

from J.E. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions*, Wiley, 1963 (Dover reprint)

**Table 7.1.<sup>a</sup> Hammett Substituent Constants,  $\sigma$ , Based on the Ionization of Benzoic Acids<sup>b</sup>**

SUBSTITUENT	Meta-Position		Para-Position	
	$\sigma_{meta}$	ESTIMATED LIMIT OF UNCERTAINTY	$\sigma_{para}$	ESTIMATED LIMIT OF UNCERTAINTY
CH <sub>3</sub>	<b>-0.069</b>	0.02	<b>-0.170</b>	0.02
CH <sub>2</sub> CH <sub>2</sub>	-0.07	0.1	<b>-0.151</b>	0.02
CH(CH <sub>3</sub> ) <sub>2</sub>	-	-	<b>-0.151</b>	0.02
C(CH <sub>3</sub> ) <sub>3</sub>	-0.10	0.03	<b>-0.197</b>	0.02
3,4-(CH <sub>2</sub> ) <sub>4</sub>	-	-	<b>0.042</b>	0.02
C <sub>6</sub> H <sub>6</sub>	0.06	0.05	-0.01	0.05
CF <sub>3</sub>	0.43	0.1	0.54	0.1
CN	<b>0.56</b>	0.05	<b>0.660</b>	0.02
COCH <sub>3</sub>	<b>0.376</b>	0.02	<b>0.502</b>	0.02
CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	0.37	0.1	0.45	0.1
CO <sub>2</sub> H	(0.37)	0.1	(0.45)	0.1
CO <sub>2</sub> <sup>-</sup>	-0.1	0.1	0.0	0.1
CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub>	-0.16	>0.1	-0.21	>0.1
Si(CH <sub>3</sub> ) <sub>3</sub>	-0.04	0.1	-0.07	0.1
Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	-	-	0.0	0.1
N <sub>2</sub> <sup>+c</sup>	1.76	0.2	1.91	0.2
NH <sub>2</sub>	-0.16	0.1	-0.66	0.1
NHCH <sub>3</sub>	-	-	-0.84	0.1
N(CH <sub>3</sub> ) <sub>2</sub>	-	-	-0.83	0.1
NHCOCH <sub>3</sub>	0.21	0.1	0.00	0.1
N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	0.88	>0.2	0.82	>0.2
NO <sub>2</sub>	<b>0.710</b>	0.02	<b>0.778</b>	0.02
PO <sub>3</sub> H <sup>-</sup>	0.2	>0.1	0.26	>0.1
OCH <sub>3</sub>	<b>0.115</b>	0.02	<b>-0.268</b>	0.02
OC <sub>2</sub> H <sub>5</sub>	0.1	0.1	-0.24	0.1
O(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	0.1	0.1	-0.25	0.1
OCH(CH <sub>3</sub> ) <sub>2</sub>	0.1	0.1	-0.45	0.1
O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	0.1	0.1	-0.32	0.1
O(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	0.1	0.1	-0.34	0.1
OC <sub>6</sub> H <sub>5</sub>	<b>0.252</b>	0.02	<b>-0.320</b>	0.02(?)
OH	<b>0.121</b>	0.02	<b>-0.37</b>	0.04
OCOCH <sub>3</sub>	0.39	0.1	0.31	0.1
SCH <sub>3</sub>	0.15	0.1	0.00	0.1
SC <sub>2</sub> H <sub>5</sub>	-	-	0.03	0.1
SCH(CH <sub>3</sub> ) <sub>2</sub>	-	-	0.07	0.1
SH	0.25	0.1	0.15	0.1
SCOCH <sub>3</sub>	0.39	0.1	0.44	0.1
SCN	-	-	0.52	0.1
SOCH <sub>3</sub>	0.52	0.1	0.49	0.1
SO <sub>2</sub> CH <sub>3</sub>	0.60	0.1	0.72	0.1
SO <sub>2</sub> NH <sub>2</sub>	0.46	0.1	0.57	0.1
S(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	1.00	>0.1	0.90	>0.1
SO <sub>3</sub> <sup>-</sup>	0.05	>0.1	0.09	>0.1
F	<b>0.337</b>	0.02	<b>0.062</b>	0.02
Cl	<b>0.373</b>	0.02	<b>0.227</b>	0.02
Br	<b>0.391</b>	0.02	<b>0.232</b>	0.02
I	<b>0.352</b>	0.02	0.18	0.1
CH=CHNO <sub>2</sub> <sup>d</sup>	<b>0.34</b>	0.03	0.26	0.03

<sup>a</sup> From the compilation of D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

<sup>b</sup> Values in bold face are sigma constants based on *thermodynamic* ionization constants in *water* at 25°. It is recommended that reaction constants,  $\rho$ , be based on these values.

<sup>c</sup> From E. S. Lewis and M. D. Johnson, *J. Am. Chem. Soc.*, **81**, 2070 (1959).

<sup>d</sup> From R. Stewart and L. G. Walker, *Can. J. Chem.*, **35**, 1561 (1957).

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**Table 7-7. Electrophilic Substituent Constants ( $\sigma^+$ )**

SUBSTITUENT	$\delta^+_{meta}$	$\sigma^+_{para}$
Dimethylamino		(-1.7)
Anilino		(-1.4)
Amino	(-0.16)	(-1.3)
Hydroxy		(-0.92)
Acetylamino		(-0.6)
Benzoylamino	-	(-0.6)
Methoxy	0.047	-0.778
Phenoxy	-	(-0.5)
Methylthio	0.158	-0.604
Methyl	-0.066	-0.311
Ethyl	-0.064	-0.295
isopropyl	-0.060	-0.280
t-Butyl	-0.059	-0.256
Phenyl	0.109	-0.179
3,4-C <sub>4</sub> H <sub>4</sub> ( $\beta$ -naphthyl)	-	-0.135
CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	(-0.01)	(-0.164)
Chloromethyl	(0.14)	(-0.01)
Hydrogen	0	0
Trimethylsilyl	0.011	0.021
Fluoro	0.352	-0.073
Chloro	0.399	0.114
Bromo	0.405	0.150
Iodo	0.359	0.135
Carboxy	0.322	0.421
Carbomethoxy	0.368	0.489
Carboethoxy	0.366	0.482
Trifluoromethyl	0.520	0.612
Cyano	0.562	0.659
Nitro	0.674	0.790
Carboxylate (K salt)	-0.028	-0.023
[(CH <sub>3</sub> ) <sub>3</sub> N] <sup>+</sup> (chloride)	0.359 <sup>c</sup>	0.408 <sup>c</sup>

<sup>a</sup> From H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 80,4979 (1958).

<sup>b</sup> Values in parenthesis are estimated from reactions other than the solvolysis of substituted 2-phenyl-2-propyl chlorides.

<sup>c</sup> The values of  $\delta^+$  for [(CH<sub>3</sub>)<sub>3</sub>N]<sup>+</sup> are surprisingly small and deserve further study.

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**Table 7-9. Substituent Constants,  $\sigma^-$**

<i>Para-SUBSTITUENT</i>	$\sigma^-$	<i>Para-SUBSTITUENT</i>	$\sigma^-$
COOH	0.728	COCH <sub>3</sub>	0.874
COOCH <sub>3</sub>	0.636	CN	1.000
COOC <sub>2</sub> H <sub>6</sub>	0.678	N <sub>2</sub> <sup>+</sup>	3.2 <sup>a</sup>
COOC <sub>4</sub> H <sub>9</sub>	0.674	NO <sub>2</sub>	1.270
COOCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	0.667	SO <sub>2</sub> CH <sub>3</sub>	1.049
CONH <sub>2</sub>	0.627	C <sub>6</sub> H <sub>4</sub> N=NC <sub>6</sub> H <sub>5</sub>	1.088
CHO	1.126	CH=CHC <sub>6</sub> H <sub>5</sub>	0.619
		CH=CHNO <sub>2</sub>	0.88 <sup>b</sup>

<sup>a</sup> E.S. Lewis and M. D. Johnson, *J. Am. Chem. Soc.*, **81**, 2070 (1959).

<sup>b</sup> R. Stewart and L.G. Walker, *Can. J.Chem.*, **35**, 1561 (1957).