THE ELECTROLYTIC DISSOCIATION OF 1,1,3,3-TETRA-CYANO-PROPENE AND 1,1,3,3-TETRACYANO-2-METHYLPROPENE.*

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Introduction. The sodium derivative of 1,1,3,3-tetracyano-propene (I) is obtained by the condensation of ethoxymethylene-malonitrile $(CN)_2C{=}CHOC_2H_5$ and sodiomalonitrile $CHNa(CN)_2$.⁽¹⁾ When recrystallized from water, it forms colourless fine needles with a molecule of water of crystallization. When the aqueous solution of this sodium compound is acidified with hydrochloric acid, no apparent change is observed. The unchanged sodium compound (with a molecule of water of crystallization) can be crystallized out from the aqueous solution acidified with hydrochloric acid, by cooling when a comparatively large amount of this compound has been dissolved by heating, or by evaporating over sulphuric acid in vacuum when the concentration is smaller. But, if the acidified solution is shaken repeatedly with ether, the aqueous layer leaves sodium chloride alone on evaporation, and on evaporating the dried ethereal extract in vacuum, the free compound, 1,1,3,3-tetracyano-propene (II), remains in colourless crystals. The free compound, isolated in this way, is extremely unstable, and decomposes quickly into a brown amorphous mass. It is, however, stable in solution. If the ethereal solution of the free compound and the aqueous solution of the equivalent amount of sodium chloride are evaporated up together in vacuum, the sodium compound (I) remains, while hydrogen chloride is driven off. These experimental facts show the strong acid character of the compound II, and the well-defined reversibility of the reaction:

$$C_7HN_4Na\ (I) + HCl \rightleftarrows C_7H_2N_4\ (II) + NaCl\,.$$

The sodium derivative of 1,1,3,3-tetracyano-2-methylpropene (III) is obtained analogously by the condensation of ethoxyethylidene-malonitrile $(CN)_2C{=}C(CH_3)OC_2H_5$ and sodio-malonitrile $CHNa(CN)_2$.⁽²⁾ As mentioned in the preceding paper,⁽²⁾ this sodium compound and the corresponding free com-

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(1) Y. Urushibara, this Bulletin, **2** (1927), 285.

(2) See p. 565 of this volume.

pound, 1,1,3,3-tetracyano-2-methylpropene (IV), behave so much similarly to I and II respectively, that the two groups can not be distinguished from each other except by analysis.

The present paper deals with the determination of the degrees of the electrolytic dissociation, and some investigations on the salts, of 1,1,3,3-tetracyano-propene (II) and 1,1,3,3-tetracyano-2-methylpropene (IV), which behave as strong acids even though they possess no carboxyl-group.

(I) $(CN)_2C=CH-CNa(CN)_2$
(II) $(CN)_2C=CH-CH(CN)_2$
(III) $(CN)_2C=C(CH_3)-CNa(CN)_2$
(IV) $(CN)_2C=C(CH_3)-CH(CN)_2$

The Preparation of the Aqueous Solutions of 1,1,3,3-Tetracyano-propene and 1,1,3,3-Tetracyano-2-methylpropene. As mentioned above 1,1,3,3-tetracyano-propene (II) and 1,1,3,3-tetracyano-2-methylpropene (IV) are extremely unstable when isolated, so that their aqueous solutions were prepared from the sodium derivatives as follows: The recrystallized sodium compound ($C_7HN_4Na\cdot H_2O$ or $C_8H_3N_4Na\cdot H_2O$) (1/160 mol) was dissolved in a little amount of water and aqueous potassium bisulphate was added in excess. The resulting solution was extracted with pure ether several times. The ethereal solution was dried with anhydrous sodium sulphate, filtered into a flask, and evaporated in vacuum to some extent. After the addition of purified water in an amount (70–80 c.c.) a little smaller than the calculated for 1/16 N, the ether was driven off in vacuum completely. The aqueous solution obtained in this way was colourless and gave no precipitate nor turbidity on adding barium chloride. Then the aqueous solution was titrated with barium hydroxide (1/20 N), and by adding the required amount of purified water, the solution was made up to 1/16 N, the titer being confirmed by titration after dilution.

The Determination of the Degrees of the Electrolytic Dissociation by Measuring the Molecular Conductivities. The 1/16 N solution (20 c.c.) was taken in a conductivity vessel. The conductivity was measured at 25.0° by the method of Wheatstone bridge. Then the concentration of the solution in the vessel was made one half by taking out half the volume of the solution and adding the same volume of pure water, and the conductivity was measured again. By repeating the same procedure the conductivities of the solutions in the concentrations down to 1/512 N were measured. The molecular conductivities were plotted against the concentrations, and the value for the infinite dilution was obtained by extrapolation of the concentration–molecular conductivity curve. Three series of measurements were carried out and the mean value of the molecular conductivity was obtained for each concentration. The degree of dissociation was calculated by dividing the molecular conductivity for each concentration by the value for the infinite dilution. From the degree of dissociation the concentration of the hydrogen ions and *p*H were calculated. The results of experiments are shown in Table 1 and Table 2. Table 3 shows the degrees of dissociation of hydrochloric acid calculated similarly from the molecular conductivities.(3) 1,1,3,3-Tetracyano-propene and 1,1,3,3-tetracyano-2-methylpropene manifest high degrees of electrolytic dissociation, comparable with those of hydrochloric acid.

Table 1. Electrolytic Dissociation of 1,1,3,3-Tetracyano-propene at 25.0°.

Concentration (N)	Molecular conductivity				Degree of dissociation	Concentration of hydrogen ions (N)	*p*H
	1	2	3	mean			
1/16	355.2	354.8	352.9	354.3	0.881	0.0551	1.26
1/32	376.2	371.2	370.4	372.6	0.926	0.0289	1.54
1/64	388.4	385.2	384.5	386.0	0.960	0.0150	1.82
1/128	399.5	396.5	395.7	397.2	0.987	0.00771	2.11
1/256	400.7	400.5	399.9	400.4	0.995	0.00389	2.41
1/512	401.3	400.5	400.4	400.7	0.996	0.00195	2.71
0	403	402	402	402.3			

Table 2. Electrolytic Dissociation of 1,1,3,3-Tetracyano-2-methylpropene at 25.0°.

Concentration (N)	Molecular conductivity				Degree of dissociation	Concentration of hydrogen ions (N)	*p*H
	1	2	3	mean			
1/16	350.1	353.9	351.1	351.7	0.879	0.0548	1.26
1/32	370.0	371.6	372.2	371.3	0.928	0.0290	1.54
1/64	380.5	383.2	382.2	382.0	0.955	0.0149	1.83
1/128	391.2	392.3	389.6	391.0	0.978	0.00764	2.12
1/256	391.4	395.3	392.9	393.2	0.983	0.00384	2.42
1/512	397.2	398.0	398.0	398.4	0.996	0.00195	2.71
0	400	400	400	400			

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(3) W. Ostwald, "Lehrbuch der allgemeinen Chemie," 1893, Vol. II, p. 1.

Table 3. The Degree of the Electrolytic Dissociation of Hydrogen Chloride at 25°.

Concentration (N)	1/8	1/16	1/32	1/64	1/128	1/256	0
Molecular conductivity(3)	378	386	393	399	401	403	407
Degree of dissociation	0.928	0.948	0.965	0.980	0.985	0.990	

The Determination of the Hydrogen Ion Concentration by Measuring the Electromotive Force. The following cell was constructed by combining a calomel electrode and a hydrogen electrode containing the 1/16 N solution of 1,1,3,3-tetracyano-propene by means of a concentrated solution of potassium chloride fixed by gelatine:

+Hg | Hg_2Cl_2 in 1 N KCl | Conc. KCl solution fixed by gelatine | 1/16 N solution of tetracyano-propene | H_2—

*p*H is obtained from the following equation:

$$pH = \frac{E-0.284}{0.0001986\,T} ,$$

where E is the electromotive force of the cell, and T the absolute temperature. The electromotive force was measured at 15°C. From the value of *p*H the concentration of hydrogen ions and the degree of dissociation were calculated. The results are shown in Table 4. For comparison *p*H of the 1/16 N hydrochloric acid was determined similarly, Table 5.

Table 4. *p*H of the 1/16 N Solution of 1,1,3,3-Tetracyano-propene at 15°C.

No. of exp.	E(volt)	*p*H	Concentration of hydrogen ions (N)	Degree of dissociation
1	0.3575	1.29	0.050	0.80
2	0.3595	1.33 } mean 1.30		
3	0.3580	1.30		

Table 5. *p*H of 1/16 N Hydrochloric Acid at 15°C.

No. of exp.	E(volt)	*p*H	Concentration of hydrogen ions (N)	Degree of dissociation
1	0.3555	1.25 } mean 1.25	0.057	0.90
2	0.3550	1.24		

Chemical Properties of 1,1,3,3-Tetracyano-propene and 1,1,3,3-Tetracyano-2-methylpropene, and the Solubilities of their Salts. The aqueous solution of 1,1,3,3-tetracyano-propene decomposes carbonates, and dissolves zinc, magnesium, and tin at the ordinary temperature with the evolution of hydrogen gas. On adding silver nitrate to the solution of the sodium salt (I) acidified with nitric acid, the silver salt of 1,1,3,3-tetracyano-propene is precipitated. The mercurous salt is also insoluble in water. The salts of other metals are soluble in water. Thus the salts of 1,1,3,3-tetracyano-propene resemble chlorides in solubilities in water. Silver and lead salts are more easily soluble in water than silver and lead chlorides respectively.

1,1,3,3-Tetracyano-2-methylpropene shows quite similar properties. Its salts are generally less soluble, and more easily crystallizable, than the salts of 1,1,3,3-tetracyano-propene, except the silver salts.

The degrees of ionization of the sodium salts (I and III) and the solubilities of the silver salts are described below.

The Degrees of the Electrolytic Dissociation of the Sodium Derivatives of 1,1,3,3-Tetracyano-propene and 1,1,3,3-Tetracyano-2-methylpropene. The molecular conductivities of the aqueous solutions of these sodium compounds in various concentrations were measured at 25.0°. The value for the infinite dilution was obtained also by extrapolating the concentration–molecular conductivity curve. The degree of dissociation was calculated by dividing the molecular conductivity for each concentration by the value for the infinite dilution. The results are shown in Table 6 and Table 7. In the 1/10 N solution the sodium derivative of 1,1,3,3-tetracyano-propene shows the degree of dissociation 0.70, while the sodium derivative of 1,1,3,3-tetracyano-2-methylpropene 0.67.

Table 6. The Electrolytic Dissociation of the Sodium Derivative of 1,1,3,3-Tetracyano-propene at 25.0°.

Concentration (N)	Molecular conductivity	Degree of dissociation
1/10	67.7	0.70
1/20	74.8	0.78
1/40	79.5	0.82
1/80	83.6	0.87
1/160	87.8	0.92
1/320	90.9	0.95
1/640	91.8	0.97
0	95.0	

Table 7. The Electrolytic Dissociation of the Sodium Derivative of 1,1,3,3-Tetracyano-2-methylpropene at 25.0°.

Concentration (N)	Molecular conductivity	Degree of dissociation
1/10	66.2	0.67
1/16	72.1	0.73
1/32	77.8	0.79
1/64	80.9	0.82
1/128	86.0	0.88
1/256	88.9	0.91
1/512	92.2	0.95
0	96.0	

The Solubilities of the Silver Derivatives of 1,1,3,3-Tetracyano-propene and 1,1,3,3-Tetracyano-2-methylpropene. The following concentration cell was constructed:

+Ag	1/10 N $AgNO_3$	Saturated solution of NH_4NO_3	Silver derivative in the solution of sodium derivative	Ag−

For the determination of the solubility of the silver derivative of 1,1,3,3-tetracyano-propene C_7HN_4Ag three measurements of the electromotive force were carried out at 18° with the cathode solutions prepared by adding one or two drops of a silver nitrate solution to the 1/10 N, 1/80 N, and 1/160 N solutions of the sodium derivative (I). For the silver derivative of 1,1,3,3-tetracyano-2-methylpropene $C_8H_3N_4Ag$ only one measurement was made at 23° with the 1/10 N solution of the sodium compound (III). The concentration of the silver ions in the cathode solution (x) was calculated from the electromotive force (E) by the following equation:

$$E = 0.058 \log \frac{0.081}{x} .$$

The solubility product was obtained by multiplying the concentration of the silver ions (x) by the concentration of the anion obtained from Table 6 and Table 7 (the value for 25°), and the solubility of the silver compound (g./l.) by multiplying the square root of the solubility product by the molecular weight of the silver compound. The results are shown in Table 8 and Table 9. The solubilities of the silver derivatives of 1,1,3,3-tetracyano-propene and 1,1,3,3-tetracyano-2-methylpropene are greater than the solubility of silver chloride (about 1.5×10^{-3}g./l.), but it takes a long time (about 2 weeks) to decompose these silver derivatives with dilute hydrochloric acid at room temperature.

Table 8. The Solubility of the Silver Derivative of 1,1,3,3-Tetracyano-propene at 18°.

No. of exp.	E (volt)	x (N)	Concentration of the anion (N)	Solubility (g./l.)	
1	0.2609	2.573×10^{-6}	0.070	0.1056	mean 0.1000
2	0.2156	1.554×10^{-5}	0.011	0.1023	
3	0.2046	2.407×10^{-5}	0.0058	0.0921	

Table 9. The Solubility of the Silver Derivative of 1,1,3,3-Tetracyano-2-methylpropene at 23°.

E (volt)	x (N)	Concentration of the anion (N)	Solubility (g./l.)
0.2431	3.315×10^{-5}	0.067	0.388

The Constitutions of 1,1,3,3-Tetracyano-propene and 1,1,3,3-Tetracyano-2-methylpropene and the Mode of Ionization. According to Hantzsch and Osswald,(4) cyanoform $CH(CN)_3$ behaves as a strong acid, showing the degree of dissociation 0.92 at 25° in the concentration 1/32 N. Further, like 1,1,3,3-tetracyano-propene and 1,1,3,3-tetracyano-2-methylpropene, cyanoform is very unstable when isolated, polymerizing rapidly, but it is stable in aqueous solution. Cyanoform is considered to exist in the form $(CN)_2C{=}C{=}NH$ in aqueous solution and to ionize as follows: (5)

$$(CN)_2C{=}C{=}NH \;=\; (CN)_2C{=}C{=}N^- + H^+.$$

This form of cyanoform has been confirmed by F. Arndt, H. Scholz, and E. Frobel,(6) who call it the ketene-imide-form or briefly the enimide-form. It may be considered that 1,1,3,3-tetracyano-propene and 1,1,3,3-tetracyano-2-methylpropene exist also in the enimide-form and dissociate in the same way:

$$(CN)_2C{=}CH{-}C(CN){=}C{=}NH \;=\; (CN)_2C{=}CH{-}C(CN){=}C{=}N^- + H^+ ,$$

$$(CN)_2C{=}C(CH_3){-}C(CN){=}C{=}NH \;=\; (CN)_2C{=}C(CH_3){-}C(CN){=}C{=}N^- + H^+ .$$

In the salts the imide hydrogen is replaced by a metal atom, the electrolytic dissociation taking place in the same way:

$$(CN)_2C{=}CH{-}C(CN){=}C{=}NNa \;=\; (CN)_2C{=}CH{-}C(CN){=}C{=}N^- + Na^+ ,$$

$$(CN)_2C{=}C(CH_3){-}C(CN){=}C{=}NNa \;=\; (CN)_2C{=}C(CH_3){-}C(CN){=}C{=}N^- + Na^+ .$$

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(4) *Ber.*, **32** (1899), 641.

(5) Hantzsch and Osswald, *loc. cit.*; also compare Baker, "Tautomerism," 1934, p. 121.

(6) *Ann.*, **521** (1935), 105.