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Elimination kinetics of *β*-hydroxynitriles in the gas phase

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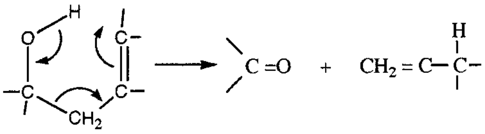
ABSTRACT: The gas-phase elimination kinetics of primary, secondary and tertiary *β*-hydroxynitriles were examined in static seasoned vessels over the temperature range 360–450 °C and pressure range 47–167 Torr (1 Torr = 133.3 Pa). These reactions are homogeneous, unimolecular and follow a first-order rate law. The rate coefficients are given by the Arrhenius equation: for 3-hydroxypropionitrile $\log k_1 = (14.29 \pm 0.47) - (234.9 \pm 6.3)$ kJ mol^{-1} $(2.303\ RT)^{-1}$; for 3-hydroxybutyronitrile $\log k_1 = (13.76 \pm 0.10) - (222.6 \pm 0.7)$ kJ mol^{-1} $(2.303RT)^{-1}$; and for 3-hydroxy-3-methylbutyronitrile $\log k_1$ (s^{-1}) $= (13.68 \pm 0.68) - (212.5 \pm 8.7)$ kJ mol^{-1} $(2.303RT)^{-1}$. The decomposition rates of the *β*-hydroxynitriles increase from primary to tertiary carbon containing the OH group. The rates for the *β*-hydroxynitriles are found to be slower than those for the corresponding *β*-hydroxyacetylene analogs. The value of log *A* from 13.7 to 14.4 and the small positive $\Delta S^{\neq}$ indicate a mechanism different from a six-centered cyclic transition state. These data appear to indicate that a four-membered cyclic transition state or a quasi-heterolytic mechanism is conceivable. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: *β*-hydroxynitriles; elimination kinetics; gas phase

INTRODUCTION

Several studies on the pyrolyses of *β*-hydroxyalkenes[1,2] and *β*-hydroxyalkynes[3] have shown that they proceed via a six-membered cyclic transition state as pictured in Eqn (1). Moreover, the replacement of the double bond with the 1,2-aromatic π-bond of benzene[4] and of pyridine[5] was also found to eliminate in a similar manner [Eqn (1)].


(1)

The increased rates found with *β*-hydroxyacetylenes compared with their olefinic analogs were attributed to the greater nucleophilicity of the triple bond toward the hydroxy hydrogen.[3] In addition, the elimination process of Eqn (1) by the nucleophilic attack of the more polar C=N bond of 2-(2-hydroxyethyl)pyridine was found, as expected, to be faster than that for the corresponding 2-hydroxyethylbenzene.[5]

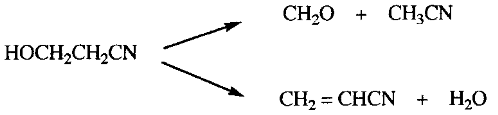
The faster rates due to the greater nucleophilicity of the C≡C with respect to the C=C bond and the C=N with respect to the C=C bond for the abstraction of the hydrogen of the OH group led us to examine the reactivity differences in elimination reaction (1) between C≡C and C≡N, that is, the *β*-hydroxyacetylenes and their corresponding *β*-hydroxynitriles. The literature cites only a patented work on *β*-hydroxynitrile decomposition.[6] These compounds when brought into contact with pumice at 300–600 °C yielded the corresponding alkyl cyanide and aldehyde or ketone.

With this background, it seemed of interest to study the homogeneous gas-phase pyrolysis kinetics of $HOCH_2CH_2CN$, $CH_3CH(OH)CH_2CN$ and $(CH_3)_2C(OH)CH_2CN$ and to make a comparison with the *β*-hydroxyacetylene analogs.

RESULTS AND DISCUSSION

3-Hydroxypropionitrile

The kinetics for the pyrolytic elimination of this substrate were reasonably determined within a temperature range of 40 °C. The reaction is described as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Stoichiometry (2) requires $P_f/P_0 = 2$, where P_f and P_0 are the final and initial pressures, respectively. The

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Table 1. Ratio of final (P_f) to initial (P_0) pressure

Substrate	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Average
3-Hydroxypropionitrile[a,b]	410.6	106	198	1.87	
	419.5	77	210.5	1.90	
	429.5	112	208.5	1.86	1.89
	439.4	73	140.5	1.92	
3-Hydroxybutyronitrile[a,b]	409.9	60.5	127	2.10	
	419.4	66	143.5	2.16	
	429.1	121.5	241	1.98	2.08
	449.9	134	279	2.08	
3-Hydroxy-3-methylbutyronitrile[a,b]	379.7	148	260.5	1.76	
	388.8	109	204	1.87	
	400.7	127	242	1.91	1.86
	410.0	104	197.5	1.90	

[a] Seasoned vessels with allyl bromide.
[b] In the presence of the free radical suppressor toluene.

Table 2. Stoichiometry of the elimination reaction[a,b]

Substrate	Parameter	Values					
3-Hydroxypropionitrile at 429.5 °C	Time (min)	4	7	10	15	20	30
	Substrate (%) (GC)	20.5	25.8	39.7	45.7	55.8	74.8
	Acetonitrile (%) (GC)	16.5	20.4	26.5	34.7	37.3	54.9
	Acrylonitrile (%) (GC)	5.0	7.1	9.6	15.0	21.8	24.9
3-Hydroxybutyronitrile at 419.4 °C	Time (min)	4	6	8	12	14	
	Reaction (%) (pressure)	20.1	30.6	39.3	49.3	54.6	
	Acetonitrile (%) (GC)	18.2	29.8	37.2	47.7	55.8	
3-Hydroxy-3-methylbutyronitrile at 400.7 °C	Time (min)	2	5	8	10	12	
	Reaction (%) (pressure)	19.3	38.1	52.7	58.5	68.8	
	Substrate (%) (GC)	21.4	38.4	55.4	61.5	70.2	
	Acetonitrile (%) (GC)	19.4	39.4	52.4	61.2	70.0	

[a] Vessel seasoned with allyl bromide.
[b] In the presence of the inhibitor toluene.

average experimental result at four different temperatures and 10 half-lives is 1.89 (Table 1). The observed $P_f/P_0 \leq 2$ of the overall elimination was found to be due to a small degree of polymerization of the formaldehyde product. Further verification of the stoichiometry of Eqn (2) was possible by comparing, up to 75% decomposition, the quantitative gas chromatographic (GC) analyses of the amount of unreacted substrate with the sum of the amount of the products acetonitrile and acrylonitrile (Table 2).

To examine the effect of the surface area on the rate of pyrolysis, several runs in the presence of at least a twofold amount of toluene inhibitor were carried out in a vessel with a surface-to-volume ratio six times greater than that of the normal vessel. The rates of formation of acetonitrile from 3-hydroxypropionitrile were unaffected in seasoned packed and unpacked vessels. However, clean packed and unpacked Pyrex vessels showed a dramatic effect on the *k* values, which could not reasonably be estimated (Table 3).

The effect of different proportions of the free radical suppressor toluene on the elimination process is shown in Table 4. No induction period was observed and the rates were reproducible with a relative standard deviation not greater than 5% at a given temperature.

Table 3. Homogeneity of the reaction

Substrate	S/V (cm^{-1})[a]	$10^4 k_1$ (s^{-1})[b]	$10^4 k_1$ (s^{-1})[c]
3-Hydroxypropionitrile at 429.5 °C	1	—[d]	5.22[e]
	6	—[d]	5.54[e]
3-Hydroxybutyronitrile at 419.4 °C	1	8.65	9.20
	6	7.08	9.57
3-Hydroxy-3-methylbutyronitrile at 388.8 °C	1	10.42[f]	8.17[e]
	6	39.54[f]	8.01[e]

[a] S = surface area, V = volume.
[b] Clean Pyrex vessel.
[c] Seasoned with allyl bromide.
[d] *k* Values very irregular.
[e] *k* Values of acetonitrile formation.
[f] Average *k* values.

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Table 4. Effect of the free radical inhibitor toluene on rates[a]

Substrate	P_0 (Torr)	P_f (Torr)	P_f/P_0	10^4k_1 (s^{-1})
3-Hydroxypropionitrile at 429.5 °C	109	53	0.5	6.93
	101	147.5	1.5	6.83
	70	157	2.2	6.31
	47	162	3.5	6.71
3-Hydroxybutyronitrile at 419.4 °C	122	—	—	9.09
	150	135	0.9	9.12
	106.5	137.5	1.3	9.68
	63	135.5	1.8	9.33
3-Hydroxy-3-methyl-butyronitrile at 400.7 °C	132	—	—	16.81
	98	110	0.9	16.88
	93.5	107	1.1	16.73
	88	171	1.9	16.79

[a] Vessel seasoned with allyl bromide.

The rate coefficients, in seasoned vessels and in the presence of toluene, were found to be independent of the initial pressure of the substrate, and the first-order plots are satisfactorily linear up to about 75% reaction (Table 5). The temperature dependence of the overall rate coefficients, at the 90% confidence level with a least-squares method, is described in Table 6.

The partial rates of the formation products as described by Eqn (2) were determined by the quantitative gas chromatographic analyses of acetonitrile and acrylonitrile. The variation of the rate coefficients for the formation of these products with temperature (Table 7) gives, by the least-squares procedure and with 90% confidence limits, the following Arrhenius equations: for acetonitrile formation $\log k_1$ (s^{-1}) = (14.37 ± 0.57) − (237.7 ± 7.7) kJ mol^{-1} $(2.303RT)^{-1}$ and for acrylonitrile formation $\log k_1$ (s^{-1}) = (13.12 ± 0.93) − (227.1 ± 12.4) kJ mol^{-1} $(2.303RT)^{-1}$.

Table 7. Variation of rate coefficients with temperature for product formation from 3-hydroxypropionitrile pyrolysis

Temperature (°C)	10^4k_1 (s^{-1}) Acetonitrile	Acrylonitrile
410.6	1.63	0.60
420.6	2.94	1.02
429.5	5.11	1.70
439.1	8.60	2.96

3-Hydroxybutyronitrile

The elimination products of the 3-hydroxybutyronitrile described by Eqn (3) suggest a theoretical P_f/P_0 ratio of 2. The average experimental P_f/P_0 value at four different temperatures and 10 half-lives is 2.08 (Table 1). Additional verification of stoichiometry (3), up to 60%

Table 5. Variation of rate coefficients with initial pressure[a,b]

Substrate	Parameter	Values				
3-Hydroxypropionitrile at 429.5 °C	P_0 (Torr)	47	70	101	109	67
	10^4k_1 (s^{-1})	6.71	6.31	6.13	6.93	6.71
3-Hydroxybutyronitrile at 419.4 °C	P_0 (Torr)	63	103	116	150	
	10^4k_1 (s^{-1})	9.46	9.11	9.37	9.47	
3-Hydroxy-3-methylbutyronitrile at 400.7 °C	P_0 (Torr)	88	93.5	112	136	
	10^4k_1 (s^{-1})	16.79	16.73	16.51	16.30	

[a] Vessel seasoned with allyl bromide.
[b] In the presence of the inhibitor toluene.

Table 6. Variation of rate coefficients with temperature[a,b]

Substrate	Parameter	Values						
3-Hydroxypropionitrile	Temperature (°C)	410.6	420.6	429.5	439.1			
	10^4k_1 (s^{-1})	2.30	3.96	6.81	11.56			
	$\log k_1$ (s^{-1}) = (14.29 ± 0.47) − (234.9 ± 6.3) kJ mol^{-1} $(2.303RT)^{-1}$							
3-Hydroxybutyronitrile	Temperature (°C)	390.9	400.1	409.9	419.4	429.5	440.1	449.9
	10^4k_1 (s^{-1})	1.78	3.09	5.50	9.35	15.85	28.84	47.86
	$\log k_1$ (s^{-1}) = (13.76 ± 0.10) − (222.6 ± 0.7) kJ mol^{-1} $(2.303RT)^{-1}$							
3-Hydroxy-3-methylbutyronitrile	Temperature (°C)	360.5	370.1	379.7	388.8	400.7	410.0	
	10^4k_1 (s^{-1})	1.51	2.67	4.35	8.17	16.30	27.51	
	$\log k_1$ (s^{-1}) = (13.68 ± 0.68) − (212.5 ± 8.7) kJ mol^{-1} $(2.303RT)^{-1}$							

[a] Seasoned with allyl bromide.
[b] In the presence of the inhibitor toluene.

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decomposition, was obtained by comparing the pressure measurements with the quantitative GC analysis of acetonitrile formation (Table 2).

$$CH_3CH(OH)CH_2CN \longrightarrow CH_3CHO + CH_3CN \qquad (3)$$

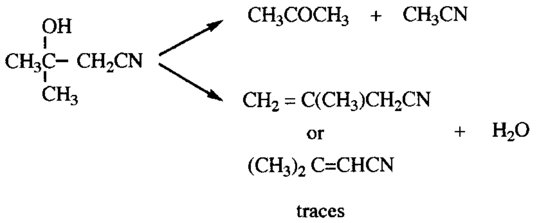
The homogeneity of this pyrolytic elimination was examined in the presence of the inhibitor toluene, by using a packed reaction vessel with a surface-to-volume ratio six times greater than that of the unpacked vessel (Table 3). The packed and unpacked Pyrex vessels seasoned with allyl bromide had no effect on rates. However, the packed and unpacked clean Pyrex vessels gave a significant heterogeneous effect.

The effect of the addition of different proportions of toluene inhibitor is shown in Table 4. Nevertheless, the pyrolysis experiments were carried out in the presence of at least twice the amount of toluene in order to prevent any possible free radical chain reactions. No induction period was observed. The rate coefficients were reproducible with a standard deviation not greater than 5% at a given temperature.

The rate coefficients of this hydroxybutyronitrile were found to be invariant with their initial pressure. The logarithmic plots are linear up to 60% decomposition (Table 5). The variation of the rate coefficients with temperature, in seasoned vessels and in the presence of the inhibitor toluene, is given in Table 6. The data were fitted to the Arrhenius equation shown where 90% confidence limits from a least-squares procedure are quoted.

3-Hydroxy-3-methyl-butyronitrile

The experimental stoichiometry for the pyrolysis of this substrate, as described by Eqn (4), with vessels seasoned with allyl bromide and in the presence of the radical chain suppresor toluene, requires $P_f/P_0 = 2$. The average experimental P_f/P_0 value obtained at four different temperatures and 10 half-lives was 1.86 (Table 1). The small departure from the stoichiometry was due to slight polymerization of the 3-methyl-3-butenenitrile. However, the stoichiometry (4) up to 70% decomposition was confirmed by comparing the percentage decomposition of the substrate from pressure measurements with those obtained by GC analysis of the unreacted substrate and the product acetonitrile (Table 2).



(4)

The homogeneity of reaction (4) was examined by using a vessel with a surface-to-volume ratio six times greater than that of the unpacked vessel. The rates were unaffected by the packed and unpacked seasoned vessels whereas a significant heterogeneous effect was observed with the packed and unpacked clean Pyrex vessels (Table 3). The effect of the free radical inhibitor toluene or cyclohexene is shown in Table 4. No induction period was observed. The rates are reproducible with a standard deviation not greater than 5% at a given temperature.

The first-order rate coefficients of this hydroxynitrile calculated from $k_1 = (2.303/t) \log P_0/(2P_0 - P_t)$ was independent of their initial pressures (Table 5). A plot of $\log (2P_0 - P_t)$ against time (t) gave a good straight line up to 75% reaction. The variation of the rate coefficients with temperature and the corresponding Arrhenius equation is given in Table 6 (90% confidence limits from a least-squares procedure).

The kinetic parameters obtained from the path leading to the formation of acetonitrile and the corresponding aldehyde or ketone in β-hydroxynitriles elimination [Eqn (5)] are compared with those of the β-hydroxyacetylene analogs [Eqn (6) (Table 8)].

$$R^1R^2C(OH)CH_2C \equiv N \longrightarrow R^1R^2CO + CH_3CN \qquad (5)$$

$$R^1R^2C(OH)CH_2C \equiv CH \longrightarrow R^1R^2CO + CH_2 = C = CH_2 \qquad (6)$$

The elimination rates of the β-hydroxynitriles increase from primary to tertiary carbon bearing an OH group (Table 8). As in the pyrolyses of β-hydroxyalkenes[1,2] and β-hydroxyalkynes,[3] the C(OH)—CH$_2$ bond polarization, in the direction of $C(OH)^{\delta +} \cdots CH_2^{\delta -}$, is the limiting factor (structures **1**–**4**).

The rates for the hydroxynitriles are found to be slower than those for the corresponding hydroxyacetylenes

Table 8. Comparative rates and kinetic parameters at 410.0 °C

Compound	10^4k_1 (s^{-1})	Relative rate	E_a (kJ mol^{-1})	Log A (s^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})
$HOCH_2CH_2CN$[b]	1.55	1	237.7 ± 7.7	14.37 ± 0.57	15.1	226.3
$HOCH_2CH_2C{=}CH$[a]	275.4	178	166.9	11.2	−45.6	155.5
$CH_3CH(OH)CH_2CN$	5.75	1	222.6 ± 0.7	13.76 ± 0.10	3.3	211.0
$CH_3CH(OH)CH_2C{=}CH$[a]	501.2	87	164.8	11.3	−43.7	153.4
$(CH_3)_2C(OH)CH_2CN$	26.7	1	212.5 ± 8.7	13.68 ± 0.68	1.87	201.1
$(CH_3)_2C(OH)CH_2C{=}CH$[a]	691.8	26	166.9	11.6	−38.0	155.5

[a] Data from Ref. 3.
[b] Parameters for acetonitrile formation.

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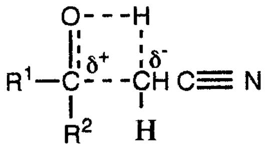
analogs. In addition, the value of log A of 13.7 – 14.4, which leads to a small positive entropy of activation, $\Delta S^{\neq}$, suggests that a four-membered cyclic transition state (**1**) or a quasi-heterolytic cleavage of the C—C bond (**2**) rather than a six-membered cyclic transition state attributed to the β-hydroxyacetylenes[3] (**3**) may occur.

The difference in mechanism of the β-hydroxynitriles may well be that the possible vinylimine formed is a six-membered cyclic transition state (**4**) and may not be a stable intermediate, leaving the H of the OH to be abstracted by the $C^{\delta-}$ as depicted in **1.** In addition, if the bond length between C and N is shorter in nitriles than the bond length of C≡C in acetylenes, it is possible to rationalize that the difference in reactivity may well be due to the nitrile bond being more rigid, thus impeding the structural deformation required for the formation of a six-membered cyclic transition state.

The small positive value of the entropy of activation of the hydroxynitriles indicates a more polar transition state. Apparently, the assumed nucleophilicity of the N of the C≡N bond does not seems to abstract the H of the OH group in a manner analogous to the behaviour of the C≡C bond. In order to describe the most probable mechanism for the elimination process of the hydroxynitrile, further work and additional data are required.



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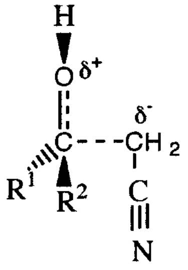

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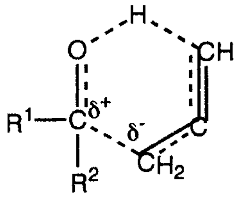

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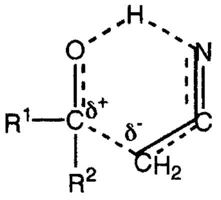

4

EXPERIMENTAL

3-Hydroxypropionitrile. The substrate 3-hydroxypropionitrile (Aldrich) was found to be of better than 99.6% purity (GC: Porapak R, 80–100 mesh). The pyrolysis products acetonitrile (Aldrich) and acrylonitrile (Aldrich) were quantitatively analyzed using the same GC column.

3-Hydroxybutyronitrile. This hydroxynitrile was prepared by treating 2-chloro-1-propanol with KCN in ethanol–water as reported.[7] The reaction product was distilled several times to 96.3% purity as determined by GC (FFAP 7%–Chromosorb G AW DMCS, 80–100 mesh) (b.p. 133–134 °C; lit.[7] b.p. 133–134 °C). The elimination product acetonitrile (Aldrich) was analyzed using a Porapak Q 80–100 mesh GC column.

3-Hydroxy-3-methylbutyronitrile. 2-Hydroxy-2-methyl-1-bromopropane was added to a solution of KCN in ethanol–water. After refluxing, water was added and the mixture was extracted with CH_2Cl_2. Distillation of the extract gave only a product which was collected at 113–115 °C at 20 Torr (1 Torr = 133.3 Pu). The corresponding nitrile was distilled several times to 99.8% purity as determined by GC (Porapak R, 80–100 mesh). NMR: δ 1.3 (s, 6H), 2.4 (s, 2H), 3.2 (s, H). The pyrolysis products acetonitrile (Aldrich) and acetone (Merck) were analyzed using the same Porapak R column.

The identities and the substrates and products were additionally confirmed by mass and NMR spectrometry.

Kinetic experiments. The kinetic experiments were carried out in a static system, seasoned with allyl bromide, and in the presence of the free radical chain inhibitor toluene. The rate coefficients were determined by pressure increase and/or by quantitative GC analyses of the unreacted substrate and products of elimination. The temperature was controlled by a resistance thermometer controller type Omega Solid State Relay SSR2-40A45 and Shinko DIC-PS maintained with ±0.2 °C and measured with a calibrated platinum– platinum–13% rhodium thermocouple. No temperature gradient was observed along the reaction vessel. The substrates were injected directly into the reaction vessel with a syringe through a silicone-rubber septum.

Acknowledgments

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