

CYCLIC VOLTAMMETRIC STUDIES

Part III. Stability of 4-Nitroaniline and 1-Nitronaphthalene Anion Radical Intermediates in Alcoholic, Nitrilic and Mixed Solvent System

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(Received November 22, 1974)

Abstract. Cyclic voltammetric investigation were carried out on 4-nitroaniline and 1-nitronaphthalene in ethanol, acetonitrile, acetonitrile-ethanol (20% ethanol) and acetonitrile-water (25% water) mixture in order to study the stability of the anion radical intermediates. It was found that, while the anion radical of 1-nitronaphthalene was stable in ethanol, ethanol-acetonitrile, acetonitrile and acetonitrile-water mixture, anion radical of 4-nitroaniline was stable in acetonitrile, acetonitrile-ethanol and acetonitrile-water mixture but unstable in pure ethanol.

The shift in $E_{1/2}$ is also qualitatively discussed.

Anion radicals of nitroaromatics have been generated and studied by several workers.¹⁻⁶ The method of generation and nature of studies varied from polarographic studies,⁴ polarographic generation of the anion radical and ESR studies,^{1,2} cyclic voltammetric studies on the stability of anion radical,³ and alkali metal reduction and the ion-pair formation.^{5,6} Polarographic studies gives us the information about the reversibility or irreversibility of process but does not tell us about a coupled chemical process and the stability (life time) of the anion-radical intermediates. Alkali metal reduction has the problem of ion-pair formation, with low concentration of the species to be studied.⁷ Use of crown-potassium to generate the ion-radical in high concentration has been found to be successful but the experiment has to be carried out at low temperature.⁸ Recently pulse technique has been finding use in generating the anion radical intermediate in high concentration.⁹ Much simpler, however, is the method of cyclic voltammetry. This method though has limitation in detecting species of life time 100 microsecond or less it can give us preliminary information about the stability of the anion radicals, if not the correct rate constant for disappearance.³

Nitrobenzene anion radical has been studied polarographically, by ESR^{1,2} and through alkali metal reduction,^{5,6} and have been found to be stable in alcoholic⁵, nitrilic,^{1,5} and ethereal solution.⁵ It has also been found stable in dimethyl formamide. No information is available on the stability of nitroaniline (4-NA) anion radical and the higher analogue of nitrobenzene: 1-nitronaphthalene (1-NN) anion radical. In the present work we have carried out such study on the above-mentioned two compound (4-NA and 1-NN) and report here the result of the investigation.

Result and Discussion

Results of cyclic voltammetric studies of 4-nitroaniline and 1-nitronaphthalene at 33 mV/sec scan

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rate, and on hanging mercury drop electrode are given in Tables 1 and 2. Since the purpose of study was to investigate stability of anion radicals only, a gold wire as quasi-reference electrode,¹⁰ was used. No quantitative interpretation of the numerical values of $E_{1/2}$'s are attempted.

4-Nitroaniline. It is quite clear that the reversibility criteria $(E_p)_a - (E_p)_c \approx 60$ mV is satisfied¹¹ to 25% ethanol. The anion so produced is stable, at least in the time scale studied (k decomposition is less than 0.01 sec^{-1}). From the reversibility criteria and the stability of anion, it can be inferred that no chemical reaction is coupled to the electron-transfer process which follows



Qualitatively, the anodic shift in $E_{1/2}$ on the addition of ethanol is interpreted as greater solvation of the anion in mixed solvent. A Born charging process $\Delta G = \frac{-A}{r} \left(1 - \frac{1}{E}\right)$ would predict a cathodic shift, since, addition of ethanol to acetonitrile will lower the dielectric constant. It should, however, be pointed out that the change in liquid junction potential is completely unknown and a contribution from liquid junction potential cannot be ignored. One, however, notes that in the case of nitronaphthalene there is no change in $E_{1/2}$. We can say, qualitatively that for the same composition (dielectric constant) the anodic shift for 4-nitronaphthalene cannot be explained on the basis of Born charging. An ion-dipole interaction may be playing more effective part. Due to smaller size of nitroaniline anion radical, there is stronger interaction of dipole of ethanol with the anion radical, and thus the anion gets more solvated. Sadek *et al.*⁴ has reported that the introduction of ethanol (in aqueous solution) shifts the polarographic (irreversible) $E_{1/2}$ cathodically due to adsorption of ethanol on the surface of electrode thus preventing nitroaniline getting reduced.

In pure ethanol, 4-nitroaniline does not give a reversible wave, thus the anion radical is unstable in

TABLE 1. ELECTROCHEMICAL DATA FOR 4-NITROANILINE IN ACETONITRILE-WATER AND ACETONITRILE-ETHANOL MIXED SOLVENT.^(a)

Solvent	Composition(b) (%)	(E _p) _a -(E _p) _c (mV)	E _{1/2} (d)	Reversibility	Stability
Ethanol	0	70	-1.25(d)	Reversible	Stable(e)
	15	67	-1.17	"	"
	20	75	-1.15	"	"
	100	—	—(f)	Irreversible	—
Water	15	55	-1.55	Reversible	Stable
	25	45	-1.11	"	"

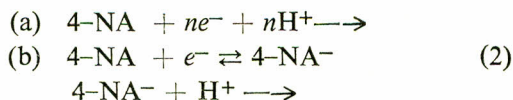
(a) On hanging mercury-drop electrode with 0.1 *t*-butammonium perchlorate as supporting electrolyte.¹² (b) Weight per cent. (c) in mV (E_p)_a-(E_p)_c ≈ 60 mV is for reversible, one electron, process. (d) v_s gold wire reference electrode (ref. 10). To convert E_{1/2} given here to SCE add -0.130 V. (e) The rate of decomposition of the anion should be less than 0.01 sec⁻¹. (f) Since the process is irreversible (or pseudoreversible) E_{1/2} cannot be calculated.

TABLE 2. ELECTROCHEMICAL DATA FOR 1-NITRONAPHTHALENE IN ACETONITRILE-WATER AND ACETONITRILE-ETHANOL MIXED SOLVENT.^(a)

Solvent	Composition (%)	(E _p) _a -(E _p) _c	E _{1/2}	Reversibility
Ethanol	0	70	-0.95	Reversible
	10	60	-0.95	"
	15	90b	-0.95	"
	25	75	-0.95	"
	100	75	-0.90	"
Water	10	70	-0.86	"
	15	80	-0.83	"
	25	70	-0.79	"

(a) See Table 1 for footnotes. (b) The reasons for such a large value could not be ascertained.

time scale of 33 mV/sec scan rate. The nonexistence of the anodic peak can be due to either of the following two processes:



Although (2b) is more likely to occur,¹² no further investigation was carried out to confirm one or the other. The main reason being that to distinguish the two processes, effect of higher scan rate on the peak potential^{1,2} had to be studied. A quasi-reference electrode is not an ideal electrode system for such a study.¹⁰

In acetonitrile-water system, the result is similar, i.e. 25% (composition) of water does not affect the reversibility of the system nor the stability of the anion (rate of decomposition is less than 0.01 sec⁻¹). Also the anodic shift in the E_{1/2} indicates a greater stabilization of the anion due to ion-solvent interaction as predicted by Born model.

1-Nitronaphthalene. This higher analogue of nitrobenzene has not been studied so far. Studies on other substituted naphthalene compounds will be interesting.

From the Table 2 it is quite clear that 1-nitronaphthalene is reduced reversibility by a one-electron process in acetonitrile-ethanol mixture in entire composition range following the process given in equation 1. The anion radical is stable (*k* decomposition is less than 0.01 sec⁻¹). It is to be noted that the E_{1/2} is unaffected on the addition of ethanol (lowering of dielectric constant). According to Born model, there should have been cathodic shift. The change in E_{1/2} indicates a compensatory liquid junction potential between reference electrode and solution phase.

The acetonitrile-water system exhibits the same feature as for 4-nitroaniline. 1-Nitronaphthalene gets reversibility reduced (one electron) and the anion radical is stable (*k* decomposition less than 0.01 sec⁻¹). The anodic shift in E_{1/2} is consistent with ion-solvent interaction stabilization as predicted by Born model.

Experimental

1-Nitronaphthalene was crystallised from ethanol (m.p. 60°C). 4-Nitroaniline was recrystallised from benzene. Ethanol (Analar grade) was used without purification. Tetrabutyl ammonium perchlorate was used directly. A gold wire (about 24 gauge and 1½ in long) was used as quasi-reference electrode. The rest of the electrode assembly and instrument was of Heath Co. A servorecorder (Heath) was used to record the cyclic voltammogram. A hanging mercury-drop electrode was constructed by sealing a piece of gold wire in a glass capillary with the help of Araldite (Ciba). The end was polished with fine emery paper, till gold was seen as shining disc. A tiny drop of mercury of radius 0.5 mm was brought in contact with the surface of gold wire. Such an electrode has been used by the author before and has been found to be completely satisfactory.¹³

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