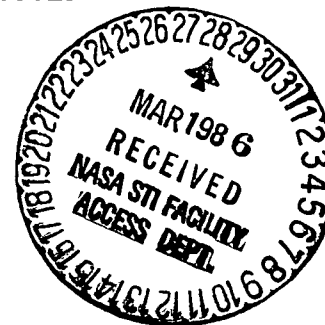


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EXPERIMENTAL STUDIES ON THE REACTION KINETICS OF
1,1-DIMETHYLHYDRAZINE AND OXYGEN

Th. Just



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Summary

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*Numbers in the margin indicate pagination in the foreign text.

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EXPERIMENTAL INVESTIGATIONS ON THE REACTION KINETICS OF UDMH AND OXYGEN

Th. Just

Deutsche Forschungs- und Versuchsanstalt für Luft- und Raumfahrt

1. Introduction

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The systems 1,1-dimethylhydrazine-oxygen (hereinafter called UDMH-O₂) and UDMH combined with nitric oxide have achieved some importance as propellant combinations for rocket engines. For the further development of rocket engines, it is often helpful to have more precise knowledge of the chemical kinetics of propellant-oxidizer combinations. For this reason, studies were undertaken to obtain some insight into the kinetics of UDMH-O₂ reactions.

Given the complexity of the UDMH molecule and the relatively limited funds available for this study, we could not expect a very precise analysis. Nevertheless, certain simple properties were found to be significant, and may be useful as pointers for more in-depth studies.

It developed that when a UDMH-O₂-Ar mixture is heated suddenly, in all cases first the UDMH molecule bursts in a unimolecular stage very probably at the N-N bond, and the subsequent reaction with oxygen occurs considerably later than the first phase, after a clearly predictable time period, in a distinct second stage. The same also applies for further reactions of the formed UDMH fractions in oxygen-free mixtures.

2. Measurement Method

First an attempt was made to obtain information on ignition

delays and reaction times as a function of pressure and temperature at the highest possible UDMH-O₂ concentrations. For this, the likely route seemed to be detonations, produced easily by initial ignition with a spark or shock wave. Good results have been obtained with this method for the systems H₂-O₂, n-hexane-O₂, etc. [1,2,3]. Corresponding experiments in the present system went astray in that under the pressure and temperature conditions of a detonation the processes occurred so fast that 8 they were no longer accessible to exact measurement. Dilution with argon or nitrogen did not significantly improve the results. The only result here was the good agreement of the calculated and measured detonation speeds.

p_{anf}^a (Torr)	x_{UDMH}	x_{O_2}	x_{N_2}	$D(m/s)$	$D(m/s)$ b berechnet
40	0.153	0.77	0.077	2 150	2 130
42	0.22	0.67	0.11	2 320	2 310

Key: a. initial b. calculated

The relatively simple theory of Chapman and Jouget for the calculation of detonation speeds (see for example Jost [4]) can thus also be applied to the system UDMH-O₂. The small amounts of N₂ were necessary for the decomposition-free evaporation of UDMH in a saturation apparatus.

To get usable results on reaction kinetics, the system, heavily diluted with argon, was studied in a shock wave apparatus. The pressure and temperature conditions behind the incoming shock wave were set so low that an preliminary reaction was prevented and the reaction was only started after the reflecting shock wave. Measurements with initially only slightly diluted mixtures of UDMH and O₂ yielded poorly reproducible results, the main cause probably being not the preliminary reaction after the incoming shock wave, but the preliminary reaction at the wall of the inlet tube and the shock tube itself. Reproducible measure-

ments were only achieved with UDMH molar fractions of less than 0.06.

The strong continuous UV absorption at 2,500 Å was used as an indicator for the decomposition of UDMH. The start of the further violent chemical reactions could subsequently be marked by recording the light emission associated with this process, in the visible spectrum range at 5,500 Å. This is largely non-thermal excitation. At concentrations that are not too low, $x_{\text{UDMH}} \geq 0.01$, a pressure increase can be observed at the end flange of the shock tube, starting at exactly the same time as the 9 light emission at 5,500 Å.

2.1. Details of Apparatus

UDMH decomposes very slowly on light metal and glass surfaces; hence the shock tube (inner diameter 72 mm) was aluminum. All tubing and the saturation apparatus were glass. The desired mixtures of UDMH, O₂ and argon were produced by charging an argon stream with UDMH vapor and then adding oxygen. The final vapor pressure of UDMH developed in two successive coil condensers, with very precise thermostatic controls ($\pm 0.1^\circ\text{C}$). The temperature in the saturator proper was ca. 5 to 6°C higher than in the condensers. By observing the condensation of excess UDMH, the exact charge of the argon stream could be determined. The argon and O₂ partial streams were measured with rotameters, accuracy $\pm 1\%$.

The speed of the incoming shock wave was determined with electronic meters specially developed for this job at the institute. Thin-film probes served as sensors.

For spectroscopic investigations, a small Zeiss quartz prism device was used. A hydrogen lamp proved well suited as a background radiator for the absorption measurements. Observation

windows installed on the side ahead of the end flange allowed measurements ca. 5 - 3 mm away from this flange.

3. Results

The initial conditions after the reflected shock wave were calculated electronically by computer program from the measurements of the speed of the incoming shock wave and the known thermodynamic data of the respective mixture.

3.1. Decomposition of UDMH

First, under the typical conditions for the experiments: T from 900 to 1,400°K, P 0.5 to 2 atm and x_{UDMH} 0.0009 to 0.005, /10 the validity of the Lambert-Beer law was checked and confirmed, i.e. in a very good approximation:

$$\frac{J}{J_0} = e^{-\alpha \cdot n \cdot l}$$

J_0 = incoming intensity

J = penetrating intensity,

... both in a narrow frequency band around $\lambda = 2,500 \text{ \AA}$

α = absorption coefficient

n = concentration in mol/l

l = layer thickness

Preliminary experiments also determined the optimum wavelength range for the transition from the fundamental state to the excited state of UDMH, which under the present conditions presented only a very low dependency of the absorption coefficient on temperature, Fig. 1.

Taking account of the influence of temperature on the absorption coefficient, which the change in temperature during the decomposition reaction generally requires, could be neglected

here. The only necessary correction was to take account of the initial absorption after filling with the mixture, before passage of the shock wave.

The evaluation of the oscillograms (Fig. 2) yielded an excellent representation of the decrease in concentration over time, according to:

$$\frac{n}{n_0} = e^{-k \cdot t}$$

t = time

n = concentration at time t

n₀ = initial concentration

k = rate constant

The first stage in Fig. 2 corresponds to compression due to the incoming shock wave.

Formally, the decomposition of UDMH can be described with a first-order law. /11

If one graphs the half-life $t_{0.5}$, obtained from $n(t_{0.5}) = n_0/2$, as a function of temperature, one gets Fig. 4.

This figure also shows experiments with a reduced UDMH concentration. The results are the same as at higher concentrations. From this one can very probably conclude an absence of effects of the decomposition products upon the UDMH decomposition process. Thus the decomposition of UDMH is observed directly according to:



A variation of the entire pressure level between 1.35 atm and 3.0 atm likewise caused no change in the measurement results. For reasons of equipment strength, the pressure level

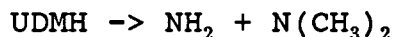
was not increased further. The measurement accuracy seemed adequate to suggest the conclusion that under the present conditions, the decomposition process is controlled practically only by the natural lifespan of highly excited UDMH molecules. The complicated UDMH molecule, with its numerous internal degrees of freedom of vibration, makes it seem plausible that at these relatively low pressures this limiting process is already achieved, while smaller molecules only present the well-known transition from the "low-" to the "high-pressure range" at considerably higher pressures.

The half-life $t_{0.5}$ can be connected to the decomposition probability of UDMH. For this value k , in Arrhenius notation we get:

$$k = k_0 \cdot e^{-E/RT}$$

with $k_0 = 7 \cdot 10^{12} \text{ s}^{-1}$
 and $E = 42\,700 \text{ cal/mol.}$

The likely result is a decomposition with a separation of the N-N bond, similar to N_2H_4 , according to:



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The found values k_0 and E seem physically reasonable, but somewhat contradict values stated by Glassmann et al. [5]. The flow method used by these authors possibly does not rule out an interfering influence of catalytic wall reactions, which certainly do not occur with the present method aside from preliminary reactions during filling. The good reproducibility of our results at different initial concentrations make such an influence appear unlikely. The scatter range of Glassmann's measurement points is considerably greater than ours. A quite justifiable adjustment of the slope of the interpolating lines through Glassmann's measurement points brings his results practically into accord with the present ones.

Since very probably the decomposition of UDMH was measured in the immediate vicinity of the so-called high-pressure range, according to the various models developed by Slater [6], Kassel, Rice, Ramsperger and Marcus [7], Troe and Wagner [8], the influence of molecular vibrations on the value of the activation energy is relatively slight. Thus the found activation energy is approximately the same as the N-N bonding energy value in the UDMH molecule. The found frequency factor k_0 is also in a range predicted by the different models. Other considerations on a certain reaction path in the decomposition of UDMH will be discussed below in connection with the measured intrinsic emission during decomposition.

3.2. Reaction of UDMH with O₂

3.2.1. Influence of O₂ on Measurements of the Unimolecular Decomposition Step of UDMH

In the studied UDMH concentration range, even an addition of six times the amount of O₂ did not perceptibly affect the decomposition of UDMH. Thus no parallel reactions occur at /13 comparable speed.

3.2.2. Light Emission at 5,500 Å in Reaction with O₂

With the laterally installed spectral apparatus, a relatively flat emission maximum was observed at ca. 5,500 - 6,000 Å. An oscillogram of the intrinsic emission is shown in Fig. 5. The oscillograph was triggered by the incoming shock wave. Here the exact time of impact of the shock wave against the end flange is shifted somewhat to the right on the oscillogram (arrow, Fig. 5). Immediately after the shock reflection, the recording shows a very quickly vanishing "peak" and then a more prolonged flash phenomenon, which is strong only in the presence of O₂. It was assumed that this is the exothermal further reaction of the decomposition products of UDMH and O₂. We can only guess at the

genesis of the first "peak." Because of the maximum of the flash at ca. 5,500 Å this might be the radiation from non-thermally excited NH_2 ("α bands of NH_3 "), which possibly results during the first decomposition step of UDMH. The fast breakdown of the peak might be explained by a shorter lifespan of the excited state of the NH_2 radical, or possibly also by relaxation upon impact with Ar. The UDMH decomposition process could be imagined in that at a concentration somewhat greater than 43,000 cal/mol in one or more appropriate normal vibrations, the N-N bond is greatly loosened precisely when energy for this is stored in the extended form of NH_2 . The extended configuration of NH_2 corresponds to the electronically excited state [9]. The emission at 6,000 Å has an activation energy of ca. 47,300 cal/mol. The measured activation energy of ca. 43,000 cal/mol is probably somewhat less than the actual energy requirements when the molecule explodes. The deficit between this and 47,300 cal/mol might be covered by the thermal energy of suitable UDMH molecules. In all, the proposed model does not seem entirely improbable. A precise clarification of these questions would require a considerably more expensive spectroscopic study, such as could not be conducted here. /14

The second flash was used to define an ignition delay, for simultaneous pressure measurements confirm that only here, in the second phase of the reaction, was noteworthy heat of reaction released.

At a constant gas pressure and constant temperature, the ignition delay decreases as the O_2 content increases. Moreover, at a constant total pressure, the dependency of ignition delay on temperature changes as the O_2 content changes. The apparent activation energy decreases. This suggests a relatively complex reaction mechanism, in which at different O_2 contents different elementary steps determine further evolution. These relatively coarse measurements allow no definitive statements about details

of the mechanism. At a constant temperature, moreover, a clear influence of the total pressure also appears. These reactions are accordingly at least bimolecular, i.e. they depend on the concentration of two kinds of molecules. Unfortunately it was not possible to get good reproducible results on ignition delay at concentrations higher than $x_{\text{UDMH}} = 0.06$, so that a high-accuracy extrapolation of ignition delay for undiluted UDMH- O_2 mixtures, which would also be desirable from the technical viewpoint, is impossible.

The results are shown in Figs. 6 and 7.

One result to bear in mind from this initial study of the UDMH- O_2 system is that in the studied range of P , T and x_{UDMH} , the reaction proceeds in two very clearly separated phases. The first phase is coupled to the fast, unimolecular decomposition of UDMH without noteworthy effects of O_2 or radicals, while the second phase is clearly connected to the exothermal reaction with O_2 . Figure 8 shows the half-lives for the decomposition of UDMH together with typical ignition delays as a function of temperature. The separation of the two reaction phases at the same temperature is clearly visible here.

Further studies apparently can only be conducted with /15 a good deal of spectroscopic equipment and using fast-recording mass spectrometers.

4. Influence of UDMH on Ignition Behavior of H_2 -Air Mixtures

The very fast decomposition of UDMh also suggests other technical applications that have nothing to do with rocket engines. As shown by the ignition delay experiments with H_2 -air mixtures at 800-1400°K and 1/2 to 2 atm at the Reaction Kinetics Department of DFVLR [10], the ignition delays at 900°K increase very rapidly as one approaches the conditions for the "second

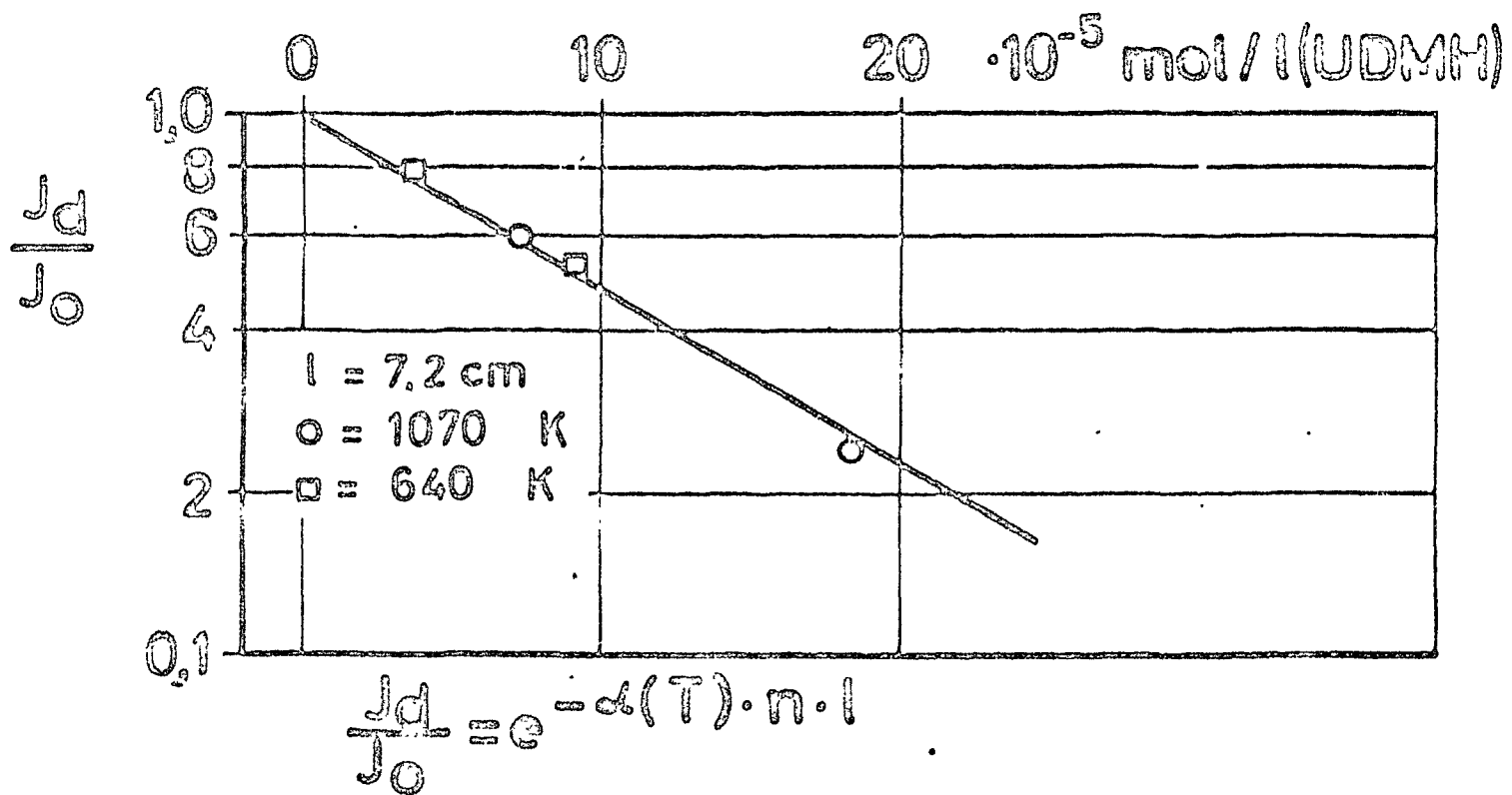
explosion limit". In developing drives for fast supersonic aircraft ($M \geq 5$), this may be an unpleasant property, since it might adversely effect the combustion or ignition behavior of a supersonic diffusion flame. Shock tube experiments verified that even small amounts of added UDMH considerably lower the ignition delays in the vicinity of the second explosion limit [11]. Within limits, this allows an expansion of the combustion range of H_2-O_2 even to low temperatures without requiring the use of expensive flame holders that increase flow losses.

As an example, consider the influence in measurements behind the reflected shock wave both with and without added UDMH (Fig. 9).

The ignition delays with added UDMH present less dependence on temperature in the vicinity of the second explosion limit. With the present relatively small-diameter shock tube, it was impossible to determine whether a second limit, similar to the second explosion limit but at lower temperature, exists with added UDMH.

Our thanks to the German Research Society for providing funds.

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Abb. 1 Prüfung des Lambert-Beerschen Gesetzes.

Fig. 1. Check of the Lambert-Beer law

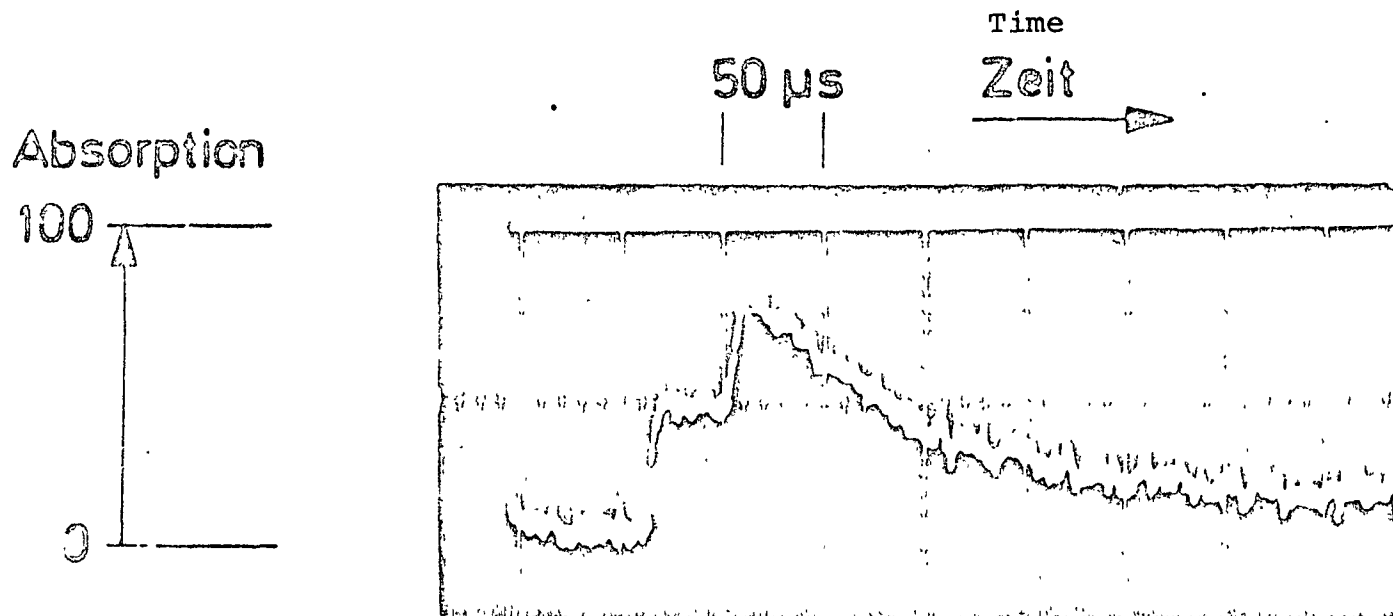
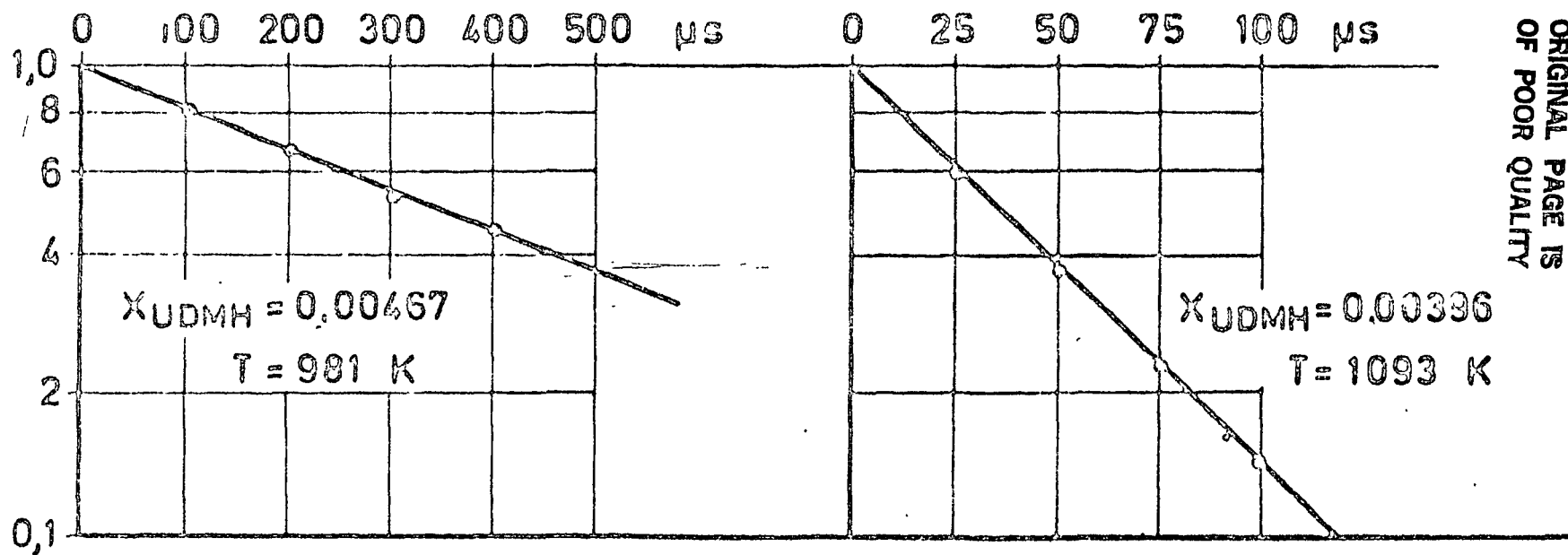


Abb. 2 Zerfall von UDMH
Absorption bei 2 500 Å.

Fig. 2. Decomposition of UDMH
Absorption at 2500 Å.

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Abb. 3 $n/n_0 = e^{-k \cdot t}$
Zerfallsgesetz von UDMH.

Fig. 3. Decomposition law for UDMH

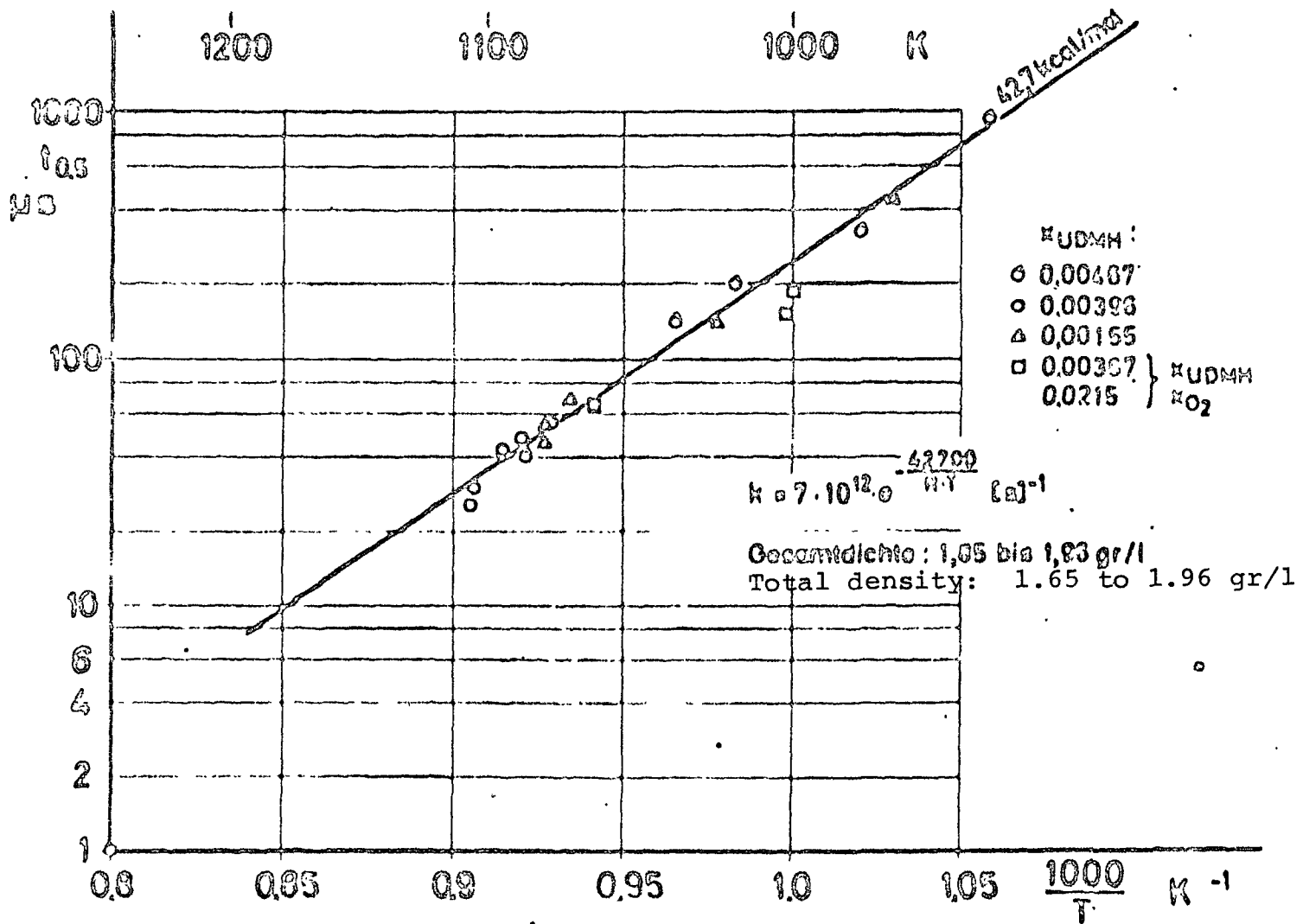


Abb. 4 Halbwertszeit des Zerfalls von UDMH gegen 1/T.

Fig. 4. Half-life of decomposition of UDMH vs. 1/T

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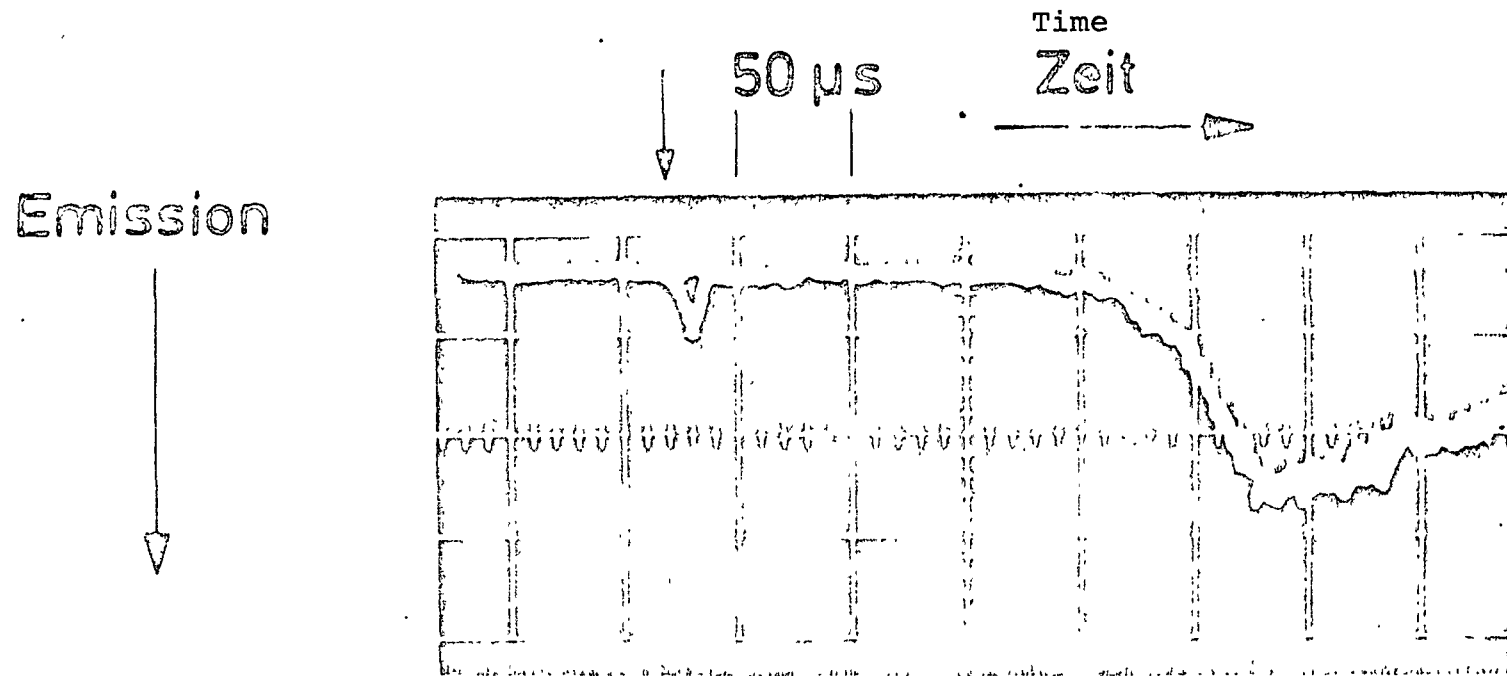
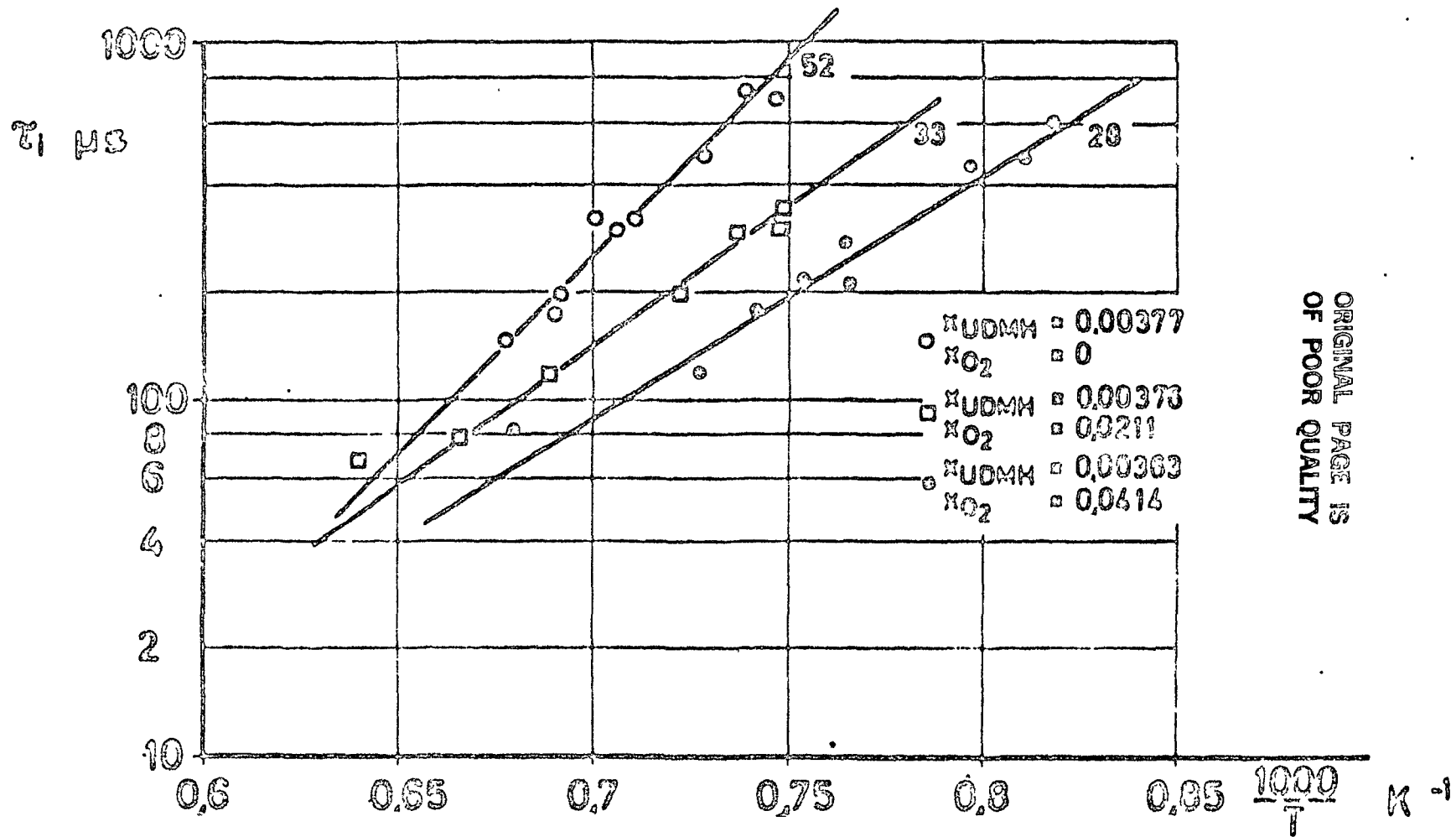


Abb. 5 Eigenemission bei 5 500 Å
UDMH-O₂.

Fig. 5. Intrinsic emission at 5500 Å.
UDMH-O₂.



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Abb. 6 Zündverzögerung von UDMH-O₂-Ar.

Fig. 6. Ignition delay of UDMH-O₂-Ar

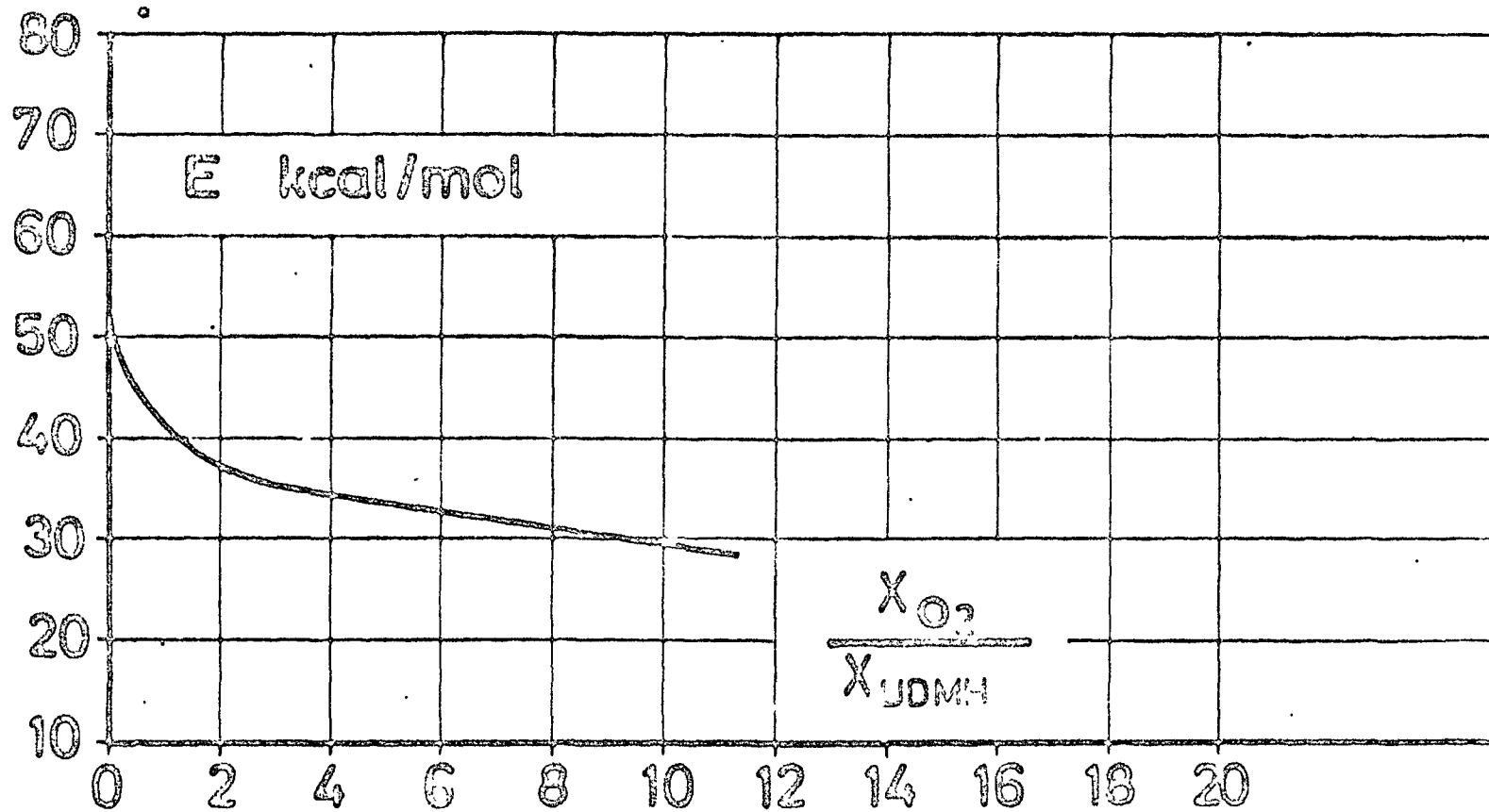


Abb. 7 "Aktivierungsenergie" des Zündverzugs gegen $\frac{x_{O_2}}{x_{UDMH}}$
 Fig. 7. "Activation energy" of ignition delay vs. ... $\frac{x_{O_2}}{x_{UDMH}}$

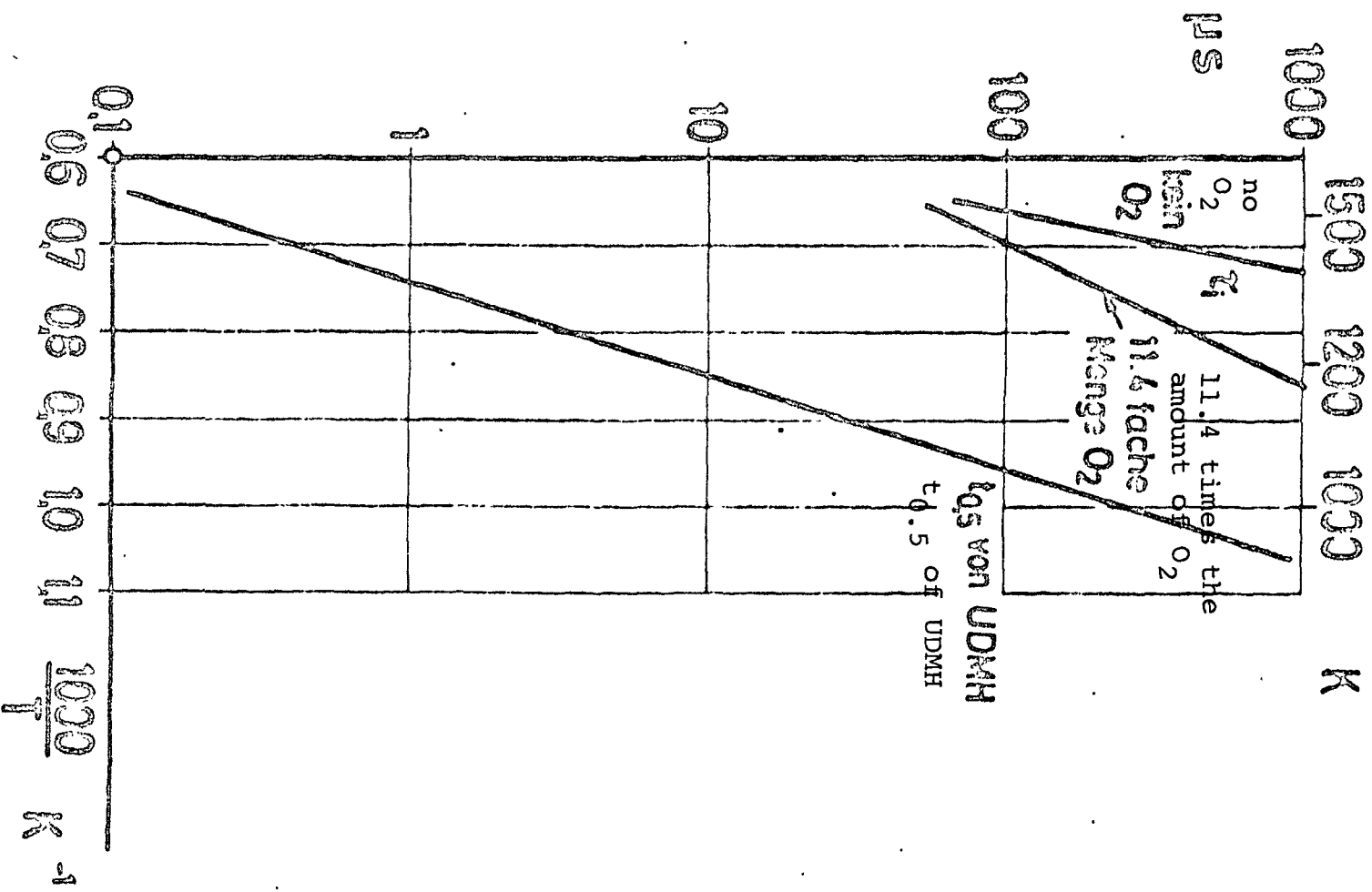
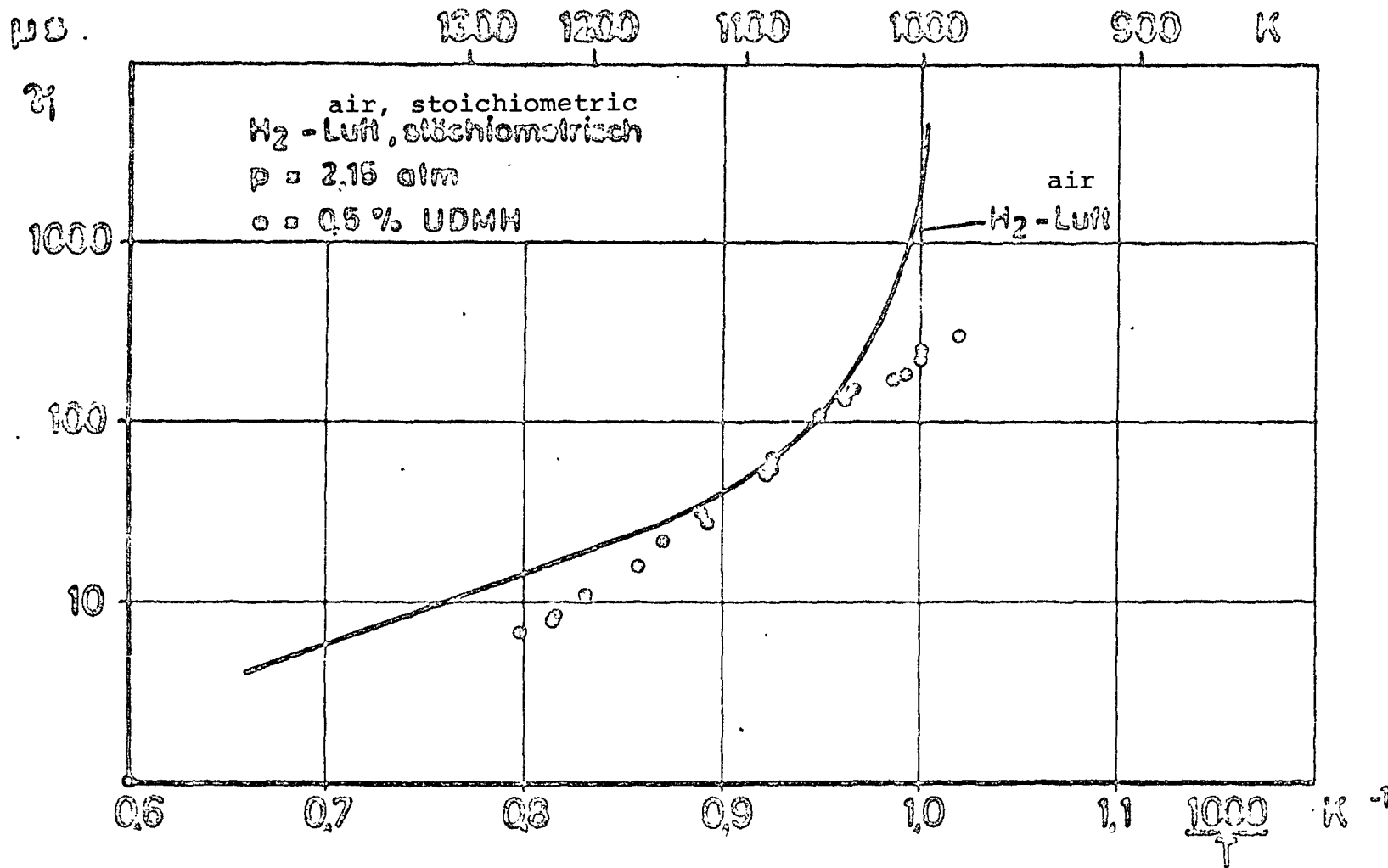


Fig. 8. Comparison of decomposition time of UDMH with "ignition delays"
 Abb. 8 Vergleich der Zerfallszeit von UDMH mit den "Zündverzügen".



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Abb. 9 Einfluß von UDMH auf die Zündverzugszeit von H₂-Luft.

Fig. 9. Influence of UDMH on ignition delay of H₂-air.