

QUANTUMCHEMICAL CALCULATIONS ON ORGANOSILICON RADICALS. V

STUDY OF ORGANOSILICON ANION RADICALS
PREPARED BY ELECTROCHEMICAL REDUCTION

By

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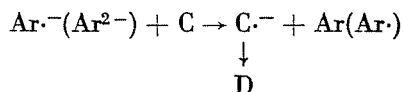
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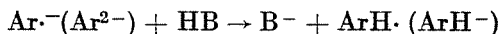
The method of polarographic reduction for the investigation of organosilicon anion radicals was first applied by BOCK and SEIDL [1] for benzochinon derivatives. The organosilicon compounds gave more positive half-wave potential values in comparison with the carbon analogues, this fact was explained by the assumption of $\text{Si} \leftarrow \text{C}_\pi$ effect. The same was concluded based on investigations of trimethylsilyl substituted butadienes [2].

Later polarographic half-wave potentials and their comparison with results of quantumchemical calculations were reported by several authors [3–6].

Investigations on anion radicals are motivated by important practical aspects. Anion radicals (and biradicals) can start electrontransfer reaction in the presence of a suitable receptor (C) according to the following equation:



where $\text{Ar}\cdot^-$ and Ar^{2-} designates the anion radical and biradical, respectively; on the other hand, anion radicals are able to abstract proton from acidic compounds (HB), whilst hydroaromatic radical ($\text{ArH}\cdot$) or hydroaromatic anion (ArH^-) is formed [7]:



The process of electron transfer is very important in polymer chemistry since it is the initial step of anionic polymerization (in this case C is the corresponding monomer).

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Experimental

The polarographic reduction generating anion radicals was carried out in a direct current polarograph (OH-102, Radelkis, Budapest). Dimethylformamide (DMF), freshly distilled after drying by K_2CO_3 , was used as solvent. The supporting electrolyte was tetra-*n*-butylammoniumiodide (TN-BAI) in concentration of 0.05 mol/l. To remove the oxygen solved in DMF, nitrogen has been bubbled through the solution before the measurement

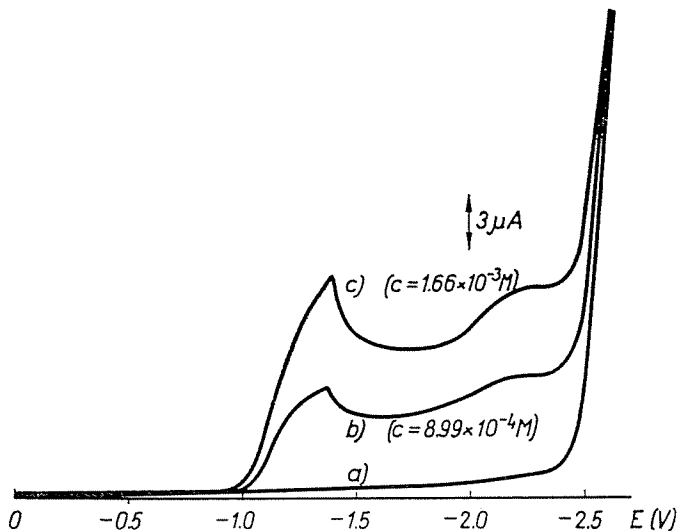


Fig. 1. Polarograms of 9,10-(TS)₂-anthracene (TS = trimethylsilyl): a) remaining current of the supporting electrolyte; b) and c) polarograms in the presence of the electroactive compound in increasing concentration

for 10–15 minutes, during the measurement the nitrogen was run over the solution. The concentration of the electroactive compound was 10^{-3} to $5 \cdot 10^{-3}$ mol/l. Mercury pool was used as reference electrode.

The polarographic maximum observed for disubstituted anthracenes (illustrated in Fig. 1) for the case of 9,10-bis-(trimethylsilyl) anthracene was eliminated by polyethylene glycol and polypropylene glycol used in 8–20%.

For the anthracene derivatives a second polarographic step was also observed because of the formation of dianion (e.g. polarogram a) in Fig. 2).

Polarograms were recorded in DMF-water system, too, in order to investigate the protonation of anion radicals. Two or 4 ml water was given to the dry DMF solution (resulting in solutions with water content of $14 \pm 1\%$ and $28 \pm 2\%$, respectively). The influence of the proton donor concentration on the polarogram was not studied in detail. The height of the first polarographic step increased considerably (Figs 2 and 3) and the second step in

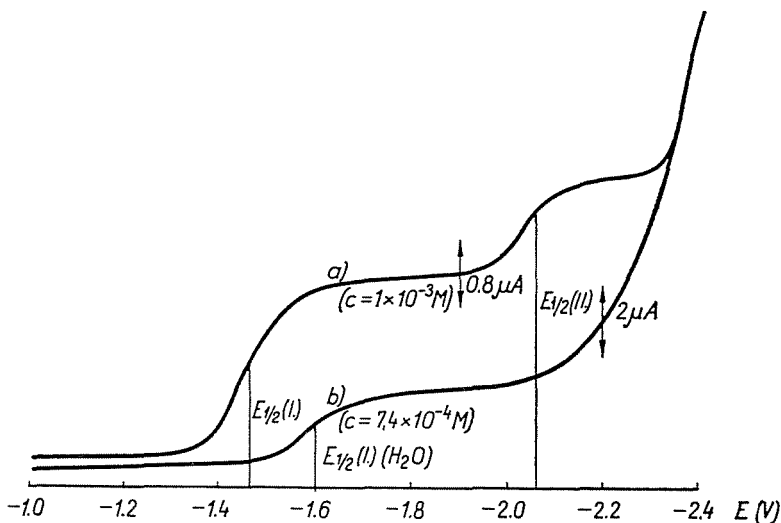


Fig. 2. The effect of water on the polarogram of anthracene: a) polarogram in dry solvent; b) polarogram with 15.8% water content

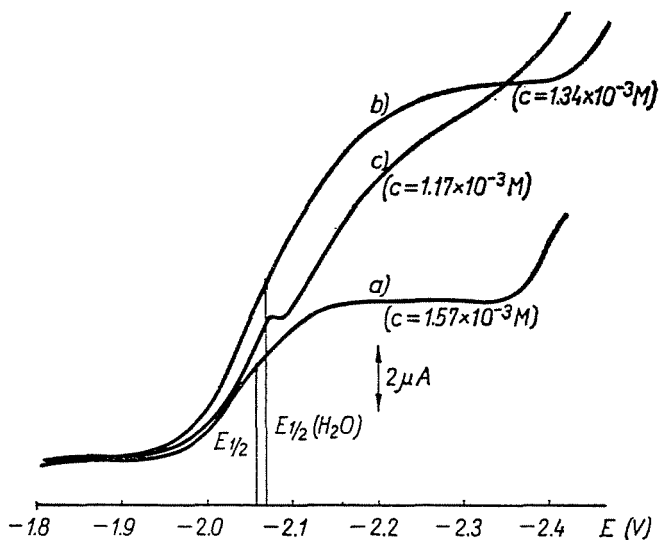


Fig. 3. The effect of water on the polarogram of 1,4-(TB)₂ naphthalene (TB = tert. butyl): a) polarogram in dry DMF; b) polarogram in solution containing 14.9% water; c) polarogram in solution containing 26.1% water

the polarograms of anthracene derivatives disappeared after water addition, in some cases the polarogram could not be evaluated if greater amount of water was added to the solution (Fig. 3, polarogram c).

In the presence of proton donor the values of half-wave potentials were by 0–0.15 V more negative.

Results and discussion

The value of the reduction half-wave potential can be connected with the energy of the lowest unoccupied π level for a molecule. HOIJTINK [8] interpreted the half-wave potential of an electrochemical reduction resulting in the formation of an anion radical as the standard potential of the reduction process ($\text{Ar} + e \rightleftharpoons \text{Ar}\cdot^-$).

The reduction half-wave potentials of some trimethylsilyl substituted benzene, naphthalene, anthracene and phenanthrene derivatives prepared in our laboratory have been summarized in Table I where the results of quantum-chemical calculations obtained for the energies of the lowest unoccupied π levels of these compounds are also presented (by HMO-McLachlan method

Table I

Benzene derivatives				Naphthalene derivatives					
Substituent	$-E_{1/2}$ (V) (Hg pool)		$-\varepsilon_{m+1}$ (β)		Substituent	$-E_{1/2}$ (V) (Hg pool)		$-\varepsilon_{m+1}$ (β)	
			A	B				A	B
None					1,4(TB) ₂	2.06	2.5	0.652	
					1(TB)	2.04	2.03	0.636	
	2.4		1.000		None	1.98	1.98	0.618	
1,4(TS) ₂					1(TS)	1.94	1.93	0.554	0.552
	2.34	2.35	0.733	0.739	2(TS)	1.97	1.97	0.585	0.584
1(TS),4-NO ₂					1,4(TS) ₂	1.84	1.83	0.489	0.484
	0.57	0.55	0.176						

with ω -technique). A good agreement is observed in comparing the experimental results with values calculated according to the regression formula given by STREITWIESER and SCHWAGER [9]:

$$E_{1/2} \left(\begin{array}{c} \text{DMF} \\ \text{TNBAI} \end{array} \right) = (2.407 \pm 0.182)\varepsilon_{m+1} - (0.396 \pm 0.093)$$

It is seen in Fig. 4 that the points are mostly found within a reliability interval.

On the basis of the data in Table I, the conclusion can be drawn that — despite the fact that the $-\text{SiMe}_3$ group has a greater inductive effect than the $-\text{CMe}_3$ group [10] — the half-wave potentials of trimethylsilyl substituted systems are less negative than those of either the analogous carbon compounds or the unsubstituted compounds. This suggests that the $+\text{I}$ effect

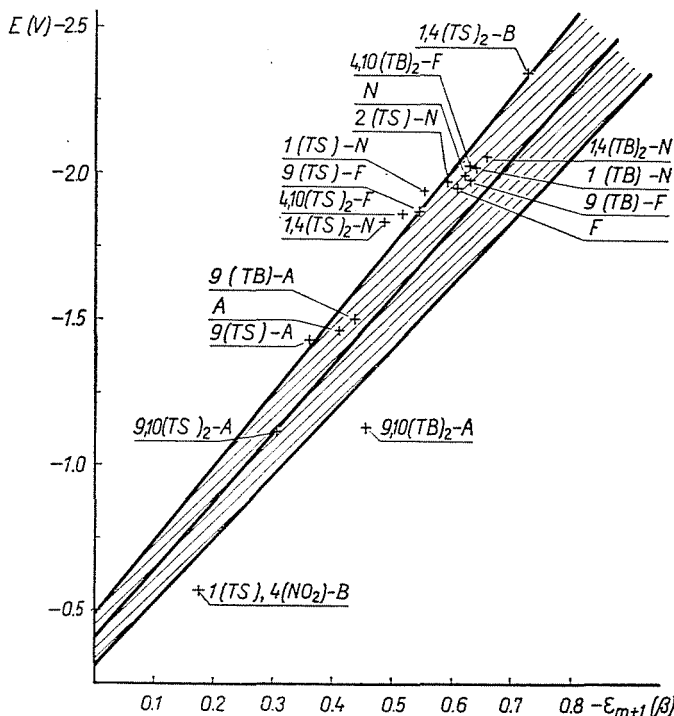


Fig. 4. Connection between the half-wave potentials and energy of the lowest unoccupied π levels (A: anthracene, B: benzene, N: naphthalene, F: phenanthrene)

Table I (contin.)

Phenanthrene derivatives			Anthracene derivatives				
Substituent	$-E_{1/2}$ (V)	$-\epsilon_{m+1}$ (β)		Substituent	$-E_{1/2}$ (V)	$-\epsilon_{m+1}$ (β)	
		A	B			A	B
4,10(TB) ₂	2.00	0.630		9,10(TB) ₂	1.13 ⁺	0.454	
9(TB)	1.98	0.623		9(TB)	1.50	0.435	
None	1.95	0.605		None	1.47	0.414	
9(TS)	1.87	0.541	0.538	9(TS)	1.45	0.359	0.356
4,10(TS) ₂	1.86	0.517	0.513	9,10(TS) ₂	1.10 ⁺	0.305	0.298

Polarographic half-wave potentials and calculated energies of the lowest unoccupied π levels for the investigated compounds

(TS: trimethylsilyl group, TB: tert. butyl group, +: polarographic maximum)
A) after [19]; B) after [5]

of the $-\text{SiMe}_3$ group is overcompensated by its $-\text{M}$ effect resulting in the formation of a $(p-d)\pi$ bond and decreasing the energy of the lowest unoccupied π level. The mentioned effects of the substituents are illustrated in Fig. 5 for naphthalene.

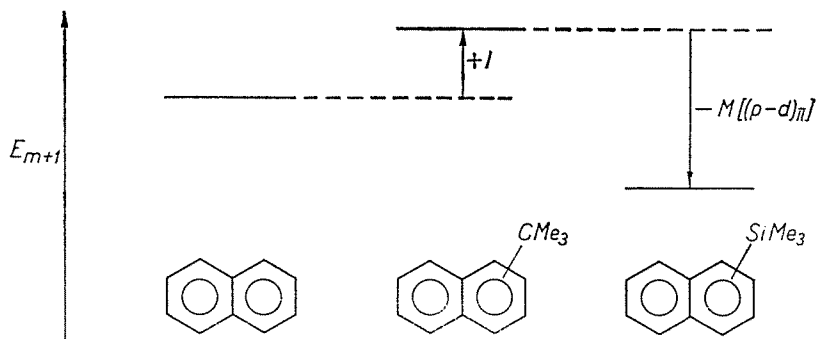


Fig. 5. The effect of $-\text{CMe}_3$ and $-\text{SiMe}_3$ substitution on the lowest unoccupied π level of naphthalene (on the basis of polarographic results)

According to our polarographic results a $(p-d)\pi^*$ link exists in anion radicals (which can be considered as being in a specially excited state). This assumption supports our quantumchemical interpretation of the ESR spectra of organosilicon anion radicals when the silicon atom was treated as a pseudo π centre and the delocalization was considered to be extended over silicon bound to aromatic system [6].

It has been a much discussed question whether the electrochemical reduction generating anion radicals was reversible or not. The problem can be investigated using the TOMES' criteria [11], or carrying out a logarithmic analysis of the polarograms [12]. The latter method indicates that the first step is a reversible reaction (Figs 6 and 7) with one electron change since instead of the $RT/2, 303 F = 0.059$ value calculated from the Nernst equation, data from Figs 6 and 7 (corresponding to reciprocal values of the slopes) are in an interval 0.059 to 0.075.

In dry DMF a second polarographic step between -2.03 and -2.05 V was observed for the anthracene derivatives. The limiting current of the second step was nearly equal to that of the first step, indicating the formation of dianion. This reduction proved to be dominantly irreversible because of the disproportionation of the dianion, desilylation or other kind of decomposition. Our assumption is supported by the fact that practically no difference was observed for the $E_{1/2(11)}$ values of various anthracene derivatives.

The characteristic features of the polarograms recorded in DMF-water system as compared to the polarograms obtained in dry solvent were the following:

- a) the height of the step increased;
- b) the half-wave potential became more negative;
- c) the reduction appeared to be irreversible (as found by logarithmic analysis, the reciprocal values of the slopes were between 0.100 and 0.140).

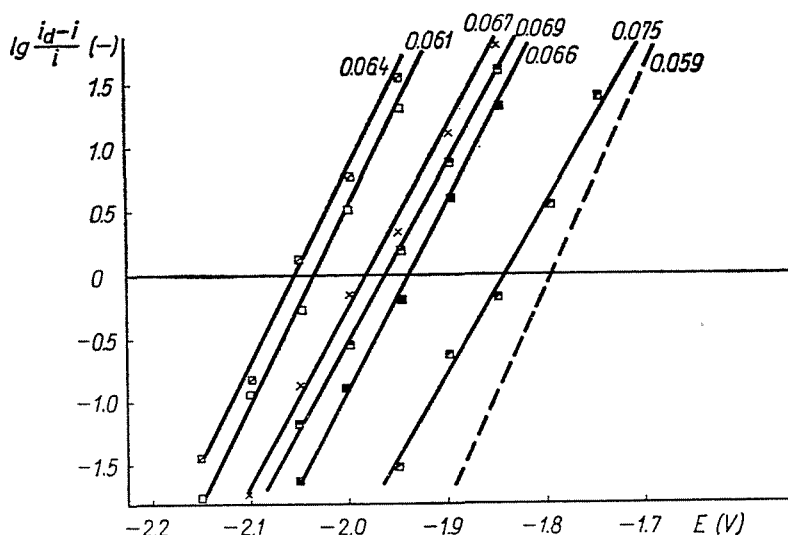


Fig. 6. Logarithmic analysis of polarograms for $-\text{SiMe}_3$ and $-\text{CMe}_3$ substituted naphthalene derivatives (\times : N, \square : 1-(TB)-N, \blacksquare : 1-(TS)-N, \square : 1,4-(TB)₂-N, \blacksquare : 1,4-(TS)₂-N, \blacksquare : 2-(TS)-N)

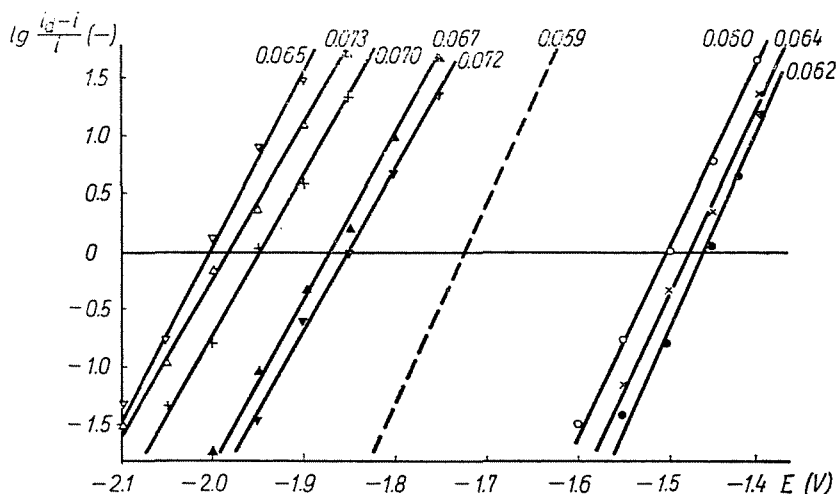
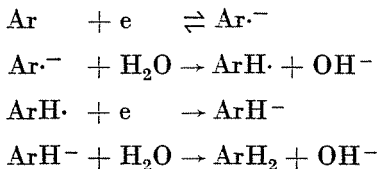


Fig. 7. Logarithmic analysis of polarograms of $-\text{SiMe}_3$ and $-\text{CMe}_3$ substituted anthracene and phenanthrene derivatives (\times : A, \circ : 9-(TB)-N, \bullet : 9-(TS)-A, $+$: F, \triangle : 9-(TB)-F, \blacktriangle : 9-(TS)-F, ∇ : 4,10-(TB)₂-F, \blacktriangledown : 4,10-(TS)₂-F; dotted line indicates the values corresponding to the theoretical reversibility

The reduction of aromatic hydrocarbons in the presence of proton donor may take place according to the following mechanisms:

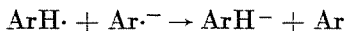
- a) PAUL—LIPKIN—WEISSMAN (PLW) [13] mechanism;
- b) disproportionation mechanism [14].

In the PLW mechanism the following processes have to be considered:



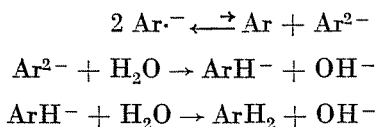
If the protonation of $\text{Ar}^{\cdot-}$ is faster than the diffusion of $\text{ArH}\cdot$ from the surroundings of the electrode, then $\text{ArH}\cdot$ can be reduced to hydroaromatic anion without a further change of the electrode potential since the electron-affinity of $\text{ArH}\cdot$ is higher than that of the initial compound [8]. According to this mechanism the half-wave potentials should be shifted toward more positive values, but we observed the opposite trend.

A variation of the PLW scheme is represented by the regeneration mechanism [15] in which the hydroaromatic radical takes part in the following reaction:



If this process occurred, the half-wave potential would not change.

In mechanism b) the protonation can be described as follows:



Both mechanisms can interpret the increase of the diffusion limiting current as a consequence of the readiness to reducibility, enhanced electron-affinity of $\text{ArH}\cdot$ in mechanism a) and the increase in the concentration of the electroactive compound (Ar) in mechanism b).

According to the PLW mechanism, the rate determining step is the protonation of the anion radical, and the apparent rate constant of the processes is proportional to the water concentration. In mechanism b) the rate-determining step is the protonation of the dianion.

In order to explain the protonation reactions, it is most important to determine spin densities on the carbon atoms of the anion radical.

Two methods have been developed for determining the position and rate constant of the protonation.

HOIJTINK used the following equation for the rate constant of the protonation [16]:

$$k_s = \kappa \cdot \exp(C \cdot e_j/kT) = \kappa \cdot \exp(\gamma \cdot e_j),$$

where α , C , γ are constant, ρ_j is the spin density on carbon atom j of the anion radical. This equation gives information on the position of the protonation (where k_s is the highest), but it does not suit estimating the correct values of the rate constants.

HAYANO and FUJIHARA [17] judged the position of the protonation on the basis of the change in localization energy. Suitable approximation of the rate constants was only carried out, however, by NAGAKURA's charge transfer mechanism [18]:

The localization energy L can be given as the difference between the total electron energy E_π of the anion radical and that of the hydroaromatic radical protonated on carbon atom j :

$$L_j = E_\pi(\text{Ar}^\cdot) - E_\pi(\text{ArH}\cdot_j).$$

The protonation takes place in a position where the change in the localization energy is the smallest.

Quantumchemical calculations were carried out by Hückel's method improved by ω -technique for each of the possible products of protonation (hydroaromatic radical, hydroaromatic anion, dihydro derivative) of naphthalene, anthracene and phenanthrene derivatives. The results have been discussed in a qualitative way.

The localization energies for the protonated products of some trimethylsilyl substituted naphthalenes are summarized in Fig. 8. The change in the localization energy is the smallest in the protonated radical \rightarrow protonated anion reaction, thus this is the fastest process. The formation of hydroaromatic radical from anion radical appeared to be the rate-determining step, in accordance with the experimental results.

In trimethylsilyl substituted naphthalenes, anthracenes and phenanthrenes, the position of protonation is the carbon atom substituted by $-\text{SiMe}_3$ group. For the unsubstituted naphthalene the protonation in positions 1 and 4 is preferential.

The comparison also involves the results of calculations for $-\text{CMe}_3$ substituted naphthalenes. According to the Hoijsink's equation, the nucleophile centres of the anion radicals of these compounds correspond to positions 5 and 8 (designated by asterisks in the Figure) if the quantumchemical parameters of the $-\text{CMe}_3$ group are chosen as described previously [6].

The reliability of our quantumchemical estimation on the rates of the particular reaction steps are supported by ESR experimental results [17] according to which the ESR spectrum of the protonated radical cannot be observed.

For anthracene and phenanthrene derivatives the protonation in positions 9 and 10 is preferential.

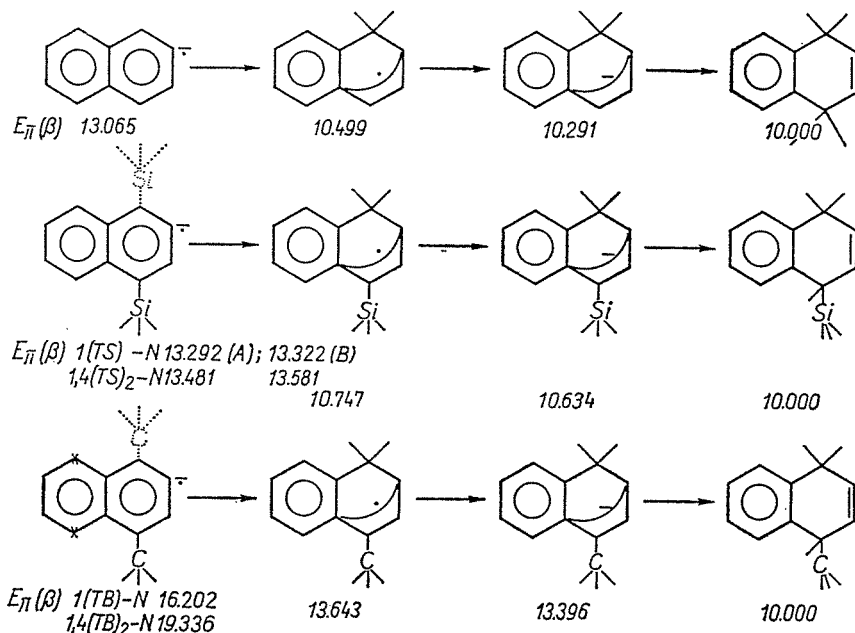


Fig. 8. Change of localization energy during protonation of naphthalene derivatives

Our quantumchemical results confirm HOIJTINK's theory [8] about the increased electron affinity of $\text{ArH}\cdot$. The value of ε_{m+1} for phenanthrene is -0.605 (in β units), for the radical protonated in position 9 is -0.213 ; the same quantities for anthracene and the 10-trimethylsilylanthracene hydroaromatic radical protonated in position 9 are -0.414 and -0.065 , respectively.

Conclusion

The HMO method appears to be suitable for the estimation of the position, rate-determining step and even the rate constant of the protonation process. Since the electronaffinity of the $\text{ArH}\cdot$ radical is lower than that of the initial compound, a positive shift is expected concerning the half-wave potentials of the polarograms recorded in DMF-water system. The observed negative shift presumably can be explained by the formation in irreversible reactions of secondary protonated products, the electronaffinity of which is lower than for the corresponding unsubstituted compound. This reasoning is supported by HOIJTINK's observation [8] according to which the process and final products of the protonation may be different depending on the field strength of the double layer of the electrode. During this process hydroaromatic compounds likely to be reduced in more negative potentials may be formed.

Summary

Several trimethylsilyl substituted naphthalene, anthracene and phenanthrene derivatives were investigated by d. c. polarography. The $-\text{SiMe}_3$ substitution caused a positive shift in the half-wave potentials compared to the unsubstituted and analogous $-\text{CMe}_3$ substituted compounds. A $d-\pi^*$ interaction was accepted to interpret this phenomenon. Logarithmic analysis of the polarograms showed the first step to be reversible. The polarograms recorded in the presence of water indicated a negative shift if the half-wave reduction potentials, attributed to lower electronaffinity species formed during irreversible reactions. The protonation mechanism of radical anions was investigated by HMO calculation.

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