

Experimental Determination of the Static Equivalent Pressures of Detonative Explosions of Cyclohexane/O₂/N₂-Mixtures in Long and Short Pipes (part 3 of 3)

Hans-Peter Schildberg*, Julia Eble

BASF SE, 67056 Ludwigshafen, Germany

hans-peter.schildberg@basf.com

The abstract of the third part of this paper is included in the abstract of part 1.

Table 2: Compilation of precompression factors found for all tests conducted. The tests are listed in the same order as in Table 1. Omitted are those tests without DDT and those with a DDT location upstream of the first pressure sensor (tests 29, 26, 24). Note that tests 22, 32 and 35 were tests in the short pipe configuration.

number of test	initial pressure of the gas mixture [bar abs]	value of last pressure measurement of precompressed zone upstream of DDT location [bar abs]	precompression factor [-]	axial position of last pressure measurement [mm]	location of DDT as inferred from pipe deformation [mm]	speed of precompressed zone as inferred from the two last pressure signals upstream of DDT location [m/s]	distance between two last pressure sensors upstream of DDT location [mm]
1	20,00	250	12,50	3300	3740	442	620
19	14,10	603	42,77	4440	4530	1280	320
20	14,00	470	33,57	2840	3060	578	630
21	14,00	> 1000	> 71,43	1580	1710	706	630
5	20,00	508	25,40	4580	4750	800	640
22	14,00	580	41,43	6040	6140	914	320
25	12,00	110	9,17	2840	3430	533	320
28	12,00	> 1000	> 83,3	2840	2980	1103	320
23	12,00	980	81,67	1580	1690	360	630
32	3,07	625	203,58	7760	7910	1736	330
35	3,17	500	157,72	7430	7540	1488	320

The final speeds of the precompressed zone relative to the pipe wall found for the long pipe configuration seem to be similar for Cyclohexane and the other mixtures. The values are in the range of 1000 m/s to 1300 m/s, which is about half of the speed of the stable detonation.

The full width at half maximum of the pressure peaks corresponding to the compressed zone of unreacted gas ahead of the accelerating deflagrative flame front is of the order of 30 μ s (see Figures 9, 10, 11) in the final stage of the run-up to detonation. This also holds for the other mixtures investigated in the past. If a final speed of 1150 m/s relative to the pipe wall is assumed, the extension of the compressed zone in axial direction is about 35 mm (34.5 mm = 1150 m/s * 30 μ s). Figure 12 provides a schematic sketch.

To allow the precompressed unreacted gas to autoignite before it is consumed by the extremely fast deflagrative flame front, its ignition delay time must drop to values of about 10 μ s or less. This results from the fact that in the final stage of flame acceleration the deflagrative flame front propagates into the unreacted, heated mixture with speeds of the order of 1000 m/s, meaning that within 10 μ s a 1 cm thick slice (in axial direction) of the shock front is converted into hot reaction products. If the thin slice of unreacted mixture still

remaining ahead of the front would need longer than about 10 μs to autoignite – and thereby generating the DDT – it would be consumed in the next 10 μs in deflagrative manner and the DDT would not occur.

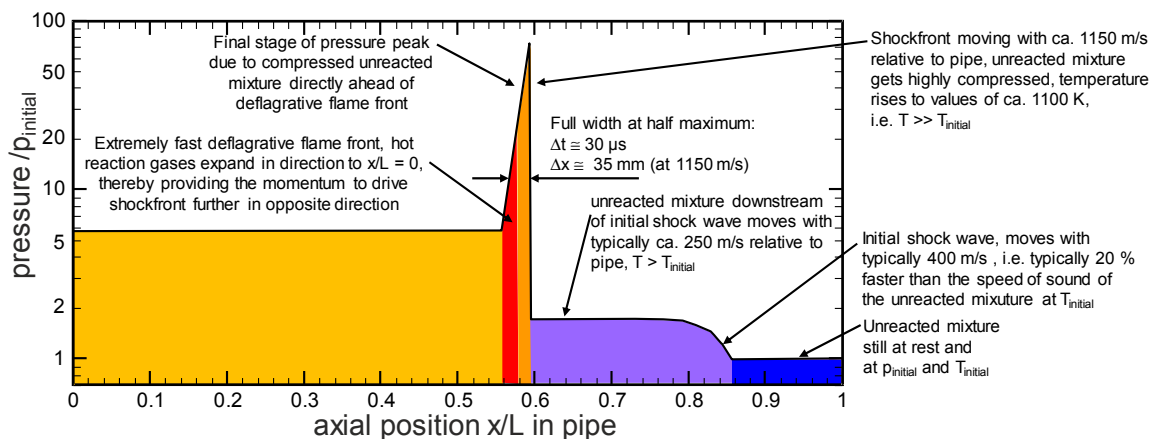


Figure 12: Schematic sketch of the pressure distribution in a long pipe when the pressure peak corresponding to the compressed unreacted mixture ahead of the deflagrative flame front has attained its maximum height, i.e. an instant just before DDT occurrence.

5. Understanding the observed precompression factors by applying reaction kinetics

The precompression factors, which are attained in the precompressed zone of unreacted mixture ahead of the deflagrative flame front at the instant of autoignition, should correlate with the values found experimentally for the ratio R . To understand quantitatively the reason why (1) the R -values of stoichiometric $\text{C}_6\text{H}_{12}/\text{O}_2/\text{N}_2$ mixtures with low O_2 concentrations differ from the R -values found for the other three stoichiometric mixtures $\text{CH}_4/\text{O}_2/\text{N}_2$, $\text{H}_2/\text{O}_2/\text{N}_2$ and $\text{C}_2\text{H}_4/\text{O}_2/\text{N}_2$ at corresponding O_2 -concentrations and why (2) the R -values drop along the stoichiometric line with rising O_2 concentrations, reaction kinetics will be applied.

5.1 Computational model

A detailed chemical kinetic mechanism taken from Silke (2007) was used to study the oxidation of cyclohexane both at high and low temperatures. The mechanism was validated against experimental data incorporating the temperature range 650-1150 K, and different pressures and equivalence ratios (Silke 2007). Based on this kinetic model, concentration-time profiles were calculated with the program package OpenSMOKE (Cuoci 2013, 2015) for an adiabatic batch reactor with constant volume. Besides, a homogenous reaction system with ideal gas behavior was assumed. The calculated ignition delay times were set equal to the times of the maximum slopes of the temperature profiles. To identify the most important reactions that influence the ignition delay times, sensitivity and reaction flux analyses were performed.

5.2 Results and discussion

Kinetic mechanisms for combustion often consist of different parts, the so-called submechanisms, to describe the consumption of the combustible, the C_1/C_6 species or the H_2/O_2 system in different temperature regimes. At lower temperatures, the dominant reaction path for cyclohexane is the H atom abstraction by OH and other radicals, followed by successive additions of oxygen leading to chain branching pathways (Silke 2007). Through the degenerate chain-branching reactions OH radicals are formed, which, in turn, lead to the consumption of the combustible. At high temperatures, the mechanism includes unimolecular combustible decomposition, H atom abstraction, alkyl radical decomposition and the subsequent oxidation reactions of the fragments. The different reaction rates can indicate whether the low- or the high-temperature mechanism is more influential.

5.2.1 Temperature dependence of the mechanism

To get an idea which mechanism is dominant in the different temperature regimes, reaction flux analyses were performed at 1100 K, 1200 K, 1300 K and 1400 K and 2000 bar for the stoichiometric $\text{C}_6\text{H}_{12}/\text{O}_2/\text{N}_2$ mixture used in tests 1 and 5 (mole fractions: 0.0228/0.20521/0.77199). The high pressure was chosen to roughly account for the pressure in the precompressed zone at the instance of DDT occurrence. The analyses were performed for the cyclohexane consumption at 90 % of the ignition delay time to get comparable results.

An indicator for the occurrence of the low-temperature mechanism is the addition of O₂ to the cyclohexyl radical. For the high-temperature mechanism the indicator is the isomerization reaction of the cyclohexyl radical followed by decomposition. The temperature dependent competition between these two reaction pathways was analyzed in this study. At 1100 K the ratio between the reaction paths is nearly 1:1, whereas at 1400 K around 90 % of the cyclohexyl radicals are consumed by the high-temperature reaction path. Therefore, it can be concluded that the transition between the low- and high-temperature mechanisms proceeds between 1100 K and 1400 K.

5.2.2 Ignition temperature of cyclohexane

The experimentally determined ignition temperature of cyclohexane in air at 1 bar abs is 533 K (=260 °C; CHEMSAFE database). The ignition temperature is the lowest temperature of a hot surface at which within 5 minutes an ignition of a flammable gas or vapor in mixture with an oxidiser (usually air) and, if applicable, an inert gas occurs. To determine the ignition temperature predicted by the kinetic mechanism, the simulations were performed with a simulation time of 5 minutes and 1 bar varying the temperature. As a result, the first ignition within 5 minutes at 1 bar occurs at 602 K. From sensitivity analyses and reaction flux analyses it becomes obvious that the most influential reactions are the low-temperature reactions (e.g. the O₂-addition to the cyclohexyl radical).

5.2.3 Ignition delay times of cyclohexane, ethylene, methane and hydrogen in mixture with air

The ignition delay times (IDT) for stoichiometric cyclohexane, ethylene, methane and hydrogen mixtures with air (or with slightly O₂-depleted air or slightly O₂-enriched air) were calculated for different compression ratios and temperatures. The temperature after compression was calculated as follows:

$$T_{\text{final}} = T_{\text{initial}} \cdot \left(\frac{p_{\text{final}}}{p_{\text{initial}}} \right)^{\frac{\kappa-1}{\kappa}} \quad \text{and} \quad \kappa = \frac{C_p}{C_v} \quad (1)$$

Here, p is the absolute pressure, T the absolute temperature and κ the isentropic exponent, calculated as the ratio between the heat capacity at constant pressure and the heat capacity at constant volume. For the different mixtures, the isentropic exponent was calculated by the thermodynamic rules of mixtures. The conditions before compression are labelled as “initial”, the conditions after compression as “final”.

The ignition delay times calculated by the kinetic simulations for the different combustible/O₂/N₂ mixtures at different compression ratios are given in Tables 3 to 6. x denotes the mole fraction of the species. For methane, ethylene and hydrogen the gas mixture must be compressed by a factor of about 200 to heat the gas from T_{initial} = 20 °C to about 1100 K. At this temperature the IDT has dropped to about 10 μs. For cyclohexane at T_{initial} = 70 °C a compression ratio of about 100 is enough to heat it to a temperature at which the IDT has dropped to about 10 μs.

It becomes obvious, that at temperatures of greater than or equal to about 1100 K the ignition delay times are of the same order for all combustible/air mixtures. At lower temperatures the difference between the ignition delay times of the individual mixtures is much higher. In this low-temperature regime cyclohexane has the shortest ignition delay times and the lowest ignition temperature compared to the other combustibles of this study. By employing reaction flux analyses it could be shown that the low-temperature reactions of cyclohexane are most influential in this temperature regime. The typical low-temperature reaction path of the cyclohexane oxidation cannot occur for methane, ethylene or hydrogen. But, in the high temperature regime at temperatures above 1100 K, ignition is caused by similar reactions for the four different combustible/air mixtures and the ignition delay times converge.

These findings show that if an explosive mixture M1 has a substantially lower AIT than an explosive mixture M2, it cannot yet be assumed that mixture M1 also exhibits an IDT sufficiently small for DDT occurrence at substantially lower temperatures (and henceforth at smaller precompression factors) than the mixture M2. The correct way to estimate whether an unknown mixture M1 exhibits smaller or larger R-values than a known mixture M2 is to compare the precompression ratios which generate temperatures for which the IDT drops to values of the order of 10 μs.

Table 3: Ignition delay times of cyclohexane. T_{initial} = 343 K = 70 °C, p_{initial} = 20 bar, x(C₆H₁₂) = 0.0228, x(O₂) = 0.2052, x(N₂) = 0.772. This is the mixture of test no. 1 in Table 1.

p _{final} /p _{initial}	p _{final} [bar]	T _{final} [K]	IDT [s]	p _{final} /p _{initial}	p _{final} [bar]	T _{final} [K]	IDT [s]
25	500	776	1.70E-03	100	2000	1104	7.40E-06
50	1000	926	6.60E-05	125	2500	1168	4.10E-06
75	1500	1026	1.70E-05	150	3000	1223	2.60E-06

Table 4: Ignition delay times of methane. $T_{initial} = 293 \text{ K} = 20 \text{ }^\circ\text{C}$, $p_{initial} = 12 \text{ bar}$, $x(\text{CH}_4) = 0.125$, $x(\text{O}_2) = 0.25$, $x(\text{N}_2) = 0.625$. This is the mixture of test no. 4 in Schildberg (2016a).

$p_{final}/p_{initial}$	p_{final} [bar]	T_{final} [K]	IDT [s]	$p_{final}/p_{initial}$	p_{final} [bar]	T_{final} [K]	IDT [s]
25	300	646	3.30E+01	125	1500	958	6.10E-04
50	600	765	1.80E-01	150	1800	1002	2.30E-04
75	900	845	1.20E-02	200	2400	1075	5.70E-05
100	1200	907	2.10E-03	300	3600	1188	9.40E-06

Table 5: Ignition delay times of ethylene. $T_{initial} = 293 \text{ K} = 20 \text{ }^\circ\text{C}$, $p_{initial} = 8 \text{ bar}$, $x(\text{C}_2\text{H}_4) = 0.0733$, $x(\text{O}_2) = 0.22$, $x(\text{N}_2) = 0.7067$. This is the mixture of test no. 10 in Schildberg (2018).

$p_{final}/p_{initial}$	p_{final} [bar]	T_{final} [K]	IDT [s]	$p_{final}/p_{initial}$	p_{final} [bar]	T_{final} [K]	IDT [s]
25	200	651	3.60E-01	125	1000	971	1.90E-04
50	400	774	2.30E-02	150	1200	1016	8.70E-05
75	600	856	2.30E-03	200	1600	1091	2.30E-05
100	800	919	5.40E-04	300	2400	1207	5.10E-06

Table 6: Ignition delay times of hydrogen. $T_{initial} = 293 \text{ K} = 20 \text{ }^\circ\text{C}$, $p_{initial} = 3.58 \text{ bar}$, $x(\text{H}_2) = 0.276$, $x(\text{O}_2) = 0.138$, $x(\text{N}_2) = 0.586$. This is the mixture of test no. 22 in Schildberg (2015).

$p_{final}/p_{initial}$	p_{final} [bar]	T_{final} [K]	IDT [s]	$p_{final}/p_{initial}$	p_{final} [bar]	T_{final} [K]	IDT [s]
25	89.5	675	2.20E+02	125	447.5	1025	4.40E-04
50	179	808	2.00E-01	150	537	1075	1.60E-04
75	268.5	898	1.10E-02	200	716	1158	3.50E-05
100	358	966	1.70E-03	300	1074	1286	5.20E-06

5.2.4 Ignition delay times of stoichiometric cyclohexane/O₂/N₂ mixtures in dependence on the O₂-concentration

In the experiments it had been found that the ratio R slightly reduces when raising the C₆H₁₂ concentration in the stoichiometric C₆H₁₂/O₂/N₂ mixtures from 2.28 vol.-% to about 4.5 vol.-% (see Fig. 7). The change in R would require that IDT-values small enough to allow for a DDT are obtained at ever smaller precompression ratios when raising the C₆H₁₂-concentrations to about 4.5 vol.-%. As shown by Tab. 7, the recompression ratios yielding the same IDT value actually exhibit a slight reduction in this concentration range.

At higher combustible concentrations R suddenly drops to 1 (see Fig. 7), which is most probably due to directly triggering the detonative mode of combustion in these highly reactive mixtures by the ignition source, i.e. there is no longer an initial deflagrative stage.

5.2.5 Qualitative variation of R to be expected as function of initial temperature of the explosive mixture

Until now no tests have been conducted to determine the variation of R with the initial temperature of the explosive mixture. In this section it will be shown what can be expected for the variation of R, when certain simplifying assumption are made.

Under the assumption that the DDT occurs as soon as the precompressed zone of unreacted mixture ahead of the flame front has reached a temperature for which the IDT is equal to 10 μs and under the assumption that an IDT of 10 μs is always attained at 1100 K, the required precompression ratios can be specified in dependence on the mean isentropic exponent κ of the mixture. Furthermore it is assumed that the formula for adiabatic compression as used in section 5.2.3 holds. Then the required precompression ratio $p_{final}/p_{initial}$ as function of $T_{initial}$ is given by:

$$\frac{p_{final}}{p_{initial}} = \left(\frac{1100 \text{ K}}{T_{initial}} \right)^{\left(\frac{\kappa}{\kappa-1} \right)} \text{ and } \kappa = \frac{C_p}{C_v} \quad (2)$$

In fact, the last assumption is presumably not perfectly justified because to some extent the compression process might be better described by the formula for temperature rise caused by shock (see e.g. Schildberg 2016a), but this formula is extremely difficult to handle for the run-up from deflagration to detonation because the ratio $p_{final}/p_{initial}$ and the Mach number M are permanently changing. Since only a qualitative understanding is sought for, the simple equation (2) is used.

Although different combustibles will have different values of κ , the mean κ value of the explosive mixture is dominated by the κ values of O_2 and N_2 , which are close to 1.4. Therefore, the κ values of stoichiometric explosive combustible/ O_2/N_2 mixtures with low O_2 -concentrations (18 to 30 vol.-%) are usually in range from 1.3 to 1.4 in the temperature interval from 20 °C to about 1000 °C. For cyclohexane/ O_2/N_2 the average κ value in this interval is about 1.34.

Table 7: Ignition delay times (IDT) calculated for different precompression ratios of the stoichiometric $C_6H_{12}/O_2/N_2$ mixtures investigated in tests 5, 22, 25, 23, 29 and 26 (see Table 1). All mixtures were at same $T_{initial} = 130$ °C but at different initial pressures between 12 and 20 bar abs. In the last 8 lines the IDT's calculated for stoichiometric mixtures with even higher O_2 -concentrations are given. These mixtures were not investigated in the tests. (Note that the IDT also drops when the final pressure rises but the temperature is kept constant. Thus, the effect of rising O_2 -concentration on the IDT can be compensated for or even overcompensated by conducting the experiment at a lower initial pressure. This explains that the IDT's in test 22 are slightly longer than in test 5).

$P_{final}/P_{initial}$	Test 5, $O_2=20,5$ vol.-%, 20 bar			Test 22, $O_2=24,3$ vol.-%, 14 bar			Test 25, $O_2=29,0$ vol.-%, 12 bar		
	p_{final} [bar]	T_{final} [K]	IDT [s]	p_{final} [bar]	T_{final} [K]	IDT [s]	p_{final} [bar]	T_{final} [K]	IDT [s]
25	500	912	1,50E-04	350	912	1,90E-04	300	912	1,70E-04
50	1000	1088	2,30E-05	700	1088	2,90E-05	600	1088	2,70E-05
75	1500	1206	6,30E-06	1050	1206	7,40E-06	900	1206	7,20E-06
100	2000	1297	2,50E-06	1400	1297	2,80E-06	1200	1297	2,80E-06
125	2500	1372	1,30E-06	1750	1372	1,40E-06	1500	1372	1,40E-06
150	3000	1437	7,20E-07	2100	1437	7,90E-07	1800	1437	7,70E-07

$P_{final}/P_{initial}$	Test 23, $O_2=38,3$ vol.-%, 12 bar			Test 29, $O_2=47,3$ vol.-%, 17 bar			Test 26, $O_2=56,2$ vol.-%, 17 bar		
	p_{final} [bar]	T_{final} [K]	IDT [s]	p_{final} [bar]	T_{final} [K]	IDT [s]	p_{final} [bar]	T_{final} [K]	IDT [s]
25	300	896	1,40E-04	425	896	8,30E-05	425	896	7,20E-05
50	600	1064	2,00E-05	850	1064	7,80E-06	850	1064	6,00E-06
75	900	1177	6,40E-06	1275	1177	2,70E-06	1275	1177	2,00E-06
100	1200	1264	2,80E-06	1700	1264	1,50E-06	1700	1264	1,20E-06
125	1500	1336	1,50E-06	2125	1336	9,00E-07	2125	1336	7,30E-07
150	1800	1398	8,60E-07	2550	1398	5,60E-07	2550	1398	4,80E-07

$P_{final}/P_{initial}$	(no test), $O_2=70$ vol.-%, 12 bar			(no test), $O_2=80$ vol.-%, 12 bar			(no test), $O_2=90$ vol.-%, 12 bar		
	p_{final} [bar]	T_{final} [K]	IDT [s]	p_{final} [bar]	T_{final} [K]	IDT [s]	p_{final} [bar]	T_{final} [K]	IDT [s]
25	300	896	7,61E-05	300	880	9,00E-05	300	863	1,14E-04
50	600	1064	6,88E-06	600	1041	6,59E-06	600	1017	7,12E-06
75	900	1177	2,47E-06	900	1148	2,10E-06	900	1120	1,98E-06
100	1200	1264	1,39E-06	1200	1231	1,15E-06	1200	1199	9,74E-07
125	1500	1336	8,47E-07	1500	1299	7,75E-07	1500	1264	6,40E-07
150	1800	1398	5,39E-07	1800	1358	5,42E-07	1800	1319	4,77E-07

In Table 8 the required precompression ratios are presented. Furthermore, a relative R-value is calculated. This value describes the relative change of the ratio R when the initial temperature of the investigated mixture is changed from 20 °C to a lower or to a higher value. To calculate the relative R-values, it was assumed that R is proportional to the precompression factor of the precompressed zone at the instant when the DDT occurs. Presumably a strict proportionality cannot be expected but rather a soft correlation in the sense that larger precompression factors entail larger R-values. We still assumed strict proportionality because only a qualitative understanding is sought for. Furthermore, to specify the relative R values it has to be recalled that R was defined as the ratio between the static equivalent pressure at the location where the DDT occurs and the static equivalent pressure in the region of the stable detonation (p_{stat_stable}). Because p_{stat_stable} is inversely proportional to the absolute temperature of the mixture, this effect has to be compensated for in the calculation of the relative R values. Thus, to give an example, the relative R-value at 100 °C for a mixture with $\kappa = 1.38$ is calculated as $50.71/121.79 * (273.15 + 100)/(273.15 + 20) = 0.53$.

Table 8: Precompression ratios required to heat a gas mixture, which is present at different initial temperatures $T_{initial}$ and which can have different values of $\kappa = c_p/c_v$, to a temperature of 1100 K.

$T_{initial}$ [°C]	Precompression ratios (PR) required for different values of $\kappa = c_p/c_v$ and relative R-values							
	PR for $\kappa = 1,4$	rel. R- value	PR for $\kappa = 1,38$	rel. R- value	PR for $\kappa = 1,36$	rel. R- value	PR for $\kappa = 1,34$	rel. R- value
-20	171,02	1,44	207,49	1,47	257,20	1,50	289,01	1,52
0	131,06	1,19	157,43	1,20	192,98	1,22	215,55	1,22
20	102,34	1,00	121,79	1,00	147,77	1,00	164,12	1,00
40	81,23	0,85	95,84	0,84	115,16	0,83	127,24	0,83
60	65,41	0,73	76,54	0,71	91,15	0,70	100,21	0,69
80	53,34	0,63	61,94	0,61	73,13	0,60	80,03	0,59
100	43,98	0,55	50,71	0,53	59,39	0,51	64,71	0,50
120	36,64	0,48	41,95	0,46	48,76	0,44	52,91	0,43
140	30,80	0,42	35,03	0,41	40,42	0,39	43,69	0,38
160	26,10	0,38	29,51	0,36	33,81	0,34	36,41	0,33
180	22,29	0,34	25,04	0,32	28,51	0,30	30,59	0,29
200	19,16	0,30	21,41	0,28	24,22	0,26	25,90	0,25

6. Conclusions

The p_{stat} -values determined for $C_6H_{12}/O_2/N_2$ confirm what had been found for other mixtures ($CH_4/O_2/N_2$, $C_2H_4/O_2/N_2$, $H_2/O_2/N_2$) in the past. In particular the estimation formulae for the p_{stat} -values of the short pipe scenarios are reassured. The smaller R-values found for C_6H_{12} at low O_2 -concentrations (3.7 instead of about 5.5 for other mixtures) are with high probability only due to the elevated initial temperature at which the tests were conducted and not a consequence of the AIT of C_6H_{12} being much lower than the AIT of the other mixtures. The autoignition process starting the DDT, which requires an IDT of not larger than about 10 μs , is due the high temperature oxidation mechanism whereas the "classical" autoignition in air at 1 bar abs is due to the low temperature oxidation mechanism. For the four mixtures investigated by reaction kinetics the IDT values became very similar at temperatures ≥ 1100 K. At this temperature the AIT dropped to about 10 μs . If other common combustibles exhibited the same AIT-behaviour, the precompression factor required for triggering the DDT would be the same and, consequently, similar R values could be expected for corresponding O_2 -concentrations.

References

- CHEMSAFE Data Base, maintained by the *Physikalisch-Technische Bundesanstalt* (PTB, Braunschweig, Germany) and the *Bundesanstalt für Materialforschung und -prüfung* (BAM, Berlin, Germany), free internet admission under <https://www.chemsafe.ptb.de/>
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