

FAST REACTION STUDIES OF CARBOCATIONS IN SOLUTION

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Abstract - The pulse radiolysis method has been used to generate and study a series of five carbocations, consisting of phenylcarbenium ions and cyclopropylphenylcarbenium ions, in chlorocarbon solvents. Rate constants for the reactions of these substituted carbenium ions with various nucleophiles such as halide ions, alkyl amines, ammonia and water, have been determined. The observed reactivity trends (or, in some cases, lack thereof) with successive substitution are discussed in relation to steric and electronic effects. Comparison of these reactivities with observations from solvolysis experiments is discussed. Solvent effects are observed.

INTRODUCTION

Organic molecular ionic species, upon which Michael Szwarc has contributed so many landmark studies (Refs. 1 & 2), play a broad and important role in organic reactions in solution. The properties of many of these reactive intermediates, in particular their reactivities, have proven to be amenable to investigation by fast reaction methods such as pulse radiolysis (Refs. 3 & 4) and flash photolysis. This paper is concerned with recent pulse radiolysis studies of carbocations in solution, specifically with the reactivity of a series of five arylcarbenium ions (Refs 5 - 8).

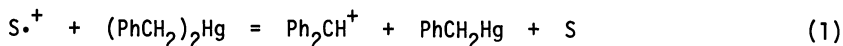
It should be pointed out, however, that the application of the method is by no means limited to the study of carbocations. Our earlier work had dealt with aromatic radical anions (Refs. 9 - 12) and cations (Refs. 13 - 15). It was then extended to carbanions (Refs. 16 & 17) and carbanion pairs (Ref. 17), and to carbocations (Ref. 8), upon which our interest has been focussed in the past few years.

Pulse radiolysis, by means of which the carbocations are generated, observed and studied, is an impulse method in which the energy perturbation on the solution is a submicrosecond pulse of high energy electrons. Upon pulse irradiation of solutions of selected solutes at sufficiently high concentration, the carbocations are generated within the period of the pulse, at an initial concentration which may range from 10^{-5} to 10^{-7} M. They are observed by fast optical absorption detection (with a time resolution of about 5 nsec.); their optical spectra may be determined, and their time-history in the solution observed directly. If no nucleophile is added to the solution, the normal lifetime of the carbocation, limited by combination with a solvent counter-ion, is on the order of a few μ secs. or longer. This time is sufficiently long to permit the observation of the reaction of the carbocation with a nucleophile, which is present, under pseudo-first order conditions (arranged by having the concentration of the nucleophile in substantial excess over that of the carbocation). By sorting out the appropriate wavelength for observation of the carbocation and the appropriate time scale for the reaction (usually tens to hundreds of nanoseconds) an individual electrophilic reaction can be observed directly and its rate constant determined absolutely. Occasionally one encounters problems of spectral overlap which have to be sorted out. It should be understood that it is the reactivity which is thus being determined directly, and that, because of the pseudo-first order conditions, this determination is usually unhindered by other transient species produced by the electron pulse.

Five arylcarbenium ions have been generated and studied: the phenylcarbenium, diphenylcarbenium, triphenylcarbenium ions, and the α -cyclopropylphenyl- and α,α -dicyclopropylphenylcarbenium ions. Rate constants for the reactions with halide ions, trialkyl amines, ammonia and water have been determined. Some solvent effects have been observed for the solvents methylene chloride (MC), 1,2-dichloroethane (DCE) and 1,1,2-trichloroethane (TCE).

FORMATION OF CARBOCATIONS

The primary species formed, which result in the formation of charged species from solute molecules, are the electron (as reducing species) and the solvent cation radical, or other cationic fragment of the solvent (as oxidizing species). Electron attachment to the solute molecule (if this occurs) would, of course, result in the formation of an anionic species. Ionization of the solute molecule by electron transfer to a solvent cation would result in the formation of a cationic species. If this ionization of the solute is *dissociative*, a carbocation will be formed from the solute. A case in point is the formation of the benzyl cation from dibenzyl mercury:



where $S^{\cdot+}$ is the solvent cation radical. The rate constant for this formation reaction in DCE is (Ref. 18) $1.3 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$. Similar reactions, to form the respective arylcarbenium ions, occur with diverse compounds such as benzhydrylbromide, trityl chloride, trityl carbinol and the cyclopropylphenyl carbinols. Rate constants for various formation reactions ranging from 4.0×10^8 to $1.6 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$ in DCE have been reported (Ref. 18). If the concentration of the solute is sufficiently high (in consideration of the value of the formation constant) and if the dissociation of the solute molecule upon ionization is sufficiently rapid, the experiment will provide a "pulse" of carbocations, as is, indeed, observed to be the case.

It will be noted that the solvents selected for use so far, are all chlorocarbons. The basis for this choice is two-fold. Firstly, it is important that the analogous carbanion, e.g. PhCH_2^- , not be formed simultaneously with the carbocation; the benzyl anion and the benzyl cation have nearly identical optical absorption bands (Ref. 8), and sorting out the kinetics in a system containing both would be difficult. To this end, the chlorocarbon solvent serves as an electron scavenger which undergoes a dissociative electron attachment, trapping the electron in the form of chloride ion, which does not react with the solute. Secondly, the electron transfer to form the carbocation, reaction (1), does occur with these chlorocarbons.

IDENTIFICATION OF THE ARYLCARBENIUM IONS

In those cases for which the optical spectrum is previously known, the carbocations are identified from their optical absorption bands in the U.V. Thus, for the benzhydryl cation in DCE, for which we find $\lambda_{\text{max}} = 445 \text{ nm}$, both the band maximum and the band shape are identical with the earlier observation in strong acid medium (Ref. 19). The trityl cation in DCE shows the same double-peaked U.V. band previously reported (Refs. 20 & 21) but slightly red-shifted. The benzyl cation, with a U.V. band at $\lambda_{\text{max}} = 363 \text{ nm}$ had not been previously observed. Its identity was confirmed in two ways. First from the fact that the same optical absorption band was obtained from a series of different compounds, the common characteristic of which was that they all contained the benzyl group. Secondly, that the optical band observed was almost identical, as expected, to the band observed for the benzyl carbanion (Ref. 16). The α -cyclopropylphenyl carbenium ion shows a band maximum (Ref. 7) at 347 nm , compared with 343 nm , previously reported (Ref. 22). The α,α -dicyclopropylphenyl carbenium exhibited a spectrum (Ref. 7) with peaks at 296 nm and 353 nm . Our assignment has been discussed in comparison with the earlier work (Ref. 22). The peaks of these optical absorption bands are listed in Table 1.

TABLE 1. Optical Absorption Bands for Arylcarbenium Ions in DCE

Cation	λ_{max} (nm)
PhCH_2^+	363
Ph_2CH^+	445
Ph_3C^+	415,439
∇ PhCH^+	343
$\nabla+$ PhC^{\leftarrow}	296,353

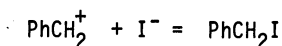
REACTIVITY OF THE ARYLCARBENIUM IONS

Our principal interest in the carbocations lay in the determination of their reactivity in a variety of electrophilic reactions. The objective of the work was to examine whether the conventional picture of decreased reactivity with increasing phenyl substitution in the

carbocation, and with cyclopropyl substitution, as related to steric effects and to electronic effects, could be sustained. Steric effects on the reactivity with a series of trialkyl amines were also examined. We have also made some observations of the effect of solvent on the reactivity. In the case of water as a nucleophile, the interesting conclusion has been reached that the state of aggregation of the nucleophile in solution is important to the kinetics. Over and above these specific objectives, it was our motive to ascertain what general correlations, if any, could be shown between our directly determined reactivities and the results of solvolysis experiments.

Reactivity with Halide Ions

Rate constants were determined (Refs. 5 & 18), in DCE only, for reaction of the phenylcarbenium ion with iodide and with bromide ion, and of the diphenylcarbenium ion and triphenylcarbenium ion with iodide, bromide and chloride ion. The reaction, which is presumably the formation of the covalent compound (no evidence of ion pair formation in DCE having been observed):



was monitored by following the decay of the carbenium ion. Iodide and bromide ion concentrations were determined by conductivity measurement, and the rate constants were obtained from first order decay curves. The rate constants for chloride ion were determined from second order rate curves representing the natural decay so that the molar extinction coefficient of the carbenium ion entered into the calculation. Accordingly no value was obtained for benzyl cation with chloride ion.

The results showed no discernible trend in reactivity with increasing phenyl substitution. The three carbocations all had rate constants, within experimental error, of $4.6 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ with iodide ion, $5.9 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ with bromide ion, and two had rate constants of $8.5 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ with chloride ion. These carbocation-anion reactions, a category of reaction which has previously been investigated for other carbocations (Refs. 23 & 24) in water, are clearly in the nature of diffusion controlled ion combination reactions, occurring in this solvent on every encounter. Successive phenyl substitution produces no observable effect. The small trend with halide ion very likely reflects the difference in mobility of the respective halide ions.

Reactivity with Trialkyl Amines

The electrophilic reactions of the arylcarbenium ions with the three trialkyl amines, triethylamine, tripropylamine, and tri-n-butylamine were investigated for all five of the carbocations listed. Moreover, the rate constants were obtained in three different solvents, MC, DCE and TCE, with some interesting results. The observed rate constants, accordingly, provide information on the effect of successive phenyl substitution, on the effect of cyclopropyl substitution in the carbocation, on the effect of the slight increase in the size of the alkyl group in the nucleophile, and on the effect of the small changes in the properties of the solvent.

There are a great many individual data items which are best considered, and more easily absorbed, in graphical rather than in numerical form, and which, for purposes of this talk, are presented in Fig. 1. The values of the rate constants determined are presented in separate groupings for PhCH_2^+ , Ph_2CH^+ , Ph_3C^+ , PhCH^+ and PhC^+ as indicated at the bottom of the figure. Within each group there are shown in separate columns, labelled E, P and B at the top, the rate constants for reaction of triethylamine, tripropylamine and tributylamine respectively, with each carbenium ion. The separate solvents are coded with a square for MC, a solid circle for DCE and an open circle for TCE.

Consider first the trend with successive phenyl substitution, for which the differences are largest in DCE. There is a decrease in rate constant from phenyl to diphenyl, but it is relatively small, amounting to slightly less than a factor of two (about the same for each amine). There is a much larger decrease from diphenyl to triphenyl substitution, ranging from 18-fold (for triethylamine) to 130-fold (for tributylamine). With the other two solvents, for which the kinetic effects are rather smaller, as will be discussed later, the decrease in going to the trisubstituted stage is also much greater than the change from phenyl to diphenyl substitution. This would seem to suggest that the decrease is to be attributed largely to a steric effect, and that electronic effects in this series of phenylcarbenium ions must be very small. The foregoing interpretation is based on the reasoning that any electronic effect ought to be evident upon doubling the number of the group (phenyl to diphenyl) into which charge delocalization would occur. The steric effect, on the other hand, may exhibit an onset at the trisubstituted stage.

Within each carbenium ion group there is also evidence of a small steric effect (largest in DCE) with increasing complexity of the alkyl group in the amine. Since the electronic effect would act to increase the rate constant with increasing size of the alkyl group, the observed decrease must indicate that the steric effect predominates.

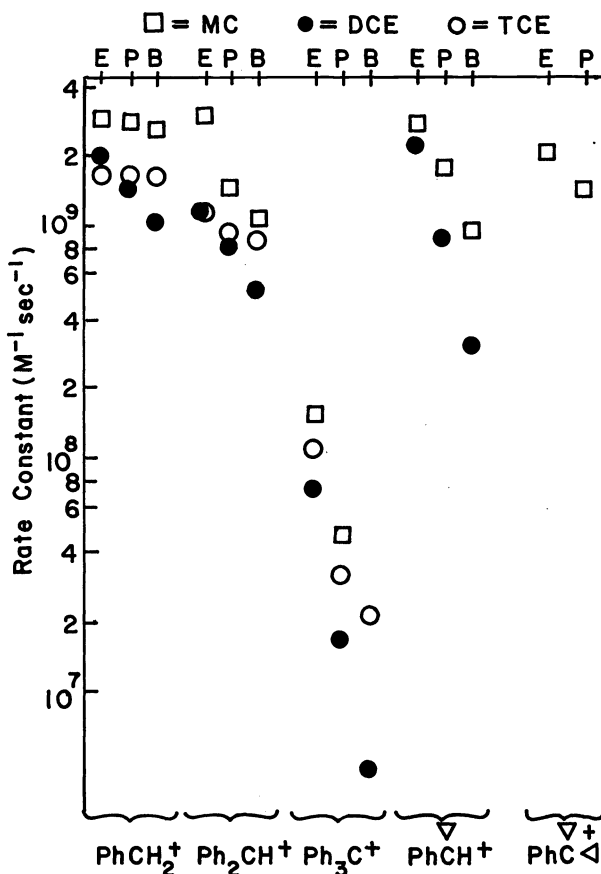


Fig. 1. Rate constants (in units of $M^{-1} \text{ sec}^{-1}$) for the reactions of the five arylcarbenium ions (indicated on the abscissa at bottom) with trialkylamines. The data for each cation are presented in separate columns. The values for each nucleophile are identified by the column positions E (triethylamine), P (tripropylamine) and B (tributylamine). The solvents are identified by \square , methylene chloride, \bullet , dichloroethane and \circ , trichloroethane. Note that the ordinate scale is logarithmic.

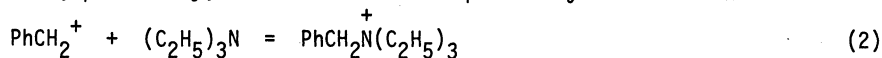
In the case of cyclopropyl substitution, we are interested in comparing our directly determined reactivity with the concept of "stability" which has its origin in either solvolysis rates or in the heats of formation of the ions. There have been a number of comments (Refs. 25 - 30, and Ref. 22), on the stabilizing effect of the cyclopropyl ring, based on the ease of formation of α -cyclopropylcarbenium ions (Refs. 25 - 28) and the resulting rapid solvolytic rates. The stabilization was reported to be greater than that of an allyl group or a phenyl ring in the carbenium ion. Steric hindrance of the cyclopropyl ring is thought (Ref. 31) to be approximately equal to that of a phenyl ring. Comparison of the rate constants in Fig. 1 for α -cyclopropylphenyl- with diphenylcarbenium ion, and of α,α -dicyclopropylphenyl- with triphenylcarbenium ion, does not reveal such an effect on the reactivity. The difference in the effect of cyclopropyl substitution compared with that of phenyl substitution is especially noteworthy at the trisubstituted stage where, from the data in MC, the cyclopropyl group has little effect compared with the phenyl ring. Our results indicate a more complex situation than solvolytic rates would reveal. Some of the effects, however, deal with small differences.

Lastly, the data in Fig. 1 show an interesting effect of solvent upon the kinetics. The effects, which are largest in DCE, are minimized, and in some cases eliminated in TCE and in MC. Note especially the data for benzyl cation in these two solvents and for benzhydryl cation in DCE. The highest rate constants, by the way, are lower than the diffusion controlled limit by a factor of about three. The solvent effect is particularly remarkable in that most of the properties of the three solvents are so similar. They show little

difference in the dielectric constant, density and enthalpy of vaporization. They do show differences in their viscosities: MC (0.429), DCE (0.800), TCE (1.20) and in their dipole moments (Ref. 32): MC (1.14), DCE (1.86), TCE (1.57). It would appear that what is involved is either polarizability or a charge-dipole interaction.

Reactivity with Ammonia

The rate constant for the reaction of trityl cation with ammonia (Refs. 18 & 7) in DCE proves to be an interesting result. The rate constants (Ref. 7) for the reaction of benzyl cation and of benzhydryl cation with ammonia are both the same, $4.2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, a value higher than the rate constants for the reaction of these cations with triethylamine, which are, respectively 2.0×10^9 and $1.2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. The rate constant for trityl cation with ammonia, however, is 2.4×10^7 compared with 7.3×10^7 for trityl cation with triethyl amine. This last result that $k_{\text{NH}_3} < k_{\text{TEA}}$ is clearly not consistent with a steric effect which would be expected to result in a lower rate constant for TEA than for ammonia. The following suggestion may explain this result. The general electrophilic reaction with the amines is, presumably, the formation of a quaternary ammonium ion:



This is not the only reaction possible; electron transfer may occur depending upon the magnitude of k_2 and the rate constant for electron transfer. For the trityl cation, the rate constant for quaternary ion formation is sufficiently reduced by the steric effect so that electron transfer may become competitive. Electron transfer is possible for TEA since its ionization potential (Ref. 33) is only 7.50 eV. Ammonia, on the other hand, has a much higher ionization potential (Ref. 33) of 10.15 eV. The electron transfer is far less likely to occur. Hence we have the reaction of type (2), with the trityl cation, with a resulting lower rate constant for NH_3 than for TEA.

Reactivity with Water

Data we have obtained (Ref. 18) for the reactivity of benzyl cation and of benzhydryl cation in DCE show a decrease in reactivity upon substitution of the second phenyl group in the carbenium ion. The data also reveal that the reactivity depends upon the state of aggregation of the nucleophile in solution.

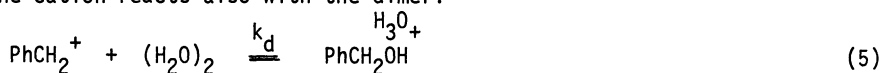
It is found that the rate data cannot be accounted for solely in terms of the reaction of the carbocation with water monomer:



as the apparent first-order rate constant exhibits an increase with increasing water concentration. The data can, however, be reconciled if the monomer-dimer equilibrium for water in DCE (for which K_e has been reported (Ref. 34) is taken into account:



and if the cation reacts also with the dimer:



with $k_d > k_m$. The values obtained at 24°C, based on this interpretation are:

	k_m	$k_d \text{ (M}^{-1} \text{ sec}^{-1}\text{)}$
PhCH_2^+	1.8×10^7	6×10^8
Ph_2CH^+	1.3×10^6	1×10^8

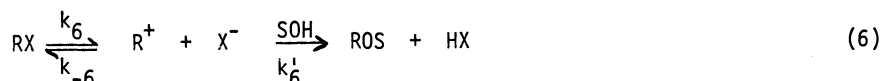
This phenomenon of higher reactivity toward the water dimer than toward the monomer was also observed for methanol and ethanol (Ref. 6) in DCE solution. The leaving group in the case of the monomer is a proton, while in the case of the dimer (reaction 5) it is a hydronium ion.

GENERAL SUMMARY

At this stage of our investigations it is appropriate to summarize some of the conclusions which are called for on the basis of the foregoing observations. First of all, the expectation that the reactivity of the arylcarbenium ions is in the order phenylcarbenium > diphenylcarbenium > triphenylcarbenium, although frequently observed, does not necessarily hold under all conditions and for all reactions. In short, this reactivity is not simply an intrinsic property of the cations themselves, but depends on the solvent as well. A case in point is the halide ion combination for which the reaction rate is mobility limited (rather than activation limited) and no difference in reactivity is seen in DCE. Secondly,

where we have observed a decreasing trend in reactivity (the trialkylamines) with successive phenyl substitution, the greater decrease at the trisubstituted stage suggests we are seeing largely a steric effect without any significant contribution from charge delocalization to the phenyl groups. Thirdly, the effect of cyclopropyl substitution (or lack thereof) on the reactivity of the arylcarbenium ions is not simply similar in magnitude to the kinetic effect of phenyl substitution, particularly at the trisubstituted stage. Fourthly, the solvent must play a very important role; even small changes in solvent properties can produce significant changes in reactivity trends. And finally, examples have been encountered in which the state of aggregation of the nucleophile in solution is an important parameter for the specific rate of the electrophilic reaction.

Considering the first three of these observations, and reflecting upon the nature of solvolysis data, it seems appropriate to ask whether "stability" of the carbenium ion should in fact be compared with the reactivity, which we determine directly. The solvolysis reaction:



consists of an auto-ionization step (k_6), followed by a fast reaction with the solvent (k'_6) such that $k'_6 \gg k_{-6}[\text{X}^-]$. The rate determining step in these solvolysis reactions is the formation of the carbenium ion. Accordingly, the solvolysis rate reflects not just the intrinsic reactivity of the carbenium ion, but rather a combination of properties of the compound from which the carbenium ion is formed, the ion itself, and the solvent in which the auto-ionization occurs.

The selectivity toward the nucleophiles does seem, from data in Fig. 1, to increase with decrease in the magnitude of the rate constant.

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