

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, COLLEGE OF ENGINEERING, CARNEGIE INSTITUTE OF TECHNOLOGY]

## Kinetic Medium and Salt Effects in Reactions between Ions of Unlike Sign. Reaction between Ammonium Ion and Cyanate Ion

BY J. C. WARNER AND EARL L. WARRICK

Although many investigations of the primary kinetic salt effect in reactions between ions have been reported, there have been no systematic studies, as far as the authors are aware, on the primary salt effect in mixed solvents over a range of dielectric constants. Studies on the influence of the dielectric constant of the solvent upon rate constants in a number of reactions between ions and uncharged molecules have been summarized by Harned and Samaras,<sup>1</sup> but practically no systematic work has been reported on the influence of dielectric constant of the solvent upon reactions between ions. The early results of Walker and Kay<sup>2</sup> and of Ross<sup>3</sup> on the velocity of conversion of ammonium cyanate into urea in mixtures of ethyl alcohol and water are not sufficiently precise for use in testing modern theories. Since this reaction is clearly one whose rate depends upon collisions between ammonium ions and cyanate ions,<sup>4</sup> we have, in this investigation, studied the primary salt effect at 50° in water ( $D$  69.85) and in mixtures of water with methyl, ethyl and isopropyl alcohols and with 1,4-dioxane at dielectric constants for the mixtures of 65, 60, 55, 45 and 40. The dependence of the rate constants at zero ionic strength upon the dielectric constant of the solvent was then compared with the predictions made by Scatchard<sup>5</sup> from the Christiansen theory.

### Materials and Experimental Procedure

Silver cyanate was prepared as follows: 50 g. of c. p. silver nitrate was dissolved in 250 cc. of water and 90 g. of Eastman "Highest Purity" urea dissolved in 350 cc. of water. The solutions were filtered and after heating the urea solution to near boiling, it was added to the silver nitrate solution in a darkened flask on a steam-bath. The mixture was then cooled to room temperature and the first small crop of colored crystals discarded. The solution was returned to the steam-bath, cooled at intervals, the silver cyanate filtered off was washed several times with ice water and dried in a vacuum desiccator. A solution of c. p. ammonium thiocyanate (approx. 0.02  $N$ ) was standardized against pure silver. Solutions of c. p. silver nitrate

(approx. 0.02  $N$ ) and c. p. ammonium chloride (approx. 0.2  $N$ ) were standardized against the ammonium thiocyanate solution.

Eastman "Highest Grade" methyl alcohol was fractionally distilled and the material used had a boiling point of 64.2° at 740 mm. in exact agreement with the vapor pressure data for this substance.<sup>6</sup> Constant boiling ethyl alcohol was used. The percentage of ethyl alcohol in the mixture was obtained from precise density measurements. Eastman "Highest Purity" isopropyl alcohol was dried and redistilled. 1,4-Dioxane was purchased from the Carbide and Carbon Chemicals Corporation and refluxed over metallic sodium for about twenty-four hours, then refluxed over phosphorus pentoxide for three hours and distilled in all-glass fractionating apparatus. All solvents were stored in such a manner that they were protected from the absorption of moisture from the atmosphere. All velocity measurements were made at  $50 \pm 0.03^\circ$ . In conducting an experiment, ammonium cyanate solutions were prepared by agitating standard ammonium chloride solution with a slight excess of silver cyanate until the solution was free of chloride ion. The solution was then filtered into a weighed reaction flask and weighed amounts of water and non-aqueous solvent added to give the desired solvent composition. The solution was heated to approximately the thermostat temperature over an open flame and then placed in the thermostat. After the establishment of temperature equilibrium, the initial sample was pipetted into an excess of standard silver nitrate solution and the mixture immediately chilled in ice water. The precipitated silver cyanate was filtered from the cold solution as soon as possible and an aliquot portion of the filtrate, made acid with 3 cc. of 3  $N$  nitric acid, was titrated with the standard ammonium thiocyanate using concentrated ferric nitrate as an indicator. As the reaction proceeded, numerous samples were treated in a similar manner. By properly adjusting the size of the sample from the reaction flask and the volume of standard silver nitrate, it was possible to maintain a comparable excess of silver nitrate in each sample. By following this procedure, it was possible to obtain results which were much more reproducible than those previously obtained.<sup>4</sup> The dielectric constants of the alcohol-water mixtures were taken from the work of Åkerlöf.<sup>7</sup> The dielectric constants of dioxane-water mixtures were determined for us by one of the industrial research laboratories and are in good agreement with those since obtained by Hooper and reported by Kraus and Fuoss.<sup>8</sup>

### Experimental Results and Discussion

By the Brönsted-Christiansen theory of the salt effect, the rate equation, neglecting the back

(1) Harned and Samaras, *THIS JOURNAL*, **54**, 1, 9 (1932).

(2) Walker and Kay, *J. Chem.*, **71**, 489 (1897).

(3) Ross, *ibid.*, **105**, 690 (1914).

(4) Warner and Stitt, *THIS JOURNAL*, **55**, 4807 (1933).

(5) Scatchard, *Chem. Rev.*, **10**, 229 (1932).

(6) "I. C. T.," Vol. III, p. 216.

(7) Åkerlöf, *THIS JOURNAL*, **54**, 4125 (1932).

(8) Kraus and Fuoss, *ibid.*, **55**, 21 (1933).

reaction which is unimportant up to 70% conversion,<sup>4</sup> is

$$-\frac{dC}{dt} = k^{\circ} C_{\text{NH}_4^+} C_{\text{OCN}^-} (f_{\text{NH}_4^+} f_{\text{OCN}^-} / f_{x^{\circ}}) \quad (1)$$

Since the activity coefficients are functions of the ionic strength, which changes during the course of the reaction, it was found impossible<sup>4</sup> to integrate the complete Equation (1). We have, however, applied Scatchard's<sup>9</sup> treatment of the rate of reaction in a changing environment with considerable success. This method involves the use of approximate equations for the activity coefficients such that, since  $z^+ z^- = -1$

$$(f_{\text{NH}_4^+} f_{\text{OCN}^-} / f_{x^{\circ}}) = \frac{1}{1 + 2A \sqrt{\mu}} \quad (2)$$

$A$  is the Debye-Hückel constant in

$$\ln f_i = -Az_i^2 \sqrt{\mu}$$

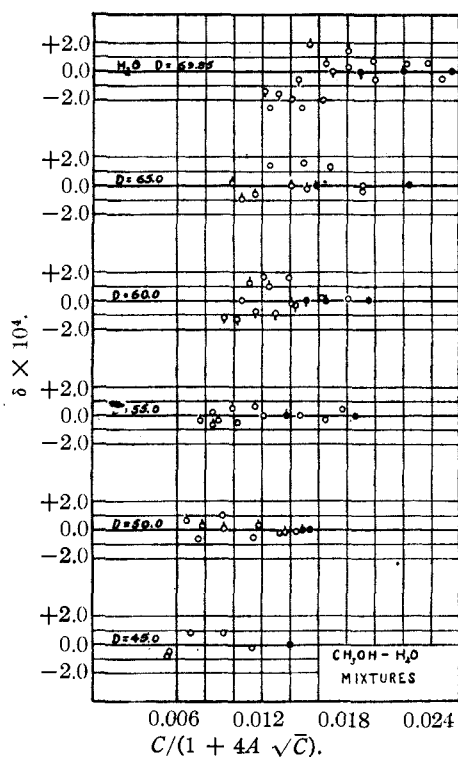


Fig. 1.—Methanol-water mixtures

If  $x$  represents the fraction of ammonium cyanate converted into urea, the concentration of ammonium cyanate and hence the ionic strength ( $\mu$ ) may be expressed in terms of the initial ionic strength ( $\mu^{\circ}$ ) and  $x$

$$\sqrt{\mu} = \sqrt{\mu^{\circ}} \sqrt{1 + gx}$$

Since for this reaction  $\mu = 0$  when  $x = 1$ , the constant  $g = -1$  and

$$\sqrt{\mu} = \sqrt{\mu^{\circ}} \sqrt{1 - x} \quad (3)$$

(9) Scatchard, THIS JOURNAL, 52, 52 (1930).

Substituting Equations (3) and (2) and the relation  $x = (C^{\circ} - C)/C^{\circ}$  in Eq. (1) we obtain

$$C^{\circ} \int_0^t k^{\circ} dt = \int_0^x \frac{dx}{(1-x)^2} + \int_0^x \frac{2A \sqrt{C^{\circ}} \sqrt{1-x} dx}{(1-x)^2} \quad (4)$$

which yields upon integration

$$k^{\circ} t = \left\{ \frac{1 + 4A \sqrt{C}}{C} \right\} - \left\{ \frac{1 + 4A \sqrt{C^{\circ}}}{C^{\circ}} \right\} \quad (5)$$

For pure water ( $D$  69.85) at 50° Equation (5) becomes

$$k^{\circ} t = \left\{ \frac{1 + 4.936 \sqrt{C}}{C} \right\} - \left\{ \frac{1 + 4.936 \sqrt{C^{\circ}}}{C^{\circ}} \right\}$$

Similar equations were obtained for each dielectric constant. Values of  $k^{\circ}$  calculated by Equation (5) from the experiments with water as solvent are given in Table I. There is no decided drift in  $k^{\circ}$  values in the various solvents. Hence we have taken as the best  $k^{\circ}$  value the average of all values of  $k^{\circ}$  obtained in the particular solvent. These average  $k^{\circ}$  values are listed in Table II. From the average  $k^{\circ}$  one may calculate the value of  $C/(1 + 4A \sqrt{C})$  at any time. The deviation ( $\delta$ ) of this from the experimental value gives a measure of variations in  $k^{\circ}$  from the average.

$$\delta = \{C/(1 + 4A \sqrt{C})\}_{\text{Expt.}} - \{C/(1 + 4A \sqrt{C})\}_{\text{Avg. } k^{\circ}}$$

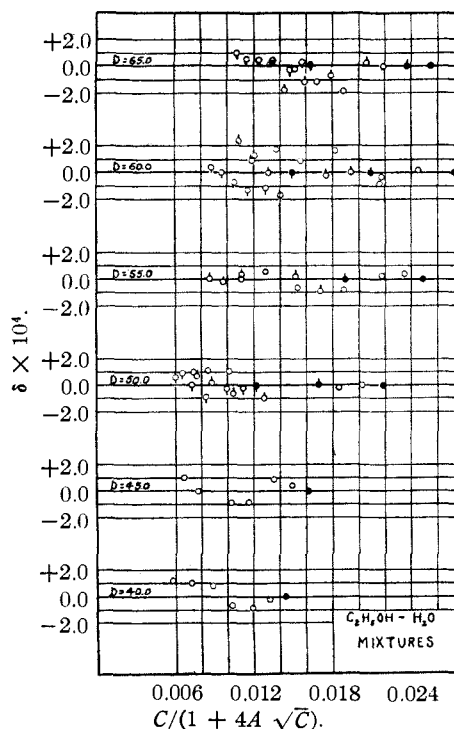


Fig. 2.—Ethanol-water mixtures.

In Figs. 1 to 4,  $\delta \times 10^4$  is plotted against experimental values of  $C/(1 + 4A \sqrt{C})$ . Differ-

ent symbols are used for each experiment in a given solvent and the filled circles represent values of  $C^\circ/(1 + 4A\sqrt{C^\circ})$ . From the information in Figs. 1 to 4 and the average  $k^\circ$  values in Table II, it is possible to obtain the original time-concentration data.

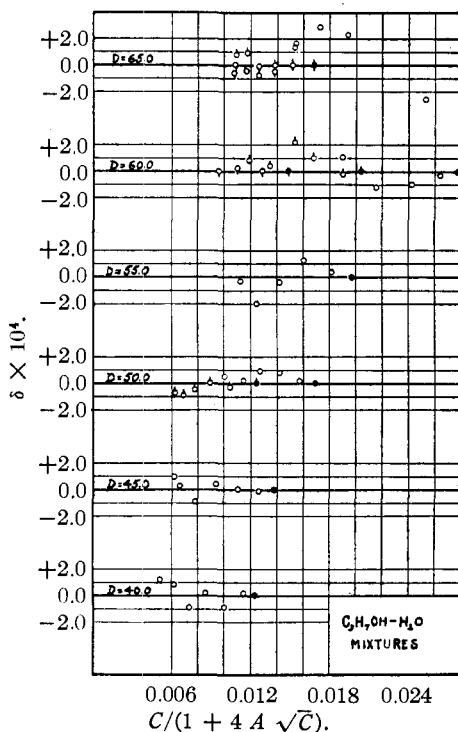


Fig. 3.—Propanol-water mixtures.

We have also obtained values of  $k^\circ$  by a method similar to that used by Warner and Stitt.<sup>4</sup> For each experiment, the reciprocal of the ammonium cyanate concentration was plotted against the time (min.). Values of  $t$  and  $1/C$  were taken from the curve at definite ionic strengths 0.005 apart and these values used for calculating the ordinary bimolecular rate constant. This constant was taken as the rate constant for the mean ionic strength of the range. Limiting rate constants at zero ionic strength were then calculated from these bimolecular constants by the Brønsted-Christiansen relation

$$\log k^\circ = \log k - \frac{6.24 \times 10^2 Z_{\text{NH}_4^+} Z_{\text{OCN}^-} \sqrt{\mu}}{D^{3/2} + 5.6 D \sqrt{\mu}} \quad (6)$$

Equation (6) assumes that  $f_{X^\circ} = 1$ ,  $b = r_{\text{NH}_4^+} + r_{\text{OCN}^-} = 2.0 \times 10^{-8}$  cm.<sup>10</sup> and that the activity coefficients of the ions at 50° may be expressed by

(10) Pauling, *Proc. Nat. Acad. Sci.*, **18**, 294 (1932); Hendricks and Pauling, *THIS JOURNAL*, **47**, 2904 (1925); Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, 1929, p. 150.

$$-\log f_i = \frac{3.12 \times 10^2 Z_i^2 \sqrt{\mu}}{D^{3/2} + 5.6 D \sqrt{\mu}}$$

Equation (6) yields somewhat higher values for  $k^\circ$  than Equation (5). The difference is small at the higher, but becomes appreciable at the lower dielectric constants. For the purpose of comparison, the ordinary bimolecular constants ( $k$ ) and the value of the limiting rate constant ( $k^\circ$ ), calculated by Equation (6) for pure water as solvent are given in Table I and values of  $k^\circ$  by Equation (6) for the solvent mixtures at  $D = 60$  and 45 are given in Table II (Rows 3 and 7). Since the calculation of  $k^\circ$  by either Equation (5) or Equation (6) assumes the Brønsted-Christiansen salt effect for reactions between monovalent ions of opposite charge, the constancy of  $k^\circ$  shows agreement with the theory of the primary salt effect.

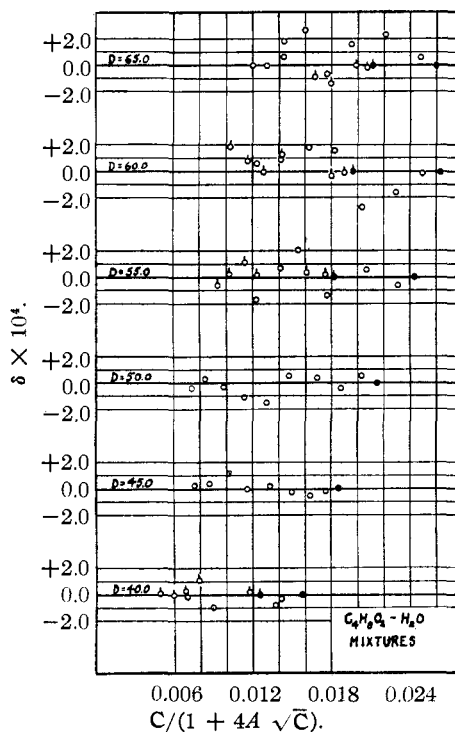


Fig. 4.—Dioxane-water mixtures.

**Kinetic Medium Effect.**—Scatchard,<sup>5</sup> from a consideration of the influence of the dielectric constant of the medium upon the concentration of Christiansen's complex, derives the following relation for reactions between ions:

$$\log k^\circ - \log k_*^\circ = \frac{e^2 Z_A Z_B}{2.3 K T r} \left[ \frac{1}{D^\circ} - \frac{1}{D} \right] \quad (7)$$

$k_*^\circ$  is the rate constant at zero ionic strength in the standard solvent of dielectric constant  $D^\circ$ ,  $k^\circ$  is the corresponding rate constant at zero ionic

strength in a solvent of dielectric constant  $D$ . If, for our purpose, water is taken as the standard solvent,  $D^\circ = 69.85$ , and we assume  $r = b \cong 2.0 \times 10^{-8}$  cm., then, since  $Z_A Z_B = -1$ , Equation (7) at  $50^\circ$  becomes

$$\log k^\circ - \log k_*^\circ = -113 \left[ \frac{1}{69.85} - \frac{1}{D} \right] \quad (8)$$

This predicts, for reactions between monovalent ions of opposite charge, an increase in velocity with decrease in dielectric constant of the solvent. An examination of the rate constants listed in Tables I and II shows that our results are in quali-

TABLE I  
RATE OF CONVERSION OF AMMONIUM CYANATE INTO UREA  
IN WATER ( $D$  69.85) AT  $50^\circ$

| $t$ ,<br>min. | $C$<br>moles/liter | $k^\circ$<br>Eq. (5) | Range of<br>concn.                | $\sqrt{}$ | Bimolecu-<br>lar $k$ | $k^\circ$<br>Eq. (6) |
|---------------|--------------------|----------------------|-----------------------------------|-----------|----------------------|----------------------|
| 0             | 0.0547             |                      |                                   |           |                      |                      |
| 16            | .0528              | 0.066                | 0.050-0.045                       | 0.218     | 0.042                | 0.072                |
| 90            | .0456              | .063                 | .045-.040                         | .206      | .045                 | .075                 |
| 165           | .0396              | .065                 | .040-.035                         | .194      | .046                 | .075                 |
| 330           | .0304              | .066                 | .035-.030                         | .180      | .047                 | .074                 |
| 422           | .0267              | .067                 | .030-.025                         | .166      | .050                 | .075                 |
| 480           | .0251              | .066                 |                                   |           |                      |                      |
| 586           | .0221              | .067                 |                                   |           |                      |                      |
| 0             | .0369              |                      |                                   |           |                      |                      |
| 42            | .0347              | .062                 | .035-.030                         | .180      | .046                 | .074                 |
| 100           | .0318              | .064                 | .030-.025                         | .166      | .049                 | .072                 |
| 250           | .0260              | .065                 | .025-.020                         | .150      | .052                 | .076                 |
| 370           | .0225              | .066                 | Average $k^\circ$ (Eq. 5) = 0.065 |           |                      |                      |
| 460           | .0205              | .066                 | Average $k^\circ$ (Eq. 6) = 0.074 |           |                      |                      |

TABLE II  
LIMITING VELOCITY CONSTANTS IN SOLVENT MIXTURES

| $D$  | CH <sub>3</sub> OH-H <sub>2</sub> O |               | C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O |               | C <sub>2</sub> H <sub>5</sub> OH-H <sub>2</sub> O |               | C <sub>4</sub> H <sub>9</sub> O <sub>2</sub> -H <sub>2</sub> O |               |
|------|-------------------------------------|---------------|---|---------------|---|---------------|--|---------------|
|      | Wt. %<br>CH <sub>3</sub> OH         | Av. $k^\circ$ | Wt. %<br>C <sub>2</sub> H <sub>5</sub> OH         | Av. $k^\circ$ | Wt. %<br>C <sub>2</sub> H <sub>5</sub> OH         | Av. $k^\circ$ | Wt. %<br>C <sub>4</sub> H <sub>9</sub> O <sub>2</sub>          | Av. $k^\circ$ |
| 65.0 | 11.1                                | 0.103         | 9.1   | 0.089         | 7.2   | 0.088         | 6.4  | 0.084         |
| 60.0 | 22.3                                | .136          | 15.4  | .125          | 14.8  | .114          | 12.7   | .115          |
| 60.0 | (Eq. 6)                             | .142          |   | .128          |   | .120          |  | .118          |
| 55.0 | 33.4                                | .192          | 27.8  | .169          | 22.6  | .145          | 19.0   | .153          |
| 50.0 | 45.0                                | .299          | 37.0  | .246          | 30.2  | .210          | 24.4   | .197          |
| 45.0 | 56.1                                | .489          | 46.2  | .361          | 37.8  | .273          | 30.1   | .282          |
| 45.0 | (Eq. 6)                             | .524          |   | .396          |   | .310          |  | .311          |
| 40.0 |                                     |               | 55.5  | .591          | 45.4  | .397          | 35.9   | .389          |

tative agreement with the theory. However, the rate constants at equal dielectric constants are

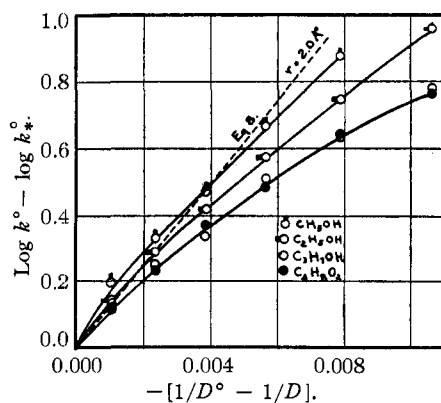


Fig. 5.

not independent of the added non-aqueous solvent. They are highest in methyl alcohol-water and lowest in isopropyl-water and dioxane-water mixtures. This dependence of  $k$  upon the non-aqueous solvent might be expected. In the simple theory, a uniform dielectric constant equal to that for the solvent mixture in the absence of salts is assumed. Actually, the non-aqueous solvent will be salted away from the ions and the resulting effective dielectric constant about the reacting ions will be somewhat higher than that assigned according to the composition of the solvent mixture. Furthermore, the order is that which one would predict from a consideration of the salting out order of the alcohols. The almost identical results obtained in isopropyl alcohol-water and dioxane-water mixtures may be attributed to the fact that although the dielectric constant of dioxane is very low due to the symmetry of the molecule, there exist in the molecule four dipoles (the C-O bonds) of considerable magnitude. Consequently, isopropyl alcohol and dioxane may be salted out to practically the same extent. Other factors might contribute to the differences observed in the various non-aqueous solvents, but it seems reasonable to assume that the salting out effect is the most important. The effective dielectric constant about the reacting ions is probably fairly independent of the ionic strength and the influence of the salting out of the non-aqueous solvent remains in the calculated limiting velocity constants ( $k^\circ$ ).

In Fig. 5, we have plotted  $\log k^\circ - \log k_*^\circ$  against the differences in the reciprocals of  $D^\circ$  and  $D$ . The curves depart somewhat from the linear relation predicted by the theory, the slope decreasing as the amount of alcohol or dioxane in the solvent mixture is increased. This may be attributed to the salting out of the non-aqueous solvent, the difference between the effective dielectric constant about the reacting ions and the dielectric constant according to solvent composition becoming greater as the amount of non-aqueous solvent is increased. The decrease in slope might also be attributed to an increase in ion association as the dielectric constant is decreased. As an additional test of the theory the slopes of the curves may be compared with the theoretical slope for  $r = 2.0$  Å. shown by the broken line in Fig. 5. One might attempt to relate the slope characteristic of an added non-aqueous solvent to a characteristic value of  $r$ .

However, there seems to be little possibility of making a quantitative explanation. Considering the possible influence of variables which have not been controlled, one may conclude that the observed influence of dielectric constant of solvent upon the rate of conversion of ammonium cyanate into urea is in better agreement with the theory than one could reasonably expect. Scatchard, for reasons similar to those mentioned in the above discussion, called attention to the approximate character of Equation (7).

### Summary

1. The rate of conversion of ammonium cyanate into urea has been studied at 50° in water ( $D$  69.85) and in mixtures of water with methyl, ethyl and isopropyl alcohols and with 1,4-diox-

ane at dielectric constants for the mixtures of 65, 60, 55, 50, 45 and 40.

2. The primary salt effect in each solvent mixture is in good agreement with that predicted by the Brønsted-Christiansen theory for a reaction between monovalent ions of opposite charge.

3. The differences between rate constants, at equal dielectric constants, in the various solvent mixtures are explained from a consideration of the salting out of the non-aqueous solvents.

4. The influence of dielectric constant of the solvent upon the rate constants is in better agreement with the Scatchard-Christiansen theory than one could reasonably expect.

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[FROM THE DEPARTMENT OF ANIMAL AND PLANT PATHOLOGY OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH, PRINCETON, N. J.]

## Some Relationships between Molecular Structure, pH and the Ability of Bacteria to Grow in Solutions of Salts of Organic Acids

BY WILLIAM F. BRUCE

Some species of bacteria can grow in a solution which contains as the only source of carbon and energy the salt of a pure organic acid dissolved in a solution of inorganic salts similar to Ringer's solution.<sup>1</sup> If an organism can grow in a solution containing a particular acid as the sole source of carbon, it must possess a mechanism for decomposing this acid. Therefore the acids which support growth are possible intermediates in the decomposition of other organic materials, such as carbohydrates, by the organism in question. In addition, the decomposition of the growth-supporting acids themselves can be followed by chemical study, and solutions of these acids may be used to advantage for the culture of bacteria.

Failure of an organism to grow in a solution containing a single organic acid allows several alternative conclusions. The organism may not be able to decompose the acid; the acid or its decomposition products may be toxic to the bacteria in the concentration used; the organism may not be able to use the decomposition prod-

ucts for growing; or the organism may require the presence of other substances for growing. Thus definite toxic action of  $\alpha$ -hydroxyisobutyric acid has been encountered in this study. Benzoic salicylic acids are, in general, toxic to organisms and Quastel<sup>2</sup> has shown by using the methylene blue technique that such molecules as formic and propionic acids can be attacked by *B. coli*, but nevertheless do not support growth by the organism. Some bacteria require hemin,<sup>3</sup> and addition of yeast extract to synthetic media may enable organisms to grow in solutions which do not support growth in the absence of yeast extract. Grey<sup>4</sup> has reported that the presence of formates may enable an organism to grow at the expense of substances which do not support growth in the absence of formate. Therefore, although failure to grow is evidence that the substance is not an intermediate in decompositions by the organism, it is not proof.

Previous studies<sup>1a,e,5,6</sup> of the growth of bacteria

(1) (a) H. Braun and C. E. Cahn-Bronner, *Centr. Bakl.*, **1**, *Abl., Orig.*, **86**, 196 (1921); (b) W. F. Bruce, *J. Biol. Chem.*, **107**, 119 (1934); (c) J. Butterworth and T. K. Walker, *Biochem. J.*, **23**, 926 (1929); (d) T. K. Walker, V. Subramaniam, H. B. Stent and J. Butterworth, *ibid.*, **25**, 129 (1931); (e) S. A. Koser, *J. Bact.*, **8**, 493 (1923).

(2) J. H. Quastel, *Biochem. J.*, **19**, 641 (1925).

(3) E. O. Jordan and I. S. Falk, "Newer Knowledge of Bacteriology and Immunology," Univ. of Chicago Press, Chicago, Ill., 1928, p. 656.

(4) E. C. Grey, *Proc. Roy. Soc. (London)*, **96B**, 156 (1924).

(5) H. C. Brown, J. T. Duncan and T. A. Henry, *J. Hyg.*, **23**, 6 (1924).

(6) J. H. Quastel and M. D. Wetham, *Biochem. J.*, **19**, 645 (1925).