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Letter

Transformation of Nitrogen-Containing Aromatic Radical Cations into Protonated Substrates

Kishan L. Handoo,[1] Jin-Pei Cheng,[2] and Vernon D. Parker*

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, USA

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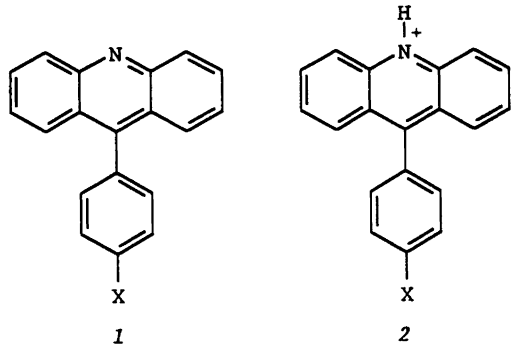
Numerous different ionic reactions of radical ions are commonly observed. On the other hand, atom transfers involving radical ions are rare. We now report preliminary results suggesting that hydrogen atom transfer to nitrogen sites in organic radical cations is a general reaction. The overall result of the process is the formation of the protonated substrate. Although we have observed this process in several classes of organic compounds, we will restrict our discussion to results that we have obtained during the oxidation of 9-arylacridines (**1**). We have chosen these substrates to illustrate this reaction because of our extensive experience with the related 9-phenylanthracene system.[3–7]

The reaction pathway resulting in a protonated substrate involves a $1-e^-$ oxidation of **1** followed by a first-order or pseudo-first-order reaction of $\mathbf{1}^{\bullet+}$. After exhaustive coulometric oxidation of **1** in either acetonitrile/Bu_4NPF_6 (0.1 M) or dichloromethane/Bu_4NPF_6 (0.1 M), the products were separated from the solvent and electrolyte and analyzed by ^1H NMR spectroscopy. In all cases, **2** was the only identified product and found to be in high yield by comparison with authentic **2** obtained by protonation of the substrates. Both the voltammetric and electrolytic behavior of **1** appear to be typical of a number of compounds with nitrogen functionalities as in acridines, 9-pyridylanthracenes and some *N*,*N*-dimethylamino-containing substrates.



1 *2*

a: X = H
b: X = OCH_3
c: X = $N(CH_3)_2$

First-order rate constants for radical cation reactions and substrate oxidation potentials were determined using derivative cyclic voltammetry (DCV)[8] in acetonitrile/Bu_4NPF_6 (0.1 M) and in dichloromethane/Bu_4NPF_6 (0.1 M) at 293 K. The data for substrates **1a–1c** are summarized in Table 1. Rate constants, which were observed to be independent of substrate concentration, are apparent values determined for the EC mechanism. It is of interest to note that significant solvent effects were observed for the reactions of $\mathbf{1a}^{\bullet+}$ and $\mathbf{1b}^{\bullet+}$ but not for those of $\mathbf{1c}^{\bullet+}$. Plots of $\log k$ vs. $\log [CH_3CN]$ in dichloromethane were reasonably linear with slopes of 1.2 ($\mathbf{1a}^{\bullet+}$) and 0.7 ($\mathbf{1b}^{\bullet+}$).[9]

The conversion of **1** into **2** formally corresponds to the addition of a hydrogen atom to the radical cation. Attempts to observe deuterium kinetic isotope effects for reactions carried out in CH_3CN and CD_3CN failed to show significant differences in the two solvents. Likewise, only small differences in rate constant were observed for changes in supporting electrolyte concentration. Furthermore, the observed rate constants for the reactions of $\mathbf{1a}^{\bullet+}$ were observed to be very nearly the same in the presence of either Bu_4NPF_6 (0.1 M) or $LiClO_4$ (0.1 M) as supporting electrolyte. These experiments were carried out in an attempt to identify possible hydrogen atom transfer reactions between radical cation and solvent or electrolyte.

Electrolysis of **1a** and **1c** in dichloromethane/Bu_4NPF_6 (0.2 M) in the presence the hydrogen atom donors, 1,3- or 1,4-cyclohexadiene, resulted in the quantitative formation of **2a**, **2c** and cyclohexadienyl dimers. The kinetic data in Table 2 show the effect of diene concentration on the rate of decomposition of $\mathbf{1c}^{\bullet+}$. The second-order rate constant for the hydrogen atom transfer reaction was observed to be equal to $1.03(6) \times 10^3\ M^{-1}\ s^{-1}$ at 298.1 K.

* To whom correspondence should be addressed.

Table 1. First-order rate constants and oxidation potentials of 9-arylacridines.

9-Aryl group	E^{p}_{rev} [a]	$10^{-2}k$(AN) [b]	$10^{-2}k(CH_2Cl_2)$ [c]
Phenyl	1.322	96	11.3
4-Methoxyphenyl	1.243	74	6.4
4-Dimethylaminophenyl	0.496	0.050	0.081

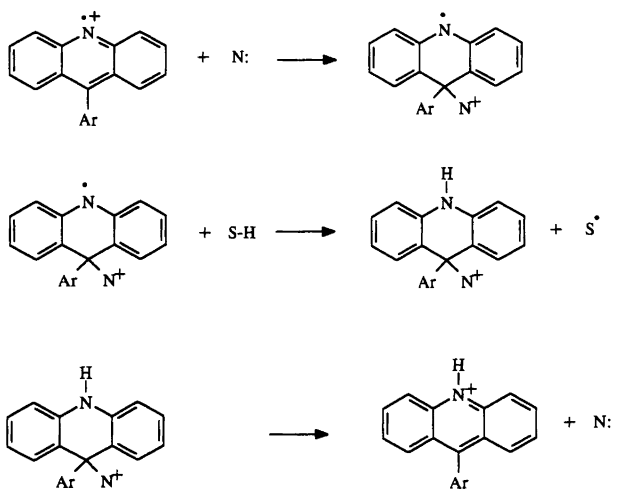
[a] Measured in acetonitrile/Bu_4NPF_6 (0.1 M) vs. ferrocene/ferrocene$^{+\cdot}$ at a voltage sweep rate of 100 V s^{-1}. [b] ln s^{-1} measured at 293 K in acetonitrile/Bu_4NPF_6 (0.1 M). [c] ln s^{-1} measured at 293 K in CH_2Cl_2/Bu_4NPF_6 (0.1 M).

Table 2. Hydrogen atom transfer reactions between 9-(4-dimethylaminophenyl)acridine radical cation and 1,3-cyclohexadiene.

[Diene]/M	(k_1/s^{-1}) [a]	$(k_2/M^{-1}s^{-1})$ [b]
0.156	176	1128
0.209	213	1019
0.260	249	958
0.312	300	962
0.365	380	1041
0.418	427	1022
0.520	555	1067
0.728	758	1041

[a] Pseudo-first-order rate constant in CH_2Cl_2/Bu_4NPF_6 (0.2 M) at 298.1 *K* measured by derivative cyclic voltammetry. [b] Second-order rate constant.

Our preliminary mechanistic conclusions based on the data described in the previous paragraphs are outlined in Scheme 1. The initial step in the reaction, in the absence of an added hydrogen atom donor, involves interaction between the radical cation and a nucleophile (N:), either water or acetonitrile. The product-forming steps are then proposed to involve hydrogen atom abstraction from the solvent or supporting electrolyte followed by dissociation of N: to give protonated substrate. The failure to observe a solvent deuterium kinetic isotope effect suggests that H-atom abstraction from solvent is not rate determining.



Scheme 1.

The initial step is written to account for the more rapid reactions either in acetonitrile or in the presence of water. In the presence of good hydrogen atom donors, such as the cyclohexadienes, nucleophilic catalysis (step 1) is not necessary and moderately rapid second-order hydrogen atom transfer reactions are observed.

We find that during the anodic oxidation of the parent compound acridine (Acr) the protonated substrate is a major product. However, in this case competing reactions, presumably resulting in coupling products, were also observed. Coupling reactions of oxidized intermediates have previously been observed during acridine oxidation in acetonitrile.[10,11] In one report[11] it was proposed that one half of the acridine was converted into protonated acridine in an acid–base reaction of the substrate with protons generated during electrolysis. However, our results suggest that the reaction pathway leading to Acr-H$^+$ is the same as that for the cation radicals of 9-arylacridines reported here.

The hydrogen atom transfer mechanism has previously been implied from the products observed during the oxidation of triethylamine in acetonitrile.[12,13] We believe that this mechanism is quite general and will be observed for most nitrogen-containing radical cations as long as other more rapid pathways are suppressed. Further work, to determine the scope and generality of this oxidation process is in progress.

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