collapse of the ice-like structure is quite evident in Fig. 3: on all curves the Stokes–Einstein domain extends to higher fluidities the higher the temperature.

Differences in the "mole fraction ratio at the break-down point" in the presence of sucrose and of glycerol are ascribed to specific effects of the viscosity controlling molecules. Three categories of interactions can be visualized by which a polyalcohol type viscosity controller may contribute to the break-down of the ice-like structure and engender closer packing in the solvent matrix[9,14,15]: (a) an "internal pressure effect" on the loosely bound tetrahedral solvent aggregates by the sucrose or glycerol molecules (which cannot fit into normal lattice positions) "wedged" between them: (b) removal of water molecules from the tetrahedral structure due to the formation of primary ("inner shell") solvate bonds between water and viscosity controller; (c) long range interactions such as secondary ("outer shell") hydration which may compete with the relatively weak "intra ice-like structure bonds." Perturbation of the tetrahedral structure by these long-range effects can be envisioned as a distortion of the normal orientation of the water dipoles under the influence of the electrostatic fields in the vicinity of the polar viscosity controller molecules. The order of magnitude of the mole fraction ratio at the break-down point in the presence of sucrose clearly indicates that the breakdown of the ice-like structure cannot be due to an internal pressure effect in this instance. Inspection of reasonable tridimensional models of sucrose and water makes it evident that a sucrose molecule cannot possibly exert a wedge effect on more than an average of 5–10 water molecules. This compares with a mole fraction ratio of 120 water molecules per sucrose at the experimentally determined breakdown point. Primary hydration can only account for about four water molecules per sucrose.[16] Consequently, long-range effects of the viscosity controlling molecules, such as outer shell hydration, apppear to be the paramount factor in the breakdown of the ice-like solvent structure upon addition of sucrose. This is the only plausible explanation for the collapse of the ice-like water matrix in the presence of only one sucrose molecule per 120 water molecules. Glycerol, with a mole fraction ratio at the breakdown point of the order of 10, presents an entirely different picture. Wedge and primary hydration effects *can* readily account for the breakdown of the ice-like structure in the presence of glycerol.

We cannot offer as yet a satisfactory rationalization for explaining the variance in the mechanisms by which glycerol and sucrose cause the breakdown of the ice-like structure of water. However, the following analogy may be pertinent. Sound velocity measurements indicate that the prevalence of the ice-like structure is affected appreciably and specifically by monohydric alcohols.[17] For instance, in an aqueous solution containing 0.4 mole fraction methanol, the mole fraction of associated water molecules was 0.2 as compared to 0.8 in pure water; *ceteris paribus*, a mole fraction of ethanol as high as 0.6 was required to reduce water association to the same level. Because of the similarity between methanol and ethanol, this difference cannot reasonably be accounted for by internal pressure effects nor by primary solvation. Long range effects of outer shell hydration or an unknown type of interaction evidently must be involved. Since convincing experimental evidence shows that such a situation can prevail in the case of two simple homolog alcohols, it is perhaps not surprising that appreciable differences were found in this study between the behavior of a disaccharide (sucrose) and a triol (glycerol).

Acknowledgment.—This investigation was supported by research grants H-2342, H-2342(C) and H-2342(C2) from the National Institutes of Health, Public Health Service.

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(14) W. E. Bauer, Thesis, Pennsylvania State University, 1959.

(15) D. G. Miller, This Journal, **80**, 3576 (1958).

(16) H. Shiio, *ibid.*, **80**, 70 (1958).

(17) O. Nomoto, *J. Phys. Soc. Japan*, **11**, 1146 (1956).

University Park, Pennsylvania

[Contribution No. 486 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company]

Polarographic Behavior of Some 1,4-Substituted-2,3,5-pyrrolidinetriones

By E. A. Abrahamson

Received December 24, 1958

A polarographic study has been made of the behavior of 1,4-substituted-2,3,5-pyrrolidinetriones at the dropping mercury electrode. A parallelism has been found between their behavior and the behavior of such compounds as pyruvic acid and phenylglyoxylic acid which can exist in both anion and undissociated forms, both of which are reducible. Application of theory derived by Delahay has given rates of recombination of the order of 10^9 to 10^{11} l. mole^{-1} sec.$^{-1}$.

Synthesis of pyrrolidinetriones having a strong electron-attracting group in the 4-position[1] prompted a polarographic study of these compounds because of the paucity of information on the polarographic reduction of tricarbonyl compounds. Although a number of experimenters have investigated dicarbonyl compounds of aliphatic, aromatic and heterocyclic types,[2] the only published work on tricarbonyl compounds has been that on the reduction of croconic acid[3] and diphenyl-

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(1) E. G. Howard, A. Kotch, R. V. Lindsey, Jr., and R. E. Putnam, This Journal, **80**, 3924 (1958).

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, pp. 676, 691, 811.

(3) F. Arcamone, C. Prevost and P. Souchay, *Bull. soc. chim. France*, 891 (1953).

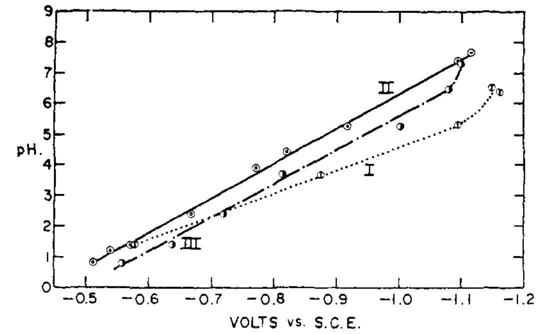


Fig. 1.—Plot of *p*H *vs.* $E_{1/2}$ for I, II and III: ......, I; ———, II; -·-·-, III.

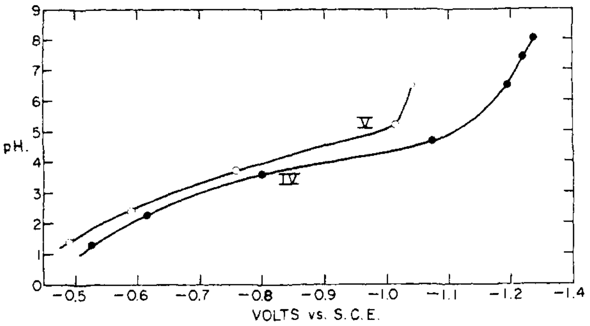
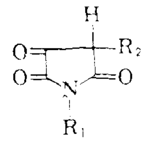


Fig. 2.—Plot of *p*H *vs.* $E_{1/2}$ for IV and V.

triketone[4]; therefore, it was of interest to explore the polarographic behavior of five 1,4-substituted-2,3,5-pyrrolidinetriones.

Experimental

Materials.—These five 1,4-substituted-2,3,5-pyrrolidinetriones, hereinafter referred to as I, II, III, IV and V, respectively, were prepared according to reference 1[5]: 1-methyl-4-(N-methylcarbamoyl)-2,3,5-pyrrolidinetrione (I); 1-phenyl-4-(N-phenylcarbamoyl)-2,3,5-pyrrolidinetrione (II); 1-(3-trifluoromethylphenyl)-4-[N-(3-trifluoromethylphenyl)-carbamoyl]-2,3,5-pyrrolidinetrione (III); 1-cyclohexyl-4-(N-cyclohexylcarbamoyl)-2,3,5-pyrrolidinetrione (IV); 1-phenyl 4-acetyl-2,3,5-pyrrolidinetrione (V). These compounds have the generalized structure

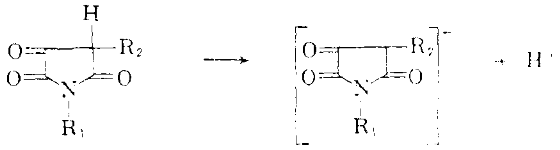


All compounds were available as the free acids, although in the case of I, the sodium salt also was used. The potassium chloride, sodium hydroxide, potassium biphthalate, monopotassium phosphate and boric acid used to make Clark and Lubs buffers were all of analytical grade quality. The nitrogen used to degas the solutions contained less than 5 p.p.m. oxygen and was not purified further. Stock solutions of the pyrrolidinetriones were made in ethanol. Aliquots were diluted with aqueous buffer and sufficient ethanol to make solutions which were 1:1 ethanol to water by volume.

Apparatus.—A Leeds and Northrup Type E Electrochemograph was used to obtain the polarographic curves. An H-type polarographic cell was employed with an agar plug and a saturated calomel electrode in one leg of the cell. The cell was not thermostated except for the temperature-controlled kinetic studies, since the room temperature remained constant within a few degrees for all measurements. All curves were run at damping position No. 1. Three capillaries were employed during the course of the measurements. Capillaries 1, 2 and 3 had the following values of *m*, respectively, 1.066, 1.605 and 2.484 mg./sec. The *m* value was measured with an open circuit in air, the mercury column having a height of 59, 57.5 and 60 cm., respectively. The drop time measured at −0.5 volt in a medium of *p*H 1.4 was 6 seconds, 3.3 seconds and 3.1 seconds for capillaries 1, 2 and 3, respectively. A Beckman Model G *p*H meter was used to measure the *p*H of the solutions prepared for polarographic analysis. The values of *p*H are apparent values since no effort was made to correct for non-aqueous effects. All half-wave potentials were measured relative to the saturated calomel electrode.

Results and Discussion

The effect of *p*H on the reduction of the five pyrrolidinetriones was studied over the *p*H range 1 to 12. The behavior of these compounds parallels that which has been observed for pyruvic acid,[6] phenylglyoxylic acid,[7] nitrosophenylhydroxylamine[8] and others. In the *p*H range 1 to 5, a single wave (A) appears and at high *p*H values, 8 to 12, a single wave (B) appears. At intermediate values of *p*H 5 to 8, two waves appear, the height of the first (A) diminishing and the height of the second (B) increasing with increasing *p*H. The total wave height (A + B) is equal to the height of A at low *p*H and the height of B at high *p*H, *i.e.*, the total current flowing remains constant. The first wave is attributed to the undissociated form and the second to the anionic form of the pyrrolidinetrione



Figures 1 and 2 show the variation of the half-wave potential with *p*H for the first wave of the five pyrrolidinetriones. These *p*H studies were carried out at low concentrations (range of 5×10^{-4} to 10^{-3} *M*) because of limited solubility of some of the pyrrolidinetriones, particularly IV, and to avoid maxima which are generally more prevalent at higher concentrations. Maxima, if present, could be suppressed with 0.005% gelatin at these concentrations. Over the *p*H range of 1 to 5 the variation of half-wave potential is essentially linear for compounds I, II and III. Calculation of the slope from Fig. 1 gives a variation of 0.130, 0.085 and 0.095 mv./*p*H unit for each of these triones, respectively. The half-wave potentials of IV and V do not shift in a completely linear manner with *p*H except over a very narrow *p*H range.

The half-wave potential of the second wave which appears at *p*H values greater than 6 appears to be independent of *p*H over the *p*H range 6 to about 10. Values of this half-wave potential for each of the triones are given in Table I. At very alkaline *p*H values, *i.e.*, above 10, the half-wave potential shifts to more negative values. This is probably

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(1) I. Tachi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **42**, 27 (1938).

(5) We are indebted to Dr. Alex Kotch for generous samples of the pyrrolidinetriones.

(6) O. H. Muller and J. P. Baumberger, THIS JOURNAL, **61**, 590 (1939); R. Brdicka, *Chem. Listy*, **40**, 232 (1946).

(7) V. Hanus, "Sbornik Mezinárod. Polarog. Sjezdu Praze, 1st Congr., 1951, Pt. I, Proc.," pp. 811–817.

(8) I. M. Kolthoff and A. Liberti, THIS JOURNAL, **70**, 1885 (1948).

TABLE I

$E_{1/2}$ FOR THE REDUCTION OF THE ANION FORM

Compound	$E_{1/2}$ vs. S.C.E., v.
I	−1.34
II	−1.25
III	−1.28
IV	−1.42
V	−1.27

due to interaction with the borate buffer used at these values of *p*H.

The position of the half-wave potential does not appear to bear any simple relationship to the substituents in the 1- and 4-positions. The variation of half-wave potential for the anion is more in accord with what one might expect for resonance stabilization of the reduction intermediate, *i.e.*, pyrrolidinetriones with phenyl substituents are more easily reduced than those with saturated substituents.

In all cases except that of III, the limiting current remained constant as alkaline *p*H values were reached. In the case of III the limiting current dropped to one-fifth of its value, indicating rather rapid hydrolysis or complex formation with the borate buffer used in this case. Compounds possessing trifluoromethyl groups are susceptible to alkaline hydrolysis.[9] At a *p*H of about 11, the wave heights of II and V were found also to diminish with time, indicating hydrolysis or reaction, but not nearly as rapidly as in the case of III.

To determine whether the reduction of these compounds obeyed the Ilkovic equation, a concentration study was run on compound II at a *p*H of 1.3. A *p*H of 1.3 was chosen since only in very acid solutions would the reduction of the undissociated acid be expected to be diffusion controlled. At more intermediate values of *p*H the current will be controlled by a combination of diffusion and rate of recombination. Over a twenty-fold range of concentration from 0.193 to 3.86 m*M* the diffusion current was found to be a linear function of concentration, an i_d/c value of 1.65 ± 0.03 being obtained. The half-wave potential appeared to be dependent on concentration, shifting to more negative potentials by about 30 millivolts for a tenfold increase in concentration.

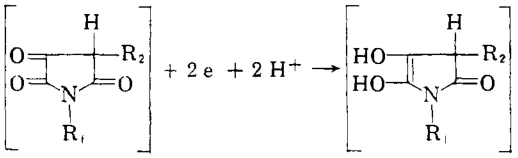
Diffusion coefficients were calculated for the undissociated form of the five triones using the Ilkovic equation and diffusion current data obtained in solutions whose *p*H was about one. The number of electrons involved in the reduction was assumed to be two since values of diffusion coefficient calculated on this basis agreed best with the known value of benzoate ion of 8.8×10^{-6} cm.²/sec. Furthermore, these values compare favorably with values of *D* reported for isatin[10] and camphorquinone[11,12] whose structures are more like the triones than benzoic acid. The values of *D* obtained for the five triones are presented in Table II.

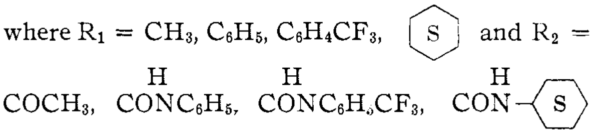
TABLE II

CALCULATED VALUES OF *D* FROM ILKOVIC EQUATION ASSUMING $n = 2$

Compound	$D \times 10^6$, cm.² sec.⁻¹
I	2.9
II	1.7
III	2.1
IV	2.0
V	2.9

Accepting $n = 2$, it is postulated that the reduction mechanism in acid medium for the undissociated acid is





where $R_1 = CH_3, C_6H_5, C_6H_4CF_3$, and $R_2 = COCH_3, CO\overset{H}{N}C_6H_5, CO\overset{H}{N}C_6H_4CF_3, CO\overset{H}{N}-$

A similar mechanism could be written for reduction of the anion in alkaline medium. This mechanism is similar to that proposed by Schwabe and Berg[13] and by Leonard, *et al.*,[11,12] for 1,2-diketones.

Since the two waves in the intermediate range are attributed to the reduction of undissociated acid and anion, respectively, the limiting current of the first wave should be controlled both by diffusion and the rate of recombination of anion with protons. If one selects a *p*H at which the concentration of undissociated acid in the bulk of solution is negligibly small, the limiting current should be controlled only by the recombination and the limiting current should then be independent of the mercury column.[14] Such a study was carried out on compound III at a *p*H of 7.3 for two different column heights and two temperatures. The results are shown in Table III. These results indicate that under the conditions of the experiment the limiting current of the first wave is essentially controlled by the rate of recombination and the second wave is essentially diffusion con-

TABLE III

STUDIES OF LIMITING CURRENT *vs.* MERCURY RESERVOIR HEIGHT FOR III AT *p*H 7.3

Concentration 6.83×10^{-4} *M*

H Cor., cm.	Wave	*id*, μamp.	*T*, °C.	$id/\sqrt{H}$
55	A	0.22	24	
30	A	.21	24	
55	A	.46	40	
30	A	.43	40	
55	B	1.23	24	0.17
30	B	0.84	24	.15
55	B	1.78	40	.24
30	B	1.16	40	.21

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[9] N. W. Buxton, *et al.*, *J. Chem. Soc.*, 366 (1954).

[10] W. C. Sumpter, J. L. Williams, P. H. Wilken and B. L. Willoughby, *J. Org. Chem.*, **14**, 713 (1949).

[11] N. J. Leonard, H. A. Laitinen and E. H. Mottus, THIS JOURNAL, **75**, 3300 (1953).

[12] N. J. Leonard, H. A. Laitinen and E. H. Mottus, *ibid.*, **76**, 4737 (1954).

[13] K. Schwabe and H. Berg, *Z. Elektrochem.*, **56**, 952 (1952).

[14] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, pp. 269–294.

trolled. The temperature coefficient for the first wave, about 6% per degree, also indicated its kinetic character, whereas the limiting current of the second wave had a normal temperature coefficient 2% per degree, indicating diffusion controlled reductions.

The theory of polarographic kinetic currents as derived by Brdicka, Weisner, Koutecky and Delahay is discussed by Delahay[15] and by Kolthoff and Lingane.[14] Delahay[16] and Weisner[17] have derived expressions for the limiting current when it is essentially controlled by the rate of recombination. The two expressions are essentially the same except that Weisner's expression considers recombination of the anion with protons from three sources, namely, H_3O^+, H_2O and from the buffer. When recombination with H_3O^+ is the only mechanism considered, the equations are essentially the same. The expression derived by Delahay is

$$i_{av} = 0.6 \times 1.255 \times 10^6\, nm^{2/3}\tau^{2/3}C_{H^+}{}^0 C_{A^-}{}^0 D_{HA}{}^{1/2}(k_r{}^{1/2}/K^{1/2}) \qquad (1)$$

in which i is the current in microamperes, n is the number of electrons involved in the reduction, m is the flowing mass of mercury in mg. sec.$^{-1}$, τ is the drop time in sec., $C_{H^+}{}^0$ and $C_{A^-}{}^0$ are the concentration of hydrogen ions and anion in moles per liter, D is the diffusion coefficient of the acid in cm.^{2} sec.$^{-1}$, K is the ionization constant of the acid in moles per liter and k_r is the rate of recombination in (moles per liter)$^{-1}$ sec.$^{-1}$. This equation is applicable when the current is essentially controlled by the rate of recombination. Under these conditions the equilibrium concentration of undissociated acid is so small that its diffusion current is negligible compared to the kinetic current. The concentration terms in the equation then represent the concentration both in the bulk of the solution as well as the concentration at the surface of the electrode.

Delahay[15] also gives an expression relating k_r to the hydrogen ion concentration when the limiting current for the undissociated acid is equal to half the diffusion current for the reduction of the anion. This expression is

$$(k_r/K)^{1/2}C_{H^+}{}^0\, \tau^{1/2} = 0.76 \qquad (2)$$

The terms have the same significance as before.

Values for the rate constant have been calculated by both of these equations and the data are presented in Tables IV and V. In general the rate constants calculated by equation 2 are higher than those calculated by equation 1, the best agreement being obtained for compounds III and IV. It is thought that the values by equation 2 are more nearly correct since there is some doubt that the experimentally determined values of i for equation 1 are currents due solely to recombination. Weisner[17] suggests that for precise measurement of the limiting current of the first wave in the region where kinetic control exists, the ratio of the current of the first to the second wave be of the order of 1:200. Solubility limitations prevented attainment of such a ratio for the compounds studied. Consequently it became impossible to measure accurately the limiting current of the first wave when the ratio of the heights of the two waves exceeded 1:6 in this study. The most favorable ratio of wave heights was obtained for compounds III and IV which undoubtedly accounts for the fact that the k values calculated for these two compounds by both equations are in the best agreement.

TABLE IV

CALCULATED VALUES OF k_r BY EQUATION 1

Compound	$i$avg., μamp.	pH at which i measd.	C_A, mmoles/l.	$K \times 10^8$, moles/l.	k_r, (moles/l.)$^{-1}$ sec.$^{-1}$
I[a]	0.88	6.5	0.83	1.0	1.46×10^8
II[a]	.26	7.7	.495	1.15	1.7×10^{10}
III[a]	.26	7.3	.683	1.3	1.3×10^9
IV[b]	.20	8.0	.473	4.8	2.1×10^{10}
V[b]	.88	6.5	1.35	1.15	8.1×10^7

[a] Value of $m^{2/3}\tau^{2/3} = 3.446$. [b] Value of $m^{2/3}\tau^{2/3} = 2.996$.

TABLE V

CALCULATED VALUES OF k_r BY EQUATION 2

Compound	pH When $i_{HA} = 0.5\, i_A$	k_r (moles/l.)$^{-1}$ sec.$^{-1}$
I	6.7	2.4×10^9
II	7.6	1.7×10^{11}
III	6.9	6.1×10^9
IV	7.4	5.3×10^{10}
V	6.4	1.3×10^9

WILMINGTON, DELAWARE

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[15] P. Delahay, "Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 87–100.

[16] P. Delahay, THIS JOURNAL, **74**, 3506 (1952).

[17] K. Weisner, *Anal. Chem.*, **27**, 1712 (1955).