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Voltammetry of (E)-1-Phenyl-2-Nitro-1-Propene in N,N-Dimethylformamide Solutions

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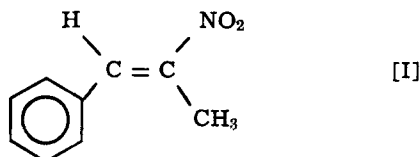
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ABSTRACT

The electrode reduction mechanism of (E)-phenyl-2-nitro-1-propene (PNP) in N,N-dimethylformamide (DMF) has been studied by polarographic, cyclic voltammetric, and rotating disk techniques. The compound is reduced in two polarographic steps in DMF and DMF-water solutions. Data taken at potentials of the first polarographic plateau suggest that the compound is reduced to a product via a mechanism involving coupling of the ion radicals of the precursor. The rate of the coupling reaction has been studied as a function of concentration of the PNP and water content of the solvent. Oscilloscopic recording of rapid cyclic voltammetry experiments demonstrate that the second polarographic step represents a two-electron reduction of the parent compound, PNP.

A wealth of electrochemical and electron spin resonance data demonstrate the great stability of the anion π -radicals of a large variety of aromatic nitro compounds in aprotic solvents such as acetonitrile, dimethylsulfoxide, and N,N-dimethylformamide (DMF) (1, 2). Nitro group elimination (3) and aromatic ring-halide elimination (4, 5) represent some decay pathways of certain species of this general type. Hoffman *et al.* (6) found that the anion radicals of various electrochemically generated tert-alkyl nitro compounds are intrinsically unstable, cleaving to nitrite ion and corresponding alkyl free radicals in glyme solvent. The small amount of data presented relative to nitroalkene π -radicals, intermediate to the above examples in extent of resonance stabilization, is inconclusive as to the general behavior of such species in aprotic media (7-9). As part of a systematic study into this matter, the compound 1-phenyl-2-nitro-1-propene (PNP) [I] was synthesized and its electrochemical behavior in DMF and DMF-water solutions observed. Techniques employed in the study include conventional d-c polarography, rotating disk, and cyclic voltammetry.



Results

Polarography.—The compound PNP features two polarographic waves in DMF containing 0.1M tetra-N-propylammonium perchlorate (TPAP) (Fig. 1). The waves exhibit half-wave potentials ($E_{1/2}$) of -0.99 and -1.68 V vs. saturated calomel electrode (SCE) and are diffusion controlled. Complete polarographic data are presented in Table I. The diffusion current constant (I_d) of the more negative potential plateau in dry DMF¹ is much less than that for a one-electron

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Key words: (E)-1-phenyl-2-nitro-1-propene, electrochemistry, dimerization.

¹ DMF containing less than 0.03% water.

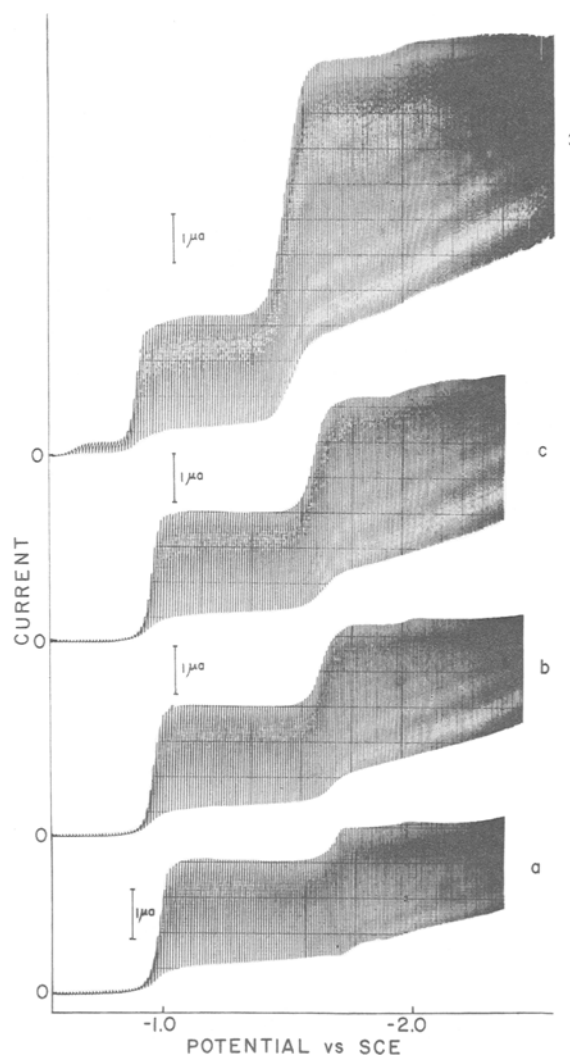


Fig. 1. Polarograms of PNP 1 mM in DMF containing (a) no water, (b) 220 mM H₂O, (c) 660 mM H₂O, (d) 6600 mM H₂O.

Table I. Polarographic data for (E)-1-phenyl-2-nitro-1-propene in DMF, DMF-H₂O, and DMF-HQ mixtures^a

H ₂ O ^b (mM)	First wave		Second wave	
	-E _{1/2} (V)	I _d (μAmM ⁻¹ sec ^{-1/6} mg ^{-2/3}) ^c	-E _{1/2} (V)	I _d (μAmM ⁻¹ sec ^{-1/6} mg ^{-2/3}) ^c
0	0.99	1.82	1.68	0.59
220	0.95	1.82	1.65	1.52
440	0.95	1.82	1.61	1.95
660	0.94	1.82	1.61	2.15
1,100	0.93	1.82	1.56	3.08
2,200	0.89	1.82	1.50	4.71
6,600	0.87	1.82	1.47	5.51
11,000	0.86	1.82	1.37	5.37
HQ (mM)				
0.0	0.99	1.82	1.68	0.59
1.82	0.99	1.82	1.43	2.52
9.10	0.98	1.83	1.35	4.22
18.20	0.97	1.81	1.29	4.81
36.40	0.97	1.81	1.25	4.81
145.60	0.92	1.81	1.24	4.81

^a All solutions were 1 mM in PNP and 0.1M in TPAP supporting electrolyte.

^b Concentration computed based on water added to solvent.

^c All diffusion currents measured at a mercury head height of 60 cm. The electrode characteristics measured at 60 cm mercury head and at open circuit were $m = 2.41$ mg/sec and $t = 3.1$ sec.

transfer process involving materials of comparable diffusion coefficients. Addition of the proton donors water and hydroquinone (HQ) to the test solution had no effect on the diffusion current or shape of the first plateau (Fig. 1). The $E_{1/2}$ of the wave is, however, shifted towards less negative potentials by large ratios of proton donor to electroactive compound. The characteristics of the second polarographic wave proved to be sensitive to added proton donors (Table I, Fig. 1). The diffusion current is increased to a limiting value, a factor of ten greater than that of the wave in pure solvent, upon addition of large quantities of water or HQ. This change is accompanied by a significant positive shift in the $E_{1/2}$ of the wave (Table I). Consistent with previously published data, HQ proved to be much more effective than water as a donor in DMF (10). Similar polarographic behavior is reported by Baizer and co-workers for several 1,2-diacetylated olefins (11, 12).

Cyclic voltammetry.—Typical cyclic voltammograms of PNP recorded at a planar platinum disk electrode (ppde) at varying concentrations in DMF are shown in Fig. 2. Data for voltammetric studies at concentrations of 0.1 and 1 mM PNP are presented in Table II.

Voltage excursion and reversal 120 mV cathodic of the first plateau revealed cyclic voltammetric waves with very little anodic current in solutions containing 1 and 10 mM PNP in dry DMF (Fig. 2). The potential sweep rate (v) ranged to a maximum of 12.48 V/min in experiments conducted on 1 mM solutions (Fig. 2). In a series of experiments conducted at 1 mM PNP the cathodic peak potential [(E_p)_c] shows negative shifts of 30 mV per tenfold increase in v . This cathodic shift is accompanied by a 9% decrease in the current function, (ip)_c/ $v^{1/2}$ (Table II).

Similar voltammetric experiments in solutions containing 0.1 mM PNP in dry DMF produced cyclic waves possessing significant anodic currents (Fig. 2). The (E_p)_c and current function of the recorded voltammograms were essentially constant with respect to a varying potential sweep rate (Table II). The cathodic to anodic peak separation [(E_p)_c-(E_p)_a] is 60 mV at all values of v .

Chronoamperometric experiments were conducted in conjunction with the cyclic voltammetric experiments at the same ppde and under identical conditions of concentration of PNP and supporting electrolyte at potentials corresponding to the first polarographic plateau. Diffusion current plots, $it^{1/2}/C$ vs. t , of data taken from current-time decay curves (0.3-1.4 sec) of the reduction of PNP at 0.1 and 1.0 mM in dry DMF correspond closely to similar plots for the known one-

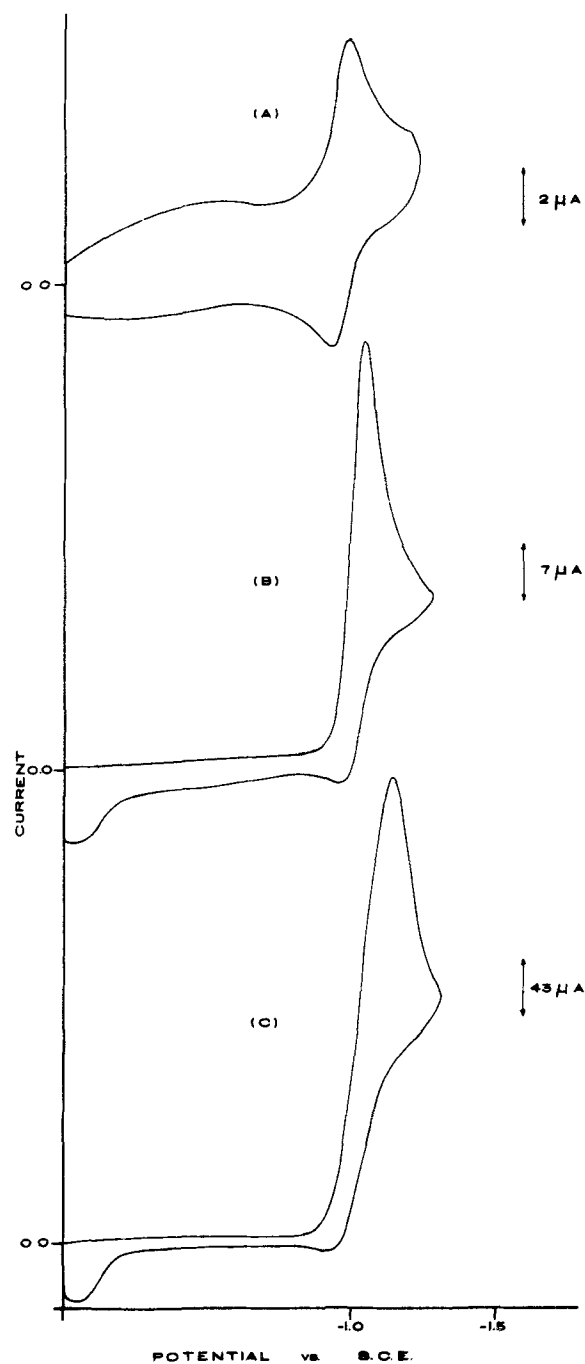


Fig. 2. Single sweep cyclic voltammograms taken at a ppde at potentials of first polarographic wave in DMF containing 0.1M TPAP and (a) 0.1 mM PNP recorded at 12.48 V/min. (b) 1 mM PNP recorded at 12.48 V/min. (c) 10 mM PNP recorded at 9.65 V/min. E_{λ} is 120 mV.

electron reduction of nitrobenzene under the same experimental conditions.

The influence of water on the process occurring at potentials of the first polarographic wave was studied with cyclic voltammetry at a ppde (Table II). Controlled quantities of water were added to solutions 0.1 and 1.0 mM in PNP and cyclic voltammograms were recorded. Addition of water to solutions 0.1 mM in PNP had a slight but discernible influence on the (E_p)_c, current function, and anodic to cathodic current ratio [(ip)_a/ (ip) _c] of the cyclic curves (Table II). At a proton donor to PNP ratio of 2.4×10^4 moles to one, a 10% decrease in the current function and a 20 mV negative shift in the cathodic wave is noted to accompany a tenfold increase in v . Only an immeasurably small anodic current is observed on the reverse sweep

Table II. Cyclic voltammetric data for (E)-1-phenyl-2-nitro-1-propene in DMF and DMF-H₂O at a ppde^a

H ₂ O ^b (mM)	ν (V/min)	$-(E_p)c$ (V)	$-(E_p)a$ (mV)	$(i_p)a/$ $(i_p)c^c$	$(i_p)c/v^{1/2}$ $\mu A \text{ volt}^{-1/2} \text{ min}^{1/2}$
(E)-1-phenyl-2-nitro-1-propene (0.1 mM)					
0	12.48	1.00	60	1.0	2.59
	9.38	1.00	60	1.0	2.46
	6.24	1.00	60	1.0	2.38
	3.12	0.99	60	1.0	2.46
	1.25	0.99	60	1.0	2.66
600	12.48	0.97	62	0.66	2.62
	9.38	0.97	60	0.64	2.50
	6.24	0.96	60	0.62	2.41
	3.12	0.96	— ^d	— ^d	2.40
	1.25	0.95	— ^d	— ^d	2.65
1200	12.48	0.95	70	0.66	2.47
	9.38	0.95	70	0.64	2.42
	6.24	0.95	70	0.61	2.38
	3.12	0.94	— ^d	— ^d	2.46
	1.25	0.94	— ^d	— ^d	2.65
2400	12.48	0.93	70	0.63	2.39
	9.38	0.93	70	0.62	2.40
	6.24	0.92	— ^d	— ^d	2.40
	3.12	0.92	— ^d	— ^d	2.43
	1.25	0.91	— ^d	— ^d	2.65
(E)-1-phenyl-2-nitro-1-propene (1 mM)					
0	4.68	1.05	— ^d	— ^d	23.25
	3.12	1.04	— ^d	— ^d	23.45
	1.56	1.03	— ^d	— ^d	25.00
	0.47	1.02	— ^d	— ^d	25.34
	0.47	1.02	— ^d	— ^d	22.80
600	4.68	1.02	— ^d	— ^d	23.90
	3.12	1.02	— ^d	— ^d	25.78
	1.56	1.01	— ^d	— ^d	25.63
	0.47	0.99	— ^d	— ^d	22.15
	0.47	0.99	— ^d	— ^d	23.68
1200	4.68	1.00	— ^d	— ^d	25.47
	3.12	0.99	— ^d	— ^d	25.05
	1.56	0.97	— ^d	— ^d	21.63
	0.47	0.97	— ^d	— ^d	22.34
	0.47	0.97	— ^d	— ^d	24.20
2400	4.68	0.97	— ^d	— ^d	23.71
	3.12	0.96	— ^d	— ^d	
	1.56	0.95	— ^d	— ^d	
	0.47	0.94	— ^d	— ^d	
	0.47	0.94	— ^d	— ^d	

^a All solutions were 0.1M in TPAP.

^b Concentration computed based on water added to solvent.

^c E_λ (switching potential) = 120 mV and ratio computed after method of Nicholson *et al.* (15).

^d Anodic current not reliably measurable.

segment of cyclic experiments conducted at a ν of less than 6.24 V/min (Table II, Fig. 3). Only a positive shift in $(E_p)c$ relative to the same values in dry solvent is noted in water addition experiments conducted at 1 mM PNP (Table II).

The dependence of cyclic peak characteristics on the concentration of PNP in dry DMF is significant to the interpretation of the electrochemical process responsible for the first diffusion plateau. In general, the cyclic voltammetric data taken at 0.1 mM PNP suggests the reversible, one-electron formation of an intermediate followed by a chemical reaction slow relative to the voltage excursion rate (13, 14). At higher concentrations of PNP (1.0 and 10.0 mM) the behavior suggests a rapid chemical reaction coupled to an initial electron-transfer process. The influence of the precursor concentration on the rate of the coupled homogeneous chemical reaction and the chronoamperometric data is consistent with second order kinetics involving dimerization of intermediate radicals of the precursor (hydrodimerization). Nicholson *et al.* (15) and Saveant *et al.* (16) have presented the theory of cyclic voltammetry for an electrochemically initiated homogeneous dimerization reaction with diagnostic criteria analogous to those developed for other electrochemical reaction mechanisms (13, 14). The cyclic voltammetric data in Table II for PNP are in general good agreement with the dimerization criteria.

Oscilloscopic recording of current response to rapid voltage excursion and reversal past the diffusion plateau of the diminished second wave, revealed data definitive of the electrochemical process responsible for the wave. Cyclic voltammograms recorded at a ppde in 1 mM PNP at 24 and 240 V/min (Fig. 4) show that the cathodic current of the second wave grows in intensity with increased sweep rate to a limiting value equal to that of the first wave, a one-electron process.

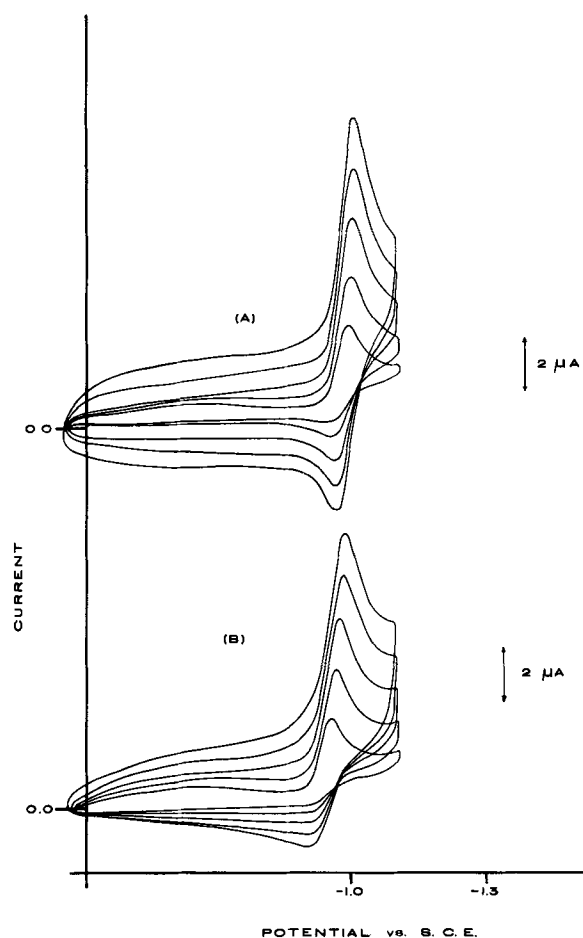


Fig. 3. Single sweep cyclic voltammograms of PNP at 0.1 mM in DMF recorded at a ppde at potentials of first polarographic wave. (a) Solution contained no added water and voltammograms recorded at 12.48, 9.38, 6.24, 3.12, and 1.25 V/min. (b) Solution contained 2.4M H₂O and voltammograms recorded at 12.48, 9.38, 6.24, 3.12, and 1.25 V/min. E_λ is 120 mV.

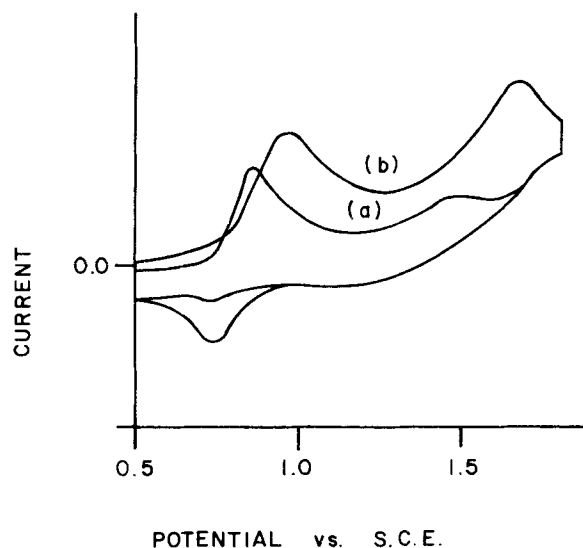


Fig. 4. Trace from film of oscilloscopic recording of single sweep cyclic voltammograms at a ppde of a 1 mM solution of PNP at (a) 24 V/min and (b) 240 V/min. E_λ is approximately 120 mV.

These data and the enhanced anodic current of the first wave recorded under the same conditions are consistent with an electrochemical reduction process involving an initial one-electron transfer to the parent

Table III. Rotating disk electrode data for the first reduction wave of (E)-1-phenyl-2-nitro-1-propene (PNP)^a

Limiting disk current $i_{d,1}$ (μA)	Rotation rate ω (sec^{-1})	$\frac{i_{d,1}}{\omega^{1/2}C}$
Concentration of PNP = 2.78 mM		
110	48	5.73
155	99	5.61
190	150	5.58
220	201	5.58
244	253	5.52
274	305	5.64
294	358	5.59
314	409	5.59
330	461	5.53
350	512	5.56
368	564	5.58
384	616	5.57
Concentration of PNP = 3.20 mM		
259	201	5.72
Concentration of PNP = 4.79 mM		
212	48	6.41
297	99	6.25
305	105	6.21
420	201	6.18
473	253	6.20
516	305	6.16
573	358	6.17
594	409	6.13
631	461	6.13
668	512	6.13
703	564	6.18
773	616	6.17

^a Solutions were 0.1M TBAI in DMF.

compound at the first wave and a subsequent one-electron addition to the ion radical at the second wave. Chemical reactions following the first transfer are not apparent at very rapid potential excursion rates. The sensitivity of the second wave to small quantities of proton donors (Fig. 1) is consistent with a rapid protonation of an initially produced dianion of PNP. In summary the cyclic voltammetric data are consistent with a general reduction scheme of the type

First Wave

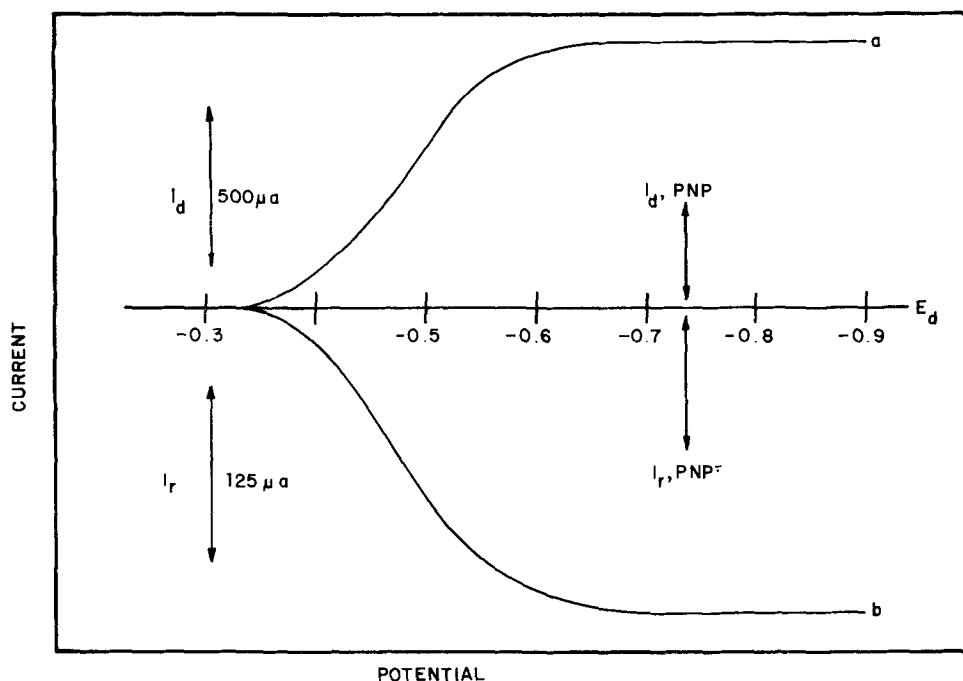
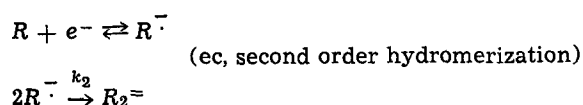
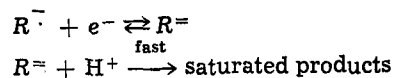


Fig. 5. RRDE voltammograms of PNP at 2.89 mM in DMF determined at a scan rate of 30 mV/sec and a rotation rate of 201 rad/sec. (a) i_d vs. E_d (b) i_r vs. E_d , $E_r = -0.10\text{V vs. Ag R.E.}$

Second Wave



Rotating ring-disk electrode studies.—Confirmation of hydrodimerization as the major reduction pathway of PNP in DMF at its first polarographic step and a determination of the rate constant for the coupling reaction (RRDE) techniques. Rotating disk electrode voltammograms taken at scan rates of 20–25 mV/sec of 1 mM solutions of PNP in DMF show a reduction wave with $E_{1/2} = -0.49\text{V vs. Ag reference electrode}$. Values of the Levich constant, $i_{d,1}/C_R\omega^{1/2}$ (where $i_{d,1}$ is the disk current on the mass transfer limiting plateau) given in Table III, show no dependence on rotation rate (ω). The diffusion coefficient for PNP, D , evaluated from the Levich equation

$$i_{d,1} = 0.62nFAD^{2/3}\nu^{-1/6}C_R\omega^{1/2}$$

(where $n = 1$, and ν , the kinematic viscosity, is $0.00849\text{ cm}^2/\text{sec}$ for DMF) was found to be $2.4 \times 10^{-5}\text{ cm}^2/\text{sec}$. Coulometry carried out at $-1.10\text{V vs. Ag-R.E.}$ shows n_{app} values of 0.97 and 0.98 for 2.78 and 4.79 mM solutions, respectively. The independence of the Levich constant with rotation rate and the above coulometry data suggest the absence of polymerization which often accompanies hydrodimerization reactions in aprotic solvents (e.g., for diethyl fumarate and fumaronitrile) (14, 20).

Rotating ring-disk electrode experiments were performed to gather additional data relative to the mechanistic characteristics of the reduction process. A typical RRDE voltammogram of this system is shown in Fig. 5. Collection efficiency (N_K) (where $N_K = i_r/i_d$) measurements as a function of disk current (CONI) (where $\text{CONI} = i_d/i_{d,1}$) were made at various rotation rates (ω) and concentrations. Representative data of these experiments are presented in Table IV. The trend of increasing N_K with decreasing CONI has been shown to be indicative of a hydrodimerization reaction proceeding by a coupling of radical anions rather than attack of the parent compound by radical anions (17, 20). The experimental points were fit by simulating such a mechanism for different values of the simulation rate constant parameter

Table IV. Experimental collection efficiency (N_K) data for (E)-1-phenyl-2-nitro-1-propene^{a,b}

i_r (μA)	i_a (μA)	N_K	CONI
Concentration PNP = 2.78 mM			
23.4	54.6	0.429	0.199
44.7	113.9	0.392	0.414
61.7	175.5	0.352	0.638
71.3	220.4	0.324	0.801
76.6	247.7	0.309	0.900
78.8	260.5	0.303	0.947
80.0	267.2	0.300	0.972
80.5	272.3	0.296	0.990
81.0	273.8	0.296	0.996
81.0	275.0	0.295	1.000
Concentration PNP = 4.79 mM			
16.5	20.0	0.525	0.047
18.0	37.0	0.486	0.086
28.0	64.0	0.438	0.149
36.0	90.2	0.400	0.209
37.8	106.8	0.353	0.249
42.5	135.1	0.315	0.314
47.5	149.9	0.317	0.349
55.0	208.0	0.264	0.484
60.0	234.7	0.255	0.547
62.0	250.0	0.248	0.581
65.0	280.3	0.232	0.651
70.0	315.0	0.222	0.732
70.0	319.7	0.219	0.744
71.0	359.8	0.197	0.837
75.0	400.0	0.189	0.930
76.0	419.9	0.181	0.977
78.0	430.0	0.181	1.000

^a Solutions were 0.1M TBAI in DMF.

^b Rotation rate = 201.1 radians/sec.

$KKTC = (0.51)^{-2/3} \nu^{1/3} D^{-1/3} D \omega^{-1} k_2$. The lines in Fig. 6 correspond to $KKTC$ values of 2.2 for line b and 0.9 for line a. These lines correspond to the following experimental conditions: line a, concentration of PNP equal to 2.78M at a rotation rate of 305 radians/sec; line b, concentration of PNP equal to 4.79 mM at a rotation rate of 201 radians/sec. Values of k_2 , determined

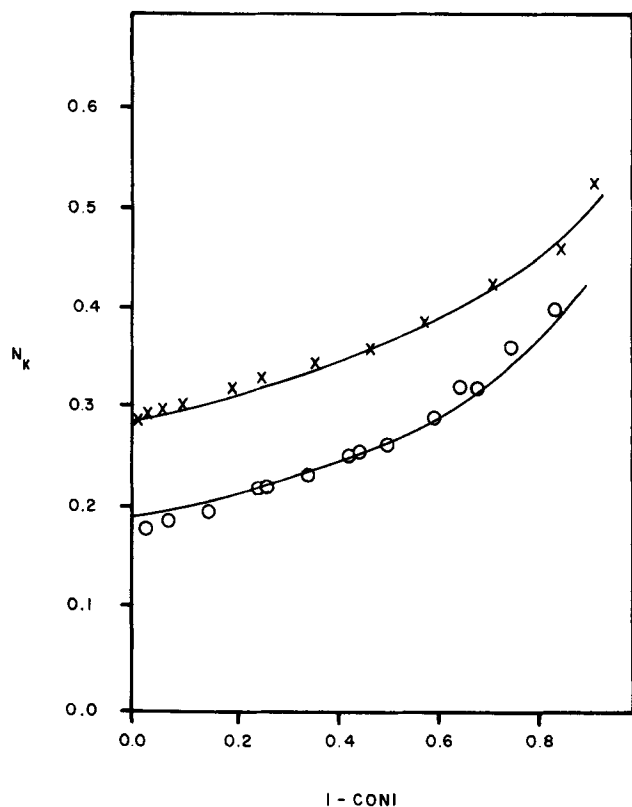


Fig. 6. Collection efficiency (N_K) vs. 1-CONI for a 2.78 mM PNP solution (X), and a 4.79 mM PNP solution (O). The rotation rates were 305 rad/sec and 201 rad/sec respectively. Solid lines are theoretical curves corresponding to dimerization mechanism and for (X) $KKTC = 2.2$ and (O) $SCTC = 0.9$.

Table V. Calculated rate constants for reactions of radical anion of PNP obtained from RRDE results^a

ω (sec ⁻¹)	Concentration (mM)	$KKTC^b$	k_2 (1/mole-sec)
99	2.78	2.1	1.5×10^4
	4.79	3.1	1.3
201	2.78	1.0	1.5
	3.20	1.3	1.6
305	4.79	2.2	1.8
	2.78	0.9	1.3
			Avg = 1.7×10^4

^a The solutions were all 0.1M TBAI in DMF.

^b $KKTC = (0.51)^{-2/3} \nu^{1/3} D^{-1/3} D \omega^{-1} k_2$, $\nu = 0.00849$ cm²/sec.

from these $KKTC$ values and the diffusion coefficient are given in Table V; an average of $1.7 \times 10^4 M^{-1} sec^{-1}$ is obtained.

Discussion of Results

Cyclic voltammetric, chronoamperometric, and rotating-ring disk data suggest that a dimeric coupling reaction (hydrodimerization) represents a major mode of decay of the anion radical of the compound PNP, produced by an initial one-electron transfer in DMF solvent. The compound is reduced also at more negative potentials via an *ec* process involving protonation of the dianion of the parent.

The radical anion coupling rate found here for PNP, $1.7 \times 10^4 M^{-1} sec^{-1}$, is intermediate to those found for other substituted olefins (17-20); the dialkyl fumarate radical anions couple with a $k_2 \approx 10^2 M^{-1} sec^{-1}$, while that for fumaronitrile radical anions is $6 \times 10^5 M^{-1} sec^{-1}$. The 1-phenyl, 2-cyano substituted olefin, cinnamionitrile, yielded a k_2 value of $9 \times 10^2 M^{-1} sec^{-1}$.

Baizer and co-workers (11) found that the radical anion of benzalacetophenone in DMF decayed most rapidly of the five, 2-substituted 1-phenyl olefins he studied ($-CO\phi > -CN > -COOC_2H_5 > -CON(CH_3)_2 > -C_6H_5$) with a lifetime approximately 1/40th of that of diethyl fumarate. Comparison of the k_2 computed for PNP with these data illustrated the relatively great reactivity of radical ions of nitrosubstituted olefins.

The cyclic voltammetric data from the study of the influence of water on the electrochemical reaction occurring at potentials of the first polarographic plateau suggests that proton donors influence the rate of chemical reactions coupled to the electron transfer but do not alter the mechanism of the processes controlling the shape and behavior of the cyclic curves (15). Similar conclusions were reached by Baizer and co-workers (11) and Bard and co-workers (18) from a variety of data. The magnitude of the influence of water is slight but data taken at precursor concentrations of 0.1, 1.0, and 10.0 mM are consistent with an increase in the rate of reactions coupled to the initial electron transfer (Table II, Fig. 3).

Studies of *cis-trans*-pairs of some activated olefins (19) have demonstrated that the anion of the *cis*-isomer may undergo a rapid isomerization to form the *trans*-radical anion as well as react more rapidly in self or cross-coupling reactions. No evidence of such behavior by the E-isomer of PNP is found in the short-term electrochemical data presented herein. The fact that only the E-isomer is produced in the synthesis of PNP, by the condensation of benzaldehyde, with nitroethane is probably pertinent to this point.

Experimental

Apparatus.—The ppde employed in the cyclic voltammetric experiments was a Beckman platinum buton electrode with an area of 80 mm². The reference electrode employed in the polarographic and cyclic voltammetry experiments, an aqueous saturated calomel electrode, made contact with the solution through an agar plug behind a Pyrex frit. Water leakage

through this tip was found to be negligible. The cyclic voltammetric data were recorded on a Bolt-Barnak-Newman X-Y Plotter using a Wenking potentiostat and exact wave form source for potential variation and control. The polarograms were recorded with a Beckman Electroscan 30 electroanalytical system.

A Tascussel Electronique Bipotentiostat, Model Bipad 2, was used for all RRDE experiments. A Digitec digital voltmeter, Model 204, and a Fairchild digital multimeter, Model 7050, were used to measure the steady-state ring and disk currents simultaneously. A Wavetek function generator provided a d-c potential ramp for voltammetric experiments recorded on a Mosley Model 2D-2 X-Y recorder. The platinum-Teflon rotating ring-disk electrode, having a disk radius (r_1) of 0.187 cm and inner (r_2) and outer (r_3) ring radii of 0.200 and 0.332 cm, respectively, was constructed by Pine Instrument Company, Grove City Pennsylvania. The maximum collection efficiency, N , for the RRDE used in these experiments was 0.555 (20). The reference electrode was a silver wire spiral.

Chemicals.—Spectroquality DMF containing approximately 0.03% water was obtained from Eastman Organic Chemicals. The solvent was vacuum distilled from anhydrous CuSO_4 before use. Hydroquinone was obtained from J. T. Baker Chemical Company and was recrystallized from a 50% water-ethylether solution. All nitroalkenes were synthesized by the method of Hass, Susie, and Heider (21). The compound PNP exhibited a melting point of 64°C after several recrystallizations from absolute ethanol.

Acknowledgment

The authors gratefully acknowledge the financial support of the Robert A. Welch Foundation; J. W. Rogers—(Grant No. AO-337), A. J. Bard—(Grant No. F-079), and National Science Foundation (GP-31414X).

Manuscript submitted May 13, 1974; revised manuscript received June 24, 1974.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1975 JOURNAL.

All discussions for the June 1975 Discussion Section should be submitted by Feb. 1, 1975.

The publication costs of this article have been assisted by the Robert A. Welch Foundation and the National Science Foundation.

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The Electrocapillary Phenomena at the Lead Electrode

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ABSTRACT

The electrocapillary phenomena was studied on the lead electrode by the method of meniscus rise in Na_2SO_4 solutions. The potential and concentration dependence of meniscus rise at potentials approximately cathodic to the pzc suggest that the electrode is polarizable. A sharp increase in the interfacial tension at -1.1V is attributed to anion adsorption. Charge density and differential capacity values are calculated from the meniscus rise data for 0.01M Na_2SO_4 solution, and are compared to the results of electrocapillary and capacity measurements on both mercury and lead electrodes, respectively. A reduction in the increase of meniscus rise with potential starting at about -1.55V with 1M Na_2SO_4 suggests the occurrence of cation specific adsorption.

An adequate understanding of the electrochemical activity of solid electrodes requires a better knowledge than is presently available of the electrode/electrolyte interface. The meniscus rise technique has been shown (1-10) to be valuable in previous studies of the inter-

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Key words: electrocapillary phenomena, lead electrode, meniscus rise, interfacial tension, double layer.

facial tension at solid electrodes. An extensive application of this technique to various systems is therefore desirable.

The development of the meniscus rise technique, and hence that of the interfacial phenomena at solid electrodes, requires, besides the examination of different systems, some comprehensive measurements on a given