At lower temperatures the decomposition is very slow, the rate increasing by a factor of about three for each 10° rise in temperature. This decomposition can become important, especially at higher temperatures in systems in which cyanide ion is undergoing another reaction, particularly if this reaction is itself fairly slow. There is at least one instance in the literature in which only approximations as the kinetics could be made owing to the lack of rate data on the decomposition of cyanide.[16] Also, there are undoubtedly instances in which this reaction was ignored as being insignificant in kinetic studies.

Experimental Section

General.—J. T. Baker "Analyzed" Reagent KCN was used in the experiments without further purification.

Kinetics.—The progress of the reaction was followed by titration of aliquots of the reaction mixture with standard $AgNO_3$ solution, KI being used as the indicator.[25] The presence of KNO_3 or ethanol in the reaction mixture did not interfere with this method of analysis.

Solutions were prepared using CO_2-free distilled water, stored under nitrogen, and protected from atmospheric CO_2 by trapping the vent with Ascarite. Stock solutions of KOH were prepared in large quantities and standardized; the KCN solutions were prepared from these KOH stock solutions immediately prior to each run.

Runs were made in triplicate under a nitrogen atmosphere in tightly stoppered 125-ml flasks. An initial volume of 100 ml of reaction mixture 0.05 M in KCN was used in each instance. The mixtures were prepared from stock solutions kept in the thermostated bath and were reimmersed in the bath immediately after preparation. After 1 hr, and at suitable intervals thereafter, 10-ml aliquots were withdrawn and titrated, the nitrogen in the flasks being replenished each time. The first point obtained after mixing was taken as $t = 0$ in the calculation of the rate constants. Determinations were made until the reactions were 55–80% complete, except for the runs at 33.1°, which were followed to only 16% completion. Runs of different mixture compositions made at the same temperature were carried out simultaneously in order that comparison of differences in rate could be made without regard to small variations in temperature over the course of the experiments.

Errors.—Titrations were read to ±0.02 ml (initial volume of titrant consumed was about 5 ml) and the average volumes of titrant, having a standard deviation of 0.03 ml or less, were used in calculation of the point-by-point rate constants. Each value of k reported in Table I is the average of all of the individual rate constants obtained in a given run. Individual rate constants obtained early in the reaction showed more scatter than those obtained later on, proably because of the very small differences in titre observed initially. The large standard deviation in k obtained at 33.1° is no doubt a reflection of this, since the reaction at this temperature was so slow. Since the accuracy of the values of K_h is uncertain, errors in k_s have not been reported.

Although it was possible to control temperatures to ±0.05°, it is doubtful that this value was realized because of the long duration of the kinetic runs. A value of ±0.1° would probably be a better estimate.

Registry No.—Potassium cyanide, 151-50-8; hydrocyanic acid, 74-90-8; potassium hydroxide, 1310-58-3.

Acknowledgments.—We wish to thank Professor G. Myron Arcand for many helpful discussions. Partial support of this project from the National Science Foundation and the Idaho State University Research Programs Committee is also gratefully acknowledged.

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[25] R. A. Day and A. L. Underwood, "Quantitative Analysis," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 106.

A Simple, Comprehensive Correlation of Organic Oxidation and Ionization Potentials

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Received August 24, 1971

We have been interested in developing new and useful organic electrooxidations. The sublime goal of this work is of course the ability to predict the products and rates of reactions for any oxidation. The most fundamental data needed for such predictions are the oxidation potentials of the reactants and possible products. One must know if the reactant will give up one or more electrons in the accessible potential range and if the possible products will survive the potential necessary to oxidize the reactant. It would, therefore, be useful to have an equation to predict oxidation potentials. This equation should be simple, use readily accessible input data, and provide oxidation potentials for a wide variety of species. We describe such an equation using ionization potentials (IP) as the only input data. Extensive tabulations of IP are available,[1-3] and photoelectron spectroscopy should provide a burgeoning source of data.[4]

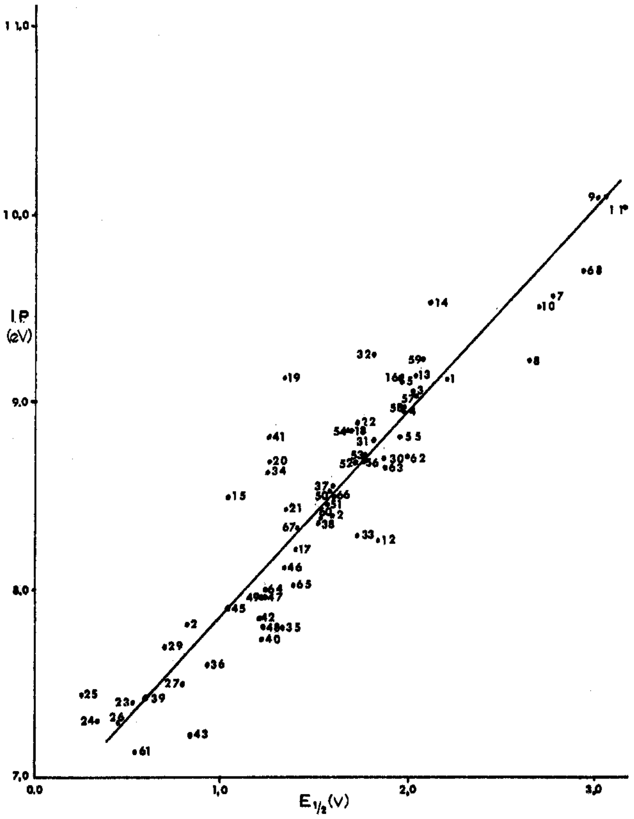

Figure 1.—Plot of vertical IP *vs.* $E_{1/2}$. Numbers refer to Table I.

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[1] R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 308.

[2] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

[3] J. L. Franklin, *et al.*, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," U. S. Department of Commerce, 1969.

[4] D. W. Turner, C. Baker, A. O. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970.

TABLE I

OXIDATION AND IONIZATION POTENTIALS

	Compd	IP, eV[a]	$E_{1/2}$, V[b]		Compd	IP, eV[a]	$E_{1/2}$, V[b]
1	2-Butene	9.13	2.21	35	Triphenylene	7.80	1.35
2	1,4-Cyclohexadiene	8.40	1.60	36	Coronene	7.60	0.93
3	1,3-Butadiene	9.07	2.03	37	*m*-Xylene	8.56	1.60
4	Cyclohexene	8.95	1.98	38	Mesitylene	8.39	1.53
5	2-Methyl-1-butene	9.12	1.97	39	Azulene	7.43[f]	0.61
6	Ethylene	10.51	2.90	40	Chrysene	7.75	1.22
7	1-Butene	9.58	2.78	41	Indene	8.81	1.25
8	2-Methylpropene	9.23	2.65	42	Hexamethylbenzene	7.85	1.20
9	2-Methylpentane	10.11	3.01	43	Anthracene	7.23	0.84
10	1-Octene	9.52	2.70	44	Tetracene	6.88	0.53
11	2,2-Dimethylbutane	10.05	3.28	45	1,4-Dimethoxybenzene	7.90[g]	1.04
12	2,3-Dimethyl-1,3-butadiene	8.27	1.84	46	Naphthalene	8.12	1.34
13	2-Iodopropane	9.17	2.04	47	1-Methylnaphthalene	7.96	1.24
14	Methyl iodide	9.54	2.12	48	Phenanthrene	7.80	1.23
15	Phenol	8.50	1.04	49	2-Methylnaphthalene	7.96	1.22
16	1,4-Dioxane	9.13	1.97[c]	50	*o*-Xylene	8.56	1.58
17	Anisole	8.22	1.40	51	*p*-Xylene	8.45	1.54
18	Thiophene	8.86	1.70	52	*p*-Bromotoluene	8.67	1.72
19	*n*-Butyl mercaptan	9.14	1.34	53	Iodobenzene	8.73	1.77
20	Dimethyl sulfide	8.69	1.26	54	Anisaldehyde	8.86[g]	1.64
21	Diethyl sulfide	8.43	1.35	55	Toluene	8.82	1.96
22	Dimethyl sulfoxide	8.84	1.73[c]	56	*p*-Chlorotoluene	8.69	1.76
23	Diphenylamine	7.40	0.53	57	Chlorobenzene	9.07	2.07
24	1-Naphthylamine	7.30	0.34	58	Bromobenzene	8.89	1.98
25	2-Naphthylamine	7.25	0.44	59	Benzene	9.24	2.04
26	Dimethylaniline	7.14	0.45	60	Biphenyl	8.27	1.48
27	Triethylamine	7.50	0.79[c]	61	Perylene	7.15	0.55
28	Trimethylamine	7.82	0.82	62	1-Propylbenzene	8.72	1.97
29	Aniline	7.70	0.70[d]	63	2-Propylbenzene	8.69	1.88
30	*n*-Butylamine	8.71	1.87[c]	64	Pentamethylbenzene	7.92	1.28
31	*N,N*-Dimethylacetamide	8.81	1.82[c]	65	1,2,4,5-Tetramethylbenzene	8.03	1.29
32	Pyridine	9.27	1.82	66	1,2,3-Trimethylbenzene	8.48	1.58
33	Quinoline	8.30	1.73[e]	67	1,2,4-Trimethylbenzene	8.27	1.41
34	Fluorene	8.63	1.25	68	*tert*-Butyl alcohol	9.71	2.94[c]

[a] Photoionization or spectroscopic values compiled by Kiser[1] except where noted. [b] Measured in acetonitrile at platinum. Reported *vs.* Ag|AgNO$_3$. Values from the compilation of C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, except where noted. [c] Measured by E. A. Mayeda. [d] C. Parkanyi and R. Zahradnik, *Collect. Czech. Chem. Commun.*, **30**, 4287 (1965). [e] R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, p. 320. [f] Reference 2. [g] A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 22 (1968).

Previous workers have correlated the IP and oxidation potentials ($E_{1/2}$) of aromatic hydrocarbons and alkenes and discussed the reasons underlying such a correlation.[5,6] In particular, the relatively small solvation energy changes and the probable monotonic variation of solvation energy with the size of the hydrocarbon and therefore its IP were mentioned.

Expansion of this idea to include all sorts of organic molecules is possible as illustrated by Figure 1. This plot includes all the reliable data that we could collect from the literature and several values determined in our laboratory. The electrochemical data all refer to acetonitrile solvent and a smooth platinum anode. The reference electrode is Ag|AgNO$_3$ in acetonitrile. Data reported *vs.* sce were corrected by adding −0.30 V. The numbers used are simple averages of all reports. Both half-wave and peak potentials are reported in the literature. We have corrected the latter by adding −0.15 V. This value is approximate but reasonable for these irreversible oxidations. Several literature values were checked and a few not on the line were not reproduced. These points were rerun several times including a determination by an independent investigator.[7] The revised values were used and several closely related points (same papers, similar structures) which appeared to need revision were excluded.[8] Only vertical IP were used (Table I).

The plot in Figure 1 fits the equation $E_{1/2} = 0.92(\mathrm{IP}) - 6.20$. As expected, the slope is less than unity. Because there are a disproportionate number of aromatic hydrocarbons included in Figure 1, we have made a more representative plot in Figure 2. The least-squares line has the equation $E_{1/2} = 0.89(\mathrm{IP}) - 6.04$. The correlation coefficient for the plot in Figure 1 is 0.92 and in Figure 2 is 0.95. Since the data came from many different sources and we know there is often considerable error in the $E_{1/2}$ values, this seems quite acceptable.

It should be realized that since the initially formed

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

(6) E. S. Psych and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2124 (1963).

(7) We thank Dr. Lloyd Jones for these measurements.

(8) The point for ethylene is not on the plot but was included in the least-squares calculation. Points 30 and 31 are revised values. $E_{1/2}$ data for several substituted anilines[9] and amides and primary amines[10] were excluded. Different sets of values for the latter are given in the original literature and in a book by the same author. Our values differ from both.

(9) S. Wawzonek and T. W. McIntyre, *J. Electrochem. Soc.*, **114**, 1025 (1967).

(10) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, Chapter 9.

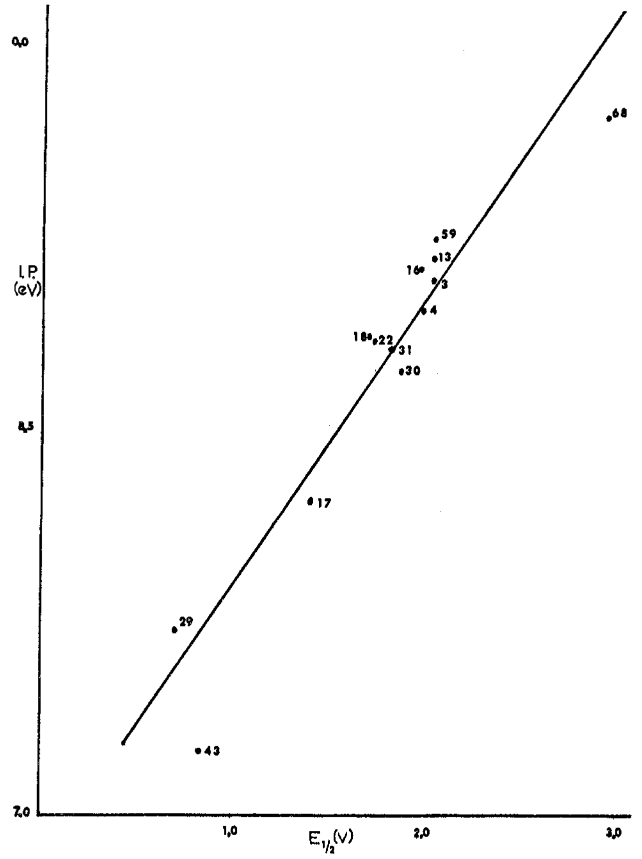

Figure 2.—Plot of selected vertical IP *vs.* $E_{1/2}$. Numbers refer to Table I.

cation radical decays much more rapidly than the time required for the measurement $E_{1/2}$ is a kinetic parameter for the overall oxidation process. If one considers this fact in addition to the possible incursion of specific surface effects and differential solvation, this simple correlation is fascinatingly accurate. The correlation results because the energy of the highest occupied molecular orbital (HOMO) primarily determines both potentials. Several groups have described correlations of IP or $E_{1/2}$ with the HOMO energy[2,11] and it is clear that either potential should be calculable. It does appear that phenol and butyl mercaptan have abnormally low $E_{1/2}$ values because of special solvation. The cation radicals of these species will be strong acids stabilized by hydrogen bonding to the basic solvent, acetonitrile. This will, of course, lower the $E_{1/2}$. Other solvation effects and specific surface effects might be uncovered by a careful study of $E_{1/2}$ variations as a function of solvent and electrode material.

This correlation should have interesting ramifications in organic electrochemistry. As indicated, decisions about synthetic feasibility can be made with some confidence based upon oxidation potential predictions for reactants and products. In a similar manner, electrooxidation can be applied selectively to the most easily oxidized functionality of a complex molecule. Photoelectron spectroscopy is of interest in this regard since it not only provides IP data but reveals the nature of the HOMO.[4] Finally, it is noted that homogeneous electron-transfer oxidation rates and the $E_{1/2}$ of radicals[12] and inorganic complexes may be amenable to a similar treatment.

Acknowledgment.—We thank the Petroleum Research Fund and the National Science Foundation for support.

[11] An extensive and modern treatment with references is M. J. S. Dewar, J. A. Hashmall, and N. Trinajstic, *J. Amer. Chem. Soc.*, **92**, 5555 (1970).

[12] H. Volz and W. Lotsch, *Tetrahedron Lett.*, 2275 (1969) report −0.47 V for the reduction $E_{1/2}$ of tropylium perchlorate on mercury. Since this couple is probably fully reversible and therefore independent of electrode, we would calculate the IP as 6.25. The reported[1] spectroscopic IP is 6.24!

Oxidative Coupling of Aldehydes and the Rearrangement of Dioxa-1,5-hexadienes

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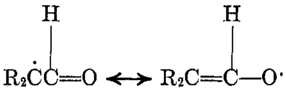
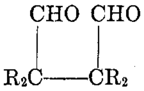
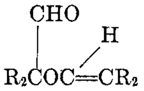
The oxidation[2] of aldehydes of the form R_2CHCHO by active manganese dioxide gives products which can be formulated as dimers of the free radical a. These are **1** and **2**. The other symmetrical coupling product, the divinyl peroxide, $R_2C{=}C(H)OOC(H){=}CR_2$, **3**, has not been observed. We have been interested in dioxa-1,5-hexadienes and their rearrangements in connection with our studies[3] of allylic carboxylates, which are 1,3-dioxa-1,5-hexadienes. Compounds **1**, **2**, and **3** are respectively substituted 1,6-, 1,4-, and 3,4-dioxa-1,5-hexadienes.


$R_2\dot{C}C(H){=}O \longleftrightarrow R_2C{=}C(H){-}O\cdot$

a


$R_2C(CHO){-}C(CHO)R_2$

1


$R_2C(CHO)OC(H){=}CR_2$

2

The Cope rearrangement would lead to the rearrangements **2** ⇄ **2** and **1** ⇄ **3**. The first is a degenerate rearrangement which could be revealed by labeling as has been done in one cyclic case;[4] in the open-chain case the completely methylated compound **2a** does not show any nmr line broadening at 150°,[2] showing by this method no degenerate rearrangement. In this note we present evidence supporting in some detail the free-radical coupling mechanism and observe some of the proposed rearrangements.

There was a possibility that the active manganese dioxide oxidation could be exploited to give products allowing a study of the rearrangement whether or not the radical coupling mechanism is correct. If the mechanism is incorrect, then oxidation of optically active α-methylbutylraldehyde might give an optically active form of the oxidation product in either of the geometrically isomeric form **2b** or **2c**. On the other hand, if the mechanism is correct, **2b** and **2c** will be optically inactive, but cross products **2d**, **2e**, and **2f** might result from the oxidation of a mixture of isobutyraldehyde and α-methylbutyraldehyde. The Cope rearrangement would be expected to be accom-

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[1] National Science Foundation Predoctoral Fellow, 1968–1971.

[2] J. C. Leffingwell, *Chem. Commun.*, 357 (1970).

[3] E. S. Lewis, J. T. Hill, and E. R. Newman, *J. Amer. Chem. Soc.*, **90**, 662 (1968).

[4] J. D. Roberts and R. P. Lutz, *ibid.*, **83**, 2198 (1961).