Hydrogen atom abstraction by radical cations. The reactions of 9-substituted acridine radical cations with cyclohexa-1,4-diene †

Kishan L. Handoo, Jin-Pei Cheng ‡ and Vernon D. Parker *

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

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9-Substituted acridine radical cations undergo facile hydrogen atom abstraction reactions with cyclohexa-1,4-diene in dichloromethane–Bu_4NPF_6 (0.2 M). The kinetics of the reaction were studied by derivative cyclic voltammetry and observed to conform to the EC mechanism (charge transfer followed by irreversible first-order reaction). The products of the reactions are the protonated acridine substrate and dimer–substrate adducts of cyclohexa-1,4-diene. A comparison is made between the reactions of 9-phenylacridine and 9-phenylanthracene radical cations. The former undergoes rapid hydrogen atom abstractions, while the latter slowly dimerizes in the absence of nucleophiles. It is suggested that localization of the odd electron in a p-orbital on nitrogen imparts the hydrogen abstraction activity of the radical cation. Since there are no free p-orbitals on the carbon atoms of the aromatic rings in arene radical cations the hydrogen atom abstraction reaction pathway is not observed.

Introduction

It has recently been pointed out[1] that although radical cations have dual functionality, their polar reactions have received very much more attention than reactions that depend upon the unpaired electron. Of the three most characteristic reactions of free radicals (dimerization, atom abstraction and reaction with dioxygen) only the former is frequently encountered with radical cations. Radical cations of a number of olefins,[2] including some tetraalkyl olefins[3] related to biadamantylidene, react with dioxygen to form dioxetanes, but the radical cations derived from most other compounds are inert to dioxygen. We have previously observed that some substituted acridine radical cations abstract hydrogen atoms from the solvent upon generation in acetonitrile.[4]

Dimerization, or coupling with substrate, reactions more commonly exhibit the radical behaviour of radical cations. But here again dimerization can only be expected when there are specific structural features, in addition to the odd electron, which promote free radical-like behavior. For example, dimerization is a common pathway of methoxy-substituted benzene radical cations, as long as there are unsubstituted positions *ortho* or *para* to the methoxy group. It has previously[1] been proposed that the most important structural feature which promotes dimerization of radical cations is the presence of substituents which effectively decouple the charge and spin by localization of the charge onto the substituent, for example on the methoxy group.

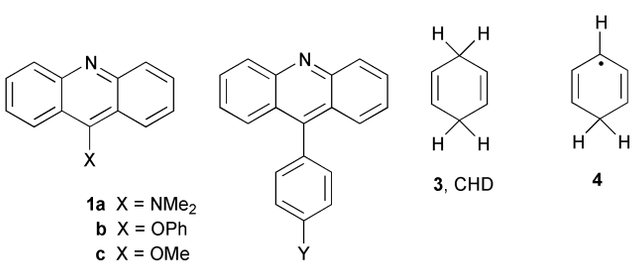
In this paper we present kinetic data for hydrogen atom transfer reactions of the only series of radical cations, substituted acridine radical cations, which have been observed to undergo the reaction. The data reported here support the hypothesis that this reaction series, like those which undergo radical cation dimerization, possess a structural feature that promotes decoupling of charge and spin, resulting in the propensity to abstract hydrogen atoms from suitable donors.

† This paper is dedicated to the memory of Professor Lennart Eberson whose many contributions had an enormous influence on the chemistry of radical cations and on the work of one of the authors (V. D. P.).
‡ Present address: Department of Chemistry, Nankai University, Tianjin 300071, China.

Results

Radical cation substrates and the hydrogen atom donor

Although the radical cation of the parent compound in the series, acridine, will most likely take part in hydrogen atom transfer reactions, we omit this substrate due to practical difficulties in obtaining kinetic data. We have used two series of substituted acridines, **1** and **2**, in our studies, along with the hydrogen atom donor cyclohexa-1,4-diene (CHD), **3**.



Reversible oxidation potentials and hydrogen atom transfer product yields

The reaction between an acridine radical cation and CHD is illustrated by eqn. (1).

$$\mathbf{1}^{+\bullet} + \text{CHD} \rightarrow \mathbf{1\text{-}H}^{+} + \mathbf{4} \qquad (1)$$

The reaction is conveniently followed using cyclic voltammetry. Before addition of CHD to the solution containing the substrate, the peak potential and peak current for the oxidation of the substrate are recorded. After exhaustive electrolysis in the presence of CHD the voltammogram is recorded before and after neutralization by the addition of a suitable base. The yield of the conjugate acid of the substrate can then be determined by the peak current for oxidation of substrate measured at the end of the procedure described above.

Peak potentials for the oxidation of the various 9-substituted acridines, along with the apparent % yields of protonated

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Table 1 Reversible oxidation potentials of 9-substituted acridines and yields of protonated substrates obtained during exhausive electrolytic oxidation in acetonitrile.[a]

Compound	E_{ox} [b]	Yield (%) [c]
9-Dimethylaminoacridine **1a**	0.478	—
9-Phenoxyacridine **1b**	1.210	83
9-Methoxyacridine **1c**	1.067	80
9-Phenylacridine **2a**	1.322	86
9-(4-Methoxyphenyl)acridine **2b**	1.243	94
9-(4-Dimethylaminophenyl)acridine **2c**	0.496	90

[a] Solvent containing Bu_4NPF_6 (0.1 M) at 298 K. [b] Reversible electrode potential measured *vs.* ferricinium/ferrocene by derivative cyclic voltammetry at 100 V s^{-1}. [c] Yield of conjugate acid of the substrate, see Experimental section for details.

Table 2 Substrate reaction order studies for the reactions of 9-substituted acridine radical cations with cyclohexa-1,4-diene in dichloromethane–Bu_4NPF_6 (0.2 M) at 298 K

Substrate	[Substrate]/mM	[Diene]/mM	v_c/V s^{-1} [a]
2a	0.50	10.0	579
	1.00	10.0	565
	1.50	10.0	569
	2.00	10.0	561
2b	0.50	20.0	158.0
	1.00	20.0	158.4
	1.50	20.0	155.3
	2.00	20.0	156.6
2c	0.50	100	81.8
	1.00	100	81.2
	1.50	100	83.9
	2.00	100	82.7

[a] Voltage sweep rate necessary to achieve a given R'_I value; $R'_I = 0.4$, 0.5 and 0.6 for 9-phenylacridine **2a**, 9-(4-methoxyphenyl)acridine **2b**, and 9-(4-dimethylamino)acridine **2c**, respectively.

products after exhaustive electrolysis in dichloromethane–Bu_4NPF_6 (0.1 M) in the presence of CHD (0.1 M) at 298 K, are summarized in Table 1. In the case of 9-dimethylaminoacridine **1a** oxidation, the conjugate acid of the substrate was not the exclusive product and the results were not reproducible. In all other cases the yield was observed to be 80% or greater.

Kinetic studies of the reactions between 9-substituted acridine radical cations with cyclohexa-1,4-diene

The kinetics of the reactions were studied by derivative cyclic voltammetry[5] (DCV), which has been used in numerous radical ion kinetic studies in our laboratory. Ordinary cyclic voltammetry is not suitable for detailed kinetic studies due to the difficulty in establishing a baseline for measurement of the reverse peak current. This difficulty is overcome with DCV, since the baselines for both forward and reverse scans are close to zero. Kinetic studies were carried out in dichloromethane–Bu_4NPF_6 (0.2 M) at 298 K. This solvent system has the advantage that it does not provide as good a source of hydrogen atoms as the acetonitrile–Bu_4NPF_6 (0.1 M) system, so the radical cations are longer lived in the absence of added hydrogen atom donor. This latter is advantageous when measuring second-order rate constants between radical cations and hydrogen atom donors, since the effect of the background reaction is eliminated at lower hydrogen atom donor concentrations.

The data in Table 2 show the effect of substrate concentration (C_A) on the voltage sweep rate (v_C) necessary for a particular value of R'_I, the ratio of reverse to forward derivative peak heights. If the reaction order in radical cation is unity, v_C is predicted by the reaction order approach[5] to be constant independent of C_A, while v_C varies directly with log C_A for reactions second-order in radical cation. The values of v_C are, within experimental error, independent of C_A in all three cases shown in Table 2. The latter provides convincing evidence that the reactions of the radical cations with CHD are cleanly first-order in radical cation.

Table 3 Effect of cyclohexa-1,4-diene concentration on apparent rate constants for the reactions with 9-methoxyacridine **1b** and 9-phenoxyacridine **1c** radical cations in dichloromethane–Bu_4NPF_6 (0.2 M) at 298 K

	1b		**1c**	
[Diene]/mM	k_1/s^{-1a}	$10^{-3}k_2$/ M^{-1} s^{-1b}	10^{-3} k_1/ s^{-1a}	10^{-4} k_2/ M^{-1} s^{-1b}
10.0	—	—	1.136	11.4
15.0	—	—	1.508	10.1
20.0	265	13.3	1.635	8.18
25.0	346	13.8	1.803	7.21
30.0	353	11.8	2.53	8.43
35.0	365	10.4	2.88	8.21
40.0	432	10.8	2.97	7.42
45.0	441	9.80	3.71	8.24
50.0	462	9.24	3.78	7.55
60.0	491	8.18	—	—
70.0	578	8.26	—	—
80.0	691	8.64	—	—
90.0	790	8.78	—	—
100	868	8.68	—	—

[a] First-order rate constants for the EC mechanism. [b] Apparent second-order rate constants for the reactions of the radical cations with cyclohexa-1,4-diene.

Table 4 Effect of cyclohexa-1,4-diene concentration on apparent rate constants for the reactions with 9-phenylacridine **2a** and 9-(4-methoxyphenyl)acridine **2b** in dichloromethane–Bu_4NPF_6 (0.2 M) at 298 K

	2a		**2b**	
[Diene]/mM	10^{-3} k_1/ s^{-1a}	10^{-5} k_2/ M^{-1} s^{-1b}	10^{-2} k_1/ s^{-1a}	10^{-4} k_2/ M^{-1} s^{-1b}
10.0	2.40	2.40	—	—
20.0	3.87	1.93	5.42	2.71
30.0	4.57	1.52	8.60	2.87
40.0	5.45	1.36	10.2	2.54
50.0	6.52	1.30	11.0	2.20
60.0	7.79	1.30	12.9	2.15
70.0	11.3	1.61	13.4	1.91
80.0	11.1	1.39	16.4	2.05
90.0	17.8	1.97	18.0	2.00
100	16.6	1.66	20.9	2.09

[a,b] See Table 3.

Since the radical cations are not long-lived in the absence of added hydrogen atom donor it is necessary to insure that the background reaction is insignificant under the conditions that second-order rate constants for hydrogen atom abstraction are determined. A convenient way to do this is to evaluate apparent second-order rate constants over a range of hydrogen atom donor concentrations, [CHD] in this work. The data in Tables 3, 4 and 5 illustrate the determination of second-order rate constants for the radical cation hydrogen atom abstractions. The first-order rate constants for the reactions of the radical cations were assigned by comparison of experimental to theoretical data for the EC mechanism, which is an irreversible first-order reaction following charge transfer. If the background reaction is not negligible, apparent second-order rate constants will be larger than the value for the reaction between radical cation and CHD. The data in all three tables show that at the low end of [CHD] the apparent second-order rate constants are large and that they decrease to a constant (within experimental

Table 5 Effect of cyclohexa-1,4-diene concentration on apparent rate constants for the reactions with 9-(4-dimethylaminophenyl)acridine **2c** in dichloromethane–Bu_4NPF_6 (0.2 M) at 298 K

[Diene]/mM	R'_I	k_1/s^{-1a}	$k_2/M^{-1}\ s^{-1b}$
0.104	0.718	131.5	1255
0.156	0.676	155.9	999
0.209	0.639	180.5	864
0.260	0.608	203.4	782
0.312	0.571	234.3	751
0.365	0.525	280.3	768
0.418	0.503	306.2	733
0.520	0.457	371.2	714
0.728	0.409	459.0	631

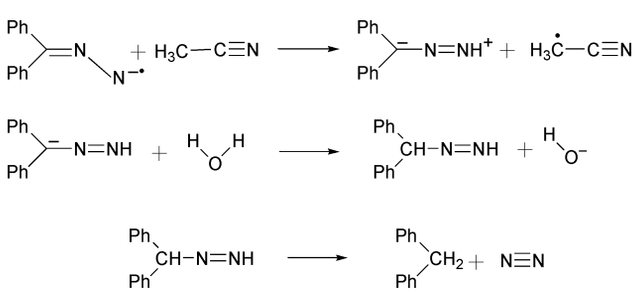
[a,b] See Table 3.

error) value as [CHD] is increased. The magnitudes of [CHD] necessary for second-order rate constant determination depend upon the particular radical cation reaction being studied.

The second-order rate constants for the reactions between 9-substituted acridine radical cations and cyclohexa-1,4-diene are: 8.63 (0.38) × 10^3 (**1b**); 7.89 (0.48) × 10^4 (**1c**); 1.56 (0.26) × 10^5 (**2a**); 4.39 (0.24) × 10^4 (**2b**); and 7.41 (0.69) × 10^2 M^{-1} s^{-1} (**2c**).

Discussion

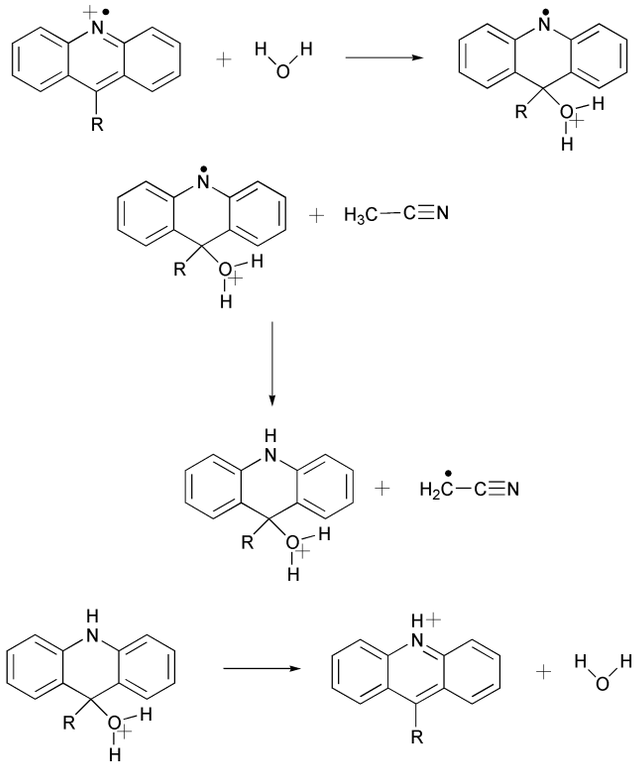
Hydrogen atom abstraction is a rare reaction of radical ions. Until now the strongest evidence for this type of reaction has been our observation of a solvent deuterium kinetic isotope effect of about 20 when the diazodiphenylmethane anion radical reacted with the solvent, either CH_3CN or CD_3CN.[6,7] The results could only be explained by a rate-determining hydrogen atom abstraction by the anion radical from the solvent. Diphenylmethane was observed to be a primary product of the reaction that involves an initial hydrogen atom abstraction, presumably followed by rapid protonation and loss of dinitrogen (Scheme 1).



Scheme 1

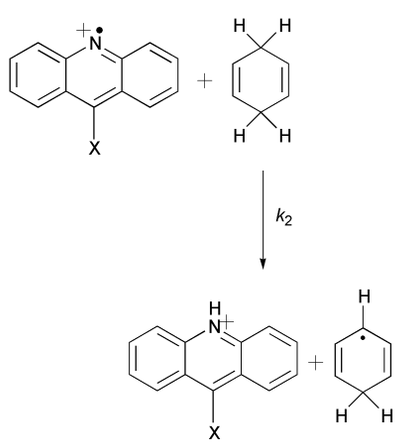
In our earlier communication we reported hydrogen atom abstraction reactions from solvent acetonitrile by 9-substituted acridine radical cations.[4] The mechanism of this reaction apparently does not involve a simple hydrogen atom transfer from the solvent, since we failed to observe significant rate differences when the solvent was changed from CH_3CN to CD_3CN. The reaction was observed to be first-order in radical cation and in H_2O and measurements in the presence of D_2O revealed a deuterium kinetic isotope effect of close to 1.5. It was proposed that the rate-determining step in the reaction was attack of the nucleophile (water) at the 9-position of the radical cation, activating hydrogen atom abstraction by the nitrogen center (Scheme 2). A similar mechanism may account for the cyclic voltammetry data reported for substituted flavin radical cations.[8]

Our study[4] did not provide evidence for the direct involvement of radical cations in hydrogen atom abstraction reactions analogous to the earlier report[7] for the radical anion reaction.



Scheme 2

The primary objective of this work was to see if conditions could be found under which acridine radical cations act as the acceptor in hydrogen atom transfer reactions. Since radical cations are prone to react with nucleophiles,[9,10] non-nucleophilic dichloromethane was selected as the solvent and cyclohexa-1,4-diene was chosen as an unambiguous hydrogen atom donor. The results presented in Table 2 verify that the reactions are first-order in radical cation. First-order behaviour in [CHD] is demonstrated in Tables 3–5. The radical cations react slowly in dicloromethane–Bu_4NPF_6 (0.2 M) in the absence of intentionally added reactants. We are not sure what the background reaction is, but the data clearly show that as [CHD] is increased the apparent second-order rate constants decrease and approach constant values, equal to k_2 (Scheme 3).



Scheme 3

Attempts to find linear Hammett relationships for the hydrogen atom abstraction reactions of the 9-substituted acridine radical cations are summarized in Table 6. The results for compounds **2a–c**, with remote subsituents, on the phenyl ring, are shown in the upper half of Table 6. Although only three rate constants are available, reasonably good correlations are found with both σ_p and σ_p^+, with the highest correlation coefficient (r^2)

Table 6 Hammett relationships for remote (Y, compounds **2**) and direct (X, compounds **1**) 9-substituents on acridine radical cations in reactions with Cyclohexa-1,4-diene

Compound	Y	log (k_2/M^{-1} s^{-1})	σ_p[a]	σ^+_p[a]
2a	H	5.19	0	0
2b	OMe	4.64	0.100	−0.80
2c	NMe_2	2.87	−0.43	−1.73
ρ			3.95	1.36
r^2			0.92	0.97
Compound	X	log (k_2/M^{-1} s^{-1})	σ_p[a]	σ^+_p[a]
1	Ph	5.19	0.039	−0.20
1b	OPh	3.94	0.063	−0.53
1c	OMe	4.90	0.100	−0.80
ρ			N.A.[b]	N.A.[b]

[a] Substitutent constants from reference 11. [b] Scatter, no correlation.

observed with the latter (0.97). Remote resonance electron donating substituents substantially decrease the rate of hydrogen atom abstraction from CHD. Linear Hammett correlations are not observed for substitution directly on the acridine ring. Both **1b** and **1c** show a decreased rate of hydrogen abstraction relative to phenyl to a small degree.

All of the results clearly show that 9-substituted acridine radical cations, in the absence of nucleophiles, undergo facile hydrogen atom abstraction reactions. What is the structural feature that promotes this unusual reaction? The 9-phenylanthracene radical cation might be considered to be structurally related to the radical cation of 9-phenylacridine. The former undergoes typical radical cation reactions including combination with nucleophiles when present and dimerization in their absence. We find no evidence for the dimerization of 9-phenylacridine radical cation and there is no evidence that the 9-phenylanthracene radical cation takes part in hydrogen atom abstraction reactions. Obviously, the structural difference between the two radical cations is the presence or absence of a nitrogen atom at the 10-position.

It has been proposed[1] that much of radical ion reactivity can be accounted for in terms of the degree of coupling between the radical and ionic centers. For example neither the radical anion nor the radical cation of anthracene undergo rapid dimerization reactions. However, localization of charge on a substituent of the radical ion promotes dimerization. 9-Cyanoanthracene radical anion and 9-methoxyanthracene cation radical undergo facile dimerization. A number of other examples of similar phenomena have been given.

Removal of an electron from the π-system of a 9-substituted acridine might be expected to produce a radical cation with the charge and the odd electron delocalized over the π-system. If this were the dominant structure of the radical cation, it seems unlikely that the unusual hydrogen atom abstraction behavior would be observed. However, if an electron from the unshared pair on nitrogen is promoted to the π-system, the odd electron becomes localized in a nonbonding orbital and is free to take part in typical radical reactions such as hydrogen atom abstraction. Obviously, there is no comparable structural feature available to the 9-phenylanthracene radical cation and it does not take part in hydrogen atom abstraction reactions.

The results from the Hammett correlations appear to be consistent with the explanation presented in the previous paragraph. The resonance donating substituents promote delocalization of the charge and the odd electron into the π-system and decrease the hydrogen abstraction activity of the radical cations. The reasonably good Hammett correlations for compounds **2a–c** (Table 6) most likely reflect the delocalization of the charge and the odd electron into the 9-aryl group; the greater the extent of delocalization, the lesser the importance of the free radical behaviour due to localization of the odd electron in a non-bonding orbital on nitrogen.

An alternative mechanism involving electron transfer between the 9-substituted acridine radical cations and CHD to give the substrate and CHD radical cation is less likely. This reaction might be expected to be followed by proton transfer from the CHD radical cation to the 9-substituted acridine. Assuming the latter, the final products are expected to be the same for the two mechanisms. On the other hand, the voltammetry response is inconsistent with the electron transfer mechanism, which is expected to show electrocatalytic behaviour.

We conclude that hydrogen atom abstraction by radical cations is not generally a favorable reaction pathway. The reaction can only be expected in cases where there is a structural feature favoring localization of the odd electron in a non-bonding orbital. The latter is expected to promote free radical-like behavior.

Experimental

Materials

Dichloromethane, after passing through active neutral alumina, was used without further purification. Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized from dichloromethane–diethyl ether before use. Cyclohexa-1,4-diene (Aldrich) was of the highest purity available and used as received. 9-Substituted acridines were prepared using standard literature methods.[12]

Instrumentation and data handling procedures

Cyclic voltammetry was performed with a Princeton Applied Research (Princeton, NJ) Model 273 potentiostat/galvanostat driven by a Hewlett Packard 3314A function generator. After passing through a Stanford Research Systems, Inc. Model SR640 dual channel low pass filter, the data were recorded on a Nicolet Model 310 digital oscilloscope with 12-bit resolution. The oscilloscope and function generator were controlled by a personal computer *via* an IEEE interface. The current potential curves were collected at selected trigger intervals to reduce periodic noise,[13] and 20 curves were averaged before being treated with a frequency domain low pass digital filter and numerical differentiation.

Cyclic voltammetry measurements

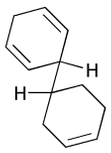
A standard three-electrode one compartment cell was used for all kinetic measurements. Positive feedback IR compensation was used to minimize the effects of uncompensated solution resistance. Reference electrodes were $Ag/AgNO_3$ (0.01 M) in acetonitrile constructed in the manner described by Moe.[14] The working electrodes, 0.4 mm Pt, were prepared by sealing wire in glass and polishing to a planar surface as described previously.[15] The cell was immersed in a water bath controlled at 25 ± 0.2 °C.

Kinetic measurements

Rate constants were obtained by comparing derivative cyclic voltammetry[5] data to theoretical data obtained by digital simulation.[16] The reactions were studied by using solutions containing substrates (0.5–2.0 mM) and cyclohexa-1,4-diene (0.01–0.8 M).

Product studies

Yields of acridinium ion products were obtained by cyclic voltammetry peak current measurements. The voltammogram was recorded before exhaustive controlled potential coulometric oxidation of substrate (1.0 mM) in the presence of a large excess of cyclohexadiene. Immediately after the oxidation



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was complete, pyridine (5 mM) was added to regenerate the substituted acridine. The cyclic voltammogram was recorded once again and the yield was determined from the relative peak-heights for oxidation of the substituted acridine before and after controlled potential oxidation. GC-MS analysis of the reaction mixture showed the presence of a single product derived from cyclohexa-1,4-diene with M^+ equal to 160. It was assumed that the product is derived from the reaction of cyclohexa-1,4-dienyl radical with the parent molecule followed by hydrogen atom abstraction to give the coupling product **5** (MW = 160).

Acknowledgements

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