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CONTROLLED POTENTIAL ELECTROLYSIS—XIII

POLAROGRAPHIC BEHAVIOUR AND CONTROLLED POTENTIAL ELECTROLYSES IN ACETONITRILE OF SEVERAL ALIPHATIC TERTIARY NITRO COMPOUNDS

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Abstract—The electrochemical reduction of aliphatic t-nitro compounds was studied in anhydrous acetonitrile by polarography and large scale controlled potential electrolysis. The first step of the electrode process involved a one-electron transfer leading to an unstable nitro anion radical which cleaved to nitrite ion and the corresponding free radical. This mechanism was substantiated by controlled potential electrolysis of t-nitrobutane and three α-nitroisobutyric acid derivatives. The difference in polarographic behaviour between t-nitrobutane and α-nitroisobutyric acid derivatives and the results of their electrolysis in the presence of a proton donor were related to the stability of the nitro anion radical and the reducibility of the nitroso derivatives. The predominant factor governing the half-wave potential was the inductive effect of the substituent. An extended Hückel MO calculation was carried out, but the results are unsatisfactory.

IN PRECEDING papers,[1,2] the difference in electrochemical behaviour between an aliphatic t-nitro group and other nitro groups was investigated, and tris(2-ethoxycarbonyl-2-propyl)hydroxylamine was obtained from controlled potential electrolysis of ethyl α-nitroisobutyrate in an alkaline aqueous solution at the plateau potential of its polarographic first wave. It was suggested for this reaction that a transfer of an electron causes a C—N bond fission and succeeding radical reaction.[2] In the present paper, the polarographic reduction and the controlled potential electrolyses of three α-nitroisobutyric acid derivatives and three related t-nitro compounds in acetonitrile were examined in detail, because the nitro anion radical which is assumed to be produced in the electrolytic reduction of the nitro compound is usually more stable in nonaqueous media than in water. Hoffmann *et al.*[3,4] studied the polarographic reduction of four aliphatic t-nitro compounds in 1,2-dimethoxyethane, but only obtained ESR signals from the electrolytic reduction of t-nitrobutane and not from other compounds. The signal was from the nitro anion radical during the electrolysis and from the nitroxide after electrolysis was discontinued. We used t-nitrobutane as reference compound, and investigated the mechanism of electrolytic reduction of the other compounds by comparing the results with those for t-nitrobutane.

RESULTS

Polarography. Polarographic reductions of t-nitrobutane (I), α-nitroisobutyronitrile (II), α-nitroisobutyramide (III), ethyl α-nitroisobutyrate (IV), 2-methyl-2-nitro-1-propanol (V), and tris(hydroxymethyl)nitromethane (VI) were investigated in acetonitrile containing 0·1 M TEAB as a supporting electrolyte. The values of the half-wave potentials and the diffusion current constants are listed in Table 1 and typical polarograms are shown in Fig. 1. (I) and (II) gave two waves, and the others, one wave. (I) and (V) showed small prewaves with wave heights which were almost independent of the concentration. The wave height of the first wave of each compound was proportional to the concentration between $2{\cdot}5 \times 10^{-4}$ and 2×10^{-3} M. Logarithmic analyses of the first wave in each case gave a straight line with the following slope (I) 0·091 v, (II) 0·071 v, (III) 0·087 v, (IV) 0·099 v, (V) 0·071 v and (VI) 0·119 v. This result shows that the first waves were all irreversible.

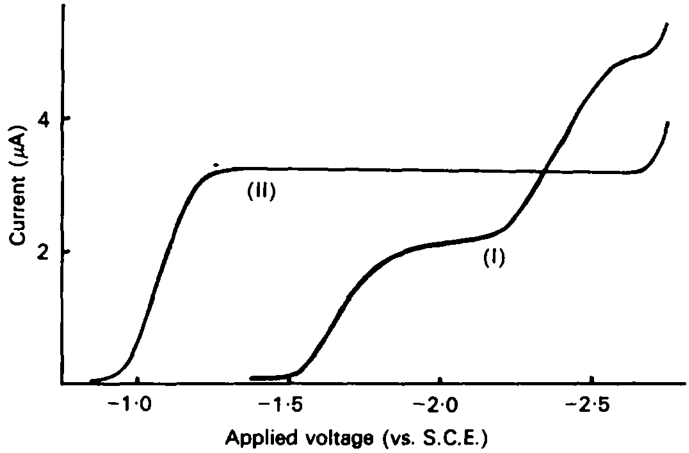


FIG. 1 Polarograms of t-nitrobutane (I) and α-nitroisobutyronitrile (II) (5×10^{-4} M) in anhydrous acetonitrile containing 0·1 M TEAB

TABLE 1. HALF-WAVE POTENTIALS ($E_{\frac{1}{2}}$) AND DIFFUSION CURRENT CONSTANTS (I_d) OF ALIPHATIC TERTIARY NITRO COMPOUNDS (5×10^{-4} M) IN ANHYDROUS ACETONITRILE

Compounds	$E_{\frac{1}{2}}$ v *vs* SCE	I_d*
t-Nitrobutane (I)	−1·62	3·34
	−2·40	4·80
α-Nitroisobutyronitrile (II)	−1·08	5·57
α-Nitroisobutyramide (III)	−1·31	3·80
	−1·71	0·92
Ethyl α-nitroisobutyrate (IV)	−1·32	4·78
2-Methyl-2-nitro-1-propanol (V)	−1·52	2·45
Tris(hydroxymethyl)nitromethane (VI)	−1·45	2·87

* $I_d = i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$ μA . l . mmol^{-1} . mg$^{-\frac{2}{3}}$. sec$^{\frac{1}{2}}$

To investigate the effect of a proton donor, the polarographic behaviour of the compounds on addition of various amounts of water were examined. The results are listed in Table 2. Compounds II and IV showed a single wave in anhydrous acetonitrile, but a second wave began to grow at a water concentration of 5% by volume and reached its maximal height at 10% water. On the other hand, I showed two waves in anhydrous acetonitrile, but the height of the second wave was greatly reduced with 5% water and only one wave was seen with 10% water. Two nitroso derivatives which are assumed to be formed by two-electron reduction of the nitro compounds were prepared, and their half-wave potentials were measured in acetonitrile and compared with those of the nitro compounds. The results are listed in Table 3. It is particularly interesting that ethyl α-nitroisobutyrate was less reducible than the corresponding nitro compound IV, whereas t-nitrosobutane and usual nitroso compounds are more easily reducible than their corresponding nitro derivatives.

TABLE 2. EFFECT OF WATER ON HALF-WAVE POTENTIALS ($E_{\frac{1}{2}}$) AND DIFFUSION CURRENT CONSTANTS (I_d)

Water added by volume, %	(I) $E_{\frac{1}{2}}$	(I) I_d	(II) $E_{\frac{1}{2}}$	(II) I_d	(III) $E_{\frac{1}{2}}$	(III) I_d	(IV) $E_{\frac{1}{2}}$	(IV) I_d
5	-1·48	3·69	-1·03	5·46	-1·25	3·80	-1·19	4·48
	-2·20	2·50	-1·90	5·16	-1·72	3·68	-2·03	9·26
10	-1·37	3·87	-0·92	6·07	-1·11	3·21	-1·18	3·88
			-1·69	6·98	-1·61	5·46	-1·97	11·20
15	-1·32	3·80	-0·92	5·46	-1·10	3·33	-1·13	4·18
			-1·61	5·77	-1·61	5·70	-1·86	8·37
20	-1·32	3·69	-0·85	4·55	-1·09	3·68	-1·07	4·48
			-1·51	6·07	-1·75	6·29	-1·65	6·72

Relationship between the half-wave potential and the inductive substituent constant. To examine the effect of substituents on the half-wave potential of the first wave of aliphatic tertiary nitro compounds, the half-wave potentials of $Me_2C(NO_2)X$, where X was —Me, —H, —CH_2OH, —$CONH_2$, —CO_2Et or —CN, were plotted against the σ_I constant of X.[5] The results are shown in Fig. 2. Though most points

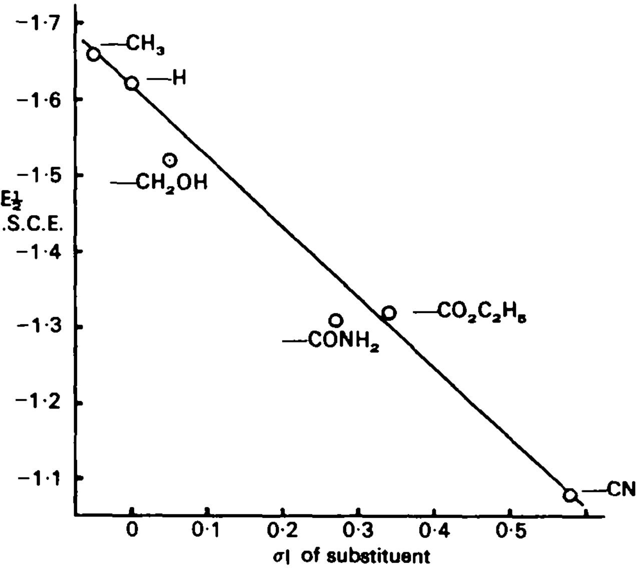


FIG. 2 Dependence of half-wave potential of the nitro compounds, $(CH_3)_2C(NO_2)X$, on the inductive substituent constant of the group X

fall on a straight line indicating that reducibility increases with increase in electronegativity of substituent, the points for —CH_2OH and —$CONH_2$ deviate from the straight line. These deviations may be ascribed to the effect of hydrogen bonding between the O of the nitro group and H of the hydroxymethyl group or amide group. The NMR chemical shift for the protons of the Me group of these compounds was plotted against the σ_I value. The results are shown in Table 4. In this case, the values for —H, —CH_2OH and —$CONH_2$ deviated from a linear relationship.

TABLE 3. HALF-WAVE POTENTIALS OF NITRO AND NITROSO COMPOUNDS (5×10^{-4} M) IN ACETONITRILE

Compounds	$E_{\frac{1}{2}}$, v *vs* SCE
t-Nitrobutane (I)	−1·62
t-Nitrosobutane	−1·36
Ethyl α-nitroisobutyrate (IV)	−1·32
Ethyl α-nitrosoisobutyrate	−1·70

Controlled potential electrolysis. Controlled potential electrolyses of I, II, III and IV were carried out in acetonitrile containing 0·1 M TEAB as supporting electrolyte at the plateau potentials of the first waves of these compounds. The results are summarized in Table 5. The concentration of the sample was in the range of 5×10^{-3} M ~ 10^{-2} M. Under these conditions, the concentration of water in the soln was comparable with that of the sample. Compounds II, III and IV behaved similarly, and their coulometric *n* values were found to be about 1·3 electrons. About 0·7 molar equivalent of nitrite ion was detected in the soln after electrolysis, Isobutyronitrile, isobutyramide and ethyl isobutyrate were isolated from the solutions of II, III and IV, respectively after electrolysis. Tetramethylsuccinonitrile and diethyl tetramethylsuccinate were also isolated from the solutions of II and IV, respectively after electrolysis. Moreover electrolysis of IV gave a small amount of ethyl methacrylate and ethyl α-nitrosoisobutyrate as determined by gas chromatography and the UV spectrum.

TABLE 4. METHYL PROTON NMR CHEMICAL SHIFT OF THE NITRO COMPOUNDS $(CH_3)_2C(NO_2)X$ AND THE INDUCTIVE SUBSTITUENT CONSTANT OF GROUP X

Substituents	σ_I	Chemical shift (τ)
−Me	−0·05	8·40
−H	0·00	8·43
−CH_2OH	0·05	8·41
−$CONH_2$	0·27	8·10
−CO_2Et	0·34	8·13
−CN	0·58	7·97

Electrolysis of I consumed about 2·7 electrons per molecule and gave 0·36 mole equivalent of nitrite ion. The electrolysed solution reduced Fehling's solution in the cold, and hence t-butylhydroxylamine was assumed to be produced. From the coulometric *n* value and the amount of nitrite ion produced, it can be assumed that most of the nitro anion radical was reduced further to t-butylhydroxylamine without the occurrence of a C—N bond fission. When the electrolysed solution was left for one day in air, it became blue, suggesting that t-butylhydroxylamine was oxidized to t-nitrosobutane by air. Compounds which might be formed from the t-butylnitro anion radical by cleavage of the C—N bond were not isolated, because these compounds were very volatile liquids or gases.

TABLE 5. THE RESULTS OF CONTROLLED POTENTIAL ELECTROLYSIS OF THE NITRO COMPOUNDS IN ACETONITRILE CONTAINING 0·1 M TEAB (0·013% WATER WAS PRESENT IN THE SOLUTION.)

Compounds	Applied potential V *vs* SCE	n	Products formed
(I)	−2·00	2·73	NO_2^- 0·36eq., t-Butylhydroxylamine
(II)	−1·40	1·34	NO_2^- 0·65eq., Isobutyronitrile Tetramethylsuccinonitrile
(III)	−1·60	1·35	NO_2^- 0·73eq., Isobutyramide
(IV)	−1·60	1·35	NO_2^- 0·63eq., Ethyl isobutryate Ethyl α-nitrosoisobutyrate Diethyl tetramethylsuccinate Ethyl methacrylate

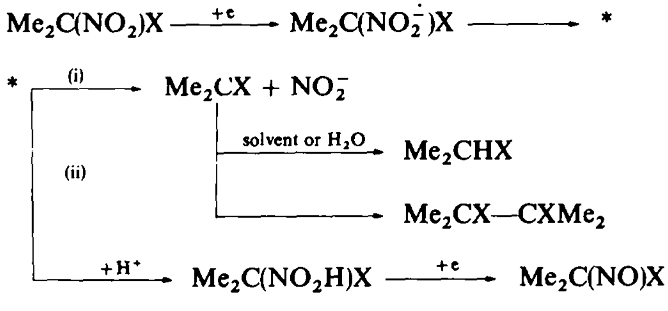
To investigate the effect of proton donors on the electrolytic reduction processes of these compounds, controlled potential electrolyses of I and IV were carried out in the presence of phenol. The results are shown in Table 6. It was found that with both compounds the coulometric *n* value increased and the amount of nitrite ion decreased with increase in the amount of added phenol. Electrolysis of I, however, produced a negligible amount of nitrite ion when 25 equivalents of phenol were present in the solution, but produced t-butylhydroxylamine in a single reduction involving four electrons. On the other hand, electrolysis of IV produced some nitrite ion and the coulometric *n* value did not exceed two.

TABLE 6. EFFECT OF A PROTON DONOR (PHENOL) ON THE CONTROLLED POTENTIAL ELECTROLYSIS OF t-NITROBUTANE (I) AND ETHYL α-NITROISOBUTYRATE (IV)

Compounds		Amount of added phenol		
		0	25 times eq.	50 times eq.
(I)	n	2·73	4·30	
	NO_2^-	0·36eq.	negligible	
(IV)	n	1·35	1·58	1·94
	NO_2^-	0·63eq.	0·42eq.	0·25eq.

DISCUSSION

The first step in the electrode reaction of the aliphatic t-nitro compounds studied is considered to be a one-electron reduction leading to a nitro anion radical. The differences in the results obtained by electrolysis of these compounds are best explained on the basis of differences in stability of the nitro anion radicals produced. The anion radical of t-nitrobutane is much more stable than that of α-nitroisobutyric acid derivatives, and hence most of the anion radicals are protonized by a trace of water and reduced further to a hydroxylamine, and the amount of nitrite ion produced decreases. Moreover, as Hoffmann *et al.* suggested,[4,6] some of the anion radicals of I react with t-Bu radicals which are formed via C—N bond fission of the anion radicals initially formed, giving di-t-butylnitroxide which is further reduced to N,N-di-t-butylhydroxylamine. This reaction process also causes a small decrease in nitrite ion formation and a small increase in the coulometric *n* value. On the other hand, in the anion radical of α-nitroisobutyric acid derivatives, homolytic C—N bond fission takes place much faster than protonation, thus producing larger amounts of nitrite ion and residual free radicals. Hence a value close to unity was obtained as the experimental *n* value. In view of these facts, the reduction processes and subsequent decomposition processes of α-nitroisobutyric acid derivatives should be expressed by Scheme 1.



(1)

$X = —CN, —CONH_2$, and $—CO_2Et$

When a proton donor is present, the reaction rate of (ii) becomes faster than that of (i), and the nitroso derivative is produced. The differences in the results of polarography and controlled potential electrolysis between I and α-nitroisobutyric acid derivatives in the presence of proton donors may be explained in terms of differences in the half-wave potentials of their nitroso derivatives. Because t-nitrosobutane is more readily reduced than I, the nitroso species formed by process (ii) is immediately reduced to t-butylhydroxylamine by the succeeding two-electron reduction, and the polarogram of I shows only one wave just as the usual nitro polarogram in aqueous solution. On the other hand, ethyl α-nitrosoisobutyrate, which is produced by process (ii), is not reduced at the potential applied, and so the coulometirc *n* value does not exceed two, whereas the polarography of IV shows two waves, representing nitro to nitroso and nitroso to hydroxylamine species.

Molecular orbital calculations. To explain the difference in stability between the nitro anion radicals of t-nitrobutane and α-nitroisobutyric acid derivatives, Hückel MO calculations were carried out for these compounds. To the first approximation, the instability of the t-nitro anion radical and rupture of the C—N bond are assumed to depend on the stability of the resulting π radicals, and hence the π electron resonance energies of the resulting π radicals were calculated. Most of the parameters used were those of Yonezawa *et al.*[7]

The value of Rieger *et al.*[8] was used for the parameter of nitrile. The hyperconjugation model was used for the Me group. The π electron resonance energies obtained were $Me_3\dot{C}$, 0·633 β; $Me_2\dot{C}CN$, 0·871 β; $Me_2\dot{C}CONH_2$, 1·136 β and $Me_2\dot{C}CO_2Et$, 1·22 β. These results are consistent with the experimental results, in that the resonance energy of the t-Bu radical is the smallest. However, the resonance energy of isobutyronitrile was calculated to be much smaller than that of the other two isobutyric acid derivatives, whereas any difference between values for compounds was scarcely observed experimentally. Secondly, to correlate the half-wave potentials with structure and to explain why C—N bond fission occurs in these nitro anion radicals, the extended Hückel MO calculation proposed by Hoffmann[9] was carried out on four t-nitro compounds. This was because the difference between these compounds is in the σ framework, and therefore, calculations must be carried out including both the σ and π electrons simultaneously. The parameters[10] used are shown in Table 7. Because the actual structure with the lowest energy under the condition was not known, calculation was carried out at first on selected reasonable structure. The same coordinates were used for the atoms of the nitro and two Me groups. The atomic distances were taken as follows:[11] C—H, 1·09A; C—C, 1·54A, C=O, 1·22A; C—N (nitro), 1·46 A, N—O, 1·21 A; N—H, 1·02 A; C—N (amide), 1·36 A; C≡N, 1·15A; CO—O (ester), 1·36 A; O—Et (ester), 1·46 A. The bond angles are assumed to be 120° for an unsaturated C-atom, the tetrahedral angle for saturated C-atom and N-atom of amide group, 127° for ∠ONO (nitro), and 113° for ∠COC (ester). The coordinates of atoms used are shown in Table 8. The results are shown in Tables 9 and 10. It has been shown that the polarographic half-wave potential can be correlated with the energy of the lowest vacant orbital.[12] Only a small difference, with a maximum of 0·076 eV, was obtained between these compounds, then the large difference between half-wave potentials, with a maximum of 0·54 V, can not be explained. Though several calculations were carried out on the modified structures, the energy of the lowest vacant orbital was not changed more than ± 0·025 eV, and a further

TABLE 7. COULOMB INTEGRALS OF VARIOUS ATOMIC ORBITALS, H_{rr} (eV), AND THE EFFECTIVE NUCLEAR CHANGES OF VARIOUS ATOMS, Z

	Orbital			
Atom	1S	2S	2P	Z
H	−13·60			
C		−21·43	−11·42	3·25
N		−27·50	−14·50	3·90
O		−35·30	−17·76	4·55

The resonance integrals $H_{rs} = 0{\cdot}875 \times (H_{rr} + H_{ss}) \times S_{rs}$

TABLE 8. GEOMETRY OF THE COMPOUNDS: CARTESIAN COORDINATES OF ATOMS

	x	y	z
Common part			
H_1	−1·603282	1·257356	0·725956
H_2	−0·149985	2·147304	0·212175
H_3	−0·149985	1·257356	1·753563
H_4	−1·603282	−1·257356	0·725956
H_5	−0·149985	−1·257356	1·753563
H_6	−0·149985	−2·147302	0·212175
C_1	0·0	0·0	0·0
C_2	−0·513282	1·257356	0·725956
C_3	−0·513282	−1·257356	0·725956
C_4	−0·513282	0·0	−1·451912
N_1	1·460000	0·0	0·0
O_1	2·009340	1·078110	0·0
O_2	2·009340	−1·078110	0·0
t-Nitrobutane			
H_7	−1·603282	−1·257356	0·725956
H_8	−0·149985	−1·257356	1·753563
H_9	−0·149985	−2·147302	0·212175
α-Nitroisobutyronitrile			
N_2	−0·869913	0·0	−2·460708
α-Nitroisobutyramide			
O_3	−1·712786	0·0	−1·674928
N_2	0·370582	0·0	−2·485648
H_7	0·956960	0·832856	−2·431483
H_8	0·956960	−0·832856	−2·431483
Ethyl α-nitroisobutyrate			
O_3	−1·712786	0·0	−1·674928
O_4	0·370582	0·0	−2·485648
C_5	−0·184384	−0·567945	−3·710750
C_6	0·879902	−0·527855	−4·823051
H_7	−0·482301	−1·600692	−3·530053
H_8	−1·053961	0·012426	−4·018897
H_9	1·749479	−1·108226	−4·514903
H_{10}	1·177820	0·504891	−5·003747
H_{11}	0·465578	−0·951869	−5·737681

modification of the structure did not give a better result. As the largest negative value of the atomic bond overlap population of the lowest vacant orbital was for the N—O bond, the C—N bond fission observed experimentally is not explained by this value, and some other factors may be contributed. The reason for the above results is considered, as suggested by Fukui *et al.*[13] to be the result of the parametrization that the coulomb integral of each atomic orbital was approximated uniformly with the negative value of the ionic potential, and so the polarization of charge became too large. To overcome this defect the coulomb integral must be varied according to AO population on the atomic orbital by means of the ω-technique.

TABLE 9. POPULATION ANALYSIS FOR THE TERTIARY NITRO COMPOUNDS

		Compound			
		(I)	(II)	(III)	(IV)
Net charge	C_1	+0·4310	+0·4832	+0·3955	+0·3998
	C_2, C_3	−0·3861	−0·3346	−0·3415	−0·3431
	C_4	−0·2805	+1·1350	+1·5806	+1·7978
	N_1	+1·6401	+1·7108	+1·6278	+1·6788
	O_1, O_2	−1·1013	−1·0898	−1·1034	−1·0954
Bond overlap population	C_1–C_2	0·7355	0·6846	0·6983	0·6971
	C_1–C_3	0·6704	0·8542	0·7648	0·7879
	C_1–N_1	0·8194	0·7794	0·8243	0·8034
	N_1–O_1	0·8019	0·8144	0·7985	0·8087

TABLE 10. NATURE OF THE LOWEST VACANT ORBITAL (L.V.)

Compound	Energy of L.V., eV	Atomic population			Overlap population	
		C_1	N_1	O_1	C_1–N_1	N_1–O_1
(I)	−11·1428	0·0307	0·6491	0·0980	−0·0540	−0·1310
(II)	−11·2077	0·0238	0·6661	0·1020	−0·0507	−0·1474
(III)	−11·1317	0·0392	0·6418	0·0966	−0·0626	−0·1294
(IV)	−11·1677	0·0285	0·6666	0·1011	−0·0544	−0·1345

EXPERIMENTAL

Materials. t-Nitrobutane, α-nitroisobutyronitrile, α-nitroisobutyramide, ethyl α-nitroisobutyrate, ethyl α-nitroisobutyrate and tris(hydroxymethyl)nitromethane were prepared and purified as described in previous papers.[2, 14] 2-Nitro-2-methyl-1-propanol was prepared from formaldehyde and 2-nitropropane and recrystallized from toluene,[15] m.p. 90·5° (lit. 90 ~ 91°).[15] Tetraethylammonium bromide (TEAB) was prepared from EtBr and Et_3N and recrystallized from isopropanol.[16] Acetonitrile was purified by the method of O'Donnell *et al.*[17] The purified acetonitrile contained 0·006% water and the acetonitrile soln containing 0·1 M TEAB contained 0·013% (7·2 mM) water as determined by Karl Fischer titration. Tetramethylsuccinonitrile and diethyl tetramethylsuccinate were prepared from 2,2′-azobisisobutyronitrile.[18] Isobutyronitrile and ethyl methacrylate were obtained from commercial sources and purified by distillation.

Apparatus. The apparatus used for measurement of IR spectra, controlled potential electrolysis, colorimetry and measurement of NMR spectra were the same as those described in the previous paper.[14] Polarograms were recorded in a Simazu RP-50 Polarograph. The gas chromatograph used was a Hitachi KLG-2 model with a thermal conductance detector. The columms were packed with Silicon DC-550. Electric conductance was measured by a Toa Dempa CM-1DB Digital Conductivity Meter. Current-time curves were recorded with a Toa Dempa EPR-2TB Recorder.

General procedure for polarographic reductions. The solns were studied in a cylindrically shaped cell with a Hg pool anode, fitted with side arms for anode connection and for admission of argon. The cell was thermostatically regulated by a water-bath controlled at 25° ± 0·05°. The dropping Hg-electrode was operated at a press of 65 cm. All measurements were carried out in acetonitrile containing 0·1M TEAB as a supporting electrolyte. The specific conductance of the soln was $1{\cdot}185 \times 10^{-2}$ $\mho$/cm. The resistance of the assembly was 625 Ω, and hence the IR drop could be ignored. The potential of the pool, when measured in an H-cell against aqueous SCE, remained constant during a run. The pool, therefore, provides a stable reference potential, and hence the potential of the pool was measured against aqueous SCE after each run. All solns were de-aerated by passage of argon through them for at least 30 min. The argon (Ar

99·99 %, N_2 0·005 %) was passed through Cu turnings (heated to 400°), then an acetonitrile soln and finally the soln. During polarogram recording argon was passed over the surface of the soln.

General procedure for controlled potential electrolysis. The electrolysis cell used was a modified H-type cell with a middle compartment separated by two fritted glass disks. The area of the mercury pool cathode was 17·8 cm^2 and the volume of catholyte was 80 ml. The anode was a Ag-wire. The soln was stirred with a magnetic stirrer. The reference electrode was an aqueous SCE connected via a sintered glass disk to a bridge containing the test soln and closed at the end by a sintered disk of fine porosity. The quantity of electricity consumed in the electrolysis was calculated by a graphical integration of a current-time curve. The concentration of the test substances was $2 \times 10^{-3} \sim 2 \times 10^{-2}$ M. After electrolysis, a part of the electrolysed soln was used for determination of nitrite ion by Griess reaction. The rest of the electrolysed soln was evaporated to dryness under reduced press and extracted with ether. After evaporation of the ether, the residue was purified by distillation or recrystallization, and identified with authentic samples by measurement of its m.p., IR spectra and NMR spectra. Volatile substances which were distilled with acetonitrile were analysed by gas chromatography and their identification was made by comparing their retention times with those of the authentic samples of expected materials.

Molecular orbital calculations. Calculations by the Hückel MO method were performed with an NEAC 2203 computer at Osaka University. Calculations by the extended Hückel MO method were performed by IBM 7090 of Japan Unicon Committee with QCPE 30 program of Quantum Chemistry Program Exchange.

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