bonding decreases; the magnitude of σ_{R,NO_2} decreases; and therefore Δ decreases.

The Exclusion of Benzoic Acid from the 2-Substituted Sets.—The pK values of benzoic acid obviously do not lie on the correlation lines obtained for 2-substituted benzoic acids. We may account for this in part in terms of coplanarity of the carboxyl group with the ring in benzoic acid as compared to the existence of a large average interplanar angle in the 2-substituted benzoic acids. We find[17] that the pK values for carboxylic acids belonging to the set XCO_2H in water at 25° can be correlated with σ_m giving $\rho = -8$. Then from eq 2 for X = Ph

$$pK_{Ph} = -8\sigma_{I,Ph} - 8/3\sigma_{R,Ph} + pK_H \qquad (16)$$

As $\sigma_{R,Ph}$ is given by eq 15, for an interplanar angle of 30° we would expect a deviation of 0.08 pK units in water. The remainder of the deviation may be due to the difference in solvation of the carboxyl group in planar benzoic acid as compared with the nonplanar 2-substituted benzoic acids. Values of pK_H calculated, pK_H observed, and Δ, the difference between calculated and observed values, are reported in Table XII. In all sets studied, pK_H calculated is less than pK_H observed.

Composition of the *ortho* Electrical Effect.—The composition of the electrical effect of a substituent may conveniently be described[3] by the parameter ϵ where

$$\epsilon = \beta/\alpha \qquad (17)$$

TABLE XII

CALCULATED AND OBSERVED pK_H VALUES FOR BENZOIC ACID

Set	pK_H Calcd	pK_H Obsd	Δ
01	3.474	4.203	0.729
02	4.449	4.820	0.371
03	5.240	5.469	0.226
04	6.978	7.029	0.051
05	3.892	4.454	0.562
06	4.548	4.996	0.448
07	6.389	6.63	0.428
08	7.219	7.647	0.428
09	8.272	9.41	1.14
010	8.581	10.25	1.67
011	8.343	8.609	0.266
012	8.282	8.603	0.321

We have previously investigated ϵ for *ortho*-substituted compounds as a function of structure.[3,4] Electrical effects of *ortho* substituents were classified as normal effects (ϵ >0.6) and abnormal effects (ϵ <0.5). From our present results for at least some sets ϵ is a function of solvent as well as of structure. For the 2-substituted benzoic acids eq 8 and 17 give

$$\epsilon = (mS + d)/\alpha \qquad (18)$$

and as α is constant

$$\epsilon = m'S + d' \qquad (19)$$

This is in contrast to the behavior of 3- or 4-substituted benzoic acids for which ϵ is not solvent dependent.

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[17] M. Charton, unpublished results.

A Linear Free-Energy Relationship for Acceptor Strength in Charge-Transfer Complex Formation. I. Substituted Benzene Donors

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Equilibrium constants for charge-transfer complex formation between 19 sets of substituted benzene π donors and various acceptors are correlated by the linear free-energy relationship

$$\log K_A = \nu\eta_A + \log K°_A$$

where η_A is a constant characteristic of the "strength of acceptor" and ν is a function of donor, solvent, and temperature. Values of η are defined from the reference system p-xylene in CCl_4 at 25° for which $\nu \equiv 1.00$. Fifty values of η are reported for acceptors including substituted 1,4-benzoquinones, nitrobenzenes, cyanobenzenes, anhydrides, and halogens. It is suggested that η_A values for π acceptors of the type $GX_1 \ldots X_n$ may be calculated from the equation

$$\eta_A = \eta_G + \Sigma\eta_{X_i}$$

where η_{X_i} is the increment in η caused by the X_i substituent and η_G is the η value of the parent compound.

In the course of a previous investigation[1] a need arose for a parameter which would serve as a measure of acceptor strength in charge-transfer complex formation. Hammond[2] has shown that the acceptor strengths of 2-substituted 1,4-benzoquinones may be adequately represented by the Hammett equation. A scale of acceptor strength which would comprise all known acceptors including halogens and SO_2, as well as organic acceptors, is required; therefore the Hammett equation cannot be used. To provide such a scale, the linear free-energy relationship (eq 1) has been defined

$$\log K_A = \nu\eta_A + \log K°_A \qquad (1)$$

where K_A is the equilibrium constant for charge-transfer complex formation of some acceptor A; η_A is a constant characteristic of the acceptor strength of A; the slope ν is a function of the donor, solvent, and temperature; and the intercept log $K°_A$ represents the logarithm of the calculated value of the formation constant for the reference acceptor A°. To determine values of η a standard donor, solvent, and temperature and a reference acceptor must be chosen. The choice of the standard system was determined by the following considerations. (1) The donor must be sufficiently reactive to permit the determination of "reliable"

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[1] M. Charton, *J. Org. Chem.*, **31**, 2991, 2996 (1966).

[2] P. R. Hammond, *J. Chem. Soc.*, 471 (1964).

TABLE I

VALUES OF η

Acceptors	η	Set[a]	K_C[e]	Ref
Iodine monochloride	0[b]		1.51	*f*
Iodine monobromide	−0.35[c]		0.67	*g*
Iodine	−0.69[c]		0.31	*f*
Bromine	−0.90[c]		0.192	*h*
Bromine monochloride	−0.32[d]			
Chlorine	−2.0	5A	0.017	*i*
Sulfur dioxide	−1.17	*c*	0.103	*j*
2,3-Dicyano-1,4-benzoquinone	0.10	5A	4.9	*k*
2,3-Dichloro-5,6-dicyano-1,4-benzoquinone	0.61	5A	19.2	*k*
2-Methyl-1,4-benzoquinone	−1.00	8A	0.57	*l*
1,4-Benzoquinone	−0.95	8A	0.71	*l*
2-Chloro-1,4-benzoquinone	−0.83	8A	1.20	*l*
2-Nitro-1,4-benzoquinone	−0.47	8A	5.51	*l*
2-Cyano-1,4-benzoquinone	−0.54	8A	4.11	*l*
2-Acetyl-1,4-benzoquinone	−0.82	8A	1.21	*l*
2-Methoxy-1,4-benzoquinone	−1.3	8A	0.18	*l*
2-Fluoro-1,4-benzoquinone	−0.91	8A	0.85	*l*
2-Bromo-1,4-benzoquinone	−0.69	8A	2.11	*l*
2-Iodo-1,4-benzoquinone	−0.71	8A	1.95	*l*
2-Carbomethoxy-1,4-benzoquinone	−0.94	8A	0.72	*l*
2,6-Dichloro-1,4-benzoquinone	−0.65	8A	2.60	*m*
2,6-Dimethyl-1,4-benzoquinone	−1.12	8A	0.34	*m*
Duroquinone	−1.07	8A	0.41	*m*
Chloranil	−0.33	8A	10.27	*m*
Bromanil	−0.43	8A	6.66	*m*
Iodanil	−0.57	8A	3.62	*m*
Nitrobenzene	−1.4	13	0.3	*h*
1,2-Dinitrobenzene	−1.2	13	0.5	*n*
1,3-Dinitrobenzene	−1.3	13	0.4	*n*
1,4-Dinitrobenzene	−1.06	4	0.14	*o*
1,3,5-Trinitrobenzene	−0.62	4	0.37	*o*
1,2,3-Trinitrobenzene	−0.77	8A	1.5	*p*
1,2,4-Trinitrobenzene	−0.71	8A	2.0	*p*
2,4,6-Trinitrotoluene	−0.76	5A	0.49	*o*
1,3,5-Trinitro-2,4-dimethylbenzene	−0.89	13	1.7	*n*
Picric acid	−0.50	8A	4.86	*q*
1,2,3,5-Tetranitrobenzene	−0.35	8A	9.4	*p*
1,2-Dicyanobenzene	−1.5	18A	1.39	*r*
1,3-Dicyanobenzene	−1.8	18A	0.77	*r*
1,4-Dicyanobenzene	−1.2	18A	2.43	*r*
1,3,5-Tricyanobenzene	−0.83	18A	5.10	*r*
1,2,4,5-Tetracyanobenzene	−0.33	12	3.0	*s*
Tetrachlorophthalonitrile	−0.64	17	0.8	*t*
Tetracyanoethylene	0.30	8A	148.3	*u*
7,7,8,8-Tetracyanoquinodimethane	−0.70	12	0.817	*v*
Pyromellitic dianhydride	−0.29	*d*		*w*
Tetrachlorophthalic anhydride	−0.25	8A	13.0	*x*
Maleic anhydride	−0.99	11	1.54	*y*
Chloromaleic anhydride	−0.74	9	0.043	*z*
Dichloromaleic anhydride	−0.55	8A	3.98	*aa*

[a] Numbers refer to the sets in Table III. [b] By definition. [c] Calculated from the standard set (*p*-xylene/CCl_4/25°). [d] M. Charton, unpublished results. [e] All K_C are in CCl_4 at 25° unless otherwise noted. [f] R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **74**, 4500 (1952). [g] At 24°; R. D. Whittaker and H. H. Sisler, *J. Phys. Chem.*, **67**, 5231 (1963). [h] Calculated from K_N; R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **72**, 4677 (1950). [i] L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 462 (1951). [j] Calculated from K_N; L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 4169 (1951). [k] P. R. Hammond, *J. Chem. Soc.*, 3113 (1963). [l] P. R. Hammond, *J. Chem. Soc.*, 471 (1964). [m] At 18–20°; R. Foster, D. L. Hammick, and P. J. Placito, *ibid.*, 3881 (1956). [n] At 18–20° in cyclohexane; B. Dale, R. Foster, and D. L. Hammick, *ibid.*, 3986 (1954). [o] Calculated from K_C at 20 and 45°; N. B. Juriniski and P. A. D. de Maine, *J. Amer. Chem. Soc.*, **86**, 3217 (1954). [p] At 20°; R. Foster, *J. Chem. Soc.*, 1075 (1960). [q] At 20°; G. Briegleb, J. Czekalla, and H. Hauser, *Z. Physik. Chem.*, **21**, 99 (1959). [r] R. Foster, and T. J. Thomson, *Trans. Faraday Soc.*, **59**, 2287 (1963); in $CHCl_3$ at 20°. [s] S. Iwata, J. Tanaka, and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 894 (1966); at 22.4° in CH_2Cl_2. [t] A. S. Bailey, B. R. Henn, and J. M. Langdon, *Tetrahedron*, **19**, 161 (1963); in $CHCl_3$ at 24°. [u] At 20°; G. Briegleb, J. Czekalla, and G. Reuss, *Z. Physik. Chem.*, **30**, 333 (1961). [v] At 22° in CH_2Cl_2; L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mechel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962). [w] At 26°, calculated from K_N; L. L. Ferstandig, W. G. Toland, and C. D. Heaton, *ibid.*, **83**, 1151 (1961). [x] J. Czekalla and K. O. Meyer, *Z. Physik. Chem.*, **27**, 185 (1961); calculated from K_N. [y] Z. Raciszewski, *J. Chem. Soc., B*, 1142 (1966); K_C in methylcyclohexane. [z] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **75**, 3376 (1953); calculated from K_N. [aa] C. H. J. Wells, *Tetrahedron*, **22**, 1985 (1966); calculated from K_C at 20.2 and 40.1°.

formation constants for very weak acceptors. (2) A symmetric donor is preferred to minimize variable steric effects arising from different complex configurations. (3) Availability of data in the literature is required. On the basis of these considerations, *p*-xylene in CCl_4 at 25° was chosen as the standard system. For the standard system $\nu_0 \equiv 1.000$, by definition.

The choice of a reference acceptor required only that a "reliable" value of its formation constant for the standard system be available. ICl was chosen as the reference acceptor for which $\eta_A \equiv 0.000$, by definition. Values of η may now be calculated from standard system formation constants extant in the literature. The values of η obtained are presented in Table I together with the formation constants from which they were calculated.

To provide a test of eq 1 and to make possible the calculation of values of η for other acceptors (for which standard system formation constants are unavailable) formation constants for other donors were correlated with eq 1 by the least mean squares method. The data used in the correlations are given in Table II; the results are reported in Table III. Additional values of η were calculated from these results and are listed in Table I with the formation constants used in obtaining them.

Results

Excellent results were obtained for sets 1–6, 8, 14, and 15. Very good correlations were obtained for sets 11, 12, 17, and 21. The results for sets 9 and 16 were good. For sets 7, 13, and 18, fair correlation is obtained, while sets 10, 21, and 24 give poor results. The results for set 5 are improved on elimination of the value for A = iodine. As set 5A seems somewhat more reliable, it has been used to calculate new values. As improvement in the results obtained for set 8 on the elimination of the value for A = iodine monochloride occurs, new η values were calculated from set 8A. Elimination of the value for A = 1,4-dinitrobenzene from set 18 gives a markedly improved correlation (set 18A) from which new values of η were calculated.

The correlation obtained for the alkyl- and aminobenzenes and for chlorobenzene with the η constants are generally satisfactory; the results obtained from naphthalene (set 19) and diphenyl (set 20) are poor. It has been suggested that the acceptor strength of polynitroaromatic compounds is dependent on the size

TABLE II

COMPLEX FORMATION CONSTANTS USED IN CORRELATIONS[a]

Set	Donor	Solvent	Temp, °C	Ke
1	PhH	CCl_4	25	A (0.15);[b] B (0.54);[b] C (0.44);[c] D (0.109);[d] E (0.054);[e] F (0.304)[f]
2	PhMe	CCl_4	25	A (0.16);[b] B (0.87);[b] C (0.51);[c] D (0.130);[e] E (0.076);[e] F (0.478)[f]
3	1,2-$C_6H_4Me_2$	CCl_4	25	A (0.27);[b] B (1.24);[b] C (0.78);[c] D (0.198);[e] E (0.136);[e] F (0.975)[f]
4	1,3-$C_6H_4Me_2$	CCl_4	25	A (0.31);[b] B (1.39);[b] C (0.78);[c] D (0.184);[e] E (0.119);[e] F (0.711)[f]
5	1,3,5-$C_6H_3Me_3$	CCl_4	25	A (0.82);[b] B (3.20);[b] C (1.47);[c] D (0.381);[g] E (1.52);[e] G (0.67)[h]
6	1,2,4,5-$C_6H_2Me_4$	CCl_4	25	A (0.63);[b] B (5.60);[b] G (1.73);[h] H (0.66);[h] I (0.45);[h] J (12.3);[i] K (72.3)[i]
7	C_6HMe_5	CCl_4	25	A (0.88);[b] B (6.43);[b] G (2.90);[h] H (1.13);[h] I (0.78)[h]
8	C_6Me_6	CCl_4	25	A (1.35);[b] B (13.2);[b] C (4.36);[c] G (4.45);[h] H (1.50);[h] I (0.86);[h] J (73.8);[h] K (574.0)[i]
9	PhH	$CHCl_3$	25	A (0.056);[j] G (0.058);[k] L (0.026);[l] M (0.25)[m]
10	PhH	c-C_6H_{12}	25	A (0.212);[n] G (0.81);[o] M (2.03);[p] O (0.79)[q]
11	C_6Me_6	c-C_6H_{12}	20	G (13.5);[r] O (28.9);[s] T (5.0);[r] U (3.9);[r] V (2.46)[r]
12	C_6Me_6	CH_2Cl_2	22	G (1.03);[j] J (13.4);[i] K (97.5);[i] M (17.0);[t] N (5.87)[j]
13	PhNHMe	c-C_6H_{12}	20	G (7.3);[u] H (3.1);[u] I (.9);[u] O (7.9)[q]
14	PhNHEt	c-C_6H_{12}	18.5–20	G (8.4);[u] H (3.8);[u] I (1.2);[u] P (0.3);[u] Q (0.8);[u] R (0.7);[u] S (2.0)[u]
15	$PhNMe_2$	c-C_6H_{12}	18.5–20	G (9.5);[u] H (5.8);[u] I (1.8);[u] P (0.4);[u] Q (1.1);[u] R (1.2)[u]
16	$PhNEt_2$	c-C_6H_{12}	18.5–20	G (6.5);[u] H (2.4);[u] I (1.7);[u] P (0.3);[u] Q (1.1);[u] R (1.4)[u]
17	$PhNMe_2$	$CHCl_3$	19–21	G (1.3);[v] M (24.8);[w] O (1.6);[x] W (0.4);[y] X (2.5)[y]
18	1,4-$(Me_2N)_2C_6H_4$	$CHCl_3$	20	G (8.16);[z] I (6.89);[z] Q (2.12);[z] R (2.18);[z] X (12.97)[z]
19	Naphthalene	CCl_4	25	A (0.25);[b] B (1.39);[b] C (0.63);[i] D (0.20);[aa] G (4.00);[bb] L (0.31);[cc] M (3.26);[dd] N (2.8);[ee] O (1.35);[dd] Y (3.59)[ff]
20	Ph_2	CCl_4	25	A (0.37);[gg] G (1.0);[hh] L (1.28);[cc] M (1.78);[dd] N (2.90);[ee] O (0.625)[dd]
21	PhCl	CCl_4	25	A (0.106);[ii] B (0.21);[b] C (0.109);[ii] D (0.08);[d] E (0.032);[e] F (0.20);[f] Z (0.04)[ii]

[a] Values of Ke are given in parentheses. Acceptors are A, iodine; B, iodine monochloride; C, iodine monobromide; D, bromine; E, sulfur dioxide; F, pyromellitic anhydride; G, 1,3,5-trinitrobenzene; H, 2,4,6-trinitrotoluene; I, 1,4-dinitrobenzene; J, 2,3-dicyano-1,4-benzoquinone; K, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; L, 1,4-benzoquinone; M, tetracyanoethylene; N, tetrachlorophthalic anhydride; O, chloranil; P, nitrobenzene; Q, 1,2-dinitrobenzene; R, 1,3-dinitrobenzene; S, 1,3,5-trinitro-2,4-dimethylbenzene; T, 1,2,4-trinitrobenzene; U, 1,2,3-trinitrobenzene; V, 1,2,3,5-tetranitrobenzene; W, 1,3,5-tricyanobenzene; X, 1,2,4,5-tetracyanobenzene; Y, picric acid; Z, chlorine.

[b] Footnote *f*, Table I.

[c] Footnote *g*, Table I.

[d] Footnote *h*, Table I.

[e] Footnote *j*, Table I.

[f] Footnote *x*, Table I.

[g] R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **76**, 3062 (1954).

[h] Footnote *c*, Table I.

[i] Footnote *k*, Table I.

[j] Calculated from the equation $\log K_C = mS + c$: M. Charton, Abstracts, 152nd National Meeting of the American Chemical Society, 1966, p 195V.

[k] Calculated from K_N (K in mole fraction units) reported by A. Bier, *Rec. Trav. Chim.*, **75**, 866 (1956).

[l] Footnote *y*, Table I.

[m] A. R. Cooper, C. P. W. Crowne, and P. G. Farrell, *Trans. Faraday Soc.*, **62**, 18 (1966).

[n] W. K. Plucknett and H. L. Richards, *J. Chem. Eng. Data*, **8**, 239 (1963).

[o] At 20°; C. C. Thompson, Jr., and P. A. D. De Maine, *J. Phys. Chem.*, **69**, 2766 (1965).

[p] P. H. Emslie and R. Foster, *Tetrahedron*, **21**, 2851 (1965); at 22°.

[q] E. A. Halevi and M. Nussim, *J. Chem. Soc.*, 876 (1963).

[r] Footnote *p*, Table I.

[s] R. Foster, D. L. Hammick, and B. N. Parson, *J. Chem. Soc.*, 555 (1956).

[t] R. E. Merrifield and W. D. Philips, *J. Amer. Chem. Soc.*, **80**, 2778 (1958).

[u] Footnote *n*, Table I.

[v] R. Foster and D. L. Hammick, *J. Chem. Soc.*, 2685 (1954).

[w] Z. Rappoport, *ibid.*, 4498 (1963).

[x] D. C. Mukherjee and A. K. Chandra, *J. Phys. Chem.*, **68**, 477 (1964).

[y] Footnote *t*, Table I.

[z] Footnote *r*, Table I.

[aa] N. W. Blake, H. Winston, and J. A. Patterson, *J. Amer. Chem. Soc.*, **73**, 4437 (1951). Calculated from K_N.

[bb] G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **59**, 184 (1955).

[cc] M. Chowdhury, *Trans. Faraday Soc.*, **57**, 1482 (1961).

[dd] Footnote *u*, Table I.

[ee] M. Chowdhury and S. Basu, *Trans. Faraday Soc.*, **56**, 335 (1960).

[ff] Footnote *q*, Table I.

[gg] B. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **54**, 1286 (1958).

[hh] C. E. Castro, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **80**, 2322 (1958).

[ii] S. U. Choi and S. J. Chang, *Daehan Hwahak Hwoejee*, **9**, 169 (1965).

of the donor.[3,4] A correlation of $\log K_C$ with η for the naphthalene–halogen complexes (A = iodine, bromine, iodine monochloride, iodine monobromide) gives excellent results (set 19A). Inclusion of the value for A = tetracyanoethylene again gives excellent results (set 19B) with no significant change in ν or $\log k°_A$. The halogen complexes, if they have the same geometry as the bromine–benzene complex, cannot be affected by the size of the donor. As the inclusion of the tetracyanoethylene does not affect the correlation, it too must be independent of donor size. These results show that eq 1 is not generally applicable to polycyclic aromatic donors. In a future paper, a modification of eq 1 will be presented which is applicable to complexes of this type. In the linear regression analysis used here, the independent variable (in this case η) is assumed to be free of error. The resulting line is the best prediction of values of the dependent variable ($\log K_C$). For the calculation of new values it is preferable to carry out a second regression analysis in which the variables are interchanged. Thus values of η have been calculated from eq 2, using the K_C values reported in Table I. This method was suggested by Jaffé[5] for the calculation of new Hammett substituent constants.

$$\eta = b(\log K_C) + d \qquad (2)$$

These results have permitted the determination of acceptor strength constants for 50 acceptors including both inorganic acceptors and a wide range of organic π acceptors. Recently, several authors have remarked about the great difficulty in the measurement of charge-transfer complex formation constants.[6–8] In view of the uncertainty regarding the values of formation constants the η values reported herein are thought to be generally reliable in the tenth's place.

Discussion

If the naphthalene and biphenyl sets (sets 19 and 20) are excluded from consideration for the reason described above, then of the remaining 19 sets, excellent correlations were obtained for nine, very good correlations for five, good correlations for two, and fair correlations for two. Only one set did not give a significant correlation. These results clearly show that eq 1 is ap-

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(3) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964.

(4) A. R. Cooper, S. W. P. Crowne, and P. G. Farrell, *Trans. Faraday Soc.*, **62**, 18 (1966).

(5) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(6) S. Carter, J. N. Murrell, and E. J. Resch, *J. Chem. Soc.*, 2048 (1965).

(7) W. B. Person, *J. Amer. Chem. Soc.*, **87**, 167 (1965).

(8) P. H. Emslie, R. Foster, C. A. Fyfe, and I. Herman, *Tetrahedron*, **21**, 2343 (1965).

TABLE III

RESULTS OF CORRELATION WITH EQ 1

Set	ν	Log $K°_A$	r[a]	s[b]	s_ν[c]	t[d]	b[e]	d[e]	n[f]	CL[g]
1	0.872	−0.205	0.977	0.0920	0.0952	9.163	1.09	0.199	6	99.9
2	0.944	−0.0443	0.989	0.0671	0.0694	13.60	1.04	0.0339	6	99.9
3	0.913	0.157	0.982	0.0852	0.0881	10.36	1.06	−0.186	6	99.9
4	0.944	0.155	0.995	0.0447	0.0462	20.42	1.05	−0.168	6	99.9
5	1.15	0.588	0.990	0.0738	0.0804	14.30	0.853	−0.513	6	99.9
5A	1.16	0.571	0.998	0.0391	0.0428	27.16	0.857	−0.492	5	99.9
6	1.35	0.925	0.983	0.165	0.114	11.88	0.715	−0.673	7	99.9
7	0.916	0.806	0.907	0.191	0.246	3.723	0.879	−0.834	5	95
8	1.71	1.50	0.966	0.272	0.187	9.157	0.545	−0.841	8	99.9
8A	1.79	1.59	0.980	0.230	0.164	10.92	0.536	−0.867	7	99.9
9	0.745	−0.804	0.989	0.0744	0.0787	9.450	1.31	1.05	4	98
10	0.753	0.112	0.842	0.267	0.341	2.207	0.941	−0.203	4	80
11	1.86	2.09	0.960	0.128	0.314	5.914	0.496	−1.08	5	99
12	1.48	0.984	0.981	0.159	0.167	8.860	0.652	−0.641	5	99
13	1.35	1.48	0.936	0.190	0.360	3.751	0.649	−1.05	4	95
14	1.67	1.88	0.987	0.0863	0.122	13.62	0.584	−1.13	7	99.9
15	1.60	1.98	0.979	0.114	0.166	9.676	0.598	−1.23	6	99.9
16	1.27	1.52	0.896	0.217	0.315	4.032	0.632	−1.17	6	98
17	1.51	0.891	0.981	0.147	0.172	8.785	0.636	−0.580	5	99
18	0.780	1.41	0.904	0.175	0.212	3.670	1.05	−1.64	5	95
18A	0.858	1.41	0.994	0.0555	0.0689	12.45	1.15	−1.64	4	99
19	0.737	0.394	0.618	0.387	0.331	2.223	0.518	−0.469	10	90
19A	0.974	0.133	0.993	0.0553	0.0808	12.05	1.01	−0.141	4	99
19B	1.03	0.169	0.996	0.0551	0.0563	18.34	0.960	−0.166	5	99.9
20	0.683	0.210	0.757	0.287	0.295	2.320	0.840	−0.357	6	90
21	0.412	−0.726	0.876	0.167	0.102	4.055	1.86	1.17	7	99
21A	0.644	−0.620	0.928	0.124	0.129	4.999	1.34	0.752	6	99

[a] Correlation coefficient. [b] Standard error of the estimate. [c] Standard error of ν. [d] Student "t" test. [e] Slope and intercept respectively of regression line for the calculation of η. [f] Number of points in set. [g] Confidence level.

TABLE IV

VALUES OF η_X

X	η_X (benzene)	η_X (1,4-benzoquinone)[f]	η_X (ethylene)
H	0[a]	0[a]	0[a]
NO_2	0.57[b]	0.48	
CN	0.50[c]	0.41	
Cl	0.22[d]	0.12	0.22[g]
—CO—O—CO—	0.41[e]		
F		0.04	
Br		0.26	
I		0.24	
CO_2Me		0.01	
Ac		0.13	
Me		−0.05	
MeO		−0.35	

[a] By definition. [b] Average of values obtained from η (1,3,5-trinitrobenzene) − η (1,2-, 1,3-, and 1,4-dinitrobenzenes). [c] From η (1,2,4,5-tetracyanobenzene − η (1,3,5-tricyanobenzene). [d] From [(η-tetrachlorophthalonitrile) − η (1,2-dicyanobenzene)]/4. [e] From η (pyromellitic dianhydride) − η (tetrachlorophthalic anhydride) = $4\eta_{Cl}$. [f] From η (2-substituted 1,4-benzoquinone) − η (1,4-benzoquinone). [g] Average of values from η (dichloromaleic anhydride) − η (chloromaleic anhydride) and η (chloromaleic anhydride) − η (maleic anhydride).

plicable to substituted benzene π donors. A modification of eq 1 which accounts for the behavior of polycyclic arene donors will be reported in a forthcoming paper in this series.

The utility of η values as a measure of acceptor strength would be very much enhanced if a method of *a priori* calculation of these values were available. As a possible method of calculation of η for π acceptors, consider eq 3. A π acceptor may be written in the

$$\eta_A = \eta_G + \epsilon\eta_{X_i} \tag{3}$$

form G ($X_1X_2 \ldots X_n$) where X_1, $X_2 \ldots X_n$ are substituents bonded to the skeletal group G. It is assumed that the acceptor strength will then be given by the sum of a contribution for the group G and contributions for all of the substituents bonded to it. It is further assumed that $\eta_H \equiv 0$.

An average value of η_G (benzene) of −2.3 can be calculated from the η_A values of substituted benzene acceptors and the η_X (benzene) values in Table IV. From η_A values for substituted ethylenes and the η_X (benzene) values an average value of η_G (ethylene) of −1.8 can be obtained.

The correlation of η_X (benzene) (set I) and η_X (1,4-benzoquinone) (set II) values with the extended form of the Hammett equation was studied with a view to the

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \tag{4}$$

estimation of η_X values and in order to determine the nature of electrical effects on π-acceptor strength. The necessary σ constants are from the sources reported in previous work[1] with the exception of σ_I and σ_R for the carboxylic acid anhydride group. For this group, σ_I and σ_R were assumed equal to the values for the benzoyloxycarbonyl group. These values were obtained by methods described elsewhere.[9] The results

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(9) M. Charton, *J. Org. Chem.*, **28**, 312 (1963); Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, p 56V.

TABLE V

RESULTS OF CORRELATIONS OF η_X WITH EQ 4

Set	α	β	h	R^a	F^b	r^c	$s_{est d}$[d]	s_α[d]	s_β[d]	s_h	n^e	CL[f]
I	0.767	0.521	−0.00709	0.998	206.0	0.181	0.0227	0.0443	0.0717	0.0216	5	99.5
II	0.668	0.529	−0.0635	0.861	11.48	0.0216	0.131	0.183	0.175	0.0789	11	99.5
IIA	0.666	0.622	−0.0272	0.913	17.64	0.0299	0.111	0.155	0.155	0.0690	10	99.5
IIB	0.620	0.788	−0.0324	0.956	31.50	0.0929	0.0866	0.122	0.141	0.0598	9	99.9

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficient of σ_I on σ_R. [d] Standard error of the estimate, α, β, and h. [e] Number of points in set. [f] Confidence level.

are presented in Table V. Excellent correlations were obtained. Some improvement in the correlation of η_X (1,4-benzoquinone) resulted from the exclusion of η_{CO_2Me} from the (set IIA). The results were further improved by the exclusion of η_{Ac} (set IIB).

The magnitude and composition of the electrical effects on π-acceptor strength are comparable with those observed previously[1] for π-donor strength. The correlations with eq 4 permit the calculation of η values for a wide range of acceptors.

A Comparison of Peroxide and Ether Groups as Proton Acceptors in Intramolecular Hydrogen Bonding of Alcohols

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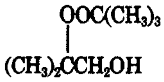
The differences in frequencies between the free and intramolecularly hydrogen-bonded O-H absorption ($\Delta\nu$) are presented along with the enthalpies of intramolecular hydrogen bonding ($-\Delta H_{IB}$) for 2-*t*-butylperoxy-2-methyl-1-propanol (I), 2-methyl-2-neopentoxy-1-propanol (II), and 3-*t*-butoxy-2,2-dimethyl-1-propanol (III) in carbon tetrachloride solution. By comparison with the model ethers (II and III), it is suggested that the hydroxy peroxide I exhibits intramolecular hydrogen bonding *via* a 1,5 interaction. Further comparison of $\Delta\nu$ and $-\Delta H_{IB}$ values for the hydroxy ether (II) and the hydroxy peroxide (I) indicates that the peroxide group is somewhat less basic than the ether group. With reference to suitable model compounds, the effect of *gem*-dimethyl substitution is discussed in light of the Thorpe–Ingold effect.

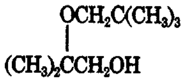
In the course of a long-range program designed to study the intramolecular reactions of substituted peroxides[1] we were led to investigate intramolecular hydrogen bonding to a peroxide group. A recent review[2] has compiled infrared intramolecular hydrogen bonding data for over 1600 compounds with the hydroxyl group as the proton donor. A number of compounds were listed having an ether oxygen as the proton acceptor. As yet no intramolecular hydrogen-bonding data has been reported for compounds with a peroxide linkage as the proton acceptor. A comparison is now made between peroxide and ether groups as proton acceptors in intramolecular hydrogen bonding where the hydroxyl group is the proton donor. The comparison is made between three stereochemically similar compounds: 2-*t*-butylperoxy-2-methyl-1-propanol (I), 2-methyl-2-neopentoxy-1-propanol (II), and 3-*t*-butoxy-2,2-dimethyl-1-propanol (III). Either 1,5 or 1,6 intramolecular hydrogen bonding is possible in I, while hydrogen bonding is restricted to a 1,5 interaction in II and a 1,6 interaction in III.

Results

In a preliminary communication, which was directed to another phase of our work, the synthetic routes to alcohols I and II were outlined.[3] The alcohols were oxidized to the corresponding acids with chromic acid, and evidence was presented for the structures of the acids.[3] Further evidence for the structures of I and II as well as III is presented in the Experimental Section.


$(CH_3)_2C(OOC(CH_3)_3)CH_2OH$

I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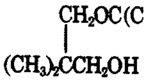
II


$(CH_3)_2C(CH_2OC(CH_3)_3)CH_2OH$

III

At the concentrations which the spectra were measured only a free and a single hydrogen-bonded oxygen–hydrogen absorption was noted for the three alcohols (I, II, and III). No significant change was observed in the ratios of absorptivity over the concentration range 4.00 × 10^{-2}–10^{-3} M for the three alcohols. This ensures that the absorption due to hydrogen bonding represents only intramolecular hydrogen bonding.

The enthalpy of intramolecular hydrogen bonding was determined from a study of the effect of temperature on the ratio of the integrated absorbancies for the hydrogen bonded to free species (A_B/A_F). The data for the three alcohols are presented in Tables I–III.

TABLE I

INTEGRATED ABSORBANCIES FOR 2-*t*-BUTYLPEROXY-2-METHYL-1-PROPANOL (I) IN CARBON TETRACHLORIDE SOLUTION[a]

Temp, °C	A_F	A_B	A_B/A_F
33.8	55.0 ± 0.2	765.3 ± 2.6	13.9
49.9	57.8 ± 0.5	752.0 ± 1.8	13.0
70.1	60.5 ± 0.5	712.5 ± 1.5	11.8

[a] 4.00 × 10^{-2} M.

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[1] Part I: W. H. Richardson, J. W. Peters, and W. P. Konopka, *Tetrahedron Lett.*, 5531 (1966).

[2] M. Tichý, *Advan. Org. Chem.*, **5**, 115 (1965).

[3] W. H. Richardson and R. S. Smith, *J. Amer. Chem. Soc.*, **89**, 2230 (1967).