

CORRELATION AND QUANTUM-CHEMICAL INTERPRETATION OF ELECTROCHEMICAL REDUCTION OF SUBSTITUTED β -CHLOROVINYL KETONES

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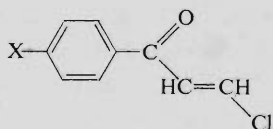
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p-Substituted phenyl-2-chlorovinyl ketones undergo two-electron reduction at mercury dropping electrode in 0.1M-H₂SO₄/CH₃OH medium. Localization energy calculations have shown the carbon-halogen bond to be the reaction centre in these molecules containing three potential reaction centres; in accordance with results of preparative electrolysis the first reaction step consists in reductive splitting off of the halogen. The half-wave potential values of individual derivatives correlate successfully with the calculated values of localization energies; the deviations found with the non-substituted and phenylsubstituted derivatives differing from the other compounds by magnitude of their π electron system are ascribed to the approximations involved in the simple HMO method.

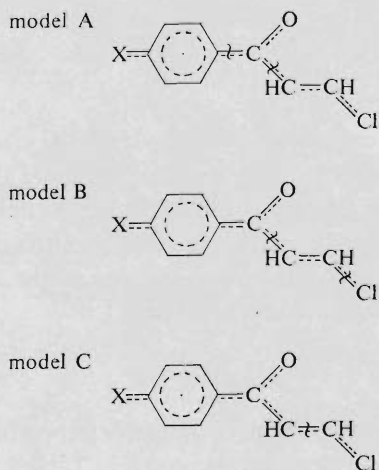
Hush and coworkers¹ dealt with a possibility of rigorous quantum-chemical interpretation of electrochemical splitting of carbon-halogen bond with the use of semiempirical methods (CNDO/2). They also discussed possibilities of calculation of rate constants of a number of electrode processes involving a bond cleavage. However, most of the papers published so far dealing with quantum-chemical interpretation of electrochemical reductions accompanied by bond cleavage use the HMO method for the same purpose. Čársky and coworkers² considered the probable reaction centre of polarographical reduction of *p*-substituted benzonitriles to be the atom with the maximum density of unpaired electron in anion radical of the corresponding molecule. This estimate agrees with experimental results in most cases. Similar approach was applied to interpretation of electrochemical reduction of aromatic and heterocyclic halogen derivatives³⁻⁵. Berdnikov and coworkers⁶ interpreted a polarographic reduction course of vinylsulfonyl chloride and styrylsulfonyl chloride on the basis of relative decrease of bond orders on accepting an electron in the LFMO. In our previous paper⁷ we dealt with correlation of electrochemical reduction potentials of halogen derivatives of benzene and biphenyl. We showed that, within the π electron approach, the reduction potentials can be correlated with the Wheland localization energies. A suitable model of the transition state of this irreversible reaction is represented by a system in which the carbon-halogen bond being split is excluded from conjugation and becomes centre of nucleophilic attack by electron. On the basis of these findings a mechanism of the electrode process was then postulated.

In the present paper we deal with electrode processes involving more complex halogen derivatives containing several centres accessible for electrode reactions.

The substances studied are aryl-2-chlorovinyl ketones of the following type:



Considering an attack by electron, these molecules contain three potential reaction centres which are known to undergo cathodic reduction in other compounds: carbonyl group, "double" bond of vinyl group, and the terminal carbon-halogen bond. Formation of the activated complex molecule-electrode during polarographic reduction is accompanied by interruption of conjugation between the reaction centre and the rest of the molecule. Activation energy of this process (within the HMO scheme) can be expressed by the Wheland localization energy which is defined as a difference of sum of π electron energies of the fragments formed by the interruption of the conjugation and π electron energy of the intact molecule. Models of the transition states corresponding to reductions at the individual theoretically possible reaction centres will be denoted as A, B, and C, respectively (Scheme 1). Electrons of the conjugated system of the molecule can be divided among the fragments formed by the interruption of conjugation in different ways. In this paper the index in symbols of localization energy (A, B or C) denotes the respective model, whereas the superscript (0 or +) denotes the π electronic charge of the fragment attacked by electron. At the same time, the fragment containing the benzene nucleus carries the opposite charge. On the basis of the calculated values of localization energies we try, in a further part, to determine the reaction centre of polarographical reduction and to find



SCHEME 1

correlation relation between half-wave potential of the polarographical reduction and the quantum-chemical characteristics of these molecules, making use of the results given in the previous paper⁷. The criterion of correctness of the chosen model is the lowest value of localization energy and, furthermore, correspondence of the calculated correlation to physical reality, *i.e.* that in a series of substituted derivatives a higher value of localization energy corresponds to a more negative potential. Results of this theoretical study are confronted with experimental results of study of electrochemical reduction course of these compounds⁸.

EXPERIMENTAL

Reagents. The compounds I to IX (Table I) were prepared by the known procedure of addition of aroyl chlorides to acetylene⁹ or by reaction of the corresponding 2-hydroxy ketones with thionyl chloride^{10,11}.

The other reagents used were commercial chemicals of *p.a.* grade; methanol was distilled under inert gas.

Polarography. The polarographical curves were recorded with a polarograph Radelkis OH 105. Methanolic solutions 0.1M-H₂SO₄ or 0.1M-LiClO₄ served as basic electrolytes. The depolarizer concentration was 10⁻³ mol l⁻¹, the half-wave potentials relate to aqueous saturated calomel electrode.

CALCULATIONS

The quantum-chemical calculations were carried out by the standard program for the HMO method using the computers Minsk 22 and Tesla 200. The regression equations and the correlation coefficients R were calculated by the least squares method. The used values of correction parameters of coulombic and resonance integrals are given in Table II.

RESULTS

Electrochemical Data

For correlation with the calculated quantum-chemical characteristics we used the half-wave potentials measured in the medium 0.1 mol l⁻¹-H₂SO₄/CH₃OH. These data were preferred to the potentials measured in the unbuffered LiClO₄ medium where the course of the electrode reaction or subsequent reactions can be accompanied by uncontrolled pH changes in the close vicinity of the electrode. The respective values of half-wave potentials are given in Table I.

Localization Energies

The calculated values of localization energies corresponding to nucleophilic attack of three potential reaction centres are also given in Table I for the individual models (Scheme 1) and for various charges of the attacked rest of the molecule.

DISCUSSION AND CONCLUSIONS

If the electron is considered to attack a neutral fragment, then the linear regression of the half-wave potentials with the localization energies results in the following

TABLE I

Half-wave potentials of polarographical reduction in 0.1M-H₂SO₄/CH₃OH and localization energies W (in $-\beta$ units) of p -X-phenyl-(2-chlorovinyl) ketones

Compound	X	$-E_{1/2}$, mV	Model A		Model B		Model C	
			W_A^0	W_A^+	W_B^0	W_B^+	W_C^0	W_C^+
I	H	445	0.9620	3.5800	0.5512	1.9371	1.7071	1.2228
II	CH ₃	460	0.9750	3.5930	0.5482	1.9619	1.7059	1.2332
III	C ₂ H ₅	463	0.9750	3.5930	0.5482	1.9619	1.7059	1.2332
IV	CH ₃ O	480	0.9809	3.5989	0.5471	1.9711	1.7038	1.2377
V	F	453	0.9705	3.5885	0.5493	1.9550	1.7071	1.2298
VI	Cl	419	0.9663	3.5843	0.5503	1.9454	1.7070	1.2263
VII	Br	413	0.9652	3.5832	0.5504	1.9429	1.7067	1.2254
VIII	I	410	0.9647	3.5827	0.5506	1.9416	1.7067	1.2257
IX	C ₆ H ₅	433	0.9713	3.2939	0.5497	1.8944	1.6974	1.2264

TABLE II

Correction parameters of coulombic (h_X) and resonance (k_{XY}) integrals

X	h_X	X—Y	k_{XY}
C	0	C—C	1.0
Cl	2.0	C—Cl	0.4
O (carbonyl)	1.0	C=O	1.0
O (ether)	2.0	C—O	0.8
F	3.0	C—F	0.7
Br	1.5	C—Br	0.3
I	1.3	C—I	0.25
CH ₃ (heteroatomic model) ^a	2.0	C—Me	0.7
		O—Me	0.6

^a The ethyl derivative was calculated with the same parameters.

relations (W in $-\beta$ units, $E_{1/2}$ in mV):

$$E_{1/2} = -3\,210W_A^0 + 2\,762, \quad R = 0.807$$

$$E_{1/2} = 13\,470W_B^0 - 7\,843, \quad R = 0.782$$

$$E_{1/2} = 1\,292W_C^0 - 2\,644, \quad R = 0.126$$

These dependences do not correspond to experimental results, since a higher localization energy corresponds to a higher activation energy; thus the localization energy should increase with a shift of the half-wave potential towards more negative values. This presumption is fulfilled only with the model A which concerns the electron attack at carbonyl group. This model, however, does not agree with the lowest values of localization energies. On the contrary, in the cases presuming the attacks of the multiple bond and carbon-halogen bond (the models B and C, respectively) the lower activation energy would correspond to a more negative value of the half-wave potential, which is in antagonism with the basic presumption of this theory. The experimental results are better interpreted by a model presuming decomposition of the conjugated system into charged fragments. In this case linear regressions of the half-wave potentials with the corresponding localization energies gave the following dependences:

$$E_{1/2} = -2\,321W_A^+ + 7\,888, \quad R = 0.710$$

$$E_{1/2} = -2\,476W_B^+ + 4\,397, \quad R = 0.995$$

$$E_{1/2} = -5\,862W_C^+ + 6\,769, \quad R = 0.979.$$

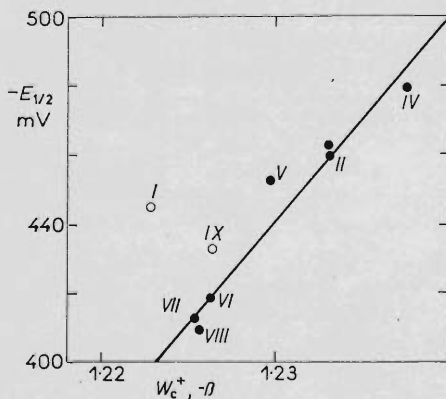


FIG. 1

Dependence of half-wave potentials on localization energies for the attack of the C—Cl fragment carrying positive charge (the derivatives are denoted as in Table I)

(With the non-substituted molecule *I* and the *p*-phenyl derivative *IX* deviations were observed from the behaviour of the other seven compounds. These deviations are most probably due to the difference between magnitude of electron systems of the compounds *I* and *IX* and those of the other seven compounds, *i.e.* in the set of the compounds *I* to *IX* the parallelity of properties of the compounds does not reach such a degree which is necessary for the HMO treatment. Therefore, the correlations of the half-wave potentials with the localization energies presuming the attack of the fragment with negative charge were calculated in the set of seven compounds *II* to *VIII*).

The lowest value of localization energy corresponds to the model C presuming the attack of carbon-halogen bond. Dependence of the half-wave potentials of the studied derivatives on the localization energy (corresponding to attack of the electron on the positive fragment of C-Cl bond with subsequent splitting off of the halogen) is given in Fig. 1.

Hence, out of the three possibilities of the attack of chlorovinyl ketone by electron that of the attack of C-Cl bond is most probable, because it is connected with the least energy requirements. This conclusion is also supported by the fact that the calculated maximum density of the unpaired electron in the anion radicals of the molecules studied is concentrated just at the carbon atom carrying the chlorine atom. Finally this conclusion also agrees with experimental results, the main products of preparative electrolysis⁸ with controlled potential being the compounds of the types $\text{RCOCH}=\text{CH}-\text{CH}=\text{CHCOR}$ and $\text{RCOCH}_2\text{CH}=\text{CHCH}_2\text{COR}$.

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