Letter to the Editor

Substituent and Solvent Effects on the Rate Constants for the Reactions of 9-Substituted Anthracene Radical Cations with Trinitromethanide

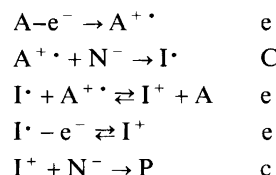## Haijiang Wang, Gang Zheng and Vernon D. Parker[†]

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The rates of the reactions between a variety of radical cations with both neutral and ionic nucleophiles have been observed to be affected by both steric and electronic factors.[1-7] For example, the second-order rate constants for the reactions of 9-cyano- and 9-nitro-anthracene radical cations with pyridine are about two orders of magnitude greater than those for the anthracene radical cation.[4] On the other hand, rate constants reported for the reactions of 9-substituted anthracene radical cations with trinitromethanide ion appear to be nearly independent of the 9-substituent.[8,9] This apparent inconsistency prompted us to examine the kinetics of the reactions of a series of 9-substituted anthracene radical cations with trinitromethanide by electrochemical methods in order to determine whether the nucleophilic activity of trinitromethanide is unusual.[10]

The electrochemical method of choice for the study of very rapid second-order reactions of electrode-generated intermediates is the prepeak method[1,11] when it is applicable.[12] The range of rate constants which can be determined using the method with a substrate concentration of 1 mM and a voltage sweep rate of 0.1 V s^{-1} is from about $10^6 \text{ M}^{-1} \text{ s}^{-1}$ up to the diffusion-controlled limit. This is the range of rate constants applicable to the reactions of 9-substituted anthracene radical cations with nucleophiles.

Prepeak data and second-order rate constants for the reactions of 9-substituted anthracene radical cations $(A^{+\cdot})$ with trinitromethanide (N^-) in acetonitrile and in dichloromethane at 298 K are summarized in Table 1. The rate constants were obtained by matching prepeak data with those obtained by digital simulation[12] of the eCec mechanism outlined in Scheme 1. In Scheme 1 $I^\cdot$ is the intermediate radical formed upon combination of the radical cation with the anionic nucleophile and I^+

$$A - e^- \rightarrow A^{+\cdot} \qquad e$$
$$A^{+\cdot} + N^- \rightarrow I^\cdot \qquad C$$
$$I^\cdot + A^{+\cdot} \rightleftharpoons I^+ + A \qquad e$$
$$I^\cdot - e^- \rightleftharpoons I^+ \qquad e$$
$$I^+ + N^- \rightarrow P \qquad c$$

Scheme 1.

results from the oxidation of the radical. The final products of the reaction under our conditions have not yet been determined but are likely to be analogous to those known for the same radical cations with other nucleophiles.[13] Products of the reactions of radical cations derived from aromatic compounds with trinitromethanide generated during photolysis of the tetranitromethane–aromatic compound charge transfer complex in most cases corresponds to the addition of the elements of $C(NO_2)_3$ and NO_2.[14,15] Aromatic compounds that are difficult to oxidize, such as benzene and toluene, have been reported to undergo anodic substitution reactions producing trinitromethyl derivatives[16] during electrolysis in acetonitrile in the presence of trinitromethanide. On the other hand, the reaction between tris(4-bromophenyl)aminium and trinitromethanide results in only nitro derivatives.[17]

Our data (Table 1) indicate that the apparent second-order rate constants vary from 10^7 up to the diffusion-controlled value in acetonitrile and encompass a slightly narrower range in dichloromethane. The Hammett ρ (log k vs. σ^+) for the data in acetonitrile was observed to be equal to 2.9 $(r = 0.95)$ and can be compared to that observed for the reactions of 9-substituted anthracene radical cations with pyridines (2.4).[5] The low correlation coefficient (0.95) is, at least in part, due to the fact that rate constants for the reactions of 9-substituted anthracene radical cations observed when the substituent is cyano

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Table 1. Prepeak potential differences and second-order rate constants for the reactions of 9-substituted anthracene radical cations with tetrabutylammonium trinitromethanide in acetonitrile and dichloromethane.[a]

9-Substituent	$v/V\ s^{-1}$	Acetonitrile		Dichloromethane	
		$\Delta E^{p\ b}$	$\log(k/M^{-1}\ s^{-1})^{c}$	$\Delta E^{p\ b}$	$\log(k/M^{-1}\ s^{-1})^{c}$
Ph	0.10	127	7.0 (9.3)	151	7.7 (11.1)
Cl	1.00	151	8.5	165	8.9
Br	1.00	144	8.4 (9.1)	165	8.9 (11.2)
CN	1.00	203	10.2	191	9.8
NO_2	1.00	187	9.7	186	9.6

[a] In solvent containing Bu_4NPF_6 (0.1 M) at 298 K. [b] Difference in prepeak and main peak potentials. [c] From comparison of experimental with theoretical data obtained by digital simulation.
Numbers in parentheses are reported in Ref. 8.

($\sigma^+ = 0.66$) are greater than when it is nitro ($\sigma^+ = 0.89$). Furthermore, changing the solvent from acetonitrile to dichloromethane has only a small effect on the apparent second-order rate constants as has previously been observed in comparable reactions.[4]

In contrast with the trends that we observe in apparent second-order rate constants for the reactions of radical cations with trinitromethanide, those reported earlier[8] are essentially independent of substituents. Rate constants in acetonitrile and dichloromethane for two of the radical cations studied here, those derived from 9-phenyl and 9-bromoanthracene, were determined earlier[8] and are given in parentheses in Table 1. Another apparent inconsistency in the two data sets for these two reactions is the solvent effect. Much greater increases in apparent second-order rate constants upon the solvent change were reported earlier than we observe here.

Our conclusion regarding the answer to the question asked at the outset of this study (does trinitromethanide exhibit unusual nucleophilic reactivity toward radical cations?) is that the answer is no. Substituent and solvent effects, observed by electrochemical techniques, for the reactions of 9-substituted radical cations with trinitromethanide parallel those observed for other nucleophiles using the same measurement techniques. The reasons for the discrepancies noted in the previous paragraph are presently unclear and require further study.

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