alcohol or water solutions. Their structure is essentially the same as that of the simple amides except for a higher contribution of the forms with a separation of charge.

Experimental

The measurements were carried out as was described in a previous paper.[16]

Materials

Dioxane.—The purification and constants of dioxane were as described previously.[16]

Urea.—A c. p. grade of urea was recrystallized twice from methyl alcohol, heated with pure dioxane to remove any alcohol; m. p. 132.6°.

Thiourea.—Eastman Kodak Co. best grade thiourea was recrystallized from methyl alcohol, heated with pure dioxane. The product gave no test for thiocyanate.

Summary

The dipole moments of urea 4.56 and thiourea 4.89 have been measured in dioxane at 25°. Plots of the dielectric constants against weight fractions were linear, showing the molecules were not associated in these solutions.

The dipole moment values indicate that urea and thiourea are resonance hybrids with a 20–30% contribution from the forms with a separation of charge.

(16) Kumler and Halverstadt, THIS JOURNAL, **63**, 2182 (1941).

The magnitude of our values for these compounds together with those for substituted ureas appearing in the literature are correlated from the standpoint of resonance. Urea and thiourea have nearly the same moments as the corresponding symmetrical disubstituted compounds. All of these compounds have two equivalent forms with a separation of charge. The moments of the monosubstituted compounds in which the two forms with a separation of charge are not equivalent are smaller, and those of the unsymmetrical disubstituted compounds still less. The low moments of the symmetrical tetrasubstituted compounds are attributed to steric hindrance.

The evidence of the existence of urea and thiourea as zwitterions is examined and it is shown that all the evidence can be adequately accounted for by the resonance hybrid structure whether urea is in the solid state or in dioxane, alcohol, or water solutions.

The structure of urea and thiourea is not essentially different from that of the simple amides except for a somewhat larger contribution of the forms with a separation of charge.

The Dissociation Constant, Dipole Moment and Structure of α-Nitrotetronic Acid

BY W. D. KUMLER

α-Nitrotetronic acid was originally assigned the isonitro form.[1] The structure of this compound is reconsidered here in the light of present day viewpoints. The dissociation constant and dipole moment have been measured and the results interpreted.

Results

TABLE I

MEASUREMENTS IN WATER AT 25°

M	% Neutralized	pH	pKa	Average pKa
0.00875	40	2.40	1.63	
.00752	50	2.55	1.70	1.68
.00710	60	2.67	1.70	

MEASUREMENTS IN DIOXANE AT 25°

ω_2	ϵ_{12}	ν_{12}
0.0005308	2.2275	0.97349
.0008488	2.2380	.97328
.0012674	2.2507	.97315
.0015091	2.2593	.97306

ϵ_1	ν_1	α	$-\beta$	$P_{2\infty}$	$P_{E_{2\infty}}$	μ
2.2100	0.97364	32.50	0.386	802	27	6.10

(1) Wolff and Lüttringhaus, *Ann.*, **312**, 133 (1900).

Discussion

The possibilities for the structure are the isonitro and the enol.
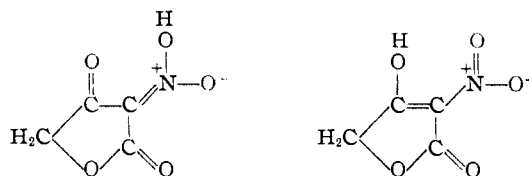
The structure of analogous compounds suggests that the enol is by far the more stable structure. Thus tetronic acid and α-halogen substituted tetronic acids are largely in the enol form[2] while no stable isonitro compound of any kind has been isolated. The isonitro compounds that have been obtained[3] change into the nitro form on standing. These facts in themselves suggest that the enol form is the more probable.

The structure of an isonitro compound is ana-

(2) Kumler, THIS JOURNAL, **60**, 857, 859 (1938).
(3) Hantzsch and Schultze, *Ber.*, **29**, 699, 2253 (1896).

logous to that of nitric acid, which is of course a strong acid.

$$=C=\overset{+}{N}\diagup\begin{smallmatrix} OH \\ O^- \end{smallmatrix} \qquad O=\overset{+}{N}\diagup\begin{smallmatrix} OH \\ O^- \end{smallmatrix}$$

The fact that the two forms with a separation of charge are not equivalent

$$=C=\overset{+}{N}\diagup\begin{smallmatrix} OH \\ O^- \end{smallmatrix} \qquad =\overset{-}{C}-\overset{+}{N}\diagup\begin{smallmatrix} OH \\ O \end{smallmatrix}$$

as they are in the case of nitric acid would cause the isonitro compound to be somewhat weaker than nitric acid. However, the compound would be much stronger than nitrous acid $Ka = 4 \times 10^{-4}$ and would probably have a Ka greater than 10^{-2}. The observed Ka of 2.1×10^{-2} therefore, does not exclude the isonitro structure.

Some of the factors likely to affect the dissociation constant of the enol form of α-nitrotetronic acid are illustrated by the ratios in Table II.

TABLE II

$$\frac{Ka\ \alpha\text{-Nitrotetronic acid}}{Ka\ \alpha\text{-Chlorotetronic acid}} = \frac{21 \times 10^{-3}}{7.4 \times 10^{-3}} = 2.8$$

$$\frac{Ka\ o\text{-Nitrophenol}}{Ka\ o\text{-Chlorophenol}} = \frac{6.8 \times 10^{-8}}{7.97 \times 10^{-10}} = 86$$

$$\frac{Ka\ p\text{-Nitrophenol}}{Ka\ p\text{-Chlorophenol}} = \frac{7.0 \times 10^{-8}}{1.46 \times 10^{-10}} = 478$$

$$\frac{Ka\ o\text{-Nitrobenzoic acid}}{Ka\ o\text{-Chlorobenzoic acid}} = \frac{6.71 \times 10^{-3}}{1.14 \times 10^{-3}} = 5.9$$

$$\frac{Ka\ p\text{-Nitrobenzoic acid}}{Ka\ p\text{-Chlorobenzoic acid}} = \frac{3.76 \times 10^{-4}}{1.05 \times 10^{-4}} = 3.7$$
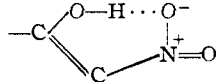
The fact that the ratios for the phenols are considerably greater than those for the benzoic acids is due to two effects. Acid strengthening groups have a greater relative effect on weak acids than on strong ones and with the phenols the nitro group is in a position to exert its rather large acid strengthening resonance effect. The nitro group cannot do this in the benzoic acids and here the major factor is the inductive effect, which is greater the nearer the groups are to the dissociating hydrogen. The ratio for the *ortho* benzoic acids is thus greater than for the *para* acids.

If a hydrogen bond is formed by the dissociating hydrogen it would weaken the acid because the hydrogen would be held by an additional force. As Branch and Yabroff pointed out,[4] this factor is reponsible for the anomalously small second dissociation constant of salicylic acid. In the *ortho* chloro and nitro benzoic acids, however, if

any hydrogen bonds are present they are quite weak and do not have a major effect on the acid strength. It is known that only weak hydrogen bonds are formed to chlorine atoms and in the case of the ortho nitro compound apparently unfavorable angles and distances cause the bond to be weak. If a strong hydrogen bond were present in this compound, the ratio for the ortho acids would be much smaller.

The acid weakening effect of a hydrogen bond formed by a dissociating hydrogen is shown very strikingly by the ratios for the phenols. Thus while the ratio Ka o-nitrophenol/Ka o-chlorophenol would be expected to be about twice that of the para compounds, or about 900, it is actually 86 or about one-tenth the expected value. The strong hydrogen bond in o-nitrophenol thus reduces the dissociation constant of the compound by a factor of more than ten.

Tetronic acids are of about the same strength as the ortho benzoic acids, so a comparison of the Ka's of the two series will not be invalidated by a great difference in acid strength. In α-nitrotetronic acid, however, the nitro group, as in the case of the ortho and para nitrophenols, is in a position to increase the acid strength due to resonance. As a result one would expect the ratio of the Ka's for the nitro and chloro compounds to be greater for the tetronic acids than for the ortho nitro benzoic acids. The fact that it is considerably less is evidence that a strong hydrogen bond is present in α-nitrotetronic acid.

In α-nitrotetronic acid the same possibilities are present for hydrogen bond formation that are present in o-nitrophenol and nitroacetophenone. The last two compounds are known to contain strong hydrogen bonds so by analogy one would expect such a bond in the first compound. In all these compounds the structure $-C\diagup\begin{smallmatrix} O-H\cdots O^- \\ \\ C-\overset{+}{N}=O \end{smallmatrix}$ is present.

The fact that α-nitrotetronic acid does not give a color with ferric chloride is evidence that a strong hydrogen bond is present in the molecule. Ordinary enols and isonitro compounds give colors with ferric chloride. Thus the α-halogen tetronic acids and the isonitro form of p-bromophenylnitromethane[5] show this reaction but compounds with strong hydrogen bonds like o-nitrophenol do not.

(4) Branch and Yabroff, THIS JOURNAL, **56**, 2568 (1934).

(5) Sidgwick, "Organic Chemistry of Nitrogen," Oxford University Press, London, 1937, p. 232.

When the moment of 6.10 for α-nitrotetronic acid is compared with that of tetronic acid 4.80, and that of α-chlorotetronic acid 5.83, it is apparent that there is a factor present in the nitro compound that is not present in the other two. The carbon–chlorine moment is about 1.5–1.8. The moment of α-chlorotetronic acid is 1.03 units higher than that of tetronic acid which seems reasonable in that the carbon–chlorine moment most probably is not directly in line with the resultant moment of the rest of the molecule. The large moment of the nitro group, 3–4, is directed along the carbon–nitrogen bond in the same direction in the nitro compound as the carbon–chlorine moment is directed in the corresponding chloro compound. This means that the moment of the nitro compound should be 1.5–2 units greater than that of the chloro compound. Actually it is only 0.27 unit greater which suggests some factor being present in the nitro compound which changes the direction and(or) magnitude of the moment of the nitro group. The formation of a hydrogen bond to one of the oxygens of the nitro group would have such an effect. Thus the dipole moment as well as the dissociation constant is consistent with the presence of a hydrogen bond in the enol form.

Experimental

The pH values of the solutions were measured with a glass electrode in connection with the pH meter of Goyan, Barnes and Hind.[6]

The dielectric constant measurements were carried out as described previously,[7] as was the purification of the dioxane.

The α-nitrotetronic acid had an equivalent weight of 145.5 and a melting point of 183–184° with decomposition.

The moment also was calculated by a method described previously[8] using the equations

$$p_{2_0} = \frac{3\alpha v_1}{(\epsilon_1 + 2)^2} + (v_1 + \beta)\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}$$
$$P_{2_0} = p_{2_0} M_2$$
$$\mu = 0.0127 \sqrt{(P_{2_0} - P_{E2_0})T}$$

The dielectric constants were linear with the weight fractions indicating no association effects in the solutions.

Summary

α-Nitrotetronic acid has a pKa of 1.68 and a dipole moment of 6.10. From considerations of general stability the enol form is more probable than the isonitro structure. Both the dissociation constant and the dipole moment are consistent with the presence of a strong hydrogen bond in the enol form.

(6) Goyan, Barnes and Hind, Ind. Eng. Chem., Anal. Ed., 12, 485 (1940).

(7) Kumler and Halverstadt, This Journal, 63, 2182 (1941).

(8) Halverstadt and Kumler, "A Critical Study of Dielectric Polarization Curves," in publication.

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[Contribution from the Chemical Laboratory of the Washington Square College of New York University]

The Absorption Spectra and the X-Ray Examination of the Isomeric Glucononitriles,

By Philippos E. Papadakis

Two forms of glucononitriles are known[1a,2,3] melting at 120.5 and 145°, and obtained by crystallization from absolute alcohol and glacial acetic acid, respectively.[3] Aqueous solutions of the two forms have initially practically the same specific rotation, but whereas that of the high melting form, to be now referred to as the A form, remains unchanged with time, that of the low melting B form shows a complex time-dependence. The present report describes investigations on the X-ray diffraction and absorption spectra of the two modifications, in an attempt to discover the reason

for this contrast in behavior. Three samples of the B form,[3] checked as to melting point and microcombustion analysis, served as material.

X-Ray Examination.—Specimens of the two forms A and B were subjected to X-ray powder analysis using focusing cameras of the Bohlin type as modified by Phragmen. Possible atmospheric action was prevented by enclosing the samples in sheaths of regenerated cellulose which themselves gave no diffraction pattern. Twenty-seven lines were observed between θ values of 15 and 45° on the photograms of both specimens, corresponding in the two cases in position and intensity. These experiments within their limits of resolution did not help much in answering the problem.

(1) Original manuscript received August 15, 1940.

(1a) Zemplén, Ber., 60, 171 (1927).

(2) Wohl and Wollenberg, Ann., 500, 281 (1932).

(3) Papadakis and Cohen, This Journal, 60, 765 (1938).