the diphenylmethyl cation is too-short lived to be detected by ns LFP in water, in methanol, and in ethanol.[12,13]

(d) Picosecond Laser Flash Photolysis (ps LFP). In such cases it is possible to employ even faster lasers, and indeed this has been done to directly observe Ph_2CH^+ in water, methanol and ethanol.[14] The primary photochemical events that lead to cations and the separation/collapse of ion pairs occur on the picosecond time scale, and ps LFP experiments have been reported probing such processes.[15,16]

(e) Solvent Effects. Protic solvents react with a given cation in the order methanol > ethanol > water >> 2,2,2-trifluoroethanol (TFE) >> 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP). These effects are large (see Table 1), and in many cases they can be exploited to increase lifetime into a range where a particular cation becomes detectable with a slower technique. We have found for example that the diphenylmethyl cation (**1**) becomes observable with ns LFP in TFE and becomes quite long lived in HFIP. The 9-fluorenyl cation (**11**) requires ps LFP even in TFE but is observed with ns LFP in HFIP.

Table 1. Effect of Solvent on Rate Constants k_s (s^{-1}, 20 °C) for Decay of Cations.

Cation	MeOH	EtOH	H_2O	CF_3CH_2OH	$(CF_3)_2CHOH$
(**10**) $(An)_2CH^+$[a]	8.6×10^6[b]	5.5×10^6[c]	1.0×10^5[b,d]	1.4×10^1[b]	
(**1**) $(C_6H_5)_2CH^+$	2.5×10^{10}[e]	1.4×10^{10}[e]	1.3×10^9[e,f]	3.2×10^6[b]	$\sim 1 \times 10^1$[c]
(**11**) 9-Fluorenyl			$>4 \times 10^{10}$[g,h]	8×10^8[i]	2×10^4[j]

[a] An = 4-$MeOC_6H_4$. [b] Ref. 12. [c] Unpublished data. [d] 4:1 H_2O:CH_3CN. [e] Ref. 14. [f] 1:1 CH_3CN:H_2O. [g] Ref. 15. [h] 9:1 H_2O:MeOH. [i] Hilinski, E., (Florida State University), Personal communication. [j] Ref. 17.

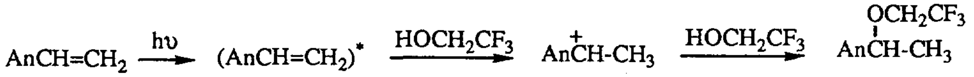
2.3 Assignment of Transient Cations

An important consideration in any flash photolysis experiment is the unambiguous assignment of structure to a particular transient that has been observed. This section considers the criteria that we have employed in such assignments where cations are involved as intermediates.

(a) Spectrum. The ideal situation is one where the cation is produced under 'stable ion' conditions and is characterized by NMR. In such cases a match of the UV-visible spectrum observed in a flash photolysis experiment with one obtained conventionally for the stable ion is excellent evidence that the transient spectrum does correspond to the cation. We have found that solvents have little influence on the UV-visible spectra of delocalized carbenium ions.[18]

(b) Kinetic Studies. Transients can also be identified on the basis of their kinetic behavior. The decay of carbenium ions in protic solvents (HOS) usually occurs in a single exponential fashion, and is accelerated by the addition of good nucleophiles. We have found that azide ion is an especially good indicator in this regard, since this anion generally reacts with carbenium ions at or near the diffusion limit.[19] Oxygen, on the other hand, an effective quencher of radicals and triplet excited states, has no effect on a carbenium ion.

(c) Products. If flash photolysis produces a cation, products appropriate to that intermediate must also be observed. The use of this criterion in an example from our work is illustrated in eq 1. Flash photolysis of 4-methoxystyrene (**12**) in TFE revealed a single transient, with quenching kinetics characteristic of a cation.[20] The obvious candidate was the 1-arylethyl cation **14**, but there was no spectrum under stable ion conditions for comparison. We therefore sought confirmation through the analysis of products. Indeed the only material obtained was the Markovnikov solvent adduct **15**, formed in 100% chemical yield[20] and 20% quantum yield.[21]



$$\mathrm{AnCH{=}CH_2} \xrightarrow{h\nu} \mathrm{(AnCH{=}CH_2)^*} \xrightarrow{\mathrm{HOCH_2CF_3}} \mathrm{An\overset{+}{C}H\text{-}CH_3} \xrightarrow{\mathrm{HOCH_2CF_3}} \mathrm{An\overset{OCH_2CF_3}{C}H\text{-}CH_3} \qquad (1)$$

12 **13** **14** **15**

(An = 4-MeOC$_6$H$_4$)

(d) Rate Constant Ratios. This criterion, which represents a combination of (b) and (c), involves the demonstration that the ratio of two rate constants directly measured by flash photolysis agrees quantitatively with a selectivity based upon product analysis. For example, Ritchie had reported in 1971 that the bis(4-methoxyphenyl)methyl cation, obtained upon solvolysis of the corresponding mesitoate in MeOH, had a selectivity k_{Az}:k_{MeOH} of 1.3×10^3 M^{-1}.[22] Our 1988 LFP studies involved the generation of this cation from a 4-cyanophenoxide precursor and gave the absolute rate constants, k_{Az} as 9.0×10^9 M^{-1}s^{-1} and k_{MeOH} as 8.4×10^6 s^{-1}.[12] Their ratio is 1.1×10^3 M^{-1} in excellent agreement with Ritchie's number.

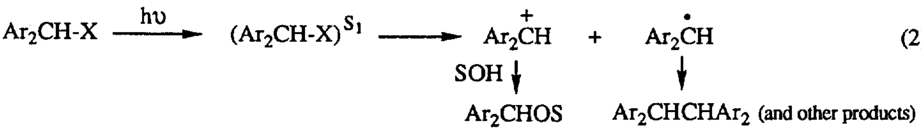
2.4 Ground State or Excited State Intermediates.

In the LFP experiments, the cation is derived from an excited state, and a question arises as to whether this cation is the same as the one produced from a ground state reaction. When ns LFP is employed, the time interval from excitation to observation is likely sufficient to ensure that this is the case. Two pieces of evidence from the previous section can be cited: the correspondence of UV-visible spectra with ones obtained for solutions of ground state cations; and the correspondence of rate constant ratios with ones measured for ground state reactions. The question of ion pairing also arises. Diffusional separation of ion pairs has been to shown to be complete within 1 - 10 ns,[16] so that a transient cation observed with ns LFP is very likely a free ion.

At shorter times, i.e. in ps LFP, it is certainly true that ion pairs can be observed.[16] However the question of the photophysical events forming the cations is still unanswered, at least unambiguously. Different selectivities have been reported for the "same" cation generated by a photochemical and by a thermal reaction.[23] This different behavior may indicate that, at least in these cases, the photochemically generated cation is not reacting from the same electronic or vibrational state as the thermally generated one. In other cases however, ps LFP studies have indicated that the cation observed after a few ps is in its ground state, at least in so far as UV-visible absorption spectrum is the criterion.[15,16b] The photochemistry of cations has been a recent focus of attention. The excited states of carbenium ions have lifetimes in some cases of 1 - 10 ns. There is quenching of these excited states by nucleophiles, and the rate constants are much larger than those observed for the same nucleophile reacting with the ground state cation.[24] In my opinion there is still a question as to whether the excited state reaction involves nucleophilic addition[24b] or some other quenching process such as electron transfer.

3. Methods for Photochemical Generation of Cationic Intermediates.

3.1 Photoheterolysis. This method involves heterolysis of a C—X bond following excitation and is the photochemical analog of the cation-forming step in an S_N1 reaction. As expected from this analogy, polar solvents such as water and the alcohols in Table 1 are normally required, although cations have been observed following photoheterolysis in acetonitrile.[18] The products are the solvent adducts, so the overall reaction amounts to a photosolvolysis. The reaction in this sense was first described by Zimmerman and co-workers in the sixties,[25] and considerable effort in elucidating its scope and mechanistic details has since ensued.[26] A common feature is that the photosolvolysis product is generally accompanied by products from a radical intermediate (eq 2).



$$\begin{array}{ccccccc} \mathrm{Ar_2CH\text{-}X} & \xrightarrow{h\nu} & (\mathrm{Ar_2CH\text{-}X})^{S_1} & \longrightarrow & \overset{+}{\mathrm{Ar_2CH}} & + & \overset{\bullet}{\mathrm{Ar_2CH}} \\ &&&& {\scriptstyle \mathrm{SOH}}\downarrow && \downarrow \\ &&&& \mathrm{Ar_2CHOS} && \mathrm{Ar_2CHCHAr_2}\ \text{(and other products)} \end{array} \qquad (2)$$

As illustrated in Fig. 1, competing heterolysis and homolysis pathways are clearly seen with LFP in the form of transient spectra corresponding to both intermediates. In such cases, the radical is clearly distinguished from the cation by criteria discussed in section 2.3, especially quenching studies. Radicals are scavenged by oxygen and not by nucleophiles, the exact opposite of cations.

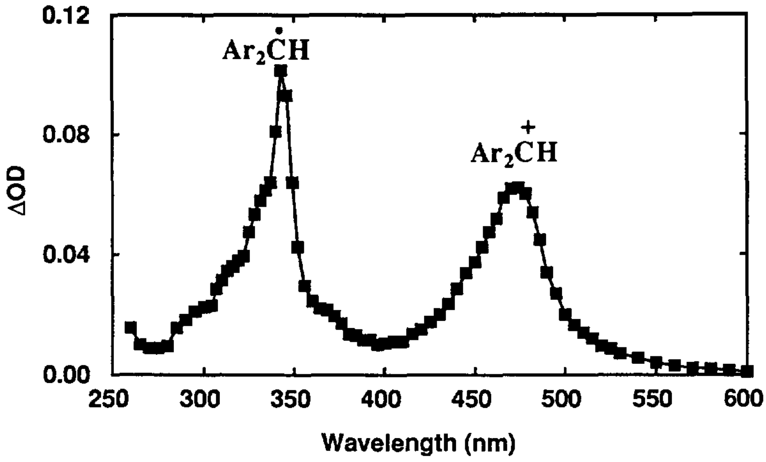


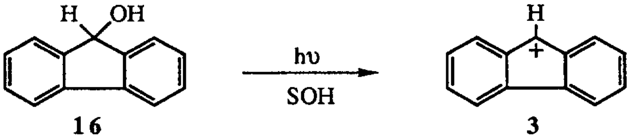
Figure 1. Transient absorption spectrum following 248 nm excitation of $(4\text{-}MeOC_6H_4)(C_6H_5)CH\text{-}OAc$ in argon-saturated 1:2 acetonitrile:water.

This approach has proven to be generally applicable, and has been used for LFP studies of a number of benzylic-type systems. Anionic leaving groups that range from bromide and chloride to acetate and 4-cyanophenoxide have been employed; neutral leaving groups such as PPh_3[27] also work. One study investigating the effect of leaving group is summarized in Table 2.[18] There is a general trend that better leaving groups yield more cation, although there are clearly exceptions. Overall the effect of leaving group is highly attenuated relative to the situation in ground state solvolysis.

Table 2. Quantum Yield of Intermediates Observed with ns LFP following 248 nm Irradiation of $Ph_2CH\text{-}X$ in CH_3CN.[18]

Leaving Group	$\Phi(R^+):\Phi(R^\bullet)$	$\Phi(R^+)$	$\Phi(R^\bullet)$
Bromide	0.63	0.12	0.19
Chloride	0.59	0.13	0.23
Fluoride	0.26	0.05	0.20
$4\text{-}NCC_6H_4O$	0.22	0.02	0.09
CF_3CO_2	0.14	0.04	0.31
$4\text{-}NO_2C_6H_4O$	<0.1		
CH_3CO_2	<0.08		
HO	<0.03		0.04

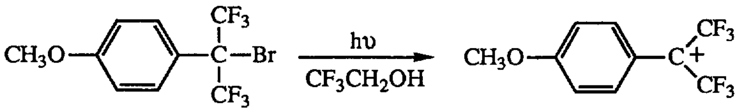
Systems that deserve special comment are illustrated in eqs 3-7 below. As shown in eq 3, irradiation of 9-fluorenol (**16**) in protic solvents results in the 9-fluorenyl cation (**3**) through loss of the poor leaving group OH^-. This unusual photochemistry was first found in product studies by Wan and co-workers, who proposed that excited **16** cleaves to form the excited state of **3**, which as an excited 4n π cyclic system is thought to take on aromatic character.[28] Later LFP studies characterizing the intermediate cation were carried out by the Hilinski group,[15] using ps LFP in methanol:water, and by our group,[17] using HFIP to bring the lifetime of the cation into the ns LFP range. The generality of this reaction has now been demonstrated with a variety of substituents at the 9-position, through our studies with 9-aryl,[29] 9-alkyl,[21] and 9-Me_3SiCH_2,[30] and a study with the electron withdrawing 9-COOMe by the Johnston group.[31]



16 **3**

(3)

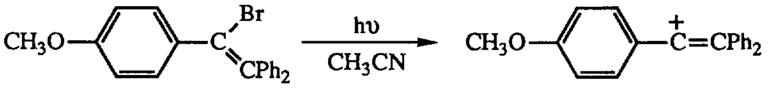
Eq 4 illustrates a second example of a cation bearing electron withdrawing groups, this time from our laboratory.[32]



17 **18**

(4)

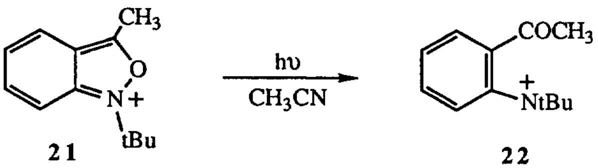
Several groups have reported the LFP characterization of vinyl cations,[33] as exemplified by eq 5.[33c]



19 **20**

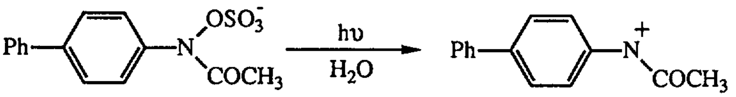
(5)

The final examples show the use of photoheterolysis for the LFP study of arylnitrenium ions, eq 6 an example from the Falvey group[34] and eq 7 from our group.[35]



21 **22**

(6)



23 **24**

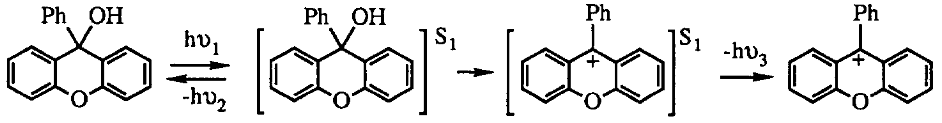
(7)

While the focus of this report is the LFP characterization of the chemistry of the cations once they are formed, there is considerable interest over the primary photophysical and photochemical events. One question, as illustrated by eq 8, is whether heterolysis occurs in the excited state along with homolysis, or whether only homolysis occurs resulting in a radical pair that in part undergoes electron transfer to give the ion pair.

$$\begin{tikzcd}
\text{R-X} \arrow[r, "h\nu"] & (\text{R-X})^{S_1} \arrow[r, "k_{homo}"] \arrow[dr, "k_{het}"'] & {[\text{R}^\bullet\ {}^\bullet\text{X}]} \arrow[r] \arrow[d, "k_{ET}"] & \text{Radical transient and products} \\
& & {[\text{R}^+\ {}^-\text{X}]} \arrow[r] & \text{Cation transient and products}
\end{tikzcd} \qquad (8)$$

Pincock and co-workers have proposed the latter sequence in the case of naphthylmethyl and benzyl carboxylates,[36] based on product analysis and a model where electron transfer competes with decarboxylation in the acyloxy radical. This interpretation however has recently been challenged by Zimmerman,[37] in favor of his original mechanism[25] involving competing pathways in the excited state. This issue in principle can be resolved with very fast LFP, and one such study involving Ph_2CHCl in acetonitrile has appeared from the Peters group.[16b] This study showed that radical and cation were fully formed within the 20 ps resolution of the equipment employed, with no indication of subsequent electron transfer. These results are indicative of direct heterolytic cleavage, although Peters cautioned that there was still uncertainty over the events at very short times (< 20 ps).

Another question is whether heterolysis can occur on the excited state energy surface to give initially an excited cation (adiabatic heterolysis). One case where this has been unequivocally demonstrated is the xanthenol system. As shown by Wan, Yates, and co-workers,[38] irradiation of **25** in neutral aqueous solution results in the fluorescence of both the excited alcohol **26** and the excited cation **27**. The concentration of ground state cation (**28**) in this solution is immeasurably small, and moreover irradiation at the λ_{max} of this cation results in no fluorescence. Thus the cation fluorescence must arise from of an excited state that has been produced through excitation of the alcohol.

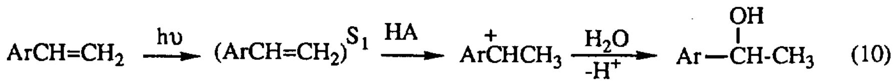


25 **26** **27** **28**

(9)

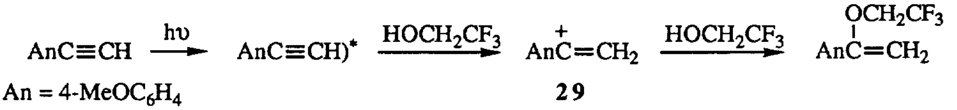
3.2 Photoprotonation of Alkenes and Alkynes

Styrenes undergo Markovnikov hydration when irradiated in aqueous acids, through a mechanism that is analogous to that of ground state hydration except that protonation occurs in the excited state.[39]



$$\text{ArCH=CH}_2 \xrightarrow{h\nu} (\text{ArCH=CH}_2)^{S_1} \xrightarrow{\text{HA}} \text{Ar}\overset{+}{\text{C}}\text{HCH}_3 \xrightarrow[-\text{H}^+]{\text{H}_2\text{O}} \text{Ar—}\overset{\text{OH}}{\overset{|}{\text{C}}}\text{H-CH}_3 \qquad (10)$$

With the aim to employ ns LFP to detect the intermediate cations we investigated the less nucleophilic solvents TFE and HFIP. To our surprise, photoaddition occurred with reasonable quantum yield without an added acid, that is, with solvent as the proton donor (see eq 1). The transient cations were indeed detected; for Ar = 4-methylphenyl and phenyl, this required HFIP,[40] whereas TFE suffices when Ar = 4-methoxyphenyl.[12,20] As shown in eq 11 we have also employed this technique to produce vinyl cations with phenylacetylenes as precursors.[20,21]

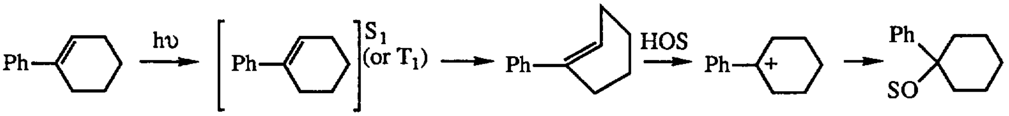


$$\mathrm{AnC{\equiv}CH} \xrightarrow{h\nu} \mathrm{AnC{\equiv}CH)^*} \xrightarrow{\mathrm{HOCH_2CF_3}} \mathrm{An\overset{+}{C}{=}CH_2} \xrightarrow{\mathrm{HOCH_2CF_3}} \mathrm{An\overset{OCH_2CF_3}{C}{=}CH_2} \qquad (11)$$

An = $4\text{-MeOC}_6\text{H}_4$

29

A second mechanism for solvent photoaddition is seen with 1-phenylcyclohexene (**30**) and involves protonation of the strained trans isomer **30** produced by cis → trans isomerization (in both the singlet and triplet excited states). In methanol, ns LFP studies carried out by Bonneau and co-workers have revealed a transient that was assigned to this trans intermediate.[41] The 1-phenylcyclohexyl cation (**31**) was not seen since its lifetime in this highly nucleophilic solvent is too short. In our experiments with HFIP, we found the reverse situation.[42] Now the trans alkene could not be observed since protonation was very fast. The low nucleophilicity of the solvent however provided a longer lifetime for the cation, and it was this intermediate that was observed.

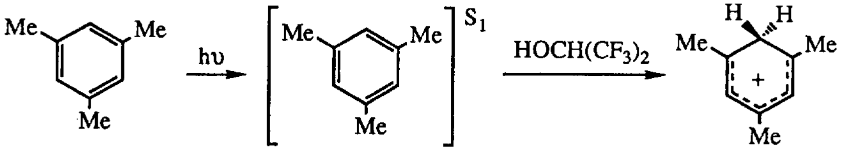


(12)

30 31 32

3.3 Photoprotonation of Aromatic Compounds

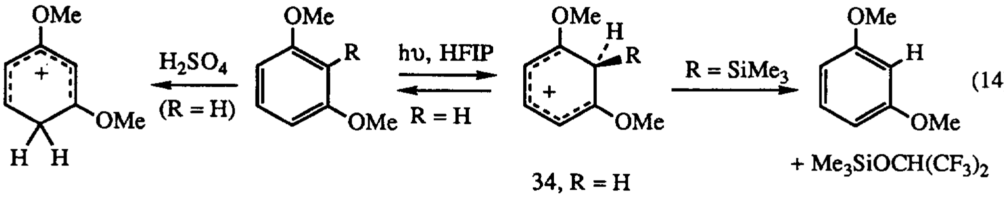
The possibility that excited aromatic compounds protonate in a manner similar to that of excited styrenes had been suggested by several observations, viz. photochemical H-D exchange,[43] fluorescence quenching by acids,[44] and ipso photosubstitution.[45] We employed HFIP to investigate this reaction, and indeed with the combination of low solvent reactivity and an acidic solvent OH group, cyclohexadienyl cations were observed with LFP.[42,46-50] As one example, irradiation of mesitylene in HFIP resulted in the transient cation **4**,[47] which was identified by comparison with the spectrum obtained on ground state protonation in strong acids.



(13)

4

Excited states and ground states of aromatic compounds can have substantially different distributions of electron density, and this gives rise to the potential for different site selectivities in their protonation.[43,47] 1,3-Dimethoxybenzene, as an example, undergoes both kinetic and thermodynamic protonation in strong acids at the 4-position. We observed photoprotonation in HFIP, but this is predominantly at the 2-position.[47] The initial indication of a difference was the transient spectrum, which showed an intermediate with cationic characteristics but with a λ_{max} at 410 nm (as compared to the cation **33** in strong acids at 315 nm). Confirmation that this transient was **34** was provided by experiments with $(CF_3)_2CHOD$ as the solvent, which showed exclusive H-D exchange at the 2-position.



(14)

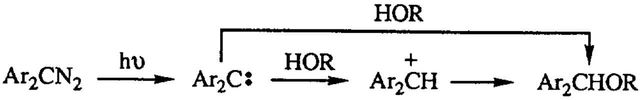
33

34, R = H
35, R = SiMe₃

Our experiments with silyl substituents at position 2 of 1,3-dimethoxybenzene provided the first examples of β-silyl-substituted cyclohexadienyl cations (e.g. **35**). In this case, the fate of the cation was desilylation, to produce 1,3-dimethoxybenzene and an ether (e.g. $Me_3SiOCH(CF_3)_2$). The detailed kinetic analysis possible with LFP established that the desilylation was a concerted bimolecular process involving the HFIP solvent displacing 1,3-dimethoxybenzene at silicon.[48]

3.4 Protonation of Photochemically-Generated Carbenes and Nitrenes.

A common reaction of singlet carbenes is insertion into OH bonds of alcohols to give ethers. With certain carbenes, this insertion appears to occur via two steps, with an initial protonation to give a carbenium ion. Direct evidence has been provided through LFP studies by Kirmse, Kilian, and Steenken, through the detection of diarylmethyl cations **38** following irradiation of diaryldiazomethanes **36**.[51]



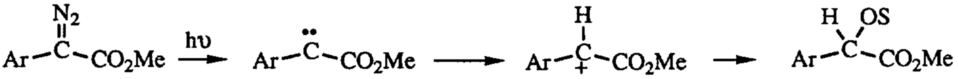
$$Ar_2CN_2 \xrightarrow{h\nu} Ar_2C\colon \xrightarrow{HOR} Ar_2\overset{+}{C}H \longrightarrow Ar_2CHOR \qquad (15)$$

$Ar_2C\colon \xrightarrow{HOR} Ar_2CHOR$

36 37 38 39

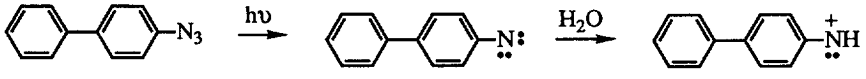
A later study by Scaiano and co-workers established that the precursor to the carbenium ion is indeed the singlet carbene **37**.[52] However quantum yields for formation of cation were not nearly as large as those for overall formation of **39**. Since collapse within the ion pair $Ar_2CH^{+}\cdot{}^{-}OR$ was excluded, the researchers suggested that parallel pathways involving protonation and direct insertion lead to the ether product from carbene **37**.

Schepp and Wirz have employed a similar route for the LFP study of α-carbomethoxybenzyl cations **42**. The parent and the 4-methyl derivative were observed upon irradiation of the diazo precursors **40** in HFIP, and the 4-methoxy analog was observed even in water.[53]



40 **41** **42** **43** (16)

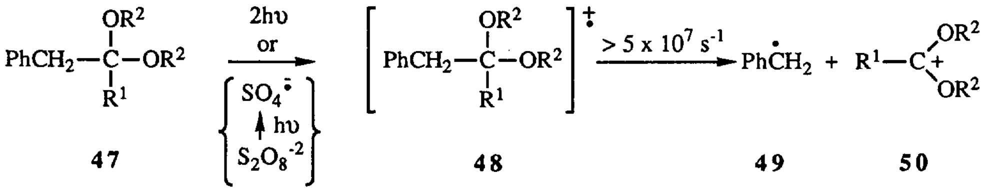
We have recently described an analogous approach for the LFP observation of nitrenium ions.[54] The 4-biphenylylnitrenium ion **46**, for example, was observed in aqueous solutions following irradiation of the azide **44**. The cation appears to form by rapid solvent protonation of an initially-formed singlet nitrene (e.g. **45**), although other routes such as protonation of excited **44** cannot be ruled out at this time .



44 **45** **46** (17)

3.5 Fragmentation of Photogenerated Cation Radicals

Cation radicals are obtained photochemically a number of ways — photoionization, one electron transfer to a photochemically-produced oxidant, or electron transfer within an excited donor-acceptor complex. There is good evidence from product analysis that one of the decay pathways open to the cation radical is C-C fragmentation, one fragment ending up as a radical and the second as a carbocation.[55] This reaction has been studied by LFP for benzylic derivatives **47**, with R_1 = H, alkyl, aryl and R_2 = alkyl (or ring).[8] The cation radicals **48** were produced in aqueous solution by biphotonic ionization or by oxidation with sulfate radical anion. The intermediates **48** could not be observed (by ns LFP), because they rapidly underwent fragmentation to the benzyl radical **49** and to the corresponding oxocarbocation **50**. Both of these species were detected as transients.



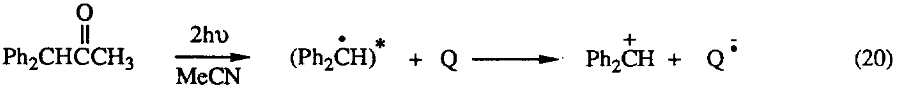
47 **48** **49** **50** (18)

3.6 Ionization of Excited Radicals

Faria and Steenken have shown that a neutral radical can be photoionized to the corresponding carbocation.[56] Their study involved the triphenylmethyl radical **52**, which was produced photochemically in several ways, including the two photon ionization/decarboxylation of triphenylacetate ion (**51**). With a second laser exciting shortly after the first, irradiation of this radical produced a transient triphenylmethyl cation **53**, identical in every respect to the same cation generated by a photoheterolysis route.

$$\underset{\mathbf{51}}{\mathrm{Ph_3C\text{-}CO_2^-}} \xrightarrow[(248\ \mathrm{nm})]{2h\nu,\ -e,\ -CO_2} \underset{\mathbf{52}}{\mathrm{Ph_3C^{\bullet}}} \xrightarrow[(308\ \mathrm{nm})]{h\nu,\ -e} \underset{\mathbf{53}}{\mathrm{Ph_3C^+}} \qquad (19)$$

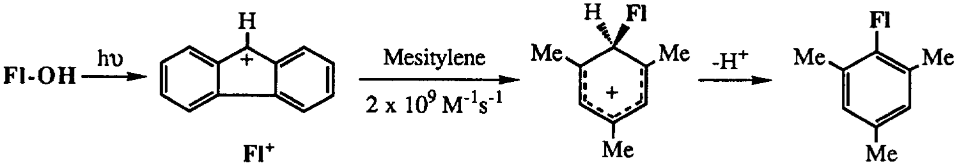
Scaiano and co-workers employed LFP techniques to generate excited diphenylmethyl radical and observed rate accelerations with electron acceptors (Q) such as p-dicyanobenzene. The LFP observation of the diphenylmethyl cation as the product established that the quenching took place by electron transfer (eq 20).[57]



$$\mathrm{Ph_2CH\overset{O}{\overset{\|}{C}}CH_3} \xrightarrow[\mathrm{MeCN}]{2h\nu} \mathrm{(Ph_2\dot{C}H)^*} + \mathrm{Q} \longrightarrow \mathrm{Ph_2\overset{+}{C}H} + \mathrm{Q^{\dot{-}}} \qquad (20)$$

3.7 Reactions of Photogenerated Cations with C=C

We have observed that carbocations formed in the weakly nucleophilic solvent HFIP can be trapped by added pi-nucleophiles to generate a second cation. As one example, the 9-fluorenyl cation obtained from the alcohol precursor reacts with added aromatic compounds to form products of electrophilic aromatic substitution.[58] This reaction is quite rapid and approaches diffusion control for electron rich aromatic compounds such as anisole and mesitylene. Moreover, with such derivatives, the cyclohexadienyl cation can be observed to grow in as the fluorenyl cation decays, so in the same experiment both cationic intermediates of a Friedel-Crafts alkylation are observed.

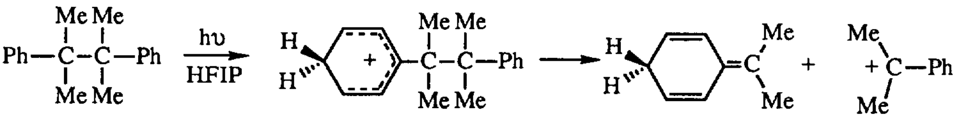


Fl⁺

(21)

3.8 Cleavage of Photogenerated Cations

A variation on this theme was found by Faria and Steenken for irradiation of biscumene (**54**) in HFIP.[59] The cumyl cation (**57**) was observed by LFP as a transient. The mechanism proposed for its generation involved protonation of excited biscumene, followed by rapid fragmentation of the derived cyclohexadienyl cation **55** so-formed to the cation and isocumene (**56**).



54 **55** **56** **57**

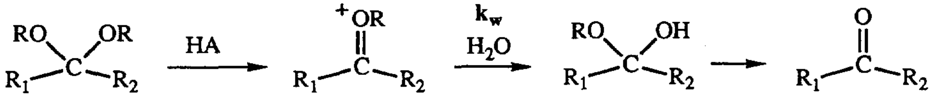
(22)

4. Carbocation Reactivities toward Solvent

We discuss in this section reactivities of carbocations with the solvent in which they are generated. The rate constants, unless otherwise noted, are given in units of s^{-1} and represent the first-order exponential decays as observed in the flash photolysis experiments.

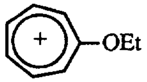
4.1 Hydration of Oxocarbocations

Oxocarbocations are intermediates of the hydrolysis of acetals, ketals and ortho esters (eq 23).

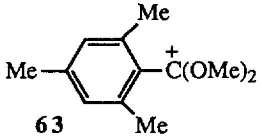


58 **59** **60** **61** (23)

The normal situation is for the cation-forming step (**58** → **59**) to be rate-limiting, although in a number of cases the third stage (**60** → **61**) has been found to be the slow step overall.[60] In our early studies of cation reactivity, we uncovered several systems where hydration of the cation (**59** → **60**) could be made rate-limiting.[61] These situations involved acetals and ortho esters that produced highly stabilized cations such as **62** and **63** that formed more rapidly than they reacted with water so that the cations were actually observed during hydrolysis.



62



63

Values of the rate constant k_w for the hydration of more reactive oxocarbocations are given in Table 3. Rate constants for the tri- and di-alkoxy cations shown are based on direct measurement, with values for the monoalkoxy derivatives estimated by use of azide as a "clock".

Table 3. Rate Constants k_w (s^{-1}) for the Decay of Oxocarbocations in Water (20 °C).

Cation	R = Me	R = Et	R = iPr	Ref.
$(RO)_3C^+$	1.4×10^3	6.3×10^1	1.0×10^0	63
$MeC^+(OR)_2$	1.3×10^5	2.8×10^4	2.0×10^3	8,64
$HC^+(OR)_2$		2.0×10^7	2.2×10^6	8
$PhC^+(OR)_2$	1.3×10^5	4.2×10^4		8,65,66
$PhC^+Me(OR)$	5×10^7			62
$PhC^+H(OR)$	2×10^9			62
$Me_2C^+(OR)$	1×10^9			62
$EtC^+H(OR)$		2×10^{10}		62

As expected, alkyl and phenyl groups attached to the C^+ center are "kinetically" stabilizing, as are additional alkoxy groups. These effects are cast in quantitative terms in Figure 2, in a plot of log k_w versus the sum of the σ^+ constants for the groups attached to the central carbon, a correlation suggested by Kresge and coworkers.[67] Clearly a single relationship is not evident: cations bearing H, alkyl, and alkoxy substituents produce one correlation line with $\rho^+ = 6.1$, whereas cations with one phenyl produce a second line with similar slope (5.5), but with lower inherent reactivity. The single points for Ph_2CH^+ and Ph_3C^+ suggest that this trend continues with additional phenyl substitution.

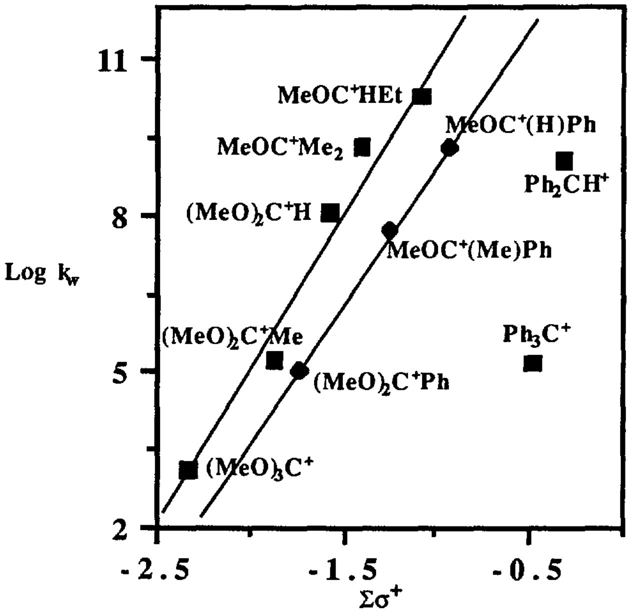
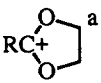
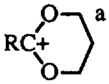
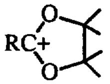
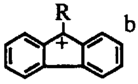
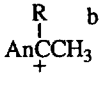


Figure 2. Correlation of log k_w with the sum of σ^+ constants for groups attached to central carbon.

As seen in Table 3, k_w varies with the O-alkyl group. In general one EtO decreases k_w by a factor of 3 relative to MeO, with a further factor of 3 when EtO is replaced by iPrO. These effects are relatively independent of cation type and are roughly additive for multiple substitutions. A reasonable correlation with the Taft σ^* parameter of the alkyl group is found, with a slope of 5 similar to that of the σ^+ correlations in Figure 2. The correlation with the steric parameters E_s is poor. These parameters predict a larger difference between Et (E_s = -0.07) and iPr (E_s = -0.49) than between Me (E_s = 0) and Et (E_s = -0.07), but this difference does not show up in the k_w values.

Alkyl substitution at the formal C^+ center results in reactivity changes that do not follow either the electronic or the steric order. As shown in Table 4, acyclic dialkoxycarbocations show little difference in reactivities for a series of straight chain substituents (Me, Et, nPr, nBu), whereas branched substituents (iPr, sBu, tBu) actually *increase* the rate. For cyclic analogs rate constants are essentially independent of the nature of the substituent. The best explanation for these effects invokes differential solvation, with the cations being stabilized by solvation in the order Me > Et > iPr > tBu, the opposite direction to the electronic/steric effect, so that differences in reactivity end up being small and variable.

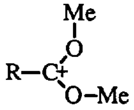
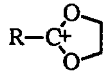
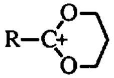
Table 4. C-Alkyl Effects on the Relative Reactivities ($k_w(R):k_w(Me)$) of Cations.

R	$R\overset{+}{C}(OMe)_2$ [a]	$R\overset{+}{C}(OEt)_2$ [a]	 [a]	 [a]	 [a]	 [b]	 $An\overset{R}{\underset{+}{C}}CH_3$ [b,c]
Me	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Et	1.2	1.0	1.0	1.1	1.5	1.6	0.6
nPr	0.9	0.8		0.9			
nBu	1.2			1.0			
iPr	5.8	2.4	1.1	1.3	1.7	0.5	0.2
sBu	4.6			0.9			
tBu	4.8	2.3	0.7	1.1	1.1	0.1	1.0

[a] Ref. 8. [b] Ref. 21, rate constants for reaction with TFE. [c] An = 4-MeOC$_6$H$_4$.

Rate constants for cyclic oxocarbocations relative to an acyclic analog are summarized in Table 5. A 1,3-dioxolan-2-ylium ion (i.e. a 5-cycle) is more reactive than a 1,3-dioxan-2-ylium ion (i.e. a 6-cycle), and when substituted with a 2-methoxy or 2-methyl group, the two cyclic cations are more reactive than the acyclic dimethoxy analog. With a 2-phenyl substituent however, the two cyclic cations are less reactive than the acyclic analog, although the 5-cycle vs 6-cycle difference remains. Cations such as PhC$^+$(OMe)$_2$ are not fully planar,[68] owing to interaction of the phenyl ortho hydrogens and the Z-alkyl group in the E,Z conformation adopted by this system (see first structure in Table 5). This steric interaction is not present in the cyclic cations, and thus the phenyl group can exert its full stabilizing effect through charge delocalization.

Table 5. Comparison of Reactivities of Cyclic and Acyclic Oxocarbocations (Refs. 8, 64).

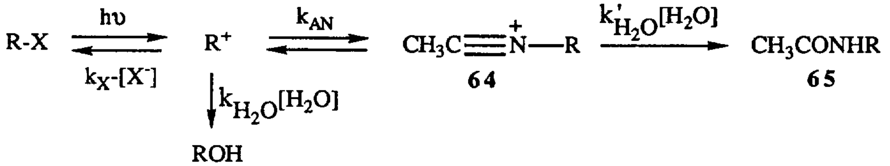
	R = MeO		R = Me		R = Ph	
	k_w (s^{-1})	$k_{cyc}:k_{acyc}$	k_w (s^{-1})	$k_{cyc}:k_{acyc}$	k_w (s^{-1})	$k_{cyc}:k_{acyc}$
	1.4×10^3	1	1.3×10^5	1	9.9×10^4	1
	2.7×10^4	19.3	1.4×10^6	10.8	3.0×10^4	0.3
	4.6×10^3	3.3	1.4×10^5	1.1	4.0×10^3	0.04

4.2 Carbenium Ions — General Reactivities and Solvent Effects.

Table 6 lists selected examples of cations that have been studied by flash photolysis, along with their k_S values. As discussed in Sect. 2.2, the solvent ROH has a profound effect on cation lifetime. Qualitatively the order follows the nucleophilicity parameters N or N_{OTs} derived from analysis of solvent effects on solvolysis reactions.[69] Quantitatively the data are insufficient to demonstrate an exact correlation. It would appear that effects on the fully formed cations are somewhat larger than predicted on the basis of these N values.

In contrast to the effect of ROH, adding acetonitrile to water has little effect. Rate constants actually increase slightly despite decreasing water concentration, but the effect amounts to only about a 1.2-fold increase in k_S from pure water to ~80% by volume acetonitrile.[13] A consequence is that second-order rate constants calculated as $k_S[H_2O]$ are not constant, and in fact change by over an order of magnitude.

The cation lifetime does increase in mixtures above 80% acetonitrile, and the behavior becomes complex as pure acetonitrile is approached.[13,18] The situation here can be explained as follows (see eq 24).



$$\begin{tikzcd} \mathrm{R{-}X} \arrow[r, shift left, "h\nu"] & \mathrm{R^+} \arrow[l, shift left, "k_X\text{-}[X^-]"] \arrow[r, shift left, "k_{AN}"] \arrow[d, "k_{H_2O}[H_2O]"] & \mathrm{CH_3C{\equiv}\overset{+}{N}{-}R} \arrow[l, shift left] \arrow[r, "k'_{H_2O}[H_2O]"] & \mathrm{CH_3CONHR} \\ & \mathrm{ROH} & \mathbf{64} & \mathbf{65} \end{tikzcd}$$

(24)

Cations such as Ar_2CH^+ bearing at least one 4-MeO do not react with acetonitrile, and they decay with complex kinetics attributable to reaction with the anion released in the photogeneration, and to trace amounts of water. Less stable cations such as Ph_2CH^+ do decay with single exponential kinetics because they react with acetonitrile to form a nitrilium ion (e.g. **64**). Interestingly, the cation-derived products observed on irradiation of Ph_2CHCl in acetonitrile are **65** and diphenylmethanol in a 1:6 ratio.[18] The carbinol, however, cannot be the product of the primary reaction, since the cation is far more short-lived than can be explained by its reaction with the trace water present. This analysis leads to the conclusion that although the carbenium:nitrilium equilibrium lies to the nitrilium side, the reaction is reversible, and the products are derived mainly from the carbenium ion. Interestingly, the solvent acetonitrile is appreciably nucleophilic, and exhibits a rate constant k_{AN} very similar to the rate constant k_{TFE} observed in trifluoroethanol solvent.

Many experiments involving carbocations are carried out with added salts present, for example to maintain ionic strength in competition experiments. These salts do have a significant retarding effect on the rate of cation decay in the solvent (and indeed on the rate of reactions with added nucleophiles).[10,27] As one example, we observed that k_{obs} for the decay of the triphenylmethyl cation in 1:2 acetonitrile:water was decreased by a factor of 2 on addition of 0.2 M $NaClO_4$.[10] This effect is presumably caused by the lowering of the solvent activity by solvation of the added ions, although a detailed theoretical analysis has not been carried out. As a cautionary note, halide salts such as NaCl usually result in rate accelerations. This outcome is caused by the halide reacting as a nucleophile, and is not a salt effect.

Table 6. Solvent Reactivities of Selected Carbocations at 20 °C.

Cation	k_w,^{a} s^{-1}	k_{TFE}, s^{-1}	k_{HFIP}, s^{-1}	Ref.
(66) $(4\text{-MeOC}_6H_4)_3C^+$	1.0×10^1	—	—	13
(53) $(C_6H_5)_3C^+$	1.5×10^5	—	—	10,13
(67) $(4\text{-CF}_3C_6H_4)_2(C_6H_5)C^+$	8.8×10^6	—	—	13
(10) $(4\text{-MeOC}_6H_4)_2CH^+$	1.0×10^5	1.4×10^1	—	12,13
(68) $(4\text{-MeOC}_6H_4)(C_6H_5)CH^+$	2.0×10^6	1.2×10^3	—	12,13
(69) $(4\text{-MeC}_6H_4)_2CH^+$	3.2×10^7	2.4×10^4	—	12,13
(1) $(C_6H_5)_2CH^+$	1.3×10^9	3.2×10^6	$\sim 1 \times 10^1$	12-14
(70) 9-Phenyl-9-xanthylium	2.3×10^1	—	—	7
(71) 9-Xanthylium	2.3×10^4	—	—	7
(72) 9-Phenyl-9-fluorenyl	1.5×10^7	1.5×10^4	—	29
(73) 9-Methyl-9-fluorenyl	—	8.6×10^6	—	30
(3) 9-Fluorenyl	$>4 \times 10^{10}$	8×10^8	2×10^4	15,17
(74) $4\text{-MeOC}_6H_4C^+(CH_3)_2$	$\sim 4 \times 10^7$	1.6×10^4	—	40
(14) $4\text{-MeOC}_6H_4C^+HCH_3$	—	3.9×10^5	—	20,40
(75) $4\text{-MeOC}_6H_4CH_2^+$	—	4.3×10^6	3×10^2	40
(76) $4\text{-MeC}_6H_4C^+(CH_3)_2$	—	1.0×10^7	6×10^2	40
(77) $4\text{-MeC}_6H_4C^+HCH_3$	—	—	5×10^4	40
(78) $4\text{-MeC}_6H_4CH_2^+$	—	—	2×10^6	40
(79) $C_6H_5C^+(CH_3)_2$	—	—	9×10^3	40
(80) $C_6H_5C^+HCH_3$	—	—	6×10^5	40
(18) $4\text{-MeOC}_6H_4C^+(CF_3)_2$	1.0×10^7	6.6×10^4	—	32
(81) $4\text{-MeOC}_6H_4C^+HCF_3$	—	9.3×10^5	—	32
(82) $4\text{-MeC}_6H_4C^+HCOOCH_3$	—	—	3.0×10^5	53
(83) 2,4,6-Trimethoxybenzenonium	5.8×10^5	7×10^2	—	46
(34) 2,4-Dimethoxybenzenonium	—	—	2×10^3	47
(84) 2-Methoxybenzenonium	—	—	7×10^5	21
(4) 2,4,6-Trimethylbenzenonium	—	—	1×10^5	46
(29) $4\text{-MeOC}_6H_4C^+{=}CH_2$	—	1.3×10^6	—	20,21
(85) $4\text{-MeOC}_6H_4C^+{=}CMe_2$	—	2.3×10^5	—	21
(20) $4\text{-MeOC}_6H_4C^+{=}CPh_2$	—	1.4×10^4	—	21

[a] Usually 4:1 or 3:1 water:acetonitrile.

4.3 Correlation of log k_w and pK_R

Cation hydration is the forward reaction of the pseudo acid-base equilibrium of eq 25, with a corresponding equilibrium constant K_R as defined in eq 26.

$$R^+ + H_2O \underset{k_H}{\overset{k_w}{\rightleftharpoons}} ROH + H^+ \qquad (25)$$

$$K_R = \frac{k_w}{k_H} = \frac{[ROH][H^+]}{[R^+]} \qquad (26)$$

A plot of log k_w vs pK_R therefore represents a linear free energy correlation where the rate constant and the equilibrium constant refer to the same reaction. Such plots have been discussed on several occasions in the past based upon data for highly stabilized cations.[2,70] With flash photolysis providing k_w for more reactive cations, a plot covering a range of 23 pK_R units now can be constructed (Figure 3). As suggested by Taft,[70a] (and in a slightly different context by the Richard group),[71] a single correlation does not exist. The data separate into families comprising structurally related ions with a decreasing order of intrinsic reactivity as follows: 9-unsubstituted-9-xanthylium ~ cyclic dialkoxycarbocation > phenyltropylium > diarylmethyl ~9-arylxanthylium > triarylmethyl ~ 9-aryl-9-fluorenyl.

The lines in Figure 3 have been drawn with the assumption that there is a linear relation within each family. There is scatter however that may mask a gentle downward curvature. Such curvature is most apparent on use of the combined data for triarylmethyl and 9-aryl-9-fluorenyl cations,[29] and is consistent with the transition state becoming more cation-like as the reactivity of the cation increases. However, even if there is curvature, it is small. The quantity d(log k_w)/dpK_R is remarkably unchanged (-0.6 ± 0.1) for a very large change in pK_R.

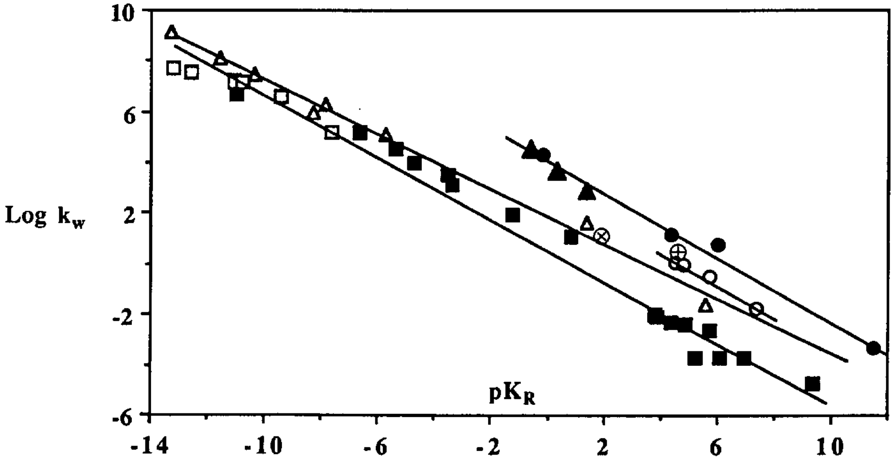


Figure 3. Rate-equilibrium correlation: triarylmethyl (■); diarylmethyl (△); 9-aryl-9-fluorenyl (□); 9-unsubstituted-9-xanthylium (●); aryltropylium (o); cyclic phenyldialkoxycarbocations (▲); 9-phenylxanthylium (⊗); parent tropylium (⊕). Lines have been drawn based upon linear regression. Dialkoxycarbocations + 9-unsubstituted xanthylium ions (slope = -0.63); aryltropylium, (-0.68); diarylmethyl (-0.54); triarylmethyl + 9-aryl-9-fluorenyl (-0.60).

4.4 Effect of Aromatic Substituents

In considering the effect of aromatic substituents on the reactivities of benzylic-type cations, we initially anticipated a reasonable correlation with σ^+, the parameter based on cumyl chloride ionization and developed for reactions that form benzyl cations. However, plots of log k_w vs σ^+ were not linear and showed significant deviations of the points for para π donors such as MeO and Me_2N.[13] These deviations moreover were in the direction that indicated that these substituents have kinetic stabilizing effects on the fully-formed cation greater than indicated by σ^+. There were in fact good correlations with σ^{C+}, a parameter due to Brown and co-workers based on ^{13}C NMR chemical shifts of benzylic-type cations measured under stable ion conditions.[72] Log k_H values on the other hand did correlate with σ^+. This outcome was not surprising since this rate constant refers to an acid-catalyzed solvolysis and hence is much more similar to the reaction used to define σ^+.

This effect was also seen through application of the two parameter Yukawa-Tsuno equation.[73] This is shown in eq 27 and constitutes a Hammett plot with a second parameter r^+. The equation was introduced for reactions that have interactions of π donors with partial positive charge that lie between those of the two reactions that define the σ and the σ^+ scales. The parameter r^+ was intended to fall between 0, a situation that would correspond to a fit to σ, and 1, where the fit is to σ^+. However, for the equilibrium hydration of benzylic-type cations, log k_w (and in some cases pK_R) requires r^+ values significantly greater than 1 (see Table 7). This is again indicating that σ^+ underestimates the stabilizing effects of π donors in the fully-formed cation.

$$\log (k/k_o) = \rho\{\sigma + r^+(\sigma^+ - \sigma)\} \qquad (27)$$

Application of the two-parameter equation introduced by Jencks and co-workers provided further insight.[4c] This relationship is shown in eq 28 and separates substituent effects into a polar or inductive contribution described by ρ_n and a resonance contribution described by ρ_r.

$$\log (k/k_o) = \rho_n\sigma + \rho_r(\sigma^+ - \sigma) \qquad (28)$$

For reactions where both rate and equilibrium constants are known, what Jencks defines as 'normalized' ρ values (ρ_{norm}) can be calculated by dividing the ρ value obtained for the fit to the rate constant by the corresponding ρ for the fit to the equilibrium constant (i.e. $\rho_n(k_w)/\rho_n(K_R)$ or $\rho_r(k_w)/\rho_r(K_R)$). Since the value of $\rho(K_R)$ measures the overall change in substituent effect on proceeding from reagent to product, ρ_{norm} measures the fraction of that change that has occurred when the transition state has been reached. These values are also provided in Table 7 and show that in the direction of cation hydration, ρ_n(norm), the fractional change in the polar effect is significantly less that 0.5, whereas ρ_r(norm), the fractional change in the resonance effect, is greater than 0.5. The inequality in the two values shows that there is imbalance in the reaction coordinate in terms of the two modes of interaction of substituents with the positive charge. When comparing the transition state to starting cation, the substituent "sees" a much larger fractional decrease in positive charge in its resonance interaction as compared to the decrease that it "sees" through the polar interaction.

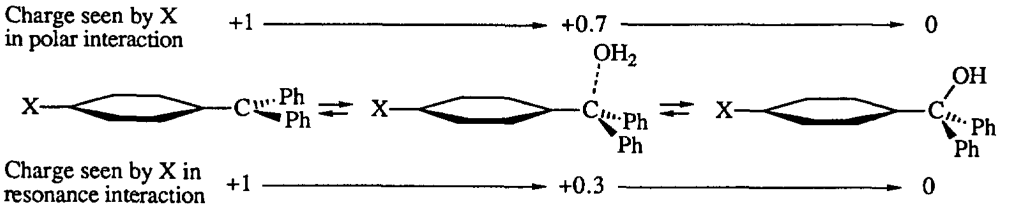
Table 7. Results of Fitting to Two Parameter Equations 27 and 28.

Parameter	Ar-$^+$CHCH$_3$[a]	Ph$_2$C$^+$-Ar[b]	9-Ar-9-fluorenyl[c]
$r^+(k_w)$	2.3	3.6	2.2
$r^+(k_H)$	0.9	0.7	0.2
$r^+(K_R)$	1.4	1.6	0.7
$\rho_n(\text{norm}) = \rho_n(k_w)/\rho_n(K_R)$	0.36	0.33	0.23
$\rho_r(\text{norm}) = \rho_r(k_w)/\rho_r(K_R)$	0.61	0.72	0.76

[a] Calculated using data of Jencks and Richard, ref. 4c, except for the point for p-dimethylamino, where a rate constant directly measured by LFP[32] has been employed. [b] Ref. 13. [c] Ref. 29.

This effect is illustrated schematically for the triarylmethyl system in eq 29. In simple terms, the starting cation bears a full positive charge that interacts with the substituent X, and the product alcohol has no charge. When the reaction proceeds from cation to transition state only 30% of this positive charge has disappeared when the polar interaction is used as the measure, but 70% of the charge has disappeared in terms of the resonance effect. Jencks and Richard were the first to observe such an imbalance[4c] and explained it by a model in which the partial bond to the incoming water in the transition state localizes the fractional positive charge remaining on the formal C$^+$ carbon. Another way of looking at this is through the change in hybridization that takes place at this carbon, and that results in less delocalization of the positive charge through the π system to the substituent. Whatever the explanation, the outcome is that as water adds to the cationic center, the resonance interaction of X with the positive charge initially decreases at a much greater rate than does the polar interaction.

This model also accounts for σ$^+$ underestimating the resonance interaction in the fully-formed cation, since in the reverse direction where the cation arises from the alcohol, only 30% of this interaction has developed when the transition state is reached. If a similar picture is true for cumyl chloride ionization, the rate constants for this ionization, and the σ$^+$ parameters derived from these, do not reflect the full resonance interaction in the cation itself.



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4.5 Effect of Alkyl Groups

As one would expect, substitution of a methyl group for hydrogen results in a decrease in the rate constant, or a "kinetic stabilization." As shown in Table 8, factors of 10 - 100 have been observed for benzylic-type cations. This factor depends somewhat on the other two substituents, with the trend that the more they stabilize the cation, the smaller the effect of the methyl group. An exception is seen in the series benzyl, phenethyl, cumyl where the second methyl substituent has approximately twice the effect of the first. This outcome is most likely related to a non-additive steric effect, with the cumyl cation being quite crowded and thus relatively more resistant to solvent addition. One surprising result, as shown by the last two entries, is that methyl substitution has an especially large influence on the (highly stabilized) dialkoxycarbocations.

Table 8. Kinetic Stabilizing Effect of Methyl versus Hydrogen for Reactivities of Carbenium Ions and Dialkoxycarbocations.

Cation	$k_s(R = H)/k_s(R = Me)$	Solvent	Reference
Ph_2C^+-R	21	TFE	12
9-R-9-fluorenyl	93	TFE	21
4-$MeOC_6H_4CMe^+$-R	24	TFE	40
4-$MeOC_6H_4CH^+$-R	11	TFE	40
4-$MeC_6H_4CMe^+$-R	83	HFIP	40
4-$MeC_6H_4CH^+$-R	40	HFIP	40
$(EtO)_2C^+$-R	7.1×10^2	W	8
$(iPrO)_2C^+$-R	1.1×10^3	W	8

The effects of variation of the alkyl group in two cations are shown in the last two columns of Table 4, alongside data for dialkoxycarbocations. As with the latter species, effects are small and variable. For example, the fluorenyl cation with a 9-t-butyl substituent is less reactive than the methyl analog, but the methyl and tert-butyl cations in the p-anisylethyl series have almost equal rate constants. Clearly, the story with respect to alkyl substitution in carbocations is far from complete, and more studies are required for a satisfactory understanding.

Also of interest is the lack of kinetic destabilization associated with substitution of electron withdrawing groups. This effect was originally observed by Richard and co-workers through use of the "azide-clock" method for reactions involving CF_3-substituted cations.[74] In collaboration with the Richard group we later verified the effect through direct measurement. For example, the p-methoxycumyl cation decays in TFE with $k_{TFE} = 1.6 \times 10^4$ s^{-1},whereas the cation 4-$MeOC_6H_4C^+(CF_3)_2$ where both methyl groups are replaced by CF_3 groups is only slightly more reactive, with $k_{TFE} = 6.4 \times 10^4$ s^{-1}. Flash photolysis studies by other researchers have shown similarly small effects on substituting the $COOCH_3$ group (e.g., in Table 6 compare **82** and **77**).[31,53] These substitutions do result in large decreases in thermodynamic stability.[74] Several explanations[53,74] have been advanced for the very small kinetic effect, and the reader is referred to the original papers for these discussions (see especially ref. 74c).

5. Carbocation Reactivities toward Added Nucleophiles

5.1 The N_+ Correlation

For relatively stable cations reacting with nucleophiles, Ritchie[1,2] proposed that the data could be satisfied by the simple relation of eq 30.

$$\log (k/k_o) = N_+ \qquad (30)$$

In this equation k and k_o are rate constants for the combination of a cation with a given nucleophile and a reference nucleophile respectively, and N_+ is a parameter dependent on the nucleophile and the reaction conditions. A feature of this equation is the implication that the relative reactivity of a given pair of nucleophiles depends only on their two N_+ values and is independent of the nature of the electrophile. In other words the selectivity does not depend on the reactivity of the electrophile. Proposals have been made that an electrophile parameter should be included,[75] although Ritchie has argued that this was unnecessary.[76] The Ritchie equation is based on heteroatom nucleophiles — oxyanions, thiolates, amines — reacting mainly in water with cations such as triarylmethyl, tropylium, and diazonium ions. As noted in the Introduction, all of these cations are highly stabilized. Flash photolysis obviously provides the opportunity to study more reactive cations, and this has been done, for example, with the parent triphenylmethyl cation[10] and the xanthylium ion.[7] In these cases plots of log k versus N_+ clearly have slopes less than unity (0.33 for the former and 0.65 for the latter) indicating a selectivity lower than that observed with the highly stabilized cations. Decreased selectivity with increased cation reactivity has also been observed in competition studies,[77] and in a flash photolysis study of amines reacting with triarylmethyl cations.[78] The conclusion is that for nucleophiles combining with reactive cations, the simple Ritchie relation of eq 30 does not hold.

5.2 Azide Ion

Azide ion was originally employed as an added nucleophile in solvolysis reactions to probe mechanism. For reactions proceeding by way of cation intermediates a typical, and widely cited, reactivity:selectivity relationship emerged. The selectivity $k_{Az}:k_s$ (as measured by the competition kinetics method) was found to decrease with decreased stability of the cation (as measured by k_{ion} for its formation).[79]

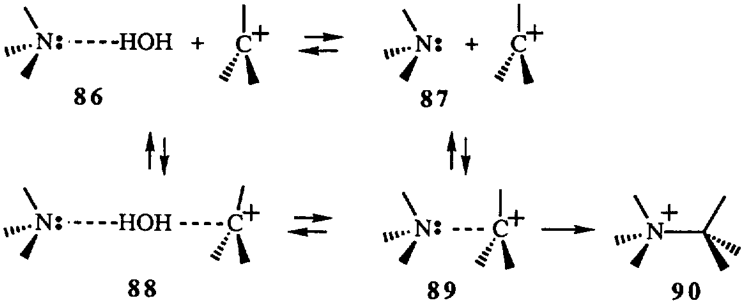
$$\begin{tikzcd} & & ROS \\ RX \arrow[r, "k_{ion}"] & R^+ \arrow[ur, "+SOH,-H^+;\ k_s"] \arrow[dr, "+N_3^-;\ k_{Az}"'] & & (31) \\ & & RN_3 \end{tikzcd}$$

Suggestions were then made that this adherence to the reactivity-selectivity principle was associated with the azide reaction being encounter controlled.[4b,4c,80] Thus, as cation reactivity increased (and the solvent rate constant k_s also increased), k_{Az} remained unchanged since it had already reached its limit. The result is a decrease in $k_{Az}:k_s$. Jencks et al. then took $k_{Az} = 5 \times 10^9\ M^{-1}s^{-1}$ as the diffusion limit, and from the rate constant ratios they calculated absolute rate constants for the solvent and other nucleophiles.[4b,c] This approach uses azide as a "clock" to obtain the rate constant for the other nucleophile. With flash photolysis, the validity of this approach can be tested since the absolute rate constants can be measured. We have done this through investigations with a series of triarylmethyl and diarylmethyl cations in aqueous acetonitrile,[19] and with p-methoxybenzyl cations in TFE:water mixtures.[32] Within each set a limit is reached where k_{Az} attains a maximum constant value, while at the same time k_s continues to change in the expected manner. The limiting k_{Az} values are in the vicinity of 10^{10} $M^{-1}s^{-1}$, the numbers being dependent on solvent composition and to a certain extent on cation structure. Theoretical models that calculate rate constants for diffusional encounter reproduce the experimental numbers, provided that non-productive encounters, i.e. collisions that do not result in combination, are included.[19]

The conclusion is that the "azide clock" method using $k_{Az} = 5 \times 10^9$ $M^{-1}s^{-1}$ does produce excellent estimates of rate constants for other nucleophiles, provided that the cation is reactive. "Reactive" in this sense would correspond to a cation with a solvent rate constant $>10^5$ s^{-1} (or a k_{Az}:k_s ratio $< 10^5$ M^{-1}).

5.3 Primary Amines

Our study of primary amines reacting with diarylmethyl cations revealed an interesting role of solvent.[78] When examined in 100% acetonitrile, these reactions were fast, with k(RNH_2) approaching the encounter limit. There was a small dependence on amine structure, and this was in the expected direction of k(RNH_2) increasing with increasing amine basicity. As water was added to the solvent, k(RNH_2) decreased regardless of the nature of RNH_2, but the effect was more pronounced the more basic the amine. By the time highly aqueous solvents were reached, reactivity no longer paralleled basicity. For example, for some cations k(n-propylamine) was smaller than k(2-cyanoethylamine) despite the lower basicity of the cyano-substituted amine. Such inversions of amine reactivity had been observed previously in competition studies,[81] and also with phosphoryl electrophiles.[82] The explanation involves a requirement for formation of an encounter complex **89** in which the amine-water hydrogen bond is broken prior to the actual C-N bond forming step (eq 31).



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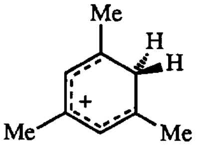
Two mechanisms for the formation of **89** can be envisaged. The first involves encounter of the cation with the free amine **87** in equilibrium with hydrogen-bonded amine **86**; and the second involves the sequence **86** → **88** → **89**, in which the hydrated amine encounters the cation, and the water molecule must then move out of the way. The former mechanism likely applies in the acetonitrile-rich solutions where there are significant concentrations of free amine. Data for all solvent compositions were fit satisfactorily by this model,[78] although the second route cannot be ruled out unambiguously for the water-rich solutions.

5.4 Halides

The importance of hydration of the nucleophile is also seen in data for the combinations of halide ions with the retinyl cation[83] and with some diarylmethyl cations.[84] In 100% acetonitrile these reactions are very fast, with rate constants near or at the diffusion limit. The diphenylmethyl cation, for example, reacts at the encounter limit ($k(X^-) = 2 \times 10^{10}\ M^{-1}s^{-1}$) with all four halides.[85] With the addition of water however, the rate constants decrease in a monotonic fashion with increasing water content. The retarding effect follows the order of anion hydration ($F^- > Cl^- > Br^- > I^-$) and is consistent with the hydrated halide being less reactive. A similar dependence on water concentration is observed with other anions such as acetate.[84] More study is required to sort out the quantitative details of solvation by water (and by other protic solvents), but many such investigations should now be possible with flash photolysis.

5.5 Cyclohexadienyl Cations

Table 9 summarizes trends observed with cyclohexadienyl cations **4** and **91** and compares them with the benzylic-type cations **92** and Ph_2CH^+ (**1**) and the vinyl cation **93**. Each of **92**, **1**, and **93** react with alcohols by C-O bond formation and exhibit the reactivity order MeOH > EtOH > iPrOH > tBuOH, a trend likely associated with the steric bulk of the nucleophile. With **4** and **91** however, there is little change across the series. The cyclohexadienyl cations react by deprotonation, and the conclusion is the kinetic basicity of the simple alkanols is about the same. The importance of basicity is reinforced by data for ethers reacting with **4**. Tetrahydrofuran, whose basicity should be similar to methanol, indeed reacts at about the same rate; the less basic 1,4-dioxane reacts significantly more slowly.[44] One interesting feature is the large rate constant observed for bromide ion. The weak basicity of bromide suggests that this may be reacting by nucleophilic addition to the ring to form a cyclohexadiene, and not by deprotonation.



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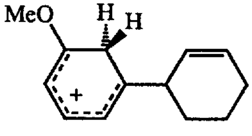

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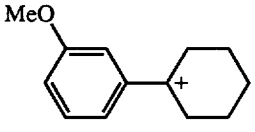

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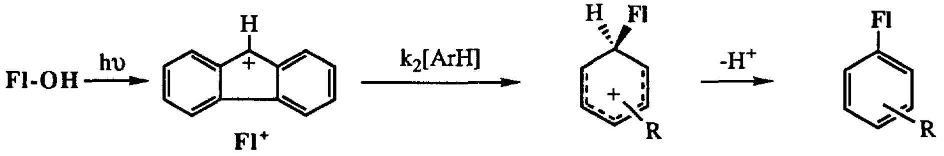
Table 9. Relative Second-Order Rate Constants for Cation Reactions with Alcohols and Bromide

Cation, solvent	MeOH	EtOH	iPrOH	tBuOH	Br$^-$	Ref.
2,4,6-Trimethylbenzenonium (**4**) (HFIP)	1.00	0.71	0.83	0.50	1.5 x 10^2	46
2-Methoxy-6-cyclohexenylbenzenonium (**91**) (HFIP)	1.00	1.27	1.20	1.13	6.7 x 10^1	42
1-(3'-Methoxyphenyl)cyclohexyl (**92**) (HFIP)	1.00	0.57	0.16	0.13	1.2 x 10^3	42
Ph_2CH^+ (**1**), AN	1.00	0.71	0.26	0.058	1.7 x 10^1	85
$An_2C{=}C^+An$ (**93**), AN	1.00	0.84	0.32	0.047		33b

5.6 Carbon Nucleophiles — Aromatic Compounds

In HFIP, benzene and other aromatic compounds compete with the solvent for cations, making it possible to observe directly the electrophilic step in a Friedel-Crafts alkylation. Our most extensive experiments have involved the 9-fluorenyl cation, obtained photochemically from 9-fluorenol (eq 33).[65,86] Product analysis upon irradiation in HFIP in the presence of aromatic compounds shows a pattern typical of electrophilic aromatic substitution. For example, Fl^+ reacted with toluene to give a 5:5:90 ratio of ortho:meta:para-(9'-fluorenyl)-toluenes; and a competition experiment with benzene led to a partial rate factor for the para position of 2.0×10^2. In the LFP experiments, first-order rate constants for the decay of Fl^+ increased in a linear fashion with the concentration of the added aromatic. The slopes of these plots provided directly the rate constants k_2.



(33)

The partial rate factor for para substitution in toluene obtained from these k_2 values for toluene and benzene is 1.8×10^2, in excellent agreement with the number measured by the competition method. This represents the first time that such a comparison has been possible for a Friedel-Crafts reaction. Rate constants k_2 for mono-substituted benzenes range from $3.3 \times 10^5\ M^{-1}s^{-1}$ for benzene itself to $1.7 \times 10^9\ M^{-1}s^{-1}$ for anisole, with a plot of log k_2 versus σ^+ linear with a slope of -5.0. These rate constants, however, are clearly approaching a plateau by the time that anisole is reached. This levelling off can be seen particularly with methylated benzenes, where k_2 lies between 1×10^9 and $2 \times 10^9\ M^{-1}s^{-1}$ for di-, tri-, tetra-, and penta-substituted derivatives. Olah (and others) have suggested that transition states in aromatic substitutions can resemble either the σ-complex or a π-complex.[87] Very fast reactions have been assumed to correspond to the latter situation and to lead to low intermolecular selectivity and ortho:para ratios with toluene near 2:1. This concept however does not apply to the 9-fluorenyl cation. Its reactions with aromatic compounds are clearly very fast, approaching diffusion control, and yet there is still significant intermolecular and intramolecular selectivity.

5.7 Carbon Nucleophiles — Alkenes

Mayr and co-workers have reported extensive kinetic studies of the reactions of alkenes with diarylmethyl cations, methoxycarbenium ions, and aldehyde-Lewis acid complexes, and have provided a comprehensive review.[88] Within a certain alkene series (for example, terminal alkenes) rate constant ratios for a given pair of cations are relatively constant over a range of alkene reactivities; i.e. there is constant selectivity similar to that expressed by eq 30 in section 5.1. This behavior, however, does not apply universally. Considering the data alongside those for the highly stabilized cations, for metal coordinated π electron systems,[89] and even for hydride transfers to cations, a reasonable fit was found to equation 34,

$$\log k = s(E + N) \qquad (34)$$

where k is the rate constant for a given electrophile and nucleophile, E and N are the electrophilicity and the nucleophilicity parameters for the two, and s is a sensitivity parameter that depends on the nucleophile. A value of s = 1 corresponds to a constant selectivity relation. In fact the values of s lie between 0.5 and 1.5, with the majority between 0.7 and 1.3.

In concluding this section, we note that a consistent theoretical model of cation:nucleophile reactions has not emerged, despite the existence of considerable data and several empirical relations (such as eqs 30 and 34) that reasonably fit the data within certain limitations. Several problems that must be addressed are as follows. (Some of these are discussed in Richard's recent Report in this journal.)[90]

(a) How does one account for solvation, particularly of the nucleophile in protic solvents?

(b) Why does the position of the transition state seemingly show so little variation over wide ranges of reactivity? This behavior is apparent in the log k_w vs pK_R correlations (Section 4.3), and also in data for enthalpies of activation for cation:alkene reactions.[88]

(c) How important is the electron affinity of the electrophile and the ionization potential of the nucleophile? For reactions of cations and π-nucleophiles that are well below the encounter limit, Mayr has demonstrated that there is little correlation with the ionization potential; but for faster reactions involving enol ethers as nucleophiles, ionization energy appears to be a important factor.[88]

(d) How does one assess the imbalance in the transition between a change in polar and a change in resonance interactions and incorporate these factors into a theoretical model? Is there also imbalance with respect to solvation?

(e) Why in some cases (Ar_2CH^+ and π-nucleophiles)[88] is there a correlation between the activation free energy and the free energy of the overall reaction, but in others (α-CF_3 substituted cations)[74] this correlation breaks down?

6. Nitrenium Ion Reactivities

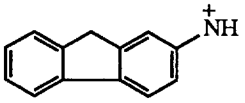
Compared to their carbon analogs nitrenium ions have seen very little direct study, under either flash photolysis conditions or under stable ion conditions. Diaryl derivatives Ar_2N^+ have been observed on 2-electron oxidation-deprotonation of the corresponding amines in acetonitrile.[91] However, no nitrenium ion has been characterized as a distinct species under stable ion conditions,[92] with the exception of the cyanodiphenylmethyl cation (Ph_2C^+-CN), which was considered to have significant nitrenium character ($Ph_2C=C=N^+$).[92b] Reactions proceeding via nitrenium ion intermediates have been investigated extensively, especially as models for processes involved in carcinogenesis by aromatic amines (see below). Only within the last two years however have routes been developed for the flash photolytic generation of these species (eqs 6,7,17), opening the way for direct studies of their reactivity.

6.1 Multiplicity of the Ground State

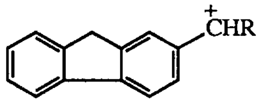
Nitrenium ions are isoelectronic with carbenes and, like the latter species, can have singlet or triplet ground states. Although the parent NH_2^+ is calculated to be a ground state triplet, phenyl substitution stabilizes the singlet; a recent high level computation has shown the singlet phenylnitrenium ion to be 21 kcal/mol more stable than the triplet.[93] An experimental method to distinguish singlets and triplets has been suggested by Falvey and co-workers; singlet arylnitrenium ions react with nucleophiles and give adducts, while triplets react with hydrogen atom donors and give amines.[94] On this basis, the majority of arylnitrenium ions that have been observed by flash photolysis (and also as intermediates in solvolysis reactions) are singlets, since they do react by adduct formation. It is not universally true however that arylnitrenium ions are singlets. A p-nitrophenylnitrenium ion that is a ground state triplet has recently been reported by the Falvey group.[94b]

6.2 Lifetime in Water — Comparison with Carbenium Analogs

Arylnitrenium ions are remarkably long-lived in water, especially when compared to carbenium analogs. As one example, we have found that the 2-fluorenylnitrenium ion (**94**) has a lifetime in water of 30 microseconds.[54] This is five orders of magnitude longer than the lifetime of the benzyl analog **96** (whose rate constant has been estimated from that for **95**, based on the effect of replacing phenyl with H in other carbocations). Part of the explanation for the kinetic stability of nitrenium ions may lie in the different site of water addition. Whereas arylcarbenium ions normally react with water at the external carbon, arylnitrenium ions avoid formation of a weak N-O bond by reacting in the ring (mainly para to N). This addition to the ring disrupts aromaticity and may significantly raise the intrinsic activation energy.



94; $k_w = 3.4 \times 10^4\ s^{-1}$ (ref. 54)



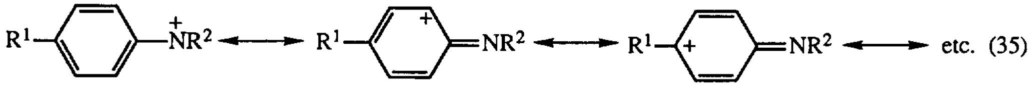
95; R = Ph, $k_w = 1.5 \times 10^7\ s^{-1}$ (ref. 35)
96; R = H, $k_w \sim 10^9\ s^{-1}$ (estimated)

6.3 Azide Ion

Like water, azide ion (Az) reacts with nitrenium ions at a ring carbon, and the products are azido-substituted aromatic compounds.[95] With LFP, k_{Az} has been measured directly as 4 - 5 x $10^9\ M^{-1}s^{-1}$ for several nitrenium ions with quite different k_w.[35,54] Thus, azide reacts with nitrenium ions at (or at least very close to) the diffusion limit. The "azide-clock" approach has been applied to solvolyses proceeding via nitrenium ions to provide absolute rate constants.[95] The direct measurements confirm that this approach is valid.

6.4 Nitrenium ion or Iminocyclohexadienyl Cation

Diffusion limited combination with azide ion is of course characteristic of most carbenium ions. An arylnitrenium ion **97** has several carbenium resonance contributors (**98**,**99**, etc.) with the positive charge delocalized in the aromatic ring.



(35)

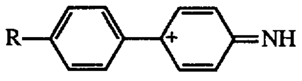
97 **98** **99**

As discussed below, there is in fact evidence that such resonance contributors are important, and that an arylnitrenium ion is perhaps better viewed as a cyclohexadienyl cation bearing an imine substituent:

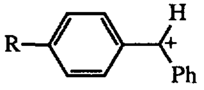
(i) The substituent R^2 at nitrogen has very little influence. In both the 2-fluorenyl and 4-biphenylyl nitrenium ions, there is no effect on λ_{max} of the cation of changing R^2 from H to acetyl.[35,54] The rate constants for water addition do increase, but only by a small factor.[35,54,95b,c]

(ii) Substituents R^1 do have pronounced effects on reactivity. However, these reactivities correlate poorly with σ^+.[95c] In other words these substituents do not interact with the positive charge as they do in a typical benzylic cation situation.

(iii) What appears to be a typical benzylic interaction is revealed by a substituent in the remote ring of the biphenylylnitrenium ion. As illustrated below, we have recently found that a 4-methoxy substituent in that ring stabilizes the cation kinetically by a factor of 2000,[96] an outcome similar in magnitude to that found in comparable benzyl cations.

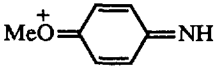


$$\frac{k_w(R{=}H)}{k_w(R{=}MeO)} = 2000$$



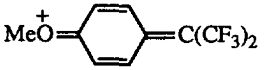
$$\frac{k_w(R{=}H)}{k_w(R{=}MeO)} = 650$$

(iv) We have also recently observed the p-methoxyphenylnitrenium ion **100** by irradiation of the precursor azide in water.[97] This cation has λ_{max} at 295 nm similar to that of the cation **18**, and also similar to that of anisole in concentrated acid, where protonation occurs on the para carbon to give **101**. Each of these cations is best viewed as an O-methylated 2,5-cyclohexadienone.



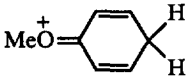
100

λ_{max} = 295 nm (ref. 97)



18

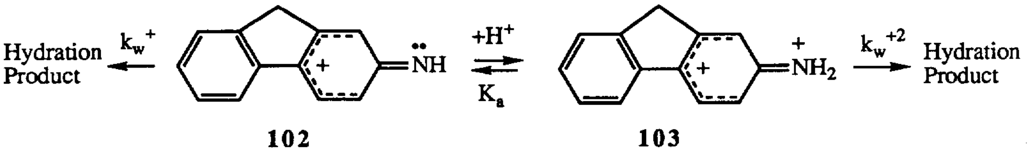
λ_{max} = 310 nm (ref. 32)



101

λ_{max} = 285 nm (ref. 47)

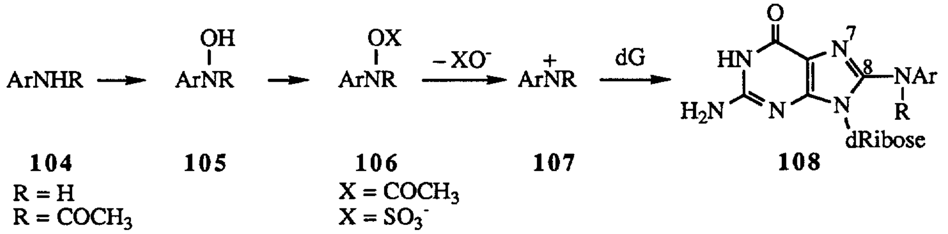
(v) The LFP studies with the 4-biphenylyl- and 2-fluorenylnitrenium ions (**102**) have revealed that the decay is accelerated by dilute solutions of H^+, and the rate constants then approach a plateau in more concentrated acids (e.g., 1 molar $HClO_4$).[96] The data can be fit by the kinetic model of eq 36, where the nitrenium ion is in equilibrium with a dication **103**. The acidity constant K_a of this dication obtained from kinetic fits is 0.25. (The value is 0.8 for 4-biphenylyl). In terms of this protonation, **102** is behaving as an imine with a nearby positive charge reducing basicity.



(36)

6.5 Guanine and π-Nucleophiles

Aromatic amines such a 4-aminobiphenyl, 2-aminofluorene, and their amides (**104**) are carcinogens. Their mode of activation is proposed to involve metabolic oxidation to a hydroxylamine derivative **105** followed by esterification to **106**. This ester reacts with DNA, predominantly at C_8 of a guanine residue, to give an adduct **108**, which has been characterized in both biological and model systems.



(37)

A nitrenium ion **107** formed by ionization of the ester has been widely assumed to be an intermediate. Convincing evidence has very recently been provided by the Novak group in experiments where derivatives of **106** (R = $COCH_3$) were solvolyzed in aqueous solutions in the presence of deoxyguanosine (dG).[98] The nucleoside did not accelerate the rate of decay of **106**, and yet significant amounts of the appropriate C8 adducts **108** were obtained – classic evidence for an intermediate formed in a rate-limiting step that does not involve the nucleoside. From the yields of **108** relative to those derived from water addition, ratios k_{dG}:k_w were calculated as 290 M^{-1} and 8000 M^{-1} for the N-acetyl-4-biphenylyl and 2-fluorenyl nitrenium ions, respectively.

These ratios imply a high reactivity for deoxyguanosine with these nitrenium ions, a feature that we have recently demonstrated through measurements of the absolute rate constants with flash photolysis (Table 10 — dGMP = deoxyguanosine-5'-phosphate).[99] Note that the ratio k_{dG}:k_w obtained with LFP for the cation **24** is 288 M^{-1}, the same as the number obtained in the competition experiment.

Table 10. Absolute Rate Constants for the Reactions of 4-Biphenylylnitrenium Ions (20 °C).

	k_w, s^{-1}	k_{dG}, $M^{-1}s^{-1}$	k_{dGMP}, $M^{-1}s^{-1}$	$k_{EtOCH=CH_2}$, $M^{-1}s^{-1}$
46, 4-C_6H_5-$C_6H_4NH^+$	1.8 x 10^6	2.1 x 10^9	1.8 x 10^9	2.3 x 10^8
24, 4-C_6H_5-$C_6H_4NAc^+$	5.9 x 10^6	1.7 x 10^9	1.3 x 10^9	2.2 x 10^8

Also apparent is that the deoxyguanosine reacts with rate constants approaching diffusion control. Both this reactivity, and the position of attachment of the electrophile contrast with results for carbenium ions. For example, the p-methoxybenzyl cation reacts at the heterocycle's external NH_2 group, and does this in very low yield in aqueous solution.[100] LFP experiments with diarylmethyl cations in the presence of dG and dGMP show very little rate acceleration,[99] under conditions where the nitrenium ions are very effectively quenched.

Collectively, these experiments have clearly established that nitrenium ions, at least those derived from carcinogenic amines, are viable intermediates in aqueous solution and react selectively with deoxyguanosine. The mechanism for the formation of the C8 adduct is still open to question. Alternatives to direct electrophilic substitution at C8 involve an initial attack at N7, and there is some evidence for this.[101]

Unusual reactivity patterns of nitrenium ions are also observed with enol ethers, π-nucleophiles that have seen investigation with carbenium ions. With diarylmethylcarbenium ions in 100% acetonitrile, the bimolecular rate constants for ethyl vinyl ether and water quenching of diarylmethyl cations are within 30% of each other, so that selectivity ($k_2(EtOCH=CH_2):k_2(H_2O)$) is ~1.[88] Were this non-selectivity to apply also in aqueous solution, the enol ether would be unable to trap more than a few percent of the cation; and even then enol ether concentrations of the order of 1 molar would be needed. However, ethyl vinyl ether is an effective quencher for the biphenylylnitrenium ions in water, even at concentrations as low as 0.01 M. Selectivities ($k_2(EtOCH=CH_2):k_2(H_2O)$) are 10^4 - 10^5, in marked contrast to those for carbenium ions.

As shown by the experiments discussed throughout Section 6, much still needs to be learned about the reactivity of arylnitrenium ions. However, this should now be possible, given recent success in generation and study of these species by the flash photolysis method.

7. Acknowledgements

Funding for this research came from the Natural Sciences and Engineering Research Council of Canada, in the form of a Research Grant, and an Equipment Grant for a Laser Flash Photolysis apparatus. Aspects of this research were also supported by the Petroleum Research Fund, administered by the American Chemical Society. I thank Dr. Steen Steenken for his collaboration in establishing the carbenium ion systems, and the skilled graduate students and post-doctoral fellows in my laboratory who performed the experimental work. I also thank Linda Johnston, Herbert Mayr, Mike Novak, John Richard, Peter Wan, and Jacob Wirz for their help and suggestions on this manuscript.

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(*Received* 7 *July* 1995)