Thermal Decomposition of 2-Ethylhexyl Nitrate (2-EHN)

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ABSTRACT: The decomposition mechanism of 2-ethyl-hexylnitrate (2-EHN), an important additive to diesel fuel to improve the cetane number, was investigated in solution and in the gas phase. In *trans*-decalin as solvent, an activation barrier for the thermal decomposition of 39 kcal/mol was determined, and thus the decomposition is slow at temperatures below 100°C. Under high pressure conditions (2.4 kbar) the decomposition rates decrease, in accordance with a radical mechanism. Flash vacuum pyrolysis with subsequent detection of the products via mass spectroscopy or matrix IR spectroscopy allows to identify NO_2, formaldehyde, and several olefins as the major decomposition products. These data allow proposing a consistent mechanistic scheme for the 2-EHN decay. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 34: 34–38, 2002

INTRODUCTION

Ignition improvers are commercially important additives to diesel fuel. An important criterion of the quality of diesel fuel is the cetane number, which describes the time delay between injection and spontaneous ignition in a standard diesel engine [1]. A high cetane number, corresponding to short delay times, is desirable to ascertain a clean ignition especially at low motor temperatures. The cetane number of diesel fuel can be improved by the addition of small quantities of radical precursors such as organic nitrates. A nitrate that has found large practical application is 2-ethylhexyl nitrate (2-EHN), which decomposes into NO_2, formaldehyde, and the heptyl radical [2]. From measuring the pressure increase as a function of the temperature of a sealed vessel, the Arrhenius parameters $E_a = 37.5 \pm 3$ kcal/mol and log $A = 15.4$ was determined for the decomposition of 2-EHN in the gas phase. Two decomposition modes of 2-EHN are of importance for the practical use as fuel additive: the slow, unwanted decomposition outside the injection system and the thermal decomposition during injection. Here we present kinetic data for the thermal decay of 2-EHN in different solvents to understand the decomposition in diesel fuel and a mechanistic study of the gas-phase processes leading to the improvement of the cetane number.

EXPERIMENTAL

2-Ethylhexyl nitrate (2-EHN) was obtained from Aral AG and the purity was checked by GC (>97%). The kinetic data were obtained by time-dependent thermolyses in sealed ampoules at various temperatures. Solutions of 2-EHN (16 mmol/l) in *trans*-decalin, benzene, and ethanol containing naphthalene (8 mmol/l) as internal standard were used in the kinetic experiments.

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Table I Kinetic Data of the Thermolysis of 2-EHN in Solution

Solvent	p (bar)	T (°C)	T (K)	k (10^{-5} s^{-1})	T^{-1} (10^{-3} K^{-1})	ln k
trans-Decalin	1.0	162.5	435.7	8.95	2.296	−9.32
		148.0	421.2	1.53	2.375	−11.09
		135.4	408.6	0.33	2.448	−12.61
		120.0	393.2	0.037	2.544	−14.81
trans-Decalin	2500.0	146.3	419.5	0.22	2.384	−13.04
Benzene	1.0	121.1	394.3	0.036	2.537	−14.84

High-pressure thermolysis were carried out in a Roth laboratory autoclave. GC analyses were performed by using a Siemens Sichromat 1–4 (column: OV 1, 29.5 m) connected with a Merck Hitachi D-2500 Chromato-Integrator. Mass spectra were measured with a VG Quadrupoles SXP Elite spectrometer. The primary ionization energy was usually 20 eV.

Flash vacuum pyrolyses were carried out by evaporating a sample of 2-EHN and passing it through a 7-cm quartz tube which was heated electrically by a tantalum wire.

The matrix isolation experiments were performed by standard techniques [3] with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by co-deposition of a large excess of argon (Messer Griesheim, 99.9999%, approximately 0.15 mmol/min) and the trapped species on top of a cold CsI (IR) window. To obtain optically clear matrices, the cold window was retained at 30 K during deposition, and the matrix was subsequently cooled to 10 K. Infrared spectra were recorded by using either a Bruker IFS66 FTIR or an Equinox 55 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range 400–4000 cm^{-1}. Irradiations were carried out with a Gräntzel mercury low-pressure spiral lamp.

2-Ethylhexyl nitrate – IR (argon, 10 K): 2973.8 (15), 2943.7 (8), 2885.2 (5), 2869.9 (2), 1644.8 (100), 1612.1 (2), 1471.4 (8), 1461.1 (6), 1382.5 (4), 1280.8 (67), 988.0 (5), 968.8 (2), 868.9 (31), 852.7 (4), 762.0 (9), 701.1 (4), 668.0 (2) cm^{-1} (relative intensity).

RESULTS AND DISCUSSION

Thermal Decomposition of 2-EHN in Solution

The kinetics of the thermolysis of 2-EHN was investigated by heating solutions in benzene, *trans*-decalin, and ethanol in sealed ampoules and following its decay with GC. Decalin and benzene were chosen as model solvents for diesel fuel, and ethanol to investigate the influence of solvent polarity and acidity.

In all solvents first-order kinetics was observed. In *trans*-decalin the decay of 2-EHN was measured at several temperatures in the range 120–162.5°C (Table I), from which the Arrhenius parameters E_a and log A were obtained (Fig. 1). However, because of the small temperature range accessible in our experiments, an accurate independent determination of both parameters was not possible. The best statistical fit was obtained with an unreasonably large log A value (log $A = 17.9$, $E_A = 43.8$ kcal/mol). If we use the frequency factor published by Pritchard (log $A = 15.4$) [2] an activation barrier of 39.0 kcal/mol is calculated, in good agreement with his gas-phase value ($E_a = 37.5 \pm 3$ kcal/mol). This indicates that the decay kinetics of 2-EHN is largely uninfluenced by unpolar solvents.

At temperatures below 100°C the decomposition of 2-EHN in decalin (and diesel fuel) is thus extremely slow, at 120°C the half-life is 522.7 h, and at 150°C it is 9.5 h. From this we conclude that 2-EHN is stable under normal storage conditions. Since the pressure inside the injection system of modern diesel engines can reach several kilobars, we also measured the decomposition of 2-EHN under high-pressure conditions. At 146.3°C and 2.4 kbar, the half-life was determined to be 88.5 ± 4 h, considerably longer than the 16 h at the same temperature and 1 bar pressure. This is in

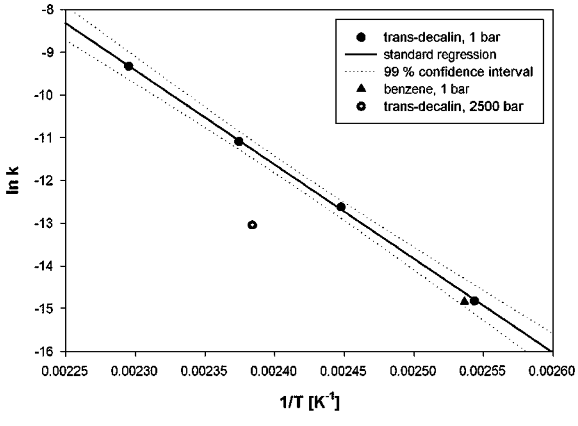


FIGURE 1 Arrhenius plot for the decomposition of 2-EHN in *trans*-decalin and benzene.

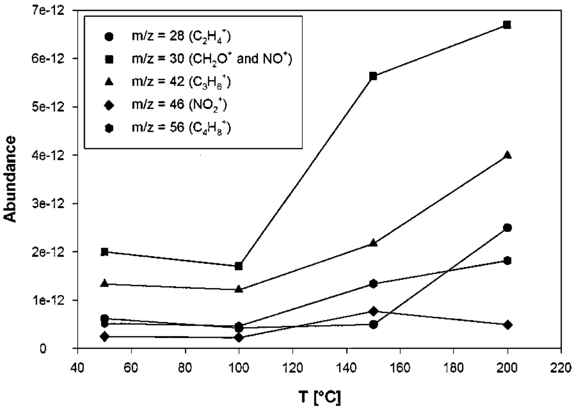


FIGURE 2 Mass spectroscopic data of the most important fragments at different pyrolysis temperatures showing the thermal decomposition of 2-EHN at 150°C.

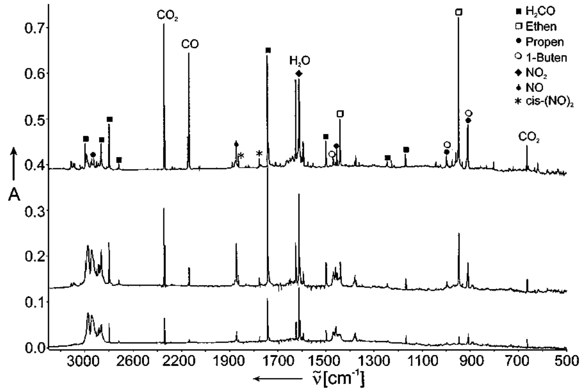
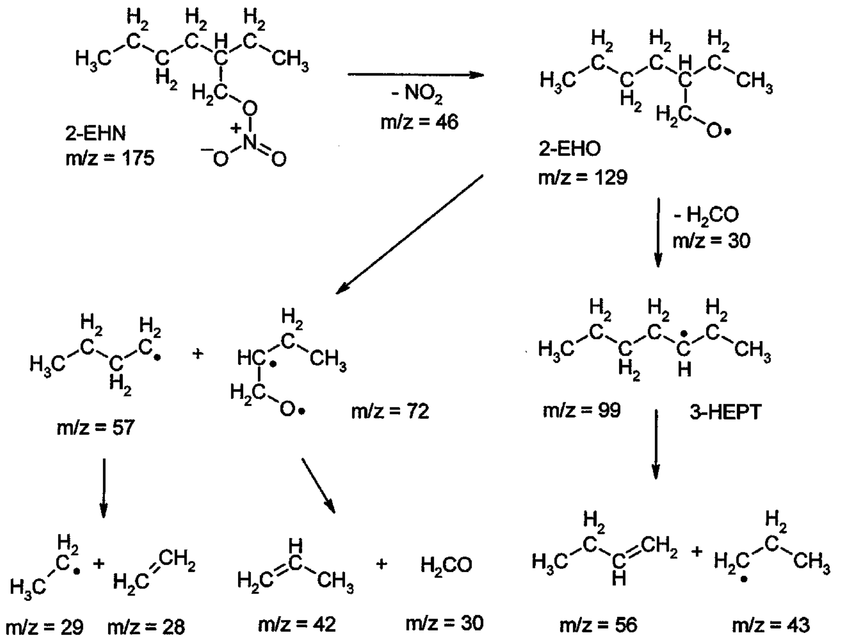


FIGURE 3 IR spectra showing the products of the gas-phase decomposition of 2-EHN in argon at 10 K. The spectra were obtained after different pyrolysis temperatures; top: 625°C, middle: 375°C, bottom: 250°C.

accordance with a fragmentation process under formation of a radical pair as the rate-determining step.

In benzene at 121°C the half-life of 2-EHN was determined to 535 h, in good agreement with the half-life of 523 h at the same temperature in decalin. The decomposition in decalin and benzene exhibits the same kinetics, and we therefore expect that in diesel fuel, with varying composition of aliphatic and aromatic constituents, also the same kinetics is followed. A major difference between thermolyses in benzene and decalin is that at higher concentrations of 2-EHN (>1%) the benzene solution turns very dark and a black coating on the surface of the glass ampoule is formed, while in decalin only a yellow coloring and no precipitate is observed. This indicates that the rate-determining step is the same in both solvents; however, as expected the secondary reactions of the radicals differ.

In ethanol as solvent, the decay of 2-EHN was determined as $k = 9.57 \times 10^{-7}\ s^{-1}$ at 121°C, corresponding to a half-life time of 201 h. Thus, in ethanol the decomposition is considerably faster than in the non-protic solvents, which indicates a change in reaction mechanisms. One of the reaction products was separated by preparative GC and identified (MS, ^{13}C NMR) as 2-ethylhexanol, the product of the ethanolysis of 2-EHN. Obviously, the activation barrier for this process is lower than that of the homolytic bond cleavage.



SCHEME 1

Table II IR Spectroscopic Data of the FVP (625°C) Products of 2-EHN, Matrix-Isolated in Argon at 10 K

Argon 10 K				Argon 10 K			
$\tilde{\nu}(\mathrm{cm}^{-1})$	I_{rel}[a]	Assignment[b]	Reference	$\tilde{\nu}(\mathrm{cm}^{-1})$	I_{rel}[a]	Assignment[b]	Reference
3112.1	5	Ethene		1552.9	2		
3091.2	2	1-Butene	[7]	1498.8	18	H_2CO	
3082.7	3	Propene	[7,8]	1468.5	5	1-Butene	[7]
3036.6	1	Propene	[7,8]	1460.0	2	1-Butene	[7]
3018.6	1	1-Butene	[7]	1452.9	10	Propene	[7,8]
2995.6	17	H_2CO		1440.4	32	Ethene	
2986.4	4	Ethene		1415.1	1	Propene	[7,8]
2983.2	4	Propene	[7,8]	1380.1	2	1-Butene	[7]
2980.1	3	1-Butene	[7]	1373.7	4	Propene	[7,8]
2976.7	2			1361.4	3		
2940.7	5	Propene	[7,8]	1345.0	1		
2922.3	3	Propene	[7,8]	1305.5	2	Methane	
2902.2	2	1-Butene	[7]	1245.1	3	H_2CO	
2885.6	2	1-Butene	[7]	1226.2	3	SiO	
2864.7	15	H_2CO		1216.4	1	Propene	[7,8]
2798.2	30	H_2CO		1168.5	9	H_2CO	
2718.9	3	H_2CO		1077.1	1	1-Butene	[7]
2345.1	97	CO_2		1043.6	2	Propene	
2339.1	34	CO_2		1033.7	1		
2149.3	17	CO		1023.1	1		
2138.5	77	CO		999.1	7	Propene/1-butene	[7,8]
1888.9	3			997.8	7		[7,8]
1872.0	13	NO	[9]	974.6	3		
1863.2	4	*cis*-ONNO	[9]	959.4	7		
1819.8	1	Propene	[7,8]	947.6	100	Ethene	
1776.2	6	*cis*-ONNO	[9]	932.4	3	Propene	[7,8]
1742.1	75			911.8	2		
		H_2CO					
1739.9	3			909.6	6	1-Butene	[7]
1737.1	2			908.6	29	Propene	[7,8]
1708.0	3			905.6	2		
1688.6	2	*cis*-ONON	[9]	855.9	1	1-Butene	[7]
1661.4	2			801.1	5		
1646.8	3	Propene	[7,8]	736.9	2		
1636.8	4	1-Butene	[7]	720.6	2		
1623.8	53	H_2O		663.5	17	CO_2	
1610.8	58	NO_2	[10]	661.9	12	CO_2	
1607.9	29	H_2O		658.5	1		
1602.4	3			631.3	2	1-Butene	[7]
1599.6	3			617.0	4		
1595.2	3			578.6	2	Propene	[7,8]
1592.9	14	H_2O		556.4	1	1-Butene	[7]
1589.4	3			533.7	3		
1572.9	3						

[a] Relative intensity based on the strongest peak.

[b] The assignment is based either on the comparison with authentic spectra or literature-known spectra.

Mechanistic Studies in the Gas Phase

The decomposition of 2-EHN in the gas phase was investigated under the conditions of flash vacuum pyrolysis (FVP). The product composition was determined using a quadrupole mass spectrometer or by trapping of the products from FVP in argon at 10 K.

The mass spectrum of 2-EHN at 20°C obtained by 20 eV electron impact shows the characteristic fragmentation pattern of alkyl nitrates [4,5]. $C_3H_7^+$

($m/z = 43$), $C_4H_9^+$ ($m/z = 57$), and $C_4H_{10}^+$ ($m/z = 58$) were observed as major ions, while signals above $m/z = 60$ were not detectable. Pyrolysis temperatures above 150°C result in a significant change of the obtained mass spectra, indicating the thermal decomposition of 2-EHN. The signal at $m/z = 57$ strongly decreases, whereas signals at $m/z = 28$ ($C_2H_4^+$), $m/z = 29$ ($C_2H_5^+$, CHO^+), $m/z = 42$ ($C_3H_6^+$), $m/z = 46$ (NO_2^+), $m/z = 56$ ($C_4H_8^+$), and particularly $m/z = 30$ (CH_2O^+, NO^+) as major ions are increasing in intensity (Fig. 2). Raising the temperature above 200°C does not lead to further significant changes in the mass spectra.

The initial step of the fragmentation of 2-EHN (both thermally and electron impact induced) is the loss of NO_2 ($m/z = 46$) to give the 2-ethylhexyloxy radical (2-EHO, $m/z = 129$; Scheme 1). This radical is rather unstable and not directly observed. Subsequent loss of formaldehyde ($m/z = 30$) produces the 3-heptyl radical (3-HEPT, $m/z = 99$) [2]. The latter radical rapidly decomposes to give 1-butene ($m/z = 56$) and the 1-propyl radical ($m/z = 43$).

The primarily formed 2-EHO radical can also react by breaking the C2—C3 bond under formation of a butoxy diradical ($m/z = 72$) and the 1-butyl radical ($m/z = 57$). The diradical decomposes immediately into formaldehyde ($m/z = 30$) and propene ($m/z = 42$), whereas the 1-butyl radical forms ethene ($m/z = 28$) and the ethyl radical ($m/z = 29$). This decomposition scheme rationalizes all of the major fragments formed at FVP temperatures higher than 150°C.

FVP of 2-EHN with subsequent trapping of the products in argon at 10 K allowed to obtain IR spectra of the thermolysis products. The FVP was performed at temperatures between 250 and 625°C. At all temperatures the decomposition of 2-EHN was quantitative and the strong and characteristic vibrations of the alkyl nitrate moiety were absent in the IR spectra (Fig. 3). The nonradical products observed by mass spectroscopy (formaldehyde, ethene, propene, 1-butene, and NO_2) were also identified in the matrix by comparison with literature data (Table II). In addition, NO, two of its van der Waals dimers, and traces of methane were observed. Species like CO, CO_2, H_2O, and SiO are not attributed to direct FVP products of 2-EHN, but rather to impurities in the sample or in the pyrolysis tube.

The pyrolysis products were stable towards UV irradiation, while annealing at 35 K resulted in significant changes in the spectra. Most of the changes are due to aggregation of the small and mobile molecules like NO and NO_2.

The pyrolysis of 2-EHN produced always the same set of products, irrespective of the pyrolysis temperature, however, the product ratio was strongly dependent on the temperature. At 625°C the IR spectrum shows high concentrations of olefins with ethene as the major product. Reduced FVP temperature results in a significant decrease of all bands assigned to the olefins, and formaldehyde and NO_2 are the main products at temperatures below 500°C.

CONCLUSION

2-EHN is an important diesel fuel additive that significantly increases the cetane number. Our kinetic measurements clearly show that it only very slowly decomposes under normal motor operation conditions and thus the loss before reaching the ignition system is negligible. Moreover, under the high-pressure conditions inside the injection system the decomposition rate is further reduced. The primary products of the thermal decay is the (2-EHO) radical, which further breaks down to formaldehyde, olefins, and smaller alkyl radicals. This decomposition mode is in line with the fragmentation path of alkoxy radicals $RCH_2O^{\cdot}$, which produce alkyl radicals $R^{\cdot}$ and formaldehyde in high yield [6]. The activation barrier for this process was determined to about 10 kcal/mol (depending on R) [2,6] and is thus much lower than that of the rate-determining step (cleavage of the NO bond) of the decomposition of 2-EHN.

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