pared with the 50% over-all monodeuteration of products indicated by mass spectrometry. This work suggests that the reaction involves transfer of a hydride ion to the acetylenic substrate, presumably *via* the transition metal cocatalyst. A high dimer–trimer ratio was obtained in this experiment. This may, in part, be due to the use of a deuterated cocatalyst (a similar experiment, in which lithium aluminum hydride in diglyme was used, gave a lower dimer–trimer ratio).

Mechanism.—While it is not at present possible to give a detailed account of the mechanism of these reactions, the following is proposed as a working hypothesis, which is at least not in disagreement with the experimental evidence.

It is assumed that, at the start of the reaction, the group VIII transition metal ion is reduced to a lower valence state by the hydridic reducing agent, at the same time accepting a hydride ion from the latter, and so forming a transition metal hydride. In fact, it is suspected that the restriction of these catalyses to group VIII of the periodic table reflects the relatively great tendency on the part of the elements in this group to form hydrides. Similarly, restriction of the effective cocatalysts to hydridic reducing agents indicates that it is the transfer of hydride ion from reducing agent to metal atom which is characteristic of the most favorable reaction paths.

The reduced transition metal species then forms complexes with acetylenes. In these complexes, the metal atom may act as a hydride transfer agent, thus permitting transfer of hydrogen from one acetylenic substrate molecule to another, two or more of which being in some way associated or complexed with the metal atom in question.

The complexes formed are probably π complexes—*i.e.*, they involve double bonding between the metal atom and the acetylenic triple bond itself.[9] The transition state for the catalytic reaction probably involves a structure very similar to that of a π complex between a metal atom and one or more acetylenic molecules, *via* such triple bonds. In view of the limited information available it is probably not justifiable to carry speculation as to the details of the reaction mechanism any further at this time.

Pyrolysis of Cyanoformates. A New Synthesis of Nitriles

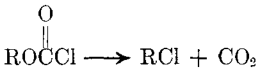
WILLIAM A. SHEPPARD

Contribution No. 790 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

Received May 23, 1962

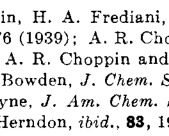
The gas phase decomposition of alkyl cyanoformates, $\mathrm{RO\overset{\overset{O}{\|}}{C}CN}$, where R is CH_3, $C_6H_5CH_2$, and $NCCH_2$, gives carbon dioxide and the corresponding nitrile. In contrast to the relatively mild conditions employed in chloroformate decomposition, this reaction requires temperatures in the range of 700 to 800°. Ethyl cyanoformate decomposes above 400° to ethylene, hydrogen cyanide, and carbon dioxide. Possible mechanisms for these decompositions are considered.

The thermal decomposition of alkyl chloroformates leads to alkyl chlorides and carbon dioxide.[1]



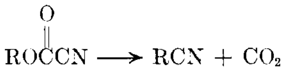
$$\mathrm{RO\overset{\overset{O}{\|}}{C}Cl \longrightarrow RCl + CO_2}$$

Chloroformates from primary alcohols generally decompose at a convenient rate in a temperature range of 150 to 250°, whereas those from tertiary alcohols are often too unstable for isolation at room temperature. At elevated temperatures, depending on the structure of the alkyl group, the competing elimination reaction can be significant. Recently, Lewis and co-workers[1d] reported extensive kinetic, optical activity, and isotopic studies, including an examination of the effect of structure of the alkyl group, and concluded that the chloroformate decomposition substitution reaction was best explained by a polar transition state of the type:



and that the elimination reaction occurred by a polar mechanism.

As a new synthetic route to nitriles, the pyrolysis of cyanoformates appeared attractive. Methyl cyanoformate, prepared from methyl chloroformate



$$\mathrm{RO\overset{\overset{O}{\|}}{C}CN \longrightarrow RCN + CO_2}$$

and sodium cyanide,[2] was passed through a heated tube at reduced pressure. However, it was found that no reaction occurred in the 200–300° region that is normal for decomposition of chloroformates, and a temperature of 700° was required to promote loss of carbon dioxide and formation of acetonitrile in a yield of 30 to 40%. Ethyl cyanoformate partly decomposed at 400° to ethylene, hydrogen cyanide, and carbon dioxide and no propionitrile was detected: complete decomposition occurred at 700°.

In order to explore the generality of this decomposition reaction, two new cyanoformates, benzyl and cyanomethyl, were prepared. Benzyl cyanoformate decomposed smoothly at 700° to benzyl cyanide in 50% yield. The conversion of cyanoformate to nitrile was higher for benzyl than for methyl but was also accompanied by an increase of by-products. Cyanomethyl cyanofor-

---

[1] (a) A. R. Choppin, H. A. Frediani, and G. F. Kirby, Jr., *J. Am. Chem. Soc.*, **61**, 3176 (1939); A. R. Choppin and G. F. Kirby, Jr., *ibid.*, **62**, 1592 (1940); A. R. Choppin and E. L. Compere, *ibid.*, **70**, 3797 (1948); (b) S. T. Bowden, *J. Chem. Soc.*, 310 (1939); (c) K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955); (d) E. S. Lewis and W. C. Herndon, *ibid.*, **83**, 1955 and 1961 (1961); E. S. Lewis, W. C. Herndon, and D. C. Duffey, *ibid.*, 1959.

[2] W. Gluud, W. Nusler, and K. Keller, German Patent 592,539 (1934), *Chem. Abstr.*, **28**, 3417 (1934).

TABLE I

PYROLYSIS OF CYANOFORMATES—MACROSCALE

Cyanoformate $\mathrm{\overset{O}{\overset{\|}{}}}$ R of ROCCN	Sample size	Pyrolysis conditions[a] Temp., °C.	Pyrolysis conditions[a] Press., mm.	Gaseous products	Liquid products: Total yield	Liquid products: Product	Liquid products: Relative %, by infrared	Liquid products: Relative %, by GC[b]	Liquid products: Over-all % yield[c]
CH_3	2 ml.	600	120	CO_2 (?)	2 ml.	$\mathrm{CH_3O\overset{O}{\overset{\|}{C}}CN}$	~99	. .	. .
CH_3	2 ml.	800	115	CO_2 (?)	1.3 ml.	CH_3CN	25	30	(40)
						$\mathrm{CH_3O\overset{O}{\overset{\|}{C}}CN}$	75	65	(42)
						Unidentified	. . .	5	. .
CH_3	7.83 g.	800	120[a]	CO_2 + HCN	4.73 g.	CH_3CN	20	25	31
						$\mathrm{CH_3O\overset{O}{\overset{\|}{C}}CN}$	80	67	41
						Unidentified[d]	. . .	7	. .
C_2H_5	2 ml.	200	20	Negligible	2 ml.	$\mathrm{C_2H_5O\overset{O}{\overset{\|}{C}}CN}$	100	. .	. .
C_2H_5	2 ml.	400	120	CO_2, HCN, $CH_2{=}CH_2$	1.3 ml.	$\mathrm{C_2H_5O\overset{O}{\overset{\|}{C}}CN}$	~99	. .	. .
C_2H_5	2 ml.	700	195	CO_2, HCN, $CH_2{=}CH_2$	0	. . .	. . .	. .	. .
$C_6H_5CH_2$	5.48 g.	800	110–120[a]	CO_2, HCN	2.72 g.	$C_6H_5CH_2CN$	95	84	57
						$\mathrm{C_6H_5CH_2O\overset{O}{\overset{\|}{C}}CN}$	5	3	1
						Unidentified (8 products)	. . .	13	. .
$C_6H_5CH_2$	7.25 g.	700	120	CO_2, HCN	3.76 g.	$C_6H_5CH_2CN$	90	80	50
						$\mathrm{C_6H_5CH_2O\overset{O}{\overset{\|}{C}}CN}$	5	3	1
						Unidentified (9 products)	. . .	17	. .
$NCCH_2$	2.80 g.	800	120	CO_2, HCN	1.11 g.[e]	$CH_2(CN)_2$[f]	10	12	8
						$\mathrm{NCCH_2O\overset{O}{\overset{\|}{C}}CN}$	70	43	17
						Unidentified (10 products)	. . .	45	. .
C_6H_5	~4 g.	600	120[a]	Trace HCN, CO_2	3 g.	$\mathrm{C_6H_5O\overset{O}{\overset{\|}{C}}CN}$	>98	0	. .

[a] Addition times were approximately 8–10 min. with exception of runs marked with *a* in which addition times were 25 min. [b] Infrared analysis are approximate by estimation from comparison with spectra of reference samples. Gas chromatographic analysis were carried out using helium carrier gas on 2-m. 20% Silicone 703 on 40–60 mesh Columpak, column temperatures 100°; or 20% Apiezon L on Columpak, column temperature 175°. [c] Calculated from gas chromatographic analysis. [d] Acrylonitrile was identified by mass spectrometric analysis as one low yield by-product. [e] The crude product gave a strong positive color test for malononitrile; W. Kesting, *Ber.*, **62B**, 1422 (1959). This test is negative for cyanomethyl cyanoformate. [f] Malononitrile was recovered unchanged from passage through the pyrolysis tube at 800°.

mate, $\mathrm{NCCH_2O\overset{O}{\overset{\|}{C}}CN}$, was prepared in a few per cent yield by the low temperature reaction of glyconitrile with phosgene followed by reaction of the intermediate chloroformate (not isolated) with hydrogen cyanide and pyridine. This cyanoformate decomposed at 700° to give malononitrile in low yield (8%). Although a large amount of starting material was recovered, more by-products were found. Phenyl cyanoformate was also prepared by reaction of phenyl chloroformate with hydrogen cyanide and pyridine, and was recovered unchanged from pyrolysis at 600°. By contrast phenyl chloroformate disproportionates during distillation at atmospheric pressure to diphenyl carbonate and phosgene and does not pyrolyze to chlorobenzene.[3]

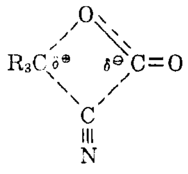
Additional studies of the pyrolysis reaction were carried out on a microscale using a pyrolysis-gas chromatographic apparatus. In this case the results from pyrolysis over quartz chips at 700° with contact times of fifteen to twenty-five seconds were comparable to those on the macroscale at 800° with shorter contact times. Although the course of pyrolysis was not changed when quartz powder was substituted as packing, the pyrolysis temperature was lowered by approximately 100°. (This temperature decrease could be in part due to a small increase in contact time.) With granular sodium

---

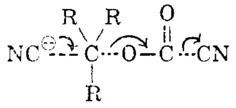
(3) E. Barral and A. Morel, *Compt. rend.*, **128**, 1578 (1899); *Bull. soc. chim.* (France), **21**, 722 (1899).

cyanide packing[4] the decomposition temperature was lowered over 300° to about 250°.

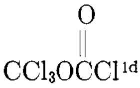
A mechanism consistent with the above data is a unimolecular decomposition with a transition state I analogous to, but of less polar character than, that proposed for chloroformate decomposition. The high reaction temperature is associated with the strong C—C bond in the cyanoformate. The minor yields of by-products, possibly derived from free radicals, and the small effect resulting from a change in surface area argue against an entirely radical course. The catalytic effect of sodium cyanide can result from a stabilization of the polar transition state on the ionic crystal surface or from direct participation of the sodium cyanide in a S_N2 type process with a transition state such as shown by II. The large by-product yield from cyanomethyl cyanoformate can be ascribed to the unfavorable effect of the cyano group (on methyl) on the charge distribution in I (for analogy see the discussion of the abnormal decomposition of



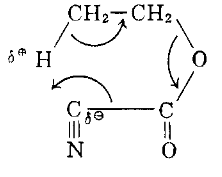
I



II



$CCl_3O\overset{O}{\overset{\|}{C}}Cl$[1d]). The cyclic polar transition state III is suggested to account for the elimination-type decomposition of ethyl cyanoformate.



III

Experimental

Synthesis of Cyanoformates. Ethyl and Methyl.—A slurry of ethyl or methyl chloroformate with an equimolar amount of powdered sodium cyanide (containing approximately 0.2% water) was heated at 40–45° under reflux for several hours, then distilled at reduced pressure. The distillate was carefully fractionated by distillation through a 45-cm. glass helices-packed column. By analysis of each fraction by gas chromatography (silicon oil on firebrick), the yields in the respective preparations were: ethyl cyanoformate (b.p. 117°, $n^{25}D$ 1.3803), 32%; methyl cyanoformate (b.p. 99°, $n^{25}D$ 1.3709), 39%; a small amount of the corresponding carbonate esters and recovered chloroformates were separated in each preparation. A method described in the older literature in which alcohol was used as solvent[5] was not found satisfactory.

Benzyl.—To 34.1 g. of benzyl chloroformate[6] was added 15 g. (0.30 mole) of sodium cyanide in portions with stirring. A slight exothermic reaction was observed, and the mixture was stirred at 45–50° for 8 hr. The product was distilled from the mixture at 30–70° (5–1.5 mm.) and fractionated through a 30-cm. spinning band still. After distillation of 17.8 g. of benzyl chloride, b.p. 74° (18 mm.), 6.7 g. (29% yield) of benzyl cyanoformate was collected, b.p. 80° (2.5 mm.), $n^{25}D$ 1.4050.

Anal. Calcd. for $C_9H_7NO_2$: C, 67.1; H, 4.38; N, 8.7. Found: C, 67.3; H, 4.75; N, 8.2.

The cyanoformate was also characterized by infrared (CN absorption at 2150 cm.$^{-1}$, carbonyl at 1750 cm.$^{-1}$) and pro-

TABLE II

PYROLYSIS OF CYANOFORMATES—MICROSCALE

Pyrolysis tube packing	Pyrolysis temp., °C.	Approx. contact time,[a] sec.	% CH_3CN[b]	% Recovered[b] $CH_3O\overset{O}{\overset{\|}{C}}CN$
a. Methyl cyanoformate[c]				
33 Mesh quartz chips	300	24	0	*ca.* 95[d]
	400	18–21	1	92
	500	21	7	86
	600	18	27	53
	700	15	38	8
Powdered quartz	300	30	0	*ca.* 95
	400	. .	2	82
	500	. .	22	38
	600	. .	44	3
Granular NaCN	200	33	3	76
	250	. .	30	29
	300	30	48	0
	400	24	41	0
b. Ethyl cyanoformate[e]				
				% $C_2H_5O\overset{O}{\overset{\|}{C}}CN$[f]
33 Mesh quartz chips	300	18		97
	400	12		90
	500	6		30
	600	6		0

[a] Estimated from nitrogen samples. [b] Analysis on 12-ft. silica grease (25%) on firebrick chromatography column; column temperature, 78°. Amount of carbon dioxide product was approximately inversely proportional to amount of recovered cyanoformate. A small amount of hydrogen cyanide was observed in addition to other by-products at higher temperature; the amount of hydrogen cyanide was greater over quartz powder. [c] 10-μl. sample, helium flow rate 47–49 ml./min. [d] Sample contained few per cent of dimethyl carbonate as an impurity. Appearance of a few per cent of carbon dioxide at 300° was also noted. [e] Pyrolysis of propionitrile under the conditions employed did not occur to any significant extent until 700°. The products were hydrogen cyanide, ethylene, acetonitrile, and acrylonitrile. [f] Estimated per cent; calibration for sensitivity of products and starting material was not carried out. Hydrogen cyanide, carbon dioxide, and ethylene, in amount corresponding to extent pyrolysis, were also detected.

---

[4] We would like to thank Dr. F. S. Fawcett of this laboratory for suggesting this experiment.

[5] J. U. Nef, *Ann.*, **287**, 308 (1895).

[6] Obtained from Mann and Co. and shown by n.m.r. proton analysis to contain 28% benzyl chloride; with correction for impurity, 0.144 mole of benzyl chloroformate.

[7] Anhydrous glycolonitrile was prepared by vacuum distillation of a 70% aqueous solution; 2% phosphoric acid was used as stabilizer.

ton n.m.r. spectra (single proton resonances at τ of 2.73 and 4.85 in ratio of approximately 2.5:1 for aromatic to methylene protons, respectively).

Cyanomethyl.—A solution of 40 g. (0.50 mole) of pyridine in 300 ml. of anhydrous ether was chilled to −5° in an anhydrous atmosphere, and 55 g. (0.55 mole) of phosgene was condensed into the reaction mixture. The phosgene formed a solid complex with the pyridine which precipitated as a white powder from the ether solution. A solution of 28.5 g. (0.50 mole) of glycolonitrile[7] in 50 ml. of ether was added dropwise to the stirred reaction mixture at a rate such that the temperature did not rise over −5°. Solutions of 19 ml. (13 g., 0.48 mole) of liquid hydrogen cyanide in 80 ml. of ether and 40 g. (0.50 mole) of pyridine in 50 ml. of ether were added to the reaction mixture simultaneously at *ca.* equal rates while the reaction temperature was maintained below 0°. After the addition was completed, the reaction was stirred for 30 min. at 0°, gradually warmed to 15°, and suction filtered to remove the pyridine hydrochloride. The ether was distilled through a 45-cm. glass helices-packed column, and the residual liquid fractionated through a 30-cm. spinning band column. After separation of 2.1 g. (5.6%) of chloroacetonitrile, b.p. 69° (96 mm.), the cyanomethyl cyanoformate, 2.96 g. (5.4%), was collected as a colorless liquid, b.p. 81° (47 mm.), $n^{25}\text{D}$ 1.4231. Further purification was accomplished by recrystallization from ether at −40° to give a white, crystalline solid which melted at room temperature.

Anal. Calcd. for $C_4N_2H_2O_2$: C, 43.6; N, 25.4, H, 1.80; Found: C, 43.8; N, 25.1, 25.2; H, 1.90.

A single proton resonance (τ of 5.13) was observed in the n.m.r. spectrum and the infrared spectrum showed absorption at 2150 cm.$^{-1}$ for CN and at 1760 cm.$^{-1}$ for carbonyl.

Phenyl.—A solution of 48 g. (0.30 mole) of phenyl chloroformate and 13 ml. (9.0 g., 0.33 mole) of liquid hydrogen cyanide in 300 ml. of ether was cooled to 0°, and a solution of 24.4 g. (0.35 mole) of pyridine in 25 ml. of ether was added dropwise at a rate such that the reaction temperature was maintained between 0 and 5°. The reaction was strongly exothermic, and pyridine hydrochloride precipitated immediately from the solution. After addition was complete the reaction mixture was warmed to room temperature and suction filtered to remove the pyridine hydrochloride. The ether was distilled, and the residual liquid fractionated through a 45-cm. spinning band column to yield 7.5 g. of phenyl cyanoformate, b.p. 66–68° (4.7 mm.). A white, crystalline residue of 14.5 g. was identified as diphenyl carbonate. The phenyl cyanoformate crystallized on standing and was recrystallized from hexane as white platelets, m.p. 51.6–53.0°.

Anal. Calcd. for $C_8H_6NO_2$: C, 64.9; H, 4.09; N, 9.5; mol. wt., 148. Found: C, 65.4; H, 3.4, 3.7; N, 9.7; mol. wt., 176, 172.

The infrared spectrum of phenyl cyanoformate had typical cyano and carbonyl absorption at 2150 cm.$^{-1}$ and 1760 cm.$^{-1}$, respectively.

Pyrolysis of Cyanoformates.—The general procedure involved dropwise addition of the cyanoformate in the top of the pyrolysis tube which was mounted vertically and connected through U-traps to a vacuum system. The pyrolysis tube was a 1-in.-diameter quartz tube, and was packed with cut quartz tubing and heated over 1 ft. of its length. The system was operated at reduced pressure, and the product was collected in a liquid nitrogen trap at the exit of the tube. The gaseous product was distilled into a second liquid nitrogen trap and transferred to a gas cell for infrared analysis. The liquid products were characterized by comparison of their infrared spectra with those of reference samples and by gas chromatographic separtion and mass spectrometric analyses. The pyrolysis conditions and results are summarized in Table I.

The microscale pyrolysis studies were carried out in a pyrolysis-gas chromatographic unit. The pyrolysis tube consisted of a $^1/_8$-in.-i.d. Iconel tube heated externally over a 10-in. length. The sample size was about 10 μl. and helium was used as carrier gas. Contact times were estimated by the difference in retention time of a nitrogen sample injected at ports in the upper and lower ends of the pyrolysis tube. The exhaust gases were fed directly into a gas chromatographic unit for analysis, and identification was accomplished by comparison of retention times with reference samples supplemented where needed by collection and characterization by infrared and mass spectrometric analysis. The results are summarized in Table II.

Acknowledgment.—We would like to thank Dr. T. J. Kealy for advice and assistance in carrying out the pyrolysis experiments and Mrs. Adah B. Richmond and Mr. J. W. Robson for the gas chromatographic analyses.