

67. Comments on Empirical Correlations between Reduction Potential of Carbon-Halogen Bonds and NQR. Frequencies of Halogen Atoms in Organic Molecules

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Summary. An empirical linear correlation exists between nuclear quadrupole resonance frequencies of halogen nuclei (^{35}Cl , ^{79}Br , ^{127}I) and the polarographic reduction potentials in series of organic halides. In terms of electronic structure this is interpreted as a significant relationship between the average p -electron population at halogen atoms and the first vacant molecular orbital of halogenated molecules. On the basis of the present correlations conclusions are drawn about some controversial mechanistic aspects of the electroreduction of the carbon-halogen bond.

A linear relationship $f_{\text{NQR}} \sim E_{1/2}$ exists between nuclear quadrupole resonance frequencies (f_{NQR}) of halogen nuclei and irreversible half-wave potentials ($E_{1/2}$) of organic halides. Correlations are observed for chloro-, bromo- and iodo-derivatives (Fig. 1, 2 and 3, resp.); the regression coefficients are reported in the Table. In cases where line-splitting occurs in the NQR. spectrum an unweighted averaged value was taken over the observed frequencies with no consideration of either crystal field effects or non-equivalent molecular sites. When available, low temperature data were used¹⁾. The $E_{1/2}$ -values originate in various sources [2] and have sometimes been obtained in different supporting electrolytes: this results in an unavoidable increase of the data dispersion. In multi-waves polarograms only the first wave was taken into consideration; all the $E_{1/2}$ are referred to the saturated calomel electrode.

The present correlations show that there exists a highly significant relationship between the *average valence p-electron distribution* at halogen atoms and the first reduction potential of the molecules to which they are bonded. For a nucleus of spin 3/2 the resonance frequency of a crystalline sample is given by

$$f_{\text{NQR}} = \frac{e^2 Q}{2} q_{zz} \left[1 + \frac{\eta^2}{3} \right]^{1/2}$$

where q_{zz} is the principal component of the field-gradient tensor, and η , the asymmetry parameter, gives a measure of the asymmetry of the p -electron distribution at the halogen nucleus; other factors are constants. The axis of the p_z -atomic orbital of the halogen is conveniently chosen to lie along the direction of the bond to carbon. Furthermore, it can be shown that the field-gradients are related to the electronic structure by the simple expression [3]

$$q_{zz} = \left(n_z - \frac{n_x + n_y}{2} \right) q_0,$$

¹⁾ All the NQR. frequencies were taken from [1].

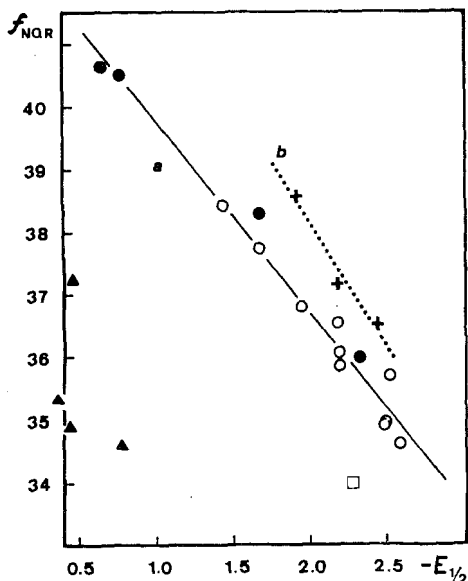


Fig. 1. Correlations between the NQR. frequencies (Mc/s) of ^{35}Cl and the polarographic reduction potentials $E_{1/2}$ (Volt) of C-Cl bonds. Compounds listed in the order of increasing absolute $E_{1/2}$ -values: ● {alkyl chlorides}: C_2Cl_6 , CCl_4 , CHCl_3 , CH_2Cl_2 , (\square CH_3Cl deviates); ○ {chlorobenzenes}: hexa-, penta-, (1, 2, 4, 5)-, (1, 2, 3)-, (1, 2, 4)-, (1, 3, 5)-, (1, 2)-, (1, 4)-, (1, 3)-, mono-; + {chloroolefines}: C_2Cl_4 , C_2HCl_3 and $\text{C}_2\text{H}_2\text{Cl}_2$; ▲ *m*-, *p*-, *o*-nitrochlorobenzene, *p*-chlorobenzaldehyde.

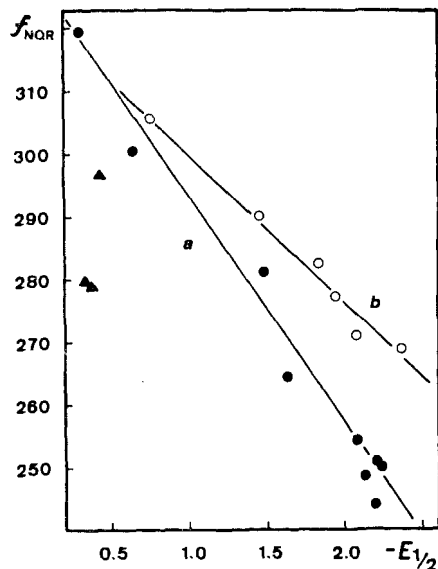


Fig. 2. Correlations between the NQR. frequencies (Mc/s) of ^{79}Br and the polarographic reduction potentials $E_{1/2}$ (Volt) of C-Br bonds. Compounds listed in the order of increasing absolute $E_{1/2}$ -values: ● {alkyl bromides}: CBr_4 , CHBr_3 , CH_2Br_2 , CH_3Br , $\text{Br}(\text{CH}_2)_5\text{Br}$, $\text{C}_2\text{H}_5\text{Br}$, cyclopentyl-Br, *n*- $\text{C}_3\text{H}_7\text{Br}$, *n*- $\text{C}_4\text{H}_9\text{Br}$; ○ {bromobenzenes}: hexa-, (1, 2, 4, 5)-, (1, 2)-, (1, 3)-, (1, 4)-, mono-; ▲ *m*-, *p*-, *o*-nitrobenzene.

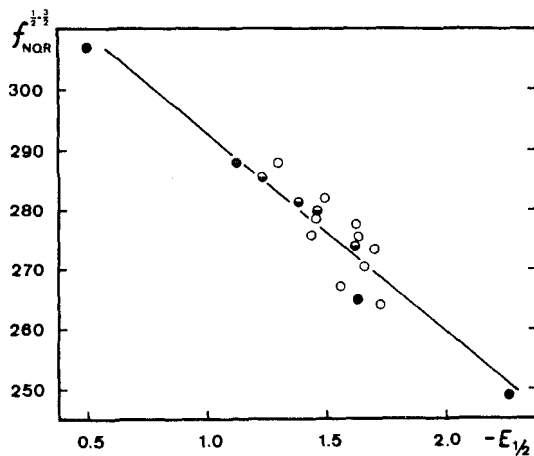


Fig. 3. Correlation between the NQR. frequencies ($3/2 \rightarrow 1/2$) (Mc/s) of ^{127}I and the polarographic reduction potential $E_{1/2}$ (Volt) of C-I bonds. Compounds listed in the order of increasing absolute $E_{1/2}$ -values: ● {alkyl iodides}: CHI_3 , CH_2I_2 , CHI_2 , *n*- $\text{C}_4\text{H}_9\text{I}$; ○ {iodobenzenes}: (1, 2)-, (1, 3)-, (1, 4)-, mono-; ○ {other aromatic iodo-compounds}: *p*- $\text{IC}_6\text{H}_4\text{NH}_3^+$, *p*- $\text{IC}_6\text{H}_4\text{COOH}$, *m*- $\text{IC}_6\text{H}_4\text{COOH}$, *o*- $\text{IC}_6\text{H}_4\text{OH}$, *o*- $\text{IC}_6\text{H}_4\text{NH}_2$, *m*- $\text{IC}_6\text{H}_4\text{OH}$, 4-iododiphenyl, *m*- $\text{IC}_6\text{H}_4\text{NH}_2$, *p*- $\text{IC}_6\text{H}_4\text{OH}$, *p*- $\text{IC}_6\text{H}_4\text{NH}_2$.

where q_0 is the field-gradient produced by one electron in a valence p-orbital, and the n 's are the electron populations in the respective p-orbitals. If the asymmetry parameters are small and the sum ($n_x + n_y$) is nearly constant within a group of related molecules, then the shifts in the frequencies f_{NQR} will be proportional to the changes in the p_z -electron population. These conditions are expected to be met in pure single bonds for most alkyl halides. In addition, MINDO-3 calculations [4a] show that these requirements also closely hold throughout the chlorobenzenes series [4b]; an experimental confirmation is to be found in the small values of the few measured asymmetry parameters. From the simplifying view-point just outlined, and considering that the core electrons density at the halogen is not likely to vary greatly, the variations in the total electron density at the halogen atom will be mainly due to changes in the valence p_z -electron population, for which f_{NQR} is a measure. This affords a useful way of looking at the empirical correlations: the greater the average electron density at the halogen atoms, the more difficult the reduction. This qualitative approach has a definite bearing on a controversial mechanistic point of the electrode process²⁾. Some authors have suggested a transition state geometry with the halogen end of the C–X dipole oriented away from the electrode, and a backside electron transfer as in a S_N2 displacement. Other investigators support instead the view that the C–X bond is oriented with the halogen atom nearest to the electrode surface. Our empirical relationships agree better with the latter view, where the penetration of the depolarisator into the double layer (penetration of which the transfer coefficient α is a measure) is expected to give rise to a repulsion energy which will increase (decrease of α) with the net electron density at the halogen atom³⁾.

In order that the electrode reaction occurs the potential must act across several energy barriers of which the greater will be rate determining [7]. The process of orientation of the electroactive species at the electrode surface is associated with a potential barrier which might become predominant when the C-halogen dipole is oriented opposite to the electric field, in which case the fraction αE of the potential favoring the electroreduction would be expected to vary in inverse order to the magnitude of the dipole. If one assumes that the electron transfer process requires the overlap of one metallic orbital with an antibonding molecular orbital [8] one can admit that the orbital interaction will increase with the electronegativity of the reaction centre (in the postulated model: the halogen atom) *i.e.* the contribution of the antibonding MO. will be larger in the transition state when the net charge on the halogen atom decreases. This approach also has a definite bearing on the expected magnitude of α [8].

It is not meant here that the few points just discussed definitely preclude the choice of another model for the electrode process. Inasmuch as quantum mechanical calculations [4b] show that a steady increase of the net average charge on chlorine atom(s)

²⁾ A detailed account of various mechanistic aspects of the electrode process is given in [5].

³⁾ A few additional remarks will serve to illustrate some aspects of the kinetic approach to the problem. For irreversible systems $E_{1/2}$ has been shown [6] to be proportional to $\ln(k_{t,h}^0 \cdot K)/\alpha n$ where $k_{t,h}^0$ is the specific rate constant of the heterogeneous electrode process, α is the transfer coefficient, n is the number of electrons involved in the activation step, and K encompasses parameters irrelevant to the present discussion. Furthermore, from the theory of absolute reaction rate the activation energy is proportional to $\ln k_{t,h}$.

is associated with a monotonous destabilization of the lowest vacant MO., and this fact might overrun the environmental energy increments of the chosen model.

Polychloroethylenes data are distributed along a line **b** which runs closely parallel to the main regression line **a** (Fig. 1). The following approximate reduction potentials (in Volt) are predicted for the experimentally non-reducible vinyl chloride: -3.3 , and 1,2-dichloroethylenes: -2.9 (*cis*); -2.8 (*trans*). The sometimes formulated statement that vinyl chlorides are more difficult to reduce than the corresponding saturated molecules is illustrated by the shift of the regression line towards negative potentials. It is noteworthy that the higher activation energy in the electron transfer process is not related to an increase of the electron density at the halogen atom since the asymmetry parameters of vinyl chloride and polychloroethylenes are substantially different from zero and π -bonding tends to place a positive charge on the halogen atom.

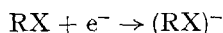
Ethyl chloride is not normally reducible within the available potential range; this is confirmed by a predicted $E_{1/2}$ of -3.3 Volt.

Allyl and benzyl chlorides, as well as benzylic geminal polyhalides, (not shown on Fig. 1), are more easily reduced than might be inferred from their observed NQR frequencies. This undoubtedly confirms the occurrence of an electrode mechanism different from the one associated with chlorobenzenes and alkylchlorides. The facile reduction of these so-called 'activated systems' is generally viewed as proceeding *via* a low energy transition state close to the resonance stabilized hydrocarbon radical as intermediate.

NQR measurements are less extensive for iodo-compounds than for the chloro- and bromo-derivatives; consequently we had to consider a more heterogeneous bulk of data. For instance, several iodobenzene derivatives are substituted by a group (*e.g.* OH or COOH) which brings about pH-dependence of the half-wave potential: it ensues an additional bias in some of the reported $E_{1/2}$ -values. Plots were made for the two transitions $f(3/2 \rightarrow 1/2)$ and $f(5/2 \rightarrow 3/2)$ of the iodine atom ($I = 5/2$); only the former correlation is reported in Fig. 3 since the information contained in the other one (see Table) is practically equivalent.

In terms of the electronic structure of the substrate, half-wave potentials can be related to the energy of the lowest unoccupied molecular orbital. Several other structural factors (*e.g.* steric interactions in the transition state), as well as experimental factors, may affect the observed half-wave potentials [9]. It is required that these factors do not vary substantially (or vary linearly with $E_{1/2}$) when changes in the electronic structure are correlated with half-wave potentials. Fortunately, experimental results show that these requirements are often fulfilled in series of related substances.

The primary rate-determining step of the overall two-electrons reduction of alkyl halides can be regarded as the irreversible formation of a metastable radical anion [7]:



Whether $(RX)^-$ is a true intermediate or merely a transition state complex is irrelevant to the present discussion since we assume that for related compounds the activation energy of the carbon-halogen bond breakage runs parallel to the energy of the lowest vacant orbital. It is seen in Fig. 1 that the aromatic compounds fit the same regression line as the saturated ones. This might be put forward as *experimental evidence*

of the initial addition of one electron to a sigma-type MO of the chlorinated aromatic molecules. This possibility had been formerly suggested by Fukui [11] on the basis of HMO-type calculations on saturated systems. At a higher level of sophistication, MINDO-3 calculations performed on chlorobenzenes fully confirm this view [4b]: ring substitution by one chlorine atom already lowers enough the energy of the first unfilled σ orbital to allow inversion with the lowest vacant π level. It is illuminating to see that the three chloro-nitro-benzenes (as well as the bromo-isologues) and *p*-chloro-benzaldehyde do not fit the main regression line. In these compounds conjugation with an adjacent unsaturated group stabilizes substantially the lowest vacant π level and no levels inversion occurs on ring substitution by one halogen atom: therefore the first electron is transferred into a π molecular orbital and the correlation breaks off.

According to Townes & Dailey's approximation [3] the ratio $f_{\text{NQR}}(\text{molecular})/f_{\text{NQR}}(\text{atomic})^4$ is a fair estimate of the p-electron deficiency ρ at a nucleus forming a pure single bond. By inserting this relationship in the empirical expression $E_{1/2} = B' \cdot f_{\text{NQR}} + A'$ the product $B' \cdot f_{\text{NQR}}(\text{atomic}) \approx \Delta E_{1/2}/\Delta \rho$ affords a measure of the 'susceptibility' of the reduction potential to a change in the average valence p-electron population at the halogen atom(s). The following values (Volt \cdot electron⁻¹) are obtained: 17.2 (chloro-compounds, average); 16.3 (chloro-benzenes); 15.9 (bromo-benzenes); 10.4 (alkyl bromides); 9.32 (iodo-compounds, average); 12.2 (iodo-benzenes). It is seen that these values parallel the electro-negativities of the halogen atoms.

Table. Regression coefficients of the linear correlations $f_{\text{NQR}}[\text{Mc/s}] = B \cdot E_{1/2}[\text{Volt}] + A$

Class of compounds	- B	A	s.d. about regression
Alkyl chlorides and chlorobenzenes (a, Fig. 1)	3.096	42,93	0.33
Chloroolefines (b, Fig. 1)	3.942	46.04	0.31
Alkyl bromides (a, Fig. 2)	36.08	328.0	4.48
Bromobenzenes (b, Fig. 2)	23.63	323.6	2,27
Iodo-compounds $f(3/2 \rightarrow 1/2)$; (Fig. 3)	33.11	326.2	4.02
Iodo-compounds $f(5/2 \rightarrow 3/2)$	64.48	646.9	7.37
Iodobenzenes (● in Fig. 3)	27.82	320.0	0.55

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4) $f_{\text{NQR}}(\text{atomic})$: ³⁵Cl = 54.80; ⁷⁹Br = 384.90; ¹²⁷I = 343.92 Mc/s.

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68. Iron Carbonyls in Organic Synthesis, I. Iron Pentacarbonyl Induced Decomposition and Transfer Hydrogenation of Aryl Azides to Substituted Ureas¹⁾

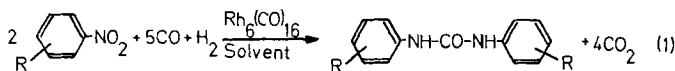
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Summary. Iron pentacarbonyl catalyzes smooth decomposition of aryl azides in the presence of acetic acid to afford good (70–90%) yields of the corresponding disubstituted ureas. Possible and alternative reaction mechanism pathways are discussed.

Introduction. – The homogeneous transition metal catalyzed deoxygenation of aromatic nitro compounds by carbon monoxide and hydrogen, under controlled conditions, affords high yields of 1,3-diarylureas [1] [2] (compare also [3]), according to equation 1 below. Such reductive carbonylation of nitrobenzenes to diphenylureas



is regarded [1] [2] [4] as occurring through the agency of nitrenoid complexes of transition metals [5–7], the phenyl-nitrene moiety most likely being generated at the coordination sphere of the metal by two subsequent reductions by carbon monoxide groups and there remaining as stabilized ligand.

In quest of more compelling evidence for the foregoing hypothesis, we subsequently looked into a few analogous reactions of aryl nitrenes, independently generated by transition metal induced decomposition of the corresponding azides.

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