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The Electrolytic Behavior of Tetrasubstituted Iminium Salt in Acetonitrile

Atsutaka Kunai,* Junji Harada, Masayasu Nishihara, Yasuo Yanagi, and Kazuo Sasaki
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Saijo, Higashi-Hiroshima, 724

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Cathodic behavior of *N*-cyclohexylidenepyrrolidinium salt (**1**) and *N*-cyclohexylideneaniline (**2**) in acetonitrile has been studied by means of dc polarography, cyclic voltammetry and preparative electrolysis under controlled potential conditions. The compound **1** exhibits a reduction wave at about −1.8 V, which is accompanied by formation of a surface compound. The products obtained from the preparative electrolysis were neither saturated amines nor dimeric compounds but were mostly polymeric materials. However, when electrophilic olefins, such as acrylonitrile or methyl acrylate, were present in the solution, coupling products were produced. The compound **2**, which cannot be reduced by itself below −2.7 V, is reduced at about −1.8 V when benzoic acid is in the solution. The reduction product in this case was *N*-cyclohexylaniline, which was replaced by a coupling product when acrylonitrile was present in the reaction system. The formation of the coupling products is considered to occur by a radical mechanism in both cases.

The formation of C–C bonds by addition of strong nucleophilic carbanion to the carbonyl carbon atom is widely used in organic synthesis. Similar addition reaction to the imino group or particularly to the iminium group, which is the *N*-analogue of carbonyl group, is frequently utilized in alkaloid synthesis.[1] Since the carbon atom at the iminium group is strongly positively polarized, the electrolytic reduction is easier than for the corresponding carbonyl group.[2] It is considered that the product is generally a monomeric amine in protic solvents while dimeric compounds are favored in aprotic solvents.[2–4] Accordingly, it is expected that the intermediate derived from the reduction of an iminium salt will add to certain kinds of electrophiles. In fact, the electrolytic reductive coupling of some aromatic iminium salt with various benzyl bromides has been reported.[5] Except for the heterocyclic iminium salt,[3,4] however, the electrode reduction of iminium salt has not hitherto been studied extensively.[2]

In the present paper, we study the reaction of *N*-cyclohexylidenepyrrolidinium perchlorate (**1**) as a representative of an iminium salt of simple aliphatic ketones. The crossed coupling with electrophilic olefins is the main subject of our interest.[6] In addition, a similar reaction of *N*-cyclohexylideneaniline (**2**) is also studied. Polarographic studies of related compounds are available in the literature.[7] The solvent used was acetonitrile in all cases, and acrylonitrile and methyl acrylate were used as the electrophilic olefins. In some cases, methyl 3-bromopropionate was also used as the electrophile.

Experimental

General. D.c. polarography using a dropping mercury electrode and linear potential sweep experiments using a platinum, gold and hanging mercury drop electrodes were utilized for studying electrochemical properties. All measurements were made in acetonitrile solutions containing 0.1 M tetraethylammonium perchlorate (1 M=1 mol dm^{-3}). The solution were degassed with nitrogen.

Preparative electrolyses were carried out in a divided cell with a mercury pool cathode at a constant potential.

Electrodes. The height of the dropping mercury electrode s was kept at 50 cm. The capillary constant was 578 mmHg s mg^{-1}.** Platinum and gold wires of 1 mm in dia meter and 5 mm in length were used for cyclic voltammetry. All the potential values cited are those referred to a saturated calomel electrode using acetonitrile as the solvent.[8]

Reagents. Reagent grade acetonitrile was distilled over phosphorus pentaoxide and the distillate was refluxed over calcium hydride. This was freshly distilled before use. *N*-cyclohexylidenepyrrolidinium perchrorate (**1**) was prepared by the condensation of cyclohexanone with pyrrolidinium perchlorate.[9] Similarly, *N*-cyclohexylideneaniline (**2**) was prepared from cyclohexanone and aniline, bp 87 °C/133 Pa.

Controlled Potential Electrolysis. *(a)* N-*Cyclohexylideneaniline (2)*: The base solution was acetonitrile containing 0.1 M. tetraethylammonium perchlorate. A solution (100 cm^3) containing 1 mmol of **2** and 2 mmol of benzoic acid was electrolyzed at −1.9 V under a nitrogen atmosphere. The telectrolysis was continued until the current fell to the background level. The electrolyzed solution was evaporated to remove the solvent and the residue was extracted with ether by use of a Soxhlet extractor. The extract was again concentrated and subjected to TLC separation. The amount of the starting material remaining was determined by means of the formation of cyclohexanone 2,4-dinitrophenylhydrazone. The conversion of **2** was 80% and the yield of *N*-cyclohexylaniline (**3**) was 66% on the base of the reacted imine.

(b) 2 in the Presence of Acrylonitrile: A similar procedure was applied as used in the above. The amount of acrylonitrile added was 2 millimoles. The products, **3** (R_f 0.85) and 1-anilino-1-(2-cyanoethyl)cyclohexane (**4**) (R_f 0.70), were isolated by using silica gel TLC plates (5% EtOAc in benzene). Results are shown in Table 1.

(c) N-*Cyclohexylidenepyrrolidinium Perchlorate (1) in the Presence of Acrylonitrile*: Solutions of 1 mmol of **1** and 3 mmol of acrylonitrile were electrolyzed at −1.80 V. Others were the same as (*a*). The product, 1-(2-cyanoethyl)-1-(1-pyrrolidinyl)-cyclohexane (**6**), was isolated by preparative GLC (5% OV-17, 2 m, 215 °C). Results are shown in Table 2.

(d) 1 in the Presence of Methyl Acrylate: A mixed solvent of 10% MeOH and 90% CH_3CN was used in this case, which contained **1** (1 mmol) and methyl acrylate (3 mmol). Products obtained were 1-[2-(methoxycarbonyl)ethyl]-1-(1-pyrrolidinyl)cyclohexane (**7**) (34%) and 1,2-bis[2-(methoxycarbonyl)-ethyl]-1-(1-pyrrolidinyl)cyclohexane (**8**) (30%).

(e) 1 in the Presence of Methyl 3-Bromopropionate: Procedure

** 1 mmHg≈133.322 Pa.

was the same as (*d*). Three millimoles of 3-bromopropionate was used. Products were **7** (3%) and **8** (3%).

Product Analyses. ***4***: IR (neat) 3420 (-NH-), 2950 (-CH_2-), 2250 (CN), 750 and 690 cm^{-1} (Ph); NMR ($CDCl_3$) δ=1.17—1.75 (10H, m), 1.75—2.60 (4H, A_2B_2), 3.37 (1H, broad), 6.53—6.95 (3H, m), and 7.00—7.30 (2H, m); MS (70 eV), *m/e* (I_{rel}), 228 (M^+, 30), 185 ($M^+-C_3H_7$, 50), 174 ($M^+-CH_2CH_2CN$, 100), and 93 ($PhNH_2$, 79). Found: C, 79.06; H, 8.82; N, 12.13%. Calcd for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27%.

6: IR (neat) 2950 (-CH_2-), 2250 (CN), and 1450 cm^{-1} (-CH_2-); NMR ($CDCl_3$) δ=0.83—2.10 (16H, m) and 2.10—2.70 (6H, m); MS (70 eV), *m/e* (I_{rel}), 206 (M^+, 6), 163 ($M^+-C_3H_7$, 4), and 152 ($M^+-CH_2CH_2CN$, 100). Found: C, 75.90; H, 10.70; N, 13.40%. Calcd for $C_{13}H_{22}N_2$: C, 75.68; H, 10.75; N, 13.58%.

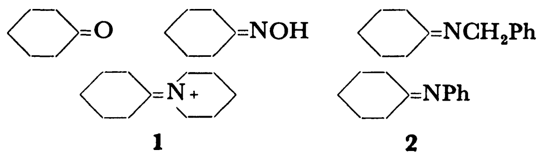
7: IR (neat) 2940 (-CH_2-), 1745 and 1190 cm^{-1} ($COOCH_3$); NMR ($CDCl_3$) δ=1.22—2.05 (16H, m), 2.22—2.88 (6H, m), and 3.65 (3H, s); MS (70 eV), *m/e* (I_{rel}), 239 (M^+, 3), 208 (M^+-OCH_3, 6), 196 ($M^+-C_3H_7$, 26), and 152 ($M^+-CH_2CH_2COOCH_3$, 100). Found: C, 70.50; H, 10.56; N, 6.16%. Calcd for $C_{14}H_{25}O_2N$: C, 70.25; H, 10.53; N, 5.85%.

8: IR (neat) 2950 (-CH_2-) and 1745 cm^{-1} ($COOCH_3$); MS (70 eV), *m/e* (I_{rel}), 325 (M^+ for $C_{18}H_{31}O_4N$, 5), 294 (M^+-OCH_3, 8), 282 ($M^+-C_3H_7$, 18), and 238 ($M^+-CH_2CH_2COOCH_3$, 100).

Other compounds were identified by comparison with authentic samples.

Results and Discussion

Polarography. The parent compound, cyclohexanone, does not show any reduction wave below the limit of solvent decomposition in acetonitrile (Fig. 1). Neither cyclohexanone oxime nor *N*-cyclohexylidenebenzylamine exhibits a reduction wave. *N*-cyclohexylideneaniline **2**, however, gives rise to a reduction wave with a half-wave potential at −2.8 V. The iminium salt **1** shows a wave with a characteristic maximum at about −1.8 V. On the other hand, all of electrophilic reagents such as acrylonitrile or methyl acrylate have their half-wave potentials at more negative than −2.2 V, indicating the possibility of selective reduction of the iminium salt **1**. *N*-Cyclohexylideneaniline (**2**) is also



1 **2**

selectively reduced when benzoic acid is deliberately added. This is shown in Fig. 2, where the effect of benzoic acid on the polarogram of the imine **2** is studied. It is clearly evident that a marked shift of reduction wave occurs upon addition of benzoic acid. Denoting the waves of $E_{1/2}$= −1.8, −2.3, and −2.8 V as the waves I, II, and III, respectively, we analyzed the height of each wave. This is shown in Fig. 3, where

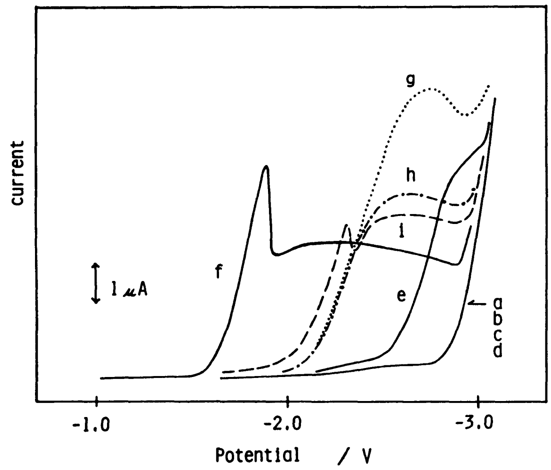


Fig. 1. Polarograms of the substrates in acetonitrile solution (1 mmol dm^{-3}).

The solution contains: a) none; b) cyclohexanone; c) cyclohexanone oxime; d) *N*-cyclohexylidenebenzylamine; e) *N*-cyclohexylideneaniline; f) *N*-cyclohexylidenepyrrolidinium perchlorate; g) acrylonitrile; h) methyl acrylate; and i) methyl 3-bromopropionate.

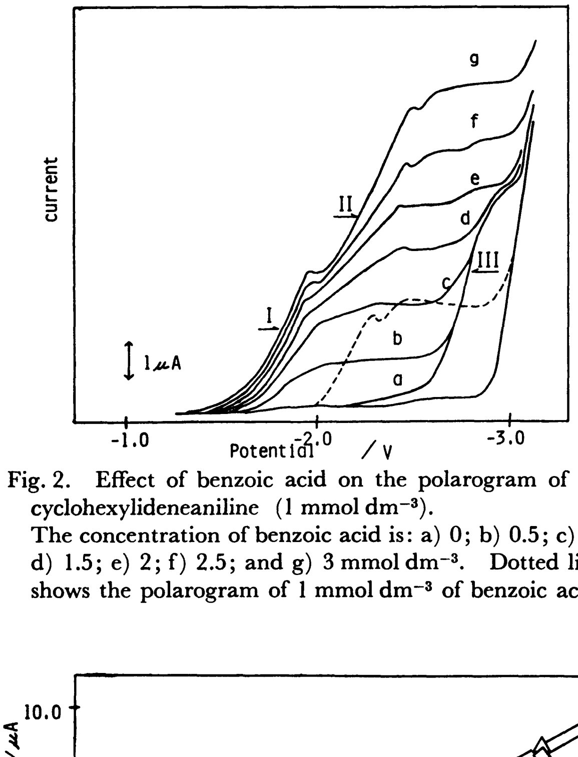


Fig. 2. Effect of benzoic acid on the polarogram of *N*-cyclohexylideneaniline (1 mmol dm^{-3}).

The concentration of benzoic acid is: a) 0; b) 0.5; c) 1; d) 1.5; e) 2; f) 2.5; and g) 3 mmol dm^{-3}. Dotted line shows the polarogram of 1 mmol dm^{-3} of benzoic acid.

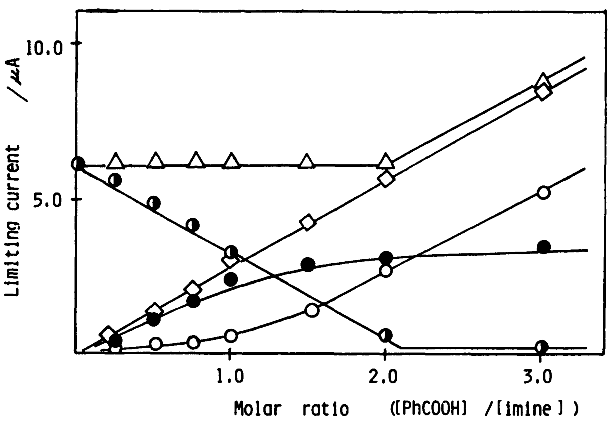


Fig. 3. Relation of the waves I through III appearing in Fig. 2.

Ordinate stands for the limiting current of: (●) wave I; (○) wave II; (◑) wave III; (◇) waves I and II; and (△) waves I, II, and III. Abscissa stands for molar ratio of benzoic acid against 1 mmol of the imine.

the scale of the abscissa indicates the molar ratio of benzoic acid to imine; $R=$[benzoic acid]/[imine].

The wave I increases monotonously until R becomes equal to 1 and then stops increasing. The final height is roughly one half of the original wave of the imine. Although the second wave (wave II) coincides with the wave of benzoic acid itself, a hasty interpretation seems to be misleading.

It should be noted that the second wave starts to grow appreciably after exceeding $R=1$ and the sum of the waves, I and II, increases exactly linearly. Moreover, the total height of waves I, II, and III remains constant until R reaches 2. In accord with the above facts, the following sequences of the reaction can be assumed, where A stands for **2** and HB is benzoic acid (Eqs. 1 through 5).

$$\mathrm{A + HB \rightleftharpoons AH^+ + B^-} \qquad (1)$$

$$\mathrm{AH^+ + e + \overset{\text{wave I}}{\rightleftharpoons} AH\cdot} \qquad (2)$$

$$\mathrm{2\,AH\cdot \longrightarrow AH_2 + A} \qquad (3)$$

$$\mathrm{AH\cdot + H^+ + e \xrightarrow{\text{wave II}} AH_2} \qquad (4)$$

$$\mathrm{A + 2e \xrightarrow{\text{wave III}} A^=} \qquad (5)$$

That the final height of the wave I is one half of the original wave height of imine suggests the process occurring in the wave I to be one-electron transfer. The follow-up chemical step (3) should occur sufficiently fast to provide wave III, where free imine is reduced by two-electron transfer. At the second wave, the primary electrode product, AH·, is further reduced as far as proton is donated from benzoic acid. The reaction of wave III is undoubtedly the reduction of free imine itself, and the wave diminishes when sufficient amount of benzoic acid is present in the solution. This mechanism agrees with the result of preparative electrolysis made at a potential of wave I. As Table 1 indicates, *N*-cyclohexylaniline (**3**) is dominated in the reaction products.

Cyclic Voltammetry of ***1***. The polarogram of **1** exhibited a wave with strong maximum (see Fig. 1). It was impossible to displace this maximum by any means. Therefore we attempted to study the effect of the electrode material on the reaction of **1**. Platinum, gold and hanging mercury electrodes were chosen and cyclic voltammetry was employed. Figure 4 indicates the results. In the case of the platinum electrode (Fig. 4a), the first cathodic wave appeared at about -0.95 V, which is very positive compared with the peaks observed with gold or mercury electrodes. Because of this, we estimate the reaction at the platinum electrode to be different from that at the mercury electrode. With platinum, the peak current showed a linear dependence on the square root of the potential sweep rate. The reaction, which is consistent with the result of preparative electrolysis is as follows (Eq. 6).

$$\mathbf{1} + \mathrm{e} \longrightarrow \mathbf{5} + 1/2\,\mathrm{H_2} \qquad (6)$$

It should be noted that only when a platinum cathode was used hydrogen evolved appreciably. This must be related to the special affinity of hydrogen on the platinum surface.

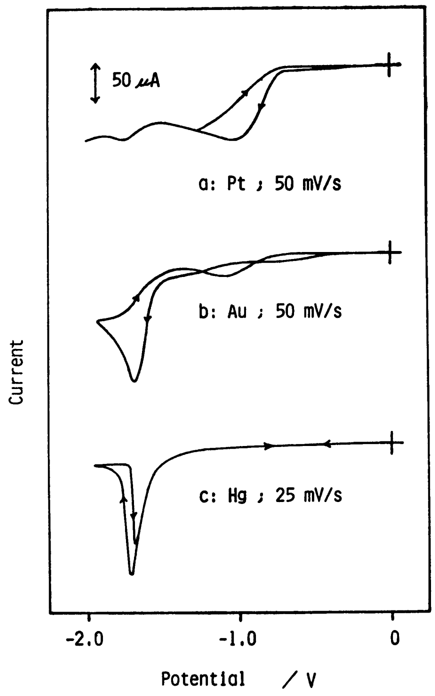


Fig. 4. Cyclic voltammograms of *N*-cyclohexylidenepyrrolidinium perchlorate in acetonitrile solution (5 mmol dm^{-3}).
Electrode is: a) platinum; b) gold; and c) hanging mercury. Sweep started from 0 V towards negative direction.

With the gold electrode (Fig. 4b), the current peak appeared at about -1.7 V. The peak current was also linear against the square root of the rate of potential sweep but did not cross the origin of the coordinate showing the contribution of some kinetic complication. The reaction at this electrode was not studied further.

At the hanging mercury drop electrode (Fig. 4c), a sharp current peak appeared at -1.72 V. The peak current, however, did not change systematically with the change of the rate of potential sweep while the peak potential value was unchanged. In addition, the current diminished rapidly after passing the peak potential, -1.72 V. When the direction of the potential sweep was reversed, the peak reappeared at a potential slightly positive to the forward sweep.

These findings lead us to assume that a surface compound was formed on the mercury surface. The surface compound would be an insulating material and the current fell steeply after it covered the mercury surface fully. A quantitative analysis of the peak current, however, failed because of the difficulty of reproducing the experiments, which was mainly caused by the poor reproducibility of the size of the hanging mercury drop.

Controlled Potential Electrolysis. N-*Cyclohexylideneaniline (**2**)*: This compound has been electrolyzed in the presence of acrylonitrile at -1.9 V, in the region of wave I, with a mercury pool electrode. In order to do this, the addition of benzoic acid was necessary as was described in the previous section. The products obtained are listed in Table 1 as a function of the molar ratio of

Table 1. Electrolysis of *N*-cyclohexylideneaniline (**2**)

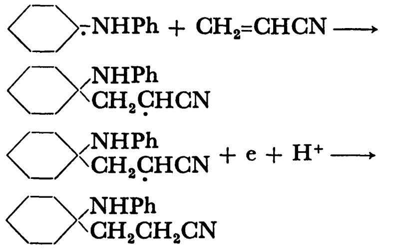
Run$^{a)}$	Additive		Electricity consumed	**2** Recovered	**3**	**4**	Conversion of **2**	Yield$^{b)}$/% of	
	Acrylonitrile (mmol)	Benzoic acid (mmol)	F mol^{-1}	(mmol)	(mmol)	(mmol)	%	**3**	**4**
1	0	2.0	2.01	0.20	0.53	—	80	66	—
2	2.0	1.0	1.05	0.56	0.02	0.30	45	4	68
3	2.0	2.0	1.89	0.39	0.04	0.44	61	6	72
4	2.0	3.0	1.91	0.12	0.10	0.53	88	12	61

a) The elcctrolyses were made for the solution (100 cm^3) containing 1 mmol of **2** at -1.90 V. b) The yields werc based on **2** unrecovered.

benzoic acid to the imine. In every case, the main product was the adduct **4** of acrylonitrile to the imine and the by-product was *N*-cyclohexylaniline (**3**). No dimeric product was observed. When the electrolysis was done in the absence of acrylonitrile but in the presence of 2 mmol of benzoic acid, the main product was *N*-cyclohexylaniline (**3**) (66%), which showed the sequence of Eqs. 2 and 3 is operating.

Isolation of both **3** and **4** was performed by the use of silica-gel TLC. The amount of unreacted imine was analyzed as its 2,4-dinitrophenylhydrazone. It is worth noting that the increasing amount of benzoic acid added improves the percentage conversion of imine to the adduct.

The reaction occurring in this system can be expressed by the following equations.



(7)

(8)

4

N-Cyclohexylidenepyrrolidinium Perchlorate (1). Referring the result of cyclic voltammetry, we electrolyzed **1** at -1.80 V in the presence of acrylonitrile with a mercury pool electrode. The results obtained are listed in Table 2. In all cases, the current reached the background level after passing about 1 F† per mole of electricity. The highest yield of the adduct **6** was 37%. No starting material remained in the electrolyzed solution. No diamine, the formation of which was suggested by Andrieux,[2] was detected. For producing **6**, an addition of methanol or 2-propanol seems to be effective.

When platinum was used as the electrode material, hydrogen evolved vigorously during the course of electrolysis. Both the GC and TLC analyses indicated that a number of compounds are produced in this case. Among these, three dominant compounds were characterized to be adiponitrile, enamine **5** (21%), and 2-(2-cyanoethyl)cyclohexanone, by comparing with the authentic samples, respectively. The amount of the adduct **6** was only 5%. These findings indicate that the primary step occurring at the platinum electrode is the reductive decomposition (Eq. 6). The enamine **5** thus produced will further undergo the follow-up chemical reaction to give a complex mixture of the products. The cyanoethylation seems to be a suitable follow-up reaction in this case.[10]

Table 2. Electrolysis of *N*-cyclohexylidenepyrrolidinium perchlorate **1** in the presence of acrylonitrile

Run$^{a)}$	Base solution	Coulometric n value	Yield$^{b)}$/% of **6**
1	MeCN	0.96	26
2	MeCN-MeOH(1%)	0.98	32
3	MeCN-MeOH(5%)	0.97	33
4	MeCN-MeOH(10%)	1.11	37
5	MeCN-MeOH(10%)$^{c)}$	1.04	31
6	MeCN-*i*-PrOH(1%)	1.09	29
7	MeCN-*i*-PrOH(5%)	1.04	31
8	MeCN-*i*-PrOH(10%)	1.04	31

a) The electrolyses were made for the solution (100 cm^3) containing 1 mmol of **1** and 3 mmol of acryronitrile at -1.80 V. b) The yields were based on the amount of **1** used. c) Ten millimoles of acrylonitrile was used in this case.

In contrast to the platinum electrode, mercury pool electrode seems to be favored for producing **6**. This may be correlated to the difference in the primary intermediates between the two electrode systems. The formation of organomercury compounds seems plausible but their detection failed.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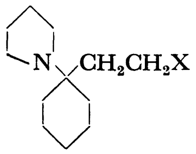
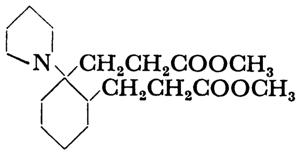


6 X = CN
7 X = COOCH$_3$



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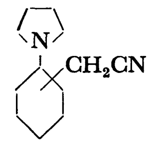

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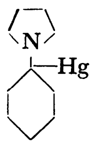

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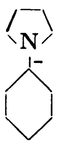
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When the electrolysis was carried out in the absence of acrylonitrile, the product was mostly a polymeric substance together with a small amount of **9**, which

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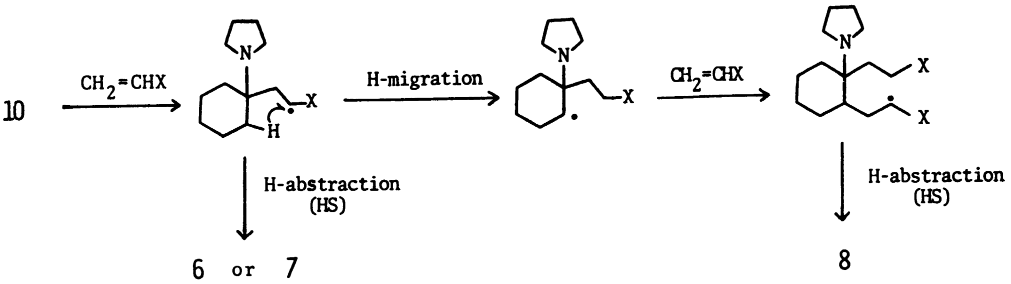
† 1 F≈96480 C.



(X= -CN or -COOCH$_3$, HS= solvent)

Scheme 1.

might be derived from **10** by a radical mechanism.

When methyl acrylate was used in place of acrylonitrile, **8** was produced in 30% yield in addition to **7** (34%).

In order to account for the formation of **6** through **9**, it seems reasonable to assume the formation of the neutral radical **10** as the primary intermediate on the mercury surface. The possibility of forming either organomercury compound **11** or carbanion **12** seems unlikely in the following reasons. 1) When methyl 3-bromopropionate was used in place of methyl acrylate, the yield of **7** and **8** was less than 3%. This means that the primary species has a poor SN_2-displacement ability. 2) No organomercury compound was detected in the electrolyzed solution.

The radical **10** will react with olefins, such as acrylonitrile or methyl acrylate to form **7**, **8** or **9** as is expressed in Scheme 1. The presence of certain co-solvents such as alcohols inhibits undesirable radical polymerization.

Conclusion

The tetrasubstituted iminium salt **1** is reduced more easily than corresponding carbonyl compounds. It forms a neutral radical when it is reduced cathodically at a mercury surface. The radical thus formed is favored to polymerize rather than to dimerize. The presence of electrophilic olefins such as acrylonitrile gives rise to the formation of radical adduct as the intermediate, which gives the final products of **6** through **8**. The latter reaction is not highly selective and the polymerization always accompanies. The addition of a hydrogen donor such as methanol is effective in inhibiting the polymerization and increasing the yield of adducts.

The compound **2** is easily reduced electrolytically when it is protonated. When acrylonitrile is present in the solution, the adduct **4** is formed in more than 70% yield.

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