

It should be noted that no differences in the infrared and nuclear magnetic resonance spectra were found for the samples of *monotrans*ester which showed complete disproportionation within a short period of time as compared to those which exhibited a much greater stability.

**Acknowledgment.**—The authors are indebted to the personnel of the Analytical Research Branch, Chemical Research Division, for the elemental analyses reported in this paper.

ARMY CHEMICAL CENTER, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRATT INSTITUTE AND BROOKLYN COLLEGE]

## Applications of the Hammett Equation to Non-aromatic Unsaturated Systems. I. *trans*-3-Substituted Acrylic Acids<sup>1</sup>

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RECEIVED MARCH 25, 1958

Dissociation constants for *trans*-3-substituted acrylic acids, *trans*-3-methyl-3-substituted acrylic acids and *trans*-3-carboxy-3-substituted acrylic acids are correlated with the Hammett equation. The  $\rho$ -values and correlation coefficients are 2.230, 0.975; 2.977, 0.991; and 1.918, and 0.925, respectively. New substituent constants are calculated for a number of substituents. The non-applicability of the Hammett equation to the dissociation constants of the corresponding *cis*-acids is discussed.

The Hammett equation has been very useful in the correlation of equilibrium and rate data, and of various physical constants.<sup>4,5</sup> It has been applied to meta and para substituted benzene derivatives and, recently, to heterocyclic compounds.<sup>6</sup> In

modified form, it also has been applied to aliphatic compounds, and ortho substituted benzene derivatives.<sup>7a-e</sup> Neither the Hammett equation nor any other linear free energy relationship has been applied to rate or equilibrium data for non-aromatic

TABLE I  
DISSOCIATION CONSTANTS OF 3-SUBSTITUTED ACRYLIC ACIDS

| Substituent                                      | Con-figuration | 10 <sup>6</sup> K   | Method of evaluation | Acid                      | Ref.  |
|--|----------------|---------------------|----------------------|---------------------------|-------|
| H  | ..             | 5.56                | Conductimetric       | Acrylic                   | 9     |
| Me   | <i>trans</i>   | 2.03                | Conductimetric       | Crotonic                  | 9, 10 |
| Me   | <i>cis</i>     | 3.6 <sup>a</sup>    | Conductimetric       | Isocrotonic               | 12    |
| Et   | <i>trans</i>   | 2.02                | Conductimetric       | 2-Pentenoic               | 11    |
| Pr   | <i>trans</i>   | 1.98                | Conductimetric       | 2-Hexenoic                | 11    |
| <i>i</i> -Pr                                     | <i>trans</i>   | 1.99                | Conductimetric       | 4-Methyl-2-pentenoic      | 11    |
| Ph   | <i>trans</i>   | 3.65                | Conductimetric       | Cinnamic                  | 12    |
| Ph   | <i>cis</i>     | 13.2                | Conductimetric       | Cinnamic                  | 12    |
| CO <sub>2</sub> H                                | <i>trans</i>   | 95.7 <sup>c</sup>   | Conductimetric       | Fumaric                   | 10    |
| CO <sub>2</sub> H                                | <i>cis</i>     | 1200 <sup>d</sup>   | Conductimetric       | Maleic                    | 10    |
| CO <sub>2</sub> <sup>-</sup>                     | <i>trans</i>   | 4.13 <sup>e</sup>   | Conductimetric       | Fumaric                   | 10    |
| CO <sub>2</sub> <sup>-</sup>                     | <i>cis</i>     | 0.0505 <sup>f</sup> | Conductimetric       | Maleic                    | 10    |
| CF <sub>3</sub>                                  | <i>trans</i>   | 70                  | Conductimetric       | 4,4,4-Trifluoro-2-butenic | 13    |
| CF <sub>3</sub>                                  | <i>cis</i>     | 33                  | From pH              | 4,4,4-Trifluoro-2-butenic | 14    |
| CO <sub>2</sub> Et                               | <i>trans</i>   | 47.3 <sup>a</sup>   | Conductimetric       | Monoethyl fumarate        | 15    |
| Cl   | <i>trans</i>   | 22.2 <sup>a,b</sup> | From pH              | Chloroacrylic             | 16    |
| Cl   | <i>cis</i>     | 47.7 <sup>a,b</sup> | From pH              | Chloroacrylic             | 16    |
| 4'-ClC <sub>6</sub> H <sub>4</sub>               | <i>trans</i>   | 3.86                | Conductimetric       | 4-Chlorocinnamic          | 17    |
| 4'-MeOC <sub>6</sub> H <sub>4</sub>              | <i>trans</i>   | 2.89                | Conductimetric       | 4-Methoxycinnamic         | 18    |
| 4'-MeC <sub>6</sub> H <sub>4</sub>               | <i>trans</i>   | 2.73                | Conductimetric       | 4-Methylcinnamic          | 18    |
| 3'-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> | <i>trans</i>   | 7.58                | Conductimetric       | 3-Nitrocinnamic           | 18    |
| 4'-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> | <i>trans</i>   | 8.99                | Conductimetric       | 4-Nitrocinnamic           | 18    |
| PhCH=CH  | ..             | 3.75                | Conductimetric       | 5-Phenyl-2,4-pentadienoic | 12    |
| CH <sub>2</sub> Cl                               | <i>trans</i>   | 7.25 <sup>a</sup>   | Conductimetric       | 4-Chloro-2-butenic        | 19    |

All data in water at 25°, reported as thermodynamic dissociation constants unless otherwise stated. <sup>a</sup> Non-thermodynamic dissociation constant. <sup>b</sup> Data at 18°. <sup>c</sup> K<sub>1</sub> of fumaric acid. <sup>d</sup> K<sub>1</sub> of maleic acid. <sup>e</sup> K<sub>2</sub> of fumaric acid. <sup>f</sup> K<sub>2</sub> of maleic acid.

(1) This work is taken in part from the thesis submitted by M. Charton to the Graduate Faculty of Brooklyn College in partial fulfillment of the requirements for the degree of M.A., June, 1956.

(2) This work was presented in part at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1956.

(3) Address all inquiries to M. Charton, Pratt Institute, Brooklyn, N. Y.

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 73, 118-123.

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

(6) H. H. Jaffé and G. O. Doak, *THIS JOURNAL*, **77**, 4441 (1955).

carbon-carbon unsaturated compounds, although many publications have appeared on the application of linear free energy relationships to non-aromatic carbonyl compounds.

(7a) R. W. Taft, *ibid.*, **74**, 2728 (1952).

(7b) R. W. Taft, *ibid.*, **74**, 3120 (1952).

(7c) R. W. Taft, *ibid.*, **75**, 4231 (1953).

(7d) R. W. Taft, *ibid.*, **75**, 4538 (1953).

(7e) R. W. Taft and D. J. Smith, *ibid.*, **76**, 305 (1954).

This work was suggested by the authors' discovery of the existence of a correlation between the oxidation-reduction potentials of quinones and the substituent constants of the Hammett equation. A search of the literature disclosed a private communication from Carter to Evans and DeHeer<sup>8</sup> reporting the existence of such a relationship. Evans and DeHeer stated that there was no apparent basis for such a relationship, as the Hammett equation was applied only to meta and para substituted aromatic compounds, and quinones are not aromatic compounds. Substituted quinones are actually *trans*-olefinic compounds as can be seen from their structure. In order to test the applicability of the Hammett equation to *trans*-olefinic compounds in general, the dissociation constants of the *trans*-3-substituted acrylic acids were examined. This choice was based on the fact that the Hammett equation is applicable to the dissociation constants of *meta* and *para* substituted benzoic acids and on the availability of these dissociation constants in the literature. The correlations between,  $\sigma_p$  and the dissociation constants were made by Jaffé's method.<sup>5</sup> The values of the dissociation constants, and the  $\sigma_p$  values used are shown in Tables I and II, respectively. The results are given in Table III. A plot of  $\log K$  against  $\sigma$  is shown in Fig. 1.

TABLE II

| SUBSTITUENT CONSTANTS USED IN CORRELATIONS              |            |              |   |            |                 |
|---|------------|--------------|---|------------|-----------------|
| Substituent   | $\sigma_p$ | Ref.         | Substituent   | $\sigma_p$ | Ref.            |
| H   | 0          | <sup>a</sup> | Me  | -0.170     | 4               |
| Et  | -0.151     | 5            | Pr  | -.126      | 4               |
| <i>i</i> -Pr  | -.151      | 4            | Ph  | .009       | 4               |
| Cl  | .227       | 4            | Br  | .232       | 4               |
| CO <sub>2</sub> H                                       | .45        | 20a          | CO <sub>2</sub> <sup>-</sup>                            | .132       | 5               |
| CO <sub>2</sub> Et                                      | .45        | 20a          | CF <sub>3</sub>   | .54        | 20 <sup>a</sup> |
| CH <sub>2</sub> Cl                                      | .184       | 5            | PhCH=CH   | -.050      | 21              |
| <i>p</i> -ClC <sub>6</sub> H <sub>4</sub>               | .081       | 22           | <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>              | -.088      | 22              |
| <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>               | -.048      | 22           | <i>m</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> | .183       | 22              |
| <i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> | .229       | 22           | OH  | -.357      | 5               |

<sup>a</sup> By definition.

The correlation coefficient,  $r$ , was found to be 0.975 for the *trans*-3-substituted acrylic acids. Jaffé has suggested an arbitrary scale for determining the degree of correlation, in which  $r > 0.99$  is excellent,  $r > 0.95$  is satisfactory and  $r > 0.90$  is fair correlation. Both thermodynamic and

- (8) E. Evans and J. DeHeer, *Trans. Faraday Soc.*, **47**, 801 (1951).  
 (9) J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1008 (1937).  
 (10) W. L. German, G. H. Jeffery and A. I. Vogel, *ibid.*, 1604 (1937).  
 (11) D. J. G. Ives, R. P. Linstead and H. L. Riley, *ibid.*, 561 (1933).  
 (12) J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939).  
 (13) R. N. Haszeldine, *J. Chem. Soc.*, 922 (1953).  
 (14) E. T. McBee, D. R. Pierce and D. D. Smith, *THIS JOURNAL*, **76**, 3722 (1954).  
 (15) J. Walker, *J. Chem. Soc.*, **61**, 714 (1892).  
 (16) H. J. Backer and A. E. Beute, *Rec. trav. chim.*, **54**, 167 (1956).  
 (17) J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1426 (1937).  
 (18) J. F. J. Dippy and J. E. Page, *ibid.*, 357 (1938).  
 (19) A. Kirrmann, R. Schmitz, P. Federlin and M. L. Dondon, *Bull. soc. chim. France*, 612 (1952).  
 (20) (a) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958); (b) G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 4761 (1956).  
 (21) J. K. Kochi and G. S. Hammond, *THIS JOURNAL*, **75**, 3542 (1953).  
 (22) E. Berliner and L. H. Liu, *ibid.*, **75**, 2417 (1953).

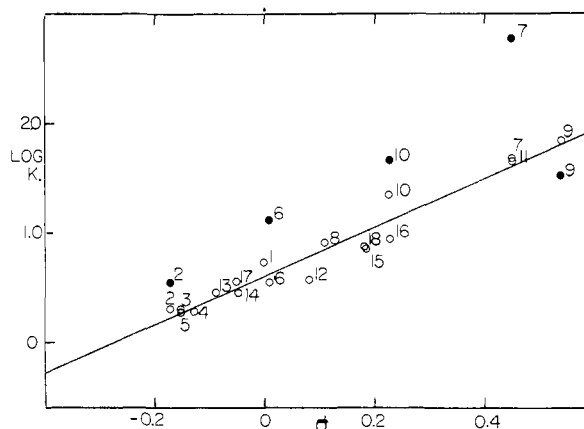


Fig. 1.—Hammett equation plot of  $\log 10^5 K$  vs.  $\sigma$  for *trans*-3-substituted acrylic acids: ●, *cis*-acids; ○, *trans*-acids. The substituents are: 1, H; 2, Me; 3, Et; 4, Pr; 5, *i*-Pr; 6, Ph; 7, CO<sub>2</sub>H; 8, CO<sub>2</sub><sup>-</sup>; 9, CF<sub>3</sub>; 10, Cl; 11, CO<sub>2</sub>Et; 12, 4-ClC<sub>6</sub>H<sub>4</sub>; 13, 4-MeOC<sub>6</sub>H<sub>4</sub>; 14, MeC<sub>6</sub>H<sub>4</sub>; 15, 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>; 16, 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>; 17, PhCH=CH<sub>2</sub>; 18, CH<sub>2</sub>Cl.

non-thermodynamic dissociation constants were used in the correlations.

The justification for this is that a comparison of the non-thermodynamic constants in those instances where both have been reported showed that the mean deviation was 1.67% and the mean absolute deviation was 10.24% for the thirteen compounds compared. As the Hammett equation correlates data with a precision of 15%<sup>4,5</sup> the utilization of both thermodynamic and non-thermodynamic constants was considered justifiable.

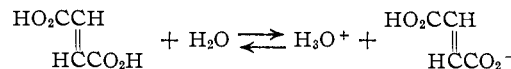
TABLE III

| RESULTS OF CORRELATIONS                        |        |       |       |            |       |
|--|--------|-------|-------|------------|-------|
| Reaction series                                | $\rho$ | $r$   | $s^a$ | $\log K^0$ | $n^b$ |
| <i>trans</i> -3-Substd. acrylic acids          | 2.230  | 0.975 | 0.117 | 0.608      | 18    |
| <i>trans</i> -3-Substd.-3-methylacrylic acids  | 2.977  | .991  | .120  | 1.390      | 5     |
| <i>trans</i> -3-Substd.-3-carboxyacrylic acids | 1.918  | .923  | .211  | 0.982      | 6     |

<sup>a</sup> Standard deviation. <sup>b</sup> Number of compounds in series.

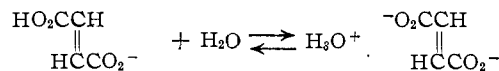
The use of  $\sigma_p$  rather than  $\sigma_m$  in these correlations is due to the fact that  $\sigma_m$  is largely (although not entirely) a measure of the inductive effects.<sup>23,24</sup>

Statistical factors were required for the correlation of the carboxyl and carboxylate groups. The first dissociation constant of fumaric acid was divided by a statistical factor of two, as there are two carboxyl groups which may dissociate. This value then was used in the correlation for the carboxyl groups



The second dissociation constant of fumaric acid was multiplied by a statistical factor of two, as the dicarboxylate anion has twice as large a chance of being protonated as have the anions of other acids.

- (23) J. D. Roberts and W. T. Moreland, *ibid.*, **75**, 2167 (1953).  
 (24) R. W. Taft in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 594-597.



As can be seen in Fig. 1, the dissociation constants of *cis*-3-substituted acrylic acids are not correlated by the Hammett equation. This is readily explained by their resemblance to *o*-substituted benzene derivatives, which are also not correlated by the Hammett equation, due to the so-called *ortho* effect. The *ortho* effect is apparently not only



steric in nature, but also involves, in some cases at least, chelation between substituent and reaction site. This easily demonstrable difference between the *cis* and *trans* compounds suggests the applicability of correlation with the Hammett equation to the assignment of *cis* and *trans* configuration to a pair of isomers, not only in the case of 3-substituted acrylic acids but, as more data become available, in other series of compounds as well.

The *trans*-3-substituted acrylic acid reaction series has been utilized for the calculation of substituent constants ( $\sigma_p$ ) for the 3'-methylphenyl, 3'-hydroxyphenyl, 3'-methoxyphenyl, 3'-chlorophenyl, ethynyl, propynyl and *trans*-propynyl groups. The substituent constant for the carbomethoxy group has been calculated from the *trans*-3-methyl-3-substituted acrylic acid reaction series. The results obtained are given in Table IV.

The dissociation constants of the 3-methyl-3-substituted acrylic acids and of the 3-carboxy-3-substituted acrylic acids (substituted maleic acids) have been correlated with Hammett's  $\sigma_p$  constants. The results of these correlations are in Table III and Figs. 2 and 3. The correlation is satisfactory

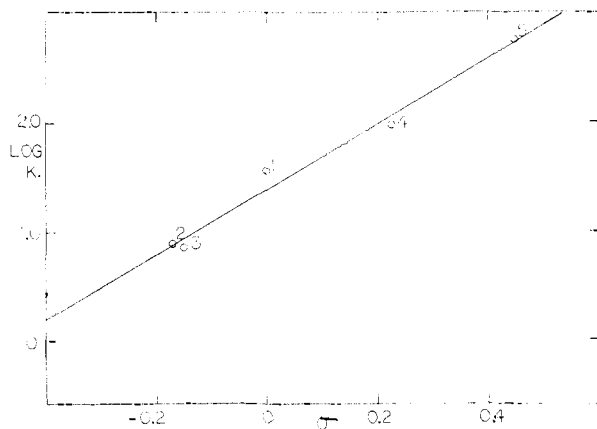


Fig. 2.—Hammett equation plot of  $\log 10^5 K$  vs.  $\sigma$  for *trans*-3-substituted-3-methylacrylic acids. The substituents are: 1, H; 2, Me; 3, Et; 4, Cl; 5,  $\text{CO}_2\text{Et}$ .

in the case of the former reaction series, but only fair in the latter. This lack of satisfactory correlation may be due in part to the known variance of the substituent constant for the hydroxyl group with reaction conditions.<sup>5</sup> Another factor, probably of greater importance, is that only six com-

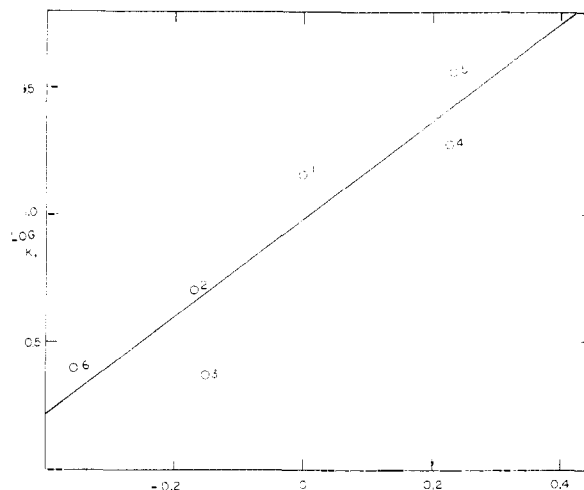


Fig. 3.—Hammett equation plot of  $\log 10^5 K$  vs.  $\sigma$  for *trans*-3-substituted-3-carboxyacrylic acids. The substituents are: 1, H; 2, Me; 3, Et; 4, Cl; 5, Br; 6, OH.

pounds have been studied, and the data are drawn from three different sources.

The successful correlation of these reaction series, having a constant substituent *cis* to the reaction site, is analogous to correlations in aromatic reaction series, in which there is a constant substituent *ortho* to the reaction site.

TABLE IV  
NEW SUBSTITUENT CONSTANTS

| Substituent                  | Acid                           | $10^5 K$ | Ref. | $\sigma_p$ calcd. |
|------------------------------|--------------------------------|----------|------|-------------------|
| $3'\text{-MeC}_6\text{H}_4$  | 3-Methylcinnamic               | 3.615    | 16   | -0.016            |
| $3'\text{-HOC}_6\text{H}_4$  | 3-Hydroxycinnamic              | 4.005    | 16   | .003              |
| $3'\text{-MeOC}_6\text{H}_4$ | 3-Methoxycinnamic              | 4.21     | 16   | .012              |
| $3'\text{-ClC}_6\text{H}_4$  | 3-Chlorocinnamic               | 5.085    | 16   | .047              |
| $\text{HC}\equiv\text{C}-$   | Pent-2-en-4-ynoic              | 17.8     | 26   | .281              |
| $\text{MeC}\equiv\text{C}-$  | Hex-2-en-4-ynoic               | 3.32     | 26   | .087              |
| $t\text{-MeCH}=\text{CH}-$   | Hexa-2,4-dienoic               | 4.47     | 26   | -.043             |
| $\text{CO}_2\text{Me}$       | 3-Methyl-3-carbomethoxyacrylic | 510      | 25   | .436              |

It is of interest to compare the effect of the constant *cis*-3-methyl group on the reaction constant for the ionization of 3-substituted acrylic acids with the effect of a constant *o*-methyl group on the reaction for the ionization of 3- or 4-substituted benzoic acids. This may be done by comparison of the ratio  $\rho_I/\rho_{II}$  with  $\rho_{III}/\rho_{IV}$  where  $\rho_I$  is the reaction constant for the ionization of *trans*-3-substituted 3-methylacrylic acids,  $\rho_{II}$  is the reaction constant for the ionization of *trans*-3-substituted acrylic acids,  $\rho_{III}$  is the reaction constant for the ionization of 2-methyl-3- or 4-substituted benzoic acids<sup>5</sup> and  $\rho_{IV}$  is the reaction constant for the ionization of 3- or 4-substituted benzoic acids,<sup>3</sup> all in water at 25°;  $\rho_I/\rho_{II}$  is found to be 1.33,  $\rho_{III}/\rho_{IV}$  is 1.43. Thus the constant *ortho* effect of the methyl group is of about the same magnitude in both the acrylic and the benzoic acids.

The results of the correlations for these reaction series are shown in Table III and Figs. 2 and 3. The data will be found in Tables V and VI.

(25) R. Anschutz, R. Hass and O. Sieplein, *Ann.*, **353**, 144 (1907).

(26) H. W. Ashton and J. R. Partington, *Trans. Faraday Soc.*, **30**, 598 (1934).

TABLE V

DISSOCIATION CONSTANTS OF 3-SUBSTITUTED-3-METHYL-ACRYLIC ACIDS

| Substituent        | 10 <sup>5</sup> K | Method of evaluation | Ref. | Acid                           |
|--------------------|-------------------|----------------------|------|--------------------------------|
| CO <sub>2</sub> Et | 553               | Conductimetric       | 25   | 3-Carboxyethyl-3-methylacrylic |
| Et                 | 7.1 <sup>a</sup>  | Conductimetric       | 11   | 3-Methyl-2-pentenoic           |
| Me                 | 7.6 <sup>a</sup>  | Conductimetric       | 11   | 3-Methyl-2-butenic             |
| Cl                 | 36                | Conductimetric       | 12   | 3-Chloro-2-butenic             |
| H                  | 95                | Conductimetric       | 12   | Isocrotonic                    |

All data in water at 25°. The configuration in these acids is such that the methyl group is *cis* to the carboxyl group. The dissociation constants are non-thermodynamic unless otherwise stated. <sup>a</sup> Thermodynamic constant.

From these correlations, it can be seen that the Hammett equation is directly applicable to the *trans*-olefinic systems. Other reaction series are now under consideration.

**Acknowledgment.**—The helpful advice and discussion of Professor H. Nechamkin, Pratt Institute,

TABLE VI

DISSOCIATION CONSTANTS OF 3-SUBSTITUTED-3-CARBOXY-ACRYLIC ACIDS (SUBSTITUTED MALEIC ACIDS)

| Substituent | 10 <sup>5</sup> K | Method of evaluation | Ref. | Acid          |
|-------------|-------------------|----------------------|------|---------------|
| H           | 14.2              | From pH              | 26   | Maleic        |
| Me          | 5.14              | From pH              | 26   | Citraconic    |
| Et          | 2.30              | Conductimetric       | 27   | Ethylmaleic   |
| Cl          | 10.0              | From pH              | 26   | Chloromaleic  |
| Br          | 35.0              | From pH              | 26   | Bromomaleic   |
| OH          | 2.505             | Conductimetric       | 28   | Hydroxymaleic |

is gratefully acknowledged. The authors wish also to acknowledge the suggestion of one of the reviewers regarding the use of the substituent constants proposed by McDaniel and Brown,<sup>20</sup> thereby making unnecessary the use in some cases of  $\sigma_p$  values.

(27) K. Von Auwers and O. Ungenach, *Ann.*, **511**, 152 (1934).

(28) A. Wohl and P. Clausner, *Ber.*, **40**, 2308 (1907).

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY AND TOXICOLOGY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES MEDICAL SCHOOL]

## Base Strengths of Cyanoamines<sup>1</sup>

BY GEORGE W. STEVENSON AND DALLAS WILLIAMSON

RECEIVED JUNE 2, 1958

Substitution of aliphatic amines with cyano groups lowers their basicities. The N-cyano,  $\alpha$ -cyano,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ -cyanoamines are weaker by approx. 13, 5.7, 3.1, 1.6, 0.8 and 0.4  $pK$  units, respectively. The  $\Delta pK_a$  of  $n$  cyanosubstituted amines = approx.  $n$  (single  $\Delta pK$ ). The lowered basicity appears due to the large inductive field effect of the cyano group. A spectrophotometric method was developed to determine the  $pK_a$ 's of the very weak bases. Because of the wide range of  $pK_a$ 's of the cyanoamines, their ease of preparation, and stability, aliphatic cyanoamines should be useful.

During the course of conversion of secondary to tertiary bases by cyanoethylation it was found that the tertiary cyanoethylamines were considerably weaker bases than the secondary amines and about 3  $pK$  units weaker than the corresponding tertiary ethylamines. That the highly electron-withdrawing cyano group should exert a base-weakening effect was to be anticipated but its magnitude was surprising.

Despite the large number of cyanoamines which have been synthesized, only one paper dealing with the base strengths of the cyanoamines, by Marxer,<sup>2a</sup> has appeared.<sup>2b</sup> Marxer found that the formation of cyanomethyl tertiary amines from several secondary amines resulted in an average decrease in  $pK_a$  of 6.5  $pK$  units.<sup>2a</sup> However, it was shown that the  $pK_a$  of  $\alpha$ -piperidine-isobutyronitrile was less than that of piperidine by only 2.0  $pK$  units.

It has been found in this investigation that the

cyano group is more effective than all others in lowering basicity, possibly excluding some in which the electronegative group is attached directly to the nitrogen. Published  $pK$  values for some other types of amines are given below. Groups also can be compared using  $\delta^*$ -values as shown below. Taft has compiled a list of  $\delta^*$ -values.<sup>3</sup>

The  $pK_a$ 's of N-chlorodimethylamine and N-chlorodiethylamine have been reported as 0.46 and 1.02 by Weil and Morris.<sup>4</sup> A series of  $\beta$ -chloroethylamines has been titrated by Cohen, *et al.*<sup>5</sup> The weakest of these was tri- $\beta$ -chloroethylamine with a  $pK_a$  of 4.39. This is a much stronger base than the corresponding cyano compound which has a  $pK_a$  of 1.1. The effect of the fluoro group is comparable with that of the chloro. The hydroxyl has a considerably smaller effect, the  $pK_a$  of hydroxylamine being 5.97<sup>6</sup> and that of triethanolamine, 7.77.<sup>7a</sup>

(1) This investigation was supported by Research Grant B-1106 from the National Institute of Neurological Diseases and Blindness of the National Institutes of Health, U. S. Public Health Service. Presented in part at the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 13-18, 1958.

(2) (a) A. Marxer, *Helv. Chim. Acta*, **37**, 166 (1954). (b) Since the completion of this work another paper dealing with the  $pK_a$ 's of N-cyano-,  $\alpha$ -cyano- and  $\beta$ -cyanoamines has been published: S. Soloway and A. Lipschitz, *J. Org. Chem.*, **23**, 613 (1958). The  $pK_a$ 's of 11 compounds are given, 5 of which are included also in this study. The  $pK_a$ 's are in reasonable agreement except for that of diethylcyanamide which is reported by the above authors as 1.2; see footnote 7b.

(3) R. W. Taft, Jr., in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

(4) I. Weil and J. C. Morris, *This Journal*, **71**, 3123 (1949).

(5) B. Cohen, E. R. Van Artsdalen and J. Harris, *ibid.*, **70**, 282 (1948).

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(7) (a) N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3473 (1932). (b) In addition to the value for the  $pK_a$  of this compound, -2.0 as determined by the spectrophotometric method, two additional observations indicate the  $pK_a$  of this compound must be less than zero. When diethylcyanamide (either Eastman No. 6326 or that prepared for this study) was dissolved in water at room temp., about 1.3 ml. saturated