6564 *J. Org. Chem.* **1994,** *59,* 6564−6566

# Aryl Proton Transfer Reactions of 9-Arylanthracene and 9-Substituted Anthracene Radical Cations with 2,6-Di-*tert*-butylpyridine

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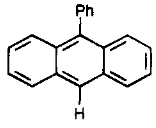
*Received July 8, 1994*[⊗]

Radical cations of anthracenes with substituents at the 9-position (Br, CN, or $NO_2$) or those of 9-arylanthracenes were observed to undergo proton transfer reactions with 2,6-di-*tert*-butylpyridine (TBP) to generate the corresponding anthracenyl radical. Under the same conditions 2,6-dimethylpyridine (LUT) undergoes combination reactions with the radical cations, and the proton transfer reactions could not be detected. The characteristic features of the reactions producing the anthracenyl radicals are as follows: (a) primary deuterium kinetic isotope effects are observed on substitution of the 10-H with 10-D, (b) the apparent Arrhenius activation energies vary from −2 to −11 kcal/mol, and (c) 10-Br-substituted anthracenes are formed during bromine atom abstraction from bromoform by the free radicals. The intermediate bromo derivatives are further oxidized under the reaction conditions. A two-step mechanism involving a reversible $\pi$-complex formation followed by rate-determining proton transfer is proposed. The results of the reactions with TBP are compared to those obtained from the corresponding reactions of the radical cations with LUT.

## Introduction

The most common reactions of radical cations of aromatic compounds involve combination with nucleophiles[2−11] and proton transfer from methyl groups.[12−16] These reactions have been studied extensively in our laboratory as well as in others. The transfer of aryl protons from radical cations of aromatic compounds was suggested some time ago,[17] but evidence for this reaction pathway has only recently[18] been presented. The feasibility of these reactions is indicated by thermochemical calculations which suggest that the benzene radical cation is expected to be a strong acid with a p$K_a$ value of the order of −4 in acetonitrile.[19]

A comparison of the reactivity of the radical cations of **1** and **2** in acid−base reactions with 2,6-di-*tert*-butylpyridine (TBP) in acetonitrile showed that the second-order rate constant for loss of the aryl proton from the 10-position of $\mathbf{1}^{\bullet+}$ is about five times as great as that for loss of a methyl proton from $\mathbf{2}^{\bullet+}$.[20] This suggests that reactions involving the loss of aryl protons from radical cations are facile. Then why are these reactions not commonly observed? The answer to this question appears to lie in the fact that even more favorable reaction pathways exist for radical cations capable of undergoing the proton transfer reaction.



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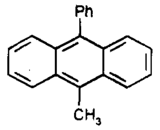

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## Results and Discussion

We chose two series of reactants to study the effect of substituents on the rates of reactions of radical cations with TBP: 9-substituted anthracenes and *para*-substituted 9-phenylanthracenes. The former series was limited due to the high reactivity toward dimerization of radical cations of anthracenes substituted at the 9-position with electron-donating substituents. The structures of the substrates used along with identifying symbols are shown below.

The radical cations of the substituted anthracenes undergo combination reactions with pyridine bases such as LUT to give mono- or bis-pyridinium salts depending upon the structure of the anthracene. The products of these reactions for a range of radical cations have been reported.[21]

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

[1] On leave from Nankai University (China).

[2] Parker, V. D. *Acc. Chem. Res.* **1984,** *17,* 243. Hammerich, O.; Parker, V. D. *Adv. Org. Chem.* **1984,** *20,* 55.

[3] Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1987,** *109,* 2521.

[4] Parker, V. D.; Reitstöen, B.; Tilset, M. *Phys. Org. Chem.* **1989,** *2,* 580.

[5] Reitstöen, B.; Norrsell, F.; Parker, V. D. *J. Am Chem. Soc.* **1989,** *111,* 8463.

[6] Reitstöen, B.; Parker, V. D. *J. Am. Chem. Soc.* **1991,** *113,* 6954.

[7] Parker, V. D.; Pedersen, M.; Reitstöen, B. *Acta Chem. Scand.* **1993,** *47,* 560.

[8] Norrsell, F.; Handoo, K. L.; Parker, V. D. *J. Org. Chem.* **1993,** *58,* 4929.

[9] Masnovi, J. M.; Kochi, J. K.; Hillinski, E. F.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1986,** *108,* 1126. Sankaraman, S.; Haney, W. A.; Kochi, J. K. *Ibid.* **1987,** *109,* 7824. Nasnovi, J. M.; Sankaraman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989,** *111,* 2263.

[10] Drewello, T.; Heinrich, N.; Maas, W. P. M.; Nibbering, N. M. M.; Weiske, T.; Schwarz, H. *J. Am. Chem. Soc.* **1987,** *109,* 4810.

[11] Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1993,** *115,* 6564.

[12] Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984,** *106,* 7472. Masnovi, J. M.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989,** *111,* 2263.

[13] Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1986,** *108,* 6371.

[14] Nelsen, S. F.; Ippoliti, J. T. *J. Am. Chem. Soc.* **1986,** *108,* 4879.

[15] Dinnocenzo, J. P.; Banach, T. E. *J. Am. Chem. Soc.* **1989,** *111,* 8646.

[16] Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1991,** *113,* 8778.

[17] Osa, T.; Yildiz, A.; Kuwana, T. *J. Am. Chem. Soc.* **1969,** *91,* 3994.

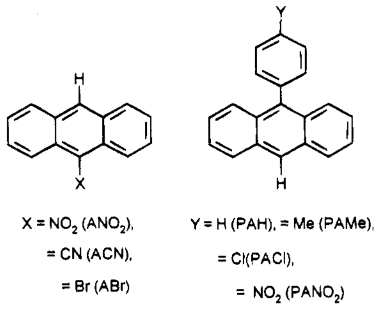
[18] Reitstöen, B.; Parker, V. D. *J. Am. Chem. Soc.* **1990,** *112,* 4968.

[19] Nicholas, A. M.; Arnold, D. R. *Can. J. Chem.* **1982,** *60,* 2165.

[20] Parker, V. D.; Chao, Y.-T.; Reitstöen, B. *J. Am. Chem. Soc.* **1991,** *113,* 2336.

[21] Reitstöen, B.; Parker, V. D. *Acta Chem. Scand.* **1992,** *46,* 464.

0022-3263/94/1959-6564$04.50/0



**Kinetic Studies.** Kinetic data for the reactions of the two series of radical cations with TBP are summarized in Table 1. All reactions were carried out in acetonitrile/$Bu_4NPF_6$ (0.1 M). The rate constants reported are for 298 K and obtained from Arrhenius plots of data measured at temperatures ranging from 253 to 303 K.

The most characteristic features of the radical cation aryl proton transfer reactions are the primary kinetic isotope effects ($k_H/k_D$) ranging from 1.4 to 2.2 and the negative Arrhenius activation energies from −2.1 to −10.6 kcal/mol. The kinetic isotope effects arise from substitution of the hydrogen at the 10-position with deuterium. These should be contrasted with those observed for the corresponding reactions with less hindered 2,6-dimethylpyridine (LUT) which are inverse in the expected range (0.7−0.8) for nucleophilic attack at the 10-position.[6,7] The activation energies are generally more negative for the 9-arylanthracene radical cations than for the 9-substituted radical cations.

An interesting contrast in the data is the fact that the rate constants for the reactions of the 9-substituted anthracene radical cations with TBP increase as the substituent becomes more electron withdrawing while those for the 9-arylanthracene radical cations do not ($PAH^{\bullet+}$ can be considered to be a member of both reaction series). In fact, in the latter series, substitution at the 4-position of the aryl group is accompanied by a decrease in the rate constant for both electron-donating and electron-withdrawing substituents. We do not have a definitive explanation for this observation but suggest that the decreased reactivity of radical cations substituted with electron withdrawing substituents is associated with the second step in the reaction (Scheme 1), *i.e.*, the rearrangement of the initially formed $\pi$-complex, rather than with the formation of the $\pi$-complex.

Another noteworthy difference in the data for the two reaction series is that the rate constant ratio $k_{LUT}/k_{TBP}$, for nucleophilic attack at the 10-position relative to abstraction of the 10-proton is very much greater for the radical cations substituted with an electron-withdrawing substitutent at the 10-position than for the 9-arylanthracene radical cations. The reason for this difference appears to be that the reactions involving LUT exhibit a greater substituent effect than the reactions of TBP. The effect is moderated when the substituent is at a remote site in the 9-arylanthracenes which gives rise to lower values of $k_{LUT}/k_{TBP}$.

**Products Derived from Aryl Radicals.** Aryl radicals are short-lived species which have not been directly observed in solution. The intermediate formation of aryl radicals is commonly confirmed by atom abstraction experiments, and the reactions of these intermediates with $CBr_4$ are believed to be diffusion controlled.[22] We have observed that α-naphthyl and 4-nitrophenyl radicals react about 1 order of magnitude slower with $CHBr_3$ than with $CBr_4$ and that the former serves as a convenient trap for these intermediates.[23] In our preliminary paper we showed that the 9-phenylanthracenyl radical, generated by proton transfer from $PAH^{\bullet+}$, reacts with $CHBr_3$ to give the corresponding bromo derivative.

**Table 1. Kinetic Data for the Reactions of Substituted Anthracene Radical Cations with 2,6-Di-*tert*-Butylpyridine in Acetonitrile**

| substrate | $\log(k/M^{-1}\ s^{-1})$ | $k_H/k_D$ | $-E_a$ (kcal/mol) | $k_{LUT}{}^a/k_{TBP}$ |
|---|---|---|---|---|
| $ANO_2$ | 2.99 | 1.5 | 2.1 | 347 |
| ACN | 2.80 | 1.5 | 2.3 | 490 |
| ABr | 2.54 | 1.4 | 2.1 | 372 |
| PAH | 2.11 | 2.1 | 7.0 | 8.5 |
| PAMe | 2.05 | 2.0 | 6.2 | 8.5 |
| PAOMe | 1.86 | 2.2 | 2.3 | 9.5 |
| PACl | 1.67 | 1.6 | 10.4 | 27 |
| $PANO_2$ | 1.80 | | 10.6 | 22 |

[a] The rate constants for the reactions of LUT are from ref 7.

**Table 2. Yields of 10-Substituted 9-Bromoanthracenes Observed in the Reactions of 9-Substituted Anthracene Radical Cations with Bromoform in the Presence of 2,6-TBP in Acetonitrile−$Bu_4NPF_6$ (0.1 M)**

| substrate | yield (%) | substrate | yield (%) |
|---|---|---|---|
| $ANO_2$ | 30 | PAMe | 28 |
| AN | 66 | PAMeO | 37 |
| ABr | 57 | PACl | 17 |
| PAH | 13 | $PANO_2$ | 15 |

During preparative electrolysis experiments, 10-bromoanthracenes formed during bromine atom abstraction by aryl radicals are further oxidized. This is a consequence of the fact that the 10-bromoanthracenes are only slightly more difficultly oxidized than the substrates from which they were derived. For example, 9-bromo-10-phenylanthracene is oxidized at a potential 70 mV more positive than 9-phenylanthracene. In order to confirm the trapping of the anthracenyl radicals by $CHBr_3$, we carried out preparative electrolyses to about 60% conversion of the substrates and then determined the yields of bromoanthracenes based upon consumed substrate. The data for the preparative experiments are summarized in Table 2. In all cases significant yields of bromoanthracenes were obtained. Yields varied from 15 to 66%. The further oxidation products, 10-hydroxy-10-aryl-9-anthrone and anthraquinone, were detected by GC/MS analysis.

**Mechanistic Conclusions.** Our interpretation of the mechanisms of bimolecular reactions of radical cations with added reagents, bases, or nucleophiles is that the initial interaction of the radical cation with the electron rich species leads to the formation of a $\pi$-complex.[2−8,13,16,18,20] Since it has not been possible to directly observe the $\pi$-complexes, it has been necessary to rely on kinetic evidence for their existence. One common indication is the observation of small or negative Arrhenius activation energies. The sometimes very large negative $E_a$ values in Table 1 show that this evidence for a two-step mechanism is accentuated for the radical cation aryl proton transfer reactions.

As depicted in Scheme 1, we propose that the mechanism of the proton transfer reactions involves a transition state of the $\pi$-complex, in which the nitrogen atom of TBP is associated with the positive charge of the radical cation. The product-forming step, involving the cleavage

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(22) Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589.

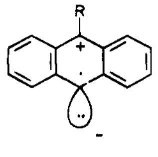
(23) Tilset, M.; Parker, V. D. *Acta Chem. Scand.* **1982**, *B36*, 281.

**Scheme 1**

$$ArH^{\bullet +} + N: \rightleftharpoons [\pi\text{-complex}]$$

$$[\pi\text{-complex}] \rightarrow Ar^{\bullet} + NH^{+}$$

of the $C_{10}$−H bond, is assisted by coordination of the nitrogen center (N:) of TBP with the acidic proton. This leads to the formation of a 10-anthracenyl radical. The departure of the 10-proton is accompanied by the reorganization of the electronic structure from a π-radical cation−σ carbanion (**3**) to an aryl radical (**4**). We suggest that this is a concerted process and that **3** is not formed on the basis of the expected relative stabilities of the two intermediates. In a related case, the phenyl cation **5** has been predicted to be more stable than **6** by 20 kcal/mol.[24,25]



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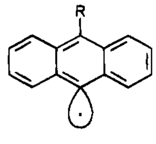

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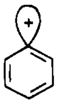

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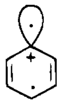

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The question arises as to how general the radical cation aryl proton transfer reaction can be expected to be. Some insight into this question can be gained by considering the data in Table 1. The largest second-order rate constant that we have observed for this reaction, between 9-nitroanthracene radical cation and TBP in acetonitrile, is $10^3$ $M^{-1}$ $s^{-1}$. Under the same conditions, the reaction of $ANO_2^{\bullet +}$ with pyridine has a second-order rate constant greater than $10^9$ $M^{-1}$ $s^{-1}$.[6] Pyridine is slightly more basic than TBP. This suggests that only TBP, or a base possessing comparable steric features, can be expected to abstract aryl protons from radical cations rather than undergo nucleophilic attack at the carbon bearing the proton. Furthermore, TBP reacts with radical cations at rather modest rates, $10^3$ $M^{-1}$ $s^{-1}$ or lower. The latter limits this reaction to reasonably long-lived radical cations. Even these will prefer to react with unhindered nucleophiles when present.

## Experimental Section

**Materials.** Reagent grade acetonitrile was distilled from $P_2O_5$ and stored over active neutral alumina. Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized from dichloromethane−ether before use. 2,6-Dimethylpyridine and 2,6-di-*tert*-butylpyridine were obtained from Aldrich and passed through a short column of active neutral alumina before use. 9-Bromoanthracene (Aldrich), 9-cyanoanthracene (Aldrich), 9,10-dibromoanthracene (Aldrich), and 9-phenylanthracene (Aldrich) were used as received. 9-Nitroanthracene,[26] 9-(4-methylphenyl)anthracene,[27] 9-(4-methoxyphenyl)anthracene,[27] 9-(4-chlorophenyl)anthracene,[27] 9-(4-nitrophenyl)-10-bromoanthracene, and 9-(4-nitrophenyl)anthracene[27] were prepared according to the published procedure. All of the 9-substituted anthracene-*10-d* derivatives were prepared from the corresponding 9-bromo-10-substituted anthracenes by halogen−lithium exchange at −78 °C with butyllithium under an argon atmosphere followed by quenching with $D_2O$. The compounds were purified by column chromatography (active neutral alumina, hexane).

**Preparative Electrolyses.** The experiments were performed using constant current coulometry between platinum mesh electrodes (~10 $cm^2$) in an H cell charged with 20 mL of solution [$CH_3CN/Bu_4NPF_6$ (0.1 M)] in each compartment. Substrates (0.05−0.1 mmol) along with TBP (0.2−0.4 mmol) and bromoform (0.4−0.8 M) were added to the anode compartment before a constant current (10 mA) was passed. The reactions were stopped when about 60% of the substrate was consumed, as monitored by CV. After removal of the solvent, the residue was extracted with ether. The 10-substituted 9-bromoanthracenes formed were identified, and yields were determined using authentic samples as standards for GC/MS and GC analyses with biphenyl as external standard or using $^1H$ NMR peak integration with hexamethylbenzene as external standard.

**Instrumentation and Data Handling Procedures.** $^1H$ NMR spectra were obtained on a Varian XL 300 spectrometer, with residual protons in the solvent ($CDCl_3$, 7.25 ppm) as an internal reference. Mass spectra were measured using a Finnigan MAT ITD GC/MS system. Gas chromatography was performed on a Varian 5880A Series instrument equipped with a flame ionization detector.

Cyclic voltammetry was performed using a JAS Instrument System, Model JDP-165A, potentiostat driven by a Hewlett-Packard 3314A function generator. The signals were filtered using a Stanford Research System, Inc., Model SR640, dual channel low pass filter before recording on a Nicolet Model 310 digital oscilloscope. An IBM AT compatible personal computer was used to control the oscilloscope and the function generator *via* an IEEE interface. The current−potential curves were collected and averaged at trigger intervals selected to reduce periodic noise.[28] The averaged signals were then treated with a digital frequency domain low pass filter before numerical differentiation.

**Derivative 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.[29] The working electrodes, 0.2−0.8 mm Pt, were prepared by sealing wire in glass and polishing to a planar surface as described previously.[30] The working electrodes were cleaned before each series of measurements with a fine polishing powder (Struer, OP-Alumina Suspension) and wiped with a soft cloth.

**Kinetic Measurements.** Rate constants were obtained by comparing experimental data to theoretical data obtained by digital simulation.[31] Derivative cyclic voltammetry[32] data for the reactions with LUT were obtained under second-order conditions (substrate (1.0 mM) and LUT (2.0 mM)) while that for the reactions with TBP were obtained under pseudo-first-order conditions (substrate (1.0 mM) and TBP (20 mM)).

**Acknowledgment.** Financial support from the National Science Foundation (Grant CHE-9106618) is gratefully acknowledged. We thank Mr. Gang Zheng for preparing some of the compounds used in this study.

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(24) Dill, J. D.; Schleyer, P. v. R.; Binkley, J. S.; Seeger, R.; Pople, J. A.; Haselbach, E. *J. Am. Chem. Soc.* **1976**, *98*, 5428.

(25) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1.

(26) *Organic Syntheses*; Wiley: New York, 1951; Collect. Vol. 31, P77.

(27) Mosnaim, D.; Nonhebel, D. C.; Russell, J. A. *Tetrahedron* **1969**, *25*, 3485.

(28) Lasson, E.; Parker, V. D. *Anal. Chem.* **1990**, *62*, 412.

(29) Moe, N. S. *Anal. Chem.* **1974**, *46*, 968.

(30) Lines, R.; Parker, V. D. *Acta Chem. Scand.* **1977**, *B31*, 369.

(31) Feldberg, S. W. *Electroanal. Chem.* **1969**, *3*, 199.

(32) Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1.