of substantial importance, such that exalted σ-values (σ^+, σ^-, or both) are always required.

There is a strong suggestion, however, that *meta* and *para* compounds do not fall on the same correlation lines. It is suggested that, in excited states, *meta* substituents enter into direct resonance interaction with a side chain and that consequently ground-state σ_m-values do not apply.

Acknowledgment.—The authors gratefully acknowledge the assistance of Messrs. John Gustafson and Myron DeLong, who have done much of the literature searching and data collecting which has been necessary. Helpful discussions with Mr. David L. Beveridge are gratefully acknowledged. Dr. John M. Vandenbelt of Parke, Davis and Company very kindly furnished us with substantial numbers of unpublished data, for which we are very grateful. All correlations were performed on an IBM 1620 computer at the University of Cincinnati Computing Center, supported by the National Science Foundation (Grant G19281).

The Application of the Hammett Equation to Amidines

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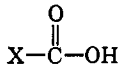
Ionization constants of C-substituted and of N-phenyl-C-substituted amidinium ions, of substituted guanidinium ions, and of 1-substituted 3-nitroguanidines were correlated with the Hammett equation using the σ_I, σ_m, and σ_p constants. The amidinium sets gave best results with σ_m, the guanidinium and nitroguanidine sets with σ_I. Correlation of the ionization constants of substituted ammonium, methylammonium, dimethylammonium, and diethylammonium ions were made, best results being obtained with σ_I. The results indicate that in guanidinium ions and guanidines which bear electron-acceptor substituents, proton transfer involves the nitrogen atom bearing the substituent. The electrical effect in C-substituted amidinium ions is believed to be due to a short-range localized effect. The major component of the localized electrical effect in substituted ammonium ions appears to be the inductive rather than the field effect.

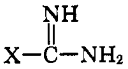
In the course of a previous investigation[1] we have studied the correlation of ionization constants of substituted carboxylic acids (I) with the Hammett equation.[2] As amides (II) are structural analogs of carboxylic acids, and are in fact iselectronic with them, it seemed of interest to study the correlation of their ionization constants with the Hammett equation. No previous correlation of simple amidines with the Hammett equation is extant in the literature. Jaffé[2] has correlated data of Lorz and Baltzly[3] on the ionization constants of 3- or 4-substituted N,N-dibutylbenzamidines (III).

$$Q_X = \rho\sigma_X + Q_H \qquad (1)$$



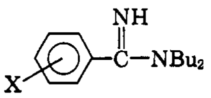
$X-C(=O)-OH$

I



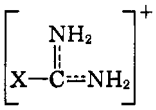
$X-C(=NH)-NH_2$

II



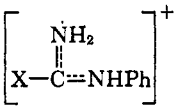
III

We have correlated ionization constants (pK_a values), obtained from the literature, for C-substituted amidinium ions (IV), C-substituted N-phenylamidinium ions (V), and 1-substituted guanidinium ions (VI), and for 1-substituted 3-nitroguanidines (VII), with the Hammett equation using the σ_I, σ_m, and σ_p constants. The correlations were made as described by Jaffé.[2] The data used are given in Table I. The σ_m and σ_p constants used were taken from the compilation of McDaniel and Brown,[4] and the σ_I constants used were from those given by Lewis and Taft,[5] whenever possible. Constants obtained from other sources are given in Table II. The results of the correlations are presented in Table III.



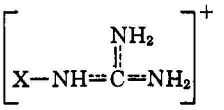
$[X-C(\overset{..}{=}NH_2)\overset{..}{=}NH_2]^+$

IV



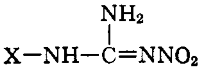
$[X-C(\overset{..}{=}NH_2)\overset{..}{=}NHPh]^+$

V



$[X-NH\overset{..}{=}C(\overset{..}{=}NH_2)\overset{..}{=}NH_2]^+$

VI



$X-NH-C(-NH_2)=NNO_2$

VII

In some cases statistical factors were necessary to provide a common basis for correlation. A statistical factor of $^2/_3$ was used for X = NH_2 in the C-substituted amidinium set as in the following reaction (i) and guanidinium (X = NH_2) is $^3/_2$ times as likely to react as are the other members of the series. When X = PhNH in the C-substituted N-phenylamidinium set, a statistical factor of $^1/_2$ was used, as the ionizable proton is assumed to be that which is attached to the nitrogen bearing the phenyl group,[6] and there are two such ionizable protons in this member of the set. When X = H in the 1-substituted guanidinium ions, a statistical factor of $^1/_6$ was used since the ionizable proton in this set is assumed to be attached to the nitrogen atom bearing the strongest electron-acceptor substituent[6]; and when X = H there are six equivalent protons. In the 3-nitro-1-substituted guanidines when X = H, a statistical factor of $^1/_4$ was used since there are four equivalent protons.

$$[X-C(NH_2)_2]^+ + H_2O = X-C(NH)NH_2 + H_3O^+ \qquad (i)$$

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[1] M. Charton, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, p. 91-Q.

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940; H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956; P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

[3] R. Baltzly and E. Lorz, *J. Am. Chem. Soc.*, **71**, 3992 (1949).

[4] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

[5] R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

[6] See discussion below.

TABLE I

IONIZATION CONSTANTS USED IN CORRELATIONS

1. C-Substituted Amidinium Ions in Water at 25°

	X									
	Ph	MeS	Me	MeO	NH_2	EtO	BuO	PrO	Me_2N	$CH_2=CHCH_2O$
pK_a	11.6[a]	9.83[a]	12.41	9.72[b]	13.86[c]	10.021	10.146	10.155	13.4	9.70
Ref.	*d*	*d*	*e*	*f*	*g*	*h*	*h*	*h*	*i*	*h*

2. C-Substituted-N-phenylamidinium Ions in Water at 25°

	X				
	H_2N	PhNH	MeO	EtO	MeS
pK_a	10.770	10.42[j]	7.41	7.71	7.14[a]
Ref.	*k*	*g*	*l*	*l*	*d*

3. 1-Substituted Guanidinium Ions in Water at 25°

	X							
	H	Ph	Ac	NO_2	H_2NCO	MeO	$OCH_2CO_2^-$	CN
pK_a	14.46[m]	10.770	8.33[a]	−0.93	7.8527	7.46[n]	7.51[n]	−0.4
Ref.	*g*	*k*	*d*	*o*	*p*	*q*	*q*	*r*

4. 1-Substituted 3-Nitroguanidines in Water at 24°; Ionic Strength = 1[s]

	X						
	H	EtO_2CCH_2	NH_2	$NCCH_2$	Bz	H_2NCO	Ph
pK_a	12.80	11.20	10.60	9.30	8.10	7.50	10.50

5. Substituted Ammonium Ion in Water at 25°

	X										
	H	Me	Et	Pr	Bu	*t*-Bu	NH_2	OH	OMe	AcNH	BzNH
pK_a	9.245	10.624	10.631	10.530	10.597	10.685	7.654	5.96	4.60	3.24[w]	2.97
Ref.	*t*	*t*	*t*	*t*	*t*	*t*	*u*	*v*	*v*	*x*	*y*

6. Substituted Ammonium Ion in 80% Methyl Cellosolve–Water at 25°[z]

	X						
	NH_2	Me	*i*-Pr	*i*-Bu	$PhCH_2$	$CH_2=CHCH_2$	OH
pK_a	7.67[u]	9.94	9.52	9.49	8.62	8.92	6.66

7. Substituted Methylammonium Ions in Water at 25°

	X						
	Me	H	OH	MeO	NHMe	$CH=CHCH_2$	$PhCH_2$
pK_a	10.774	10.624	5.96	4.75	7.22[aa]	10.11	9.58
Ref.	*t*	*t*	*v*	*v*	*bb*	*cc*	*dd*

8. Substituted Dimethylammonium Ions in Water at 25°

	X									
	H	Me	Pr	$CH_2=CHCH_2$	HC_2CH_2	$PhCH_2$	OH	MeO	Cl	Me_2N
pK_a	10.774	9.800	9.25	8.72	7.05	8.93	5.20	3.65	0.46	6.00[aa]
Ref.	*t*	*t*	*ee*	*ee*	*ee*	*ff*	*v*	*v*	*gg*	*hh*

9. Substituted Diethylammonium Ions in Water at 25°

	X						
	Et	Me	H	$PhCH_2$	Cl	CH_2CN	NH_2
pK_a	10.867	10.73	10.933	9.48	1.025	4.55	7.71
Ref.	*t*	*ii*	*t*	*ff*	*gg*	*jj*	*bb*

[a] At 20°. [b] At 24°. [c] Statistical factor of 2/3 included. [d] A. Albert, R. Goldacre, J. Phillips, *J. Chem. Soc.*, 2240 (1948). [e] G. Schwartzenbach and K. Lutz, *Helv. Chim. Acta*, **23**, 1162 (1940). [f] M. Zieff and J. T. Edsall, *J. Am. Chem. Soc.*, **59**, 2245 (1937). [g] N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932). [h] S. Basterfield and J. W. Tomecko, *Can. J. Res.*, **8**, 458 (1933). [i] S. J. Angyal and W. K. Warburton, *J. Chem. Soc.*, 2492 (1951). [j] Includes statistical factor of 1/2. [k] T. L. Davis and R. C. Elderfield, *J. Am. Chem. Soc.*, **54**, 1499 (1952). [l] W. M. Bruce, *ibid.*, **26**, 449 (1904). [m] Includes statistical factor of 1/6. [n] At 23°. [o] Ref. 6; see also L. M. Hall, J. E. DeVries and E. S. Gantz, *J. Am. Chem. Soc.*, **77**, 6507 (1955). [p] M. Yamashita and K. Sugino, *J. Chem. Soc. Japan*, **63**, 1665 (1942). [q] E. Borek and H. T. Clarke, *J. Biol. Chem.*, **125**, 483 (1938). [r] R. C. Hirt, R. G. Schmitt, H. L. Straw, and J. G. Koren, *J. Chem. Eng. Data*, **6**, 610 (1961). [s] All data from J. E. DeVries and E. St. C. Gantz, *J. Am. Chem. Soc.*, **76**, 1008 (1954); pK_a for X = H includes statistical factor of 1/4. [t] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 65. [u] N. Yui, *Bull. Inst. Phys. Chem. Res.* (Tokyo), **20**, 256 (1941). [v] T. C. Bissot, R. W. Parry, and D. H. Campbell, *J. Am. Chem. Soc.*, **79**, 796 (1957). [w] At 24 ± 1°. [x] C. R. Lindegren and C. Niemann, *J. Am. Chem. Soc.*, **71**, 1504 (1949). [y] R. Weber, W. Hofer, W. Heer, and M. Brenner, *Helv. Chim. Acta*, **44**, 2154 (1961). [z] P. F. Sommer and W. Simon, "Zusammenstellung von scheinbaren Dissoziation Konstanten im Losungsmittelsystem Methyl Cellosolve–Wasser," Vol. II, Juris-Verlag, Zurich, 1961. [aa] Includes statistical factor of 2. [bb] R. L. Hinman, *J. Org. Chem.*, **23**, 1587 (1958). [cc] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957). [dd] W. H. Carothers, C. F. Bickford, and G. J. Hurwitz, *ibid.*, **49**, 2908 (1927). [ee] K. N. Campbell and F. C. Fatora, *J. Org. Chem.*, **17**, 1141 (1952). [ff] H. Goldschmidt and Z. Salcher, *Z. physik. Chem.* (Leipzig), **29**, 89 (1899). [gg] I. Weil and J. C. Morris, *J. Am. Chem, Soc.*, **71**, 3123 (1949). [hh] J. B. Class, J. G. Aston, and T. S. Oakwood, *ibid.*, **75**, 2937 (1953). [ii] G. Bredig, *Z. physik. Chem.* (Leipzig), **13**, 191, 322 (1894). [jj] G. W. Stevenson and D. Williamson, *J. Am. Chem. Soc.*, **80**, 5943 (1958).

For comparison, we have also correlated the ionization constants of substituted ammonium, methylammonium, dimethylammonium, and diethylammonium ions. A statistical factor of 2 was used for symmetrical hydrazines owing to the presence of two equivalent basic sites. No statistical factor was used for 1,1-diethylhydrazine since Evans and Kynaston[7] have shown on the basis of infrared spectra that protonation of 1,1-dimethyl- and 1,1-diisopropylhydrazine occurs at N-1.

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(7) R. F. Evans and W. Kynaston, *J. Chem. Soc.*, 3151 (1963).

Table II

Substituent Constants from Sources Other Than Ref. 4 and 5

Substituent	σ_I	Ref.	σ_m	Ref.	σ_p	Ref.
EtO	0.27	*a*				
PrO	0.27	*a*				
BuO	0.27	*a*				
$CH_2{=}CHCH_2O$	0.33	*b*	0.13	*c*	−0.27	*c*
Me_2N	0.10	*b*				
PhNH	0.02	*a*	−0.12	*d*	−0.40	*d*
H_2NCO	0.27	*a*			0.36	*e*
$^-O_2CCH_2O$	0.32	*f*	0.08	*f*	−0.39	*f*
$PhCH_2$			−0.01	*h*	−0.10	*g*
$PhCH_2CH_2$	−0.01	*a*	−0.05	*h*	−0.14	*i*
EtO_2CCH_2	0.05	*a*	0.05	*h*	0.05	*i*
$NCCH_2$	0.18	*a*	0.18	*h*	0.17	*g*
i-Pr	−0.03	*a*	−0.07	*h*		
BzNH	0.29	*a*				
i-Bu	−0.03	*a*	−0.06	*h*		
$CH_2{=}CHCH_2$	0.00	*a*	−0.04	*h*	−0.13	*j*

[a] M. Charton, *J. Org. Chem.*, **29**, 1222 (1964). [b] Estimated from the equation: $\sigma_I = (3\sigma_m - \sigma_p)/2$: ref. 5. [c] Calculated as described in M. Charton, *J. Org. Chem.*, **28**, 3121 (1963); from σ_m and σ_p for $CH_2{=}CHCH_2$ (see below). [d] Calculated as described in ref. *c*. [e] Ref. *c*. [f] A value for σ_I of $CH_2CO_2^-$ was estimated from $\sigma_{I,CH_2X} = m\sigma_I + c$; a value for $\sigma_{p\text{-}CH_2CO_2^-}$ from $\sigma_{p\text{-}CH_2X} = n\sigma_I + d$ (M. Charton, unpublished result); a value for $\sigma_{m\text{-}CH_2CO_2^-}$ from $\sigma_m = (2\sigma_I - \sigma_p)/3$: ref. 5; σ_m and σ_p for $OCH_2CO_2^-$ were then calculated as in *d;* and σ_I obtained from these values as in *b*. [g] O. Exner and J. Jonas, *Collection Czech. Chem. Commun.*, **27**, 2296 (1962). [h] Estimated from $\sigma_m = (2\sigma_I - \sigma_p)/3$: ref. 5. [i] Estimated from $\sigma_{p\text{-}CH_2X} = n\sigma_I + d$. [j] Estimated as in *i* from σ_p for $CH_2{=}CH$ obtained from $\sigma_{p\text{-}XCH=CH} = p\sigma_{p\text{-}X} + q$ (M. Charton, dissertation, Stevens Institute of Technology, 1962).

Results

Amidinium Sets.—The results of the correlations in the two sets of amidinium ions clearly show that the σ_m constants give the best results. This is in accord with the results previously obtained with the substituted carboxylic acids.[1]

No direct comparison between the ρ-values for the ionization of carboxylic acid and of amidinium ions is possible since the two reactions are not analogous. The reaction of amidines analogous to the ionization of carboxylic acids is

$$X{-}C(NH)NH_2 + H_2O = [X{-}C(NH)_2]^- + H_3O^+ \quad \text{(ii)}$$

whereas the reaction of carboxylic acids which is analogous to the ionization of amidinium ions is

$$X{-}C(OH)_2^+ + H_2O = X{-}CO_2H + H_3O^+ \quad \text{(iii)}$$

It is interesting to note that the ratio of ρ for the amidinium ions (12.0) to ρ for the carboxylic acids (8.03 in water at 25°, correlation with σ_m[8]) is 1.5, about the same as the ratio of ρ for substituted guanidinium ions to ρ for 1-substituted 3-nitroguanidines (see below). In both cases we are comparing charged to uncharged acids. This agreement may well be fortuitous. Apparently, the constant N-phenyl substituent in set 2 has little or no effect on the sensitivity of the reaction to substituent effects since the ρ-values for sets 1 and 2 are not significantly different.

Substituted Guanidinium Ions and 1-Substituted 3-Nitroguanidines.—The substitute guanidinium ions give an excellent correlation with the σ_I constants, the results are significant at the 99.9% confidence level.

Table III

Results of Correlations

Set	σ	ρ	r[a]	s[b]	t[c]	Q_H	n[d]
1	I	−11.01	0.815	0.988	3.985	13.17	10
	m	−11.98	0.965	0.449	10.37	11.46	
	p	−4.644	0.619	1.34	2.230	9.79	
2	I	−14.63	0.931	0.742	4.402	11.29	5
	m	−12.08	0.999	0.0856	40.97	8.90	
	p	−6.372	0.877	0.974	3.159	6.69	
3	I	−24.09	0.990	0.801	17.05	14.20	8
	m	−17.70	0.908	2.36	5.295	11.83	
	p	−7.800	0.648	4.29	2.083	8.47	
4	I	−16.44	0.980	0.401	10.99	12.33	7
	m	−8.282	0.779	1.26	2.780	10.89	
	p	−2.833	0.559	1.67	1.507	10.15	
5	I	−20.64	0.979	0.682	14.31	9.59	11
	m	−21.12	0.881	1.57	5.587	8.12	
	p	−20.44	0.131	3.29	0.397	7.51	
6	I	−12.64	0.994	0.155	21.19	9.11	7
	m	−8.788	0.555	1.23	1.493	8.24	
	p	4.127	0.631	1.14	1.817	9.60	
7	I	−19.36	0.971	0.641	9.023	10.06	7
	m	−4.947	0.288	2.55	0.673	8.30	
	p	8.013	0.652	2.02	1.923	10.30	
8	I	−18.77	0.965	0.891	10.38	9.16	10
	m	−14.62	0.717	2.36	2.910	7.45	
	p	−0.402	0.036	3.39	0.101	6.91	
9	I	−20.21	0.973	0.959	9.465	9.89	7
	m	−17.93	0.856	2.16	3.697	8.52	
	p	−6.053	0.464	3.70	1.170	7.31	1

[a] Correlation coefficient. [b] Standard deviation. [c] Student t test. [d] Number of points in set.

The 1-substituted 3-nitroguanidines are also best correlated by the σ_I constants. Again the results are significant at the 99.9% confidence level. The ionization of the guanidinium ions is significantly more sensitive to substituent effects than is the ionization of 1-substituted 3-nitroguanidines, the ρ-values being 24.1 and 16.4, respectively.

Substituted Ammonium Ions.—Correlation of the pK_a values of substituted ammonium ions with σ^* constants have been reported by Hall.[9] The results of Hall were unsatisfactory for our purpose, as correlations were made with $\Sigma\sigma^*$ for secondary and tertiary amines. The amines included in the correlations are not indicated other than that they have minimum steric requirements. Furthermore, there are no values of correlation coefficient, standard deviation, or other measure of degree of correlation reported. We have therefore studied the correlation of these several sets of substituted ammonium ions with σ_I, σ_m, and σ_p in order to provide a check on our method of investigating substituent effects, since these sets would be expected to give best correlation with σ_I. The ρ-values for these sets are required for purposes of comparison with those of the amidinium, guanidinium, and nitroguanidine sets. Only substituents which do not show large resonance effects or are electron donor by resonance have been included in these sets. The results show best correlation with σ_I in all the cases studied. The ρ-values for all of those sets in water at 25° are about the same magnitude. Although ρ decreases steadily as N-methyl groups are introduced, the change is probably too small to be significant. As ρ for the substituted diethylammonium ions is approximately equal to ρ for substituted

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(8) M. Charton, unpublished results.

(9) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957).

TABLE IV

PHYSICAL EVIDENCE FOR THE STRUCTURE OF N-SUBSTITUTED AMIDINES

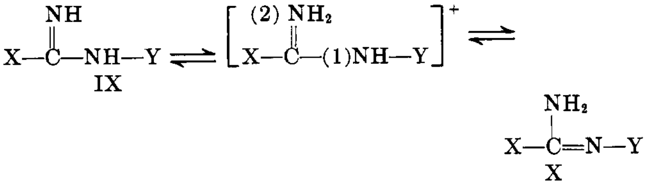
X	Y	Structure	Evidence	Ref.
CN	NH_2	X	X-Ray crystallography	*a*
Cl	—N=N—CNH_2=NCl	X	X-Ray crystallography	*b*
NO_2	NH_2	X	X-Ray crystallography	*c*
		X	Ultraviolet spectra	*d*
(RO)(R^1O)P=O	NH_2	X	Infrared and n.m.r. spectra	*e*
Ph	R	X	Infrared spectra	*f*
		IX	Ultraviolet spectra	*g*
OH	R	X	Infrared spectra	*f*
Et	R	IX[h]	Infrared spectra	*f*

[a] E. W. Hughes, *J. Am. Chem. Soc.*, **62**, 1258 (1940). [b] J. H. Bryden, *Acta Cryst.*, 11, 158 (1958). [c] J. H. Bryden, L. A. Burkhardt, and E. W. Hughes, *ibid.*, 9, 573 (1956). [d] T. G. Bonner and J. C. Lockhart, *J. Chem. Soc.*, 3858 (1958). [e] V. M. Clark, *Proc. Chem. Soc.*, 129 (1964). [f] D. Prevorsek, *J. chim. phys.*, 840 (1958); *J. Phys. Chem.*, **66**, 769 (1962). [g] Ref. 12. [h] IX predominates; X is also found.

ammonium ions, it seems unlikely that the changes in ρ due to the introduction of N-methyl groups are real.

Discussion

Site of Ionizable Proton.—The application of the Hammett equation to sets capable of prototropic tautomerism was first studied by Jaffé.[10] Kabachnik[11] and his group have investigated several systems capable of exhibiting this phenomenon. Sets 2 and 3 are both capable of exhibiting tautomerism, which may be presented as follows.



$$X{-}C({=}NH){-}NH{-}Y \rightleftharpoons \left[X{-}C({=}\overset{(2)}{N}H_2){-}\overset{(1)}{N}H{-}Y\right]^+ \rightleftharpoons X{-}C(NH_2){=}N{-}Y$$

IX

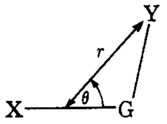
X

In carrying out the correlations it has been assumed that, when Y is an electron acceptor, the tautomer X will predominate as the result of loss of the N-1 proton. When Y is an electron donor, tautomer IX is considered predominant. On this basis, compounds with Y = alkyl were excluded from set 3. Physical evidence in support of these assumptions has been reported by several authors and is summarized in Table IV. To this physical evidence may be added the following arguments.

(1) The ρ-value for the substituted guanidinium ions (set 3) is very much larger than that for the substituted N-phenylamidinium ions (set 2), and is in fact comparable with the ρ-values obtained for substituted ammonium ions (sets 5–9). The magnitude of ρ is a function of the quantity correlated, the conditions under which it is measured, the structure of the set, and its molecular geometry. In comparing sets 2 and 3 the only variable is the molecular geometry. The variation of ρ with molecular geometry is given by eq. 2.

$$\rho_G = \frac{r_{G^0}{}^2 \cos \theta_G \rho_{G^0}}{r_G{}^2 \cos \theta_{G^0}} \tag{2}$$

We may write the set under consideration in the form XGY where X is the substituent, Y the reaction site, and G some group to which they are both attached. Similarly, we may consider some reference set XG^0Y. Then in general r and θ are defined in XI. For acid-base equilibria, r represents the distance between the midpoint of the X–G bond and the ionizable proton, θ the angle made by this distance with the X–G bond dipole.



XI

The comparison between the ρ-values of substituted ammonium ions and those of sets 2 and 3 is not so well justified. Furthermore, correlation of pK_a values of substituted phenylimines (XII) (PhXC=NH) with σ_m results in a ρ-value of about 19. Nevertheless, it does not seem possible to account for the large difference in ρ between sets 2 and 3 except in terms of the difference in r and θ between the two sets.

(2) The best correlation of the pK_a values of substituted ammonium ions is obtained with the σ_I constants. Set 3 also gives best correlation with σ_I. If ionization in set 3 were to occur at N-3 rather than N-1, then set 3 would constitute a subset of set 1; this would require that the relationship

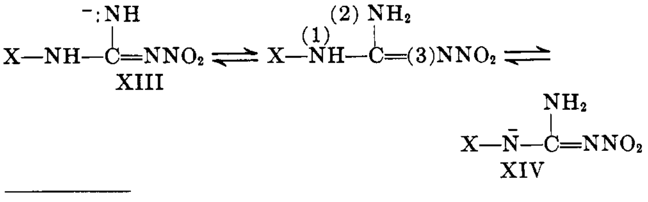
$$\sigma_{m\text{-XNH}} = m\sigma_{I,X} + c \tag{3}$$

be fulfilled. Actually the equation

$$\sigma_{m\text{-XNH}} = m\sigma_{m\text{-X}} + c \tag{4}$$

gives best results. At this point we may also note that, although Koike[12] has reported on the basis of ultraviolet data that phenylguanidine has the structure X, he finds for the ionization of 4-substituted phenylguanidines in water, a ρ-value of 2.30 (compare ρ for substituted anilines = 2.767). Ionization at N-3 should probably gave a ρ-value less than 1.

The ionization of the 3-nitroguanidines (set 4) may also show tautomerism. Here again we have assumed that, when X is an electron acceptor, XIV is predomi-



$$X{-}NH{-}C({=}NNO_2){-}\ddot{N}H^- \rightleftharpoons X{-}\overset{(1)}{N}H{-}C(\overset{(2)}{N}H_2){=}(3)NNO_2 \rightleftharpoons X{-}\bar{N}{-}C(NH_2){=}NNO_2$$

XIII

XIV

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[10] H. H. Jaffé, *J. Am. Chem. Soc.*, **77**, 4445 (1955); H. H. Jaffé and G. O. Doak, *ibid.*, **77**, 4441 (1955).

[11] M. I. Kabachnik, T. A. Mastrukova, A. E. Shipov, and T. A. Melentyeva, *Tetrahedron*, **9**, 10 (1960).

[12] H. Koike, *Nippon Kagaku Zasshi*, **83**, 917 (1962); *Chem. Abstr.*, **58**, 13301*e* (1963).

nant, whereas, when X is an electron donor, XIII is the predominant tautomer. On the basis of this assumption, compounds with X = Me, $PhCH_2$, and $PhCH_2CH_2$ were excluded from the set. These assumptions are more difficult to justify as no physical evidence is available. They seem reasonable in view of the previous discussion. Furthermore, the second argument of the previous discussion is applicable here, as again decidedly best correlation is obtained with the σ_I constants. We therefore consider that in set 4 the ionizable proton is situated at N-1.

Electrical Effects in C-Substituted Amidinium Ions.—It has previously been shown that *trans*-vinylene sets are best correlated by the σ_p constants.[13] The amidinium ions may be considered to be vinylene sets in which the reaction site is the nitrogen bearing the transferable proton. Thus the amidine set is analogous to the vinylene in the same sense that pyridine is analogous to benzene. The question then arises as to why the best results are obtained with σ_m constants rather than σ_p. In the course of another investigation[14] we have observed that, although the "normal" electrical effect of *ortho* substituents is proportional to that of *para* substituents

$$\sigma_o = m\sigma_p + c \tag{5}$$

in *ortho* substituted pyridines and quinolines, an "abnormal" electrical effect is observed.

$$\sigma_o = m\sigma_I + c \text{ or } \sigma_o = m\sigma_m + c \tag{6}$$

We believe that the amidinium ions represent an analogous situation. The geometry of the amidinium ions shows a strong resemblance to that of the 2-substituted pyridinium or quinolinium ions. Thus the explanation we have proposed for the "abnormal" *ortho* effect may be applied also to this unexpected electrical effect in amidinium ions. This explanation presumed the existence of a short-range localized electrostatic effect which we believe to be the classical inductive effect. The total electrical effect of a substituent may be represented as

$$\sigma_T = \lambda\sigma_I + \delta\sigma_R \tag{7}$$

where σ_I is a constant characteristic of the localized effect and σ_R is a constant characteristic of the delocalized effect, λ and δ being the coefficients which determine the contribution of these effects to σ_T. Over more then two bond lengths, we believe that the localized effect is largely a field effect. Over the short distance involved in the amidinium ions, the short-range localized (inductive) effect also makes a significant contribution, thus increasing the magnitude of λ and presumably leaving δ unaffected. This will result in a change in ϵ where

$$\epsilon = \delta/\lambda \tag{8}$$

As can be seen from the values of ϵ in Table V, a decrease in ϵ could lead to an electrical effect better represented by σ_m than by σ_p.

TABLE V

VALUES OF ϵ[a]

Substituent constant	ϵ	Substituent constant	ϵ
σ_I	0	σ_o	1
σ_m	0.3–0.5	$\sigma_p{}^+$	1.73[b]
σ_p	1		

[a] Ref. 14, unless otherwise noted. [b] M. Charton, unpublished results.

Electrical Effects in Substituted Ammonium Ions.—It seems significant that the ρ-values of the substituted ammonium ions are almost unaffected by the presence of N-alkyl groups. While the electrical effect of such groups would not be greatly different from that of hydrogen (σ_I for Me and Et is -0.05, for H it is 0), the variation in size and shape on introduction of N-alkyl groups should change the effective dielectric constant of the ammonium ion. Thus, if the predominant component of the localized effect in these species was the field effect, some significant change in ρ might be expected. Using the Kirkwood–Westheimer equation,[15] and assuming that the N–H bond length, the X–N bond lengths, and the XNH angle are about the same

$$\log \frac{K_X}{K_H} = \frac{e\mu_X \cos \theta}{2.303RTD_E r^2} = \rho\sigma_X \tag{9}$$

for some N-alkyl set, while for the unsubstituted set

$$\rho^0\sigma_X = \frac{e\mu_X \cos \theta}{2.303RTD_E{}^0 r^2} \tag{10}$$

and

$$\rho = \frac{D_E{}^0\rho^0}{D_E} \tag{11}$$

The absence of such an important change in ρ can be explained in terms of the inductive effect as the major component of the localized effect in the substituted ammonium ions.

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(13) M. Charton and H. Meislich, *J. Am. Chem. Soc.*, **80**, 5940 (1958); J. Hine and W. C. Bailey, *ibid.*, **81**, 2075 (1959); J. Hine and W. C. Bailey, *J. Org. Chem.*, **26**, 2098 (1961); P. B. D. de la Mare, *J. Chem. Soc.*, 3823 (1960).

(14) M. Charton, *J. Am. Chem. Soc.*, **86**, 2033 (1964).

(15) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).