

Review Article

Radical and Polar Reactivity of Radical Ions in Solution. A New Look at an Old Problem

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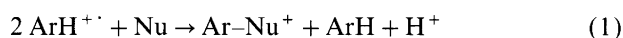
Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

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It is proposed that both polar and radical reactions should be considered when discussing radical ion reactivity. The fact that only the polar reactivity has dominated previous discussions is pointed out. It is argued that if the configuration mixing model is applicable for the estimation of radical cation–nucleophile (or cation–nucleophile) combination reaction barriers, the theory should also explain the reactivity of the proton toward anionic nucleophiles. The model severely overestimates reaction barriers for the latter reactions. The discussion is centered around the following hypothesis: In the absence of severe steric effects, the reactivity of radical ions, especially evident in the reactions with radicals (for example very few radical cations react with dioxygen at measurable rates), is dominated by the degree of coupling between charge and radical centers. Evidence from the literature supporting the hypothesis is presented for a number of different classes of radical ion reactions. Further work to test the validity of the hypothesis is proposed for many of the reaction types. Triarylmethyl radicals and carbenium ions are suggested as models to which the radical and polar reactivities of 9,10-diarylanthracene radical cations may be compared. It is concluded that the radical cation/carbenium ion comparison (for the reaction with acetate ion) would show similar reactivities while the radical cation/free radical comparison (for the reaction with dioxygen) would fail, since no reaction at all would be observed with the radical cation while the free radical reacts rapidly.

Radical ion reactivity has stimulated a great deal of interest over the past 30 years. Kinetic studies of the reactions of persistent radical cations with nucleophiles revealed that the most commonly observed reaction pathway corresponds to the half-regeneration mechanism (1), and is accompanied by the observation of rate laws with second-order terms for radical cation concentration.¹ These, and other observations led Ebersson² to propose that radical cations are from 10³ to 10⁷ times less reactive than expected for carbenium ions of related structure. Even earlier, Szwarc³ had shown that reactions of radical anions in the presence of alkali metal cations are dominated by the more reactive dianions generated by the disproportionation reaction. Disproportionation of arene radical anions was observed to be thermodynamically unfavorable in the presence of tetraalkylammonium counter ions in aprotic solvents, and reactions observed then correspond to those of the

radical anions.⁴



The provocative conclusion by Pross,⁵ which relied heavily for support on previous experimental observations,^{1,2} that direct reactions between radical cations and nucleophiles are ‘forbidden’ and cannot take place provoked an immediate response with a report of ‘rapid, low activation energy’ radical cation–nucleophile combination reactions.⁶ The prediction of ‘forbidden’ radical cation–nucleophile combination was later discussed in more detail in terms of the configuration mixing model.⁷ In order to circumvent the dilemma posed by the very rapid ‘forbidden’ reactions Shaik and Pross⁷ proposed an alternative mechanism involving rate-determining electron transfer between radical cation and nucleophile.

Over the past ten years, we have been able to show that reactivity in radical cation–nucleophile combination

Table 1. Initial gaps, equilibrium constants and rate constants for the reactions of protons with anionic nucleophiles.

Cation/solvent	Anion	IG, kcal mol ⁻¹ ^a	log K_{comb} (M ⁻¹)	log k_{comb} (M ⁻¹ s ⁻¹)
H ⁺ /H ₂ O	HO ⁻	297	15.75 ^c	11.15 ^c
H ⁺ /H ₂ O	HS ⁻	261	7.24 ^c	10.88 ^c
H ⁺ /H ₂ O	F ⁻	292	3.15 ^c	11.00 ^c
H ⁺ /CH ₃ CN	Cl ⁻	273 ^b		
H ⁺ /CH ₃ CN	Br ⁻	261 ^b		
H ⁺ /CH ₃ CN	I ⁻	242 ^b		

^aFor calculation of initial gaps see Refs. 7 and 14; solvation energies are from Ref. 22. ^bFree energies of solvation used in the calculation of IG in acetonitrile are from Ref. 23. ^cRef. 24.

reactions does not conform to the predictions of the configuration mixing model.⁸⁻¹⁸ Electron transfer followed by radical attack was ruled out as an alternative mechanism for the reaction between 9-phenylanthracene radical cation and acetate ion.⁸ In the same study it was shown that 9,10-diphenylanthracene radical cation reacts faster with acetate ion than the carbenium ion resulting from the initial attack reacts with the nucleophile, an observation which contradicted earlier conclusions on the relative reactivities of radical cations and carbenium ions toward nucleophiles. Kinetic studies of the reactions of a series of arene radical cations with anionic nucleophiles revealed that all of the reactions are very rapid and that some of the radical cations are exceptionally 'hot' electrophiles.⁹ For example, 9-nitroanthracene radical cation reacts at diffusion control with good nucleophiles, very rapidly with the weak nucleophile nitrate ion and moderately rapidly with the poor nucleophile, perchlorate ion. A detailed study of the reactions of 9-phenylanthracene radical cation with pyridine nucleophiles, including the analysis of steric and secondary kinetic isotope effects, confirmed that in all cases the rate-determining step is the second-order combination of radical cation with the nucleophile and that steric effects often are more important than electronic effects in determining reaction rates.¹¹ The general conclusion from this extensive series of studies of radical ion–nucleophile combination is that in the absence of rate-retarding steric effects the reactions are very rapid and do not conform to the predictions of the configuration mixing model.^{5,7}

The fact that radical cation reactivity does not conform to the predictions of the configuration mixing model⁸⁻¹⁸ suggests that the apparent success of the model to predict carbenium ion reactivity^{19,20} may be fortuitous. Benchmark values of 60 and 100 kcal mol⁻¹ for the initial gap (IG), which corresponds to a vertical charge-transfer transition between ground state and first excited state reactant configurations, have been set for rapid and slow reactions, respectively.⁷ The carbenium ion reactions considered were found to have IG lower than 60 kcal mol⁻¹.⁷ We propose²¹ that if the model is indeed applicable to the estimation of cation–anion combination barriers that the model should predict low (< 60 kcal mol⁻¹) IG for the known diffusion-controlled

reactions of the hydronium ion. Initial gaps* along with published²⁴ rate and equilibrium constants for proton–anion combination reactions in water are summarized in the table. Initial gap data are also included for proton–anion combination reactions in acetonitrile. This exercise results in enormous IG for the cation–anion combination reactions which are experimentally found to be diffusion controlled. Why are the IG for these reactions so large, while those for comparable carbenium ion–anion combinations are much smaller? The most significant quantity responsible for the large IG is the very large solvation energies of the proton, which are of the order of 200 kcal mol⁻¹ greater than typical solvation energies of carbenium ions.

The point of the discussion in the previous paragraph is to show that the only theory that has been offered to explain differences in cation and radical cation reactivity is not consistent with experimental kinetic data for radical cation–nucleophile combination⁸⁻¹⁸ and also fails completely to account for the absence of reaction barriers for proton–anion combination.²¹

A less than satisfying result of our work⁸⁻¹⁸ on radical cation reactivity is that it pointed out the failures of the configuration mixing model to account for reaction barriers, but no alternative explanation for the observed radical ion reactivity was apparent. In this paper an alternative experimentally verifiable hypothesis is put forth which provides valuable insight into radical ion reactivity. The hypothesis follows:

'In the absence of severe steric effects, the reactivity of radical ions, especially evident in the reactions with radicals (for example very few radical cations react with dioxygen at measurable rates), is dominated by the degree of coupling between the charge and radical centers. Decoupling of these functions, charge and radical centers, is expected to enhance the reactivity of one or both of the centers.' For example, dimerization rates of arene radical cations are observed to be greatly enhanced by methoxy and *N,N*-dimethylamino substituents, which separate the charge and radical centers. Studies of the reactivities of radical ions with varying degrees of spin-

* For calculation of initial gaps, see Refs. 7 and 14; solvation energies are taken from Ref. 22.

charge coupling are expected to provide strong kinetic support for this hypothesis.

The observation that triggered the conception of the hypothesis was that a number of persistent free radicals, including triphenylmethyl, react very rapidly with dioxygen,²⁵ while we were unable to observe any reaction between dioxygen and structurally related radical cations such as that derived from 9,10-diphenylanthracene. In terms of the configuration mixing model, a significant barrier is not predicted for either of these radical-radical combination reactions. Thus, we have observed that 'forbidden' radical cation-nucleophile combination reactions can be barrier free while 'allowed' radical cation-dioxygen combinations cannot usually be observed with arene radical cations. The hypothesis described above addresses reactivities of both the ionic and radical centers of ion radicals.

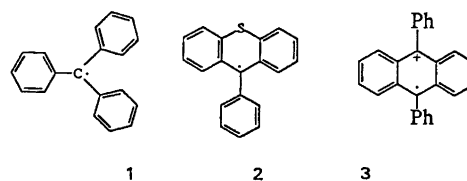
The configuration mixing model successfully predicts the stereochemical course of nucleophilic displacement of one-electron σ -bonds.²⁶ These reactions are accompanied by an inversion of configuration and it was concluded that the stereochemistry is governed by the σ^* -orbital of the one-electron bond. This work was recently extended to include the analysis of the stereochemical course of σ -radical cations in general.²⁷ Analysis of the stereochemical and regiochemical course of radical cation reactions is a very useful area in which the configuration mixing model appears appropriate. However, the fact remains that the model fails to predict reaction barriers for radical cation-nucleophile combination for the arene radical cations of the type, for which extensive kinetic data are available.⁸⁻¹⁸

All the discussion that follows is focused on the validity of the hypothesis, that in the absence of severe steric effects, radical ion reactivity is dominated by the degree of coupling between charge and radical centers. The effect of radical ion structure on reactivity is thus necessarily central to the argument. In order to design experimental systems and evaluate results, it will be necessary to use reliable methods to predict charge and spin densities in radical ions. Early work on methoxy-substituted benzene radical cations²⁸ showed that spin densities could be related to Hückel calculated values using the McLachlan method.²⁹ Modern semi-empirical methods³⁰ are expected to give reliable spin and charge densities of the radical ions of interest here. A number of programs are now readily available, for example the methods supported by Hyperchem,³¹ which allow the non-expert to make reliable calculations. Theoretical methods have been used to relate both rate constants and product distributions in radical ion dimerization reactions to charge and electron densities.^{32,33} Recent examples of relating radical cation reactivity to structural features obtained by MO calculations can be found in the extensive work of Effenberger.³⁴

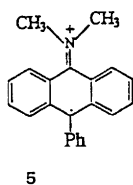
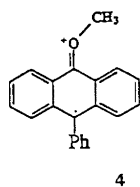
The most detailed discussion of radical ion reactivity in the literature has dealt with the reactivity of the ionic centers. In the sections that follow the data presently

available are discussed, and we suggest further work which relate to testing the hypothesis for reactivity of both the radical and the ionic centers. For emphasis, radical ion structures are drawn with the charge on one atom and the radical center on another. These structures are resonance forms of the radical ions but do not imply that they give the electron distributions; rather, they indicate that the atoms indicated are expected to be positions of either high charge or spin density.

'Allowed' radical ion reactions: radical-radical combination. Persistent free radicals such as triphenylmethyl (**1**) and related arylmethyl radicals (**2**) react very rapidly with dioxygen. The radical centers in both **1** and **2** are expected to be structurally similar to that in diphenylanthracene radical cation (**3**). Free radical **1** reacts with dioxygen in dichloromethane at 298 K with a second-order rate constant equal to $1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.²⁵ Since radical-radical combination reactions of radical ions are 'allowed', the barrier for the reaction of **3** with dioxygen might be expected to be similar to that for the free radicals **1** and **2**. However, we were unable to detect any reaction between **3** and dioxygen. A possible explanation of our failure to observe this reaction is that in **3** the charge and radical centers are delocalized over the central anthracene ring which has the effect of greatly decreasing the reactivity of the radical center. It is possible that the reaction of **3** with dioxygen takes place reversibly with a small equilibrium constant, and that the reaction goes undetected. Our attempts to trap the resulting hydroperoxyl radical with good hydrogen atom donors have failed, and we believe that if reaction takes place at all it does so very slowly.

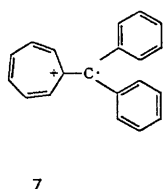
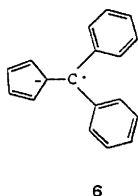


Substitution with heteroatom substituents at the 9-position of radical cations derived from anthracenes is expected to decouple the charge and radical centers. Experimental evidence that this is the case can be derived from the fact that anthracene radical cations show little tendency to dimerize while 9-methoxyanthracene radical cation undergoes dimerization at near diffusion controlled rates (dimerization reactions are discussed in another section). This suggests that the charge on 9-methoxy-10-phenylanthracene radical cation may be localized on the methoxy oxygen as in **4** which would be expected to make the 10-position susceptible to attack by dioxygen. The 10-phenyl substituent precludes dimerization in this case. We therefore suggest that both **4** and **5** are more suitable radical cations for comparison with radicals (**1**) in reactivity toward dioxygen. Work is in progress to determine the radical reactivity of **4** and **5** in



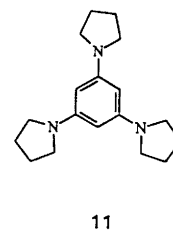
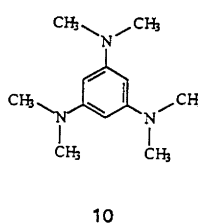
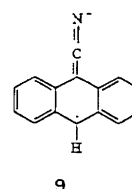
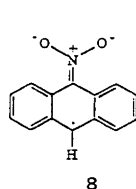
order to determine whether or not the same structural factors that lead to dimerization of radical cations also enhance the reactivity of the radical cations toward dioxygen.

Radical reactivity of distonic radical anions and cations. Distonic radical ions are those in which charge and radical centers separately exist in different regions of the structure.³⁵ For radical ions generated from conjugated π -systems we would expect that structural features which strongly stabilize either ions or radicals might result in radical ions in which charge and radical centers are decoupled to the extent that they resemble distonic structures. We suggest that the radical centers in the radical anion generated from **6** and in the radical cation generated from **7**, by virtue of charge localization on the Hückel aromatic cyclopentadiene (**6**) and tropylium (**7**) rings, may approach the radical reactivity shown by triphenylmethyl radical. Hückel calculations on the radical ions predict that more than 80% of the negative charge in **6** and more than 80% of the positive charge in **7** resides in the five-membered or seven-membered rings, respectively. Studies of both the radical and polar reactivities of **6** and **7** would be of interest.



The thermochemistry of the formation of radical ions such as **6** and **7** is expected to be of interest. We have previously shown that the entropies of formation of radical ions are strongly dependent upon the degree of delocalization of charge.³⁶⁻⁴² For example, formation of highly delocalized radical ions such as those derived from the highly symmetrical molecule, triphenylene, is accompanied by very small ΔS values while that for the formation of the thianthrene radical cation in which the charge and radical centers are localized on sulfur was observed to be as great as -25 e.u. The distonic-like structures, **6** and **7**, suggest that ΔS accompanying the formation of these radical ions should be very large. The measurement of the temperature dependencies of the reversible electrode potentials for the formation of **6** and **7** is expected to provide insight into the degree of separation of charge and radical centers.

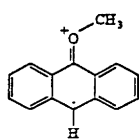
Radical ion dimerization reactions. The chemistry of arene radical ions is an area in which evidence is already available to support the hypothesis that decoupling the charge and radical centers is expected to enhance the reactivity of one or both of the centers. Anthracene is reversibly reduced in proton deficient solvents to give the persistent anion radical. On the other hand, both 9-nitro and 9-cyanoanthracene anion radicals rapidly dimerize.^{43,44} This observation can be accounted for by assuming that the charge and radical centers of the former are delocalized over the central anthracene ring while **8** and **9** contribute strongly to the structures of the substituted anion radicals. These observations are especially intriguing when one considers the fact that the simpler structures, nitrobenzene and benzonitrile, give rise to radical anions which are very persistent and show no tendency to undergo dimerization reactions. In general we might expect π -electron withdrawing substituents such as nitro or cyano, to stabilize radical anions. We interpret the change in effect of substituents in going from the anthracene to benzene systems to indicate that separation of the charge and radical centers is much less in the substituted benzene radical anions than in the corresponding anthracene derivatives. Since there is a wealth of experimental data already available on these reactions, semi-empirical MO calculations would be of value in order to better interpret structure-reactivity relationships. Such an approach has been taken by Effenberger³⁴ to rationalize trends in dimerization reactivity of radical cations of **10** and **11**.



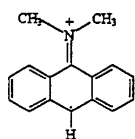
Methoxy and other π -donating substituents are expected to stabilize radical cations. However, we have observed that the radical cation derived from 9-methoxyanthracene is short-lived under conditions where radical cations of most anthracene derivatives are readily observed during cyclic voltammetry (CV) at low voltage sweep rates. This contradiction can be explained by assuming that localization of the positive charge on the 9-methoxy group promotes rapid dimerization at the 10-position. We presume that similar behavior will be

observed for 9-(*N,N'*-dimethylamino)anthracene radical cation.

It would be of interest to confirm the reaction pathways followed by **12** and **13**. Kinetic studies of the dimerization reactions could readily be studied by CV. The rate constants and activation energies for the reactions of **12** and **13** could be compared to those obtained for the dimerization of 9-phenylanthracene radical cation which is known to dimerize slowly.⁴⁵ The activation energy comparison is expected to provide further evidence for separation of charge and radical centers in **12** and **13** while this is not expected for the 9-phenylanthracene radical cation. Recent studies of radical cation⁴⁶ and radical anion⁴⁷ dimerization reactions illustrate the current approach to mechanism studies in this area.



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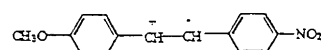
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Proton transfer reactions of methylarene radical cations. Radical cations derived from several of the methylbenzenes^{48,49} are sufficiently long-lived in the absence of intentionally added bases to be observed by cyclic voltammetry. On the other hand, 4-methoxytoluene radical cation which one might have expected to be less reactive by virtue of the cation stabilizing methoxy group cannot be observed by cyclic voltammetry in acetonitrile at voltage sweep rates as great as 1000 V s^{-1} . The reaction pathway followed by the radical cation under these conditions is proton loss followed by dimerization to form the corresponding bibenzyl. Preliminary studies indicate that the radical cation is not sufficiently long lived in acetonitrile to study the kinetics of proton loss by CV. A possible explanation of the high reactivity of the 4-methoxytoluene radical cation is that it is a consequence of the decoupling of the charge and the radical centers. If this explanation is valid, it is very interesting that proton loss must occur at the methyl group which is remote to the methoxy group on which the charge is localized.

Aryl olefin radical cations. Rotation about the ethylenic double bond in radical cations derived from tetraaryl olefins gives rise to spin-charge decoupling. This is evident from the fact that while the difference in electrode potentials for the second ($\text{ArH}^{2+}/\text{ArH}^{\cdot+}$) and first ($\text{ArH}^{\cdot+}/\text{ArH}$) charge transfers of arenes is generally about 600 mV or greater,⁵⁰ this quantity for tetraaryl olefins such as tetrakis(4-methoxyphenyl)ethylene (TAE) is zero or negative.^{51,52} The latter is due to the fact that increased rotation about the ethylenic double bond brings about spin and charge separation in the radical cation and to an even greater extent charge

separation in the dication. A number of other examples of inverted electrode potentials have been observed for the formation of radical cations and dications, and some have been discussed in detail.^{53,54}

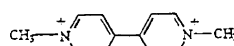
Another approach to the separation of the charge and radical centers in radical cations derived from diaryl olefins would be to design substrates in which one of the aryl groups stabilizes the positive charge while the other destabilizes the charge and at the same time provides stability to the radical center. Radical cation **14** is expected to be of this type; the methoxy group is expected to localize the charge on one side of the central bond while the nitro in the other aryl group will reinforce the charge localization and provide stabilization of the radical center.



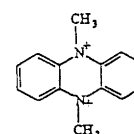
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Radical cation – dication reactivity comparisons. In general, arene dianions and dications are of the order of 10^6 times as reactive toward electrophiles or nucleophiles than the corresponding radical ions.^{55,56} The reactivity difference is without doubt partly due to coulombic factors but in terms of our hypothesis, coupling of the charge and radical centers to reduce the radical cation reactivity is also a factor. One problem in making comparisons of radical cation/dication reactivity is that it is often not possible to find reactants for which the rate constants can be measured with both of these reactive intermediates. Another problem is that the dications of most arenes are short-lived.

The dications **15** and **16** along with the corresponding radical cations would appear to be ideal for this comparison. The dication **15** is available as a stable salt, and **16** is readily observed at low scan rates in acetonitrile. The reactions on which the relative reactivity comparison might be made is proton transfer to suitable bases. We have observed that substituted *N,N*-dimethylaniline radical cations undergo proton transfer with both acetate ion and pyridine in acetonitrile.¹³ The rate constants for the reactions with acetate ion are of the order of 10^4 greater than those observed with pyridine as the base. It would appear likely on the basis of the similarities in structures of **15** and **16** to the *N,N*-dimethylaniline radical cations that these two bases may be applicable in this case as well.



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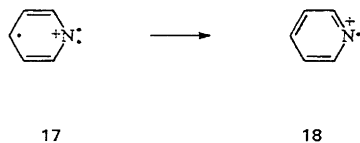


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Diarylacetylene radical ion activity. Qualitatively, it has been known for some time that radical anions derived from aryl substituted acetylenes and allenes, both of which have sp-hybridized carbon atoms, undergo protonation more rapidly than those derived from aromatic compounds or aryl olefins.⁵⁷ It seems likely that the enhanced protonation rates of radical anions derived from the sp-hybridized systems result from a basic difference in radical anion structure as compared to the more familiar sp²-systems. It is possible that the former have characteristics of vinyl carbanions, very basic species. This suggests that the radical ions derived from the sp-systems may acquire distonic like structures with two sets of orthogonal π -systems.

Hydrogen atom abstraction reactions of heteroaromatic radical cations. In a preliminary study⁵⁸ we have shown that radical cations derived from acridine and 9-substituted acridines undergo hydrogen atom abstraction reactions with solvent or intentionally added hydrogen atom donors. Our hypothesis on radical ion reactivity allows us to explain this unusual reaction. As illustrated below for the radical cation of pyridine, decoupling of charge and radical centers can be accomplished by a $n \rightarrow \pi$ transition, which has the effect of localizing the positive charge on nitrogen and removing the odd electron from the π -system localizing it in a non-bonding orbital on nitrogen. The radical cation then behaves as a reactive free radical readily abstracting hydrogen atoms from donor molecules. Since the charge is localized on nitrogen, **18** does not dimerize due to charge-charge repulsion.

The energetics of the $n \rightarrow \pi$ transitions of the radical cations of the aza-aromatic compounds can be studied by MO calculations of the π - and n -ionization potentials in the gas phase coupled with the estimation of the solvation energies of the two forms of the radical cations. For example the solvation energy of **17** can be estimated from the adiabatic ionization potential of pyridine along with the electrode potential for the oxidation of pyridine. The solvation energy of pyridinium ion is expected to be a close approximation to that of **18**.



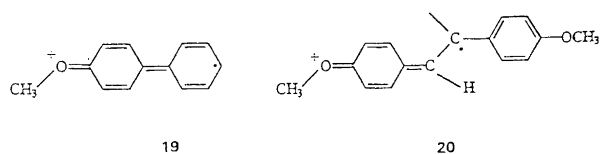
Radical ion - substrate coupling. The observation of the formation of radical ion dimers is not evidence for the radical ion dimerization mechanism, illustrated here for arene radical cations [reaction (3)]. There have been a number of cases where the preferred pathway is the radical ion-substrate coupling mechanism [reactions (4) and (5)]. The coupling reaction (4) is an interesting case to which the CM model can be applied. A single electron

transfer between $\text{ArH}^{\cdot+}$ and ArH is a degenerate reaction giving products identical to reactants. Therefore, a single electron shift in this case goes nowhere. The IG in this case is then simply the singlet-triplet energy (ΔE_{ST}) of ArH . Another pertinent aspect of comparing these two mechanisms for a system is that the steric barriers for reactions (3) and (4) are expected to be equal, so that electronic effects will dominate in determining which of the two mechanisms are preferred.



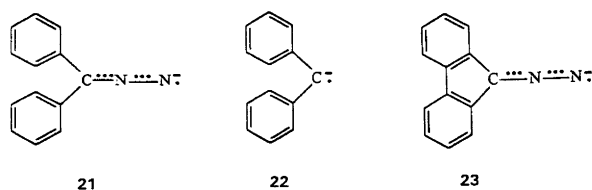
The CM model does not predict a reaction barrier for radical ion dimerizations such as reaction (3). There is a small charge-charge repulsion barrier, but a number of radical ion dimerizations take place at diffusion-controlled rates. The singlet-triplet energies of typical arenes range from about 40–90 kcal mol⁻¹; that for anthracene is 42 kcal mol⁻¹.⁵⁹

The radical ion-substrate coupling mechanism has been observed to take place, rather than the radical ion dimerization, in a number of cases for both radical cations^{60–62} and for radical anions⁶³ in aprotic solvents. Resonance structures of the radical cations of 4-methoxybiphenyl (**19**)^{61,62} and 4,4'-dimethoxystilbene (**20**)⁶⁰ show the separation of charge and radical centers to account for the radical reactivity of these radical ions. As an extension of this work^{60–63} it would be of interest to have reliable estimates of the relative rate constants, k_4/k_3 , for dimerization (k_3) and radical-substrate coupling (k_4). What is presently known is that the radical-substrate mechanism dominates and radical ion dimerization is not observed. The linear sweep voltammetry (LSV) responses for the two mechanisms differ significantly⁶¹ in that the dependence of the peak potential on substrate concentration is 39.3 (radical-substrate) and 19.7 (radical ion dimerization) mV/decade change. Recent advances in digital simulation of electrode processes^{64–66} has resulted in an algorithm suitable for the simulation of complex competitive electrode mechanisms. It is feasible, using the Rudolph method, to analyze competitive radical-substrate and radical ion dimerization in order to evaluate the minimum rate constant ratio $(k_4/k_3)_{\min}$, consistent with the experimental LSV results. Having access to $(k_4/k_3)_{\min}$, along with the experimental value of k_4 , would provide an estimate of the maximum value of the rate constant for dimerization, $(k_3)_{\max}$. This analysis would then provide an estimate of the relative barriers for the two mechanisms.



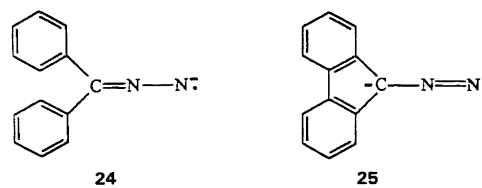
The question which cannot be avoided in considering the fact that radical ion–substrate coupling dominates over radical ion dimerization in the cases discussed above is as follows: Why does the reaction (radical ion–substrate coupling) predicted to have an appreciable barrier ($IG = \Delta E_{ST}$) by the CM model readily take place while that predicted to be barrier free (radical ion dimerization) is not observed? I believe that the answer to this question is clear, as it was for the large IG for proton–anion combination: Barriers predicted by the CM model are not observed in experimental studies.

Radical reactivity of diazoalkane radical ions. The reactions of diazoalkane radical ions in solution is a topic on which considerable work has been carried out.^{67–86} Our work in this area was initiated after the intriguing reports^{67–69} that the radical anion (**21**) decomposes in DMF solution to the corresponding carbene radical anion (**22**). We were able to show that the first-order reactions of **21** in either DMF or acetonitrile involve abstraction of hydrogen atoms from solvent rather than unimolecular decomposition to **22**.^{71,73} Studies on the related radical anion **23**, derived from 9-diazoanthracene, resulted in a still different mechanism, second-order dimerization, as the initial step.

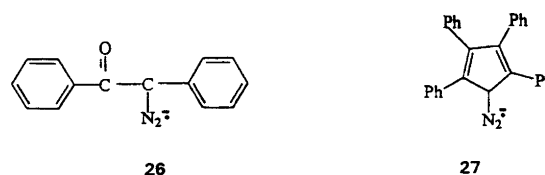


The fact that **21** abstracts hydrogen atoms from solvent while **23** undergoes dimerization was regarded as a mystery at the time. Our more recent observations of hydrogen atom abstraction reactions of acridine radical cations discussed in a previous section suggests an explanation for this unexpected result. The fact that hydrogen atom abstraction, with a relatively high activation energy, takes place in preference to dimerization of **21** indicates that there is a significant barrier to the latter. In analogy to the acridine radical cation reactions it seems reasonable to conclude that resonance form **24** with charge, and the odd electron on N contributes strongly to the structure of the radical anion and gives rise to hydrogen atom abstraction and a large barrier to dimerization. Separation of charge and the radical center for radical anion **23** can be depicted by resonance form **25** which is not predicted to have a substantial barrier for dimerization.

Unimolecular decompositions of two different radical anions (**26** and **27**) were later observed.^{76,77,85} The characteristic features of these unimolecular reactions include (i) first-order kinetics in the absence of proton donors, (ii) increased reactivity in the presence of hydroxylic compounds, (iii) the absence of solvent kinetic deuterium isotope effects, ruling out rate-determining proton or



hydrogen atom transfer from the solvent, and (iv) enthalpies of activation of the order of 10–12 kcal mol⁻¹. Point (ii) contributes to the separation of charge and radical centers accompanied by localization of charge during hydrogen bonding to hydroxylic compounds.

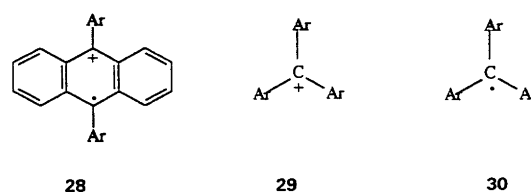


Several related radical cations of diazoalkanes were observed to undergo unimolecular loss of dinitrogen to generate the corresponding carbene radical cation.⁸⁴ The outstanding features of these radical cation decompositions were observed to be (i) first-order kinetics independent upon the presence of nucleophiles and (ii) Arrhenius activation energies of the order of 16 kcal mol⁻¹.

In connection with the hypothesis put forth here it would be of considerable interest to have charge and spin distributions on the numerous diazoalkane radical ions which have been studied to consider in light of the known reaction pathways that these species take part in.

Concluding remarks

The objective of this paper is to take a new look at an old problem, the radical and polar reactivity of radical ions in solution. In retrospect, it is clear that the direction that these studies have taken would have been quite different if the problem of radical ion reactivity had been looked at from a different perspective 20 years ago. The reactivity problem has been centered around the question of polar reactivity only. Suppose that both the polar and radical reactivities of radical cations had been considered simultaneously. The discussion could have been based on the reactivity of the 9,10-diarylanthracene radical cation (**28**). Comparisons could then have been made to the triarylmethyl carbenium ion (**29**) for polar reactivity and to the triarylmethyl radical (**30**) for radical reactivity. If the polar reactivity of **28** and **29** had been compared



toward an anionic nucleophile such as acetate ion, **28** would have been observed to react very fast with a rate constant of perhaps $10^7 \text{ M}^{-1} \text{ s}^{-1}$, while **29** would probably have been observed to react even faster, perhaps with a rate constant of about $10^9 \text{ M}^{-1} \text{ s}^{-1}$. Since free radicals are known to react rapidly with dioxygen, this reaction could have been selected for the radical reactivity comparison between **28** and **30**. What would have been observed is much more dramatic than observed for the polar reactivity comparison. The rate constant observed for the reaction between **30** and dioxygen would probably have been of the order of $10^7 \text{ M}^{-1} \text{ s}^{-1}$, while no reaction at all would have been observed between the radical cation **28** and dioxygen.

Had the polar and radical reactivity comparison discussed in the previous paragraph been available in 1986, it is likely that the CM model discussion of radical cation reactivity would have included both polar and radical reactions. On the basis of this comparison, the question that might have been asked is: Why is the polar reactivity of radical cations so high while the radical reactivity is so low? It is apparent that it is the low radical reactivity of radical cations **28** not the polar reactivity that most clearly distinguishes the radical cations from the triaryl-methyl models.

All of the discussion in this paper is focused on the hypothesis which relates radical ion reactivity to the degree of coupling between the charge and radical centers. A very appealing aspect of this hypothesis is that it is subject to verification by the study of a wide variety of reaction types which depend upon either radical or polar reactivity. There is already considerable fragmentary evidence in the literature to support most of the ideas expressed here.

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