

Table II. First-Order Rate Constants for the Methanolysis of $5 \times 10^{-4} M$ Methoxyphenoxyethylphenylsilane in Buffered Methanol at $25.00 \pm 0.01^\circ$

$[\text{HO}_2\text{CH}], M$	$[\text{NaO}_2\text{CH}], M$	$10^5 k, \text{sec}^{-1}$
0.0600	0.0200	1.89 ± 0.09
0.0900	0.0300	4.06 ± 0.08
0.1200	0.0400	7.59 ± 0.19
0.1500	0.0500	12.0 ± 0.04
0.0200	0.0200	0.81 ± 0.02
0.0300	0.0300	1.45 ± 0.05
0.0400	0.0400	2.60 ± 0.06
0.0500	0.0500	3.58 ± 0.26

^a Ionic strength maintained at 0.05 M with added lithium perchlorate. Error limits are standard deviations.

ponent. Figure 2 shows that the rate law of eq 3 is

$$v = k_{\text{BBH}}[\text{R}_3\text{SiOAr}][\text{NaO}_2\text{CH}][\text{HO}_2\text{CH}] \quad (3)$$

obeyed with $k_{\text{BBH}} = 1.62 \pm 0.08 \times 10^{-2} M^{-2} \text{sec}^{-1}$. This is in agreement with structure 3 and the displacement is therefore concerted.

To reconcile simultaneous acid-base catalysis with an Si-5 intermediate would require either (a) that formic acid interacts with the O of Si-OAr to catalyze nucleophilic attack, in formation of the intermediate, although this oxygen is much less basic than formate ion in both R_3SiOAr and the intermediate⁴ or (b) that formate ion removes the proton of a rapidly and reversibly formed methanol adduct of the reactant as the Si-OAr bond breaks. The latter would necessitate that this oxonium-like proton not be rapidly transferred to an adjacent solvent molecule but that it await the arrival of formate ion; this seems quite unlikely. We therefore conclude that this reaction is concerted.

The initially surprising conclusion that the methanolysis and hydrolysis reactions of very similar compounds proceed by different mechanisms is probably related to the equally surprising base catalysis of expulsion of the good leaving group aryloxy in the hydrolysis reaction (eq 1). The base may catalyze a critical pseudorotation of the addition compound. Lack of opportunity for such catalysis in methanol may open the way for competition by the concerted mechanism.

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(4) Cf. W. P. Jencks, *Chem. Rev.*, **72**, 702 (1972).

Dr. H. Jayaraman for his measurements on *p*-nitrophenyl acetate.

(5) Exchange student from the University of Bonn, Bonn, Germany.

(6) Holder of a Research Career Development Award of the National Institute of General Medical Sciences (1968-1973).

C. Gardner Swain

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Klaus-Richard Pörschke,⁵ Wasi Ahmed, Richard L. Schowen*⁶

Department of Chemistry, University of Kansas
Lawrence, Kansas 66045

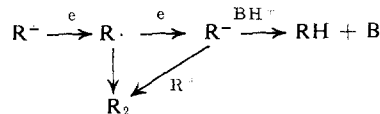
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Trapping of Electrochemically Generated Cyclopropenyl and Cycloheptatrienyl Anions by Charged Reagents

Sir:

We have described¹ the use of electrochemical reduction to generate the cycloheptatrienyl anion and a series of cyclopropenyl anions and the use of the electrochemical data in the determination of their basicities. The anions were generated from the corresponding cations, and two clear waves could be discerned by cyclic voltammetry corresponding to reduction first to the radical and then to the anion. However, controlled potential electrolysis at either the first or second wave afforded only the reductive dimer, a bis(cycloheptatrienyl) or bis(cyclopropenyl). At the first wave this is the expected product from dimerization of the radical, but at the second wave it corresponds to reaction of the anion with the starting cation. Remarkably, this was the only product at the second wave even when hydroxylic solvents, such as acetic acid, were employed in an attempt to capture the anion by protonation.

This result suggested that the trapping of the products occurs in the inner Helmholtz plane of the electrical double layer at the electrode and that solvent is not present in this region. Accordingly, to put an acidic reagent at the electrode surface we have used a novel supporting electrolyte, guanidinium perchlorate,² and have found that it is able to trap these anions by protonation even when it is present in low nominal concentration relative to more acidic solvents. Some trapping of the anions by protonation was also observed using triethylamine hydrobromide or dimethylamine hydrochloride as electrolytes, but they were not usable over as wide a negative potential range as is guanidinium ion and were thus not examined further. The result has some general significance for both mechanistic and synthetic organic electrochemistry.



The electrolyte was prepared from guanidine hydrochloride in methanol by reaction with stoichiometric amounts of KOH (filter) and then perchloric

(1) R. Breslow and W. Chu, *J. Amer. Chem. Soc.*, **95**, 411 (1973).

(2) K. V. Titova and Y. Ya Rosolovskii, *Zh. Neorg. Khim.*, **10**, 446 (1965).

acid, with recrystallization from CH_3CN . At a mercury cathode, but not at Pt, it was stable to -1.9 V vs. sce. As before,¹ electrolytic reduction of tropylium fluoroborate in CH_3CN with any supporting electrolyte (0.4 M) at -1.40 V, before the second wave, resulted in the passage of 1 faraday/mol and the production of 7,7'-bis(cycloheptatrienyl) in 98–99% isolated yield, with <1% cycloheptatriene. The same result was obtained at -1.70 V, after the second wave, with tetrabutylammonium perchlorate (TBAP) supporting electrolyte, even in the presence of 50% acetic acid. However, with 0.4 M guanidinium perchlorate as the supporting electrolyte in CH_3CN , electrolysis at -1.6 V, after the second wave, led to the uptake of 1.30 faradays/mol and the production of 29% cycloheptatriene in addition to 65% of the dimer (which is stable under these conditions). Similarly, triphenylcyclopropenyl cation affords the 3,3'-bis(triphenylcyclopropenyl) with all electrolytes at the first wave and, under most conditions, at the second wave as well, but with guanidinium perchlorate as electrolyte 12% of 1,2,3-triphenylcyclopropene is also formed.

These trapping³ experiments thus support our interpretation that the second electrochemical wave for these species does correspond to production of the anion. More interestingly, the fact that 0.4 M guanidinium ion can trap these anions, even though the more acidic and abundant acetic acid fails, confirms the idea that the medium in which the electrochemistry occurs is essentially a fused salt, from which solvent is excluded.

It is striking that even with guanidinium perchlorate some dimer persists, and the proportion is not changed by going to more negative potentials. Since the bulk guanidinium cation concentration is 200 times that of the tropylium cation, and carbon-carbon bond formation should be subject to more steric hindrance than is proton transfer, the ability of the tropylium ion or triphenylcyclopropenyl cation to compete in the trapping is remarkable. The most likely explanation is that it reacts with the anion by rapid prior electron transfer, followed by coupling of the resulting radicals.

Ordinary polarography of tropylium cation with TBAP supporting electrolyte shows almost no trace of the second wave (which was clearly visible by cyclic voltammetry, both in DMSO solvent¹ and in CH_3CN at a Pt electrode). This behavior is extremely unusual and reflects the fact that even at the second wave the overall chemical process is conversion of two tropylium cations to the dimer with two electrons, albeit by a different sequence from that observed at the first wave. Thus, the current does not increase. In polarography, an increase in diffusion current at the second potential can be observed only if some process other than coupling with the starting material takes place, and of course guanidinium perchlorate as the supporting electrolyte permits such a process. As Figure 1 shows, the ac polarogram⁴ of tropylium fluoroborate has only the first wave with TBAP electrolyte, while with guanidinium perchlorate present a second wave can be seen at

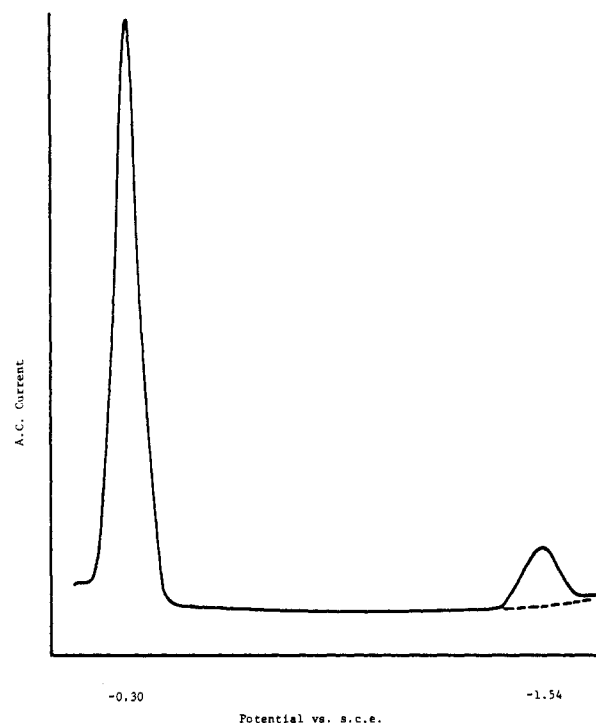


Figure 1. AC polarogram of tropylium fluoroborate in CH_3CN : solid line, with guanidinium perchlorate as supporting electrolyte; dashed line, with tetrabutylammonium perchlorate as supporting electrolyte. The two polarograms are identical except at the second wave, as shown.

the potential we have observed previously using cyclic voltammetry. Similarly, in dc polarography the very small second wave is substantially increased using guanidinium perchlorate. Thus, this new supporting electrolyte is also of significance in permitting determinations of such potentials. The second wave could be seen in cyclic voltammetry even without a special electrolyte, since cyclic voltammetry is not a steady-state process. At the first potential essentially all the cation near the electrode is converted to radical, while at the second potential extra current passes as the surviving radicals are reduced to anions. Their subsequent precise chemical fate does not affect the current.

Finally, these data indicate clearly that the most effective traps for electrochemically generated intermediates are those whose charge puts them into the double layer at the electrode. In other electroorganic syntheses this charge effect could also play an important role.⁵

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Ronald Breslow,* Robert F. Drury
Department of Chemistry, Columbia University
New York, New York 10027
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Microenvironment of Histidine 12 in Ribonuclease-S as Detected by ^{13}C Nuclear Magnetic Resonance

Sir:

Histidine 12 is an essential amino acid residue for catalytic activity in bovine pancreatic ribonuclease-A

(3) Some unusual solvent acidity effects in trapping of electrochemically generated anions are reported by A. J. Fry and R. G. Reed, *J. Amer. Chem. Soc.*, **94**, 8475 (1972). It should also be noted that triphenylmethyl anions can be trapped¹ by acetic acid, in contrast with the tropylium and cyclopropenyl cases.

(4) D. E. Smith, *Electroanal. Chem.*, **1**, 1 1966.