Thermal Decomposition of Ethyl Cyanoformate: Kinetics and Mechanism

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The thermal decomposition of ethyl cyanoformate was investigated between 310 and 405 °C at subambient pressures. Two parallel reactions account for the observed products CO_2, C_2H_4, HCN, and EtCN, the last being the result of internal substitution with simultaneous loss of carbon dioxide, the reaction occurring heterogeneously, while the olefin-forming elimination was found to be homogeneous and molecular. The temperature dependence for this reaction is given by equation (i). The energy of activation of this and analogous reactions of compounds of

$$k_e/\mathrm{s}^{-1} = 10^{11.44 \pm 0.25} \exp -42,600 \pm 610/RT \ (340\text{—}405\ ^\circ\mathrm{C}) \qquad \text{(i)}$$

formula $XCO_2C_2H_5$ are linearly correlated with Taft's polar constants σ^* for the group X.

THE production of alkyl chlorides in the pyrolysis of the corresponding chloroformates [1-3] suggests the possibility of obtaining nitriles *via* the analogous reaction of cyanoformates. Such a possibility has been investigated by Sheppard [4] who has reported some qualitative results on

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[1] E. S. Lewis and K. Witte, *J. Chem. Soc.* (*B*), 1968, 1198.

[2] V. R. Stimson and R. L. Johnson, personal communication.

[3] M. Matzner, R. P. Kurkjy, and R. J. Cotter, *Chem. Rev.*, 1964, **64**, 645.

[4] W. A. Sheppard, *J. Org. Chem.*, 1962, **27**, 3756.

the thermal decomposition of a series of cyanoformates containing no β-hydrogen atom, except for the ethyl compound, which was believed to decompose entirely through the elimination route to give HCN, CO_2, and C_2H_4. This is contrary to our finding,[5] that in a Pyrex glass batch reactor, the yield of propionitrile can be made as high as desired by appropriate treatment of the reaction vessel. We now report a detailed study of the mechanism of pyrolysis of ethyl cyanoformate, and in more general terms this paper also deals with a hypothesis that pyrolysis of compounds of formula XCO_2R ($X = H, C_nH_m, C_nH_mO, Cl$, or CN, $R = C_nH_m$) can be explained by a common mechanism. According to this, at least two parallel reactions compete more or less successfully depending upon the nature of X and R. For X groups other than alkyl, for which one reaction, namely the olefin-forming elimination, is overwhelmingly predominant, a search of the literature yields very poor results. With few exceptions, the different alternative reaction paths have not been well identified and only very recently have reliable quantitative data been published [2,6-8] on these compounds.

RESULTS

When ethyl cyanoformate at pressures of 50—300 mmHg is heated between 300 and 420 °C it decomposes at measurable rates according to equation (1). The stoicheiometry

$$NCCO_2C_2H_5 \xrightarrow{k_e} HCN + CO_2 + C_2H_4 \qquad (1a)$$

$$NCCO_2C_2H_5 \xrightarrow{k_s} CO_2 + EtCN \qquad (1b)$$

being confirmed, chromatographic determination of ethylene and carbon dioxide allowed the partition of the rate constant for disappearance of cyanoformate into reactions (1a) and (1b). Alternatively, the ratio of final to initial pressure can be used for the same purpose [5] and both methods are successful although for very long reaction times the first procedure has been preferred for practical reasons. Calculations were carried out using equations (2)—(4). As t tends to 0 the derivative of equation (3)

$$\frac{P_\infty}{P_0} - 2 = \frac{\text{Pressure of } C_2H_4}{\text{Pressure of } CO_2} = \frac{k_e}{k_e + k_s} \qquad (2)$$

$$-k_{\text{total}} = -(k_e + k_s) = \frac{1}{t}\ln\frac{(2 + F_1)P_0 - P_t}{(1 + F_1)P_0} \qquad (3)$$

reduces to (4) where F_1 is the selectivity for products of

$$k_{\text{total}}{}^0 = V_0/P_0(1 + F_1) = k_e{}^0 + k_s{}^0 \qquad (4)$$

reaction (1a), P_∞ is total final pressure, P_0 is the initial pressure of the reactant, and P_t is the total pressure at time t.

In practice, the pressure–time curve was fitted by computer to a polynomial of the fourth degree from which P_0 and V_0 were directly evaluated. Both rate constants k_e and k_s are first order with respect to concentration as shown by the linear relationship found between log (initial rate) and log (initial pressure of reactant) with slopes 1·09 (correlation coefficient r 0·992) and 0·970 (r 0·990) at 341 and 382 °C respectively. Nevertheless, at temperatures below 340 °C the calculated first-order rate constants decrease significantly as the reaction proceeds (Figure 1)

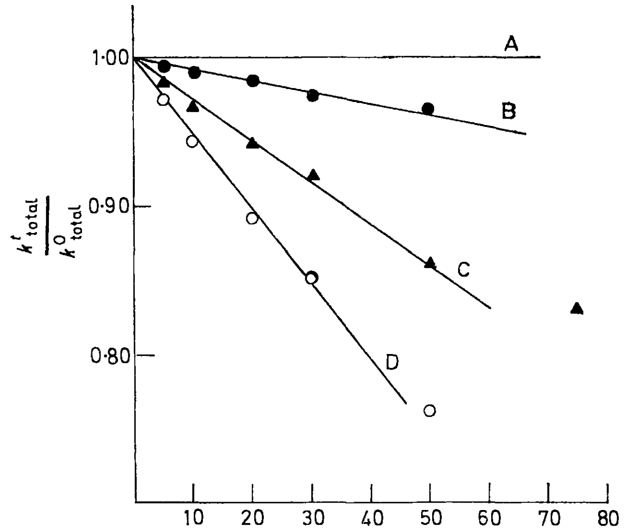

FIGURE 1 Fall off in the first-order rate constant with increasing conversion: A, higher temperature showing no trend; B, 340 °C; C, 330 °C; D, 310 °C

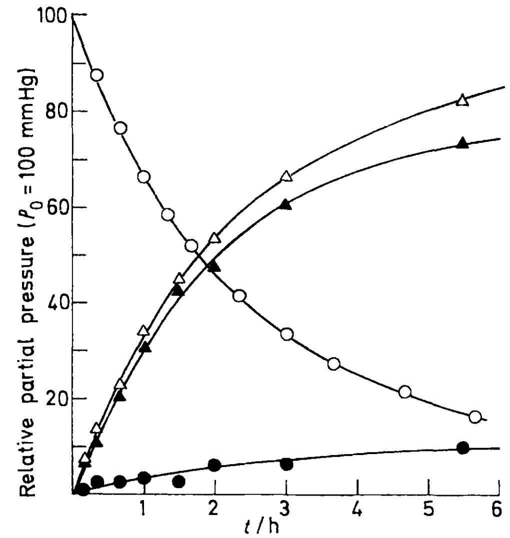

FIGURE 2 Reaction profile at 331 °C: ○, cyanoformate; ▲, ethylene; △, carbon dioxide; ●, propionitrile

so that between 310 and 340 °C only the limiting specific rates for t approaching zero, $k_e{}^0$ and $k_s{}^0$, are well defined, although neither addition of the products of the reaction nor changes in the initial concentration of reactant seem to have any significant effect on the value of $k_e{}^0$. The effect on $k_s{}^0$ is more difficult to estimate as this constant is extremely variable and depends on several other factors.

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[5] N. Barroeta and V. De Santis, paper presented at the IIIrd Iberoamerican Symposium on Catalysis and Thermal Reactions, Caracas, 1972.

[6] N. J. Daly and F. Ziolkowski, *J.C.S. Chem. Comm.*, 1972, 911.

[7] N. J. Daly and F. Ziolkowski, *Austral. J. Chem.*, 1971, **24**, 2541.

[8] D. B. Bigley and C. N. Wren, *J.C.S. Perkin II*, 1972, 2359.

This point, however, was not investigated in greater detail as we chose to concentrate on the upper part of the temperature interval, from 340 to 405 °C

As reaction (1b) is very sensitive to changes in the reaction vessel, we find it useful to define the ' normal conditions ' as employing a Pyrex vessel (*ca.* 250 ml) with a surface : volume ratio of 1·0 cm^{-1} and whose walls are covered by carbonaceous material resulting from the pyrolysis of t-butyl thiocyanate, carefully preserved from contact with air. A reaction profile obtained with this reaction vessel is shown in Figure 2.

In order to ascertain the exact form in which heterogeneous processes influence the overall reaction, we conducted the pyrolysis in a variety of vessels in which not only the type of surface but also the area : volume ratio was varied. This included PbO, Pt, NaCN, and Ag coated vessels but all these experiments confirmed the homogeneous nature of the elimination leading to CO_2, HCN, and C_2H_4.

TABLE 1

Variation of the rate constants with temperature *

Temp. (°C)	Selectivity (F_1)	$10^4k_e{}^0$/s^{-1}	$10^4k_e{}^t$/s^{-1}	$10^4k_s{}^0$/s^{-1}	$10^4k_s{}^t$/s^{-1}
310·0	0·699	0·317 ± 0·15		0·137 ± 0·006	
318·8	0·795	0·593 ± 0·013		0·153 ± 0·007	
330·7	0·853	1·02 ± 0·066		0·182 ± 0·011	
341·0	0·887	1·87 ± 0·073	1·85 ± 0·044	0·238 ± 0·010	0·235 ± 0·006
351·2	0·915	3·42 ± 0·142	3·37 ± 0·062	0·318 ± 0·013	0·308 ± 0·014
361·3	0·934	5·93 ± 0·215	5·92 ± 0·141	0·418 ± 0·015	0·418 ± 0·011
371·6	0·942	9·60 ± 0·568	9·65 ± 0·356	0·592 ± 0·035	0·595 ± 0·022
382·5	0·943	15·6 ± 1·10	17·1 ± 1·03	0·943 ± 0·066	0·958 ± 0·060
394·1	0·927	25·5 ± 1·11	26·0 ± 1·15	2·00 ± 0·084	2·05 ± 0·085
404·6	0·872	53·7 ± 2·41	55·6 ± 2·13	7·83 ± 0·313	8·17 ± 0·408

* All values refer to ' normal conditions ' (see text).

Ethyl cyanoformate was also pyrolysed in the presence of the reaction products, oxygen, and cyclohexene but none of these had any significant effect on the overall kinetics of the reaction with the exception of cyclohexene which in large quantities (>*ca.* 130%) is able to suppress the production of propionitrile.

When examining the effect of temperature on the rate constants (Table 1) it was observed that the Arrhenius plots for $k_e{}^0$ and $k_e{}^t$, gave somewhat different results, but this is unexceptional, especially considering that the temperature ranges are different. The actual equations are (5) and (6); we consider $k_e{}^t$ the more representative of the reaction.

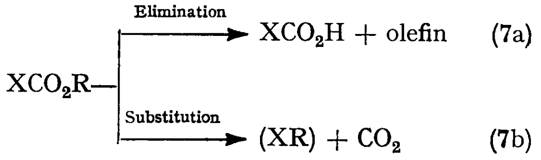
$$\log k_e{}^0/\mathrm{s}^{-1} = 11{\cdot}00 \pm 0{\cdot}21 - 41{,}340 \pm 580/2{\cdot}303RT \ (310\text{—}450\ ^\circ\mathrm{C}) \quad (5)$$

$$\log k_e{}^t/\mathrm{s}^{-1} = 11{\cdot}44 \pm 0{\cdot}25 - 42{,}600 \pm 610/2{\cdot}303RT \ (340\text{—}405\ ^\circ\mathrm{C}) \quad (6)$$

DISCUSSION

After studying a series of cyanoformates without a β-hydrogen atom Sheppard showed that the main products of pyrolysis are nitriles and carbon dioxide.[4,8] On the other hand, ethyl cyanoformate was believed[4] to decompose entirely *via* the elimination mode into ethylene, hydrogen cyanide, and carbon dioxide with no traces of propionitrile, even when the reaction took place on quartz powder or sodium cyanide catalyst.

We have found, however, that the yield of propionitrile can be varied at will by a proper choice of the reaction conditions. This concurs with the idea that compounds of general formula XCO_2R in which R has at least one β-hydrogen atom decompose according to reaction (7)



$$XCO_2R \xrightarrow{\text{Elimination}} XCO_2H + \text{olefin} \quad (7a)$$

$$XCO_2R \xrightarrow{\text{Substitution}} (XR) + CO_2 \quad (7b)$$

providing X does not contain a hydrogen-bearing nitrogen atom next to the carbonyl group in which case an isocyanate may be formed as well. The relative importance of elimination *versus* substitution for a given set of conditions is determined by the type and structure of X and R.

A summary of the literature data for some ethyl compounds of formula XCO_2R is presented in Table 2 but owing to the wide scatter in log *A* and the use of different techniques when studying these reactions the relative rates cannot be directly correlated. However, it is apparent that the higher the electron-attracting ability of the group X the lower the activation energy for elimination, but also the greater the tendency for substitution. The activation energies for elimination in compounds $XCO_2C_2H_5$ where X = NC, Cl, MeO, Me, EtO, or Et (Table 2) are linearly related to the Taft's polar substituent constants (σ^*)[9] by the equation

TABLE 2

Kinetic data for decomposition of $XCO_2C_2H_5$

X	E_a/kcal mol^{-1}	log (A/s^{-1})	Ref.
H	44·14	11·33	11
H [a]	48·3	12·4	13
Me	48·0	12·59	*c*
Et	48·5	12·72	*c*
MeO [b]	46·0	13·7	*d*
Cl	43·7	12·57	2
NC	42·6	11·44	This work
Bu^t	44	11·24	12
Bu^t [a]	48·1	12·6	13

[a] These are the preferred values of ref. 13. [b] These values are considered high in ref. 13 but very recently Bigley *et al.*[8] have obtained new evidence which supports the activation parameters of footnote *d* for diethyl and ethyl methyl carbonates. [c] A. T. Blades and P. W. Gilderson, *Canad. J. Chem.*, 1960, **38**, 1407. [d] A. S. Gordon and W. P. Norris, *J. Phys. Chem.*, 1965, **69**, 3013.

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[9] V. A. Palm, *Russ. Chem. Rev.*, 1961, **30**, 471.

E_a/kcal mol^{-1} = 48·19 − 1·548σ^* with r 0·999 and it is precisely for those compounds with the highest σ^* value where the substitution reaction has been well identified. The implications of the relationship between E_a and σ^* parallel that demonstrated by Emovon[10] between the rate constant for elimination from t-butyl esters and the pK_a of the acid.

Considering the wide range of σ^* values to which the correlation of E_a with σ^* applies, this relationship has a large predictive potential. It is noteworthy, for example, that when literature values for ethyl formate[11] (X = H) and ethyl pivalate[12] (X = Bu^t) are added to the graph they fall far from the line. However, these values have been considered too low by Benson and O'Neal[13] who prefer the estimated ones which do agree reasonably well with those predicted by our correlation.

As mentioned above reaction (1a) is homogeneous whereas reaction (1b) is, at least to a large extent, heterogeneous although the details of the latter process are by no means clear. Carbonaceous surfaces are most effective in avoiding propionitrile formation but this inhibitory effect can be eliminated by air, even in amounts far below that required to burn all the carbon. On the other hand NaCN is the most active catalyst, leading to selectivities in propionitrile as high as 0·66. We feel, however, that in order to make precise proposals about the mechanism of reaction (1b) experiments have to be designed in which the heterogeneous character of the reaction is exploited. This will be a subject for our further research. On the other hand reaction (1a) follows the general pattern of carboxylic ester pyrolysis. In this sense we do not think there is enough evidence to support Sheppard's transition state in which the six-membered ring is closed by cyano-carbon attack on the β-hydrogen atom. In fact the charge distribution within the cyano-group makes the nitrogen atom more likely to interact with the β-hydrogen, leading to a seven-membered ring transition state. This is an attractive possibility in view of the relatively low pre-exponential factor obtained in this study. Nevertheless, with the evidence we have we prefer the transition state for normal ester pyrolysis[13] for the elimination. Such a mechanism implies the elimination of cyanoformic acid which will then decompose into the observed products. This decarboxylation is a special case of the substitution of XCO_2R with R = H. The decarboxylation of unsaturated acids[14] occurs readily below 300 °C through a six-centre transition state, all of which is a consequence of the presence of the double bond in the group X. In those acids in which X has great electron-attracting power such as Cl, CN, or HO_2 this becomes the driving force for decarboxylation, probably proceeding through a four-centre transition state and taking place at relatively low temperatures. Oxalic acid for example, in which X = HO_2C, has σ^* 2·9 and decomposes below 150 °C.[15] Cyanoformic acid, its mononitrile, having an X group with an even higher σ^* is expected to be more unstable as is the case.

For a normal ester type transition state one would expect a pre-exponential factor somewhat higher than obtained here. It is possible that the figure we report is affected by some systematic and so far hidden complication, probably related to the simultaneous heterogeneous substitution.

EXPERIMENTAL

Commercial ethyl cyanoformate (Aldrich) distilled to give purity >99·5% was used throughout.

The products were analysed by g.l.c. in a 4 ft × 1/8 in Porapak Q column at 80—100 °C. Under these conditions all products were separated with the exception of the starting material which was retained in the column. The composition of the reaction mixture was fully determined by mass and i.r. spectrometry as well as by chemical analysis of the individual components.

The kinetics were followed manometrically according to techniques described elsewhere[16] and most of the rate constants were calculated using an IBM-1130 computer.

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[10] E. V. Emovon, *J. Chem. Soc.* (*B*), 1967, 1246.

[11] A. T. Blades, *Canad. J. Chem.*, 1954, **32**, 366.

[12] J. T. Cross and V. R. Stimson, *Austral. J. Chem.*, 1967, **20**, 177.

[13] S. Benson and H. O'Neal, 'Kinetic Data on Unimolecular Reactions,' U.S. Dept. of Commerce, Pub. No. NSRDSNBS–21, Washington, 1970.

[14] D. B. Bigley and R. W. May, *J. Chem. Soc.* (*B*), 1967, 557.

[15] G. Lapidus, D. Barton, and P. Yankwich, *J. Phys. Chem.*, 1964, **68**, 1863.

[16] N. Barroeta, V. De Santis, and R. Mazzali, *J.C.S. Perkin II*, 1972, 769.