

Kinetics and mechanisms of the gas-phase elimination of 2-substituted primary, secondary and tertiary hydroxy groups in nitroalkanes

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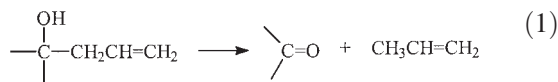
ABSTRACT: The kinetics of the gas-phase elimination of several 2-substituted primary, secondary and tertiary hydroxy groups in nitroalkanes were determined in a static reaction system over the temperature range 220–400 °C and pressure range of 29–235 Torr. The reactions, in seasoned vessels, are homogeneous and unimolecular and obey a first-order rate law. The presence of secondary and tertiary hydroxy substituent at the 2-position of the nitro group in nitroalkanes leads to a retro-aldol type of decomposition. The mechanism may be rationalized in terms of a six-membered cyclic transition state to give the corresponding aldehyde or ketone and the nitroalkane, respectively. However, some of the primary 2-hydroxy groups in nitroalkanes undergo a dehydration process with very limited isomerization to the corresponding alkyl nitrate. The mechanism of dehydration is believed to proceed through a six-membered rather than the already reported four-membered cyclic transition state to give the nitroalkene and water. In the case of the primary hydroxy substituent in 2-methyl-2-nitro-1-pentanol, the products of elimination are HNO₂ gas and 3-hydroxy-2-methyl-1-propene. This reaction is rationalized in terms of a four-membered cyclic transition state type of mechanism. The kinetic and thermodynamic parameters of the hydroxynitroalkane substrates are presented and discussed. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: gas-phase kinetics; eliminations; pyrolyses; 2-hydroxynitroalkanes

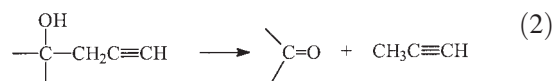
INTRODUCTION

Previous investigations on the gas-phase elimination of different series of primary, secondary and tertiary 2-hydroxy compounds have been reported as follows: 2-hydroxyalkenes,^{1–6} 2-hydroxyacetylenes,^{7,8} 2-hydroxy esters,^{2,9–13} 2-hydroxy ketones,^{4,9,14–17} 2-hydroxynitriles^{18,19} and 2-hydroxyalkylbenzenes²⁰ [reactions (1)–(6)]. From experimental kinetic data and some theoretical studies of these substrates, a six-membered cyclic transition state type of mechanism was suggested as depicted in reaction (7).

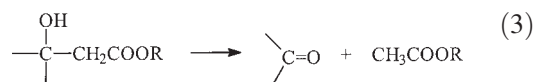
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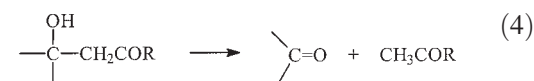
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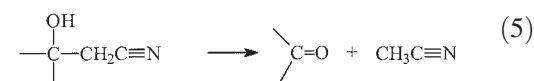
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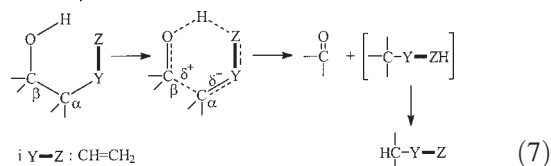
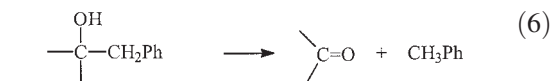
2-Hydroxy ketones



2-Hydroxynitriles



2-Hydroxyalkylbenzenes



- i Y–Z : CH=CH₂
- ii Y–Z : C≡CH
- iii Y–Z : C(OR)=O
- iv Y–Z : C(R)=O
- v Y–Z : C≡N
- vi Y–Z : C₆H₅

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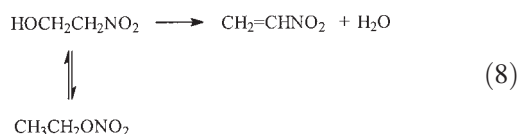
The $C_\alpha-C_\beta$ bond is believed to be polarized $C_\alpha^{\delta-} \dots C_\beta^{\delta+}$ in the reaction transition state. The decomposition rates increase from primary to tertiary C_β consistent with stabilization of the $\delta+$ charge.

August *et al.*⁴ were able to demonstrate, by comparing different series of primary, secondary and tertiary 2-hydroxy compounds, mainly 2-hydroxy ketones, 2-hydroxy esters and 2-hydroxyalkenes, that the higher the nucleophilicity of the main group the faster is the rate of elimination. In other words, the $C=O$ bond is a better nucleophile than the $C=CH_2$ bond, which accounts for the difference in reactivity in the order ketones > esters > alkenes. Among the types of compounds containing 2-substituted hydroxy groups as described in reactions (1)–(6), it seemed of interest to determine the gas-phase elimination kinetics of several primary, secondary and tertiary 2-hydroxynitroalkanes and to consider their mechanisms.

RESULTS AND DISCUSSION

Primary 2-hydroxy substituent

2-Nitroethanol. According to the elimination products of 2-nitroethanol described in reaction (8), the final pressure, P_f , should be approximately twice the initial pressure, P_0 , i.e. $P_f = 2P_0$.



The average experimental P_f/P_0 at several different temperatures and after 10 half-lives is 2.2 (Table 1). The small departure from stoichiometry was due to the formation of trace amounts of unidentified reaction products. $\text{HOCH}_2\text{CH}_2\text{NO}_2$ also yields a small amount of the isomer $\text{CH}_3\text{CH}_2\text{ONO}_2$. However, the stoichiometry of reaction (8), up to 50% reaction, was confirmed by comparing the percentage decomposition of the substrate from pressure measurements with that obtained by chromatographic analysis of nitroethene formation (Table 2).

The homogeneity of this elimination was examined by using a packed reaction vessel with a surface-to-volume ratio six times greater than that of the unpacked vessel (Table 3). The rates were unaffected by the packed and unpacked seasoned vessels, whereas a significant heterogeneous effect was obtained with the packed and unpacked clean Pyrex vessels. The effect of the free radical inhibitor toluene 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 coefficient of nitroethanol 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 $\log[P_0/(2P_0 - P_t)]$ against time t gave a good straight line up to 50% reaction. The variation of the rate coefficients with temperature and the corresponding Arrhenius equation is given in Table 6 (95% confidence limits from a least-squares procedure).

2-Nitro-1-propanol

The elimination products of 2-nitro-1-propanol described in reaction (9) require approximately a twofold increase

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

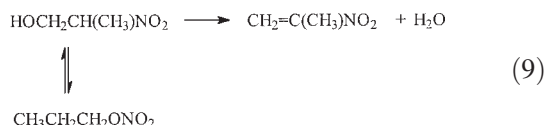
Substrate	Temperature (°C)	P_0 (Torr) ^a	P_f (Torr) ^a	P_f/P_0	Average
2-Nitroethanol	303.2	65	127	2.0	2.2
	314.0	70	157	2.2	
	320.5	106	239.5	2.3	
	329.5	65	162	2.5	
2-Nitro-1-propanol	270.0	98	192.5	2.0	2.1
	280.2	110	214	2.0	
	290.3	111.5	228.5	2.1	
	298.5	59.5	124	2.1	
2-Methyl-2-nitro-1-propanol	260.4	49.5	103	2.1	2.3
	270.2	40	91	2.3	
	279.3	61.5	150	2.4	
	240.2	92.5	159.5	1.9	
3-Nitro-2-butanol	250.4	98	186	1.9	1.9
	260.5	110	210.5	1.9	
	270.3	68	134	2.0	
	360.5	183	368	2.0	
3-Nitro-2-pentanol	370.8	155	304	2.0	2.0
	380.7	84	165	2.0	
	400.8	198	386	2.0	
	245.6	55	101.5	1.9	
2-Hydroxy-2-methylnitropropane	255.5	70	133.5	1.9	1.9
	264.8	82	155	1.9	
	270.0	72	138	1.9	

^a 1 Torr = 133.3 Pa.

Table 2. Stoichiometry of the elimination reaction

Substrate	Temperature (°C)	Parameter	Value			
2-Nitroethanol	303.2	Time (min)	5	10	14	18
		Reaction (%) (pressure)	23.7	30.2	41.5	51.6
		Nitroethene (%) (GLC)	26.3	30.1	38.7	48.5
2-Nitro-1-propanol	270.0	Time (min)	5	10	15	20
		Reaction (%) (pressure)	16.9	30.6	43.1	52.8
		2-Nitropropene (%) (GLC)	19.8	34.0	47.0	53.9
2-Methyl-2-nitro-1-propanol	235.7	Time (min)	5	10	15	18
		Reaction (%) (pressure)	20.1	37.0	51.5	57.1
		3-Hydroxy-2-methyl-1-propene (%) (GLC)	21.6	39.3	52.8	60.1
3-Nitro-2-butanol	260.5	Time (min)	3	4.5	7	10
		Reaction (%) (pressure)	17.8	30.7	41.8	50.5
		Nitroethane (%) (GLC)	19.6	31.4	39.4	53.3
3-Nitro-2-pentanol	380.7	Time (min)	1	3.5	7	15
		Reaction (%) (pressure)	25.0	34.9	55.1	74.5
		3-Nitropropane (%) (GLC)	21.2	30.0	55.4	76.5
2-Hydroxy-2-methylnitropropane	235.7	Time (min)	10	15	20	25
		Reaction (%) (pressure)	25.3	36.1	42.6	51.4
		Acetone (%) (GLC)	23.2	34.2	40.9	49.8

in the final pressure, P_f , i.e. $P_f/P_0 = 2.0$. The actual experimental results for P_f/P_0 at four different temperatures and 10 half-lives is 2.1 (Table 1). Although 2-nitropropanol produces small amounts of the isomer propyl nitrate, the stoichiometry of reaction (9), up to 70% decomposition, was confirmed by comparing the pressure measurements with the quantitative chromatographic analyses of 2-nitropropene (Table 2).

**Table 3.** Homogeneity of the elimination reaction

Substrate	S/V (cm^{-1}) ^a	$10^4 k_1$ (s^{-1}) ^b	$10^4 k_1$ (s^{-1}) ^c
2-Nitroethanol at 303.2 °C	1	21.61	5.96
	6	21.20	6.07
2-Nitro-1-propanol at 270.0 °C	1	22.41 ^d	6.15
	6	26.16 ^d	6.31
2-Methyl-2-nitro-1-propanol at 270.0 °C	1	14.53	7.79
	6	23.13	8.25
3-Nitro-2-butanol at 260.5 °C	1	15.02	12.85
	6	41.13	13.23
3-Nitro-2-pentanol at 381.0 °C	1	6.03	5.60
	6	11.92	5.87
2-Hydroxy-2-methylnitropropane at 235.7 °C	1	18.64	4.26
	6	19.26	4.10

^a S = surface area; V = volume.

^b Clean Pyrex vessel.

^c Vessel seasoned with the products decomposition of allyl bromide (420–450 °C).

^d Average k values.

The effect of the surface area on the rate of elimination was tested by carrying out several runs in a vessel with a surface-to-volume ratio of 6.0 relative to that of the normal vessel, which is equal to 1.0 (Table 3). Packed and unpacked Pyrex vessels seasoned with allyl bromide showed no effect on rates. However, the packed and unpacked clean Pyrex vessels had a marked heterogeneous effect on the rate coefficients of 2-nitro-1-propanol.

The addition of different proportions of the free radical inhibitor toluene (Table 4) showed no effect on rates. No induction period was observed. The rate coefficients were reproducible with a relative standard deviation of 5% at any given temperature.

The rate coefficient also calculated from $k_1 = (2.303/t) \log[P_0/(2P_0 - P_f)]$ was invariable with respect to their initial pressures (Table 5). On plotting $\log[P_0/(2P_0 - P_f)]$ against time t , a good straight line, up to 70% reaction, was obtained. The temperature dependence of the rate coefficients is given in Table 6. The data were fitted to the Arrhenius equation shown where 90% confidence limits from a least-squares procedure are given.

2-Methyl-2-nitro-1-propanol

The unimolecular elimination of this substrate, in a seasoned reaction vessel and in the presence of the free radical suppressor toluene, proceeds according to reaction (10). The stoichiometry demands $P_f/P_0 = 2.0$. The average P_f/P_0 at three different temperatures and 10 half-lives was 2.3. The departure from the theoretical stoichiometry increases with increase in temperature. The variation was due to the formation of trace amounts of nitropropane, isobutyl nitrite, isobutyl nitrate, 1-hydroxy-2-methyl-1-propene, 1-hydroxy-2-methyl-2-propene and isobutyraldehyde. However, it was possible to check the stoichiometry of reaction (10), up to 50% reaction, by comparing the pressure measurements with quantitative

Table 4. Effect of the free radical chain inhibitor on rates

Substrate	Temperature (°C)	P_s^a (Torr)	P_i^b (Torr)	P_i/P_s	$10^4 k_1$ (s ⁻¹)
2-Nitroethanol	314.0	88.5	—	—	6.25 ^c
		96	53.5	0.6	9.64
		70	87	1.2	9.61
		71.5	244	3.4	9.36
2-Nitro-1-propanol	290.3	85	—	—	24.10
		195	84	0.4	23.75
		126	123.5	0.9	23.55
		111.5	185	1.7	23.73
2-Methyl-2-nitro-1-propanol	270.2	73	199.5	2.5	23.52
		72	—	—	7.12
		53	64.5	1.2	7.62
		45.5	113	2.5	7.79
3-Nitro-2-butanol	260.5	40	121	3.0	7.72
		38	133	3.5	7.80
		103	—	—	12.55
		128	62.5	0.5	12.68
3-Nitro-2-pentanol	380.5	90.5	82.5	0.9	12.78
		93.5	138.5	1.5	12.47
		71.5	163.5	2.4	12.90
		235	—	—	6.10
2-Hydroxy-2-methylnitropropane	245.6	84	134	0.6	5.51
		160	168	1.1	5.08
		63	182	2.9	5.25
		94	—	—	7.47
		101	59	0.6	7.56
		61	79.5	1.3	7.67
		64.5	112	1.7	7.51

^a P_s = pressure of substrate.^b P_i = pressure of free radical inhibitor.^c Average k value.**Table 5.** Invariability of the rate coefficients from initial pressure

Substrate	Temperature (°C)	Parameter	Value				
2-Nitroethanol	320.5	P_0 (Torr)	40	66	92	106	
		$10^4 k_1$ (s ⁻¹)	14.00	14.06	14.32	14.36	
2-Nitro-1-propanol	290.3	P_0 (Torr)	73	87	111	126	195
		$10^4 k_1$ (s ⁻¹)	23.52	23.23	23.41	23.55	23.75
2-Methyl-2-nitro-1-propanol	260.4	P_0 (Torr)	29	49	54.5	66	97
		$10^4 k_1$ (s ⁻¹)	4.34	4.38	4.16	4.17	4.16
3-Nitro-2-butanol	260.5	P_0 (Torr)	44.5	71.5	103	128	150
		$10^4 k_1$ (s ⁻¹)	12.15	12.90	12.55	12.68	12.56
3-Nitro-2-pentanol	380.5	P_0 (Torr)	84	157	182	210	235
		$10^4 k_1$ (s ⁻¹)	5.51	5.15	5.07	5.70	5.60
2-Hydroxy-2-methylnitropropane	270.0	P_0 (Torr)	66.5	74	89.5	105	
		$10^4 k_1$ (s ⁻¹)	31.81	31.73	31.40	31.65	

chromatographic analysis of the main product 3-hydroxy-2-methyl-1-propene (Table 2). The homogeneity of this pyrolytic elimination was examined using a reaction vessel with different surface-to-volume ratios, i.e. the packed vessel had a 6.0 times greater surface-to-volume ratio than the unpacked vessel (Table 3). The packed and unpacked clean Pyrex vessels resulted in a marked heterogeneous effect. The packed seasoned vessel showed a very small surface effect. This substrate was always pyrolyzed in the unpacked seasoned Pyrex vessel. The elimination of this nitro alcohol substrate was not

affected by the presence of different proportions of the free radical inhibitor toluene (Table 4). No induction period was observed. The k values are reproducible with a relative standard deviation not greater than 5% at a given temperature.

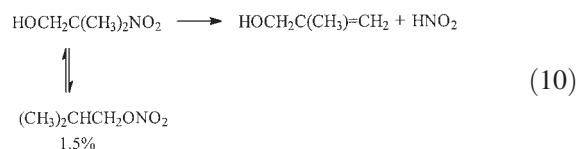


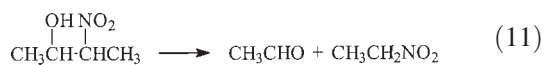
Table 6. Variation of the rate coefficients with temperature

Substrate	Parameter	Value						
2-Nitroethanol	Temperature (°C)	291.2	296.2	303.2	314.0	320.5	329.5	
	$10^4 k_1$ (s ⁻¹)	2.68	3.37	5.96	9.56	14.28	22.91	
	Rate equation	$\log k_1$ (s ⁻¹) = (11.14 ± 0.48) - (158.9 ± 5.3) kJ mol ⁻¹ (2.303 RT) ⁻¹ , $r = 0.9978$						
2-Nitro-1-propanol	Temperature (°C)	248.2	259.8	270.0	280.2	290.3	298.7	
	$10^4 k_1$ (s ⁻¹)	1.44	3.16	6.15	13.24	23.41	37.75	
	Rate equation	$\log k_1$ (s ⁻¹) = (12.40 ± 0.47) - (162.1 ± 5.0) kJ mol ⁻¹ (2.303 RT) ⁻¹ , $r = 0.9995$						
2-Methyl-2-nitro-1-propanol	Temperature (°C)	239.4	249.5	260.4	270.2	279.3		
	$10^4 k_1$ (s ⁻¹)	1.01	2.04	4.24	7.79	13.61		
	Rate equation	$\log k_1$ (s ⁻¹) = (11.64 ± 0.06) - (153.4 ± 0.6) kJ mol ⁻¹ (2.303 RT) ⁻¹ , $r = 0.9998$						
3-Nitro-2-butanol	Temperature (°C)	220.4	230.9	240.2	250.4	260.5	270.3	
	$10^4 k_1$ (s ⁻¹)	0.86	1.70	3.55	7.00	12.85	24.52	
	Rate equation	$\log k_1$ (s ⁻¹) = (11.84 ± 0.21) - (150.4 ± 2.1) kJ mol ⁻¹ (2.303 RT) ⁻¹ , $r = 0.9996$						
3-Nitro-2-pentanol	Temperature (°C)	340.7	351.1	360.7	370.8	380.8	391.0	400.8
	$10^4 k_1$ (s ⁻¹)	0.50	0.90	1.62	2.91	5.24	9.44	17.37
	Rate equation	$\log k_1$ (s ⁻¹) = (12.93 ± 0.24) - (202.8 ± 3.0) kJ mol ⁻¹ (2.303 RT) ⁻¹ , $r = 0.9995$						
2-Hydroxy-2-methylnitropropane	Temperature (°C)	225.7	230.4	235.7	245.6	255.5	264.8	270.0
	$10^4 k_1$ (s ⁻¹)	1.79	2.43	4.26	7.55	14.25	24.92	31.81
	Rate equation	$\log k_1$ (s ⁻¹) = (11.66 ± 0.40) - (146.9 ± 4.0) kJ mol ⁻¹ (2.303 RT) ⁻¹ , $r = 0.9981$						

The rate coefficients, in seasoned vessel, from $k_1 = (2.303/t) \log[P_0/(2P_0 - P_t)]$ were found to be independent of the initial pressure of the substrate (Table 5), and the first-order plots of $\log[P_0/(2P_0 - P_t)]$ versus time t are satisfactorily linear up to 50% reaction (Table 5). The temperature dependence of the rate coefficients and the corresponding Arrhenius equation is described in Table 6 (90% confidence levels with a least-squares method).

Secondary 2-hydroxy substituent

3-Nitro-2-butanol. The experimental stoichiometry for the elimination of 3-nitro-2-butanol in the gas phase [reaction (11)] is $P_f = 2P_0$. The average P_f/P_0 at four different temperatures and 10 half-lives was 1.9. The small departure from the theoretical stoichiometry was due to the very slight polymerization of acetaldehyde. Further verification of the stoichiometry of reaction (11) was possible by comparing, up to 70% decomposition, the measurements of pressure increase with the quantitative analysis of nitroethane formation (Table 2).



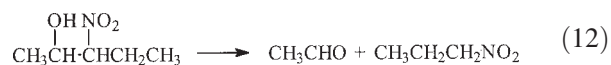
The homogeneity of this elimination was investigated by using a packed reaction vessel with a surface-to-volume ratio six times greater than that of the unpacked reaction vessel (Table 3). The rate coefficients are very similar in the packed and unpacked vessels seasoned with allyl bromide. However, the packed and unpacked clean Pyrex vessels showed a marked effect on the rates.

The process of elimination of this substrate was not affected by the presence of different proportions of a free radical inhibitor such as toluene (Table 4). No induction

period was detected. The rate coefficients are reproducible with a relative standard deviation not greater than 5% at a given temperature.

The rate coefficients of decomposition of 3-nitro-1-butanol were calculated from $k_1 = (2.303/t) \log[P_0/(2P_0 - P_t)]$ and were found to be independent of the initial pressure (Table 5). A plot of $\log[P_0/(2P_0 - P_t)]$ against time t gave a good straight line up to 70% reaction. The variation of the rate coefficients with temperature and the corresponding Arrhenius equation are given in Table 6 (90% confidence limits from a least-squares procedure).

3-Nitro-2-pentanol. The elimination reaction of this substrate, in a seasoned vessel and in the presence of a free radical inhibitor [reaction (12)] implies $P_f/P_0 = 2.0$. The average experimental P_f/P_0 value measured after 10 half-lives and at four different temperatures was 2.0 (Table 1). A further verification of the stoichiometry of reaction (12), up to 75% decomposition, is that the quantitative chromatographic analysis of nitropropane formation corresponds to the pressure increase (Table 2).



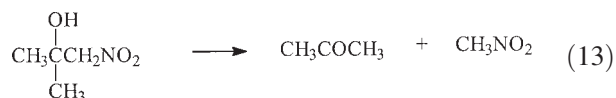
To examine the effect of surface area on the rates, several runs in the presence of toluene inhibitor were performed in a vessel with a surface-to-volume ratio six times greater than that of the normal vessel (Table 3). The packed clean Pyrex vessel resulted in a significant heterogeneous effect. This nitropentanol substrate was always pyrolyzed in seasoned vessel and in the presence of at least a twofold excess of the free radical inhibitor toluene (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.

The first-order rate coefficient of this substrate calculated from $k_1 = (2.303/t) \log[P_0/(2P_0 - P_t)]$ was independent of the initial pressure (Table 5). A plot of $\log[P_0/(2P_0 - P_t)]$ against time t gave a good straight line up to 75% decomposition. The temperature dependence of the rate coefficients together with the corresponding Arrhenius equation are given in Table 6 (90% confidence limits from a least-squares method).

Tertiary 2-hydroxy substituent

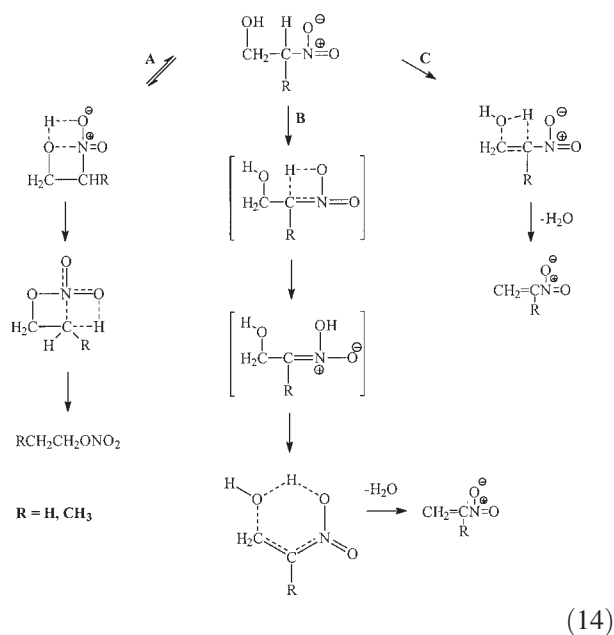
2-Hydroxy-2-methylnitropropane. The product formation of this nitro alcohol is described in reaction (13). The stoichiometry requires that, for long reaction time, $P_t/P_0 = 2.0$. The average experimental P_t/P_0 values at four different temperatures and 10 half-lives was 1.9 (Table 1). Further verification of the above stoichiometry, up to 50% reaction, was possible by comparing the percentage decomposition of the substrate from pressure measurements with that obtained from the quantitative chromatographic analyses of the product acetone (Table 2).



The homogeneity of this pyrolytic elimination was examined in a vessel with a surface-to-volume ratio six times greater than that of the normal vessel (Table 3). The rates of formation of acetone and/or nitromethane were unaffected in seasoned packed and unpacked Pyrex vessels. However, clean packed and unpacked Pyrex vessels showed a significant effect on the rates. The effect of different proportions of the free radical inhibitor toluene on the elimination reaction is given in Table 4. 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 estimated from $k_1 = (2.303/t) \log[P_0/(2P_0 - P_t)]$ were invariant with respect to their initial pressure (Table 5). On plotting $\log[P_0/(2P_0 - P_t)]$

versus time t , a good straight line, up to 50% decomposition, was obtained. The variation of the rate coefficients with temperatures is shown in Table 6. The experimental data were fitted to the Arrhenius equation (Table 6), where 90% confidence limits from a least-squares procedure are given.



The experimental results and the data specified in Table 7 require careful analyses for mechanistic interpretations. In the case of the substrates with primary 2-substituted hydroxy groups, as in 2-nitroethanol and 2-nitro-1-propanol, the likely process for nitrate formation is an abstraction of the H of the OH by the oxygen of the NO₂ group as shown in reaction (14A). This process of isomerization was found to be extremely rapid and a kinetic determination was not possible. However, the main elimination product is the dehydration reactions (8) and (9). Because of the low-temperature pyrolysis work on primary nitro alcohols and the values of $\log A = 11.28$ and 12.40 (Table 7) of these substrates, the water elimination through a four-membered cyclic state transition state type of mechanism [reaction (14C)] appears to be unlikely. Moreover, primary aliphatic alcohols with a C_β—H bond are difficult to dehydrate

Table 7. Kinetic and thermodynamic parameters for pyrolysis of the 2-hydroxynitroalkanes at 280 °C

Z	$k_1 \times 10^4$ (s ⁻¹)	E_a (kJ mol ⁻¹)	Log A (s ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
HOCH ₂ CH ₂ NO ₂	1.35	158.9 ± 5.3	11.14 ± 0.48	-45.0	154.3	179.2
HOCH ₂ CH(CH ₃)NO ₂	12.30	162.1 ± 5.0	12.40 ± 0.47	-20.9	157.5	169.1
HOCH ₂ C(CH ₃) ₂ NO ₂	14.13	153.4 ± 0.6	11.64 ± 0.06	-35.5	148.8	168.4
CH ₃ CH(OH)CH(NO ₂)CH ₃	42.66	150.4 ± 2.1	11.84 ± 0.21	-31.6	145.8	163.3
CH ₃ CH(OH)CH(NO ₂)CH ₂ CH ₃	0.006	202.8 ± 3.0	12.93 ± 0.24	-10.8	198.2	204.2
(CH ₃) ₂ C(OH)CH ₂ NO ₂	60.26	146.9 ± 4.0	11.66 ± 0.40	-35.1	142.3	161.7

Table 8. Kinetic and thermodynamic parameters for pyrolysis of HOCH₂CH₂Z at 280 °C

Z	$k_1 \times 10^4$ (s ⁻¹)	E_a (kJ mol ⁻¹)	Log A (s ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
COCH ₃	43.9	155.7	12.35	-21.9	151.1	163.2
CN	0.0000478	227.0	13.12	-7.1	222.4	226.3
C ₆ H ₅	0.00000563	229.2	12.40	-20.9	224.6	236.2
NO ₂	1.35	158.9	11.14	-45.0	154.3	179.2

even at temperatures higher than 500 °C, for a four-membered cyclic transition state elimination in the gas phase.²⁰ Ethanol was difficult to pyrolyze, but under maximum inhibition and at a single temperature of 525 °C gave a k value of 1.1×10^{-5} . However, propanol showed a variation of the rate coefficient with temperature according to the following Arrhenius expression: $\log k_1(\text{s}^{-1}) = 13.64 - 279.4 \text{ kJ mol}^{-1} (2.303 RT)^{-1}$. Comparison of the rate coefficients of ethanol, propanol and 2-nitroethanol at 525 °C are given in Related Comparison 1.

Propanol: $\log k_1(\text{s}^{-1}) = 13.64 - 279.4 \text{ kJ mol}^{-1} (2.303 RT)^{-1}$
 2-Nitroethanol: $\log k_1(\text{s}^{-1}) = 11.28 - 160.6 \text{ kJ mol}^{-1} (2.303 RT)^{-1}$

	Ethanol	Propanol	2-Nitroethanol
k_1 (s ⁻¹) at 525 °C	1.1×10^{-5}	2.3×10^{-5}	5.85

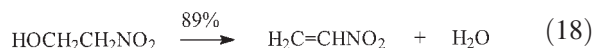
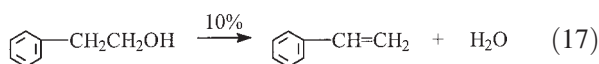
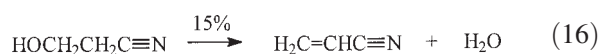
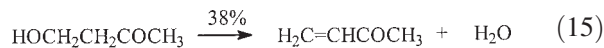
Related Comparison 1

The replacement of the H of ethanol by an NO₂ group cannot be a factor in increasing the dehydration process of the alcohol through the same mechanistic process of a four-membered cyclic transition state with a rate as fast as $500\,000 \text{ s}^{-1}$. This dramatic difference is hardly obtained in gas-phase elimination reactions in the same series of compounds. Consequently, the high dipole of the NO₂ group, as O=N⁺—O⁻ and the proximity of the adjacent C_α—H for charge stabilization through isomerization must not be overlooked. Therefore, it is not unreasonable to believe that the mechanism of dehydration may well go through a six-membered cyclic transition state as described in reaction (14B).

The rate of dehydration of 2-nitro-1-propanol was found to be faster than that of 2-nitroethanol (Table 7). This marked difference apparently arises from the abstraction of the acidic H of the —ONOH group by OH to form a water molecule [reaction (14B)], thus leaving the adjacent C_β atom partially positive. This positive C_β atom may then be stabilized through the electronic release of the CH₃ in the nitropropanol for augmentation in elimination.

The dehydration process of the primary 2-hydroxy compounds has also been observed as a parallel reaction described in reactions (1)–(6). The authors concerned assumed a four-membered cyclic transition state mechanisms for this side-reaction. Complete kinetic studies of these

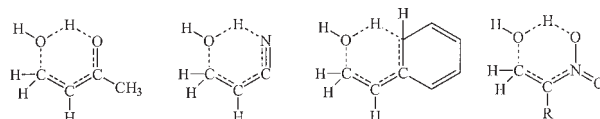
parallel reactions have only been reported for hydroxy esters,⁴ hydroxy ketones,^{4,16} hydroxynitriles¹⁸ and hydroxylalkylbenzenes¹⁹ [reactions (15)–(18)].



According to the data in Table 8, where the range of log A is 11.28–12.40, with the apparent exception of 2-hydroxypropionitrile (13.12), a six-membered rather than a four-membered cyclic transition state appears to be the most probable mechanism for water elimination. This assumption appears to be supported by the very negative entropy of activation. In addition to this consideration, when estimating the rate of elimination of water molecule of the hydroxy compounds listed in Table 8 at 525 °C, the difference is found to be extremely large (Related Comparison 2). With the same arguments for the transition state of dehydration of nitroethanol, the substrates described in Table 8 may well be undergo a similar six-membered cyclic transition state as pictured in Scheme 1.

Relative	H	CH ₃	C ₆ H ₅	CN	NO ₂	CH ₃ CO
rate at 525 °C	1	2.1	166	226	532×10^3	13100×10^3

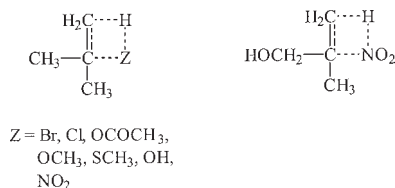
Related Comparison 2



Scheme 1

With regard to the other primary 2-hydroxynitroalkane, i.e. 2-methyl-2-nitro-1-propanol, there is no H attached to C_α; instead, there are two CH₃ group, i.e. —C_α(CH₃)₂. Consequently, no isomerization of the H for dehydration

may take place. This appears to support the mechanism in reaction (14B), based on the importance of the H at the C $_{\alpha}$ atom. In this case, the NO $_2$ group is found to be attached to a tertiary carbon atom. Consequently, the nitro group is displaced by the C $_{\beta}$ —H bond of the CH $_3$ group through a four-membered cyclic transition state type of mechanism (Scheme 2). This type of elimination is similar to the known and well-established mechanism for tertiary butyl compounds containing a leaving group Z attached to the tertiary carbon atom (Scheme 2).



Scheme 2

2-Methyl-2-nitropropane has been reported to produce isobutene and HNO $_2$ in the gas phase²¹ with the following Arrhenius expression: $\log k_1 \text{ (s}^{-1}\text{)} = 13.63 - 179.3 \text{ kJ mol}^{-1} (2.303 RT)^{-1}$. The reaction rate of this compound is expected to be faster than that of 2-methyl-2-nitro-1-propanol (Table 7) at 280 °C. However, the result is the contrary (Related Comparison 3). The effect of the HOCH $_2$ group attached to the tertiary C atom should destabilize the polarization of the C—Z bond, which is rate determining. Therefore, the reaction rate of 2-methyl-2-nitro-1-propanol should be slower than that of 2-methyl-2-nitropropane. Some additional work is needed to account for such a difference.

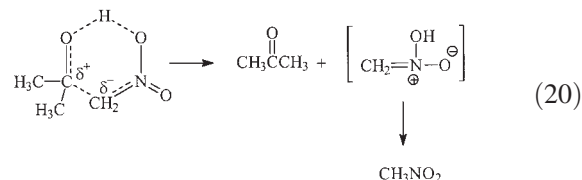
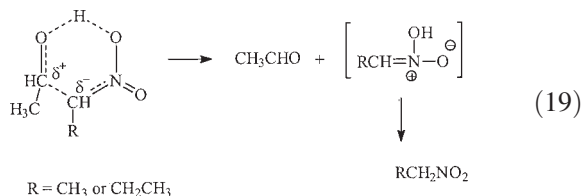


At 280 °C 4.90×10^{-4} 14.13×10^{-4}

Related Comparison 3

According to the product formation from the secondary [reactions (11) and (12)] and tertiary hydroxynitroalkane [reaction (13)], a retro-aldol type of decomposition takes place, which is similar to the elimination process

described in reactions (1)–(6). Therefore, secondary and tertiary hydroxy groups at the 2-position of nitroalkanes appear to proceed through a six-membered cyclic transition state type of mechanism as described in reaction (7). Therefore, the process of decomposition may be depicted as in reactions (19) and (20).



The comparative kinetic and thermodynamic parameters for the gas-phase elimination of different series of 2-substituted secondary and tertiary hydroxy compounds are given in Tables 9 and 10. These results seem to provide an additional support for August *et al.*'s⁴ idea about the fact that the faster elimination rate of the substrate is due to the higher nucleophilic nature of the main group. This view accounts for the difference in reactivity in the order hydroxy ketone > hydroxynitroalkane > hydroxyester > hydroxyalkyne > hydroxyalkane > hydroxynitrile > hydroxyalkylbenzene.

EXPERIMENTAL

2-Hydroxy-2-methyl-1-nitropropane. This substrate was prepared by treating nitromethane (1.03 mol) with LiAlH $_4$ (0.0014 mol) in 15 ml of dry tetrahydrofuran. The reaction mixture was stirred under an argon

Table 9. Comparative kinetic and thermodynamic parameters for pyrolysis of secondary hydroxy substituent at 360 °C

Z	$k_1 \times 10^4$ (s $^{-1}$)	E_a (kJ mol $^{-1}$)	Log A (s $^{-1}$)	$\Delta S^\ddagger$ (J mol $^{-1}$ K $^{-1}$)	$\Delta H^\ddagger$ (kJ mol $^{-1}$)	$\Delta G^\ddagger$ (kJ mol $^{-1}$)	Ref.
CH $_3$ CH(OH)CH $_2$ CH=CH $_2$	5.56	162.2	10.13	−65.5	156.9	198.4	4
	27.86	162.2	10.83	−52.1	156.9	189.9	5
CH $_3$ CH(OH)CH $_2$ C≡CH	50.16	164.8	11.30	−43.1	159.5	186.8	6
CH $_3$ CH(OH)CH $_2$ COCH $_3$	8196.8	142.1	11.64	−36.6	136.8	160.0	16
	7253.1	139.2	11.10	−46.9	133.9	163.6	4
CH $_3$ CH(OH)CH $_2$ COOCH $_3$	21.55	164.4	10.90	−50.8	159.1	191.3	4
CH $_3$ CH(OH)CH $_2$ COOCH $_2$ CH $_3$	61.76	163.1	11.25	−44.1	157.8	185.7	11
CH $_3$ CH(OH)CH $_2$ C≡N	0.25	222.6	13.76	3.97	217.3	214.8	18
CH $_3$ CH(OH)CH $_2$ C $_6$ H $_5$	0.0017	240.1	13.04	−9.81	234.8	241.0	20
CH $_3$ CH(OH)CH(CH $_3$)NO $_2$	2683.6	150.4	11.84	−32.8	145.1	165.9	This work

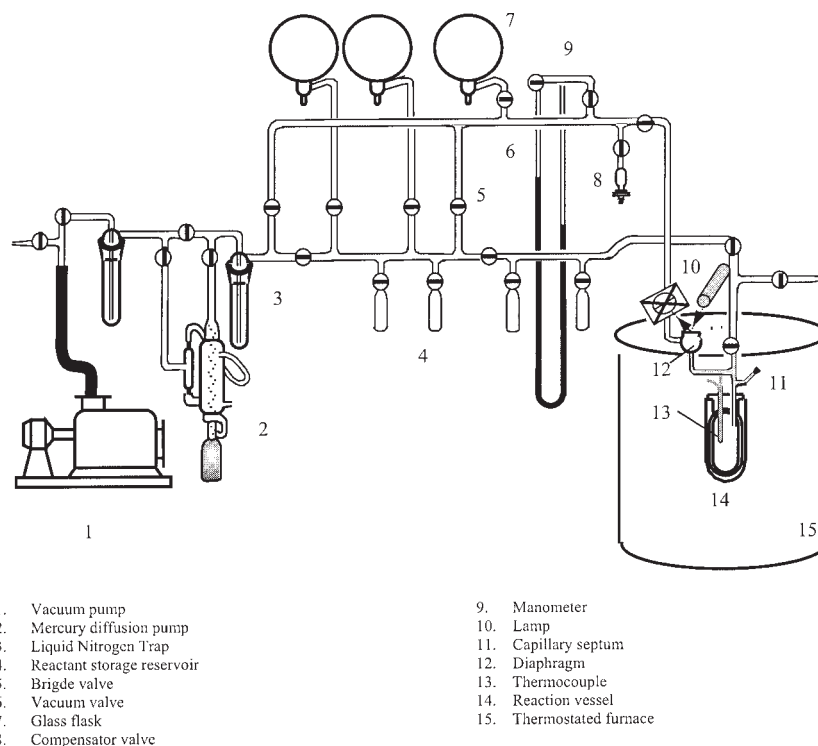
Table 10. Comparative kinetic and thermodynamic parameters for pyrolysis of tertiary Hydroxy substituent at 300 °C

Z	$k_1 \times 10^{-4}$ (s ⁻¹)	E_a (kJ mol ⁻¹)	Log A (s ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	Ref.
(CH ₃) ₂ C(OH)CH ₂ CH=CH ₂	1.94	160.3	10.90	-50.0	155.5	184.2	4
	1.94	160.3	10.90	-50.0	155.5	184.2	5
(CH ₃) ₂ C(OH)CH ₂ C≡CH	2.43	166.9	11.60	-36.6	162.1	183.1	6
(CH ₃) ₂ C(OH)CH ₂ COCH ₃	1583.3	133.4	11.36	-41.2	128.6	152.2	16
	839.4	133.9	11.13	-45.6	129.1	155.2	4
(CH ₃) ₂ C(OH)CH ₂ COOCH ₃	4.02	159.9	11.18	-44.6	155.1	180.7	4
(CH ₃) ₂ C(OH)CH ₂ COOCH ₂ CH ₃	3.04	174.5	12.39	-21.5	169.7	182.2	13
(CH ₃) ₂ C(OH)CH ₂ C≡N	0.020	212.5	13.68	3.21	207.7	205.9	18
(CH ₃) ₂ C(OH)CH ₂ C ₆ H ₅	0.00021	222.9	12.65	-16.51	218.1	227.6	20
(CH ₃) ₂ C(CH ₂ OH)NO ₂	185.8	146.9	11.66	-35.46	142.1	162.1	This work

atmosphere at 0 °C for 30 min. Anhydrous acetone (2.05 mol) was then slowly added (5 h) while stirring at 0 °C. The reaction mixture was kept overnight to reach room temperature, then 30 ml of 1M HCl and 25 ml of distilled water were added to stop the reaction. The mixture was extracted with three portions of CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated at 55 °C. The excess of nitromethane was removed at 75 °C under vacuum. The liquid product (12% yield) was found to be of 99.1% pure as determined by GC-MS (Saturn 2000, Varian) with a DB-5MS capillary column, 30 m × 0.53 mm i.d., 0.53 μm film thickness. ¹H NMR: δ 1.3 (s, 6H), 3.3 (s, 1H), 4.4 (s, 2H). MS: *m/z* 119 (M⁺), 104 [CH₃C(OH)CH₂NO₂⁺], 59 [(CH₃)₂COH⁺], 43 (CH₃C≡O⁺).

2-Nitroethanol (Aldrich), 2-nitro-1-propanol (K&K Labs), 2-methyl-2-nitro-1-propanol (Aldrich), 3-nitro-2-butanol (Aldrich) and 3-nitro-2-pentanol (Aldrich) were shown to be better than 98.5% pure when analyzed by GC-MS (Saturn 2000, Varian) with a DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). Quantitative chromatographic analyses and identifications of products were also performed by GC-MS (Saturn 2000, Varian) with a DB-5MS capillary column (30 m × 0.53 mm. i.d., 0.53 μm film thickness).

Kinetics. Kinetic experiments were carried out in a static reaction system as depicted in Fig. 1, as reported,^{22,23} with an Omega DP41-TC/DP41-RTD high-performance digital temperature indicator. The rate coefficients were

**Figure 1.** Static reaction system

determined manometrically or by the quantitative analyses of the starting material and/or by the corresponding product. The temperature was controlled by a Shinko DC-PS resistance thermometer controller and an Omega SSR280A45 solid-state relay, maintained $\pm 0.2^\circ\text{C}$, and measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was observed along the reaction vessel. The starting materials were all injected directly into the reaction vessel with a syringe through a silicone-rubber septum. The amount of substrate used for each reaction was ~ 0.05 – 0.2 ml.

REFERENCES

1. Smith GG, Yates BL. *J. Chem. Soc.* 1965; 7242–7246.
2. Arnold RT, Smolinsky G. *J. Am. Chem. Soc.* 1959; **81**: 6443–6445.
3. Smith GG, Taylor R. *Chem. Ind. (London)* 1961; 949–950.
4. August R, McEwen I, Taylor R. *J. Chem. Soc., Perkin Trans. 2* 1987; 1683–1689.
5. Failes RL, Shapiro JS, Stimson VR. In *The Chemistry of the Hydroxy Group*, Patai S (ed). Wiley: Chichester, 1980; 449–468.
6. Quijano J, David J, Sanchez C, Rincon E, Guerra D, Leon LA, Notario R, Abboud JL. *J. Mol. Struct. (Theochem)* 2002; **580**: 201–2057.
7. Viola A, MacMilan JH, Proverb RJ, Yates BL. *J. Am. Chem. Soc.* 1971; **93**: 6967–6974.
8. Quijano J, Sanchez C, David J, Leon LA, Notario R, Abboud JL. *J. Mol. Struct. (Theochem)* 2001; **572**: 135–139.
9. Quijano J, Rodriguez M, Yepes M del S, Gallego LH. *Tetrahedron Lett.* 1987; **28**: 3555–3558.
10. Yates BL, Quijano J. *J. Org. Chem.* 1970; **35**: 1239–1240.
11. Yates BL, Ramirez A, Velazquez O. *J. Org. Chem.* 1961; **36**: 3579–3582.
12. Quijano J, Restrepo I, Gallego LH, Yepes M del S. *Tetrahedron Lett.* 1994; **35**: 4735–4738.
13. Dominguez RM, Chuchani G, Quijano J, Orozco LJ, Restrepo I. *React. Kinet. Catal. Lett.* 1996; **57**: 191–196.
14. Smith GG, Yates BL. *J. Org. Chem.* 1965; **30**: 2067.
15. Yates BL, Quijano J. *J. Org. Chem.* 1969; **34**: 2506–2508.
16. Rotinov A, Chuchani G, Machado R, Rivas C, Quijano J, Yepes M del S, Restrepo I. *Int. J. Chem. Kinet.* 1992; **24**: 909–915.
17. Feng W, Wang Y, Zhang S. *Int. J. Quantum Chem.* 1997; **62**: 297–3027.
18. Chuchani G, Dominguez RM, Rotinov A, Quijano J, Valencia C, Vicente B, Franco D. *J. Phys. Org. Chem.* 1999; **12**: 19–23.
19. Chuchani G, Rotinov A, Dominguez RM. *Int. J. Chem. Kinet.* 1999; **31**: 401–407.
20. Maccoll A, Thomas PJ. *Prog. React. Kinet.* 1967; **4**: 119–148.
21. Nazin GM, Manelis GB. *Russ. Chem. Rev.* 1994; **63**: 313–322.
22. Maccoll A. *J. Chem. Soc.* 1955; 965–973.
23. Swinbourne ES. *Aust. J. Chem.* 1958; **11**: 314–330.