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SHORT COMMUNICATION

ANIONIC NUCLEOPHILE–CATION RADICAL COMBINATION REACTIONS. THE SUPER-ELECTROPHILIC PROPERTIES OF CATION RADICALS IN SOLUTION

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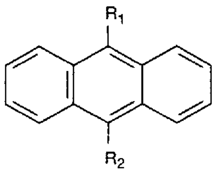
ABSTRACT

Rate constants were determined for the combination reactions of a series of cation radicals derived from substituted anthracenes with acetate, *p*-nitrobenzoate, trifluoroacetate, nitrate and perchlorate ions. Rate constants, depending on the identities of the cation radicals and the nucleophiles, ranging from about 200 to $2 \times 10^{10}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ were observed in acetonitrile at 293 K. The key steps in the reaction are (1) reversible complex formation between the anion and the cation radical followed by (2) irreversible bond formation.

$$\mathrm{Ar}^{+\cdot} + \mathrm{X}^- \rightleftharpoons \mathrm{Ar}^{+\cdot}/\mathrm{X}^- \tag{1}$$

$$\mathrm{Ar}^{+\cdot}/\mathrm{X}^- \rightarrow \mathrm{Ar}^{\cdot} - \mathrm{X} \tag{2}$$

The preliminary results show that cation radical–anionic nucleophile reactions can be very facile. The cation radicals of 9-nitro- and 9-cyanoanthracene are particularly reactive, giving rise to rate constants close to the diffusion-controlled limit with all anionic nucleophile studied and even react moderately rapidly with perchlorate ion. The reaction with perchlorate ion can be compared to the behavior of stable carbenium ions that coexist with the anion in solution and in crystalline salts.



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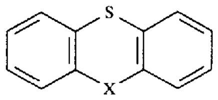

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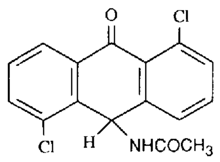

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The reactions of cation radicals in solution are of intense current interest. Pertinent publications since our reviews[1] have described extensive studies of cation radical acidity,[2] evidence for a cation radical mechanism for electrophilic aromatic substitution,[3] evidence for the existence of carbene cation radicals in solution,[4] and conflicting views on the reactivity of cation radicals toward nucleophiles.[5-7]

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The conflicting views on cation radical–nucleophile reactivity arise from the fact that reactions of cation radicals derived from substituted anthracenes (**1**) and from certain heteroaromatic compounds (**2**) with neutral nucleophiles such as pyridine are often second order in cation radical, implicating the formation of dicationic intermediates.[1] This has been interpreted to be a general phenomenon[5] and a theoretical explanation was offered. Our earlier interpretation[1] was that the sometimes slow cation radical–nucleophile kinetics are due to unfavourable equilibria involving the stable cation radicals and the nucleophiles rather than inherently low reactivity of cation radicals in general. In particular, if the nucleophile has an easily expelled proton or is negatively charged, rearrangement of the initially formed π-complex to the covalently bonded adduct would be expected to be more favorable than further oxidation to the dication. It is also important to realize that the early studies purposely employed cation radicals of low reactivity in order to make kinetic measurements possible.

More recently, it has been shown that equilibrium constants for the reactions of 9,10-diphenylanthracene dication with nucleophiles are of the order of 10^{20} greater than those of the cation radical with the same nucleophiles.[6] Hence it appears that the much greater reactivity of the dication compared with the cation radical derives from thermodynamic rather than intrinsic barriers. Also, it has been shown that cation radicals of 9-phenylanthracene, which are unhindered sterically toward nucleophilic attack at the 10-position, undergo reactions with nitrogen-centred nucleophiles at rates up to the diffusion-controlled limit.[7]

We now report kinetic studies of the combinations of transient cation radicals with anionic nucleophiles. The cation radicals studied are those derived from a series of substituted anthracenes (**1**). The reactions of the cation radicals with acetate, *p*-nitrobenzoate, trifluoroacetate, nitrate and perchlorate ions were studied in acetonitrile–$Bu_4N^+ PF_6^-$ (0·1 M) at 293 K.

The kinetic methods[8–10] used to study the reactions are illustrated in Figure 1. The derivative linear sweep voltammogram (A) is for the oxidation of 9,10-diphenylanthracene (APh_2) (0·5 mM) in the presence of *p*-nitrobenzoate ion (0·125 mM) at 40 mV s^{-1}. The rate constant for the reaction can be calculated from the difference in peak potentials for the prepeak (O_1') and the main oxidation peak (O_1).[7,8] We shall refer to this as the 'prepeak' method. The derivative cyclic voltammogram (B) is for the same process measured at 500 V s^{-1} with a nucleophile concentration of 1·0 mM. In this case the rate constant is obtained from R_1', the ratio of derivative peak heights R_1/O_1. We shall refer to this method as DCV.[9,10] The prepeak method is applicable for second-order rate constants ranging from about 10^6 mol l^{-1} s^{-1} up to the diffusion-controlled limit while DCV can be applied to reactions having rate constants up to about 10^7 l mol^{-1} s^{-1}.

Prepeaks are a result of the kinetic potential shifts due to reactions of the electrochemically generated intermediates with reactants in limiting concentrations. In the present case, a prepeak is only observed when insufficient nucleophile is present to react with all the cation radical generated in the diffusion layer. The potential of the prepeak depends on the voltage sweep rate and as the latter is increased the prepeak moves toward and in the limit merges with the main oxidation peak. An additional significant feature of the prepeak method is that the mere observation of a prepeak shows that the chemical follow-up reaction is first-order in both the electrode generated intermediate and the limiting reagent.[7]

Rate constants for the processes studied are summarized in Table 1. The values without parentheses were obtained by the prepeak method and those in parentheses by DCV. The anthracenes are identified by the symbols AR and AR_2 when the substituents are in the 9- and 10- positions, respectively. For example, APh refers to 9-phenylanthracene and APh_2 to 9,10-diphenylanthracene. ACl_2-1,5 identifies 1,5-dichloroanthracene. The products of many,

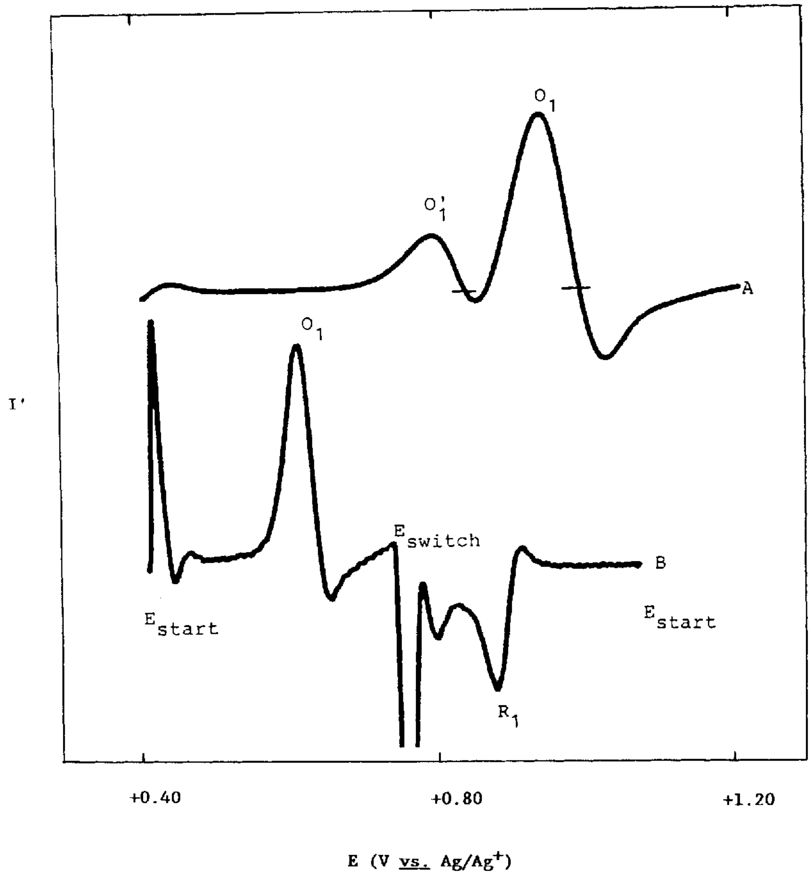

Figure 1. Derivative linear sweep and cyclic voltammograms for the oxidation of 9,10-diphenylanthracene (0·5 mM) in CH_3CN–Bu_4NPF_6 (0·1 M) at 293 K, (A) in the presence of $O_2NC_4H_4CO_2^-$ (0·125 mM) at a voltage sweep rate of 40 mV s^{-1} and (B) in the presence of $O_2NC_4H_4CO_2^-$) (1·0 mM) at a voltage sweep rate of 500 V s^{-1}. The potential scale refers to (A) and I' is the first derivative of the current–potential curve

Table 1. Second-order rate constant for anion–cation radical combination[a]

Cation radical from[b]	Nucleophile/log k(l mol^{-1} s^{-1})				
	$CH_3CO_2^-$	$O_2NC_4H_4CO_2^-$	$CF_3CO_2^-$	NO_3^-	ClO_4^-
APh_2	7·96 (7·26)	6·42	(3·48)	(2·34)	
APh	9·53	9·10	6·56	6·18	
ACl_2	9·11	9·66	6·64	6·70	
ABr_2	9·15	9·48	7·11 (6·58)	6·15	
ACl_2(-1,5)	9·96	9·30	8·42	7·30	
ANO_2	10·28	9·86	9·89	8·80	(2·46)
ACN	10·11	9·99	10·15	9·00	(2·32)

[a] In CH_3CN–Bu_4NPF_6 (0·1 M) at 293 K. Values in parentheses are from DCV and those without parentheses are from prepeak measurements. Acetate ion and p-nitrobenzoate ion were used as salts of the corresponding conjugate ion (A^-/HA).

[b] A indicates anthracene and the substituents are in the 9- or 9,10-positions unless noted otherwise; APh is 9-phenylanthracene and APh_2 is 9,10-diphenylanthracene.

but not all, of the reactions have been characterized and in most cases these are consistent with the stoichiometric equation

$$2Ar^{+\cdot} + 2X^{-} \rightarrow ArX_2 + Ar \qquad (1)$$

as the primary reaction. The final products of the reactions of the cation radicals of ACl_2-1,5 and ACN with perchlorate ion are **3** and anthraquinone, respectively. The acetamide derivative **3** has previously been found to be the major oxidation product from ACl_2-1,5 under similar conditions.[11] The products are readily accounted for by an initial attack of perchlorate ion on the cation radical followed by further oxidation, addition and elimination reactions. The oxidation of ACN is an overall four-electron process in which 9-hydroxy-10-cyanoanthracene is presumably an intermediate that is more easily oxidized than substrate.

The most outstanding feature of the data is that the reactions are very rapid. The last three lines in Table 1 show that three of the cation radicals are exceptionally 'hot' electrophiles. These react at diffusion control, or nearly so, with all those anions usually considered to be good nucleophiles (acetate, *p*-nitrobenzoate and trifluoroacetate), very rapidly with nitrate ion and reasonably fast with perchlorate ion. Another feature of the data requires comment. In the two cases where it was possible to evaluate rate constants by both kinetic methods, the prepeak method was observed to give higher rate constants. The cause of this discrepancy is being investigated.

In analogy with other recent work,[7] we suggest that the reactions follow a two-step mechanism involving a pre-equilibrium complex formation [equation (2)] followed by irreversible bond formation [equation (3)]. The product-forming reactions do not take part in the kinetics.

$$Ar^{+\cdot} + X^{-} \rightleftharpoons Ar^{+\cdot}/X^{-} \qquad (2)$$

$$Ar^{+\cdot}/X^{-} \rightarrow Ar^{\cdot} - X \qquad (3)$$

A rate constant has been reported for the combination of $DPA^{+\cdot}$ with chloride ion, but the reaction was observed to be second order in cation radical, leaving some doubt as to the interpretation in terms of the primary step in the reaction.[12] More recently, geminate ion pairs obtained by photoexcitation of charge-transfer complexes of tetranitromethane with anthracene derivatives (A–R) were observed to undergo cage combination when R is NO_2, CHO or H [equation (4)] but to diffuse apart when R is phenyl.[13]

$$[A{-}R^{-\cdot}, C(NO_2)_3^{-}] \rightarrow R{-}A^{\cdot}{-}C(NO_2)_3 \qquad (4)$$

In conclusion, this work has shown that the reactivity of cation radicals derived from substituted anthracenes with anionic nucleophiles is generally high and very dependent on structure. Some of the cation radicals are very reactive even with ClO_4^-, which serves as an inert counter ion for carbenium ion salts such as those derived from triarylmethyl cations.

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