pyridine with solutions of 2-acetyl-1,3-dimethylbenzimidazolium chloride in water. To our chagrin, complete deacylation occurred within a few seconds, as was evidenced in the NMR spectra of the solutions by the appearance of the characteristic C-2 proton of the unsubstituted 1,3-dimethylbenzimidazolium ion at δ 9.1 and the shift of the acetyl singlet from δ 2.9 to 2.0. Removal of water and pyridine under reduced pressure, followed by solvent extraction, left a residue which was quickly identified with an authentic sample of 1,3-dimethylbenzimidazolium chloride, but no trace of acetanilide or of *N*-benzylacetamide was to be found anywhere. In fact, the acetyl group seemed to have disappeared almost entirely. It was located in due course in the trapped volatiles, was rendered nonvolatile with sodium hydroxide, and was authenticated as acetic acid by NMR comparisons and by conversion into crystalline *p*-bromophenacyl acetate,[2] identical with authentic material.

Aqueous solutions of glycine and phenylalanine, as well as of aniline and benzylamine, also brought about rapid deacylation, and in all cases acetic acid and the deacylated benzimidazolium ion were the products. Only when reaction was carried out with benzylamine in water-free dimethyl sulfoxide was *N*-benzylacetamide obtained.

Further experimentation revealed that the quaternary 2-acetylbenzimidazolium ion is quite stable in weakly acidic aqueous solution. Less than 5% deacylation occurs during 3 weeks at pH 2. If the pH is raised to neutrality, however, deacylation is rapid, the half-life at pH 7.7 (HEPES) being no more than 20–30 s. The deacylation rate constant, k_2^{OH}, is about 3×10^6 M^{-1} min^{-1}. At pH 5.2 and 4.5, half-lives were 2.5 and 12 h, respectively, confirming that deacylation is brought about by hydroxide ion, even at concentrations of 10^{-9}–10^{-6} M, and hardly, if at all, by water.

Aniline (0.3 M) and pyridine (0.1 M) produced no detectable increase in the deacylation rate, which was indistinguishable (<5%) over four half-lives from that in buffer (HEPES, pH 7.7; MES, pH 5–6) alone. Rate constants for reaction of these nucleophiles thus cannot be determined in the usual way, but it is easily calculated that they cannot at the outside be greater than 5×10^{-4} (aniline) and 1×10^{-3} (pyridine) M^{-1} min^{-1}. These values contrast sharply with published rate constants[9] for *p*-nitrophenyl acetate, a typical active ester acylating agent. The hydroxide constant is 3000 times greater (pNPA, 1×10^3 M^{-1} min^{-1}), while the aniline and pyridine constants are 50–100 times less (pNPA–aniline, 2.3×10^{-2}; pNPA–pyridine, about 10^{-1} M^{-1} min^{-1}).

That the 2-acetyl-1,3-dimethylbenzimidazolium ion is subject to ready deacylation is not particularly surprising. The 1,3-dimethylbenzimidazolium 2-carbanion should be quite a good leaving group.[3] The C-2 proton of 1,3-dimethylbenzimidazolium salts exchanges rapidly in very weakly basic solution.[4] Analogous quaternary 2-acylthiazolium salts examined in the course of the classic work on the mechanism of function of thiamin 25 years ago are deacylated in neutral water just about as readily as the benzimidazolium compound is.[5] And indeed, the deacylation of 2-acetyl-1,3-dimethylbenzimidazolium iodide by water, alcohols, phenols, and amines had been reported previously,[6] although the conditions utilized were so vigorous as to give no hint as to the facility with which reaction would take place.

What is exceptional, however, is the lack of reactivity toward primary aliphatic and aromatic amine nucleophiles in water, and toward water itself for that matter, in contrast to a reactivity toward the hydroxide ion thousands of times greater than that of a typical active ester and not far short of that exhibited by typical acid anhydrides.

Hydroxide ion is a remarkably poor nucleophile toward acylating agents.[7] Even weakly basic amines such as aniline and *p*-anisidine are acylated quite satisfactorily in aqueous sodium carbonate by such reagents as acetic anhydride and benzoyl chloride, yet if nucleophilic competitiveness merely reflected concentration multiplied by basicity, nothing but hydrolysis products should result.[8] Brönsted plots for hydrolysis and aminolysis reactions of esters show hydroxide 2, 3, even 5 log units off the lines (slopes typically about 0.8) for amines and well off the lines for other oxyanion nucleophiles in many cases.[9] Comparable plots of the present data would have hydroxide not more than 1 log unit at the outside below a line of unit slope or on, or even above, a line of slope 0.9. It has been suggested[10] that the anomalous behavior of hydroxide, which is exhibited to some extent by other strongly basic oxyanions also, might be attributed to a requirement for rate-influencing or rate-controlling desolvation of these strongly solvated ions, and further evidence and cogent arguments continue to appear.[11] Most noticeable, however, is the dearth of exceptions to the anomaly. The low reactivity of hydroxide ion is so commonplace, so ubiquitous, as to seem the norm. As best we can ascertain, the 2-acetyl-1,3-dimethybenzimidazolium ion is the first acylating agent to exhibit the reactivity it properly should toward the hydroxide ion as opposed to other nucleophiles.

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Rapid, Low Activation Energy, Selective, Direct Reactions of Cation Radicals with Nucleophiles. An Experimental Test of Theory

Vernon D. Parker* and Mats Tilset

Laboratory for Organic Chemistry
Norwegian Institute of Technology, University of
Trondheim, N-7034 Trondheim-NTH, Norway

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A number of reactions of cation radicals with nucleophiles are second order in cation radical and first order in nucleophile.[1a,b] When these reactions are studied by homogeneous kinetic techniques the stoichiometry which must be considered is the half-regeneration scheme (1).[2a–e,3ab] The apparent low reactivity of

$$2A^{\bullet +} + Nu \rightarrow A^{+}\text{–}Nu^{+} + A \tag{1}$$

some cation radicals as compared to the corresponding carbocations was noted by Eberson.[4]

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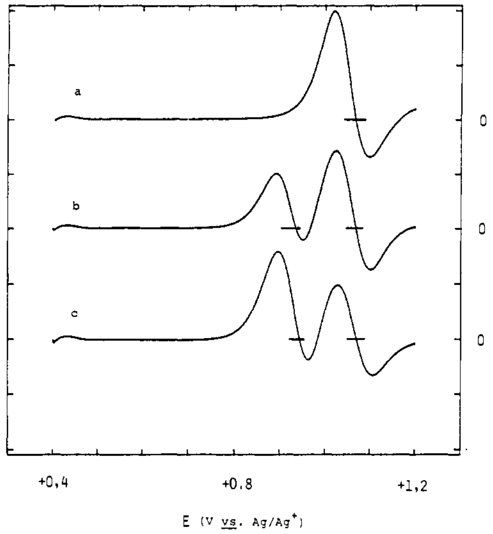

Figure 1. Derivative linear sweep voltammograms for the oxidation of 9-phenylanthracene (1.00 mM) in the presence of pyridine (a, 0.0 mM; b, 0.25 mM; c, 0.5 mM) in CH_3CN/Bu_4NPF_6 (0.10 M) at a voltage sweep rate of 100 mV/s at 293.2 K.

A consideration of these observations[1-4] recently led Pross[5] to analyze cation radical–nucleophile reactivity using the elements of the configuration mixing (CM) model.[6a-c] This analysis resulted in the general conclusion that the direct reaction between a cation radical and a nucleophile is a high-energy process and therefore classified as "forbidden".

Although we find this novel approach to ion radical reactivity very interesting, we do not believe that the conclusions are consistent with some experimental observations. For example, there are cation radical–nucleophile reactions which are very rapid and follow rate law 2. The kinetics of these reactions can only be explained by the direct reaction of the cation radical with the nucleophile.[2c,7]

$$-d[A^{\bullet +}]/dt = k_{app}[A^{\bullet +}][Nu] \qquad (2)$$

All bimolecular reactions in solution pass through an encounter complex.[8] Whether or not the presence of the encounter complex is manifested in the observed kinetics depends upon the relative magnitudes of k_p and k_{-en} (eq 3 for this case). Previous studies[2c,7]

$$A^{\bullet +} + Nu \underset{k_{-en}}{\overset{k_{en}}{\rightleftharpoons}} (\text{encounter complex}) \xrightarrow{k_p} Ar^{\bullet}\text{-}Nu^{+} \qquad (3)$$

on cation radical–nucleophile reactions have not provided information on this point. The observation of rate law 2 suggests a test of theory based on the CM model. According to the theory, reactions following (3) can take place *but* are predicted to have high activation energies.

In this paper, we examine the kinetic and activation parameters for one series of reaction 3 where $A^{\bullet +}$ is 9-phenylanthracene (PA) cation radical and Nu's are nitrogen centered nucleophiles. We show that these very rapid reactions have small activation energies and show considerable selectivity. These observations appear to be inconsistent with the conclusions[5] based upon the CM analysis.

Table I. Peak Potential Differences and Rate Constants for the Reaction of 9-Phenylanthracene Cation Radical with 4-Methylpyridine in Acetonitrile[a]

T/K	ν/V s^{-1}	ΔE_p[b]/mV	$(\Delta E_p)_{298}$[c]/mV	$10^{-7}k_7$/M^{-1} s^{-1}
293.2	0.100	159.2	161.9	4.63
293.2	0.200	148.5	151.0	4.32
293.2	0.400	136.2	138.5	3.70
283.2	0.100	151.2	159.2	3.82
283.2	0.200	142.7	150.3	4.11
283.2	0.400	131.2	138.2	3.63
273.2	0.100	145.7	159.0	3.82
273.2	0.200	137.7	150.3	4.11
273.2	0.400	127.2	138.8	3.77
				av 3.99 ± 0.33

[a] Derivative linear sweep voltammetry data for the oxidation of 9-phenylanthracene (1.00 mM) in the presence of 4-methylpyridine (0.25 mM) in solvent containing Bu_4NPF_6 (0.1 M). [b] The potential difference between the prepeak and the peak for the reversible oxidation. [c] The measured potential differences converted to values at 298.15 K for comparison with theoretical values.

Table II. Rate Constants and Activation Parameters for the Reactions of 9-Phenylanthracene Cation Radical with Nucleophiles

nucleophile (pK_a)	k_{AN}[a]/M^{-1} s^{-1}	$k_{CH_2Cl_2}$[b]/M^{-1} s^{-1}	E_a[c]	k_{PA}/k_{DPA}[d]
pyridine (12.3)[f,g]	1.1×10^7	8.0×10^6	2.6	5000
4-methylpyridine (14.3)[g]	4.0×10^7	3.3×10^7	0	7000
piperidine[e] (18.9)[f]	1×10^9	2×10^9		500
4-cyanopyridine (8.0)[g]	1.4×10^5		0.1	6000

[a] Rate constant in CH_3CN/Bu_4NPF_6 (0.1 M) at 293.2 K. [b] Rate constant in CH_2Cl_2/Bu_4NPF_6 (0.2 M) at 293.2 K. [c] Arrhenius activation energy (kcal/mol) in CH_3CN/Bu_4NPF_6 (0.1 M) for measurements at 273.2, 283.2, and 293.2 K. [d] Relative rate constants for the reactions of 9-phenylanthracene and 9,10-diphenylanthracene cation radicals, the latter from ref 2c and 15. [e] The rate constants measured with piperidine were dependent on the sweep rate, indicating charge-transfer kinetic problems at potentials so far removed from $E°$. The rate constants reported here are most likely minimum values for this reason. [f] From ref 16. [g] Values quoted in ref 17.

The kinetics of the reactions were studied by derivative linear sweep voltammetry (DLSV)[9] and the rate constants were evaluated by the differences in the potentials of the prepeak and that for the reversible process when insufficient quantities of the nucleophile were present to react with all of the cation radicals generated.[10] The analysis is illustrated by the voltammograms in Figure 1. The reversible oxidation of PA (1.00 mM) to the cation radical was observed with a peak potential (E_p) equal to +1.17 V vs. Ag/Ag$^+$ (Figure 1a). The peak potential is defined by the point where the rapidly descending derivative curve passes through 0. The addition of pyridine (0,25 mM) to the solution resulted in the oxidation process dividing into two peaks, a prepeak and one for the reversible oxidation (Figure 1b). Further addition of pyridine (0.50 mM) resulted in an enhancement of the prepeak at the expense of the main oxidation peak (Figure 1c). Since peak potentials can be measured to a high degree of precision,[9] precise rate constants can be evaluated by comparing experimental peak potential differences (ΔE_p) with the theoretical values obtained by digital simulation.[10]

The observation of a prepeak during linear sweep voltammetry is overwhelming evidence for a reaction first order in the electrode-generated intermediate. A prepeak is only observed when the second-order rate constant is 10^6 M^{-1} s^{-1} (at 0.1 V/s) or greater. Simulations of second-order (in $A^{\bullet +}$) or third-order (second order in $A^{\bullet +}$ and first order in Nu) reaction schemes *do not* give rise to prepeaks. In fact, for a purely second-order reaction, (4), the peak potential is shifted by only 107 mV with

$$2A^{\bullet +} \xrightarrow{k} \text{products} \qquad (4)$$

k equal to 10^9 M^{-1} s^{-1} (C_A = 1 mM, 0.1 V/s). A third-order reaction with limiting concentrations of Nu would give rise to smaller peak potential shifts.

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The data in Table I for the reaction of $PA^{\bullet+}$ with 4-methylpyridine illustrate the excellent fit of experimental data with theory for rate-determining reaction 3 and the overall stoichiometry shown in (5).[11] The apparent rate constants were observed to be in-

$$2PA^{\bullet+} + 2Nu \rightarrow PA(NU)_2^{2+} + PA \qquad (5)$$

dependent of voltage sweep rate (ν) and essentially independent of the temperature (average value equal to 4,0 (±0,3) × 10^7 M^{-1} s^{-1}) indicating a very low or zero activation energy. Kinetic data for the reactions of $PA^{\bullet+}$ with pyridine, 4-methylpyridine, and piperidine, obtained by the prepeak method, in both acetonitrile and dichloromethane are summarized in Table II. Data for the reaction of $PA^{\bullet+}$ with 4-cyanopyridine obtained by conventional double-potential-step chronoamperometry in acetonitrile are included as well,

The features of the data of most interest are the very large rate constants, low activation energies, and high selectivities, A plot of log k vs. pK_a (of the nitrogen bases) for the reactions in acetonitrile is curved, indicating decreased selectivity as the rate approaches diffusion control,[13] The data show that reactions 3 are not only "allowed" but also quite facile. The relative rate constants for the reactions of $PA^{\bullet+}$ and 9,10-diphenylanthracene cation radical (k_{PA}/k_{DPA}) suggest a substantial steric effect for reactions 3 when $DPA^{\bullet+}$ reacts with the nitrogen-centered nucleophiles.

The near zero or very low apparent activation energies suggest that the formation and dissociation of of the π complex (eq 6)

$$PA^{\bullet+} + Nu \underset{k_b}{\overset{k_f}{\rightleftharpoons}} PA^{\bullet+}/Nu \xrightarrow{k_p} PA^{\bullet}\text{-}Nu^{+} \qquad (6)$$

$$-d[PA^{\bullet+}]/dt = 2k_p(k_f/k_b)[PA^{\bullet+}][Nu] \qquad (7)$$

must be taken into account in the detailed rate law (7). This sequence can give rise to low or even negative activation energies.

The fact that the rate constants obtained for Nu being 4-cyanopyridine by the direct kinetic method, which would detect $PA^{\bullet+}/Nu$ as well as $PA^{\bullet+}$, are in accord with the expectation based on the log k vs. pK_a plot confirms that the reaction is going to completion on the time scale of the kinetics. Thus, relationship 8 is valid. This rules out the unlikely possibility that K ($=k_f/k_b$)

$$-d([PA^{\bullet+}] + [PA^{\bullet+}/Nu])/dt = -d[PA^{\bullet+}]/dt = k_{app}[PA^{\bullet+}][Nu] \qquad (8)$$

is large and thus k_p does not contribute to the kinetics. Complexes such as $PA^{\bullet+}/Nu$ have been proposed to account for kinetic observations in numerous other cases,[1] but it has not yet been possible to observe them. This has been attributed to small equilibrium constants for their formation. The results reported here are consistent with these observations and suggest that the low activation energies are a consequence of a negative ΔH° associated with the preequilibrium masking the positive E_a of the bond-forming step.

Our general conclusion is that cation radical–nucleophile reactions can be very rapid, approaching diffusion control, and have low activation energies. The rapid reactions are first order in cation radical, The detailed structures of the initial products of the reactions are not known and the products may or may not form via a kinetically observable intermediate π complex. In any event, it would appear that the general conclusion[5] that cation radical–nucleophile reactions are high-energy reactions is not correct,

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Intramolecular Photoinduced Diene–Diene Cycloadditions: A Selective Method for the Synthesis of Complex Eight-Membered Rings and Polyquinanes

Paul A. Wender* and Carlos R, D, Correia[1]

Department of Chemistry, Stanford University
Stanford, California 94305

Received September 9, 1986

The photoinduced [$2\pi + 2\pi$] cycloaddition of alkenes is one of the most commonly used strategy-level reactions for complex molecule synthesis. Its utility has been established for cycloadditions of ground-state alkenes with excited-state alkenes, dienes, and chromophores incorporating these groups.[2] Intermolecular diene–diene cycloadditions have also been studied[3] and a few have practical value[3b] but most are reported to produce complex mixtures. Sensitized dimerization of isoprene, for example, gives seven products and at least 15 dimers are obtained from piperylene.[3c] While unexplored, the intramolecular version of this reaction has the potential for circumventing these selectivity problems and for providing a facile route to substitutionally complex eight-membered rings[4] through rearrangement of the divinylcyclobutane photoproducts.[5] Described herein are the first examples of this photochemical reaction which delineate its scope and stereoselectivity and establish its merit in cyclooctane and polyquinane synthesis, the latter through a formal synthesis of the antitumor, antibiotic coriolin (**20**).[6]

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