

## CORRELATION OF ELECTROCHEMICAL AND QUANTUM CHEMICAL DATA FOR REDUCTION OF HALOGEN DERIVATIVES OF BENZENE AND BIPHENYL

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Electrochemical splitting of the  $sp^2$  hybrid carbon-halogen bond was chosen as a typical example of an irreversible electrode reaction. It was shown in the series of chloro derivatives of benzene and biphenyl and bromo derivatives of benzene that the correlation of the electrochemical reduction potentials with the energies of the lowest unoccupied  $\pi$ -orbital are in these cases not physically grounded, whereas correlations with quantum-chemical parameters characterizing the carbon-halogen bond turned out to be real. Most suitable is the correlation with Wheland's localization energies calculated with the assumption of separating the carbon-halogen group from the total delocalized  $\pi$ -electron system in forming the transition state.

The study of the relations between reactivity of organic compounds on an electrode and their structure has moved from empirical correlations, expressed with the aid of empirical constants characterizing various substituents<sup>1</sup>, toward correlations with molecular parameters calculated by quantum chemical methods. The authors, beginning with Maccoll<sup>2</sup>, mostly correlated the reduction or oxidation potentials with energies of the frontier orbital (highest occupied (HOMO) in the case of oxidation, or lowest free orbital (LFMO) in the case of reduction). Several assumptions have been used: *a*) According to Koopmans' theorem<sup>3</sup>, the energies of these orbitals are close to the ionization potentials or electron affinities of the molecules. *b*) The electrochemical reduction or oxidation potential is determined by the ionization potential or the electron affinity, *i.e.*, it is a thermodynamic quantity. This implies that the electrode process is reversible. *c*) The properties and the behaviour of a molecule during an electrode reaction can be derived from the properties of the isolated molecule in the ground state (*i.e.*, the solvation of the molecule, the changes in the strong electrostatic field of the electrode or other changes play no role).

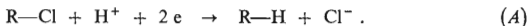
In a large number of cases, the validity of a linear relationship between polarographic half-wave potentials of reduction and LFMO energies was proved for series of structurally related compounds (*e.g.*, benzenoid and conjugated hydrocarbons, aromatic aldehydes, pyridine derivatives, aromatic nitrocompounds). Although the general validity of the conditions (*b*) and (*c*) cannot be *a priori* assumed, the validity of the mentioned correlations is an evidence that eventual changes of the properties of the molecules in the electrode interface were in the studied reaction series either constant or proportional to the correlated quantity. In a number of other cases, however, the energy of the frontier orbital is not quite characteristic for the behaviour of the molecule on the electrode; for some of these cases, we derived the following equation for the reduction half-wave potential, based on the concept about interaction between the molecule and the electrode during the formation of the transition state:

$$E_{1/2} = a + b\varepsilon_{\text{LFMO}} + cq_r + d\pi_{\text{rr}}, \quad (1)$$

where  $\epsilon_{\text{LFMO}}$  denotes energy of the lowest free orbital,  $q_r$  charge in the reaction center of the molecule,  $\pi_{rr}$  autopolarization of this center, and  $a, b, c, d$  are constants. This equation was verified on reduction of molecules with a rather complicated electron structure such as pyrimidines, pteridines, *etc.*<sup>4</sup>

All the mentioned cases involved the reduction of molecules with a  $\pi$ -electron system, where in the first, potential-determining step the electron is accepted into the lowest free  $\pi$ -orbital. During reduction in nonaqueous media, a more or less stable  $\pi$ -radical (anion radical) is formed transitionally, whose existence was in many cases proved by the electron spin resonance<sup>5</sup>.

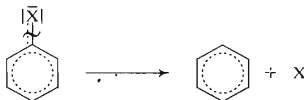
In the present work we attempt to correlate the electrochemical data of halogen derivatives (their  $E_{1/2}$  values or potentials of their cathodic peak,  $E_p$ , in cyclic voltametry) with their quantum chemical characteristics as a case of totally irreversible reaction with splitting of the  $\sigma$ -bond. It is known<sup>6</sup> that the reduction of aromatic halogen derivatives proceeds much more slowly than that of aliphatic halogen derivatives; the reduction is facilitated by the presence of other halogen atoms in the molecule and increasing polarity of the carbon-halogen bond. The half-wave potential is independent of pH, hence protons do not participate in the potential-determining step. The overall reaction scheme can be expressed as follows:



The results of published work dealing with this field were discussed recently by Beland and coworkers<sup>7</sup>. It follows that attempts to correlate the reduction potentials of halogen derivatives with the energies of  $\pi$ -orbitals do not lead to satisfactory results. The authors correlated the reduction potentials of chlorobenzenes with the energies of the lowest free  $\sigma$ -orbitals calculated by the CNDO/2 method. We assume again that the properties of compounds with a conjugated  $\pi$ -electron system can be most simply explained on the basis of the characteristics of just this system, however in the given case we do not consider only the energetic parameters of the isolated molecule in the ground state but during interaction with the electrode. Since the simple Hückel molecular orbital method is most accessible and in our case physically plausible, we made use of it in the present work. Since we have to deal with irreversible reactions whose potential is determined by kinetic rather than thermodynamic parameters, we are concerned also with relations between reduction potentials and quantum-chemical quantities determining the reaction rate, *i.e.* charges in the potential reaction centers, bond orders, and localization energies.

According to Wheland<sup>8</sup>, the  $sp^2$  hybridization of an atom in the reaction center changes during formation of the activated complex to  $sp^3$  hybridization, whereby it is disconnected from conjugation. The localization energy  $W$ , which is a measure of the activation energy of the given reaction, is given by the difference of the  $\pi$ -electron energies of the two fragments thus formed and the  $\pi$ -electron energy of the original molecule. For the electrode reaction of chloro derivatives, the molecule can split

into fractions in the following two ways:



SCHEME 1

The total number of  $\pi$ -electrons can be divided between these two fractions in different ways. The calculated localization energies ( $W_1$  for Scheme 1 and  $W_2$  for Scheme 2) will be denoted by a superscript corresponding to the charge of the larger fraction. Based on analysis of the results, it is possible to propose a more detailed mechanism of the reductive splitting of the carbon-halogen  $\sigma$ -bond on the electrode.

#### Electrochemical Data

Electrochemical reduction potentials of the halogen derivatives were taken from the literature<sup>9,10</sup>. Current-voltage curves of the chloro derivatives of benzene and biphenyl<sup>9</sup> were obtained by cyclic voltametry in 0.1M-N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Br in the medium of dimethyl sulfoxide, the depolarizer concentration was  $5 \cdot 10^{-4}$ M. The reduction potentials were determined from the differentiated  $i$ - $E$  curve against s.c.e. The reduction mechanism was checked by preparative electrolysis, the products were analysed by gas chromatography. It was found that the reduction of the studied compounds proceeds in steps with gradual splitting off of the Cl atoms. Two series of compounds were thus followed: 1) Chloro derivative of benzene — the relevant data are in Table I, and 2) chloro derivatives of biphenyl — the relevant data are in Table II; the position of the Cl atom eliminated in the first step of the cathodic process is also given.

The polarographic half-wave potentials for reduction of substituted bromobenzenes (series 3) were measured in dimethylformamide<sup>10</sup> containing 0.2M-N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>Br and the depolarizer concentration was  $5-11 \cdot 10^{-4}$ M; the relevant data are given in Table III.

#### Calculations

Quantum-chemical calculations were carried out on a Minsk 22 computer with the use of a standard program for the HMO method. Regression equations and correlation coefficients  $R$  were calculated by the least squares method. The following values of coulombic and resonance integrals were used for the heteroatoms:

$$\begin{aligned} \alpha_{Cl} &= \alpha_C + 2\beta_{CC}, & \beta_{C-Cl} &= 0.4\beta_{CC}, \\ \alpha_{Br} &= \alpha_C + 1.5\beta_{CC}, & \beta_{C-Br} &= 0.3\beta_{CC}. \end{aligned} \quad (2)$$

#### RESULTS

The quantum-chemical parameters for the three studied types of compounds are summarized in Tables I-III, namely charges on the potential reaction centers ( $q_C, q_{Cl}, q_{Br}$ ), HMO orders of the bonds ( $p_{C-Cl}, p_{C-Br}$ ), and localization energies.

TABLE I

Electrochemical Data and Calculated Quantum-Chemical Parameters for the First Series

Localization energies (in  $-\beta$  units) calculated for the center with the highest positive charge on the C atom are given in parentheses,  $r$  denotes position of the atom eliminated in the first step of the cathodic process.

No	Compounds	$r$	$-E_p, V$	$q_C$	$q_{Cl}$	$\rho_{C_{Cl}}$	$\epsilon_{LFMO}$	$W_1$	$W_2^0$	$W_2^-$	$W_2^+$
I	chlorobenzene	1	2.440	0.0121	0.0152	0.1228	1.0000	0.049	2.508	2.431	2.585
II	1,2-dichlorobenzene	1	2.218	0.0020	0.0150	0.1213	0.0090	0.048	2.495	2.444	2.551
III	1,3-dichlorobenzene	1	2.197	0.0126	0.0152	0.1213	1.0888	0.049	2.509	2.432	2.586
IV	1,4-dichlorobenzene	1	2.199	0.0047	0.0149	0.1215	1.0000	0.049	2.502	2.451	2.552
V	1,2,3-trichlorobenzene	1	1.962	0.0024	0.0149	0.1213	1.0259	0.049	2.497	2.446	2.548
VI	1,2,4-trichlorobenzene	2	1.997	0.0026	0.0149	0.1200	1.0113	0.048	2.496	2.445	2.547
VII	1,3,5-trichlorobenzene	1	1.985	0.0132	0.0152	0.1230	1.0267	(0.048	2.549	2.499	2.598)
VIII	1,2,3,4-tetrachlorobenzene	2	1.764	-0.0078	0.0147	0.1198	1.0261	0.048	2.486	2.461	2.511
IX	1,2,4,5-tetrachlorobenzene	1	1.808	-0.0048	0.0147	0.1201	1.0178	(0.048	2.491	2.466	2.516)
X	1,2,3,5-tetrachlorobenzene	1	1.794	0.0050	0.0149	0.1214	1.0268	0.048	2.490	2.465	2.515
XI	pentachlorobenzene	2	1.573	-0.0150	0.0145	0.1185	1.0352	(0.048	2.502	2.451	2.553)
XII	hexachlorobenzene	1	1.332	-0.0145	0.0145	0.1186	1.0524	(0.048	2.481	2.481	2.481
								0.047	2.481	2.481	2.481

In the first series we made the common correlation of  $E_p$  with  $\epsilon_{LFMO}$  (Fig. 1). Of the mentioned three parameters, only the dependence of  $E_p$  on  $p_{C-C1}$  has a trend corresponding to physical reality, however with a low correlation coefficient,

$$E_p = -161.92p_{C-C1} + 17.64; \quad R = 0.819, \quad (3)$$

whereas  $q_{C1}$  remains practically constant with all compounds. Further a linear correlation with two variables was considered, namely with  $\epsilon_{LFMO}$  and  $q_C$ , and the following regression equation was obtained:

$$E_p = -16.47 + 14.28\epsilon_{LFMO} - 12.57q_C; \quad R = 0.965. \quad (4)$$

Although the correlation coefficient is here higher, the slope does not correspond to physical reality. The corresponding localization energies  $W_1$ ,  $W_2^0$ ,  $W_2^+$ , and  $W_2^-$  calculated according to the concept about the structure of the transition state (Schemes 1 and 2) are given in Table I. Since with the compounds VI, VIII, X, and XI the experimentally found position of the reaction center does not coincide with the position of the C atom bearing the highest positive charge, the localization energies  $W_2^{0,+,-}$  were calculated also for this atom, and both values are given in Table I for these compounds. The value of  $W_1$  is in the whole reaction series practically

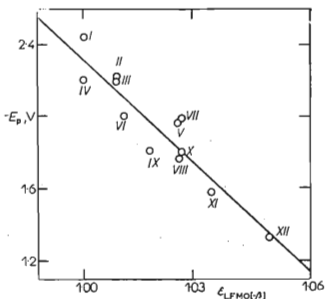


FIG. 1

Dependence of  $E_p$  on  $\epsilon_{LFMO}$  in the First Series

$$E_p = 18.94\epsilon_{LFMO} - 21.26; \quad R = 0.32.$$

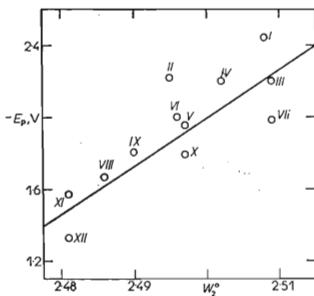


FIG. 2

Dependence of  $E_p$  on  $W_2^0$  in the First Series

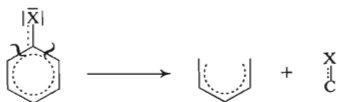
$$E_p = -25.66W_2^0 + 62.12; \quad R = 0.832.$$

constant; relations between the reduction potentials and localization energies of the general form

$$E_p = a + bW_2^{0,+,-} \quad (5)$$

are with the results for the other series summarized in Table IV. This shows that the found correlation with  $W^-$  is only apparent since on physical grounds the sign of the  $b$  value in (5) should be negative. The found proportionality between  $W^0$  and  $W^+$  results in correlations with both of them, however the correlation with  $W_2^0$  (Fig. 2) is more easily interpreted as shown in the discussion below.

In an attempt to correlate the reduction potentials in the second series, the dependences were differentiated according to the position of the splitted bond with respect to the position of the bond of both benzene rings. Therefore, we divided the compounds of the second series into five classes:



SCHEME 2

2a reaction center in *o*-position: XIII, XVI, XVII, XXII

2b reaction center in *m*-position: XIV, XVIII-XXI, XXVII

2c reaction center in *p*-position: XV, XX, XXIV, XXVI, XXXI

2d reaction centers in both *p*-positions: XIX, XXIII, XXV, XXX

2e reaction centers in *o*- and *p*-positions: XXVIII, XXIX.

This sequence is observed in Table II. As in the first series, it is possible to find a certain relation with the order of the splitted bond with various correlation coefficients (0.891 for class 2a, 0.615 for 2b, and 0.950 for 2c). Correlations between the peak potentials and localization energies according to Eq. (5) are given in Table IV; a typical correlation between  $E_p$  and  $W_2^0$  is shown in Fig. 3. A similar interdependence of different types of the localization energy as in the first series and differentiation of the correlations into classes according to the position of the reaction center is observed.

In the third series, the correlations with the charges and orders of the bonds (Table III) have a similar character as in the preceding two series but the correlation coefficients are too low ( $R = 0.680$  for correlation with  $p_{C-Br}$  and 0.648 for correlation with  $q_C$ ); the charge on the Br atom,  $q_{Br}$ , is practically constant in the whole series. The mentioned coefficients were calculated with exclusion of the *m*-derivatives, which deviate from the graphical correlation. The values of the localization energies

for the individual models of the transition state (Table III) imply similar dependences as in the preceding series (Table IV). Fig. 4 represents a typical relation between the half-wave potential and  $W_2^0$ .

## DISCUSSION AND CONCLUSIONS

According to our results, more or less close relationships exist in the studied reaction series between the reduction potentials and energies of the lowest unoccupied orbital. The same applies for relations between reduction potentials and the charge on the C atom bearing halogen. The electron acceptance as a nucleophilic attack should be easier when the charge in the reaction center is more positive, and the necessary energy should be directly proportional to the LFMO energy. However, the slopes of these dependences in reduction of aromatic halogen derivatives have an opposite sign and hence these dependences appear to be only empirical and not physically substantiated. It follows that the dependences valid generally for reversible reductions of conjugated compounds do not hold for irreversible splitting of the  $\sigma$ -bonds. That the order of the carbon-halogen bond can be correlated with the corresponding

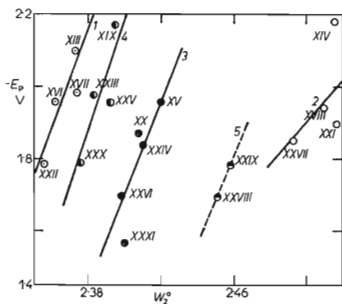


FIG. 3

Dependence of  $E_p$  on  $W_2^0$  in the Second Series

1 Class 2a,  $E_p = -12.83W_2^0 + 28.41$ ,  $R = 0.863$ ; 2 class 2b,  $E_p = -6.06W_2^0 + 13.26$ ,  $R = 0.602$ ; 3 class 2c,  $E_p = -19.70W_2^0 + 45.61$ ,  $R = 0.934$ ; 4 class 2d,  $E_p = -13.72W_2^0 + 30.78$ ,  $R = 0.921$ ; 5 class 2e,  $E_p = -15.00W_2^0 + 33.09$ .

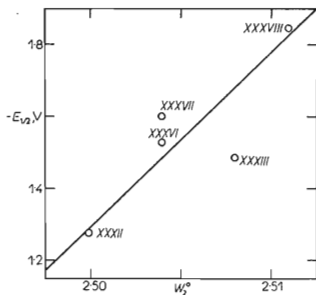


FIG. 4

Dependence of  $E_{1/2}$  on  $W_2^0$  in the Third Series (without *meta*-derivatives)

$E_p = -41.31W_2^0 + 101.95$ ,  $R = 0.847$ .

reduction potentials suggests a significant role of the parameters related to this bond for judging the electrochemical reducibility of the compounds in question.

The most suitable correlations are those with the localization energies for the transition state model according to Scheme 2, *i.e.*, separation of the carbon-halogen bond from the conjugated system. The correlation coefficients and slopes of the

TABLE II

Electrochemical Data and Calculated Quantum-Chemical Parameters for the Second Series

The value of  $r$  denotes the position of the Cl atom eliminated in the first step of the cathodic process. If two Cl atoms are splitted off simultaneously at the same potential, static characteristics of both reaction centers (A, B) are given.

No	Compound	$r$	$-E_p$ , V
<i>XIII</i>	2-chlorobiphenyl	2	2.097
<i>XVI</i>	2,3-dichlorobiphenyl	2	1.956
<i>XVII</i>	2,4-dichlorobiphenyl	2	1.983
<i>XXII</i>	2,3,5-trichlorobiphenyl	2	1.783
<i>XIV</i>	3-chlorobiphenyl	3	2.108
<i>XVIII</i>	2,5-dichlorobiphenyl	3	1.942
<i>XXI</i>	3,5-dichlorobiphenyl	3	1.897
<i>XXVII</i>	2,3,4-trichlorobiphenyl	3	1.852
<i>XV</i>	4-chlorobiphenyl	4	1.956
<i>XX</i>	3,4-dichlorobiphenyl	4	1.871
<i>XXIV</i>	2,4,5-trichlorobiphenyl	4	1.837
<i>XXVI</i>	3,4,5-trichlorobiphenyl	4	1.696
<i>XXXI</i>	pentachlorobiphenyl	4	1.566
<i>XIX</i>	2,6-dichlorobiphenyl	2,6	2.107
<i>XXIII</i>	2,3,6-trichlorobiphenyl	2,6	1.973
<i>XXV</i>	2,4,6-trichlorobiphenyl	2,6	1.966
<i>XXX</i>	2,3,5,6-tetrachlorobiphenyl	2,6	1.787
<i>XXVIII</i>	2,3,4,5-tetrachlorobiphenyl	2,4	1.679
<i>XXIX</i>	2,3,4,6-tetrachlorobiphenyl	2,4	1.784

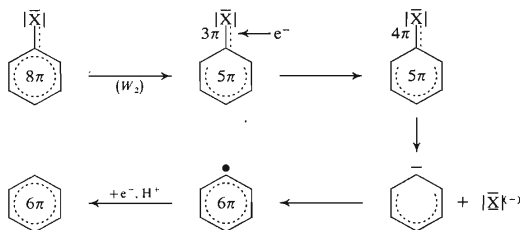


regression lines for the individual reaction series and transition state models with differently localized  $\pi$ -electron charge on the bond torso are given in Table IV. From this it follows that the slope of the correlation with the energies  $W^-$  is not in accord with the idea that a higher localization energy means a higher activation energy and hence a more difficult reduction, whereas the correlation with the values of  $W^0$

TABLE II  
(Continued)

	$q_C$	$q_{Cl}$	$p_{CCl}$	$W_2^0$	$W_2^-$	$W_2^+$
	0.0137	0.0159	0.1255	2.373	2.296	2.450
	0.0032	0.0157	0.1239	2.362	2.306	2.418
	0.0146	0.0159	0.1256	2.374	2.297	2.451
	-0.0038	0.0155	0.1227	2.356	2.321	2.391
	-0.0120	0.0151	0.1226	2.516	2.439	2.593
	0.0049	0.0159	0.1214	2.510	2.460	2.562
	0.0126	0.0151	0.1227	2.517	2.440	2.594
	-0.0085	0.0146	0.1195	2.493	2.468	2.518
	0.0130	0.0155	0.1241	2.420	2.343	2.497
	0.0032	0.0153	0.1226	2.408	2.352	2.464
	0.0041	0.0153	0.1227	2.410	2.354	2.465
	-0.0068	0.0151	0.1211	2.398	2.363	2.433
	-0.0051	0.0151	0.1213	2.400	2.365	2.435
A	0.0139	0.0159	0.1255	2.395	2.317	2.472
B	0.0139	0.0159	0.1255			
A	0.0034	0.0157	0.1239	2.383	2.325	2.440
B	0.0068	0.0157	0.1243			
A	0.0148	0.0159	0.1256	2.392	2.315	2.469
B	0.0148	0.0159	0.1256			
A	-0.0036	0.0155	0.1227	2.376	2.338	2.418
B	-0.0036	0.0155	0.1227			
A	-0.0030	0.0155	0.1228	2.451	2.427	2.475
B	-0.0059	0.0151	0.1211			
A	0.0042	0.0157	0.1240	2.458	2.419	2.497
B	0.0049	0.0153	0.1228			

and  $W^+$  has the right slope. That scheme appears more probable which corresponds to an electron attack on the carbon-halogen bond as suggested by the relation with the order of this bond. From the calculation of the localization energies it is also possible to predict the position of the splitted carbon-halogen bond in the case of polysubstituted derivatives, for example of the compounds VI, VIII, X, and XI in Table I. The mechanism of the electrode process can be hence formulated as



SCHEME 3

It can be concluded that the reduction potentials of conjugated halogen derivatives cannot be determined from the energies of the lowest free  $\pi$ -orbitals (in Fig. 1 the higher orbital energy is in disagreement with the easier reducibility of the molecule), but they can be expressed on the basis of the simple HMO method from the calculated  $\pi$ -localization energies necessary to form a substrate-electrode complex.

TABLE III

Half-Wave Potentials and Calculated Quantum-Chemical Characteristics for the Third Series  
Localization energies are in  $-\beta_{CC}$  units.

No	Compound	$-E_{1/2}^0$	$q_C$	$Q_{Br}$	$p_{CBr}$	$W_1$	$W_2^0$	$W_2^-$	$W_2^+$
XXXII	<i>o</i> -dibromobenzene	1.28	0.0001	0.0119	0.1078	0.032	2.500	2.462	2.539
XXXIII	<i>o</i> -bromochlorobenzene	1.49	-0.0030	0.0118	0.1073	0.032	2.508	2.466	2.530
XXXIV	<i>m</i> -dibromobenzene	1.40	0.0076	0.0120	0.1088	0.032	2.511	2.453	2.569
XXXV	<i>m</i> -bromochlorobenzene	1.41	0.0078	0.0122	0.1088	0.033	2.511	2.453	2.569
XXXVI	<i>p</i> -dibromobenzene	1.53	0.0019	0.0119	0.1079	0.032	2.504	2.466	2.543
XXXVII	<i>p</i> -bromochlorobenzene	1.60	-0.0002	0.0118	0.1075	0.032	2.504	2.462	2.535
XXXVIII	bromobenzene	1.85	0.0072	0.0120	0.1088	0.033	2.511	2.511	2.569

TABLE IV

Correlation Coefficients  $R$  and Regression Slopes  $b$  for Correlation of Reduction Potentials of Aromatic Halogen Derivatives with Localization Energies  $W_2$  with Different Charge Distribution in Transition State

Series	Localization energy type					
	$W_2^0$		$W_2^+$		$W_2^-$	
	$R$	$b$	$R$	$b$	$R$	$b$
1	0.832	-25.66	0.791	-6.56	0.851	15.08
2a	0.863	-12.83	0.904	-4.08	0.944	10.59
2b	0.602	-6.06	0.628	-1.96	0.627	4.82
2c	0.934	-19.70	0.957	-6.76	0.991	20.00
2d	0.921	-13.72	0.903	-4.62	0.861	10.83
2e	—	-15.00	—	-4.74	—	8.75
3	0.847	-41.31	0.778	-10.85	0.462	16.14

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