tetrachloride showed a B_2 multiplet of an AB_2 system at 7.47 τ, a doublet at 6.84 τ (hydroxyl proton), a singlet at 6.37 τ (benzyl protons), a multiplet at 5.50 τ and aromatic protons at 2.81 τ.

Anal. Calcd. for $C_{15}H_{16}OS$: C, 73.73; H, 6.60; S, 13.12. Found: C, 73.55; H, 6.29; S, 12.96.

Allyl Phenyl Sulfide XXVIII with Diborane.—Analyses of the reaction mixture of XXVIII[34] with diborane, carried out by the procedure described for XII except with a reaction time of 72 hr., on Carbowax, Theed and GE SF-96 columns at 110°, 90°, and 150°, respectively, showed the presence of 5.2% XIV, no XIII, no hexanols and 8.1% II. The ether solution was then repeatedly washed with water and dried and the solvent was removed under reduced pressure. The residue was distilled at 111° at 0.45 mm., giving a viscous colorless liquid (55%). N.m.r. analysis indicated the product was a mixture of γ-hydroxypropyl phenyl sulfide[35] and β-hydroxypropyl phenyl sulfide.[34]

Maintaining the reaction mixture of XXVIII with diborane in diglyme at 100° for 18 hr., followed by the work-up and analysis described above, showed the formation of 9.7% XIV, no XIII, no hexanols and 21% II.

Reaction of Allyl Benzyl Sulfide (XXXI) with Diborane. A.—The reaction mixture from 0.1 mole of XXXI[23] and diborane was allowed to stand for 3 days. The reaction mixture was hydrolyzed (considerable hydrogen evolution), oxidized and diluted with ether as described for XII. An aliquot of the ethereal solution was dried over magnesium sulfate. Analysis by G.L.C. on a Carbowax 20 M column at 100° showed no XIII or XIV. Analysis at 160° showed the presence of no XXIV.

The original ether solution was washed repeatedly with water and dried over magnesium sulfate. Removal of the solvent and distillation of the residue at 129° at 0.2 mm. gave 10.1 g. (56%) of a mixture of XXXII[36] (13%) and XXXIII[36] (87%) as analyzed by n.m.r.

B.—The reaction mixture from 0.1 mole of XXXI and diborane in diglyme was maintained at 100° for 24 hours. Analysis by the procedure above showed a trace of XIII, 2.1% XIV and 1.7% II.

The ether solution was washed repeatedly with water, dried and the solvent was removed under reduced pressure. The residue was distilled at 105–108° (0.35 mm.), giving a viscous colorless liquid (60%). The n.m.r. spectrum of the distillate indicated the product to be a mixture of XXXIII (92%) and XXXII (8%).

1,1-Diphenyl-2-thiophenylethylene (XXXIV).—A solution of 50.8 g. (0.33 mole) of phenacyl chloride in 300 ml. of absolute ethanol was added to 0.36 mole of sodium thiophenoxide in 300 ml. of absolute ethanol and allowed to stand for 3 hr. at room temperature and finally 1 hr. on a steam-bath. The ethanol was removed under reduced pressure and the residue poured into water and extracted with ether. The ether was evaporated and the material was recrystallized from benzene–petroleum ether to give 57.5 g. of colorless plates, m.p. 44–46°.

(34) C. D. Hurd and H. Greengard, *J. Am. Chem. Soc.*, **72**, 3356 (1950).

(35) By comparison with authentic materials (M. A. Kim and R. D. Schuetz, *ibid.*, **74**, 5102 (1952)).

(36) E. Rothstein, *J. Chem. Soc.*, 686 (1934).

A solution of 57 g. of ketosulfide in 400 ml. of ether was slowly added to a 20% excess of phenyllithium in 500 ml. of ether. The reaction mixture was stirred overnight and was then hydrolyzed with 100 ml. of 10% sulfuric acid. The ether layer was removed and washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on 2 lb. of Merck activated alumina. Elution with 0 to 37.5% benzene–petroleum ether gave 15 g. of starting material. Elution with 37.5 to 75% benzene–petroleum ether gave 8.5 g. of a mixture of starting material and product alcohol. Elution with 75% benzene–petroleum ether to 37.5% chloroform–benzene gave 25.5 g. of 1,1-diphenyl-2-thiophenylethanol as colorless needles, m.p. 74.6–75.0° from petroleum ether.

A mixture of 16 g. of 1,1-diphenyl-2-thiophenylethanol and 0.5 g. of *p*-toluenesulfonic acid was heated at 169° under aspirator vacuum until the reaction mixture was clear. The mixture was cooled, dissolved in ether and the ether phase was washed with water and dried over magesium sulfate. The solvent was removed under reduced pressure. The residue was recrystallized four times from petroleum ether and finally twice from ethanol, giving 8.0 g. of very fine colorless needles, m.p. 71.1–71.5°.[37]

Anal. Calcd. for $C_{20}H_{16}S$: C, 83.29; H, 5.59. Found: C, 83.08; H, 5.75.

1,1-Diphenyl-2-thiophenylethylene (XXXIV) with Diborane.—The crude reaction product (2.55 g.) from 4.5 g. of XXXIV and 0.55 molar equivalent of diborane was analyzed by G.L.C. on a GE SF-96 column at 238° showing the presence of XXXV (60%) and XXXVI (4%). No 1,2-diphenylethanol (XXXVII) was detected.

As a further check for the presence of XXXVII, 0.50 g. of crude product was dissolved in 30 ml. of acetone and dichromate in 30% sulfuric acid was added until an excess was present. The mixture was stirred for 15 min. at room temperature and methanol was added to decompose the excess oxidizing agent. The mixture was poured into 200 ml. of water and extracted with ether. Extraction of the ether layer with 5% sodium hydroxide, followed by acidification and extraction with ether, gave 0.27 g. of diphenylacetic acid, m.p. 137.8–148.5° (lit.[38] 148°). The original ether layer was dried over magnesium sulfate and the solvent was removed under reduced pressure leaving 0.16 g. of neutral material. Although the infrared spectrum showed a weak carbonyl peak at approximately 6.0 μ the n.m.r. spectrum showed no peak for the methylene group of desoxybenzoin. Treatment of the neutral fraction with 2,4-dinitrophenylhydrazine reagent gave a small amount of a derivative, m.p. (crude) 233–237° (2,4-dinitrophenylhydrazone of desoxybenzoin m.p. 204°).[39]

(37) It was necessary to recrystallize the material repeatedly to remove a small amount of 1,2-diphenyl-1-thiophenyl ethylene, formed by thiophenyl and phenyl migration, which would lead to erroneous results and interpretations.

(38) Reference 17, p. 560.

(39) Reference 17, p. 666.

Polarographic Oxidation Potentials of Aromatic Compounds

By E. S. Pysh and N. C. Yang[1]

The oxidation half-wave potentials of fifty-three organic compounds have been determined in acetonitrile at a rotating platinum electrode. These values are correlated with ionization potentials, with interaction energies of charge-transfer complexes with trinitrofluorenone, with Hückel coefficients of the resonance integral in the expression for the highest occupied molecular orbital energy level, and with p-absorption band spectra. The correlations yield linear relations for alternant hydrocarbons. On the basis of these correlations, the values of the oxidation half-wave potentials are applied to calculate ionization potentials for aromatic hydrocarbons and to verify the values of molecular orbital calculations.

Introduction

Polarographic oxidation half-wave potentials of organic compounds are, within certain limits, directly related to ionization potentials, charge-transfer spectra, absorption spectra and molecular orbital energy levels.[2] Ionization potentials of large organic molecules

(1) Fellow of the Alfred P. Sloan Foundation.

(2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," J. Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 7.

are difficult to determine. Although ionization potentials have been calculated through study of charge-transfer spectra, it would be useful to have another easily accessible experimental measure of relative ionization potentials. Polarographic half-wave potentials can also provide, in some cases, an experimental measure to check various molecular orbital calculations. Considering the potential usefulness of polarographic oxidation potentials, very few experimental measure-

ments have been carried out. In this investigation, the oxidation potentials of fifty-three organic compounds were measured in acetonitrile at a rotating platinum electrode and correlated with experimental photo-ionization potentials, with the appropriate charge-transfer data, with the Hückel coefficient of the resonance integral in the expression for the highest occupied molecular orbital energy level, and with absorption spectra.

A necessary condition for any correlation of polarographic data with any other parameter of electron-donating ability is that electrochemical equilibrium be achieved at the electrode and that a "reversible" wave be obtained, since then the half-wave potential is related in a simple manner to the change in free energy involved in the electrode process. When the free energy term in the simple expression for the half-wave potential is replaced by an equivalent expression one obtains

$$E_{1/2(ox)} = IP + \Delta E_{(sol)} - \frac{T\Delta S^0}{\mathfrak{F}} - \frac{RT}{\mathfrak{F}} \ln \frac{f^+ D}{f D^+} + \text{constant}$$

(1)

where IP is the ionization potential of the compound, $\Delta E_{(sol)}$ is the difference in solvation energy between the compound and that of its positive ion, f^+ and f are the activity coefficients of the ion and uncharged molecule, respectively, and D^+ and D the respective diffusion constants. $E_{1/2(ox)}$, IP and $\Delta E_{(sol)}$ are expressed in electron volts. For a series of aromatic hydrocarbons the range of ionization potentials will be from 7 to 9 e.v.; $\Delta E_{(sol)}$ will vary from about 1 to 2 e.v.; and the logarithmic term will be small since f^+ is less than f but not by an order of magnitude, and D is greater than D^+ but not by an order of magnitude. Variation in IP will be much more significant than variations in the other terms, and a plot of $E_{1/2(ox)}$ against IP might be expected to yield a straight line. If $\Delta E_{(sol)}$ were an approximately linear function of IP the linearity would be enhanced.

Experimental values for IP are available for only a few polynuclear aromatic hydrocarbons. However, in simple molecular orbital theory the ionization potential is equal to the energy of the highest occupied molecular orbital. The energies of the orbitals of polycyclic hydrocarbons are of the form $\alpha + x\beta$; the relative energies of the highest occupied orbital depend on the product $x_n\beta$ where x_n is a number calculated theoretically and β is the resonance integral. We can then write, dropping the small entropy and logarithmic terms in eq. 1

$$E_{1/2(ox)} = x_n\beta + \Delta E_{(sol)} + \text{constant}$$

(2)

Hoijtink[3] has in fact shown that a plot of polarographic reduction half-wave potentials against x_{n+1}, corresponding to the lowest vacant molecular orbital, is linear, and that a similar relationship holds when a few oxidation half-wave potentials obtained by Lund[4] are plotted against x_n, corresponding to the highest occupied molecular orbital.[5] The degree of success of this correlation reflects the degree to which the variation in the solvation energy in eq. 2 can be neglected, or the degree to which the variation is a function of IP itself.

The oxidation half-wave potentials can also be related to charge-transfer spectra. In a series of charge-transfer complexes between a single acceptor and a series of polynuclear hydrocarbon donors, if the interactions between the donor and acceptor are small, the transition energy, ΔE_{ct}, for the first charge-transfer band should be given by

$$\Delta E_{ct} = IP - EA + \text{constant}$$

(3)

where EA is the electron affinity of the acceptor molecule. The linearity of a plot of ΔE_{ct} against IP has been demonstrated for a series of aromatic hydrocarbon complexes with a given acceptor molecule.[6] Replacing IP with the molecular orbital expression suggests a linearity in the plot of ΔE_{ct} against x_n. Such a correlation has been made by Dewar and Lepley[7] using aromatic hydrocarbon complexes with trinitrobenzene, by Dewar and Rogers[8] for aromatic hydrocarbon complexes with tetracyanoethylene, and by Lepley[9] for aromatic hydrocarbon complexes with trinitrofluorenone. Beukers and Szent-Gyorgyi have also collected data from various sources to demonstrate the same relationship.[10]

From eq. 2 and 3

$$E_{1/2(ox)} = \Delta E_{ct} + \Delta E_{(sol)} + \text{constant}$$

(4)

The degree of linearity of a plot of $E_{1/2(ox)}$ against ΔE_{ct} has not yet been demonstrated. The success of such a correlation would suggest that half-wave potentials could provide a more than qualitative measure of relative electron-donating ability in forming charge-transfer complexes.

Experimental

Materials.—Samples of each of the monomethylated derivatives of 1,2-benzanthracene were provided by Prof. Melvin S. Newman. Pyrene, naphthalene, triphenylene and 1-naphthylamine were purified by sublimation; 7,12-dimethylbenzanthracene was purified by chromatography on alumina; mesitylene, o-, m- and p-xylene, toluene and benzene were purified by vapor phase chromatography; azulene and fluoranthene were crystallized from alcohol; coronene was crystallized from benzene; and 2-naphthylamine was crystallized from hot water. Anthracene was purified according to the method of Fieser.[11] 3-Methylcholanthrene and 9-methylanthracene were used as supplied by the Eastman Chemical Co. and the remaining hydrocarbons were used as supplied by the Aldrich Chemical Co. Practical grade acetonitrile, obtained from the Eastman Chemical Co., was purified as described by Kolthoff and Coetzee,[12] or spectrograde was used without further purification. Sodium perchlorate from the G. Frederick Smith Chemical Co. was dried at 120–130° for 24 hr., then at 144° under vacuum over P_2O_5 before use.

Measurements.—All polarograms were obtained with a Sargent model XV polarograph. The reference electrode was a calomel cell contained in a glass tube 15 mm. in diameter placed in a second glass tube 22 mm. in diameter which was fitted with a glass frit and which contained an agar plug and saturated KCl solution. Electrolytic contact was made through a small hole in the side of the inner tube. The entire assembly was placed in one arm of an H-cell containing acetonitrile 2.0 M in $NaClO_4$. Into the other arm, separated by a glass frit, was placed the test solution. The resistance was measured after each test with an a.c. bridge. For one cell used the resistance remained constant during any single recording, but varied from 700 to 900 ohms throughout the experiment. One cause for the slow change observed in the resistance of such a cell is the precipitation of KCl, insoluble in acetonitrile, onto the glass frit of the reference electrode. The indicator electrode consisted of a platinum wire 2.0 mm. in length and 0.8 mm. in diameter sealed into a bulb at the end of a hollow glass tube. This was fixed to a Sargent synchronous motor rotating at a speed of 600 r.p.m. A circulated water-bath maintained the temperature at 25.0 ± 0.1°.

The hydrocarbon (1 to 2 mg.) was placed in a 25-ml. volumetric flask and a solution of acetonitrile 2.0 M in $NaClO_4$ was added. For certain hydrocarbons 5 ml. of this solution was diluted fivefold to provide another solution for testing. The range of final hydrocarbon concentrations was from 3.0×10^{-5} to 7.0×10^{-4} M. In a few cases saturated solutions were used owing to low solubility. No wave could be obtained for pentacene under these conditions owing to its insolubility. The voltage was increased automatically from zero volts at the rate of one hundred millivolts per minute. During the rising portion of each curve

(3) G. J. Hoijtink, Rec. trav. chim., **74**, 1525 (1955).

(4) H. Lund, Acta Chem. Scand., **11**, 1323 (1957).

(5) G. J. Hoijtink, Rec. trav. chim., **7**, 555 (1958).

(6) H. McConnell, J. S. Ham and J. R. Platt, J. Chem. Phys., **21**, 66 (1953); also references in G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin-Göttingen-Heidelberg, 1961.

(7) M. J. S. Dewar and A. R. Lepley, J. Am. Chem. Soc., **83**, 4560 (1961).

(8) M. J. S. Dewar and H. Rogers, ibid., **84**, 395 (1962).

(9) A. R. Lepley, ibid., **84**, 3577 (1962).

(10) R. Beukers and A. Szent-Gyorgyi, Rec. trav. chim., **81**, 255 (1962).

(11) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., Boston, Mass., 1941, p. 344.

(12) I. M. Kolthoff and J. F. Coetzee, J. Am. Chem. Soc., **79**, 870 (1957).

the voltage increase was interrupted several times and the potential between the indicator and reference electrodes and the potential between the reference electrode and an external calomel electrode were measured with a Sargent potentiometer.

The final portion of the current–voltage curve was recorded automatically. Five polarograms were obtained consecutively for each solution. Between tests the platinum electrode was carefully cleaned with tissue. If the electrode was not cleaned, the current measured during the next run was greatly reduced, but with cleaning the current was reproducible to within 3 to 5%. This variation is caused by the inability to reproduce the same electrode surface at the beginning of each test. Only in the cases of azulene, pyrene, fluoranthene and 1,2-benzpyrene were dark layers of oxidation products visible.

A linear relationship between the voltage and current near the middle of the rising portion of the curve was assumed, and the potential corresponding to half the diffusion current was read by extrapolation. This potential was corrected for iR drop across the electrodes. The potential reported for compounds with large maxima (perylene, pyrene, naphthalene, phenanthrene, fluoranthene, triphenylene, benzene, toluene and 1,2-benzpyrene) is the potential at half the maximum current. Usually a tendency for maxima to appear in the more concentrated solutions could be eliminated on dilution. The half-wave potential was found to be independent of concentration.

The mean deviation in half-wave potentials obtained in five consecutive determinations was usually from 0.002 to 0.005 v., and always less than 0.010 v., but including values for the same compound obtained on different days or with different solutions of the same concentration the mean deviation was from 0.005 to 0.010 v. All the values in this experiment should be considered accurate to within 0.01 v., except for benzene and its methyl derivatives which may be accurate to only 0.02 v., since in this voltage range the supporting solvent began to decompose. The experimental error in these polarographic measurements is much less than that encountered in obtaining transition energies of charge-transfer complex formation from absorption curves.

Results

Table I lists the oxidation potentials of the compounds studied in this experiment. Lund's values[4] were measured against a silver–silver ion (0.1 N) electrode in acetonitrile with a vibrating platinum electrode. For purposes of comparison they should be increased by 0.30 v. which is the potential of his reference electrode measured against the saturated calomel electrode.[13] Table I also lists the Hückel coefficient, x_n, of the highest occupied molecular orbital for those compounds for which the data are available. Most of the values are taken from Coulson and Daudel[14]; others were reported by Dewar[7] or by Szent-Gyorgyi.[15] In the final column are given the transition energies of complexes formed with trinitrofluorenone.[9]

TABLE I

Compound	Symbol	$E^{1/2}(ox)$, v. vs. s.c.e. in acetonitrile	$x_n{}^a$	ΔE_{ct}, e.v.^{b}
2-Aminoanthracene	1	0.44		
2-Fluorenamine	2	.53		
1-Naphthylamine	3	.54	0.394^c	
2-Naphthylamine	4	.64	.460^c	
Azulene	5	.71	.477	2.32 ± 0.06
Tetracene	6	.77	.295	1.90 ± .01
Perylene	7	.85	.347	2.00 ± .02
3-Methylcholanthrene	8	.87	.388^c	
9,10-Dimethylanthracene	9	.87		
3,4-Benzpyrene	10	.94	.371^d	2.11 ± .02
9-Methylanthracene	11	.96		
7,12-Dimethylbenz-anthracene	12	.96	.387^c	
3,4-Benztetraphene	13	1.01	0.405^d	2.22 ± 0.02
1,12-Benzperylene	14	1.01	.439	2.18 ± .02
1,2,4,5-Dibenzpyrene	15	1.01	.422^d	2.22 ± .01
12-Methyl-1,2-benz-anthracene	16	1.07		
7-Methyl-1,2-benz-anthracene	17	1.08		
Anthracene	18	1.09	.414	2.30 ± .02
8-Methyl-1,2-benz-anthracene	19	1.13		
1-Methyl-1,2-benz-anthracene	20	1.14		
2-Methyl-1,2-benz-anthracene	21	1.14		
3-Methyl-1,2-benz-anthracene	22	1.14		
10-Methyl-1,2-benz-anthracene	23	1.14		
11-Methyl-1,2-benz-anthracene	24	1.14		
4-Methyl-1,2-benz-anthracene	25	1.15		
5-Methyl-1,2-benz-anthracene	26	1.15		
6-Methyl-1,2-benz-anthracene	27	1.15		
9-Methyl-1,2-benz-anthracene	28	1.15		
1,2,3,4-Dibenzpyrene	29	1.15	.398^d	2.27 ± .03
Pyrene	30	1.16	.445	2.39 ± .02
1,2-Benzanthracene	31	1.18	.452	2.38 ± .02
1,2,5,6-Dibenzanthracene	32	1.19	.474	2.37 ± .07
Acenaphthalene	33	1.21	.638	3.00 ± .11
Coronene	34	1.23	.539	2.43 ± .02
1,2,3,4-Dibenzanthracene	35	1.25	.499	2.46 ± .02
1,2,7,8-Dibenzanthracene	36	1.26	.492	
1,2-Benzpyrene	37	1.27	.497^d	2.44 ± .05
Picene	38	1.33	.502	2.65 ± .05
Chrysene	39	1.35	.520	2.58 ± .05
2,3-Dimethylnaphthalene	40	1.35		
2,6-Dimethylnaphthalene	41	1.36		
1-Methylnaphthalene	42	1.43		
2-Methylnaphthalene	43	1.45		
Fluoranthene	44	1.45	.618	2.89 ± .10
Phenanthrene	45	1.50	.605	2.86 ± .10
Naphthalene	46	1.54	.618	2.89 ± .11
Triphenylene	47	1.55	.684	2.92 ± .11
p-Xylene	48	1.77	.852	
Mesitylene	49	1.80		
o-Xylene	50	1.89	.879	
m-Xylene	51	1.91	.891	
Toluene	52	1.98	.923	
Benzene	53	2.30	1.000	

^{a} Hückel coefficient of the highest occupied molecular orbital. ^{b} Transition energy of charge-transfer complex formation with trinitrofluorenone, ref. 9. ^{c} Reference 15. ^{d} Reference 7; others, ref. 14.

In Fig. 1 the observed half-wave potentials are plotted against Watanabe's photoionization potentials.[16] Electron impact values of Wacks and Dibeler are also shown.[17] The observed half-wave potentials are plotted against the transition energies of trinitrofluorenone complexes in Fig. 2 and against the values of x_n in Fig. 3. The least squares line in Fig. 2 excludes the points for azulene (5) and acenaphthalene (33) for reasons given below; the slope is 0.73. The line in Fig. 3 also excludes methyl-substituted compounds for reasons given below; the slope is 2.13 e.v.

(13) R. C. Larson, R. T. Iwamoto and R. N. Adams, Anal. Chim. Acta, 25, 371 (1961).

(14) C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," 2nd Ed., Mathematical Institute, Oxford, Eng., and the Centre de Mechanique Ondulatoire Applique, Paris, France, 1959.

(15) A. Szent-Gyorgyi, "Introduction to a Submolecular Biology," Academic Press, Inc., New York, N. Y., 1960.

(16) K. Watanabe. J. Chem. Phys., 26, 542 (1957).

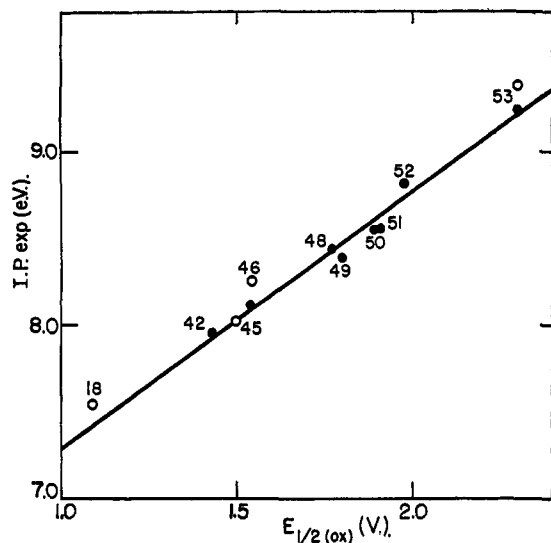(17) M. E. Wacks and V. H. Dibeler, ibid., 31, 1557 (1959).

Fig. 1.—Plot of experimental ionization potentials against $E_{1/2(ox)}$: ●, photoionization potentials, ref. 16; O, electron impact data, ref. 17. Numbers refer to list in Table I.

Discussion

Ionization Potentials.—The equation in Fig. 1 correlating photoionization potentials and oxidation potentials is

$$IP = (1.473 \pm 0.027)E_{1/2(ox)} + (5.821 \pm 0.009) \quad (5)$$

The electron impact values of Wacks and Dibeler are, except for phenanthrene, slightly above the correlation line. From eq. 5, ionization potentials can be calculated for polynuclear aromatic hydrocarbons for which no direct measurements exist. Some of these values are given in Table II together with values calculated by Briegleb and Czekella from charge-transfer data.[18] The agreement is good in all cases. Since the experimental error in the polarographic measurements is less than in measuring λ_{max} in charge-transfer spectra, there is less uncertainty in the ionization potentials calculated from polarographic data.

TABLE II

Compound	Calculated ionization potentials, e.v. Polarographic[a]	Charge transfer[b]
Tetracene	6.96	7.0
Perylene	7.07	7.15
Anthracene	7.43	7.4
Pyrene	7.53	7.55
1,2-Benzanthracene	7.57	7.6
Coronene	7.63	7.6
Chrysene	7.81	7.8
Phenanthrene	8.03	8.1
Triphenylene	8.10	8.1

[a] Calculated from eq. 5. [b] Ref. 18.

The ionization potentials calculated from eq. 5 can also be compared with values calculated by various molecular orbital techniques and can provide a check on the calculations in cases where direct photoionization values are not available. Two recent sets of calculations are those by Streitwieser[19] and those by Ehrenson.[20] Since these calculated ionization potentials were fitted to electron impact data, the values are not directly comparable to those calculated by eq. 5, which was fitted to photoionization data. Nevertheless, a plot of ionization potentials calculated by Ehrenson

(18) G. Briegleb and J. Czekella, Z. Elektrochem., 63, 6 (1959).
(19) A. Streitwieser, Jr., and P. M. Nair, Tetrahedron, 5, 149 (1959); J. Am. Chem. Soc., 82, 4123 (1960).
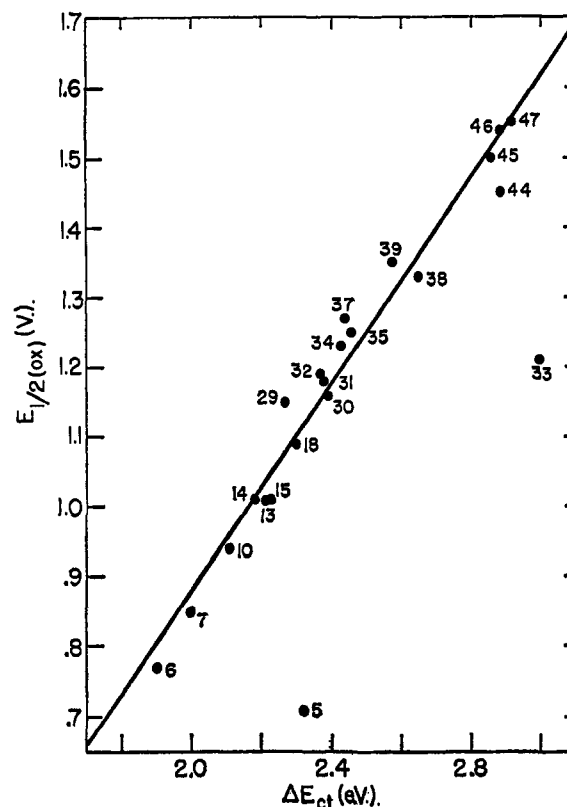(20) S. Ehrenson, J. Phys. Chem., 66, 706 (1962).

Fig. 2.—Plot of transition energies of trinitrofluorenone complexes[9] against $E_{1/2(ox)}$. Numbers refer to list in Table I.
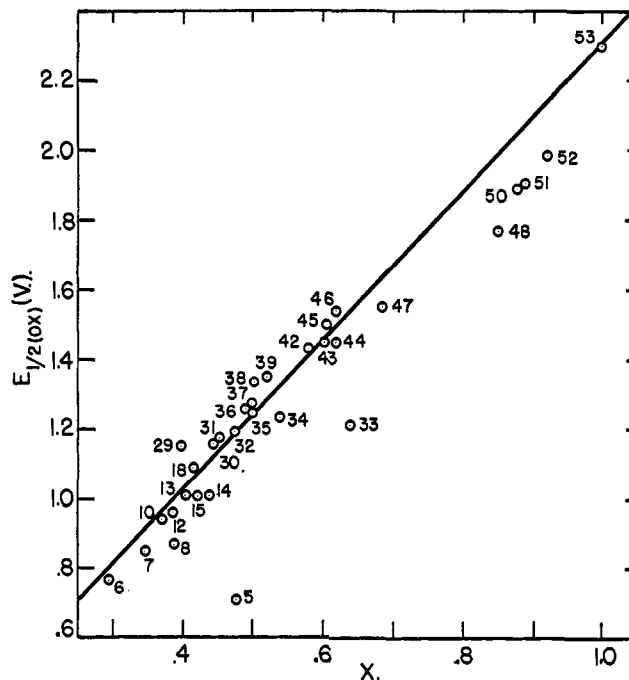

Fig. 3.—Plot of the molecular orbital parameter x_n against $E_{1/2(ox)}$. Numbers refer to list in Table I.

against $E_{1/2(ox)}$ yields a very satisfactory straight line, see Fig. 4. When Streitwieser's values are used the agreement is nearly the same except for the methyl derivatives of benzene.

The success of the correlation between $E_{1/2(ox)}$ and I_A and the success of the correlations in the following sections imply that either the solvation energy variations are small as compared with ionization potential variations or the solvation energy term varies in an approximately regular manner with the ionization potential for a large
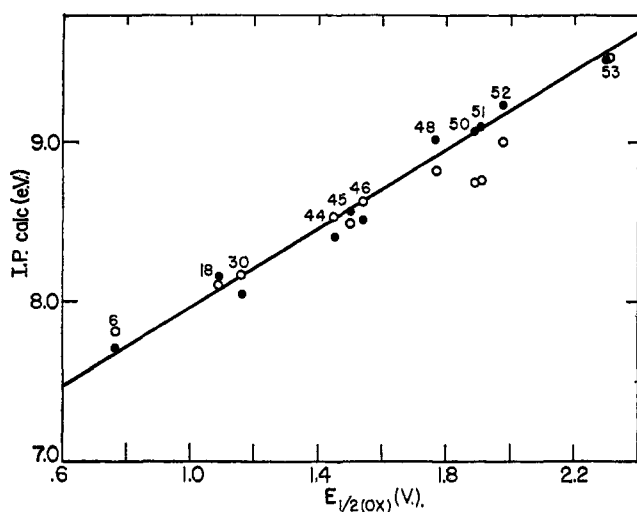
Fig. 4.—Plot of ionization potentials calculated by m.o. theory against $E_{1/2(ox)}$: ●, Ehrenson[20]; ○, Streitwieser.[19] Least squares line is drawn through Ehrenson's values. Numbers refer to list in Table I.

number of aromatic hydrocarbons. A regular dependence would tend to preserve the linearity of eq. 1 but would change the slope from unity. The observed slope of 1.47 in Fig. 1 suggests that there is a regular dependence. A possible explanation is that both the ionization potential and the solvation energy are functions of the number of rings in the compound.

Correlation with Charge-Transfer Transition Energies and Values of x_n.—The slope of Fig. 2, 0.73, when compared with the inverse of the slope of Fig. 1, 0.68, emphasizes the similarity between the behaviors of IP and ΔE_{ct} implied by eq. 1 and 4. The deviation of these slopes from unity may be accounted for by the variation in solvation energy. The slope in Fig. 3 may be defined in terms of a parameter $\beta = \beta_0 - \beta^1$, where β_0 is the normal value of the resonance integral obtained from calculations on the isolated molecule and β^1 is related to the effect of the solvent polarization on the adjacent atom electron interaction of the molecule. From the slopes of Fig. 1 and Fig. 2 the value of β^1 in acetonitrile is $0.30 \pm 0.03\ \beta_0$. The observed slope, β, in Fig. 3 is 2.13 e.v., so that the value of β_0 obtained in this correlation is 3.05 ± 0.13 e.v.

In Fig. 2 two compounds are very far from the least-squares line, azulene (5) and acenaphthalene (33). Since the charge-transfer transition energies of these two compounds correlated well with the calculated molecular orbital energies,[7-9] their behavior in Fig. 2 and Fig. 3 is due probably to the solvation energy term in eq. 4. For the cations of these two compounds, the following structures can be drawn.

(5) (33)
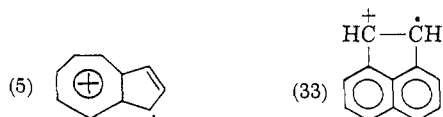
Such structures would contribute additional stabilization energy to the solvated species.

Toluene (53) and the xylenes (48, 50, 51) fall substantially below the line of Fig. 3. Such behavior would be caused by either: (i) inaccurate experimental determinations of $E_{1/2(ox)}$, (ii) unusually large solvation energies for the singly charged cations or (iii) inadequacies of the molecular orbital calculations. Our experimental value of $E_{1/2(ox)}$ for benzene agrees with that obtained by Lund,[4] but he did not determine the half-wave potentials of the xylenes. While our value for toluene is 0.20 v. lower than that obtained by Lund,

our value was reproducible to within 0.02 v. Since benzene, naphthalene and all the methyl derivatives of benzene fall on the same straight line in Fig. 1, the solvation energies of the methyl derivative cations could not be unusually large. Finally, Fig. 4 shows that molecular orbital calculations for methyl derivatives are more sensitive to the technique of calculation than unsubstituted compounds. Inadequacies of the molecular orbital treatment of methyl-substituted compounds could account for the deviation of toluene, o-, m- and p-xylene, and 3-methylcholanthrene.

In Fig. 3, coronene (34) and triphenylene (47) lie slightly below the line. It was found in the charge-transfer studies[7-10] that coronene and triphenylene were the only compounds which consistently fell off the correlation line relating charge-transfer spectra with highest occupied molecular energy levels. Lepley[9] noted that for these two compounds there is a degeneracy in their two highest occupied orbitals which should lead to a splitting of states. The calculations do not take the degeneracy into consideration. Therefore the value for the highest filled x_n is higher than it should be, $i.e.$, the calculated energy level is too low. The fact that the two compounds fall on the line in Fig. 2 where two experimental parameters are correlated supports this argument. The changes in the two values of x_n which would move coronene and triphenylene onto the line in Fig. 3 are the same as those which would effect agreement with the charge-transfer correlations.

Amino compounds are oxidized at much lower voltages than hydrocarbons because the electrons are removed from the non-bonding orbitals of the nitrogen atoms rather than from the π-systems. Thus their half-wave potentials cannot be correlated with molecular orbital calculations. Several amino compounds are included in Table I as an illustration. It is interesting that, for the amino compounds studied, second waves were observed at potentials corresponding to the oxidation of the parent compound. A second wave appeared at 1.56 v. in the case of 1-naphthylamine, at 1.28 v. for 2-naphthylamine and at 1.13 v. in the case of 2-aminoanthracene.

Effect of Methyl Substitution.—The effect of replacing a boundary hydrogen atom by a methyl group may be considered as a decrease in the electronegativity of the carbon atom. An altered Coulomb integral can be defined as

$$\alpha_r = \alpha_0 + h_r \beta_0$$

where h_r is negative. The change in the energy of the highest occupied orbital, ϵ_n, is given to a first approximation by[21]

$$\delta\epsilon_n = \sum_r c_{n,r}^2\, \delta\alpha_r$$

where $c_{n,r}$ is the coefficient of the rth atomic orbital in the nth molecular orbital. Then

$$\delta\epsilon_n = \sum_r c_{n,r}^2\, h_r \beta_0$$

since $\delta\alpha_r = \alpha_r - \alpha_0$, and the change in energy level should be proportional to $\sum_r c_{n,r}^2$, where the $c_{n,r}$'s are those of the parent hydrocarbons.

This formulation, which ignores the conjugative ability of the methyl group, has been tested by Streitwieser using changes in ionization potentials and changes in polarographic reduction half-wave potentials.[22]

(21) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A191**, 39 (1947).

(22) A. Streitwieser, Jr., *J. Phys. Chem.*, **66**, 368 (1962); A. Streitwieser, Jr., and I. Schwager, *ibid.*, **66**, 2316 (1962).

Table III

Compound	$E^{1/2}(ox)$, v.	$I.P.,^a$ e.v.	$-\Delta E^{1/2}(ox)$, v.	$\sum_r c_{n,r}^{2b}$
Benzene	2.30	9.245 ± 0.01	...	...
Toluene	1.98	$8.82 \pm .01$	0.32 ± 0.04	0.333
m-Xylene	1.91 ± 0.02	$8.56 \pm .01$	.39	.500
o-Xylene	$1.89 \pm .02$	$8.56 \pm .01$	.41	.500
p-Xylene	$1.77 \pm .02$	$8.445 \pm .01$	.53	.667
Mesitylene	$1.80 \pm .02$	$8.39 \pm .02$	.50	.500
Naphthalene	$1.54 \pm .01$	$8.12 \pm .02$	...	...
2-Methylnaphthalene	$1.45 \pm .01$	$7.95 \pm .02$	$.09 \pm .02$	.069
1-Methylnaphthalene	$1.43 \pm .01$	$7.96 \pm .02$	$.11 \pm .02$	.181
2,3-Dimethylnaphthalene	1.35		$.19 \pm .02$	.138
2,6-Dimethylnaphthalene	1.36		$.18 \pm .02$	.138
Anthracene	$1.09 \pm .01$		...	...
9-Methylanthracene	$0.96 \pm .01$		$.13 \pm .02$	.194
9,10-Dimethylanthracene	$0.87 \pm .01$		$.22 \pm .02$	.388
1,2-Benzanthracene	$1.18 \pm .01$		...	...
1-CH₃-Benzanthracene	$1.14 \pm .01$		$.04 \pm .02$	$<.001$
2-CH₃-Benzanthracene	$1.14 \pm .01$		$.04 \pm .02$	.041
3-CH₃-Benzanthracene	$1.14 \pm .01$		$.04 \pm .02$	.009
4-CH₃-Benzanthracene	$1.15 \pm .01$		$.03 \pm .02$	.026
5-CH₃-Benzanthracene	$1.15 \pm .01$		$.03 \pm .02$	.083
6-CH₃-Benzanthracene	$1.15 \pm .01$		$.03 \pm .02$	.089
7-CH₃-Benzanthracene	$1.08 \pm .01$		$.10 \pm .02$	.198
8-CH₃-Benzanthracene	$1.13 \pm .01$		$.05 \pm .02$	.104
9-CH₃-Benzanthracene	$1.15 \pm .01$		$.03 \pm .02$	.038
10-CH₃-Benzanthracene	$1.14 \pm .01$		$.04 \pm .02$	.056
11-CH₃-Benzanthracene	$1.14 \pm .01$		$.04 \pm .02$	.090
12-CH₃-Benzanthracene	$1.07 \pm .01$		$.11 \pm .02$	.155
7,12-Dimethylbenzanthracene	$0.96 \pm .01$		$.21 \pm .02$	.353

a Photoionization, ref. 16. *b* The values of $c_{n,r}$ were obtained from ref. 14. In carrying out the summation for the methyl-substituted benzenes, the degeneracy of energy levels was taken into account in the appropriate manner.

In Table III data are collected for testing this inductive model of methyl substitution for polarographic oxidation potentials. The polarographic data are in complete agreement with the photoionization potentials. The agreement with the model is fair except in the series of methylated benzanthracenes. Experimentally, substitution in the 7- or 12-position lowers the ionization potential by 10–12% and in other positions by 3–5%. However the spread of $\sum_r c_{n,r}^2$ for the latter group is larger than the spread of $\Delta E^{1/2}(ox)$. Whether the disagreement is due to inadequacies in the model or in the Hückel coefficients or in both is not yet possible to determine. It may prove, however, that new calculations of coefficients for 1,2-benzanthracene, using approximate self-consistent field techniques, will show a smaller spread of values of $c_{n,r}$ for the non-meso positions. From symmetry arguments, one would expect that calculations for 1,2-benzanthracene will depend more on the technique of calculation than would the results for the more symmetrical molecules of naphthalene or anthracene.

While the difference between the two oxidation potentials of 7-methylbenzanthracene and 12-methylbenzanthracene is not greater than twice the mean deviation, the oxidation potential of the 12-methyl compound may in fact be disproportionately lowered by the partial relief of the strain in the ion which is caused by steric repulsion between the methyl group and the neighboring hydrogen atom in the 12-methyl compound. No such steric hindrance is possible in the 7-methyl compound.

Comparison of Polarographic Data with p-Absorption Band Spectra.—The p-absorption band of aromatic hydrocarbons may be associated with the transition of an electron from the highest occupied to the lowest vacant molecular orbital but not necessarily between the two lowest vibrational states. The solvation energy of the positive ion of an organic molecule will

not be equal to that of its negative ion, but for a series of hydrocarbons the variation in the difference will not be large. If the variation in this difference is small, the difference in the polarographic reduction and oxidation half-wave potentials should give the transition energy between the lowest vibrational levels of the highest occupied and lowest vacant molecular orbitals plus a constant, so that

$$h\nu - E^{1/2}(ox) + E^{1/2}(red) = k$$

where $h\nu$ is measured from the p-absorption band of the molecule. A variation in k would represent, besides accumulated experimental error, transitions other than those between lowest vibrational levels in the p-absorption band spectra. In Table IV calculated values of k

Table IV

Compound	$h\nu,^a$ e.v.	$E^{1/2}(ox) -$ $E^{1/2}(red)$, v.^{b}	k, e.v.
Tetracene	2.64	2.35	0.29
Perylene	2.85	2.52	.33
3,4-Benzpyrene	3.22	2.78	.44
Anthracene	3.31	3.05	.26
1,2-Benzanthracene	3.46†	3.19	.27
Fluoranthene	3.47	3.22	.25
1,2,5,6-Dibenzanthracene	3.53†	3.22	.31
Coronene	3.64†	3.28	.36
Pyrene	3.72	3.26	.46
1,2-Benzpyrene	3.74	3.37	.37
Phenanthrene	4.24	3.98	.26
Naphthalene	4.35	4.12	.23
Triphenylene	4.36	4.03	.33
		Mean	.32
		Mean deviation	.047

a From p-absorption band; ref. 23. Those marked † were measured in benzene, others were measured in ethanol. *b* $E^{1/2}(red)$ in 96% dioxane; ref. 3.

are given. The reduction potentials in 96% dioxane were taken from Hoijtink.[3] The collected list of transi-

tion energies was taken from Bergman.[23] Reduction half-wave potentials in dimethylformamide[22] and in 2-methoxyethanol[23] yield similar results. The difference in polarographic oxidation and reduction potentials plus the mean value of k gives the transition energy of the absorption band to within 3% in most cases and to within 5% in all cases.

Monomethylated Benzanthracenes.—The monomethyl derivatives of 1,2-benzanthracene have been studied with respect to many theoretical and experimental parameters. Theoretical calculations of free valence numbers using both molecular orbital[24] and valence bond[25] methods, self-polarizabilities[26] and excitation energies[27] have been reported. Experimental measurements of the ultraviolet spectra and shifts with respect to the spectrum of unsubstituted 1,2-benzanthracene,[26,28] rates of reaction with osmium tetroxide,[29] rates of reaction with silver ion[30] and dissociation constants of charge-transfer complexes with trinitrofluorenone[31] have been reported.

Most of the investigators have been concerned with the varying degree of carcinogenicity within the series. In studies using both injection and skin painting techniques, the 7-, 8- and 12-methyl derivatives were found to be moderately potent, the 5-, 6-, 9-, 10- and 11-methyl derivatives were found to be weakly carcinogenic and the 1-, 2-, 3- and 4-methyl derivatives were found to be inactive. Thus the monomethylated benz-

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

(24) G. Berthier, C. A. Coulson, H. H. Greenwood and A. Pullman, *Compt. rend.*, **226**, 1906 (1948).

(25) A. Pullman, *Ann. chim.* (Paris), **2**, 5 (1947).

(26) G. M. Badger, R. S. Pearce and R. Pettit, *J. Chem. Soc.*, 1112 (1952).

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(28) R. N. Jones, *J. Am. Chem. Soc.*, **62**, 148 (1940); **63**, 151 (1941); *Chem. Rev.*, **32**, 1 (1943).

(29) G. M. Badger, *J. Chem. Soc.*, 456 (1949); 1809 (1950).

(30) R. E. Kofahl and H. J. Jones, *J. Am. Chem. Soc.*, **76**, 3931 (1954).

(31) K. H. Takemura, M. D. Cameron and M. S. Newman, *ibid.*, **75**, 3280 (1953).

anthracenes provide a structurally similar group of compounds with varying degrees of carcinogenicity, against which variation in any other parameter can reasonably be compared.

In several attempts to establish a purely electronic theory of carcinogenicity, data on the methylbenzanthracenes have been presented. The activity of 8-methylbenzanthracene cannot reasonably be attributed to a negligible difference in the calculated free valence numbers or self-polarizabilities. When carcinogenicity is compared with a calculated excitation energy, a significant separation appears between the 8-methyl derivative and the other non-*meso*-methylated compounds, but this is not supported by any experimental measurements.

Polarographic evidence helps clarify the problem. As noted above, the values of $E_{1/2(ox)}$ for the 7- and 12-methyl derivatives are significantly lower than those of the remaining compounds of the series. The variation in the remaining compounds is not more than two times the mean deviation of the values. The difference, however, between the 7-methyl compound and the 8-methyl compound is 0.05 v., which is five times the experimental mean deviation. The experimental results would tend to suggest that the calculations of excitation energies for the series result in a misleading spread of values. It would seem that the potency of the 8-methyl derivative of benzanthracene must be ascribed to non-electronic factors.[32]

(32) N. C. Yang, A. J. Castro, M. Lewis and T. Wong, *Science*, **134**, 386 (1961).

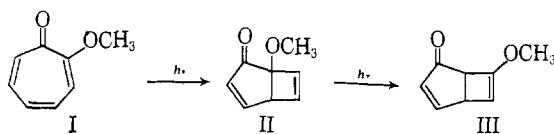[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

Photochemical Transformations. XIV. Isocolchicine[1,2]

BY WILLIAM G. DAUBEN AND DAVID A. COX

Ultraviolet irradiation of isocolchicine (VII) in methanol gives the valence isomer VIII as the major product, showing the desire of a phenyl-substituted tropolone to retain the styrene chromophore. In addition, a methanol adduct possessing structure XXV, related to γ-lumicolchicine, was formed in lesser amounts.

The photochemical-induced transformation of the tropolone nucleus has been shown to be an excellent synthetic route to the preparation of the $\Delta^{3,6}$-bicyclo[3.2.0]heptadiene-2-one system.[3] For example, α-tropolone methyl ether (I) upon irradiation in methanol by a mercury arc gives rise first to 1-methoxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadiene-2-one (II) which, in turn, is isomerized to the 7-methoxy derivative III. In a

I   II   III

similar manner, γ-tropolone methyl ether is transformed into 5-methoxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadiene-2-one.[4] In both of these series the first formed valence isomer is the one in which the methoxy group occupies a ring juncture position. In a similar manner to these simple materials, the tropolone ring of the naturally occurring alkaloid colchicine (IV) upon irradiation undergoes a valence isomerization to a bicyclo[3.2.0]-heptadiene. The products, β- and γ-lumicolchicine,[5,6] instead of having the isomeric structures with the methoxy group of a ring juncture such as V, were shown to possess the structure VI, differing only in the stereochemistry. This result raised the question as to whether the different reaction course followed was due to the undue steric strain in V or whether the con-

(1) For the previous paper in this series, see W. G. Dauben and F. G. Willey, *Tetrahedron Letters*, 893 (1962).

(2) This work was supported, in part, by Grant No. A-709, U. S. Public Health Service.

(3) W. G. Dauben, K. Koch, O. L. Chapman and S. L. Smith, *J. Am. Chem. Soc.*, **83**, 1768 (1961).

(4) O. L. Chapman and D. J. Pasto, *ibid.*, **82**, 3642 (1960).

(5) E. J. Forbes, *J. Chem. Soc.*, 3864 (1955), and references contained therein.

(6) P. D. Gardner, R. L. Brandon and G. R. Haynes, *J. Am. Chem. Soc.*, **79**, 6334 (1957).