führt. Für Temperaturen oberhalb von 1000 K wird die Abstraktionsreaktion, insbesondere bei $1-C_4H_8$ mit der niedrigen Bindungsenergie des allylischen H-Atoms, an Bedeutung gewinnen.

3.6. Vergleich mit bisherigen Untersuchungen

Mechanismen und Geschwindigkeiten der Reaktion von OH-Radikalen mit Alkenen sind ausführlich diskutiert und in jüngsten Zusammenfassungen dargestellt (siehe [21, 22]). Für niedrige Temperaturen ergibt sich allgemein eine schwach negative Temperaturabhängigkeit und eine Abhängigkeit vom Druck, was ebenfalls auf einen Additionsmechanismus hinweist. Ein Vergleich zur Bildung der Primärprodukte von OH + C_4H_8 bei niedrigen Drücken ist mit den Arbeiten [23, 24] möglich. Gutman et al. wiesen bei OH + trans-2-C₄H₈ bei sehr niedrigen Drücken (Massenspektrometer, Photoionisation) ebenfalls die Ionen $C_4H_7^+$, CH_3^+ , $C_2H_5^+$, $C_3H_7^+$, $C_2H_5O^+$ nach, die Zerfallsreaktionen und der Abstraktionsreaktion zugeordnet wurden. (Das Nichtauftreten des Ions C₄H₉O⁺ muß nicht als Abwesenheit des Adduktes C₄H₈OH bei niedrigen Drücken gedeutet werden, da die massenspektrometrische Empfindlichkeit des C₄H₉O⁺-Ions klein gegenüber den Fragment-Ionen sein kann; siehe Abb. 3.) Pitts et al. [24] (Massenspektrometer, Photoionisation) fanden bei OH + $1-C_4H_8$ bei p = 2 Torr ebenfalls das Addukt und Fragment-Ionen, woraus jedoch eine Beteiligung der Abstraktionsreaktion von 20 \pm 6% abgeleitet wurde. Die experimentellen Befunde der beiden Arbeiten [23, 24] und der vorliegenden Arbeit sind ähnlich; Unterschiede bestehen in der Interpretation der Spektren, insbesondere der Bildung des $C_4H_7^+$ -Ions bei der Ionisierung und damit des Anteils des Abstraktionskanals. Nach der vorliegenden Arbeit ist aufgrund der Fragmentierung des C4H9O+-Ions und der Spektren der Alkoholradikale C4H8OH die Abstraktionsreaktion eine untergeordnete Nebenreaktion.

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E 5519

Thermal Decomposition of Ethylbenzene in Shock Waves

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Absorptionsspektren, sichtbar und ultraviolett / Freie Radikale / Reaktionskinetik / Stoßwellen

The thermal decomposition of ethylbenzene has been investigated under high dilution by Ar in incident and reflected shock waves in the temperature range 1250 - 1600 K. At $4 \cdot 10^{-6} \le [Ar] \le 2.4 \cdot 10^{-4}$ mol cm⁻³ the reaction was found to be in the fall-off regime of the unimolecular reaction. At the highest experimental density a first order rate constant

$$k = 10^{17.1 \pm 0.3} \exp(-340 \pm 10 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$$

has been derived. Based on observations of the UV spectra of the primary dissociation fragment and the final product styrene, as well as the kinetics of formation and consumption of the intermediate species, a dominant formation of benzyl radicals can be excluded. Instead it was shown that the dissociation starts with a C - H bond split.

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Introduction

The pyrolysis of alkyl-substituted benzene molecules in general follows complex reaction paths. The mechanisms in most cases have been studied on the basis of the rates of disappearence of the parent molecules and of appearence of stable final products. Improved thermochemical data of intermediate radicals have provided additional arguments for the establishment of the mechanism. It would, of course, be of considerable value, if single steps from these mechanisms could be separated out and studied with respect to the nature of the products. We have, therefore, started to investigate a series of thermal dissociations of alkyl-substituted benzenes under shock wave conditions where the mechanisms often simplify. After studies of the pyrolysis of toluene [1, 2], p-xylene [2], benzyl [3] and p-methylbenzyl [2] radicals we now have investigated the pyrolysis of ethylbenzene.

For the pyrolysis of ethylbenzene, the principal steps have been traced in particular by the toluene [4, 5] and aniline [6, 7] -carrier techniques. Careful product analysis in flow system studies [8] gave additional information. By means of the very low pressure pyrolysis technique the rate of the initial fragmentation could be singled out [9-11]. Thermochemical arguments have been applied to identify the products of the primary fragmentation [9, 12]. As the result of these earlier studies the primary step of the pyrolysis of ethylbenzene generally is assumed [4-12] to be the C-C bond split

$$C_6H_5CH_2CH_3 \longrightarrow CH_3 + C_6H_5CH_2.$$
(1)

The radicals formed then either react with the carrier in the carrier-techniques, or they react with the parent molecule starting a complex series of secondary reactions.

Since in our earlier work on the pyrolysis of toluene and benzyl radicals, we have collected much information on the kinetic [2, 3] and UV spectroscopic [3, 13] properties of benzyl radicals, we started our present work with the goal of monitoring simultaneously the disappearence of ethylbenzene and the appearence of the dissociation fragments. So far, an alternative primary C - H bond split of the type

$$C_6H_5CH_2CH_3 \longrightarrow H + C_6H_5CHCH_3$$
 (2)

has mostly been ruled out on the basis of thermochemical arguments [8, 9, 14]. However, the heats of formation of the radicals formed after a C-H bond split are not well known such that the conclusion is not completely clear. For this reason it appeared worthwhile to investigate wether benzyl radicals are primary reaction products or not.

Experimental

In our experiments we used a stainless steel shock tube of 10 cm inner diameter, length of the test section 4.15 m, lenght of the driver section 2.80 m. The shock waves were initiated by pressure bursting of Al-diaphragms. The shock speed was measured by Pt-resistor gauges; the shock wave conditions were calculated from the shock speed accounting for the attenuation of the waves. More details of our shock tube have been given in earlier work [1]. In the shock tube, before and during the experiments, ethylbenzene and the products were monitored by UV absorption spectroscopy through oberservation windows made of quartz. These windows were placed 5 cm before the reflecting end plate. A Xe arc lamp (Varian VIX 150 W with Al reflector and sapphire window) was used as a light source for absorption measurements. Absorption signals were recorded with a grating monochromator (GCA-Mc Pherson) with 2400 lmm^{-1} grating, spectral width <1 nm (FWHM), photomultiplier (1P28A) and storage oscilloscope (Tektronix 7633) arrangement.

Since in our experiments we observed the formation of styrene in the decomposition of ethylbenzene, we used reaction mixtures of ethylbenzene in Ar as well as, for a control, of styrene in Ar (see below).

We employed ethylbenzene, styrene and Ar of high purities. The purities of ethylbenzene and styrene (Merck Schuchard) were controlled by gaschromatography and found to be better than 99.5%. Mixtures of 10-200 ppm ethylbenzene or styrene in Ar (Messer Griesheim, purity of 99.9999%) were prepared in 100 l storage bulbs. The concentrations of the mixtures were determined spectroscopically before entering the shock tube and in the tube before the shock was initiated. Whereas no wall adsorption was observed for ethylbenzene, our analysis indicated a loss of styrene from the mixtures in the tube up to 50%. Therefore the exact concentrations of the mixture were always measured in the tube before each experiment.

Results

Fig. 1 shows a typical absorption-time profile recorded at 200 nm during a shock wave experiment. The absorption of ethylbenzene increases behind the incident and reflected waves due to the shock compression of the mixture in the tube, and due to an increase of the absorption coefficient with temperature. Whereas there is no reaction behind the incident wave, behind the reflected wave reaction sets in, characterized by absorption decrease of the reaction product. At longer wavelengths, see Fig. 2, the absorption of the reaction product is so much stronger than that of the parent molecule that the latter can hardly be noticed. Figs. 1 and 2 show the formation of a propably primary reaction product. At higher temperatures, Fig. 3, this product forms very fast and later is consumed either by dissociation or bimolecular reactions. Fig. 3 shows a marked residual absorption which does not change over considerable time intervals. In order to identify the nature of this final product, we have compared the dependence of its absorption spectrum on the wavelength with the corresponding spectrum of styrene. Fig. 4 shows an absorption profile of styrene under similar conditions like Fig. 3. No reaction is observed. The high temperature absorption coefficient of styrene then follows directly from the absorption steps.

Absorption-time profiles like the oscillograms in Figs. 1-4 have been recorded in the spectral range 200-320 nm. Assuming complete conversion of ethylbenzene into the primary reaction product such as observed in Fig. 2, and complete conversion of the primary product



Fig. 1

Oscillogram of ethylbenzene UV-absorption behind the incident and reflected shock wave (light absorption at 195 nm, $[Ar] = 3.4 \cdot 10^{-5}$ mol cm⁻³, 1380 K, [ethylbenzene]/ $[Ar] = 10^{-4}$)



Fig. 2 Absorption profile of product formation by ethylbenzene decomposition. (270 nm, $[Ar] = 8 \cdot 10^{-5} \text{ mol cm}^{-3}$, 1430 K, [ethylbenzene]/[Ar]= $1.5 \cdot 10^{-5}$)





Oscillogram of the decomposition of the primary product of ethylbenzene-pyrolysis behind the reflected shock (260 nm, $[Ar] = 7 \cdot 10^{-5}$ mol cm⁻³, 1590 K, [ethylbenzene]/ $[Ar] = 3.7 \cdot 10^{-5}$)

into the final stable product such as observed in Fig. 3, the absorption coefficients have been calibrated via the concentration of ethylbenzene in the heated reaction mixture. Fig. 5 at short wavelengths shows the temperature dependence of the UV spectrum of ethylbenzene. It is characterized by the typical broadening of the UV continuum similar to earlier observations for toluene and xylene [13]. At longer wavelengths the high temperature spectra of the benzyl radicals and of the primary reaction product of the ethylbenzene pyrolysis are compared for similar temperatures near 1600 K. The two spectra show similar positions of the different continua, but strongly differing values and structures of the absorption coefficients. This comparison demonstrates clearly, that the primary product of the ethylbenzene pyrolysis under our conditions cannot be benzyl radicals. Fig. 6 compares the absorption spectrum of the final product of the pyrolysis with that of styrene under shock wave conditions at 1540 K. The striking agreement in spectral shape and absolute value proves that with nearly 100% yield ethylbenzene finally



Absorption-time profile of styrene behind the incident and reflected shock wave (260 nm, $[Ar] = 3 \cdot 10^{-5} \text{ mol cm}^{-3}$, 1540 K, $[styrene]/[Ar] = 5 \cdot 10^{-5}$)



Absorption coefficients of ethylbenzene (● 780 K, ▲ 1420 K) and the primary decomposition product (× 1400 K, ■ 1540 K) compared to benzyl radicals (solid line, 1600 K)



Absorption spectrum of the final product of ethylbenzene pyrolysis (\bigcirc) in comparison to styrene (\triangle) under equal conditions (T = 1540 K); solid line: styrene at 300 K

is converted into styrene. Table 1 summarises our measured absorption coefficients of ethylbenzene, styrene and the intermediate radical which is not benzyl but possibly phenylethyl as shown by reaction (2).

 Table 1

 Measured absorption coefficients of ethylbenzene, styrene and the intermediate radical (phenylethyl); ε in 1 mol⁻¹ cm⁻¹; approx. every third experiment is given

Ethylbenzene					
λ/nm	ε(300 K)	ε(780 K)	ε(1420 K)		
196	4800	11000	18100		
197	4900		-		
200	5150	6850	12600		
205	5460	5600	9200		
210	4000	4700	6800		
215	1250	3700	5200		
220		1850	4200		
225		900	2900		

Styrene			
λ/nm	ε(300 K)	є(1540 K)	
 215	3650	6000	
220	4800	5600	
225	7500	6000	
230	10400	6400	
235	12600	6500	
240	12500	6250	
245	10500	5200	
250	7100	3900	
255	3100	2800	
260	400	2000	

Intermediate product (prenyletny)					
λ/nm	ε(1400 K)	ε(1540 K)			
240	2400	2400			
250	4100	4000			
260	5600	5000			
270	3100	3400			
280	1900	2100			
290	1200	1300			
300	1000	1100			
305	780	1000			
310	1200	980			
320	750	780			

The observations about the structures and absolute values of the absorption coefficients of ethylbenzene, styrene and the intermediate reaction product can be further supported by investigations of the kinetic properties of these species. It was not possible to record seperately the spectrum of ethylbenzene and to study its disappearence via this spectrum. Instead, we measured the rate of the primary dissociation via the rate of formation of the primary reaction product.

This technique is fully adequate because at the wavelengths of Figs. 1 and 2, with overlapping spectra in Fig. 1 and separate product spectra in Fig. 2, the same rate constants are obtained. The formation of the primary reaction product follows a time law

$$C = C_{\infty} \left(1 - \exp(-k_1 t)\right).$$

Fig. 7 shows an Arrhenius plot of the rate constants k_1 at various inert gas pressures. The rate constants did not depend on the ethylbenzene concentration over the concentration range 15 – 200 ppm at temperatures above 1350 K. At lower temperatures a concentration dependence was observed such that only measurements with 20 ppm or less are included in Fig. 7 below 1350 K. At higher concentrations an increase of the rate constants by a factor of 2 is observed. The rate constants shown in Fig. 7 exhibit the typical properties of a unimolecular reaction in the fall-off range but close to the high pressure limit. Table 2 summarises the rate constants which we attribute to the primary



Fig. 7

First-order rate constants of reaction (2) monitored via the formation of the intermediate product: • $[Ar] = 4 \cdot 10^{-6} \text{ mol cm}^{-3}$, • $[Ar] = 3.1 \cdot 10^{-5} \text{ mol cm}^{-3}$, • $8 \cdot 10^{-5} \leq [Ar] \leq 2.4 \cdot 10^{-4} \text{ mol cm}^{-3}$

 Table 2

 I) Measured first-order rate constants of ethylbenzene decomposition (every third experiment is given)

[Ar] = mo	$= 4 \cdot 10^{-6}$ l cm ⁻³	[Ar] a	$\approx 3 \cdot 10^{-5}$ ol cm ⁻³	8 · 10 ⁻⁵ ≤ [A mol	$[t] \le 2.4 \cdot 10^{-4}$ cm ⁻³
T/K	k_1/s^{-1}	T/K	<i>k</i> ₁ /s ⁻¹	T/K	k_1/s^{-1}
1330	3.3 · 10 ³	1300	3.5 · 10 ³	1300	2.9 · 10 ³
1360	7.1 · 10 ³	1330	4.2 · 103	1320	4.2 · 103
1410	1.9 104	1400	2.2 · 10 ⁴	1350	8.6 · 10 ³
1430	2.9 · 10 ⁴	1420	3.7 · 104	1400	$2.1 \cdot 10^{4}$
1470	3.5 · 104	1470	8.4 · 104	1430	4.1 · 10 ⁴
1490	8.5 · 10 ⁴	1510	2.0 · 10 ⁵	1480	1.1 - 105
1530	9.8 · 104	1550	2.9 · 10 ⁵	1500	1.4 · 10 ⁵
1560	1.7 · 10 ⁵	1570	4.1 · 105	1520	3.1 · 10 ⁵
				1530	3.5 · 105

II) Measured first-order rate constants of phenylethyl decomposition

			or cm °	mol	cm ⁻³
<i>T</i> 7K	k_2/s^{-1}	T/K	k ₂ /s ⁻¹	<i>T</i> /K	k_2/s^{-1}
1440	1.6 · 10 ³	1520	4.5 · 10 ³	1390	1.5 · 10 ³
1530	3.4 · 10 ³	1580	1.0 · 104	1460	2.8 · 10 ³
1550	5.3 · 10 ³	1660	1.8 · 10 ⁴	1510	6.6 · 10 ³
1590	7.0 · 10 ³	1710	4.5 · 104	1560	$1.2 \cdot 10^{4}$
1640	1.3 · 104	1760	5.9 · 104	1590	1.8 · 104
1670	1.8 · 10 ⁴	1800	9.2 · 104	1610	2.0 · 10 ⁴
1710	2.7 · 10 ⁴	1820	1.2 · 105	1720	5.5 - 104
1780	5.4 · 10 ⁴	1960	3.0 · 10 ⁵	1770	1.0 · 10 ⁵
1930	1.6 · 10 ⁵	2020	4.3 · 105	1810	1.5 · 105
				1850	2.8 · 105

decomposition of ethylbenzene. These rate constants can be represented by

$$k_{1} = 10^{15.8 \pm 0.5} \exp(-311 \pm 14 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$$

at [Ar] $\approx 4 \cdot 10^{-6} \text{ mol cm}^{-3}$,
 $k_{1} = 10^{16.5 \pm 0.3} \exp(-326 \pm 10 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$
at [Ar] $\approx 3 \cdot 10^{-5} \text{ mol cm}^{-3}$,
 $k_{1} = 10^{17.1 \pm 0.3} \exp(-340 \pm 10 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$
at $8 \cdot 10^{-5} \leq [\text{Ar}] \leq 2.4 \cdot 10^{-4} \text{ mol cm}^{-3}$.

The error limits indicate statistical 2σ deviations.

At higher temperatures the disappearence of the primary product can be measured. No interference with the formation reaction occurs. However, disappearence of the spectrum of the primary product and appearence of the spectrum of the final product at all wavelengths overlaps. Nevertheless, the residual absorption signal is always approached, following a first order rate law. From this one derives rate constants k_2 for decomposition of the primary product and formation of the final product styrene which are shown in Fig. 8. They are compared with decomposition rate constants of benzyl radicals from Ref. [3] and remeasured in the present work. The marked differences of the rates of disappearence confirm our conclusion, that benzyl is not the primary product of ethylbenzene decomposition. In order to exclude possible bimolecular reactions of the primary dissociation products, we varied ethylbenzene concentrations between 15 and 300 ppm and found no influence on k_2 .





First-order rate constants of the decomposition of the intermediate phenylethyl radical (reaction (3)): • $[Ar] \approx 3 \cdot 10^{-6} \text{ mol cm}^{-3}$, • $[Ar] \approx 1.5 \cdot 10^{-5} \text{ mol cm}^{-3}$, • $7 \cdot 10^{-5} \leq [Ar] \leq 2.5 \cdot 10^{-4} \text{ mol cm}^{-3}$; × remeasured rate constants of the benzyl decomposition $[Ar] \approx 2.5 \cdot 10^{-5} \text{ mol cm}^{-3}$

The pressure dependence again corresponds to a unimolecular reaction in the fall-off range. The rate constants are included in Table 2. They can be represented by

$$k_{2} = 10^{11.0 \pm 0.3} \exp(-215 \pm 10 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$$

at [Ar] $\approx 3 \cdot 10^{-6} \text{ mol cm}^{-3}$,
 $k_{2} = 10^{11.8 \pm 0.3} \exp(-235 \pm 12 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$
at [Ar] $\approx 1.5 \cdot 10^{-5} \text{ mol cm}^{-3}$, and
 $k_{2} = 10^{12.4 \pm 0.4} \exp(-250 \pm 15 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$
at $7 \cdot 10^{-5} \leq [\text{Ar}] \leq 2.5 \cdot 10^{-4} \text{ mol cm}^{-3}$.

These values differ surprisingly from the typical rate coefficients for bond fission of ethylbenzene and benzyl radicals. Nevertheless, we have no indication that the disappearence of the primary reaction product forming styrene is not a unimolecular reaction.

Styrene appears to be a particularly stable reaction product. We have tried to monitor its thermal decomposition at temperatures above 2000 K. However, due to overlap of the UV spectra of styrene and reaction products we have not been able to investigate this reaction with the present spectral technique.

Discussion

Our failure to observe benzyl radicals in the decomposition of ethylbenzene rules out reaction (1) as the primary decomposition step. The stoechiometry of the reaction under our conditions clearly shows a complete conversion of ethylbenzene into styrene. These observations can only be reconciled by a reaction scheme with a sequence of two hydrogen atom losses

$$C_6H_5CH_2CH_3 \longrightarrow C_6H_5CHCH_3 + H$$
, (2)

$$C_6H_5CHCH_3 \longrightarrow C_6H_5CHCH_2 + H$$
. (3)

In this scheme we cannot indicate at which position the primary H-atom split occurs, whether H-atom shifts or other isomerisations play a role. In the following we tentatively assume that the primary dissociation product observed in our work corresponds to the 1-phenylethyl radical. The dissociation energy of ethylbenzene in reaction (2) can be estimated by means of the heat of formation of phenylethyl radicals as postulated dissociation products of isopropylbenzene [9, 14]. This leads to a value of $\Delta H^0 \simeq 340$ kJ mol⁻¹ for reaction (2) [14, 16] in contrast to an estimate value of $\Delta H^0 \approx 313 \text{ kJ mol}^{-1}$ for reaction (1) based on the new heat of formation of benzyl radicals of $\Delta H_{\rm f}^0$ = $200 \pm 6 \text{ kJ mol}^{-1}$ [15]. Our measured activation energies of k_1 do correspond completely to the high values observed for the C-H bond splits in toluene [1] and p-xylene [2]. Therefore our kinetic data appear fully consistent with the assumption of predominant reaction (2).

One has, of course, to ask why under our conditions reaction (2) predominates over (1). The C-C bond split is expected to have a markedly lower preexponential factor and a slightly lower activation energy. One, therefore, cannot rule out that the present reaction is a two-channel system where the benzylforming channel (1) dominates at the lower temperatures of earlier experiments [4-12] whereas channel (2) dominates under shock wave conditions. However, in order to prove this statement, better attempts to conclude on the nature of the primary product under low temperature conditions should be undertaken. It should be emphasized that our results for k_1 after extrapolation to the conditions of low temperature experiments agree well with the earlier data of Refs. [4-12]. Therefore, if the reaction is a two-channel system, the transition from dominant reaction (1) to dominant reaction (2) would not be abrupt. Nevertheless, we believe that justifications for assuming a dominant role of reaction (1) at temperatures below about 1200 K still have to be given.

Although our experiments about the conversion of ethylbenzene via phenylethyl into styrene appear to be very conclusive, there is a problem with the measured values of k_2 . Our spectral observations show convincingly a simple sequence of formation and dissappearence of phenylethyl, suggesting thus reaction (2) and (3). The measured values of k_2 however, do not appear to correspond to a unimolecular C-H bond split as indicated by reaction (3). At present, we cannot resolve this dilemma. It appears premature to speculate about an overlap of several reactions at this place. We, therefore, intend to study the possible formation of phenylethyl from the thermal decomposition of isopropylbenzene in shock waves and to investigate its subsequent thermal decomposition under our conditions.

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Modeling Studies of the Homogeneous Formation of Aromatic Compounds in the Thermal Decomposition of n-Hexane

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Kohlenwasserstoffe / Modellierung / Pyrolyse / Reaktionskinetik

The pyrolysis of n-hexane - as well as the thermal decomposition of n-hexane with addition of propene and 1-butene - was studied at 819 K up to very high conversions. A reaction model, consisting of elementary reactions, was developed. With this model the experimental results including the formation of benzene and toluene can be described. Inhibition effects, the rates of formation of various products and the effects of products on the reacting system are discussed.

Introduction

As is well known, product distribution in pyrolysis of higher hydrocarbons shows predominantly the formation of low-molecular-weight products like hydrogen, methane, ethane, ethylene, propene. With increasing conversion the formation of products with higher-molecular-weight and low hydrogen content i.e. benzene, toluene become important.

The interpretation of experimental data for such complex reaction systems is only possible by model simulations. If the model is based on elementary reactions, the number of elementary reactions neccessarily becomes high, and the development of such reaction models should be supported by sensitivity studies. In an earlier study, model simulations of n-hexane pyrolysis up to medium conversions were carried out [1]. The aim of this work was to extend the model to higher conversions including the formation of the aromatic compounds benzene and toluene.

Experimental

Experiments on the thermal decomposition of n-hexane were carried out in a conventional static quartz apparatus. The initial conditions of the experiments were varied by adding equal molar amounts of helium, propene or 1-butene to study their influence on the reaction. The experimental conditions were 819 K and 238 mbar. The variation of the total pressure with reaction time was recorded, and the product composition was determined by gas chromatography (steel column, 1/4 inch, aluminiumoxid 80/100 mesh).

The pressure rise in the different experiments is shown in Fig. 1. Curve a represents the n-hexane decomposition with added helium, which was found to be identical with the decomposition of pure n-hexane. Addition of propene causes a strong inhibitory effect (curve



Total pressure rise of different experiments at 819 K with reaction time a) n-hexane/helium; b) n-hexane/propene; c) n-hexane/1-butene

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