Ionization Constants and Hydrolytic Degradations of Cyameluric and Hydromelonic Acids

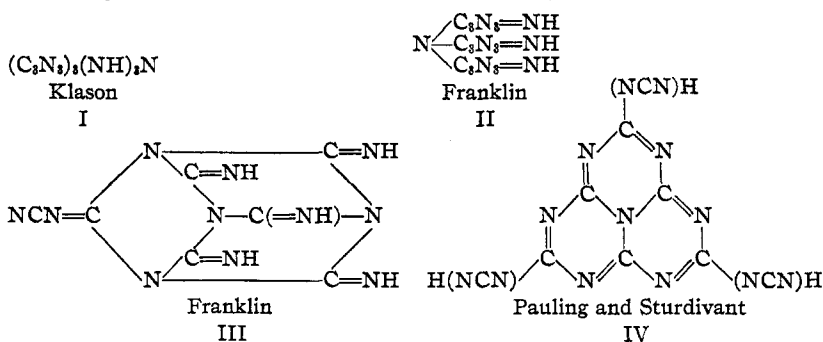BY C. E. REDEMANN AND H. J. LUCAS

Recently the question of the structure of cyameluric and hydromelonic acids has been reopened by Pauling and Sturdivant.[1] It is rather surprising that cyameluric acid and related compounds, for example melon, melam, melem, and hydromelonic acid, should have received so little attention at the hands of organic chemists. With the exception of a limited amount of work by E. C. Franklin[2] and students, the problems in this field have been neglected for many years. Since most of these compounds are insoluble both in organic solvents and in water, show neither melting nor boiling points, are inert chemically with the exception that they undergo hydrolytic cleavage, and do not yield derivatives which are readily identified, it is probable that the reasons for this neglect bear some relation to their physical and chemical properties.

Tripotassium melonate, the potassium salt of hydromelonic acid, first described by Gmelin[3] as an undesirable by-product when too high a temperature was used in the preparation of potassium thiocyanate by the fusion of sulfur, potassium ferrocyanide and potassium carbonate, was obtained also by Liebig, who dissolved melon in fused potassium thiocyanate.[4,5] Potassium melonate is formed also by heating antimony or bismuth trichloride with potassium thiocyanate. As the result of numerous careful analyses of potassium and silver melonate, Liebig[6] proposed the empirical formula $C_9H_3N_{13}$[7] for hydromelonic[8] acid. Attempts to prepare the pure acid have not been entirely successful due to the great tendency of the acid to polymerize in concentrated aqueous solution.

Cyameluric acid is probably the most important of the compounds discussed in this paper since its nucleus appears to be common to most members of the series. Potassium cyamelurate is formed by the alkaline hydrolysis of melon, or of potassium melonate.[5] When the potassium salt is acidified with a strong acid, sparingly soluble cyameluric acid separates. Henneberg named the acid and assigned to it the formula $H_3C_6O_3N_7$ on the basis of analyses of the salts and of the acid. It seems probable that Liebig[6] was the first to prepare this acid, but he was unable to obtain constant analyses for his product, probably because he recrystallized the acid from a hot hydrochloric acid solution, a procedure now known to cause rapid hydrolysis.

**Structures of Hydromelonic Acid.**—Only four structures have been proposed

Structure I was proposed by Klason[8] in 1886, and II by Franklin[2a] in 1922. The latter appears to be nothing more than an interpretation of the former. His second structure,[9] III, proposed in 1935, is essentially the structure of hexamethylenetetramine in which three of the six pairs of hydrogen atoms are replaced by the cyanimino group, (=NCN), and the other three by the imino group, (=NH). Structure IV, proposed by Pauling and Sturdivant[1] in 1937, is based upon their belief that hydromelonic acid, $C_6N_7(NCNH)_3$, bears to cyameluric acid, $C_6N_7(OH)_3$, the same relation that

(1) Pauling and Sturdivant, Proc. Natl. Acad. Sci., 23, 615 (1937).

(2) (a) Franklin, THIS JOURNAL, 44, 507 (1922); (b) Burdick, ibid., 47, 1485 (1925).

(3) Gmelin, Ann., 15, 252 (1835). This salt is also called potassium hydromelonate in the older literature.

(4) (a) Liebig, Ann., 50, 337 (1844); (b) 61, 262 (1847).

(5) Henneberg, ibid., 73, 228 (1855).

(6) Liebig, Ann., 95, 257 (1855).

(7) Actually $C_{18}H_6N_{26}$ on the basis of the atomic weights of that time.

(8) The name was assigned by Gmelin on the basis that the polymer was converted to melon by loss of water when heated, hence the acid was thought to be a hydrate of melon. Klason, J. prakt. Chem., [2] 33, 289 (1886), called this compound cyamelon, under which name some of the literature appears.

(9) E. C. Franklin, "The Nitrogen System of Compounds," The Reinhold Publishing Corp., New York, 1935, p. 107.

cyanuric tricyanamide, $C_3N_3(NCNH)_3$, bears to cyanuric acid, $C_3N_3(OH)_3$. The planar cyameluric nucleus is shown to have, according to quantum mechanical calculations, a high degree of stability. The stabilization due to resonance is approximately 150 kcal. per mole.

Structures of Cyameluric Acid.—Only three structures have been proposed for cyameluric acid

$(CN)_6O(NH)(OH)_2$
Klason, V

Franklin, VI

Pauling and Sturdivant, VII
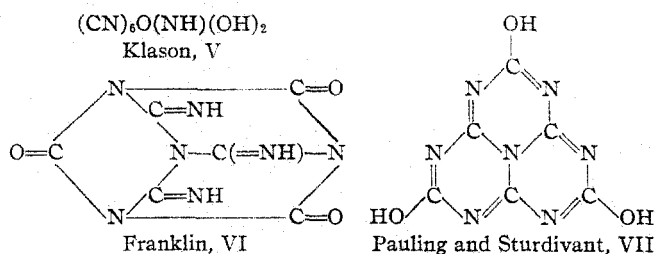
Structure V, proposed by Klason,[8] was thought by him to represent the anhydride of an acid having the formula $(HO)_2(CN)_3NH(CN)_3(OH)_2$ (VIII). In structure VI, proposed by Franklin, the central group of atoms has the hexamethylene arrangement as in the hydromelonic acid structure proposed by him, III, and in structure VII, proposed by Pauling and Sturdivant, this group has the planar cyameluric arrangement, as in their structure for hydromelonic acid, IV.

Hydrolytic Degradations

If hydromelonic acid is correctly represented by Structure I or II, then on hydrolysis to cyameluric acid of structure V (the anhydride of VIII), one mole of I or II should yield approximately one mole of cyanuric acid, one mole of cyameluric acid, three moles of ammonia and no carbon dioxide on the assumption that the C_3N_3 groups represent cyanuric acid nuclei and that the cyanuric and cyameluric acids undergo no further hydrolysis. Cyameluric acid of structure V on further hydrolysis should be capable of yielding two moles of cyanuric acid, since in the acid VIII, of which V is the anhydride, there are two C_3N_3 nuclei.

On the other hand, if hydromelonic acid is either III or IV, on hydrolysis to cyameluric acid of structure VI or VII, respectively, one mole should yield not more than one mole of cyameluric acid and at the same time, six equivalents each of ammonia and carbon dioxide. Further hydrolysis of cyameluric acid should yield not more than one mole of cyanuric acid and, at the same time, four equivalents of ammonia and

six equivalents of carbon dioxide if converted to cyanuric acid. Actually Liebig[6] isolated from the alkaline hydrolysis of cyameluric acid ammeline, ammelide, and cyanuric acid by progressively increasing the duration of hydrolysis.

Hydromelonic Acid.—When potassium melonate was hydrolyzed in 6 N nitric acid, 0.72 mole of cyanuric acid per mole of potassium melonate in the form of the insoluble cupric ammonium salt was obtained. Some hydrolysis of cyanuric acid took place at the same time. When hydrolyzed under alkaline conditions, the ratio of equivalents of carbon dioxide to those of ammonia varied from 1.25 to 1.11 (Table I). Even when hydrolysis was only a fraction of that possible, the $CO_2/2NH_3$ ratio was greater than unity. If hydromelonic acid had structure I or II, this ratio presumably would be below unity at the beginning of the hydrolysis, because carbon dioxide could come only from the breakdown of a C_3N_3 nucleus which is quite stable to further hydrolysis. Since

TABLE I
ALKALINE HYDROLYSIS OF POTASSIUM MELONATE

Sample, g.	KOH, N	Time, hrs.	NH₃ equiv.	CO₂ equiv.	Ratio CO₂/2NH₃	Extent of hydrolysis,[a] %
0.6531	5.45	1	0.00151	0.00188	1.25	15.7
1.6319	6.0	2	.01796	.02091	1.17	74.7
2.0526	3.5	2	.01464	.01628	1.11	59.3
2.5338	3.7	4	.0328	.0376	1.14	107

[a] Expressed as percentage of theoretical amount of ammonia, on the basis of structure III or IV, if the hydrolysis stopped at cyameluric acid.

potassium cyamelurate, under these conditions, was found to yield carbon dioxide and ammonia in the ratio of 2.24 (equivalents), the deviation from unity in the case of potassium melonate can be ascribed to the partial hydrolysis of the cyamelurate formed. The deviation from the ratio $^6/_4$ in the case of the latter compound probably is due to the formation of ammeline and ammelide, giving theoretical ratios of 3 and 2, respectively. Thus, the data from both acid and alkaline hydrolysis of hydromelonic acid favor structures III and IV over I and II. The hydrolysis is probably best represented by the equation

$$K_3C_9N_{13} + 6KOH + 6H_2O \longrightarrow$$
$$K_3C_6O_3N_7 + 6NH_3 + 3K_2CO_3$$
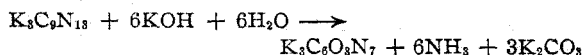
Henneberg[5] attempted to write an equation expressing this hydrolysis involving ammelide as one of the products and omitting carbonate.

Cyameluric Acid.—Hydrolysis at 100° in concentrated nitric acid, conditions under which cyanuric acid is attacked but slowly, yielded 0.935 mole of cyanuric acid per mole of cyameluric acid. These results show that cyameluric acid may be represented by either structure VI or structure VII, for only one mole of cyanuric acid would result, but not by structure V, for two moles of cyanuric acid should result if the acid has the last structure.

Ionization Constants of the Acids

On the basis of the Franklin structures III and VI, the two respective acids, hydromelonic and cyameluric, should resemble each other closely as regards their acid strengths, because the atomic groupings responsible for acidity are identical in the two cases, and the groups responsible for the difference in structure, i. e., C=NCN and C=O, respectively, are somewhat remote from the acid groups. Since the inductive effect of each of these two groups, before it can have an influence upon the acidic imino group, must pass through a tertiary nitrogen atom and a double bond, each of which alone has a pronounced damping effect upon induction, the acid strengths of III and VI would be expected to be similar. On the other hand, on the basis of the Pauling and Sturdivant structures, hydromelonic acid IV would be expected to be a much stronger acid than cyameluric acid VII. The hydromelonate ion, $C_9N_{13}^≡$, should have a much higher stability with respect to hydromelonic acid, $H_3C_9N_{13}$, than cyamelurate ion, $C_6O_3N_7^≡$, has with respect to cyameluric acid, $H_3C_6O_3N_7$. This is due to the fact that in the former case there are additional structures among which resonance can take place, for in the group of atoms IX, $(CNCN)^-$, the negative charge may be on either of the two nitrogen atoms as shown by X $\left(C—\overset{..}{\underset{..}{N}}—C≡N:\right)$ and XI $\left(C—\overset{..}{N}=C=\overset{..}{\underset{.}{N}}:\right)$. Since there are three such groups in the hydromelonate ion, the multiplicity of forms is markedly enhanced in comparison to the forms of the free acid, in which this additional type of resonance is not so important. Thus, from structural considerations, one would expect hydromelonic acid to be much stronger than cyameluric acid on the basis of the Pauling and Sturdivant structures, and to be little if any stronger on the basis of the Franklin structures.

Moreover, as Pauling and Sturdivant have pointed out, hydromelonic acid (IV) would bear the same relationship to cyameluric acid, VII, that tricyanomelamine bears to cyanuric acid. Tricyanomelamine is such a strong acid that the constant cannot be determined by conductimetric methods,[10] thus approaching the strong mineral acids in strength, whereas cyanuric acid is a weak acid.

The apparent ionization constants of hydromelonic, cyameluric and cyanuric acids were determined by titration of the potassium salts with standard hydrochloric acid, using a glass electrode to measure the pH. The solubility of the acids is too low to permit of their use for making titration curves and, in addition, hydromelonic acid polymerizes irreversibly. The cyanuric acid curve was made for the purpose of comparison. From the titration curves, apparent ionization constants were estimated for the acids by taking the pH at the "half-neutralization" points. These approximate values for the apparent ionization constants were then adjusted until the calculated titration curves fitted the observed curves very accurately. In this way a value of 1.66×10^{-7} was found for the first ionization constant of cyanuric acid, a value which is in fairly good agreement with that of 1.8×10^{-7} found by Hantzsch[11] but in poor agreement with that of 3.8×10^{-7}, found by Bader.[12]

The curves for the titrations are shown in Fig. 1 and the values for the ionization constants of hydromelonic and cyameluric acids are listed in Table II. Those for the second ionization constant of hydromelonic and the first ionization constant of cyameluric acid are approximations only, because of the separation of a solid phase in the titration shortly before the respective "half-neutralization" points were reached. On this account the assumed values of these two constants, which have been adjusted so as to fit the remainder of the respective curves, are subject to some error.

TABLE II
Ionization Constants

	Hydromelonic acid	Cyameluric acid	Cyanuric acid
K_1	Large	Ca. 1.0×10^{-3}	1.66×10^{-7}
K_2	Ca. 3.16×10^{-3}	6.30×10^{-7}	
K_3	1.26×10^{-5}	1.12×10^{-9}	

Hydromelonic acid is a much stronger acid than cyameluric, as the curves and table show. These results favor structures IV and VII of Pauling and

(10) Madelung and Kern, Ann., **427**, 26 (1922).
(11) Hantzsch, Ber., **39**, 139 (1906).
(12) Bader, Z. physik. Chem., **6**, 289 (1890).

Sturdivant for these acids. That the cyameluric nucleus is strongly electronegative is shown by the comparison of ionization constants in Table III.

TABLE III
COMPARISON OF IONIZATION CONSTANTS

	K_A			K_A
Hydromelonic acid	Large		Cyameluric acid	1×10^{-3}
Benzoylcyanamide[12]	1.86×10^{-2}		Benzoic acid	6×10^{-5}
Acetylcyanamide[12]	1.54×10^{-4}		Acetic acid	1.6×10^{-5}

In the first column, the common radical is the substituted cyanamino group, $H(NCN)$[13] and in the second, the OH group.

In a subsequent communication the results of attempts to prepare derivatives of cyameluric acid will be presented. The authors gratefully acknowledge the inspiration of Professor Linus Pauling, who suggested the investigation of cyameluric and hydromelonic acids.

Experimental

Melon.—The following procedure based upon that of Henneberg[5] was most satisfactory. Chlorine gas was passed into a vigorously stirred solution of 1 kg. (12.3 moles) of pure[14] sodium thiocyanate in 2.5 liters of water. The temperature was maintained below 70–80° by external cooling. When the mixture became so thick that stirring was no longer effective, it was cooled to room temperature, the sludge of "pseudothiocyanogen"[15] was filtered off and the filtrate was treated again with additional chlorine. This process was repeated until no further pseudothiocyanogen was formed. The combined precipitate of pseudothiocyanogen was well washed with boiling water to remove all soluble salts, then dried at 120°, giving 512 g. of product.

The 512 g. of pseudothiocyanogen, divided into two batches, was converted into melon by heating in 25-cm. porcelain evaporating dishes with a large brush flame from a Meker type burner until all volatile products were expelled. The light yellow residue of crude melon weighed 240 g.

Other methods of preparing melon were less satisfactory on a laboratory scale. The slow heating of ammonium thiocyanate is reported to give good yields[16] but requires special equipment and much time.

Potassium Melonate.—The following modification of Liebig's[4b] method was most satisfactory. Eighty grams

(13) Madelung and Kern[10] believe that the group present in tricyanomelamine is —NH—C≡N, and not —N=C=NH. However, resonance between these two structures would be expected, and Dr. E. W. Hughes has verified this for the group in the molecule of dicyandiamide (private communication).

(14) A crude grade of sodium thiocyanate prepared by dissolving sulfur in fused sodium cyanide gave only slightly smaller yields.

(15) The name "pseudothiocyanogen" is here applied to the crude mixture composed of isoperthiocyanic acid, kanarin, and various polymers of isoperthiocyanic acid obtained by this procedure instead of to the part insoluble in alkali.

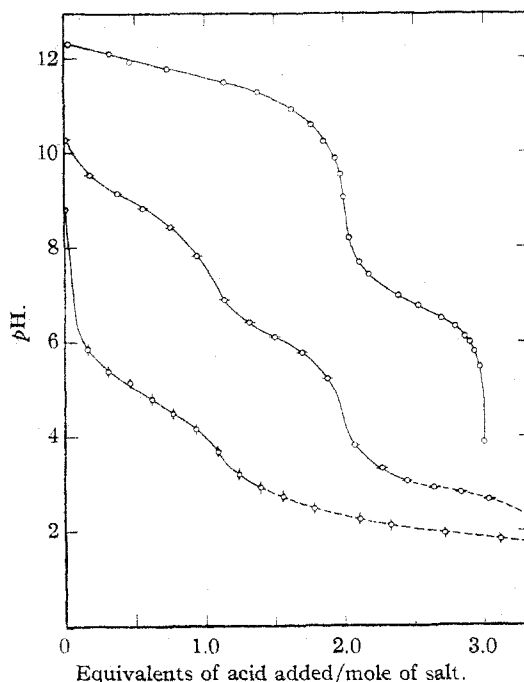(16) Gludd, Keller and Klempt, Z. angew. Chem., **39**, 1071 (1926).

Fig. 1.—O, Cyanuric acid; ·O·, cyameluric acid; φ, hydromelonic acid; – – –, solid separating out.

of pure potassium thiocyanate was slowly melted in a 10-cm. porcelain casserole and held at a moderate temperature until all moisture was expelled and a quiet melt was obtained. The temperature was then increased to a dull red heat and 40 g. of melon was added in portions of 5 to 10 g., each portion being allowed to dissolve before another was added. The carbon disulfide which is evolved was allowed to burn. When all the melon had dissolved the mixture was heated more strongly until only very little more carbon disulfide was produced. At this point a few drops of the melt were removed on the end of a Pyrex rod and its solubility[17] in hot water tested. Heating was continued until a 0.1 to 0.2 g. portion of the salt was completely soluble in 5 ml. of hot water. The entire operation required approximately one-half hour. After cooling, the salt was ground into coarse particles, dissolved in hot water, decolorized with carbon, filtered and allowed to cool. The fine felted needles, when air dried, weighed 38.8 g. Repeated crystallization gave a snow-white product.

Liebig's method using potassium thiocyanate and antimony trichloride gave a product which was hard to free from antimony salts.

Sodium Melonate.—Burdick[2b] prepared this salt by heating sodium thiocyanate with antimony trichloride. By dissolving 26 g. of melon in 50 g. of fused sodium thiocyanate, 11 g. of pure white fine needle crystals of sodium melonate was obtained. The sodium salt is very similar in appearance to and less soluble than the potassium salt.

Potassium Cyamelurate.—Two methods, both suggested by Henneberg,[5] were used.

(17) The test for solubility is very essential, for if heating has been for too short a time or at too low a temperature an insoluble product is formed.

A.—A solution of 20 g. (0.04 mole) of hydrated potassium melonate in 80 ml. of 4 N potassium hydroxide solution was boiled under reflux for two hours. A crop of slightly colored crystals of potassium cyamelurate was filtered off after cooling, and a second crop after concentrating the filtrate to one-third its initial volume. The two crops of crystals were washed with alcohol and air-dried; weight 11 g. or 70%. Crystallization from a hot moderately dilute solution with generous use of decolorizing carbon yielded pure white stout needles.

B.—A suspension of 30 g. of crude melon was boiled with 300 ml. of 3 N potassium hydroxide for forty-five minutes and the undissolved solid was filtered out. The crystals which separated from the filtrate were filtered off, washed with alcohol and air-dried. Boiling the original undissolved solid with the last filtrate and proceeding as above gave an additional amount. The total weight of potassium cyamelurate was 23 g.

Sodium Cyamelurate.—This salt, which was mentioned casually by Henneberg, is easily prepared in the same manner as the potassium salt by substituting 4 N sodium hydroxide for the potassium hydroxide in method (A) above. The yield is 50 to 60% of the theoretical assuming structure (IV) for hydromelonic acid and (VII) for cyameluric acid.

Anal. Calcd. for $Na_3O_3C_6N_7 \cdot 5^1/_2H_2O$: Na, 17.8; H_2O, 25.6. Found: Na, 17.7, 17.8; H_2O, 25.3, 25.4.

Cyameluric Acid.—Acidification of a moderately dilute aqueous solution of the sodium or potassium salt with 6 N hydrochloric acid added very slowly from a buret with effective stirring, followed by chilling in an ice-bath, gave a white crystalline powder. This was filtered off, washed well with cold water and air-dried.

Anal. Calcd. for $C_6H_3O_3N_7 \cdot 3H_2O$: C, 26.17; H, 3.27. Found: C, 25.88; H, 3.24.

Precipitation from a hot solution yields an impure product due to the rapid hydrolysis of cyameluric acid to ammelide and ammeline in acid solution. Crystallization from boiling water causes considerable decomposition due to the low pH of the solution of this comparatively strong acid.

The acid does not reduce alkaline permanganate either in the cold or upon prolonged boiling; it gives no enol reaction with ferric chloride. Most of its metallic salts are very sparingly soluble.

Acid Hydrolysis of Hydromelonic Acid.—A solution of 2.231 g. of potassium melonate in an excess of 6 N nitric acid was gently boiled for one and one-half hours. The solution was made alkaline with a slight excess of 15 N ammonium hydroxide, then sufficient cupric ammonium sulfate solution was added to color the solution a dark blue. The amethyst-red precipitate which gradually separated was filtered off, dried and weighed; weight 0.454 g. (72.5% of theoretical, assuming one mole of cyanuric acid per mole of hydromelonic acid).

The Alkaline Hydrolysis of Potassium Melonate.—A series of quantitative determinations of the amount of ammonia and carbon dioxide produced in the hydrolysis of potassium melonate to potassium cyamelurate was made as follows. The ammonia was carried over into standard hydrochloric acid by a current of purified air. The excess acid was then titrated with a standard sodium hydroxide solution using the mixed indicator, p-nitrophenol—methyl red. The amount of carbonate formed was determined by the method of Winkler as follows. The alkaline solution in the boiler was diluted to 250 ml., then an aliquot portion was taken. An excess of barium chloride solution was added to the aliquot, then the sodium hydroxide was carefully titrated with a standard hydrochloric acid solution using phenolphthalein as indicator. The data thus obtained are given in Table I.

As a check on the method, potassium melonate was replaced by urea. In this case the ratio of equiv. CO_2/equiv. NH_3 was 1.03. The difference between 1.03 and 1.00 represents about the accuracy to be expected from this method of analysis.

When potassium cyamelurate replaced potassium melonate, 2.24 was the ratio of equiv. CO_2/equiv. NH_3. This would indicate that the cause of a ratio greater than unity in the case of the hydrolysis of potassium melonate is a further hydrolysis of the potassium cyamelurate.

Acid Hydrolysis of Cyameluric Acid.—Two grams of cyameluric acid, purified through the copper ammonium salt, was digested with 10 ml. of concd. nitric acid on a steam-bath for four hours. The solution was diluted to 20 ml., cooled to 0°, saturated with the oxides of nitrogen obtained from the action of concd. nitric acid on metallic copper in order to destroy ammonium ions and make sure that all —NH_2 groups were converted into —OH groups, and evaporated to dryness on a water-bath. The residue was washed onto a weighed Gooch crucible, using 18 ml. of water, dried and weighed; weight 0.975 g. This represents 93.5% of that theoretically obtainable assuming one mole of cyanuric acid per mole of cyameluric acid. The residue gave the characteristic insoluble amethyst-colored copper ammonium salt of cyanuric acid.[18]

Electrometric Titrations of Hydromelonic and Cyameluric Acids.—Potassium melonate, 0.3707 g. (7.45 × 10^{-4} mole) crystallized four times from water, was dissolved in 50 ml. of water. Potassium cyamelurate, 0.2576 g. (6.62 × 10^{-4} mole) thrice crystallized from water, was dissolved in 50 ml. of water. In each solution was placed a glass electrode, a standard calomel electrode, and a mechanical stirrer. The former was titrated with 0.2899 N, the latter with 0.2493 N hydrochloric acid. The e. m. f. measurements were made with a student type potentiometer and a high sensitivity galvanometer in the former case, and with a Beckman pH meter in the latter case. Conversion to pH values in the former case was made by comparison with standard buffer solutions. The results are shown as the curves in Fig. 1.

Summary

Improved methods have been described for the preparation of melon, potassium and sodium melonate, potassium and sodium cyamelurate, and cyameluric acid. Titration of potassium melonate and cyamelurate, using the glass electrode, shows that hydromelonic acid is much stronger than cyameluric acid.

The titration data and results of hydrolysis

(18) S. P. Mulliken, "Identification of Pure Organic Compounds," Vol. II, John Wiley and Sons, Inc., New York, 1916, p. 84.

indicate that the molecules of these two acids contain the planar cyameluric nucleus of Pauling

and Sturdivant.

PASADENA, CALIFORNIA   RECEIVED AUGUST 10, 1939

The Addition of N-Haloamides to Olefins

BY M. S. KHARASCH AND HILL M. PRIESTLEY

An unsuccessful attempt to add N-haloamides to olefins is recorded by Seliwanoff.[1] Foldi,[2] however, showed that 1-phenylpropene and N-bromo-N-methylbenzenesulfonamide ($C_6H_5SO_2NBrCH_3$) react to give at least two addition isomers. The reaction was considered by Földi to be of limited applicability, since all the purely aliphatic olefins tried by him yielded the dibromo derivatives when treated with the N-bromo-N-methylbenzenesulfonamide.

We have succeeded in extending this interesting reaction to include aliphatic olefins such as propene, 2-methylpropene, and vinyl chloride, as well as styrene. We have also demonstrated that in the reaction

$$R''{-}N{-}SO_2R' + RCH{=}CH_2 \longrightarrow$$
(Br)
$$R{-}C{-}C{-}N{-}SO_2R'$$
(H H R'')
(Br H)
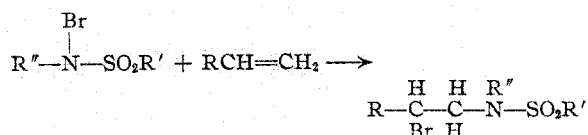
the radicals R, R' and R'' play only a minor part, since we have employed in these reactions with equal success the phenyl-, *p*-tolyl-, and benzyl-sulfonyl derivatives of methylamine, benzylamine, phenethylamine, and β-bromo-α-phenylethylamine.

The addition of the bromo derivatives of the sulfonamides to olefins appears to be a unique reaction. We have been unable to obtain addition products of olefins with the following N-bromo-compounds: N-bromobenzamide, N-bromo-N-methylbenzamide, N-bromo-N-methyl-N-carbobenzoxamine, N-bromo-triphenylmethylamine, N-bromosaccharine, N-bromophthalimide, and N-bromosuccinimide.

In addition to standardizing the conditions of addition of N-bromosulfonamides to olefins, we have succeeded in effecting the addition of N,N-dibromo derivatives of aromatic sulfonamides, e. g., N,N-dibromo-*p*-toluenesulfonamide, to styrene, anethole, and isosafrole.
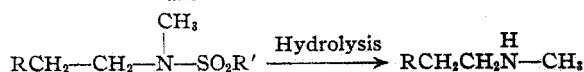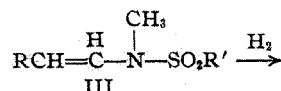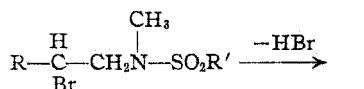
The positions taken by the nitrogen and bromine atoms of the N-bromo- and N,N-dibromo-sulfonamides is of considerable theoretical interest. The N-bromo-N-methyl aromatic sulfonamides add to propene, 2-methylpropene, vinyl chloride, and styrene to yield products in which the bromine atom takes the same position as the bromine atom in the "normal" addition[3] of hydrogen bromide to these olefins

$$RC{=}CH_2 + Br{-}N{-}SO_2R' \longrightarrow R{-}C{-}C{-}N{-}SO_2R'$$
(H)(CH₃)   (H H CH₃)
                (Br H)
                   I
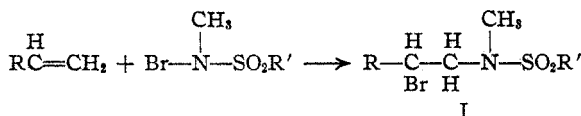
The N,N-dibromosulfonamides, on the other hand, add to olefins to yield products in which the bromine takes the same position as in the "abnormal" addition of hydrogen bromide. A brominated olefin is formed at the same time.

$$2R{-}CH{=}CH_2 + Br{-}N{-}SO_2R' \longrightarrow$$
(Br)
$$R{-}C{-}CH_2Br + RC_4H_2Br$$
(H)
$$HN{-}SO_2R'$$
II
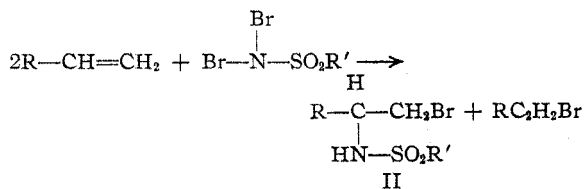
The structure of the products of reaction I was proved by conversion into known compounds by the following series of reactions. The intermediates cited were all isolated and characterized.

$$R{-}C{-}CH_2N{-}SO_2R' \xrightarrow{-HBr}$$
(H CH₃)
(Br)

$$RCH{=}C{-}N{-}SO_2R' \xrightarrow{H_2}$$
(H CH₃)
III

$$RCH_2{-}CH_2{-}N{-}SO_2R' \xrightarrow{Hydrolysis} RCH_2CH_2N{-}CH_3$$
(CH₃)   (H)

The elimination of hydrogen bromide from I usually was effected by heating the addition product with quinoline or with sodium ethoxide in al-

(1) Seliwanoff, *Ber.*, **26**, 426 (1893).

(2) Földi, *ibid.*, **63**, 2257 (1930).

(3) For definition of "normal" and "abnormal" additions of hydrogen bromide consult the paper by Kharasch, Englemann, and Mayo, *J. Org. Chem.*, **2**, 288 (1937); Kharasch, Kleiger and Mayo, *ibid.*, **4**, 428 (1939).