Synthesis and Thermochemistry of Tricyanomethyl and Other Polycyano Compounds

by

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ABSTRACT

A series of tricyanomethyl compounds were prepared in refluxing acetonitrile by the alkylation of potassium tricyanomethanide with alkyl iodides, allyl, propargyl, and benzyl bromides. Yields of 20-57% were obtained for mono and difunctional halides with a reflux time of 72 hours.

The heats of combustion of these tricyanomethyl compounds as well as of two polycyano compounds were measured using a Dickenson type calorimeter and heats of formation were calculated with a precision of approximately ±1.0%. From Pitzer's values for C-C and C-H bond energies, that of the tricyanomethyl moiety is calculated to be about 810 kcal/mole. Also the tricyanomethyl group is less stable than expected from comparison with ΔH_f^0 of propylcyanide.

As a result of the synthesis of tetracyanoethylene,[1] a large class of organic molecules heavily substituted with cyano groups has become available. Many of these have interesting physical and chemical properties. The only known tricyanomethyl compounds are the salts of tricyanomethane,[2-8] bromotricyanomethane,[9] 1,1,1-tricyanoethane,[3] 2,2,2-tricyanoethylbenzene,[3] and hexacyanoethane.[10] Tricyanomethane, itself, is an unstable compound and has not been isolated in the free state, although aquoethereal solutions of tricyanomethane have been used for synthetic reactions.[7] This paper describes the synthesis and thermochemistry of a new series of tricyanomethyl compounds.

I SYNTHESIS

A. Discussion

Hantzsch and Oswald[3] prepared 1,1,1-tricyanoethane and 2,2,2-tricyanoethylbenzene in very low yields from a heterogeneous mixture of silver tricyanomethanide with methyl and benzyl iodides, respectively. It was apparent that the silver salt of tricyanomethane was unsuitable for alkylation reactions because of its virtual insolubility in organic solvents. A search was made to find a salt of tricyanomethane which was partially

soluble in organic solvents. Since a ready preparation of potassium tricyanomethanide was now available,[8] attention was turned to studying the solubility characteristics of this salt. It was found that potassium tricyanomethanide was soluble to the extent of 19% in refluxing acetonitrile and that the salt could be alkylated in this medium with alkyl iodides, allyl, propargyl, and benzyl bromides. Optimum yields of 20-57% were obtained for mono and difunctional halides with a reflux time of 72 hours. The importance of the reactivity of the organic halide was demonstrated by the fact that 1,4-dibromobutyne-2 was converted to 1,1,1,6,6,6-hexacyanobutyne-3 in 43% yield while diiodomethane gave only a 2% yield of the monoalkylated product, 1,1,1-tricyanoethyl iodide, and none of the dialkylated product.

As an alternative method of introducing the tricyanomethyl group into organic compounds, the Michael reaction of cyanoform and α,β-unsaturated compounds was studied. Cyanoform was generated in situ by the addition of a stoichiometric amount of 100% sulfuric acid to an acetonitrile solution of potassium tricyanomethanide and the α,β-unsaturated compound. Under these conditions, addition of cyanoform to acrylonitrile, acrylic acid, methyl acrylate, acrylamide, and acrolein did not occur, for only the red polymer of cyanoform was isolated. However, methyl vinyl ketone did react in the expected manner to give 1,1,1-tricyano-4-pentanone.

The tricyanomethyl compounds are a stable class of organic compounds. The solid products can be purified by sublimation. Their exceptional thermal stability is evidenced by the fact that 1,1,1,6,6,6-hexacyanobutyne-3 was sublimed at $170^{\circ}/0.05$ mm. The infrared spectra of these compounds show a weak absorption for cyano at 4.4μ. The properties of the compounds are summarized in Table I.

In addition to the above tricyanomethyl compounds, 1,4-dicyanobutyne-2[11] and 1,1,2,2-tetracyanocyclopropane[12] were also prepared for the thermochemical studies.

B. Experimental

All analyses were made by Stanford University, Stanford, California. Melting points are uncorrected.

Alkylation of Organic Halides with Potassium Tricyanomethanide

The preparation of 1,1,1-tricyanobutene-3 is given as a typical example of the experimental procedures that were used in the reaction of organic halides with potassium tricyanomethanide.

A mixture of 29.0 g (0.225 mole) of potassium tricyanomethanide,[8] 26.6 g (0.32 mole) of allyl bromide, and 500 ml of acetonitrile was refluxed with stirring for 72 hours. The mixture was cooled and filtered

Table I

PROPERTIES OF TRICYANOMETHYL COMPOUNDS

Compound	m.p. °C	Recryst. Solvent	Yield %	Formula	Analyses					
					Calculated			Found		
					C	H	N	C	H	N
$(NC)_3CCH_3$	94-95	(a)	53.0	$C_5H_3N_3$	57.14	2.88	39.99	57.10	2.88	39.60
$(NC)_3CCH_2I$	102-103	(b)	2.2	$C_5H_2N_3I$	26.00	0.87	18.20	26.25	0.85	18.73
$(NC)_3CCH_2CH_2\overset{O}{\overset{\|\|}{C}}CH_3$	50-51	Ethanol	64.5	$C_8H_7N_3O$	59.62	4.38	26.07	59.58	4.50	26.23
$(NC)_3CCH_2C_6H_5$	140-141	(c)	55.3	$C_{11}H_7N_3$	72.91	3.89	23.19	72.89	3.99	23.40
$(NC)_3CCH_2CH{=}CH_2$	30[d]	(e)	57.8	$C_7H_5N_3$	64.11	3.84	32.04	64.00	3.85	32.30
$(NC)_3CCH_2CH{=}CHCO_2C_2H_5$	60-61	Isopropyl Alcohol	56.4	$C_{10}H_9N_3O_2$	59.11	4.47	20.68	59.35	4.82	20.86
$(NC)_3CCH_2C{\equiv}CH$	61-62	Isopropyl Alcohol	47.3	$C_7H_3N_3$	65.11	2.34	32.55	64.87	2.51	32.74
$(NC)_3CCH_2CH{=}CHCH_2C(CN)_3$	258-259	Acetonitrile	22.4	$C_{12}H_6N_6$	61.52	2.58	35.88	61.40	2.83	36.11
$(NC)_3CCH_2C{\equiv}CCH_2C(CN)_3$	219-220	(f)	43.4	$C_{12}H_4N_6$	62.07	1.74	36.20	62.11	1.83	36.30
$(NC)_3CCH_2C{\equiv}C{-}C{\equiv}CCH_2C(CN)_3$	177-178	Chloroform	27.2	$C_{14}H_4N_6$	65.62	1.57	32.80	64.95	1.47	32.22

(a) Sublimed at 40°/0.10 mm, (Lit[2], m.p. 93.5°)

(b) Sublimed at 70°/0.2 mm

(c) Sublimed at 100°/0.05 mm, (Lit[2], m.p. 138°)

(d) b.p. 95°/26 mm, $n^{20}D$ 1.4419

(e) Sublimed at 50°/1 mm

(f) Sublimed at 170°/0.05 mm

to give 21.8 g (83.5%) of precipitated potassium bromide. The filtrate was concentrated and diluted with ether to precipitate the residual potassium salts. After filtering, the filtrate was concentrated and distilled to give 16.7 (57.8%) of colorless liquid, b.p. 95°/26 mm, $n^{20}D$ 1.4419.

1,1,1-Tricyano-4-pentanone

To a stirred solution of 200 ml of acetonitrile containing 14.4 g (0.11 mole) of potassium tricyanomethanide was added 7.74 g (0.11 mole) of methyl vinyl ketone. Then 5.84 g (0.055 mole) of sulfuric acid was added dropwise at ambient temperature. There was an immediate precipitation of potassium sulfate. The reaction mixture was stirred for two hours and filtered to remove 8.86 g (92.6%) of potassium sulfate. The filtrate was concentrated to give 15.3 g of semi-solid product. This slurry was treated with isopropanol to give 11.4 g (64.5%) of white crystals, m.p. 49-50°. Recrystallization from ethanol raised the melting point to 50-51°.

1,4-Dicyanobutyne-2[11]

A mixture of 55.0 g (0.615 mole) of dry cuprous cyanide, 55.0 g (0.26 mole) of 1,4-dibromobutyne-2, and 175 ml of acetonitrile was heated under reflux with good mechanical stirring. After two hours a clear brown solution was attained. The solution was refluxed for an additional 1.5 hours, cooled, and treated with 500 ml of ether. The precipitated cuprous bromide was separated and the filtrate was treated four times with charcoal. The light yellow ether solution was then concentrated to give 12.4 g of yellow crystals. The product was recrystallized from 36 ml of benzene-hexane (80/20) to give 3.6 g (13.3%) of colorless needles, m.p. 91-92°.

Anal. Calc'd. for $C_6H_4N_2$: C, 69.2; H, 3.9; N, 26.9.

Found: C, 68.96; H, 3.73; N, 26.68.

The infrared spectrum showed a strong absorption for C≡N at 2280 cm^{-1}.

II THERMOCHEMISTRY

A. Experimental

A Parr Model 1221 oxygen bomb calorimeter was modified for isothermal operation and to ensure solution of nitrogen oxides.[13] The space between the water jacket and the case was filled with Vermiculite (exploded mica) to improve insulation. A flexible 1000 watt heater (Cenco No. 16565-3) was bent in the form of a circle to fit just within the jacket about 1 cm above the bottom. Heater ends were soldered through the orifices left by removing

the hot and cold water valves. A copper-constantan thermocouple and a precision platinum resistance thermometer (Minco Products Model S37-2) were calibrated by comparison with an NBS-calibrated Leeds & Northrup Model 8164 platinum resistance thermometer. The thermometer was used to sense the temperature within the calorimeter bucket; the thermocouple sensed the jacket temperature. A mercury-in-glass thermo-regulator (Philadelphia Scientific Glass Model CE-712) was used to control the jacket temperature.

Jacket temperature was controlled by connecting the thermoregulator and the heater to an American Instrument Co. Relay Model No. 4-5300. Power to the heater was supplied by a 60 cycle variable transformer normally operated at about 10 volts. Jacket temperature was recorded by feeding the thermocouple output through a Leeds & Northrup D.C. amplifier (Cat. No. 9835-B) to a Speedomax H Azar strip chart recorder.

Calorimeter temperature was measured with a Leeds & Northrup G-1 Mueller Bridge used in conjunction with a D.C. Null Detector (Cat. No. 9834) or with a moving coil galvanometer (Cat. No. 2284-D) and lamp and scale.

Time was measured with a 60 cycle synchronous motor clock. Sample weight was determined using an analytical balance and a set of Class S stainless steel weights.

B. Procedure

General

The samples were burned in the Parr bomb (360 ml capacity), containing, initially, 3 ml of water in the cup over the combustion crucible and 99.99% pure oxygen at 450 psi and about 23°C. The air was flushed out by filling several times with oxygen to 450 psi. The weight of the water for the calorimeter, 2000 g, was measured to 0.1 g on a high-capacity balance.

Sample pellets were weighed in the combustion crucible to 0.05 mg after overnight storage, in a desiccator, over anhydrous calcium sulfate. We do not know any of the compounds to be hydroscopic. The sample was ignited using the usual iron wire supplied by Parr.

For all samples except one the jacket temperature, during a run, was maintained constant to ±0.01°C at about 29°C and the calorimeter temperature at the start of a run was generally of the order of 25°C. 1,1,1-tricyanobutene-3 was treated specially because of its melting point ~30°C. (See below)

The temperature of the calorimeter was obtained by using the detector as a null instrument or the galvanometer in more conventional fashion. During the fore and after periods resistance was measured each minute. During the heating period the time was noted at which several predetermined values of resistance were attained. Resistance could be measured to within 3×10^{-4} ohms or about 0.0015°C.

The nitric acid produced in the combustion was determined by titration with standardized alkali using a methyl orange indicator. The thermal correction was calculated on the basis 14.0 kcal/mole evolved for each mole of aqueous acid formed. A correction was made for the average firing energy, 12.2 cal.

Calibration

The calorimeter was calibrated by burning standardized benzoic acid obtained from the Parr Instrument Co. (ΔH_c = 197.72 kcal/mole). Measurements were made under conditions paralleling as closely as possible those used during a run. For reasons explained below it was also necessary to determine the heat of combustion of Nujol brand mineral oil. For this purpose the contents of two one-pint bottles of Nujol were mixed thoroughly and stored in a one-liter bottle. Runs were made on aliquots withdrawn from this new mixture. Table II includes the results obtained both for the benzoic acid and the Nujol and gives an indication of the precision of the experiment.

Sample Preparation

Samples were purified by recrystallization; we believe each substance to be of better than 99% purity.

The 1,1,1-tricyanobutene-3 formed a glassy solid below 29°C with an unsharp transition. It was run as a liquid with the calorimeter jacket maintained at about 35°C. A small weighed pellet of benzoic acid was heated to above 30°C and the pellet wet with the liquid by dropwise addition. The weight of liquid added was determined by difference. The wet pellet was maintained above 29°C until ignition. Thus uncertainty as to the physical state of the liquid was avoided. No attempt was made to correct results for the heat of wetting.

All other samples were prepared by pressing solid pellets which were then wet with the calibrated Nujol.

C. Results

All computations were made according to the method described by Jessup.[14] The unit of energy used is the defined calorie = 4.183 int. joules. The unit of mass is the gram true mass derived from the weight in air against stainless steel weights and buoyancy corrections were made. Molecular weights were calculated using 1959 values of the Commission on Atomic Weights. Heats of formation were calculated from heats of combustion. The results of individual combustions and corrected values of the heats of formation are presented in Table II.

D. Discussion

It is now possible to compare the measured heats of formation with those predicted on the basis of bond or group additivity. We use the same method

Table II

Energies of Combustion[a]

Compound	State	Mass of Addend, g	Ms g	Es cal/g	E cal/°C	Cz Cal	Q_v 25°C cal/g	Q_p 25°C cal/g	ΔH°_f @25°C kcal/mole, in vacuo	ΔH°_f average @25°C, in vacuo
Benzoic Acid	solid		1.0494	2434.1	2434.5	1.8				
			0.9843	2435.7	2436.1	1.7				
			1.0006	2434.0	2434.4	1.8				
			1.0426	2434.1	2434.6	1.9				
			0.9934	2438.3	2438.7	1.8				
Nujol	liquid		0.9379	2439.8	2440.4	3.3	10976.8			
			0.9541	2439.8	2440.4	3.2	10962.1			
			0.9647	2439.8	2440.4	3.2	10982.0			
1,4-Dicyanobutyne-2	solid	1.1348	0.3300	2434.9	2435.7	17.1	7590.2	7590.2	88.7	
		1.1315	0.3325	2434.9	2435.7	17.1	7558.0	7558.0	85.3	87.0 ± 1.7
Tetracyanoethylene	solid	0.5902	0.9302	2438.4	2439.1	33.4	5585.0	5594.3	151.8	
		0.0964	1.0929	2438.4	2438.9	32.4	5577.9	5587.2	150.9	151.4 ± 0.5
1,1,2,2-Tetracyanocyclopropane	solid	0.6351	0.6678	2434.9	2435.5	26.6	6131.9[b]	6138.2	145.0	
		0.7467	0.7313	2434.9	2435.6	28.2	6096.6	6102.9	140.0	142.5 ± 2.5
1,1,1-Tricyanoethane	solid	0.7063	0.7560	2435.5	2436.2	30.3	6263.4	6267.7	85.6	
		0.6812	0.6957	2435.5	2436.2	27.6	6240.7	6245.0	83.2	84.4 ± 1.2
1,1,1-Tricyanobutene-3[c]	liquid	1.0932	0.3191	2445.5	2446.1	14.5	7148.5	7149.6	108.0	
		1.0902	0.3222	2445.5	2446.1	14.0	7187.0	7188.1	112.9	110.3 ± 2.5
1,1,1-Tricyanobutyne-3	solid	1.0402	0.4275	2434.9	2435.7	21.7	7002.9	7006.4	143.3	
		1.0373	0.4230	2434.9	2435.7	21.3	7030.9	7034.4	146.9	145.1 ± 1.8
1,1,1,6,6,6-Hexacyanohexene-3	solid	1.0315	0.4490	2434.9	2435.7	22.0	6578.2	6582.0	207.1	
		0.9573	0.4983	2434.9	2435.7	23.2	6525.3	6529.1	194.5	200.8 ± 6.3
1,1,1,6,6,6 Hexacyanohexyne	solid	0.7415	0.7839	2435.5	2436.2	28.9	6494.5	6499.6	242.8	
		1.1114	0.3212	2434.9	2435.7	19.2	6483.0	6488.1	240.5	241.7 ± 1.2
1,1,1,8,8,8-Hexacyanooctadiyne-3,5	solid	1.1165	0.3362	2434.9	2435.7	18.3	6825.0[d]	6829.7	295.0	
		1.1254	0.3309	2434.9	2435.7	17.6	6801.6	6806.3	289.0	292.0 ± 3.0

a. Notation is that of Jessup (loc. cit.)

b. Unburned carbon correction: 4.7 cal.

c. A separate calibration, not given, was performed with benzoic acid, because of the high temperature used. Benzoic acid was used as the addend.

d. Unburned carbon correction: 4.7 cal.

as that discussed by Boyd.[15] Assume ΔH for the following reaction is zero:

$$m\ R\text{-}CN + C_1H_{m+n} \longrightarrow mR\text{-}H + C_1\ (CN)_mH_n$$

R-CN is taken to be proplycyanide (gas) for which ΔH_f^o = 7.45 kcal/mole.[16] The heats of formation used for the compounds C_1H_{m+n} are given in Table III. The heats of sublimation of all the solids were estimated to be 20.0 kcal/mole; for the one liquid we used an estimated value for the heat of vaporization of 5.0 kcal/mole.

Table III

Compound	ΔH_f^o (kcal/mole) (gas)	Reference
Ethane	-20.236	17
Propane	-24.826	18
Ethylene	12.496	17
Cyclopropane	12.74	20
Butyne-1	39.70	18
Hexyne-3	25.84	19
Hexyne-1	29.55	18
Hexane	-39.96	18
Butyne-2	35.37	18
Hexene-3 (cis)	-11.56	18
(trans)	-12.56	18
Average	12.06	
Butene-1	0.28	18
Octadiyne-3,5	93.8*	

*Calculated from ΔH_f^o octane = -49.82 kcal/mole (Ref. 17)

ΔH hydrogenation (octa - 1,7 diyne) = 139.7 (Ref. 21, p. 53)

and ΔH hydrogenation (dodeca - 1,7 diyne) minus

ΔH hydrogenation 3,9 isomer = -3.9 kcal/mole (Ref. 21, p. 54)

The results of the comparison are shown in Table IV where the last column, Δ, represents the excess of the measured heat of formation over that calculated. Accordingly, the positive values are evidence of the decreased stability of the polysubstituted cyanocarbons.

Table IV

Compound	ΔH_f^o (gas), (kcal/mole) Measured	Calculated	Δ
1,4-Dicyanobutyne-2	107.0	99.9	7.1
Tetracyanoethylene	171.4	141.6	29.8*
1,1,2,2-Tetracyanocyclopropane	162.5	141.8	20.7
1,1,1-Tricyanoethane	104.4	76.6	27.8
1,1,1-Tricyanobutene-3	115.3	97.1	18.2
1,1,1-Tricyanobutyne-3	165.1	136.5	28.6
1,1,1,6,6,6-Hexacyanohexene-3	220.8	181.6	39.2
1,1,1,6,6,6-Hexacyanohexyne-3	261.7	219.5	42.2
1,1,1,8,8,8-Hexacyanooctadiyne-3,5	312.0	287.4	24.6

*See R.H. Boyd[15] for comparison.

It is also possible to calculate the bond energy of the tricyanomethyl moiety in each of the molecules. To do this we calculate standard heats of formation at 0^oK from the values given in Table III for 298^oC. In the absence of reliable data we note the following reported[23] specific heats, c:

Acetonitrile: 0.54 cal/g
Propionitrile: 0.538 cal/g
Butynonitrile: 0.547 cal/g

Taking an average value for c = 0.54 cal/g, we can, for each compound, calculate $H^o_{298}-H^o_o$ = 298 Mc where M = molecular weight. The bond energy of the $-C(CN)_3$ group is then calculated using values for other bond energies as given by Pitzer[22] and values for the heats of formation of H, N, and C atoms as given in reference 13. The results of these calculations are listed in Table V.

Table V

Compound	$E(-C(CN)_3)$ kcal
1,1,1-Tricyanoethane	800
1,1,1-Tricyanobutene-3	816
1,1,1-Tricyanobutyne-3	819
1,1,1,6,6,6-Hexacyanohexene-3	814
1,1,1,6,6,6-Hexacyanohexyne-3	814
1,1,1,8,8,8-Hexacyanooctadiyne-3,5	822

The following are our conservative estimates, expressed in kcal, of the uncertainties in the calculated values of the stabilization energies:

Combustion process	1.0
Heat of vaporization	1.0
Heat of sublimation	4.0

The bond energy calculations are in error, in addition, because of the uncertainty in the enthalpy calculation. For, not only is c estimated at 25°C but the further assumption is made that c is temperature-independent. This may introduce an error as large as 2 or 3 kcal. Consequently neither the scatter in the stabilization energies nor the apparently increasing trend in the bond energy with increasing unsaturation is significant. Nevertheless, assigning a bond energy to the tricyanomethyl group is reasonable. To calculate the heat of formation of linear or cyclic hydrocarbons with the group substituted in one or more locations, an average value of 810 kcal for the $-C(CN)_3$ bond energy would appear to introduce an error of about 10 kcal. We are in the process of determining the latent heats and heat capacities necessary to improve the significance of the data.

ACKNOWLEDGEMENT

Research reported in this publication was supported by the Advanced Research Projects Agency through the U.S. Army Research Office-Durham. The authors wish to thank Dr. Harry S. Mosher for his interest and helpful suggestions throughout the course of this work.

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