trans-bent configuration, we point out that the former has a less repulsive alignment of the $F_2C{=}CF$ group dipole moments than does the latter. However, the final answer to this question is bound to be much more complicated.

Acknowledgments. It is a pleasure to thank Dr. S. L. Manatt for a sample of 1,1,4,4-tetrafluorobutadiene, and Mr. N. A. Kuebler for running the optical spectra for us. Additionally, discussions with Professor V. W. Laurie and Dr. A. Andreassen are acknowledged with thanks.

Ground States of Conjugated Molecules. XXII. Polarographic Reduction Potentials of Hydrocarbons[1]

Michael J. S. Dewar, J. A. Hashmall,[2a] and N. Trinajstić[2b]

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received July 18, 1969*

Abstract: The polarographic reduction potentials of 76 aromatic hydrocarbons correlate well with electron affinities calculated by a recently described semiempirical SCF MO procedure. Points of attachment of the first two hydrogen atoms are predicted; in the few cases where data are available they confirm the predictions. The available values for polarographic oxidation potentials correlate well with calculated ionization potentials.

Correlations between the polarographic reduction half-wave potentials ($-E_{1/2}$) of conjugated hydrocarbons and the lowest unoccupied HMO orbital energies ($-m_{n+1}$) have been described by many authors,[3-7] giving in all cases reasonably good correlations with experiment, and some analogous correlations have also been reported using the Pariser–Parr method.[8] Here we present a correlation between the polarographic reduction half-wave potentials and electron affinities calculated by the variable-β SCF MO method recently developed in this laboratory.[9-12] We have also used this procedure to calculate the points of attachment of the first two hydrogen atoms during reduction by electron transfer, and finally, the available data concerning polarographic oxidation potentials have been correlated with calculated ionization potentials.

Theoretical Method

Reduction of an aromatic hydrocarbon (R) by a reversible one-electron transfer leads to the radical anion (R^-)

$$R + e \rightleftharpoons R^- \qquad (1)$$

The free energy change ($\Delta F°$) for the above process in solution is as follows

$$\Delta F° = (F°_R)_{gas} - (F°_{R^-})_{gas} + (F°_{electron})_{Hg} + (\Delta F°)_{solv} \qquad (2)$$

The difference $(F°_R)_{gas} - (F°_{R^-})_{gas}$ is equal to the electron affinity (A) of the molecule R in the gas phase, if we neglect entropy effects.

On the other hand, one can write down the half-wave potential ($E_{1/2}^{red}$) for a reversible one-electron electrode process as follows

$$-E_{1/2}^{red} = \frac{\Delta F°}{\mathfrak{F}} - \frac{RT}{\mathfrak{F}} \ln \left(\frac{D_R}{D_{R^-}}\right)^{1/2} + \frac{RT}{\mathfrak{F}} \ln \frac{F_R}{F_{R^-}} \qquad (3)$$

where $\mathfrak{F}$ is the Faraday constant, R is the gas constant, T is temperature in degrees Kelvin, and D_R and D_{R^-} and F_R and F_{R^-}, are, respectively, the diffusion coefficients and activity coefficients of R and R^-. Since these should be very similar, terms involving them may reasonably be neglected; *e.g.*, (3) then becomes

$$-E_{1/2}^{red} = \frac{\Delta F°}{\mathfrak{F}} \qquad (4)$$

Substituting A into eq 2 using eq 4

$$-E_{1/2}^{red}\ \frac{1}{\mathfrak{F}}[A + (F°_{electron})_{Hg} + (\Delta F°)_{solv}] \qquad (5)$$

The last two terms in eq 5, for polarographic reduction of a series of similar compounds under similar experimental conditions, should be constant. In this case

$$-E_{1/2}^{red} = \frac{A}{\mathfrak{F}} + \text{constant} \qquad (6)$$

A plot of $-E^1/_2{}^{red}$ *vs.* A should then be linear.

A similar relationship should hold between the polarographic oxidation potentials of hydrocarbons ($E_{1/2}^{ox}$) and calculated ionization potentials (I); *i.e.*

$$E_{1/2}^{ox} = I + \text{constant} \qquad (7)$$

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[1] Part XXI: M. J. S. Dewar, A. J. Harget, N. Trinajstić, and S. D. Worley, *Tetrahedron*, in press. This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-70-1881.

[2] (a) Physikalische-Chemisches Institut der Universität Basel, Basel, Switzerland; (b) Robert A. Welch Postdoctoral Fellow; on leave of absence from The Rudjer Bošković Institute, Zagreb, Croatia, Yugoslavia.

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Table I. Calculated Heats of Atomization of Hydrocarbons and Hydrocarbon Radical Anions, Electron Affinities, Observed Polarographic Half-Wave Reduction Potentials, and the Lowest Unoccupied HMO Orbital Energies

	Heat of atomization, eV				
Molecule	Hydrocarbon	Radical anion	A, eV	$-E_{1/2}^{\text{red}}$, V[a]	$-m_{n+1}$[b]
I	90.612	81.025	0.074	1.98	0.6180[c]
II	123.300	114.893	0.653	1.46	0.4142[c]
III	157.112	148.512	1.060	1.14	0.2950[c]
IV	190.294	181.975	1.341	0.86	0.2197[c]
V	124.222	114.835	0.273	1.94	0.6052[c]
VI	157.580	148.560	0.640	1.53	0.4523[c]
VII	190.853	182.196	1.003	1.19	0.3271[d]
VIII	224.031	215.663	1.292	0.95	0.2436[e]
IX	157.943	148.535	0.251	1.97	0.6840[c]
X	191.348	182.257	0.568	1.54	0.4991[c]
XI	224.636	215.923	0.948	1.21	0.3557[f]
XII	257.825	249.420	1.254	0.93	0.2621[e]
XIII	191.238	182.232	0.654	1.55	0.4735[c]
XIV	224.555	215.851	0.956	1.25	0.3584[f]
XV	257.760	249.341	1.242	0.85	0.2691[e]
XVI	157.772	148.628	0.516	1.81	0.5201[c]
XVII	191.113	182.253	0.800	1.44	0.4048[f]
XVIII	224.431	215.735	0.964	1.33	0.3482[f]
XIX	157.781	148.505	0.384	1.75	0.5676[c]
XX	191.238	182.161	0.583	1.57	0.4917[c]
XXI	191.458	182.398	0.600	1.65	0.5319[f]
XXII	224.982	215.927	0.605	1.57	0.5224[f]
XXIII	225.108	216.229	0.781	1.59	0.5115[f]
XXIV	191.361	182.201	0.500	1.73	0.5498[f]
XXV	191.113	182.210	0.757	1.40	0.4186[f]
XXVI	191.361	182.292	0.591	1.79	0.5019[c]
XXVII	190.980	182.027	0.707	1.53	0.4372[c]
XXVIII	224.263	215.577	0.974	1.22	0.3357[e]
XXIX	224.618	215.709	0.751	1.50	0.4287[j]
XXX	258.263	249.382	0.779	1.52	0.4321[j]
XXXI	257.991	249.129	0.798	1.47	0.3940[c]
XXXII	172.146	163.442	0.956	1.25	0.3473[c]
XXXIII	205.488	197.076	1.248	0.97	0.2648[f]
XXXIV	238.805	230.607	1.463	0.88	0.2135[f]
XXXV	239.095	230.731	1.296	1.00	0.2673[e]
XXXVI	186.893	178.011	0.779	1.49	0.4392[c]
XXXVII	220.594	211.749	0.815	1.52	0.4631[j]
XXXVIII	254.131	245.432	0.961	1.35	0.4114[j]
XXXIX	201.527	192.506	0.640	1.64	0.5392[c]
XL	239.390	230.776	1.046	1.28	0.3557[j]
XLI	249.232	240.960	1.388	0.92	0.2539[f]
XLII	287.091	279.095	1.665	0.68	0.1826[j]
XLIII	287.099	279.042	1.603	0.70	0.1916[j]
XLIV	138.627	129.631	0.664	1.61	0.4450[c]
XLV	172.380	164.330	0.610	1.67	0.4970[c]
XLVI	172.111	163.381	0.930	1.36	0.3711[c]
XLVII	205.810	197.077	0.926	1.08	0.3983[f]
XLVIII	205.902	197.093	0.851	1.45	0.4216[j]
XLIX	206.114	197.015	0.562	1.69	0.5550[d]
L	205.533	197.057	1.185	1.16	0.3027[d]
LI	205.646	197.043	1.057	1.32	0.3420[d]
LII	205.805	196.664	0.519	1.51	0.5053[e]
LIII	205.499	196.987	1.148	1.15	0.3202[e]
LIV	272.233	264.088	1.515	0.78	0.2130[g]
LV	272.483	263.978	1.155	1.15	0.2734[e]
LVI	239.461	230.762	0.961	1.35	0.3957[j]
LVII	220.270	211.856	1.247	1.18	0.2846[d]
LVIII	287.749	279.279	1.190	1.15	0.3445[j]
LIX	186.431	177.951	1.180	1.19	0.2910[d]
LX	253.537	245.261	1.384	1.06	0.2580[h]
LXI	253.177	245.153	1.636	0.80	0.1891[j]
LXII	138.668	129.848	0.840	1.35	0.3709[c]
LXIII	171.987	163.558	1.231	0.98	0.2521[d]
LXIV	205.236	197.178	1.603	0.65	0.1604[d]
LXV	172.279	163.555	0.935	1.38	0.3770[d]
LXVI	172.148	163.512	1.024	1.17	0.3116[d]
LXVII	172.118	163.291	0.834	1.39	0.4007[d]
LXVIII	205.445	196.930	1.146	1.06	0.2666[i]
LXIX	205.405	196.597	0.852	1.38	0.3966[h]
LXX	186.710	178.420	1.371	0.90	0.1859[d]
LXXI	220.050	212.092	1.702	0.60	0.0880[d]
LXXII	253.322	245.702	2.040	0.34	0.0000[i]
LXXIII	109.753	100.156	0.063	2.08	0.7046[c]
LXXIV	162.352	153.106	0.414	1.91	0.5926[c]
LXXV	214.951	205.859	0.568	1.77	0.5361[c]
LXXVI	205.221	196.967	1.406	0.46	0.1987[d]

[a] The experimental half-wave potentials are taken from I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954). [b] $\alpha + m_{n+1}\beta$ is the energy of the lowest unoccupied HMO orbital. [c] C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press, Oxford, 1965. [d] A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. I and II, Pergamon Press, Oxford, 1965. [e] P. Hochmann, J. Dubský, J. Koutecký, and C. Párkányi, *Coll. Czech. Chem. Comm.*, **30**, 3560 (1965). [f] R. Zahradník and C. Párkányi, *ibid.*, **30**, 3536 (1965). [g] M. Titz and P. Hochmann, *ibid.*, **31**, 4168 (1966). [h] P. Hochmann, J. Koutecký, and R. Zahradník, *ibid.*, **27**, 3053 (1962). [i] R. Zahradník, J. Michl, and J. Koutecký, *ibid.*, **29**, 3184 (1964). [j] Calculated by us.

The reduction of a hydrocarbon R to its dihydro derivative RH_2, by electron transfer in the presence of a source of protons, normally takes place in two steps *via* an intermediate radical RH· ; *viz.*

$$\begin{aligned} R + e &\longrightarrow R^- \\ R^- + H^+ &\longrightarrow RH\cdot \\ RH\cdot + e &\longrightarrow RH^- \\ RH^- + H^+ &\longrightarrow RH_2 \end{aligned} \tag{8}$$

Since protonation of a mesomeric carbanion is an extremely facile process, it should take place preferentially at the position with maximum formal negative charge.[13] The point of attachment of the first proton should then be the position with maximum π-electron density in the ion radical R^-, and the point of attachment of the second proton the corresponding position in the ion RH^-.

The electron affinities (A) and ionization potentials (I) of hydrocarbons (R) were calculated from the following expressions

$$A = \Delta H_a(R^-) - \Delta H_a(R) \tag{9}$$

$$I = \Delta H_a(R) - \Delta H_a(R^+) \tag{10}$$

where the ΔH_a's are heats of atomization calculated by our SCF MO π approximation,[11] those for the ion radicals R^+ and R^- being found by the "half-electron" variant.[14]

Results

In Table I are shown heats of atomization calculated for the 76 aromatic hydrocarbons listed in Figure 1, and for the radical anions formed by their reduction; some of these values had already been reported in part IX of this series.[14] In comparing the corresponding electron affinities (third column of Ta-

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[13] (a) M. J. S. Dewar, *Discuss. Faraday Soc.*, **2**, 261 (1947); (b) "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

[14] M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, **90**, 1953 (1968).

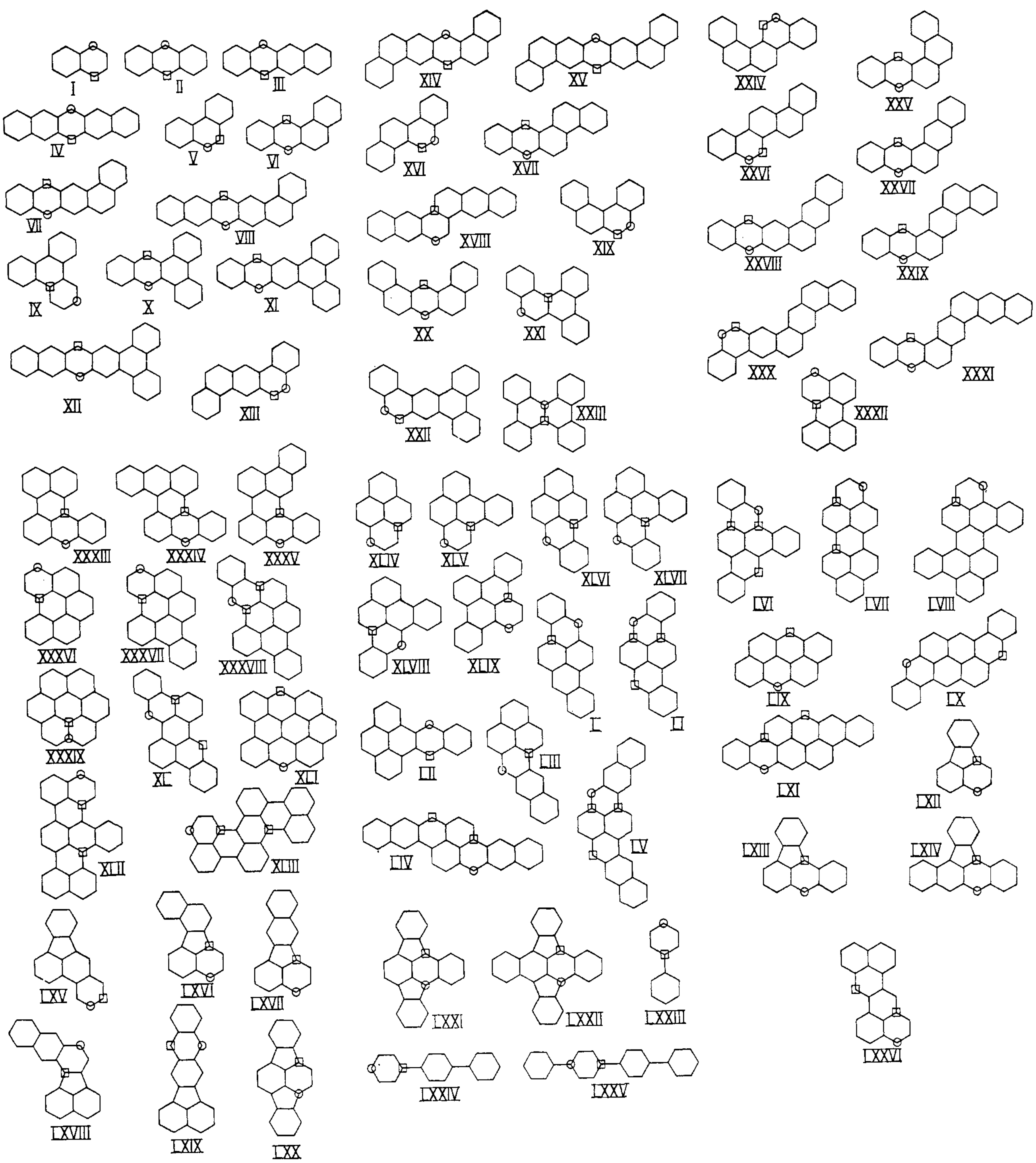

Figure 1. Geometries of molecules studied. Circles denote the predicted point of addition of the first proton and squares that of the second proton.

ble I) with experiment, it is necessary to use reduction potentials measured under identical experimental conditions, for although the relative values for different hydrocarbons seem to be the same in different solvents, etc.,[15] their absolute values vary. We have therefore confined ourselves to the values reported by Bergman,[16] since no other measurements refer to so large a number of hydrocarbons. His values for $E_{1/2}^{\mathrm{red}}$ are shown in the fourth column of Table I, while Figure 2 shows a plot of them *vs.* our calculated electron affinities.

It will be seen that there is an excellent linear relation between the electron affinities and reduction potentials, the correlation coefficient being 0.97 and the standard deviation only 0.028 V. The slope of the least-squares line (0.92) is slightly less than the theoretical value of unity (eq 6), but the difference is within the limits of experimental error[16] in the measured values of $E^{1}/_{2}^{\mathrm{red}}$. The calculated electron affinities also agree closely with experiment.[14,17]

The fact that the slope of the line in Figure 2 is so close to unity must mean that the differences in solva-

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(15) P. A. Given, *J. Chem. Soc.*, 2684 (1958).

(16) I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954).

(17) R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2409 (1966).

tion energy between the hydrocarbons and the corresponding radical anions either vary little or are small; the latter seems to be more likely in view of the insensitivity of the relative values for different hydrocarbons to changes in the solvent,[15] and because the aprotic solvents used in these studies should not solvate anions at all efficiently. However, the small deviation in the slope of the line in Figure 2 from the theoretical value of unity may reflect small changes in solvation effects along the series.

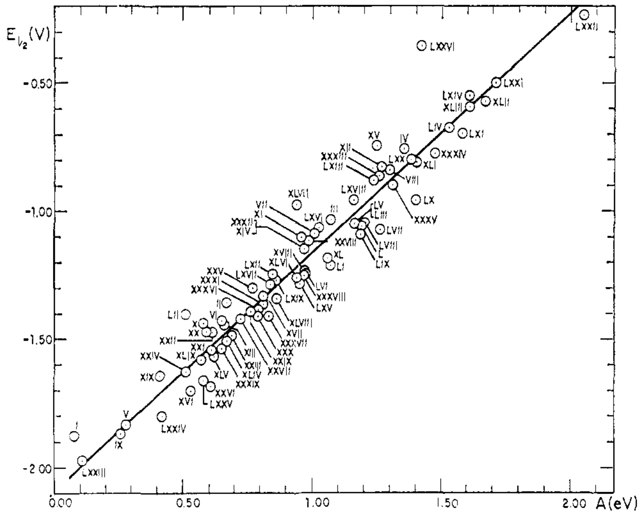

Figure 2. Plot of electron affinities (*A*) *vs.* polarographic half-wave reduction potentials ($E_{1/2}^{\mathrm{red}}$) for the compounds listed in Figure 1.

As we remarked earlier, there is also a good linear relation between $E_{1/2}^{\mathrm{red}}$ and the energies of the lowest unoccupied Hückel MO's;[3–7,18] in order to compare this with the one indicated in Figure 2, we had to carry out HMO calculations for many of the hydrocarbons since these were not listed in the available compilations.[19] Energies of the corresponding lowest unoccupied MOs are shown in the fifth column of Table I. The correlation between them and the observed reduction potentials is quite good (correlation coefficient, 0.97) but the standard deviation (0.077 V) is almost three times ours; moreover, the HMO results are expressed in terms of a parameter (β), whereas ours are absolute values, in electronvolts. This difference is quite an important one, for deviations of the slopes of plots such as that of Figure 2 from the theoretical value provide a good indication of any interference due to solvent effects. And finally, the success of HMO theory in this connection is almost certainly due to the fact that nearly all the compounds studied here are alternant hydrocarbons; it is well known[13b] that the HMO method is reasonably reliable only for this particular class of compound, whereas the procedure used here should be equally applicable to compounds containing heteroatoms. Indeed, a good example of both these points is provided by a recent study of reduction potentials of quinones.[20] Here again there is a good linear relation between the observed reduction potentials and electron affinities calculated by our SCF MO method, but the slope of the line (0.39) was much less than the theoretical value (0.5); here the reductions are carried out in protic solvents where the anions are very strongly solvated.

As indicated earlier, we also studied the reduction of the hydrocarbons to dihydro derivatives by the process indicated in eq 8. The first hydrogen should attach itself to the atom with the highest π-electron density in the radical anion R^-; these positions are indicated by circles in Figure 1. The second hydrogen should likewise attach itself to the position with maximum π-electron density in the intermediate anion RH^-; this is indicated in Figure 1 by a square. In some cases two or more positions in RH^- have essentially identical π-electron densities; all of them are then marked in Figure 1. Unfortunately, few of the reduction products of these hydrocarbons have been studied; indeed, data seem to be available only for benzene and naphthalene. The former reduces 1,4 exclusively, as we predict (the well-known Birch reduction[21]), and the same is also true of naphthalene.[22] In both cases the HMO method predicts equal ease of 1,2 and 1,4 addition. There are a number of other similar discrepancies between our predictions and those[6] of HMO theory; we hope that our calculations may stimulate further experimental work in this area.

The polarographic oxidation potentials of hydrocarbons should be related to their ionization potentials in the same way that the reduction potentials are to electron affinities (eq 6). Polarographic oxidation potentials have been measured by several groups of workers,[23–26] and the results correlate quite well with the energies of the highest occupied Hückel MO's for the hydrocarbons.[27] Gleicher and Gleicher[28] have also applied an earlier version[10] of the present SCF MO treatment to this problem; they found a good correlation between their calculated orbital energies and the oxidation potentials of Pysh and Yang.[25]

Table II shows ionization potentials calculated by Koopmans' theorem, which has been shown[14] to give results very similar to those from direct calculations using the "half-electron" method,[14] together with the polarographic oxidation potentials ($E_{1/2}^{\mathrm{ox}}$) of Pysh and Yang;[25] these were chosen since they represent the most complete series of measurements made under identical experimental conditions. As will be seen from Figure 3, there is an excellent linear relation between the calculated ionization potentials and the measured

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[18] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 173–185.

[19] (a) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press, Oxford, 1965; (b) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. I and II, Pergamon Press, Oxford, 1965; (c) P. Hochmann, J. Dubský, J. Koutecký, and C. Párkányi, *Coll. Czech. Chem. Commun.*, **30**, 3560 (1965); (d) R. Zahradník and C. Párkányi, *ibid.*, **30**, 3536 (1965); (e) M. Titz and P. Hochmann, *ibid.*, 31, 4168 (1966); (f) P. Hochmann, J. Koutecký, and R. Zahradník, *ibid.*, 27, 3053 (1962); (g) R. Zahradník, J. Michl, and J. Koutecký, *ibid.*, 29, 3184 (1964).

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[21] (a) A. J. Birch, *Quart. Rev., Chem. Soc.*, **4**, 69 (1950); (b) ref 13b, p 292.

[22] S. Wawzonek and H. A. Laitinen, *J. Amer. Chem. Soc.*, **64**, 2365 (1942).

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[25] E. S. Pysh and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2124 (1963).

[26] W. C. Neikam, G. R. Dimeler, and M. M. Desmond, *J. Electrochem. Soc.*, **111**, 1190 (1964).

[27] G. J. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, **77**, 555 (1955).

[28] G. J. Gleicher and M. K. Gleicher, *J. Phys. Chem.*, **71**, 3693 (1967).

Table II. Calculated Vertical Ionization Potentials, Observed Polarographic Half-Wave Oxidation Potentials, and the Highest Occupied HMO Orbital Energies

Molecule	−(Vertical ionization potential), eV	$-E_{1/2}^{\mathrm{ox}}$, V[a]	$+m_n$[b]
Benzene (0)[c]	9.368	2.30	1.0000
I	8.541	1.54	0.6180
II	7.972	1.09	0.4142
III	7.597	0.77	0.2950
V	8.434	1.50	0.6052
VI	8.037	1.18	0.4523
IX	8.454	1.55	0.6840
X	8.098	1.25	0.4991
XIII	8.070	1.19	0.4735
XVI	8.193	1.35	0.5201
XVII	7.875	1.01	0.4048
XX	8.095	1.26	0.4917
XXVI	8.157	1.33	0.5019
XXXII	7.724	0.85	0.3473
XXXVI	7.846	1.01	0.4392
XXXIX	7.976	1.23	0.5392
XLIV	7.951	1.16	0.4450
XLV	8.028	1.27	0.4970
XLVI	7.747	0.94	0.3711
XLVII	7.777	1.15	0.3983
XLVIII	7.841	1.01	0.4216
LXII	8.337	1.45	0.6180

[a] E. S. Pysh and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2124 (1963). [b] HMO values from tables cited in Table I. [c] Polarographic half-wave reduction potentials were not measured owing to experimental difficulties; its reduction potential is too high.

$E_{1/2}^{\mathrm{ox}}$, the correlation coefficient being 0.98 and the standard deviation only 0.035 V; indeed, the latter is comparable with the claimed experimental error.[24]

The slope of the line (0.87) in Figure 3 is, however, much less than unity; this presumably reflects the fact that carbonium ions are strongly solvated even in an aprotic solvent such as that (acetonitrile) used here. The more delocalized the charge in the radical cation formed by oxidation of a given hydrocarbon, the lower should be its energy; one would therefore expect a correlation between oxidation potential and energy of solvation of the radical cation formed by oxidation. Such a correlation would leave the relation between ionization potential and $E_{1/2}^{\mathrm{ox}}$ linear but reduce its slope; a similar reduced slope was observed[20] in a correlation of reduction potentials of quinones with calculated electron affinities and explained in the same way.

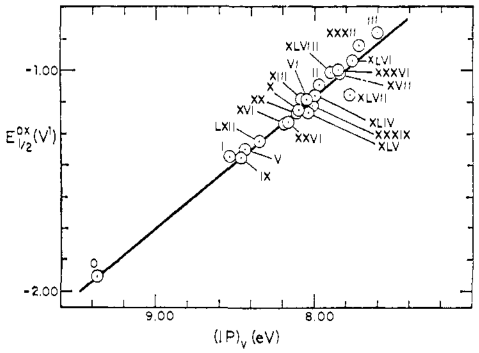

Figure 3. Plot of vertical ionization potentials (IPv) *vs.* polarographic half-wave oxidation potentials ($E_{1/2}^{\mathrm{ox}}$).

Here again the HMO method is clearly inferior. The best linear relation between $E_{1/2}^{\mathrm{ox}}$ and the energy of the highest occupied Hückel MO shows a standard deviation of 0.092 V, nearly three times ours, and the HMO method also suffers from the deficiencies pointed out above in the discussion of reduction potentials. The present procedure also gives a slightly better correlation than that of Gleicher and Gleicher,[28] as might be expected, since it is known to give even better estimates of heats of atomization of molecules.