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ELECTROCHEMICAL DISK GENERATION AND RING IDENTIFICATION OF CARBANIONS FROM ORGANOMERCURIALS IN ACETONITRILE *

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Summary

A rotating disk—ring electrode was used for study of a series of organomercury compounds R_2Hg, where R = CN, $CF(NO_2)_2$, C_6F_5, PhC≡C, p-$NO_2C_6H_4OC$≡C, $PhSCH_2C$≡C, $PhCOCH_2$, CH_2CN, CCl_2=CCl, 2-phenyl-*o*-carboranyl. Reduction of these compounds at a Pt-disk in acetonitrile is a two-electron process and results in generation of the carbanion R^-. The carbanions generated at the disk interact with the solvent during their convective diffusion to the ring electrode where there may be oxidized. The main reaction in solution, shown using chromatography—mass spectrometry techniques, is acid—base interaction of carbanions with the solvent acetonitrile, which acts as a Brönsted acid. Reaching the ring, the carbanions may be oxidized at anodic potentials of the ring; oxidation potentials depend significantly on carbanion structure (e.g. +0.28 V (vs. SCE), for $PhC≡C^-$ and +2.20 V for CN^-). It is shown that pK_a value of the carbanions do not correlate with the oxidation potentials, however, a linear correlation is observed between pK_a values and a special parameter called the efficiency coefficient.

Introduction

Experimental study of carbanion stability and reactivity is often a rather difficult problem because most of the carbanions (with exception of relatively stable ones such as Cp^-, X_3C^-, X_2CH^-, where X = NO_2, CN, COR, etc.) react readily with electrophiles and electrophilic sites of many molecules, with atmospheric oxygen and moisture, and, besides that, may undergo transformations that result in carbanion stabilization by intramolecular rearrangements or by elimination of relatively stable negatively charged species (e.g., $ClCH=CH^- \rightarrow CH≡CH + Cl^-$). Therefore, the important task arises to find methods which make possible the generation of carbanions in a given system from some stable precursors by some standard mode, and then, using some indicator device, to

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* Dedicated to Professor A.N. Nesmeyanov on the occasion of his 80th birthday.

study processes that transfer the carbanion-containing system into the stable state.

In this work we wish to report the application of a rotating disk—ring electrode for the generation and electrochemical oxidation of carbanions. The rotating disk—ring electrode was first described by Frumkin and Nekrasov in 1959 [1]. The ring allows the detection and identification of stable and unstable species which arise at the disk, if these species are electrochemically active. This method is widely adopted to investigate, first of all, the kinetics and mechanism of complex electrochemical as well as homogeneous chemical reactions in which one of the reagents is a species that is electrochemically generated at the disk (see ref. 2 for a review).

In the present work the rotating disk—ring electrode has been used for the study of carbanions in which some electrochemical reaction at the disk was to result in generation of carbanions. As an example, one might use electrochemical reduction of organic halides,

$$\mathrm{R{-}X} + 2\,e^- \rightarrow \mathrm{R}^- + \mathrm{X}^- \ (\mathrm{X} = \text{halogen})$$

or electrochemical reduction of organomercurials,

$$\mathrm{R_2Hg} + 2\,e^- \rightarrow 2\,\mathrm{R}^- + \mathrm{Hg} \qquad (1)$$

or other reactions resulting in formation of carbanions. We used the reduction of organomercury compounds (eq. 1), which is attractive because only carbanions R^- arise in solution in this reaction, whereas in the organic halide reduction besides R^-, halide ions X^- arise which may also be oxidized at the ring * and, therefore, a more complex picture would need to be interpreted.

Electrode

We used the electrode with a platinum disk and platinum ring. Schematic representation of the apparatus is given in Fig. 1 and its detailed description in the Experimental section. The disk—ring electrode had the following geometrical parameters: disk radius r_{10} 2.57 mm, inner ring radius r_{20} 2.65 mm, outer ring radius r_{30} 3.68 mm. For such an electrode, the theoretical value of the efficiency coefficient, N, calculated with formula [4]:

$$N \approx [(r_{30}/r_{10})^3 - (r_{20}/r_{10})^3]^{2/3}$$

is equal to 0.46 ± 0.03, taking into account the radii measurement errors. The efficiency coefficient is an important characteristic of the electrode; N is independent of experimental conditions, it depends only on the geometry of the electrode. The physical sense of the efficiency coefficient is shown by formula 2

$$N = \frac{n_\mathrm{D} i_\mathrm{R}}{n_\mathrm{R} i_\mathrm{D}} \qquad (2)$$

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* Cl^-, Br^- and I^- anions may be oxidized at platinum electrode in acetonitrile; they shows two anodic waves on polarograms [3].

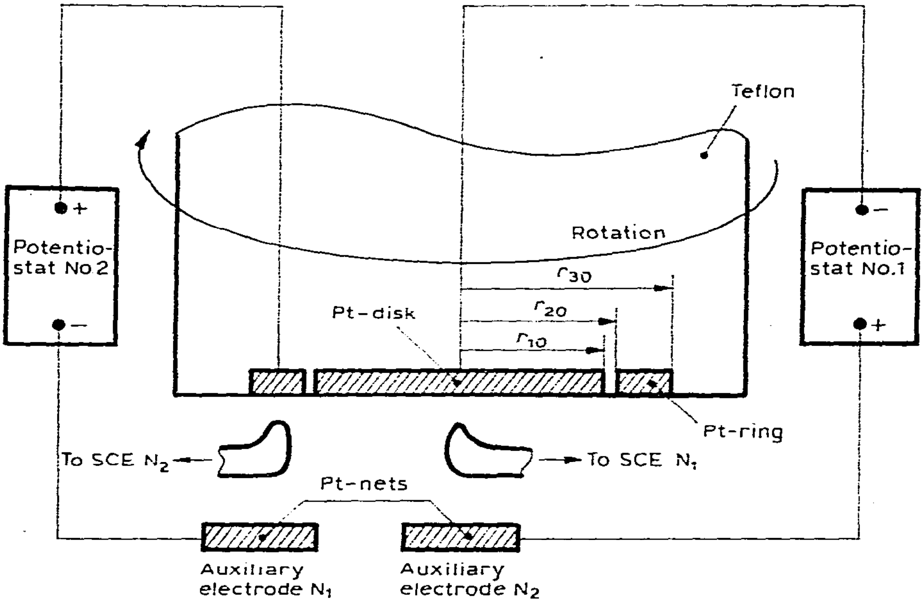


Fig. 1. Schematic representation of rotating disk—ring electrode. N_1 = No. 1; N_2 = No. 2.

where i_R and i_D are the limiting currents at the ring and at the disk, and n_D and n_R the numbers of electrons which take part in the electrochemical processes at the disk and at the ring, respectively. Thus, if a stable compound is formed at the disk and this compound is oxidizable or reducible at the ring, the efficiency coefficient shows what proportion of the total amount of the reaction product reaches the ring electrode surface (the rest of the product dissolves). If the disk reaction product is insufficiently stable, the observed value of the efficiency coefficient will be lowered as compared with the theoretical one.

Experimental determination of the efficiency coefficient with the ferrocene/ferricinum pair in aqueous alcohol, acetonitrile or dimethylsulphoxide gives $N = 0.43$, which is in good agreement with the value calculated from geometrical parameters of the electrode.

Reduction of organomercury compounds results in mercury metal which deposits on the platinum disk. At the end of the run, one can see helix-shaped figures on the disk which are formed by deposited mercury. Thus, excluding the initial run, the reduction of organomercury compounds occurs in fact at mercury not at platinum. Because of mercury deposition the only species which originally transfer from the disk surface are carbanions R^- arising from reaction 1.

Results

sp-Carbanions

Electrochemical reduction of mercurated compounds with a triple bond results in carbanions in which an orbital bearing the negative charge has roughly *sp*-hybridization. Such carbanions are more stable when compared with the corresponding sp^2- or sp^3-carbanions, due to the high percentage of *s*-character of the non-bonding orbital. We studied the behaviour of four compounds of (sp-R)$_2$Hg type: Hg(CN)$_2$, (p-NO$_2$C$_6$H$_4$OC≡C)$_2$Hg, (PhSCH$_2$C≡C)$_2$Hg, and (PhC≡C)$_2$Hg. The solvent was acetonitrile contaminated with 0.03% water (Fischer titration), the supporting electrolyte was 0.05 M Bu$_4$NBF$_4$. The results obtained are given in Table 1 and in Figs. 2—5.

Mercury (II) cyanide. Polarisation curves for Hg(CN)$_2$ are given in Fig. 2a. The compound may be reduced in acetonitrile at $E_{1/2}$ −0.45 V (SCE) at the disk which results in a clearly expressed wave. If the electrolysis at the disk is carried out at potentials of the limiting current, e.g. at E_D −1.6 V, one may register an anodic wave at the ring, which has $E_{1/2}$ +2.20 V. Under the same conditions, oxidation of KCN at the ring gives also one anodic wave which has $E_{1/2}$ +2.20 V. Thus, the anodic wave, which arises at the ring in the Hg(CN)$_2$ solution when the disk is working, is due to oxidation of carbanions CN$^-$. The yield of CN$^-$ anions is independent of the speed of electrode rotation, which means that CN$^-$ anions are stable species in acetonitrile. The observed coefficient N is equal to 0.43 (Table 1) at rotation speeds from 800 to 3960 rpm which shows that $n_D = n_R$ (eq. 2), i.e., the cyanide ion oxidation is a one-electron process. The electrochemical reduction of CN$^-$ is a process of oxidative dimerization and, apparently, results in dicyane production (cf. ref. 49).

Oxidative dimerization is a common characteristic of oxidation of spatially non-ridged carbanions. It was observed in the electrochemical oxidation of anions

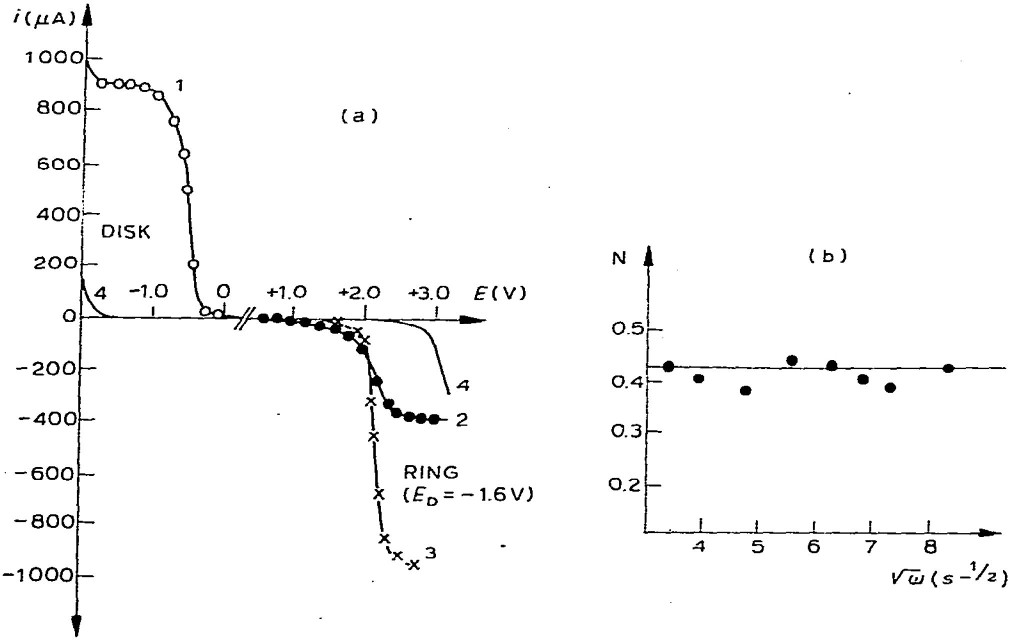


Fig. 2. (a) Polarization curves for reduction of Hg(CN)$_2$ at the disk (curve 1), oxidation of CN$^-$ anions, which are formed from Hg(CN)$_2$ at the disk (E_D −1.6 V), at the ring (curve 2) and KCN oxidation (curve 3). CH$_3$CN, 0.05 M Bu$_4$NBF$_4$, 25°C. Concentiations of R$_2$Hg and KCN, 2 × 10^{-3} M; ω 2080 rpm Curve 4 for 0.05 M Bu$_4$NBF$_4$ in CH$_3$CN. (b) Experimental dependence of the efficiency coefficient on rotation speed for Hg(CN)$_2$.

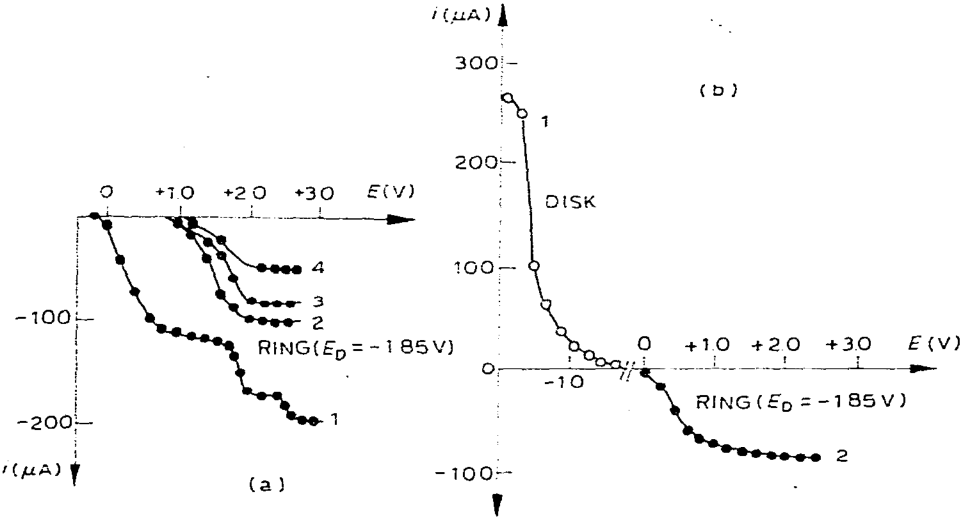


Fig. 3. (a) Anodic polarization curves for $(PhC{\equiv}C)_2Hg$ (1×10^{-3} M) reduction products at the ring electrode in $CH_3CN/0.05$ M Bu_4NBF_4. Disk potential E_D —1.85 V, disk current 495 mA; ω 2080 rpm. Contents of water in solvent: (1) 0.03, (2) 3.5, (3) 4.7, (4) 21%. (b) Polarization curves for $(PhC{\equiv}C)_2Hg$ reduction at the disk (curve 1) and oxydation of $PhC{\equiv}C^-$ carbanions at the ring (curve 2) in dimethoxyethane: 0.05 M Bu_4NBF_4, 20°C, ω 2080 rpm.

of β-dicarbonyl compounds [5], nitroalkanes [6] and substituted cyclopentadienes and fluorenes [7,8].

Bis(phenylethynyl)mercury. For $(PhC{\equiv}C)_2Hg$ the anodic curve for oxidation of reduction products coming to the ring from the disk electrode is more complex than that for $Hg(CN)_2$. With the disk not working, no electrochemical process is observed at the ring and the polarisation curve is the same as for the unchanged electrolyte solution, without R_2Hg (Fig. 2a). With the disk working at E_D —1.85 V, three anodic waves are observed with $E_{1/2}$ 0.28, 2.00 and 2.55 V (Fig. 3a, Table 1). The plot of i_R against electrode rotation speed is a straight line passing through the origin (Fig. 4a). The yields of current at the ring (YCR)

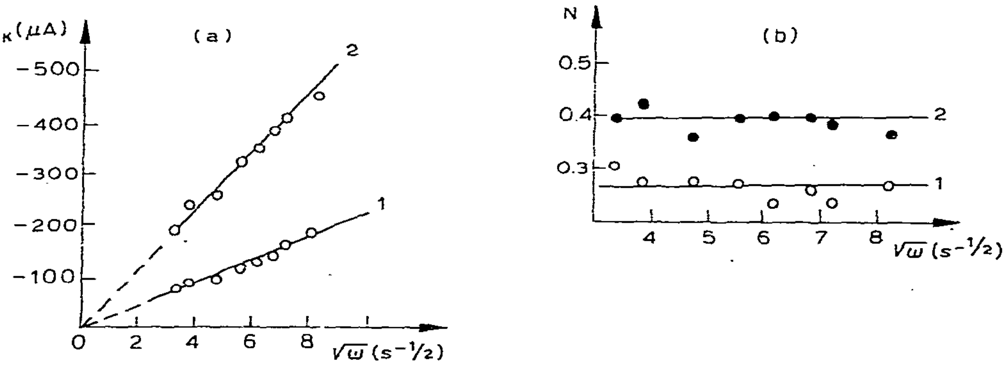


Fig. 4. (a) Dependence of i_R on electrode rotation speed for $(PhC{\equiv}C)_2$ Hg. E_D —1.85 V, E_R +0.7 (curve 1) and +2.6 V (curve 2) in CH_3CN with 0.05 M Bu_4NBF_4. (b) Dependence of the efficiency coefficients N_1 (curve 1) and N_2 (curve 2) on electrode rotation speed for $(PhC{\equiv}C)_2Hg$.

TABLE 1

ELECTROCHEMICAL PARAMETERS FOR $(sp\text{-R})_2$Hg AT ROTATING DISK–RING ELECTRODE IN CH_3CN

0.05 *M* Bu_4NBF_4, 25°C ω 2080 rpm; $E_{1/2}$ vs. SCE.

R	Disk		Ring (E_D −1.6 V)			N_1	N_2
	$E_{1/2}$ (R_2Hg) (V)	i_D (μA)	$E_{1/2}$ (R^-)[c] (V)	Other anodic waves $E_{1/2}$ (V)	Total anodic current i_R (μA)		
CN (2×10^{-3} *M*)	−0.45	870	2.20	—	370[d]	0.43	—
p-$NO_2C_6H_4OC{\equiv}C$[a, b]	−1.08	330	1.25	2.10	145[e]	0.40	0.43
$PhSCH_2C{\equiv}C$[a] (2×10^{-3} *M*)	−1.14	730	0.60	1.70; 2.15	295[e]	0.22	0.42
$PhC{\equiv}C$ (1×10^{-3} *M*)	−1.42	495	0.28	2.00; 2.55	200[g,f]	0.27	0.40

[a] These compounds were prepared by A.Kh. Filippova and K.G. Naumova in Irkutsk Institute of Organic Chemistry. [b] This compound dissolves sparingly in CH_3CN and therefore the saturated solution was used. [c] See the text. [d] At ring potential E_R 2.6 V. [e] At E_R 2.4 V. [f] Disk potential E_D −1.85 V. [g] At E_R 2.7 V.

at the limiting current of the first anodic wave (N_1) and at that of the most anodic (third) wave (N_2) were independent of rotation speed (Fig. 4b). Thus, because the cathodic current at the disk has a diffusion limitation, the anodic waves are also diffusion-controlled.

Multiplicity of the anodic curve may be explained, if we assume that disk-generated carbanions $PhC{\equiv}C^-$ are less stable than CN^- and therefore can react with solvent molecules. This results in a number of products which are oxidizable at the ring. That $PhC{\equiv}C^-$ is less stable than CN^- is shown from the pK_a values of the corresponding CH acids: in DMSO pK_a (HCN) = 12.9 [9]; pK_a ($PhC{\equiv}CH$) = 28.8 [10], 29.2 [11], 26.5 [12], or 22.6 [13]. Thus, $PhC{\equiv}C^-$ is by 10—16 powers of ten stronger than CN^- as a base, and apparently also as a nucleophile.

In contrast to the results in acetonitrile solutions, in dimethoxyethane (DME) the only anodic wave was observed with $E_{1/2}$ 0.30 V and YCR $N = 0.34$ (Fig. 3b). Because carbanions $PhC{\equiv}C^-$ are stable in DME [14], one may suppose that the anodic wave at the ring in DME arises from oxidation of these carbanions. $E_{1/2}$ of the anodic wave in DME is close to $E_{1/2}$ of the first, least anodic wave in CH_3CN, which therefore corresponds apparently to oxidation of the carbanion $PhC{\equiv}C^-$. The second and the third anodic waves are due probably to oxidation of the products of reaction of $PhC{\equiv}C^-$ anions with the solvent. Acetonitrile may react with carbanions in different ways: acid—base reaction (eq. 3) and/or condensation at CN group (eq. 4) are the most probable. It should be

$$R^- + CH_3CN \rightarrow RH + CH_2CN^- \qquad (3)$$

$$R^- + CH_3CN \rightarrow CH_3C(R){=}N^- \qquad (4)$$

noted that both anions to the right in eqs. 3 and 4 are oxidizable at the ring electrode.

TABLE 2

RESULTS OF CHROMATOGRAPHIC—MASS SPECTROMETRIC ANALYSIS OF ELECTROLYSIS PRODUCTS OF $(PhC{\equiv}C)_2Hg$ AND $(C_6F_5)_2Hg$ IN CH_3CN. Figures in parentheses correspond to compounds in Scheme 1.

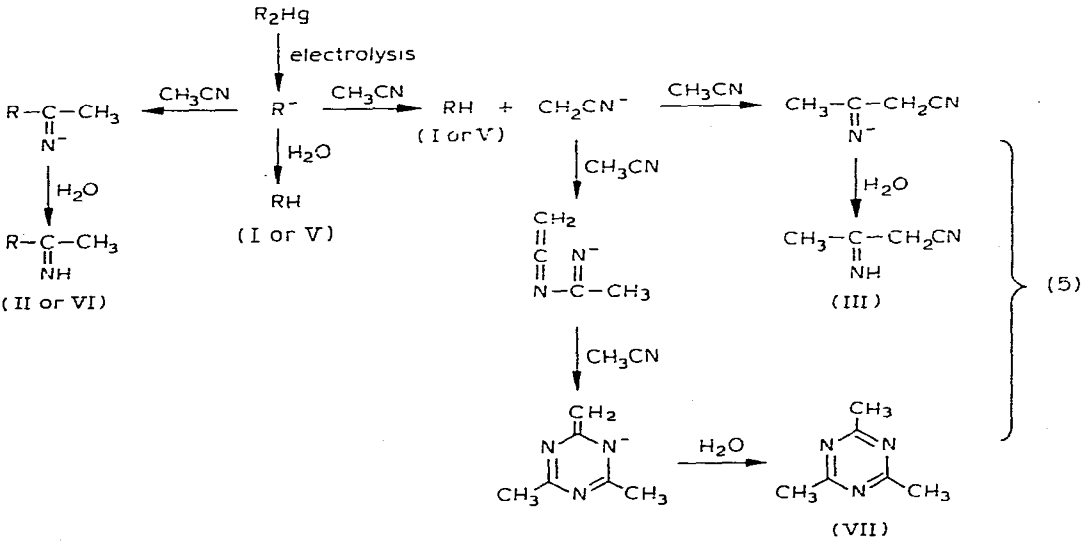
Initial compound	Electrolysis product	Yield (%)
$(PhC{\equiv}C)_2Hg$	$PhC{\equiv}CH$(I)	31
	$PhC{\equiv}CC({=}NH)CH_3$ (II)	4
	2,4,6-Trimethyltriazine (VII) [a]	12
	$PhCOCH_3$ [b] + PhCHO	40
	Non-identified products [c]	13
$(C_6F_5)_2Hg$	C_6F_5H (V)	44
	$C_6F_5C({=}NH)CH_3$ (VI)	5
	$CH_3C({=}NH(CH_2CN$ [d] (III)	7
	$CH_3CH_2(NH_2)CH_2CH_2NH_2$ [e] (IV)	
	Other products (butylene, tributylamine, and unidentified)	44

[a] The cyclotrimerization product of acetonitrile. [b] The hydratation product of phenylacetylene. [c] See experimental. [d] The condensation product of two molecules of acetonitrile. [e] The reduction product of compound III; see text.

In order to ascertain the composition of the reduction product, the electrolysis of $(PhC{\equiv}C)_2Hg$ was carried out at a controlled potential with a mercury cathode. The electrolysis products were identified using chromatography—mass spectrometry techniques. The results are given in Table 2 together with the data for $(C_6F_5)_2Hg$ (vide infra). As follows from Table 2, carbanions $PhC{\equiv}C^-$ (and $C_6F_5^-$) are removed in solution via reactions 3 and 4. It is noticable that there is much more hydrocarbon $PhC{\equiv}CH$ (and C_6F_5H) than imine II (and VI) (see Table 2 and eq. 5) in the mixture of electrolysis products. The ratio of hydrocarbon to imine $RH/RC(=NH)CH_3$, is 8/1 for $PhC{\equiv}C^-$ and 9/1 for $C_6F_5^-$. It means that the acid—base interaction of carbanions with CH_3CN is the main carbanion stabilization reaction in our system, i.e., reaction 3 is faster than reaction 4. Abstraction of a proton from the solvent molecule (reaction 3) results in acetonitrile anions, CH_2CN^-, which may condense with one or two CH_3CN molecules to give compounds III and VII (Table 2; eq. 5) *. The self-condensation of acetonitrile molecules has been shown by Becker and Fritz [19] in the reaction of acetonitrile with sodium metal deposited on platinum, via electrolysis of $NaBF_4$ in CH_3CN at −3.0 V.

Thus, Scheme 1 may explain the structures of the electrolysis products of R_2Hg in acetonitrile.

SCHEME 1



All nitrogen anions in eq. 5 can be oxidized at the platinum anode in acetonitrile and, if reactions resulting in their formation are sufficiently fast so that they may proceed within the time that is necessary for the transfer of reduction products from the disk to the ring, the second and third waves might be due to oxidation of the N-anions.

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* We used the solvent with 0.03% (1.5×10^{-2} M) water content therefore H_2O might also be a proton donor molecule. However, all reactions discussed, occur in the electrical double layer where, owing to the hydrophobic properties of unaltered electrolyte, the water content is much less than in the bulk of the solution. See refs. 15—18 for an introduction to this problem.

The YCR value on the plateau of the limiting current of the most anodic wave (N_2 0.40, Table 1) corresponds within experimental error, to the electrode efficiency coefficient as determined for the ferrocene/ferricinium pair. This means that mass balance is maintained; as many coulombs are consumed for the reduction of $(PhC{\equiv}C)_2Hg$ at the disk as are released in the ring oxidation of the disk reduction products.

Further evidence that the first wave at the ring is due to oxidation of carbanions $PhC{\equiv}C^-$ comes from a study of the effect on the polarization curve of small quantities of water. When a small amount (3.5 wt.%) of water was added to a 10^{-3} *M* solution of $(PhC{\equiv}C)_2Hg$ in CH_3CN, the first anodic wave immediately disappeared and simultaneously the anodic polarization curve changed its initial form. Subsequent additions of water results in slower changes of the polarisation picture (Fig. 3a). Apparently, the disappearance of the first wave is due to a fast proton abstraction from water by $PhC{\equiv}C^-$ anion at the disk and thus it is the less easily oxidizable phenylacetylene molecules, not $PhC{\equiv}C^-$ anions, that now convect to the ring electrode surface. If the disappearance of the first wave is due to removal of $PhC{\equiv}C^-$ anions by acid—base reaction with water, then hydroxide ions should arise near the electrode which might be rather more easily oxidized ($E_{1/2}$ = +0.65 V/SCE) in CH_3CN (Fig. 5). However, as with the analogous situation with $C_6F_5^-$ (vide infra), oxidation of OH^- ions was not observed by us in the disk—ring study of $(PhC{\equiv}C)_2Hg$ in aqueous acetonitrile (Fig. 3). Why this is so, is not clear. A possible explanation of this fact is the following. In DMSO $pK_a(H_2O) = 27.5$ [20] and $pK_a(PhC{\equiv}CH)$ = 23 to 29 [10—13], i.e., OH^- and $PhC{\equiv}C^-$ are both strong bases in dipolar aprotic solvents. It is possible that OH^- reacts with the solvent molecules CH_3CN much faster than $PhC{\equiv}C^-$, because proton transfer to O-bases is often a faster process than to C-bases with the same pK_a's [9,21]. As a result, the system OH^-/CH_3CN transfers to H_2O/CH_2CN^- while the system $PhC{\equiv}C^-/CH_3CN$ cannot transfer completely to $PhC{\equiv}CH/CH_2CN^-$ in the time that is necessary for transport of species from the disk to the ring.

Bis(p-nitrophenoxyethynyl)mercury and bis(phenylthiomethylethynyl)-mercury. Polarization curves for $(p\text{-}NO_2C_6H_4OC{\equiv}C)_2Hg$ and $(PhSCH_2C{\equiv}C)_2Hg$

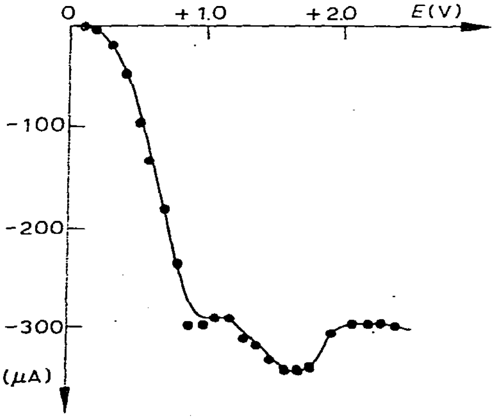


Fig. 5. Anodic polarization curve for KOH oxidation at the ring in CH_3CN/H_2O mixture (34/1 v/v). KOH concentration is 2×10^{-3} *M*. 0.05 *M* Bu_4NBF_4. ω 2080 rpm.

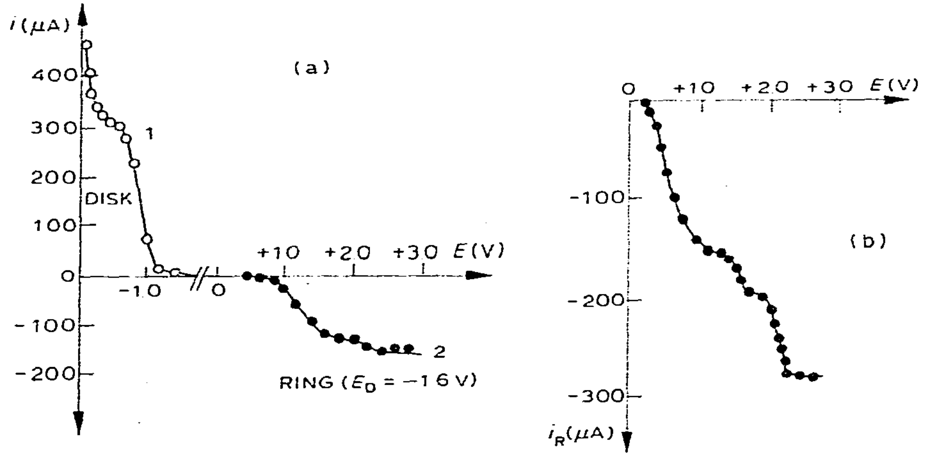


Fig. 6. (a) Polarization curves for $(p\text{-}NO_2C_6H_4OC{\equiv}C)_2Hg$ (saturated solution) reduction at the disk (curve 1) and oxidation of the reduction products at the ring (curve 2): CH_3CN, 0.05 M $BuNBF_4$, ω 2080 rpm. (b) Anodic polarization curves for reduction products of $(PhSCH_2C{\equiv}C)_2Hg$ (2×10^{-3} M) under the same conditions. E_D −1.6 V, disk current 730 μA.

are given in Fig. 6. The anodic curve for the first compound shows two waves with $E_{1/2}$ 1.25 V (N_1 = 0.40) and 2.10 V (N_2 0.43) (Table 1). The high value of N_1 allows us to ascribe the first wave to oxidation of $p\text{-}NO_2C_6H_4OC{\equiv}C^-$ carbanions because such carbanions should be sufficiently stable and have little ability to react with CH_3CN.

Phenylthiomethylethynylic anion, $PhSCH_2C{\equiv}C^-$, is of course much less stable than $p\text{-}NO_2C_6H_4OC{\equiv}C^-$, therefore, it will readily react with the solvent, As a result, a relatively low N_1 value and three anodic waves were observed (Table 1).

The limiting currents of all the anodic waves in Figs. 6a, b are linearly dependent on $\sqrt{\omega}$, the straight line passing through the origin. It means that the waves are not kinetic. The YCR's N_1 and N_2 were practically independent of the electrode rotation speed.

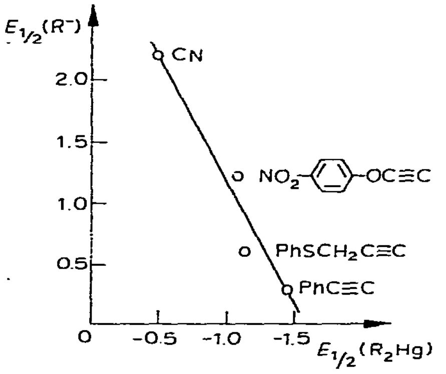


Fig. 7. Correlation between oxidation potentials of *sp*-carbanions R^- and reduction potentials of the respective organomercury compounds, R_2Hg.

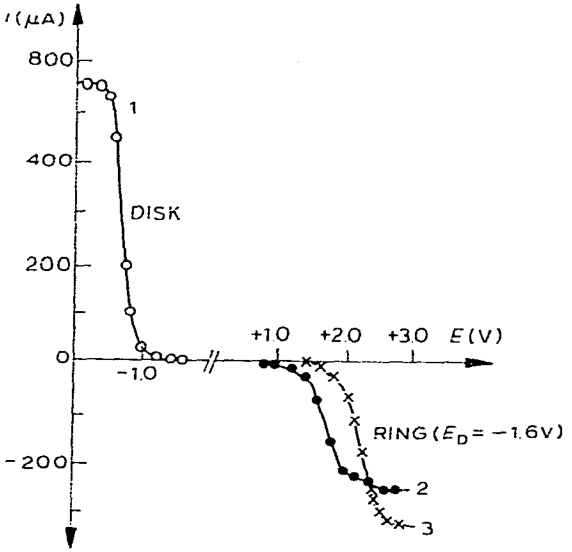


Fig. 8. Polarization curves for $(ClC{=}CCl)_2Hg$ reduction at the disk (1) and oxidation of the reduction product at the ring (2) in $CH_3CN/0.05$ *M* Bu_4NBF_4. Concentration of R_2Hg 2×10^{-3} *M*; ω 2080 rpm. Curve 3, oxidation of chloride ion (LiCl, 2×10^{-3} *M*) under the same conditions.

In order to ascertain what wave from the three anodic ones which are registered at the ring when $(PhSCH_2C{\equiv}C)_2Hg$ is reduced at the disk, is due to oxidation of $PhSCH_2C{\equiv}C^-$ carbanions, the following approach may be used. It has been shown [22] that there is a linear dependence between the susceptibilities of organomercury compounds R_2Hg to electrochemical reduction and the stabilities of the corresponding carbanions R^-:

$$\Delta(\alpha E_{1/2}) = \rho \Delta pK_a$$

where α is electrochemical transfer coefficient, $E_{1/2}$ is the half-wave potential of R_2Hg, pK_a is the acidity of RH and ρ is proportionality constant. One may

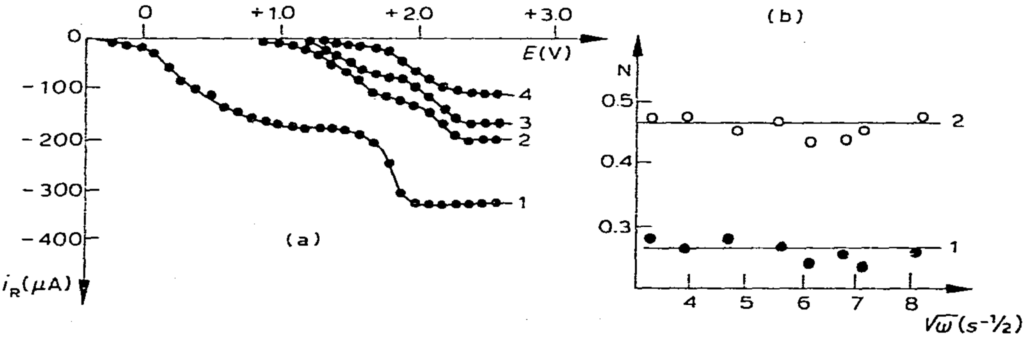


Fig. 9. (a) Anodic polarisation curves for reduction products of $(C_6F_5)_2Hg$ (2×10^{-3} *M*) at the ring electrode in $CH_3CN/0.05$ *M* Bu_4NBF_4. Disk potential E_D −1.6 V, disk current 810 μA, contents of water in solvent: (1) 0.03, (2) 3.5, (3) 7, (4) 21%. (b) Dependence of the efficiency coefficients of the first (1) and the second (2) anodic waves on rotation speed for $(C_6F_5)_2Hg$.

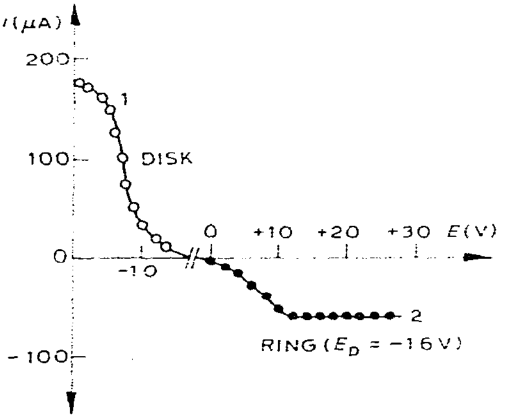


Fig. 10. Polarization curves for $(C_6F_5)_2Hg$ reduction at the disk (1) and $C_6F_5^-$ anion oxidation at the ring (2: E_D −1.6 V) in dimethoxyethane with 0.05 *M* Bu_4NBF_4. Concentration of R_2Hg 1×10^{-3} *M*, ω 2080 rpm.

also propose that in a series of similar carbanions a more stable carbanion will be oxidized more readily than a less stable one. If so, and if the following limitations are valid: (1) transfer coefficients, α, are approximately the same for all compounds R_2Hg in a given series of structurally similar organomercury compounds and (2) dimerization constants are approximately the same for all radicals $R^{\cdot}$ (which arise on oxidation of the respective carbanions R^-) in the given structural series, then there should be a correlation between reduction potentials of R_2Hg and oxidation potentials of R^-. The plot in Fig. 7 shows that such a correlation for four *sp*-carbanions is, indeed, linear. The point for $PhSCH_2C{\equiv}C^-$ lies near the correlation line, if $PhSCH_2C{\equiv}C^-$ anion has $E_{1/2}$ = 0.6 V. Thus, the first anodic wave is due to oxidation of this carbanion.

*sp*²-*Carbanions*

Bis(trichlorovinyl)- and bis(pentafluorophenyl)-mercury were chosen as precursors of sp^2-carbanions. The corresponding unsubstituted compounds, divinyl- and diphenyl-mercury, were found to be inconvenient for studying with disk—ring electrode techniques because they may be reduced only at the

TABLE 3

ELECTROCHEMICAL PARAMETERS FOR $(sp^2\text{-R})_2Hg$ AT ROTATING DISK—RING ELECTRODE IN CH_3CN

(0.05 *M* Bu_4NBF_4, 25°C: ω 2080 rpm, concentration of R_2Hg 2×10^{-3} *M*, $E_{1/2}$ vs SCE).

R	Disk		Ring (E_D −1.6 V)			N_1	N_2
	$E_{1/2}$ (R_2Hg) (V)	i_D (μA)	$E_{1/2}$ (R^-) V	Other anodic waves, $E_{1/2}$ (V)	Total anodic current, i_R (μA)		
$Cl_2C{=}CCl$	−1.33	700	1.72	2.15	260	0.34	0.37
C_6F_5	−1.26	810	0.38	1.81	335	0.25	0.46

very negative potentials (ca. −2.5 V at pure mercury [23]) and, therefore, do not give any cathodic wave on the platinum disk.

Experimental data are given in Table 3 and Figs. 8—10.

Bis(trichlorovinyl)mercury. The two pK_a values for trichloroethylene quoted in the literature are 18 [23] and 25 [24]. The first figure was obtained in the polarographical pK_a scale where $pK_a(PHC{\equiv}CH) = 18.5$, the second one in cyclohexylamine where $pK_a(PhC{\equiv}CH) = 23.2$ [25].

Thus, it is inconclusive as to which anion is more stable (relative to their CH acids), $Cl_2C{=}CCl^-$ or $PhC{\equiv}C^-$. Electrolysis of $(CCl_2{=}CCl)_2Hg$ at the disk results in two waves registered at the ring, the second wave being far less than the first. For the first wave $E_{1/2} = 1.72$ V and for the second $E_{1/2} = 2.15$.

One more path of trichloroethylene anion stabilization may be proposed which involves elimination of chloride ion and formation of dichloroacetylene:

$$CCl_2{=}CCl^- \rightarrow Cl^- + CCl{\equiv}CCl \qquad (6)$$

The chloride ion is capable of oxidation at Pt in CH_3CN. As is shown in Fig. 8, the oxidation wave for LiCl has $E_{1/2} = 2.17$ V, that is approximately the same as $E_{1/2}$ of the second anodic wave of the reduction product of bis(trichlorovinyl)-mercury. Chromatographic—mass spectrometric analysis of the electrolysis product of $(CCl_2{=}CCl)_2Hg$ in CH_3CN at the mercury cathode shows that the reaction mixture contains only $CCl_2{=}CClH$ and $(CCl_2{=}CCl)Hg$ among chlorine-containing compounds. It means that reaction 6, if it occurs, is slow.

Also, the mass spectrum shows the absence of a molecular ion m/e 82 and/or 123 (dimer and trimer of acetonitrile, III and VII, eq. 5) as well as a compound of the type II and/or VI (eq. 5). The conclusion may be drawn that carbanion $CCl_2{=}CCl^-$ is relatively stable in acetonitrile, i.e., reaction 3 may be unimportant or negligible. It is noteworthy that the height of the second anodic wave in Fig. 8 is 11 times less than the height of the first one.

Bis(pentafluorophenyl)mercury. Pentafluorobenzene has a reported pK_a = 23 [22]; pK_a (C_6F_5H) = 24.2 or 25.8 [25]. Electrolysis of $(C_6F_5)_2Hg$ at the disk results in the appearance of two anodic waves at the ring (Fig. 9a) with $E_{1/2}$ 0.38 and 1.81 V (Table 3). In DME, as for $(PhC{\equiv}C)_2Hg$, the anodic curve shows only one wave (Fig. 10) with $E_{1/2} = 0.52$ V and $N = 0.34$ which probably corresponds to a one-electron oxidation of the $C_6F_5^-$ anion:

$$2\ C_6F_5^- - 2\,e^- \rightarrow 2\ C_6F_5^{\bullet} \rightarrow C_6F_5{-}C_6F_5$$

Taking into account that $E_{1/2}$ in DME is close to the $E_{1/2}$ of the first wave in CH_3CN, the latter may be ascribed to oxidation of carbanion, $C_6F_5^-$. This was confirmed by adding one drop of water (3.5 wt.%) to a solution of $(C_6F_5)_2$-Hg in CN_3CN which resulted in disappearance of the first anodic wave (Fig. 9a).

Electrolysis at controlled potential on the plateau of the limiting current of the reduction wave of $(C_6F_5)_2Hg$ (Table 2) and the chromatography—mass spectrometric analysis showed that the main C_6F_5-containing product is C_6F_5H, i.e., $C_6F_5^-$ reacts with the solvent mainly via the acid—base interaction. The ratio of the yields $C_6F_5H/C_6F_5C({=}NH)CH_3$ is 9/1.

It was found that N_1 and N_2 are practically independent of electrode rotation speed (Fig. 9b).

Probably the second anodic wave is due to oxidation of the products which appear on interaction of $C_6F_5^-$ anions with the solvent. In the system $(C_6F_5)_2Hg$ (10^{-3} *M*)/CH_3CN/Bu_4NBF_4 (0.05 *M*), after the disk had been working for several minutes at —1.6 V and the ring was switched off and then the disk was switched off and the ring was switched on at +2.0 V, one might observe an increase in the rest current. If the disk had been switched on (with the ring switched off) for an hour, the increase in the rest current (disk switched off, ring working) was 100—150 mA at +2.0 V. Moreover, the clearly expressed wave might be observed in those potential regions where the most anodic wave is in Fig. 9a. Obviously, this wave is a wave of the carbanion—solvent interaction products. With the appearance and the increase of the anodic wave at the ring the limiting cathodic current at the disk simultaneously increased. Thus, when the disk had been working at —1.6 V for an hour, the limiting current of $(C_6F_5)_2Hg$ reduction increased from 650 to 810 mA. This is obviously due to the fact that the carbanion—solvent reaction products are not only able to be oxidized but also to be reduced. Identification of 1,3-butylenediamine (compound IV in Table 2) confirms this proposition. It is rather difficult to suppose any other pathway for this diamine formation besides reduction of aminonitrile III (Table 2).

($sp^3 \leftrightarrow sp^2$)-Carbanions

The titled carbanions are mesomeric (ambidental) anions in which both carbon and the heteroatom bear partial negative charges, e.g.:

$\bar{C}H_2—C\equiv N \leftrightarrow CH_2=C=N^-$

$Ph—C(=O)—\bar{C}H_2 \leftrightarrow Ph—C(—O^-)=CH_2$

Among the organomercury compounds that give such carbanions, bis(dinitro-

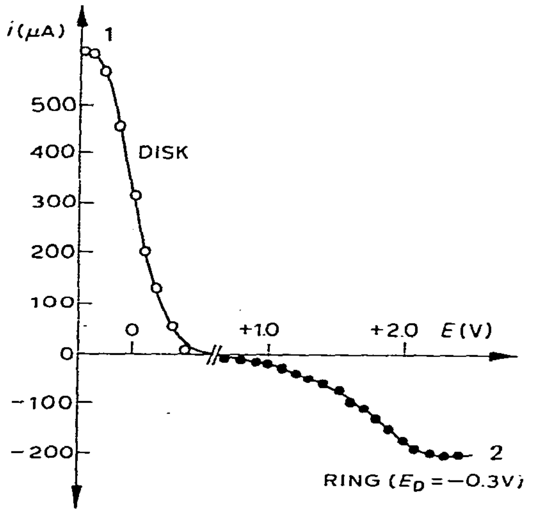


Fig. 11. Polarization curves for $[(NO_2)_2FC]_2Hg$ reduction at the disk (curve 1) and $(NO_2)_2FC^-$ anion oxidation at the ring (curve 2; E_D —0.3 V). CH_3CN; 0.05 *M* Bu_4NBF_4, 25°C. Concentration of R_2Hg 2×10^{-3} *M*, ω 2080 rpm.

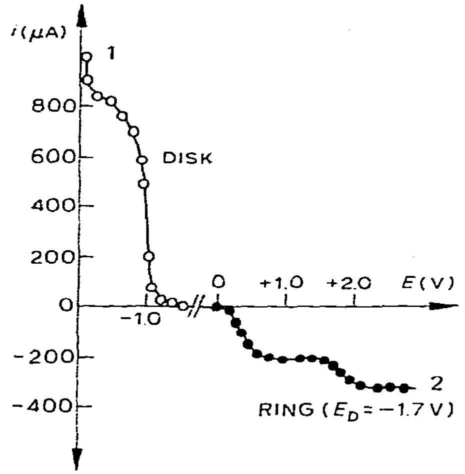


Fig. 12. Polarization curves for $(PhCOCH_2)_2Hg$ reduction at the disk (curve 1) and oxidation of products, formed at the disk, at the ring (curve 2, $E_D = -1.7$ V). CH_3CN 0.05 *M* Bu_4NBF_4. Concentration of R_2Hg is 2×10^{-3} *M*, ω 2080 rpm.

fluoromethyl)-, bis(benzoylmethyl)- and bis(cyanomethyl)-mercury were chosen for this study. Experimental data are given in Table 4 and Figs. 11–13.

Bis(dinitrofluoromethyl)mercury. $[(NO_2)_2CF]_2Hg$ can be reduced very readily at approximately zero potential vs. SCE (Table 4). The reduction product gives

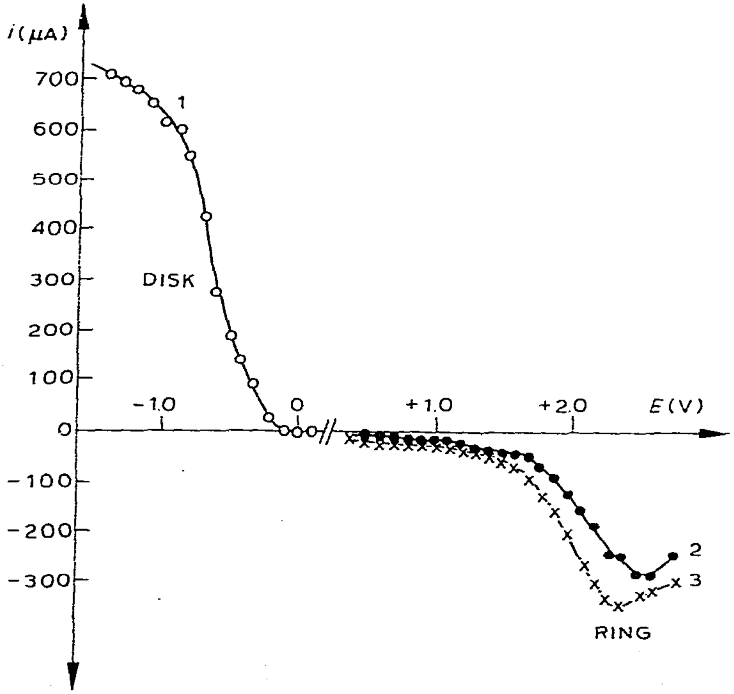


Fig. 13. Polarization curves for $Hg(CH_2CN)_2$ reduction at the disk (curve 1) and CH_2CN^- anion oxidation at the ring (curve 2; E_D −1.0 V). CH_3CN, 0.05 *M* Bu_4NBF_4. Concentration of R_2Hg 2×10^{-3} *M*, ω 2080 rpm. Curve 3, ring polarization curve obtained when $NaBF_4$ (5×10^{-3} *M*) was reduced at the disk (E_D −3.0 V; i_D 5500 μA) under the same conditions.

TABLE 4

ELECTROCHEMICAL PARAMETERS FOR (sp^3-R)$_2$Hg AT ROTATING DISK—RING ELECTRODE IN CH_3CN

(0.05 *M* Bu_4NBF_4, 25°C; ω 2080 rpm, concentration of R_2Hg 2×10^{-3} *M*. $E_{1/2}$ vs. SCE).

R	Disk		Ring			N_1	N_2
	$E_{1/2}$ (R_2Hg) (V)	i_D (μA)	$E_{1/2}$ (R^-) (V)	Other anodic waves, $E_{1/2}$ (V)	Total anodic current, i_R (μA)		
$CF(NO_2)_2$	+0.05	580	1.67 [a]	—	200	0.35	—
$PhCOCH_2$	−1.05	800	0.42 [b]	1.99	340	0.26	0.42
CH_2CN	−0.62	640	2.03 [c]	—	260	0.42	—

[a] $E_D = -0.3$ V. [b] $E_D = -1.7$ V. [c] $E_D = -1.0$ V.

one anodic wave at the ring (Fig. 11) with YCR 0.35, that is, 81% of the theoretical efficiency coefficient value calculated previously from the electrode geometry. This wave ($E_{1/2}$ 1.67 V) may be thought to correspond to oxidation of carbanions $(NO_2)_2FC^-$ which are relatively stable (pK_a 7.70 in water [26]) and probably do not react with the solvent, because YCR is practically independent of the electrode rotation speed or addition of water.

Bis(benzoylmethyl)mercury. Acetophenone has a pK_a = 24.4 in DMSO [10], i.e., the respective carbanion is of "moderate stability" relative to acetophenone (like $C_6F_5^-$ relative to C_6F_5H or $PhC{\equiv}C^-$ relative to $PhC{\equiv}CH$). In water, where pK_a(H_2O) = 15.7, $PhCOCH_3$ has a pK_a of 15.8 [27] and for the enol form pK_a = 11.0 [27].

Bis(benzoylmethyl)mercury can be reduced at a potential of about −1 V. The reduction products give two well expressed anodic waves with $E_{1/2}$ 0.42 and 1.99 V (Fig. 12, Table 4), the first wave (N_1 = 0.26) being higher than the second one ($N_2 - N_1$ = 0.14). Boht N_1 and N_2 are independent of the electrode rotation speed.

Bis(cyanomethyl)mercury. This compound can be reduced rather readily at −0.62 V vs. SCE (in DMF/$LiClO_4$, $E_{1/2}$ −0.8 V [28]). The product of electrochemical reduction of $Hg(CH_2CN)_2$ gives one wave at the ring (Fig. 13) with $E_{1/2}$ 2.03 V and YCR 0.42. Carbanion CH_2CN^- is relatively unstable (pK_a 29.1 [9] or 31.3 [10] in DMSO) and the fact that only one wave is observed at the ring, not two or three as for the other more stable carbanions such as $PhC{\equiv}C^-$, $PhSCH_2C{\equiv}C^-$, $C_6F_5^-$ and $PhCOCH_2^-$, is due to the fact that in this case the solvent/carbanion interaction is a degenerate reaction, because reagents and products are the same:

$$CH_2CN^- + CH_3CN \rightleftharpoons CH_3CN + CH_2CN^-$$

Thus, the anodic wave with $E_{1/2}$ = 2.03 V may be ascribed to oxidation of carbanion CH_2CN^-.

Cyanomethyl anions can also be generated by another mode. Electrolysis of $NaBF_4$ in CH_3CN at very negative potential, −3.0 V vs. SCE, results in deposition of sodium metal on the disk, after which sodium reacts with acetonitrile [19]:

$$2\ Na + 2\ CH_3CN \rightarrow 2\ Na^+ + CN^- + CH_2CN^- + CH_4$$

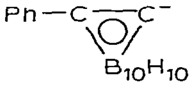
Thus, oxidation of the anions CN^- and CH_2CN^- must be observed at the disk. In fact, one anodic wave was observed (Fig. 13) because the oxidation potentials of CN^- and CH_2CN^- are very similar (cf. Tables 3 and 4). Quarter wave potential of this wave, $E_{1/4} = 1.90$ V is similar to $E_{1/2} = 2.03$ V for CH_2CN^- and three-quarter wave potential $E_{3/4} = 2.18$ V to $E_{1/2} = 2.20$ V for CN^-. Note that no anodic wave was observed at the ring when $LiClO_4$ was reduced at the disk at —3.0 V. Thus lithium does not react with acetonitrile.

Anion of 1-phenyl-o-carborane

This anion has an icosahedral skeleton with formally six-valent carbon and boron atoms. 1-Phenyl-*o*-carborane has pK_a 21.5 [29] on Streitweiser's scale where $pK_a(PhC{\equiv}CH) = 23.20$ [25].

The cathodic wave at the disk has $E_{1/2} = -1.00$ V (SCE), disk current 415 μA at 10^{-3} M concentration of the depolariser in solution.

The anodic wave at the ring shows two well defined waves with $E_{1/2}$ 0.50 V, N_1 0.33 and $E_{1/2}$ 2.04 V, N_2 0.45. The overall anodic ring current is 185 mA at a disk potential of 1.6 V (Fig. 14). The dependences of i_D and i_R on $\sqrt{\omega}$ were linear and passed through the origin. Probably the anodic wave with $E_{1/2}$ = 0.50 V is due to oxidation of carbanion (see below).



Discussions

Yield of current at the ring

Some experimental data obtained for organomercury compounds at the disk—

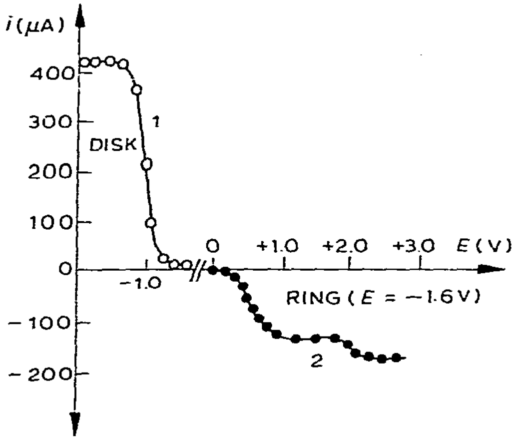
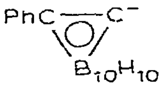


Fig. 14. Polarization curves for reduction of bis(1-phenyl-*o*-carboranyl) mercury at the disk (curve 1) and oxidation of the reduction products at the ring (curve 2). E_D —1.6 V. CH_3CN, 0.05 M Bu_4NBF_4, ω 2080 rpm. Concentration of R_2Hg is 1×10^{-3} M.

TABLE 5

EXPERIMENTAL DATA ON ELECTROCHEMICAL OXIDATION OF CARBANIONS

R^-	$E_{1/2}(R^-)$[a] (V)	pK_a(RH) in DMSO	ΔpK_a[b]	$\log(N_1/N_2)$	$E_{1/2}$[a] (V) of the second wave
CN^-	2.20	12.9 [9]	16.2	—	—
CH_2CN^-	2.03	29.1 [9]; 31.3 [10]	0	−0.30	—
$Cl_2C{=}CCl^-$	1.72	18 [22]; 25 [24]	8.9	−0.04	2.15
$CF(NO_2)_2^-$	1.67	7.70 [26][c]	20	—	—
p-$NO_2C_6H_4OC{\equiv}C^-$	1.25	(18.5)[de]	10.6	−0.03	2.10
$PhSCH_2C{\equiv}C^-$	0.60	(27.0)[d]	2.1	−0.28	2.15[f]
	0.50	21.5 [29][e]	7.6	−0.13	2.04
$PhCOCH_2^-$	0.42	21.5 [13]; 22.5 [12]. 24.4 [10]	4.9	−0.21	1.99
$C_6F_5^-$	0.38	23 [22]; 25.8 [25][f]	3.5	−0.27	1.81
$PhC{\equiv}C^-$	0.28	22.6 [13]; 26.5 [12]; 28.8 [10]; 29.2 [11]	5.9	−0.17	2.00

[a] vs. SCE. [b] pK_a difference between CH_3CN and RH. [c] In water. [d] As determined from the plot in Fig. 7. [e] In dimethoxyethane. [f] $E_{1/2}$ for the third anodic wave.

ring electrode are listed in Table 5. The second column of the table lists the oxidation potentials ($E_{1/2}$) of carbanions measured vs. aqueous saturated calomel electrode. The attribution of these potentials to the carbanion oxidation process is made on the basis of the argument already presented (see Results).

The third column of Table 5 lists the thermodynamic characteristic of carbanion stability, the pK_a values of the corresponding CH acids in DMSO. pK_a was measured in DMSO, not in CH_3CN, because the latter solvent is unstable to the action of such strong bases as carbanions (cf. Results) and no pK_a value has been reported in the literature for carbanions in CH_3CN. We chose pK_a in DMSO as a measure of the relative carbanion stability in CH_3CN because Parker's experimental data [30] have shown that chemical properties of anions in different dipolar aprotic solvents often change in parallel with the slope of the correlation line often close to unity. Thus, pK values in two dipolar aprotic solvents, DMSO and CH_3CN, may be similar to one another, or may differ sharply if the acidities are compared in CH_3CN and H_2O (see also ref. 31).

The last column of Table 5 lists $E_{1/2}$ values for the second anodic waves at the ring. Except for the pentafluorophenyl compound, $E_{1/2}$ values for the second waves of all other compounds are close to 2.07 ± 0.08 V. It may be supposed that these waves are due to oxidation of the anion CH_2CN^- ($E_{1/2}$ 2.03 V) which arises as a result of acid—base interaction of carbanions with the solvent (eq. 3).

Carbanion stability may simply be determined from the electrochemical data; we suggest use of the logarithm of YCR ratio, $\log(N_1/N_2)$. The N_1 quantity gives the relative amount of R^- while N_2 the relative amount of R^- plus interaction products of R^- with solvent. In almost all cases N_1 was close to the theoretical efficiency coefficient calculated from the electrode geometry (0.46 ±

0.03) or the experimental efficiency coefficient (0.43) determined in the system ferrocene/ferricinium. It means that if all anodic waves correspond to one-electron processes, all ($R^- + CH_3CN$) interaction products are identified at the ring. If, as has already been supposed above, the second anodic waves may be attributed to CH_2CN^- anion oxidation, then $\log(N_1/N_2)$ must be proportional to ΔpK_a between CH_3CN and RH. Such a statement is justified when the rate of the acid—base equilibria, $R^- + CH_3CN \rightarrow RH + CH_2CN^-$, is sufficiently high compared with the rate of mass transfer from the disk to the ring. The minimal time of mass transfer from disk to ring for electrodes of usual constructions may be estimated as about 10^{-3} s [32,33], consequently the rate of pseudomonomolecular reaction 3 should be $\leqslant 10^3$ s^{-1}. Unfortunately, the rates of proton transfer in acetonitrile have not been measured, therefore we have again used the respective data in DMSO. Data by Ritchie and Uschold [34] on proton transfer between substituted fluorenes, triphenylmetane or nitromethane and different C-bases or methoxide ion in DMSO or MeOH enables us to draw the Brönsted plots for forward and back reactions. In both solvents the Brönsted coefficients, α and β, changed smoothly from 1 to 0 with an increase in ΔpK_a between a donor and an acceptor, in accordance with Eigen's theory [21]. Using the Brönsted plot of Ritchie and Uschold and taking into account that the concentration of CH_3CN molecules in pure acetonitrile is about 19 *M*, one may calculate that reaction 3 in DMSO under pseudomonomolecular conditions proceeds with a rate of 10^3 s^{-1} at $\Delta pK_a = pK_a(CH_3CN) - pK_a(RH) = 5$. At higher ΔpK_a, the rate of reaction 3 is less than 10^3 s^{-1} and at $\Delta pK_a < 5$ it is $>10^3$ s^{-1}. The ΔpK_a values that are listed in Table 5 are less than 5 for four cases out of eight with ΔpK_a determined from the plot in Fig. 7 and for six cases out of eight if in the ΔpK_a calculations one uses $pK_a(CH_3CN)$ 29.1 and the maximum value of $pK_a(RH)$ given in Table 5.

There was no case when N_1 or ($N_2 - N_1$) depended on the electrode rotation

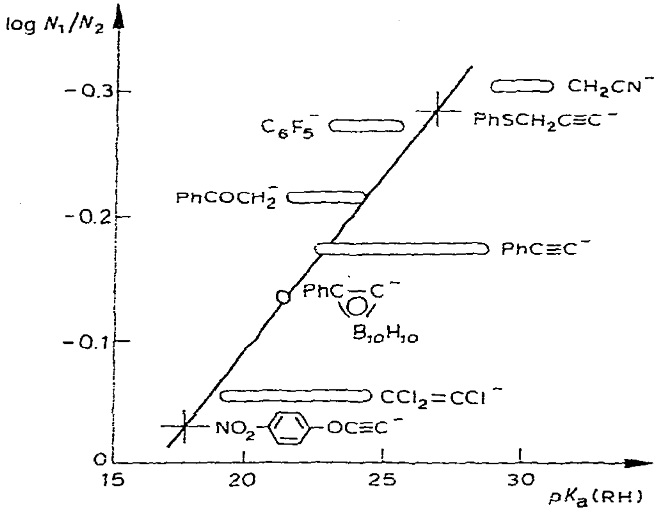


Fig. 15. Correlation between $\log(N_1/N_2)$ and $pK_a(RH)$.

speed, i.e., the systems under study did not get into the "kinetic region" in which N_1 increases while $(N_1 - N_2)$ decreases with an increase in the rotation speed.

In Fig. 15 the values of $\log(N_1/N_2)$ was taken to be -0.3 because the equilibrium constant for the reaction

$$CH_2CN^- + CH_3CN = CH_3CN + CH_2CN^-$$

is exactly unity. The correlation observed (Fig. 15) shows that the $\log(N_1/N_2)$ values may, indeed, be used as a measure of the carbanion stability and, furthermore, the attribution of the first anodic waves to carbanion oxidation processes is correct.

Note, that for compounds VI and X in Table 5, $\log(N_1/N_2)$ is a measure of the relative carbanion stabilities only for the case when the products which are oxidized at the potentials of the second anodic wave in the case of $R = PhSH_2\text{-}C{\equiv}C$, or the third anodic wave in case of $R = PhC{\equiv}C$, do not, to any appreciable extent, influence the acid—base equilibrium (eq. 3).

Half-wave potentials

Half-wave potentials in Table 5 do not correlate with the relative carbanion stability, if the pK_a value of the respective CH acids is taken as a measure of the latter. The plot of $E_{1/2}$ vs. pK_a in Fig. 16 shows that the largest "discrepancy" between $E_{1/2}$ and pK_a is observed for the anion CH_2CN^-.

There is also no correlation between $E_{1/2}$ of carbanions R^- and electron affinities (EA) of the respective radicals $R^\cdot$, in the gas phase. The following figures are used as illustrations:

R^-	CN^-	CH_2CN^-	$PhCOCH_2^-$	$PhC{\equiv}C^-$	FLU^-	Cp^-
EA of $R^\cdot$ (kcal/mol^{-1})	77 [35]	37.3 [36]	52.4 [36]	65 [35]	45 [36]	24.4 [36]
$E_{1/2}$ (V)	2.20	2.03	0.42	0.28	-0.71 [37]	-0.36 [37]

One possibility to explain the discrepancy in the electrochemical oxidation potentials to the carbanion structures is to consider the radical dimerization rates. The dependence of $E_{1/2}$ on the dimerization rate constant k_d is defined by eq. 7 [2].

$$E_{1/2} = E^0_{1/2} - \frac{RT}{3\,nF} \ln k_d + \text{const} \tag{7}$$

The following approach may be used for an estimation of changes in k_d values in transfer from one radical to another. Consider the two reactions 8 and 9, that occur in the gas phase:

$$2\,R^\cdot \overset{K}{\rightleftharpoons} R{-}R \tag{8}$$

$$2\,R'^\cdot \overset{K'}{\rightleftharpoons} R'{-}R' \tag{9}$$

In eqs. 8 and 9, K and K' are the equilibrium constant of the dimerization of the radicals $R^{\cdot}$ and $R'^{\cdot}$ respectively. The free energy difference between reactions 8 and 9 may be expressed by (eq. 10).

$$(\Delta G^0 - \Delta G^{0'}) = -RT\ln(K/K') \tag{10}$$

One may write the two thermodynamical cycles 11 and 12 for reactions 8 and 9 in the gas phase.

$$\left.\begin{array}{llll}
2\,RH & \longrightarrow R{-}R + H_2; \Delta H & & (11a) \\
2\,R^{\cdot} + 2\,H^{\cdot} & \longrightarrow 2\,R{-}H; & -2\,D(RH) & (11b) \\
H_2 & \longrightarrow 2\,H^{\cdot}; & D(H_2) & (11c) \\
\hline
2\,R^{\cdot} & \longrightarrow R{-}R; \Delta Hd = \Delta H{-}2\,D(RH) + D(H_2) & &
\end{array}\right\} \tag{11}$$

$$\left.\begin{array}{llll}
2\,R'H & \longrightarrow R'{-}R' + H_2; \Delta H' & & (12a) \\
2\,R'^{\cdot} + 2\,H^{\cdot} & \longrightarrow 2\,R'{-}H; & -2\,D(R'H) & (12b) \\
H_2 & \longrightarrow 2\,H^{\cdot}; & D(H_2) & (12c) \\
\hline
2\,R'^{\cdot} & \longrightarrow R'{-}R'; \Delta H'_d = \Delta H' - 2\,D(R'H) + D(H_2) & &
\end{array}\right\} \tag{12}$$

In expressions 11 and 12, ΔH and $\Delta H'$ are the enthalpy changes in dehydrogenation reactions 11a and 12a; $D(RH)$ and $D(R'H)$ the bond energies of R—H and R′—H; ΔH_d and $\Delta H'_d$ the enthalpy changes for the dimerization of radicals $R^{\cdot}$ and $R'^{\cdot}$, respectively; $D(H_2)$ the dissociation energy of hydrogen molecule.

From eqs. 11 and 12,

$$\Delta H_d = \Delta H - 2\,D(RH) + D(H_2)$$

and

$$\Delta H'_d = \Delta H' - 2\,D(R'H) + D(H_2)$$

therefore

$$\Delta H_d - \Delta H'_d = (\Delta H - \Delta H') - 2[D(RH) - D(R'H)] \tag{13}$$

Let us suppose that the entropy changes in reactions 8 and 9 are the same. Then, from eqs. 13 and 10,

$$-RT\ln(K/K') = (\Delta H - \Delta H') - 2[D(RH) - D(R'H)] \tag{14}$$

When all the parameters to the right of eq. 14 are known, this equation may be used as a rough estimate of the K/K' ratio in the gas phase (neglecting entropy). The ΔH values for reactions 11a and 12a are not available, therefore, one needs to use some indirect approach for an estimation of these. One of the approaches is use of Benzon's group contributions to thermodynamic properties in the gas phase [38] for an estimation of $\Delta H - \Delta H'$. In eq. 11a $\Delta H = \Delta H_f^0(RR) - 2\,\Delta H_f^0(RH)$, where $\Delta H_f^0(RR)$ and $\Delta H_f^0(RH)$ are the enthalpies of formation of RR and RH from the elements. According to Benson [38] the $\Delta H_f^0(\mathrm{RR})$ and $\Delta H_f^0(\mathrm{RH})$ values may be represented as an additive sum of the group contributions; these values differ from one another only in that the former involves two group contributions $[C_i(\mathrm{R})]$, while the latter, instead of those, two group contrubution, $[C_i(\mathrm{H})]$. (The symbol C_i refers to the terminal unsaturated carbon atom of group R. The other group contributions, both to $\Delta H_f^0(\mathrm{RR})$ and to $\Delta H_f^0(\mathrm{RH})$, are the same, therefore for reaction 11a

$$\Delta H = 2\{[C_i(\mathrm{R}(] - [C_i(\mathrm{H})]\} \tag{15}$$

and for reaction 12a

$$\Delta H' = 2\{[C_i'(\mathrm{R}')] - [C_i'(\mathrm{H})]\} \tag{16}$$

From eqs. 15 and 16

$$\Delta H - \Delta H' = 2\{\Delta[C(\mathrm{C})] - \Delta[C(\mathrm{H})]\} \tag{17}$$

where $\Delta[C(\mathrm{C})] = [C_i(\mathrm{R})] - [C_i'(\mathrm{R}')]$ and $\Delta[\mathrm{C(H)}] = [C_i(\mathrm{H})] - [C_i'(\mathrm{H})$

From eqs. 17 and 14, when the bond energy different $D(\mathrm{RH}) - D(\mathrm{R'H})$ is denoted as $\Delta D(\mathrm{CH})$, one obtains

$$RT\ln(K/K') = 2\{\Delta D(\mathrm{CH}) + \Delta[C(\mathrm{H}) - \Delta[C(\mathrm{C})]\} \tag{18}$$

The difference between the enthalpy changes in the reactions 2 $CH_3CN \rightarrow (CH_2CN)_2 + H_2$ and 2 $HCN \rightarrow (CN)_2 + H_2$ as calculated using Benson's group

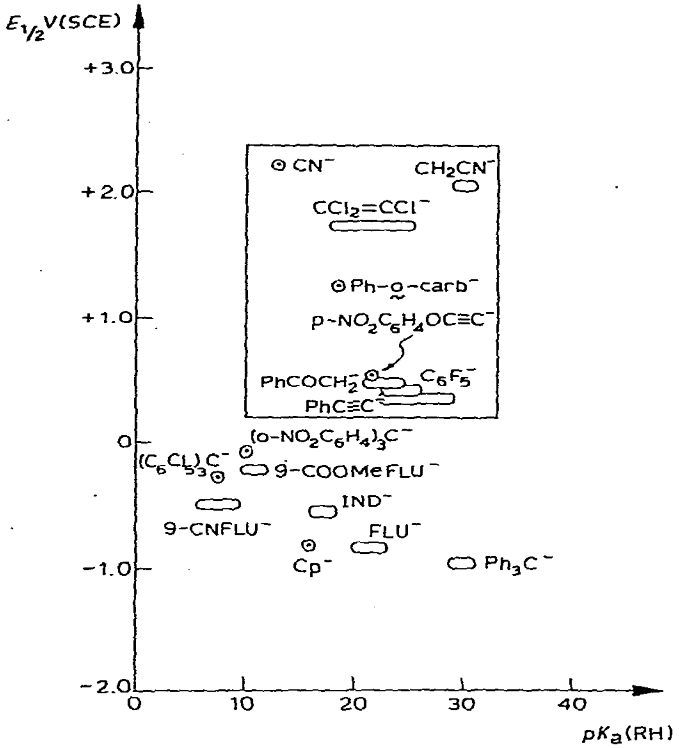


Fig. 16. Lack of relation between $E_{1/2}$ and pK_a.

contributions, is equal to 66 kcal/mol^{-1}. One may further calculate that

$RT\ln(K(CH_2CN)/K(CN)) = 8$ kcal mol^{-1}.

Hence, if the dimerization were absent, the half-wave potential difference $E_{1/2}(CN^-) - E_{1/2}(CH_2CN^-)$ should be by $(8/1.38) \times 0.02 = 0.112$ V less positive than that observed experimentally. The analogous correction for $E_{1/2}(CN^-) - E_{1/2}(PhCOCH_2^-)$ is +0.34 V *. The conclusion may be drawn that these corrections are too small to improve the correlation in Fig. 16.

The lack of correlation between $E_{1/2}$ and pK_a of carbanions is unfortunate because in the Edwards equation [40] the relative rates of interaction of nucleophilic agents with a standard electrophile are represented as the sum of two terms:

$$\log(k/k_{\text{stand.}}) = \alpha E + \beta H$$

where α and β are parameters which characterize the reaction type and the electrophile nature, while H and E are nucleophile properties, H being related to pK_a and E to the redox potential of a nucleophile. Thus, pK_a and redox potential of nucleophiles are independent parameters.

Conclusions

The data obtained allow us to conclude that organomercury compounds are convenient materials for the electrochemical synthesis of carbanions. The disk—ring electrode permits us to identify the carbanions and to estimate their relative stability in a given solvent. The method we applied differs advantageously from the pulse electrochemical techniques. The advantages of the disk-ring techniques over the pulse electrochemical ones lies in the fact that in the case of the disk-ring electrode the sites of generation (disk) and oxidation (ring) of carbanions are separated in space and therefore mercury metal, which deposits on the disk during the electrolysis, does not hinder the detection of carbanions at the ring.

Experimental

Materials

Tetra-n-butylammonium tetrafluoroborate was prepared by adjusting 10% aqueous Bu_4NOH ("Chemapol") with a solution of hydrogen tetrafluoroborate to an acidic reaction on litmus. A white precipitate was filtered and carefully washed with cold water. Dried Bu_4NBF_4 was recrystallized three times from ether acetate/diethyl ether mixture and dried in vacuo over P_2O_5 for 3 days; m.p. 162°C (lit. [41], 162—162.5°C). *Sodium perchlorate* and *sodium tetrafluoroborate*, "Chisty" grade, were recrystallized twice from methanol and dried over P_2O_5. *Acetonitrile* (Chisty) was stirred with CaH_2 (10 g l^{-1}) for 20 h, decanted and distilled twice over fresh portions of P_2O_5; b.p. 81.5°C. The purified solvent contained 0.03 wt.% water (Fisher titration). *Dimethoxyethane*

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* The Brönsted coefficient for the dimerization rates was chosen to be equal to 1; that gives the largest correction factors. Really, α lies in the region from 0.1 to 0.5 for most of the radical dimerizations [39].

"Technichesky") was purified as follows. 20—25 g solid KOH was added to 1 l in the solvent, then after several hours the liquid was carefully decanted and a fresh portion of KOH was added. This operation was repeated several times until the solid phase became colourless. The decanted reddish-brown solvent was distilled and then distilled again over sodium metal. The colourless solvent obtained was distilled over $LiAlH_4$ and kept with a small addition of benzophenone and sodium metal. Before using, the solvent was distilled, b.p. 79°C.

Bis(cyanomethyl)mercury [28] was prepared from mercury(II) chloride and $LiCH_2CN$ [42] in THF and was purified by recrystallizating twice from ethanol, m.p. >200°C (dec.).

Bis(perfluorophenyl)mercury was prepared as in ref. 43 and was recrystallized twice from CCl_4; m.p. 135—136°C (lit. [43], 135—136°C).

Bis(phenylethynyl)mercury was prepared as in ref. 44, and was purified by a 5-fold recrystallization from ethanol; m.p. 124—125°C (lit. [44], 124.5—125°C).

Bis(perchlorovinyl)mercury [45] was recrystallized twice from pentane; m.p. 72—73°C.

Bis(fluorodinitromethyl)mercury was prepared as in ref. 46, m.p. 147°C.

Bis(2-phenylo-carbonaryl)mercury was prepared as in ref. 47, the other organomercury compounds were prepared as described in ref. 48 and were recrystallized several times until their melting points were the same as those quoted in the literature.

Measurements

The electrochemical cell consisted of a cylindrical water-jacketed vessel of 40 cm^3 capacity with four symmetrically arranged tube-bends. Two of these were separated from the main volume with porous glass filtered No. 2; two auxiliary electrodes and 10 X 10 mm platinum nets were placed into these tube-bends. Two other tube-bends were made into thin capillaries inside the cell, the outlet of one being about 1 mm from the disk, while that of the other was about 1 mm from the ring. In the latter two tube-bands, two electrolytical keys, with stop-cocks, to connect the cell with two saturated calomel electrodes, were introduced. The cell had also an inlet and an outlet for bubbling argon through the solution.

Apparatus

Two potentiostates II-5848 and two galvanometers M-254 were used to plot the polarization curves. Readings were taken at potential intervals of 40 or 100 mV. One of the potentiostates drove the disk electrode and the other the ring electrode. In order to minimise interexcitation of the potentiostates, one of them was not earthed.

Two sets of pulleys of different diameters connected by thin silk thread were used to rotate the electrode. One set of pulleys was on the shaft of the rotating electrode, the other on the shaft of a synchronous electromoter D-1. The set of pulleys used enabled us to change the number of revolutions of the driven-shaft from 800 to 3960 rpm.

Measurement procedures

Preparation of the electrode. As we were working with organomercurials the surface of the disk electrode became covered by a mercury layer; the anodic demercurisation was carried out before use in saturated aqueous solution of potassium chloride (current 1.5 A for 20 min). Then the surfaces of the disk and the ring were polished using a velvety glass-paper No. 0 and a filter paper, washed carefully with water and acetone and dried with cotton.

Generation and oxidation of carbanions. 35 cm^3 of a 0.05 M solution of Bu_4NBF_4 were placed in the electrochemical cell, blown through for 40 min with dried argon and the polarization curve of the phonon was read at the disk at cathodic potentials and at the ring at anodic potentials. Then, an amount of an organomercury compound was poured into the solution so that its concentration was 1 or 2×10^{-3} M and the polarization curve was read at the ring. The latter was necessary in order to determine the possibility of oxidation of the organomercury compound. From the cathodic curve at the disk, $E_{1/2}$ and the limiting current at R_2Hg reduction were determined. Then the limiting current potential was set at the disk and the full polarization curve at the ring was read from which oxidation potentials and limiting currents of the disk reaction products were found.

Electrolysis of organomercury compounds

Electrolysis at controlled potentials was carried out in a 100 cm^3 cell supplied with a water-jacket for thermostating at 25°C; stirring was carried out with Ar bubbling through the solution. The working electrode was mercury, the auxiliary platinum electrode was separated from the working electrode with a cellophane diaphragm, the reference electrode was SCE. Electrolysis of 0.8338 g (1.5 mmol) $(C_6F_5)_2Hg$ in 50 cm^3 of CH_3CN with 0.05 M Bu_4NBF_4 as supporting electrolyte was carried out at —1.6 V for 6 h. After the electrolysis, current flowing through the cell decreased from the initial 1.35 mA to 0.08 mA. Electrolysis of 1.5 g (3.7 mmol) $(PhC{\equiv}C)_2Hg$ in 100 cm^3 of CH_3CN was carried out over 7.5 h at —1.8 V.(current at the beginning of the electrolysis 4.45 mA, and 0.105 mA at the end). After the electrolysis was complete mercury metal was separated from the reaction mixture, and the solvent, CH_3CN, was distilled off together with other low-boiling products (e.g. C_6F_5H, d.p. 88—89°C). The solid or tarish residue was extracted with ether and the ether distilled off. Thus, the catholyte was divided into three fractions: (i) distilliation product, (ii) extract, and (iii) residue after extraction. The fractions were analyzed using chromatography—mass spectrometry techniques.

Chromatography—mass spectrometry analyses

Analysis were carried out using a Varian MAT-111 spectrometer at ionizing tension 80 V and emission current 270 mA; the column of OV-1 was 1.5 m in length (He, 30 cm^3/h). The reaction products were identified from their fragmentation characteristics. The results are given below.

$(C_6F_5)_2Hg$. (i) Distillation product. Two peaks were observed on chromatography. The first corresponds to CH_3CN (m/e 41 (M^+), 42 ($M^+ + 1$), 40 ($M^+ - 1$)), the second to C_6F_5H (m/e 168 (M^+), 149 ($M - F$), 137 ($M - CF$), 118 ($M - CF_2$), 117 ($M - CF_2H$), 99 ($M - CF_3$), 75, 31. (ii) Extract. Besides CH_3CN and ether (m/e 74, etc.) two other compounds were detected in the extract: probably dimers of CH_3CN_3, $CH_3C(=NH)CH_2CN$, (m/e 82 (M^+), 55 ($M - HCN$)) and

diamine, $CH_3CH(NH_2)CH_2CH_2NH_2$, (*m/e* 88 (M^+), 73 ($M - CH_3$), 61) which arises in the dimer reduction. (iii) Residue. The chromatogram of the residue after extraction with ether shows six peaks. (a) *m/e* 156, 105, 104, 90 (not identified); (b) *m/e* 168, 149, 137, 99 (C_6F_5H); (c) *m/e* 56, 41 (butylene); (d) *m/e* 156, 107, 89, 88 (not identified); (e) *m/e* 186, 143, 100, 57 (Bu_3N); (f) *m/e* 209, 194, 168, 149, 137, 118, 117, 99, 93, 75, 31 ($C_6F_5C(=NH)CH_3$).

$(PhC{\equiv}C)_2Hg$. (i) Distillation product consisted of only CH_3CN (*m/e* 41). (ii) Extract. The chromatogram of the extract showed four peaks: (a) $PhC{\equiv}CH$ (*m/e* 102 (M^+), 76 ($M - C_2H_2$)); (b) *m/e* 123 (probably M^+ for *sym*-trimethyltriazine), 82 ($M - CH_3CN$), 41 ($M - 2\ CH_3CN$); (c) $PhCOCH_3$ (*m/e* 120 (M^+), 105 ($M - CH_3$), 77 ($M - CH_3CO$)); (d) the latter peak is not identified. (iii) Residue was a mixture of three compounds: (a) $PhC{\equiv}CH$ (*m/e* 102, 76); (b) PhCHO (*m/e* 106 (M^+), 105 ($M - H$), 77 ($M - CHO$); (c) probably $PhC{\equiv}CC(=NH)CH_3$ (*m/e* 143, 102).

$(CCl_2{=}CCl)_2Hg$. (i) Distillation product was pure CH_3CN (*m/e* 41). (ii) Extract. Chromatogram showed five peaks: (a) diethyl ether (*m/e* 74); (b) $CCl_2{=}CHCl$ (*m/e* 130, 131, 132 (M^+), *m/e* 95, 96, 97 ($M - Cl$), *m/e* 60, 61, 62 ($M - 2\ Cl$)); (c) non-identified compound (*m/e* 92, 91; toluene?); (d) non-identified compound (*m/e* 107; xylene?); (e) $(CCl_2{=}CCl)_2Hg$ which underwent decomposition in the column at about 200°C, so that the spectrum showed the masses corresponding to ions $HgCl_2^+$, $HgCl^+$, Hg^+, $CCl_2{=}CHCl^+$, $CCl_2{=}CH^+$, $CCl{=}CH^+$; (f) a small amount of non-identified compound with *m/e* 148 and without chlorine. (iii) Residue consisted of CH_3CN (*m/e* 41) and a compound with *m/e* 139, 101, 100, 98 (non-identified).

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