The Estimation of Hammett Substituent Constants[1]

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Hammett substituent constants can be estimated from the equation, $\sigma_{XG_2} = m\sigma_X + c$, where X is some substituent, G_2 is a group to which it is attached, m is the slope, and c the intercept. This equation has been shown to apply with G_2 equal to O, S, NH, CO, and *o*-, *m*-, and *p*-phenylene. This equation greatly increases the number of σ-values available, and also makes possible the estimation of σ-values for groups for which experimental determination by means of the pK_a of the corresponding substituted benzoic acid would be difficult.

In the course of work on other problems, values of the Hammett substituent constants[3] for certain groups were required. In order to develop useful methods of estimating substituent constants, relationships between series of substituent constants were sought. McDaniel[4a] and Bauld[4b] have pointed out that certain series of substituents show a linear relationship between $\sigma_{m\text{-X}}$ and $\sigma_{p\text{-X}}$. These relationships, while theoretically interesting, are of limited use in predicting new substituent constants. We have sought for relationships between substituent constants for structurally related substituents.

We can consider almost any reaction series to which the Hammett equation is applicable as consisting of a substituent X, and a reaction site Y; both of which are attached to some group G. Thus, for substituted benzoic acids, X represents the substituent, Y the carboxyl group, and G the phenylene group. In some reaction series we may find it convenient to divide G into the sub-groups G_1, G_2, ... G_n. In the cinnamic acids, for example, we may choose to consider the series to be of the form XGY where G is the styrylene group, or of the form XG_2G_1Y, where G_1 is the *trans*-vinylene group and G_2, the phenylene group. If we write the Hammett equation in its most general form

$$Q_X = \rho\sigma_X + Q_H \tag{1}$$

where Q is the quantity being correlated, we can now consider two ways of correlating data for the series described above. In the first case, we may consider the substituent constant to include only the effect of X, the reaction constant accounting for G_2G_1Y and the reaction conditions. In the second case, we may include G_2 with the substituent constant, leaving the reaction constant to account for G_1Y and the reaction conditions. Thus in the first case, the unsubstituted compound may be written as HG_2G_1Y, whereas in the second case, it would be written as HG_1Y. Then for a given X, the Hammett equation would be written for the first case as

$$Q_X = \rho_{G_1G_2}\sigma_X + Q_{HG_1G_2} \tag{2a}$$

while for the second case,

$$Q_{XG_2} = \rho_{G_1}\sigma_{G_2X} + Q_{HG_1} \tag{2b}$$

obviously

$$Q_{XG_2} \equiv Q_X \tag{2c}$$

Combining 2a and 2b and rearranging, gives

$$\sigma_{G_2X} = \frac{\rho_{G1G2}}{\rho_{G_1}}\sigma_X + \frac{Q_{HG_2G_1} - Q_{HG_1}}{\rho_{G_1}} \tag{3a}$$

or

$$\sigma_{G_2X} = m\sigma_X + c \tag{3b}$$

This implies a straight line relationship between the two constants. At first glance, this relationship appears obvious and uninteresting. If we choose certain G_2 values however, this relationship could provide us with σ-values which are otherwise difficult to obtain. When for example, G_2 is the carbonyl group, it should be possible to calculate σ_m and σ_p for the chlorocarbonyl(COCl) group. Such a value would be difficult to obtain by measurement of an ionization constant. Again, if G_2 is an oxygen atom, the σ-values for the hypobromite(BrO) group could be calculated.

To test eq. 3b, least mean square correlations of σ_{G_2X} have been made with $\sigma_{m\text{-X}}$, $\sigma_{p\text{-X}}$, and σ_{IX} for G_2 equal to *o*-, *m*-, and *p*-phenylene, carbonyl, oxygen, sulfur, and imino.

The results of these correlations are given in Table III, and the σ-constants used are given in Table II. The reaction series studied are listed in Table I.

TABLE I

SERIES CORRELATED

1	*m*-XCO	X = OH, H, NH_2, O^-, Me, OMe, OEt, Ph
2	*m*-XO	X = H, Ac, Me, CF_3, Et, Ph
3	*m*-XNH	X = Me, Ac, Et, Bu, Bz, H, OH, NH_2
4	*m*-XS	X = CF_3, Me, Ac, H
5	*p*-XCO	X = OH, NH_2, O^-, Me, OMe, OEt, Ph
6	*p*-XO	X = CF_3, Me, Ac, Et, Pr, Bu, H
7	*p*-XNH	X = Me, Ac, Et, Bu, Bz, H, OH, NH_2
8	*p*-XS	X = CF_3, Me, Ac, Et, *i*-Pr, CN, H
9	*p*-X(*p*-C_6H_4)-X	X = NO_2, Cl, Br, OH, Me, OMe, H, NH_2
10	*p*-X(*m*-C_6H_4)	X = NO_2, Cl, Br, OH, Me, OMe, H
11	*p*-X(*o*-C_6H_4)	X = H, Me, OH, OMe, Cl. NO_2

Discussion

The results of the correlations show that σ_{XG_2} is indeed a linear function of $\sigma_{m\text{-X}}$, $\sigma_{p\text{-X}}$, or σ_{IX}. In some cases it is not yet possible to determine which of the three σ_X-constants gives the best correlation. It should be pointed out that the Hammett $\sigma_{m\text{-X}}$ and $\sigma_{p\text{-X}}$ values are not necessarily identical with the values of σ_X of eq. 3. However σ_X may be represented by

$$\sigma_X = \lambda_I + \delta_R$$

The data do not warrant the use of a four-parameter equation. They were, therefore, studied in terms of $\sigma_{m\text{-X}}$, $\sigma_{p\text{-X}}$, and σ_I. This is equivalent to $\lambda = 1$,

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[1] (a) Abstracted from part of the Doctoral Dissertation of M. Charton, Stevens Institute of Technology; (b) presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

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[3] (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940; (b) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953); (c) R. W. Taft, Jr., in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

TABLE II

SUBSTITUENT CONSTANTS USED IN CORRELATIONS

X	σ_m	σ_p	σ_I
H	0^{a}	0^{a}	0^{a}
Me	-0.069^{b}	-0.170^{b}	-0.05^{c}
Et	-0.07^{b}	-0.157^{b}	-0.05^{c}
Pr	-0.05^{d}	-0.126^{e}	-0.02^{f}
i-Pr	-0.07^{d}	-0.151^{b}	-0.03^{f}
Bu	-0.07^{d}	-0.161^{e}	-0.02^{f}
Ph	0.06^{b}	-0.01^{b}	0.10^{c}
CF_3	0.43^{b}	0.54^{b}	0.41^{c}
Ac	0.376^{b}	0.502^{b}	0.28^{c}
Bz	0.343^{g}	0.459^{e}	0.29^{h}
CO_2Me	0.315^{e}	0.436^{i}	0.30^{c}
CO_2Et	0.37^{b}	0.45^{b}	0.30^{c}
CO_2H	0.37^{b}	0.45^{b}	0.30^{c}
CO_2^-	-0.1^{b}	0.0^{c}	^{h}
CHO	0.382^{j}		
$CONH_2$	0.280^{e}	0.36^{k}	^{h}
CN	0.615^{l}	0.660^{b}	0.58^{c}
OH	0.121^{b}	-0.37^{b}	0.25^{c}
OMe	0.115^{b}	-0.268^{b}	0.25^{c}
OEt	0.1^{b}	-0.24^{b}	0.27^{h}
OPr	0.1^{b}	-0.25^{b}	
OBu	0.1^{b}	-0.32^{b}	
OCF_3	0.36^{m}	0.32^{m}	
OAc	0.39^{b}	0.31^{b}	
O^-	-0.708^{e}	-0.519^{e}	-0.80^{h}
OPh	0.252^{b}	$(-0.028)^{e}$ $(-0.320)^{b}$	
NH_2	-0.16^{b}	-0.26^{b}	0.10^{b}
NHMe	-0.302^{e}	-0.592^{e} $(-0.84)^{b}$	
NHEt	-0.240^{e}	-0.607^{n}	
NHBu	-0.344^{e}	-0.512^{n}	
NHOH	-0.044^{e}	-0.399^{e}	
$NHNH_2$	-0.31^{o}	-0.550^{e}	
NHAc	0.21^{b}	0.00^{b}	
NHBz	0.217^{e}	0.078^{e}	
SH	0.25^{b}	0.15^{b}	0.25^{c}
SMe	0.15^{b}	0.00^{b}	0.25^{c}
SEt		0.03^{b}	0.25^{c}
S(*i*-Pr)		0.07^{b}	0.25^{c}
SCN		0.52^{b}	
SAc	0.39^{b}	0.44^{b}	
SCF_3	0.35^{m}	0.38^{m}	
NO_2	0.710^{b}	0.778^{b}	0.63^{c}
Cl	0.373^{b}	0.227^{b}	0.47^{c}
Br	0.391^{b}	0.232^{b}	0.45^{c}
F	0.337^{b}	0.062^{b}	0.52^{c}
I	0.352^{b}	0.27^{r}	0.39^{c}
$SiMe_3$	-0.04^{b}	-0.07^{b}	-0.12^{c}
SO_2Me	0.60^{b}	0.72^{b}	0.59^{c}
SOMe	0.52^{b}	0.49^{b}	0.52^{c}
$2\text{-}MeC_6H_4$		-0.025^{p}	
$2\text{-}HOC_6H_4$		-0.090^{p}	
$2\text{-}MeOC_6H_4$		-0.004^{p}	
$2\text{-}ClC_6H_4$		0.126^{p}	
$2\text{-}O_2NC_6H_4$		0.173^{p}	
$3\text{-}O_2NC_6H_4$		0.183^{q}	
$3\text{-}ClC_6H_4$		0.092^{p}	
$3\text{-}BrC_6H_4$		0.093^{q}	
$3\text{-}HOC_6H_4$		0.033^{p}	
$3\text{-}MeC_6H_4$		0.008^{p}	
$3\text{-}MeOC_6H_4$		0.045^{p}	
$4\text{-}O_2NC_6H_4$		0.229^{q}	
$4\text{-}ClC_6H_4$		0.081^{q}	
$4\text{-}BrC_6H_4$		0.083^{q}	
$4\text{-}HOC_6H_4$		-0.242^{q}	
$4\text{-}H_2NC_6H_4$		-0.303^{q}	
$4\text{-}MeC_6H_4$		-0.048^{q}	
$4\text{-}MeOC_6H_4$		-0.088^{q}	

[a] By definition. [b] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958). [c] R. W. Taft, Jr., and I. C. Lewis *J. Am. Chem. Soc.*, **80**, 2436 (1958). [d] Calculated from $\sigma_m = (\sigma_p + 2\sigma_I)/3$. Footnote *c*. [e] See ref. 3b. [f] Calculated from $\sigma I = \sigma^*/6.23$: R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960). [g] W. N. White, R. Schlitt, and D. Gwynn, *J. Org. Chem.*, **26**, 3613 (1961). [h] Calculated from $\sigma_I = (3\sigma_m - \sigma_p)/2$. Footnote *c*. [i] M. Charton and H. Meislich, *J. Am. Chem. Soc.*, **80**, 5940 (1958). [j] See ref. 3a. [k] Calculated from data of J. D. Roberts and C. M. Regan, *ibid.*, **76**, 939 (1954). [l] M. M. Fickling, A. Fischer, B. R. Mann, J. Packer, and J. Vaughan, *ibid.*, **81**, 4226 (1959). [m] L. M. Yagupolskii and L. N. Yagupolskaya, *Dokl. Akad. Nauk SSSR*, **134**, 1381 (1960). [n] M. Charton, Abstracts, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, p. 78-P. [o] H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Am. Chem. Soc.*, **75**, 2209 (1953). [p] Calculated from correlation of K_a of *trans-m-* and *p*-cinnamic acids. These results will be reported elsewhere. [q] E. Berliner and L. H. Liu, *J. Am. Chem. Soc.*, **75**, 2417 (1953). [r] R. A. Robinson and K. P. Ang, *J. Chem. Soc.*, 2314 (1959).

$\delta = 0$; $\lambda = 1$, $\delta = {}^1/_3$ to ${}^1/_2$; $\lambda = 1$, $\delta = 1$; for σ_I, σ_m, σ_p, respectively.

Results of Correlations.—When G_2 is *meta* or *para* -O, -NH, or -CO, the best correlation is obtained with the $\sigma_{m\text{-}X}$-constants. In the case of G_2 = -CO, this is in accord with the observation that vinylidene reaction series are correlated by the $\sigma_{m\text{-}X}$-constants,[5] as the carbonyl group may be considered to be a hetero vinylidene group. When G_2 is *m*- or *p*-S, the best correlation is obtained with the $\sigma_{p\text{-}X}$-constants. It is premature to attempt to account for the difference in behavior between S and -O, -NH or -CO. It has been pointed out by one of the referees, however, that those series which show significant correlation with σ_p contain, except for H, only carbon substituents, and he has suggested that the $\sigma_{m\text{-}X}$ values be used for all calculations of new σ-constants in series 1 through 8. As there is no way to evaluate this proposal from the available data, values of m_m and c_m are given as footnotes to Table III.

For G_2 equal to *p*-phenylene, best results were obtained with σ_{p-X} as is expected. Similarly, for *m*-phenylene best results were obtained with $\sigma_{m\text{-}X}$. In accord with the successful correlation of *o*-phenylene reaction series (in which no steric effect is present) with the σ_p-constants,[6a] best results for the *o*-phenylene series were obtained with $\sigma_{p\text{-}X}$.

It should be noted that when G_2 is -CO the correlations are very sensitive to the value for X = O^-. Exclusion of this value from series 1 and 5 gives poorer correlation, and best results are now obtained with σ_p. The results are still significant, however (90% and 95% confidence levels for series 1 and 5, respectively). The difficulty in these series is the small range of σ_{XG_2} when the value for O^- is excluded (0.10 and 0.14 n-units, respectively for series 1 and 5 as compared with 0.29, 0.53, 0.24, 0.69, 0.74, and 0.52 for series 2, 3, 4, 6, 7, and 8, respectively).

Calculation of New Substituent Constants.—The values of *m* and *c* given in Table III are for the σ_X-constant which gave the best correlation, as deter-

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(4) (a) D. H. McDaniel, *J. Org. Chem.*, **26**, 4692 (1961); (b) N. L. Bauld, Abstracts, 139th Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

(5) M. Charton, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961, p. 91-Q.

(6) (a) M. Charton, *Can. J. Chem.*, **38**, 2493 (1960); (b) A. C. Farthing and B. Nam, "Steric Effects of Conjugated Systems," Academic Press, New York, N. Y., 1958, p. 131 and ref. 3.

TABLE III

RESULTS OF CORRELATIONS

Series	G_2	r_m[a]	r_p[a]	r_I[a]	s[b]	m	c	n	d
1	m-CO	0.943	0.544	0.904	0.0581	0.553	0.329	1.61	−0.538
2	m-O	0.956	0.935	0.945	0.0427	0.555	0.156	1.65	−0.246
3	m-NH	0.982	0.803	0.874	0.0467	1.11	−0.187	0.871	0.165
4	m-S[c]	0.933	0.962	0.880	0.0362	0.290	0.222	3.19	−0.692
5	p-CO	0.942	0.576	0.904	0.0637	0.546	0.422	1.62	−0.693
6	p-O	0.969	0.953	0.955	0.0808	1.29	−0.218	0.727	0.163
7	p-NH	0.938	0.738	0.894	0.107	1.33	−0.476	0.662	0.322
8	p-S[d]	0.978	0.988	0.954	0.0358	0.567	0.128	1.72	−0.216
9	p-C_6H_4	0.828	0.970	0.634	0.0457	0.384	−0.0262	2.45	0.0626
10	m-C_6H_4	0.984	0.857	0.941	0.0128	0.237	0.00792	4.09	−0.0249
11	o-C_6H_4	0.867	0.933	0.778	0.0402	0.221	0.0211	3.94	−0.0787

[a] r = correlation coefficient. [b] s = standard deviation. [c] $m_m = 0.393$, $c_m = 0.213$. [d] $m_m = 0.719$, $c_m = 0.103$.

TABLE IV

CALCULATED SUBSTITUENT CONSTANTS

	G_2 = O		G_2 = NH		G_2 = S	
X	σ_m	σ_p	σ_m	σ_p	σ_m	σ_p
F	0.34	0.22	0.19	−0.03	0.24	0.16
Cl	0.36	0.26	0.23	0.02	0.29	0.26
Br	0.37	0.29	0.25	0.04	0.29	0.26
I	0.35	0.24	0.20	−0.01	0.30	0.28
CN	0.50	0.58	0.50	0.34	0.41	0.50
$SiMe_3$	0.13	−0.27	−0.23	−0.53	0.20	0.09
NO_2	0.55	0.70	0.60	0.47	0.45	0.57
SMe	0.24	−0.02	−0.02	−0.28	0.22	0.13
SOMe	0.44	0.45	0.39	0.22	0.36	0.41
SO_2Me	0.49	0.56	0.48	0.32	0.43	0.54

TABLE V

CALCULATED VALUES OF m

Series	G_1	G_2	ρ_{G_1}	$\rho_{GG_{12}}$	m (calcd.)	m (observed)
11	*trans*-C_2H_2	o-C_6H_4	1.64[a]	0.389[b]	0.237	0.221
10	*trans*-C_2H_2	m-C_6H_4	1.64[a]	0.466[b]	0.284	0.237
9a	*trans*-C_2H_2	p-C_6H_4	1.64[a]	0.466[c]	0.284	0.384
9b	p-C_6H_4	p-C_6H_4	1.415[b]	0.482[b]	0.341	0.384

[a] See footnote p, Table II. [b] See ref. 3b. [c] See ref. 6a.

TABLE VI

CALCULATED VALUES OF c

Series	$Q_{HG_2G_1}$	Q_{HG_1}	c (calcd.)	c (observed)
11	−4.413[a]	−4.448[b]	0.0213	0.0211
10	−4.447[c]	−4.448[b]	0.000610	0.00792
9a	−4.447[c]	−4.448[b]	0.000610	−0.0262
9b	−5.636[c]	−5.627[c]	−0.00636	−0.0262

[a] See ref. 6a. [b] See footnote p, Table II. [c] See ref. 3b.

TABLE VII

t TESTS OF m AND c

Series	t_m	Confidence level	t_c	Confidence level
11	0.375	20	0.014	20
10	2.452	90	1.508	80
9a	2.561	95	1.658	80
9b	1.097	70	1.226	70

mined by the value of r. These are the preferred values for use in estimating new σ_{XG_2}-values.

To illustrate the utility of the method, a number of new substituent constants have been calculated for groups for which experimental determination would be difficult. These values are given in Table IV.

It is also possible to calculate new values of σ_X from the appropriate σ_{XG_2}. For this purpose the equation

$$\sigma_X = n\sigma_{XG_2} + d \tag{4}$$

is required, n and d being the slope and intercept obtained by linear regression of σ_X on σ_{XG_2}[3b] (that is, by assuming σ_{XG_2} free of error). Values of n and d are given in Table III.

It has been reported (see footnote f, Table II) that σ_I and σ_R values can be estimated from the equations

$$\sigma_I = (3\sigma_m - \sigma_p)/2 \tag{5}$$

and

$$\sigma_p = \sigma_I + \sigma_R \tag{6}$$

Calculation of m and c.—The existence of a linear relationship between σ_{XG_2} and σ_X does not in itself constitute proof of the validity of eq. 3, as the observed linear relationships might be purely empirical. Although this would not in the slightest diminish their utility, it is of interest to determine whether or not the derivation of eq. 3 is valid. One test of its validity is the calculation of m and c from the appropriate values of ρ and Q_H. Calculated values of m and c are given in Tables V and VI for G_2 equal to o-, m-, and p-phenylene.

To determine the significance of the difference between the calculated and observed values of m and c, t tests were performed.[7] The values of t and the confidence levels obtained are given in Table VII. In general, the results of the t tests support the validity of eq. 3. In 9a and 10, however, the calculated and observed values of m and significantly different. As the $\rho_{G_1G_2}$ and $Q_{HG_1G_2}$ values for 9a and 10 are identical and represent an average of m-phenylene and p-phenylene, it is more reasonable to compare average

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(7) A. Hald, "Statistical Theory with Engineering Applications," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 540.

observed m- and c values with the calculated values. For these series, $\bar{m} = 0.311$, $\bar{c} = -0.0914$. These average values are obviously in good agreement with the calculated values of m and c.

Equation 3 is thus supported, at least for series 9, 10, and 11. Although it is true that these are the series least likely to deviate from the equation, it is nevertheless encouraging to find such agreement.

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Thiolesters by Anhydride Reduction with Hydrogen Sulfide

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Phthalic anhydride (or acid) can be reduced by hydrogen sulfide to thiophthalide in high yields. Hydrogen may be substituted for part of the hydrogen sulfide. The reaction appears general, but gives lower yields for other anhydrides. Reduction of cyclohexane-1,2-dicarboxylic anhydride gives 3,4,5,6-tetrahydrothiophthalide. Other aromatic acids or nitriles are reduced completely to hydrocarbon, while aliphatic acids are inert under reaction conditions. While metal sulfides may catalyze the reaction, they are not essential. In their absence, a homogeneous reduction with hydrogen is realized.

In the course of studying the oxidation of organic compounds with sulfur and water, but in the absence of a base, it was found that the reaction was reversible.[1] For example, toluene is oxidized by sulfur and water at 315°. A similar equilibrium exists in the reaction

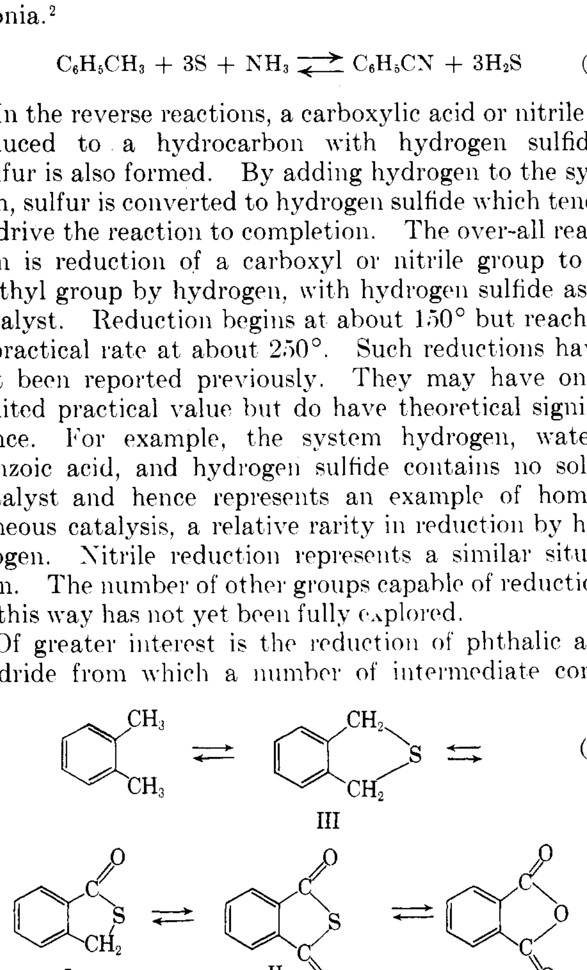
$$C_6H_5CH_3 + 3S + 2H_2O \rightleftharpoons C_6H_5CO_2H + 3H_2S \qquad (1)$$

producing nitriles from hydrocarbon, sulfur, and ammonia.[2]

$$C_6H_5CH_3 + 3S + NH_3 \rightleftharpoons C_6H_5CN + 3H_2S \qquad (2)$$

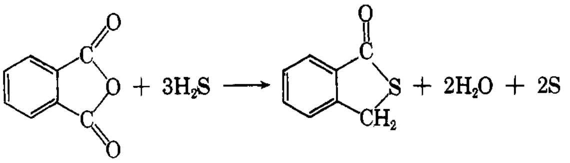
In the reverse reactions, a carboxylic acid or nitrile is reduced to a hydrocarbon with hydrogen sulfide. Sulfur is also formed. By adding hydrogen to the system, sulfur is converted to hydrogen sulfide which tends to drive the reaction to completion. The over-all reaction is reduction of a carboxyl or nitrile group to a methyl group by hydrogen, with hydrogen sulfide as a catalyst. Reduction begins at about 150° but reaches a practical rate at about 250°. Such reductions have not been reported previously. They may have only limited practical value but do have theoretical significance. For example, the system hydrogen, water, benzoic acid, and hydrogen sulfide contains no solid catalyst and hence represents an example of homogeneous catalysis, a relative rarity in reduction by hydrogen. Nitrile reduction represents a similar situation. The number of other groups capable of reduction in this way has not yet been fully explored.

Of greater interest is the reduction of phthalic anhydride from which a number of intermediate compounds were isolated. The yield of any one may be enhanced by the proper choice of conditions and the recycling of undesired intermediates. These intermediate compounds shed light on a probable mechanism of sulfur oxidations. The major reaction sequence involves the following compounds, all of which have been isolated (run 10, Table I).



(3)

Small amounts of o-toluic acid also have been found. It has not been established whether this is part of the above sequence or a competing reaction. The most stable entity at 315° in the presence of water, sulfur, and hydrogen sulfide is thiophthalide (I). It can be obtained in 94% yields by reduction of phthalic anhydride or phthalic acid.



(4)

I

Some typical results are given in Table I. The reverse reactions, the oxidation of o-xylene to thiophthalide with sulfur and water, has been described.[1]

An example of the spectrum of intermediates (3) is given in run 10 of Table I. In this case, their concentrations were enhanced by adding o-xylene to the system and limiting the amount of hydrogen sulfide employed. As a result, the major products were thiophthalic anhydride (II), thiophthalide (I), and o-xylylene sulfide (III); identification was by a high mass spectrometer. Minor peaks matched masses for di- and trithiophthalic anhydride. Benzoic acid, a major product, probably resulted from decarboxylation of phthalic acid at this temperature. Reduction of the intermediate thiophthalic anhydride with hydrogen sulfide at atmospheric pressure gave thiophthalide.

Table I shows that hydrogen sulfide alone as the reducing agent gives good yields of thiophthalide over the temperature range of 175–315°. Conversions increase with temperature while yields decrease. Above 315°, decarboxylation and reduction to o-xylene and o-xylylene sulfide occurs. The ratio of hydrogen sulfide

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[1] W. G. Toland, *J. Org. Chem.*, **26**, 2929 (1961).

[2] W. G. Toland, *ibid.*, **27**, 869 (1962).