Applications: Free Radical Initiators

Thermal Initiators: Decomposition Rate and Half-Life

Ideally, a thermal free radical initiator should be relatively stable at room temperature but should decompose rapidly enough at the polymer-processing temperature to ensure a practical reaction rate. In addition to temperature, the decomposition rate (k_d) of the initiator will depend on the solvent/monomer system used. The confining effect of solvent molecules (the cage effect) causes secondary "wastage" reactions including recombination of radicals to regenerate the initiator. The cage effect becomes more significant as viscosity increases.

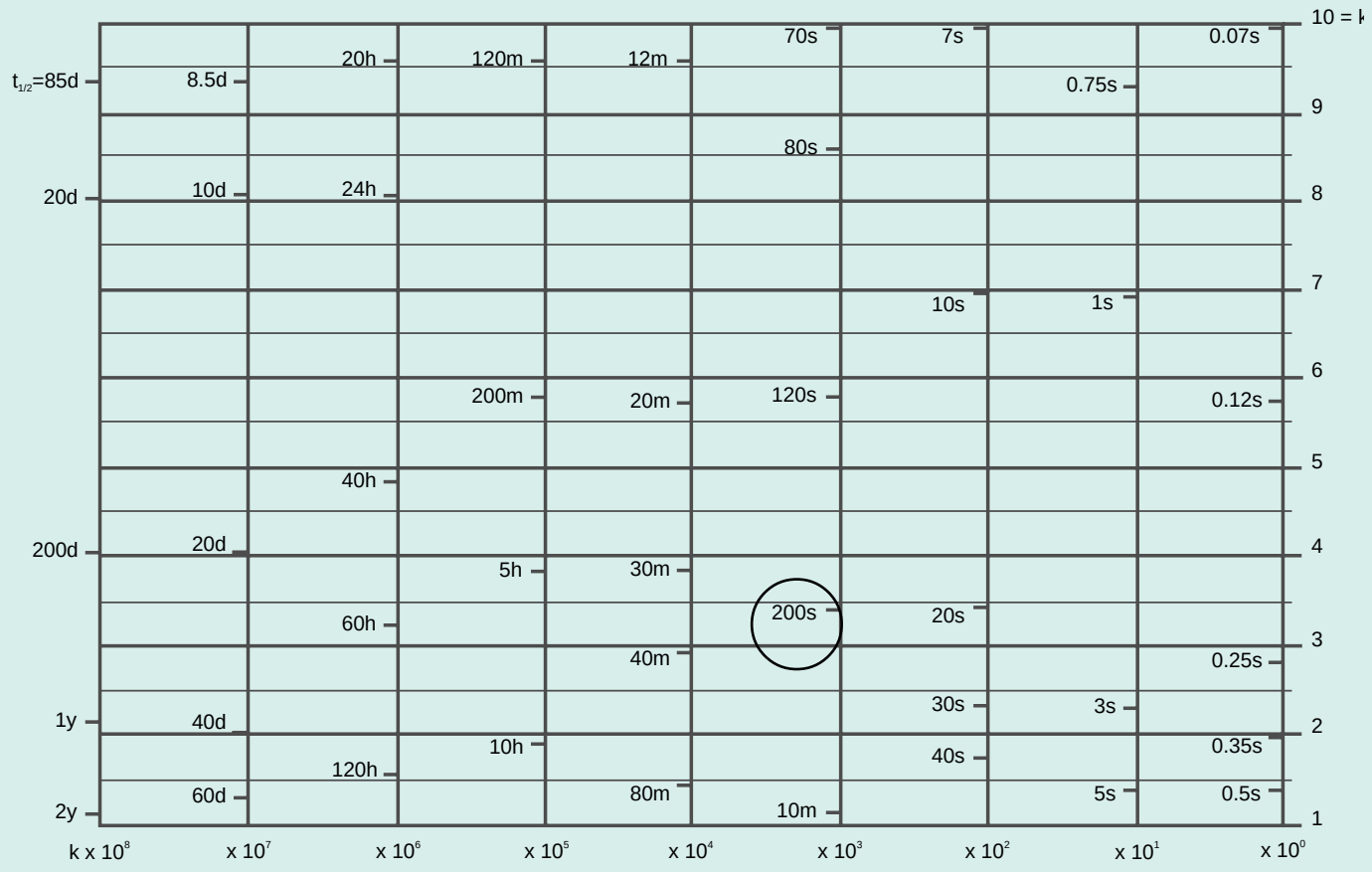
The most important indicator of activity of an initiator is its half-life ($t_{1/2}$). It is the time required to reduce the original initator content of a solution by 50%, at a given temperature.

Assuming first order decomposition kinetics, which is true for most free radical organic initiators, the half-life ($t_{1/2}$) is related to the initiator decomposition rate (k_d) as follows:

$$t_{1/2} = \ln 2/k_d$$

Table I lists the decomposition rate (k_d) data[1] for several commonly used free radical initiators, at specific temperatures and solvents. To further assist you in your selection of a thermal initiator, the temperature corresponding to a 10 hour half-life in a specific solvent is also shown. Fig. 1 relates the initiator decomposition rate (k_d) in s^{-1} to the half-life for a broad range of k_d values, including those found in Table I.

Fig 1: Relationship of Half Life ($t_{1/2}$) to Decomposition Rate (k_d).



This chart is reprinted with permission from Wiley Interscience.

How to read the chart:

See circled example: Half lives are to the left of each vertical line.

A half life of 200s has a rate constant of 3.4×10^{-3}

Key:

y = years
d = days
h = hours
m = minutes
s = seconds

Applications: Free Radical Initiators

Thermal Initiators: Decomposition Rate and Half-Life (continued)

Table I: Decompositon Rates and 10-Hour Half-lif e Temperatures of Common Thermal Initiators (arranged alphabetically by initiator)

Aldrich Cat. No.	Initiator	Solvent	T(°C)	$k_d(s^{-1})$	10h Half-life °C (Solvent)
441465	*tert*-Amyl peroxybenzoate				99 (benzene)
118168	4,4-Azobis(4-cyanovaleric acid)	Acetone Water Water	70 69 80	4.6×10^{-5} 1.9×10^{-5} 9.0×10^{-5}	69 (water)
380210	1,1'-Azobis(cyclohexanecarbonitrile)	Toluene	80 95 102	6.5×10^{-6} 5.4×10^{-5} 1.3×10^{-4}	88 (toluene)
441090	2,2'-Azobisisobutyronitrile (AIBN)	Benzene	50 70 100	2.2×10^{-6} 3.2×10^{-5} 1.5×10^{-3}	65 (toluene)
179981	Benzoyl peroxide[2]	Benzene	60 78 100	2.0×10^{-6} 2.3×10^{-5} 5.0×10^{-4}	70 (benzene)
441694	2,2-Bis(*tert*-butylperoxy)butane				100 (benzene)
388149	1,1-Bis(*tert*-butylperoxy)cyclohexane	Benzene	93	1.9×10^{-5}	
388092	2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane	Benzene	115 145	1.1×10^{-5} 4.7×10^{-4}	120 (benzene)
329533	2,5-Bis(*tert*-Butylperoxy)-2,5-dimethyl-3-hexyne				125 (benzene)
441716	Bis(1-(*tert*-butylperoxy)-1-methylethyl)benzene				115 (benzene)
388084	1,1-Bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane				85 (dibutyl phthalate)
416665	*tert*-Butyl hydroperoxide	Benzene	130 160 170 183	3×10^{-7} 6.6×10^{-6} 2.0×10^{-5} 3.1×10^{-5}	170 (benzene)
388076	*tert*-Butyl peracetate	Benzene	85 100 130	1.2×10^{-6} 1.5×10^{-5} 5.7×10^{-4}	100 (benzene)
168521	*tert*-Butyl peroxide	Benzene Benzene Benzene	80 100 130	7.8×10^{-8} 8.8×10^{-7} 3.0×10^{-5}	125 (benzene)
159042	*tert*-Butyl peroxybenzoate	Benzene	100 130	1.1×10^{-5} 3.5×10^{-4}	103 (benzene)
441473	*tert*-Butylperoxy isopropyl carbonate				98 (aliphatic hydrocarbons)
247502	Cumene hydroperoxide	Benzene	115 145	4.0×10^{-7} 6.6×10^{-6}	135 (toluene)
289086	Cyclohexanone peroxide	Benzene			90 (benzene)
329541	Dicumyl peroxide	Benzene			115 (benzene)
290785	Lauroyl peroxide	Benzene	40 60 85	4.9×10^{-7} 9.2×10^{-6} 3.8×10^{-4}	65 (benzene)
441821	2,4- Pentanedione peroxide				125 (triethyl phosphate)
269336	Peracetic acid				135 (toluene)
216224	Potassium persulfate[3]	Water 0.1*M* NaOH	80 50 60 80 90	6.9×10^{-5} 9.5×10^{-7} 3.2×10^{-6} 9.2×10^{-5} 3.5×10^{-4}	60 (H_2O) 70 (0.1*M* NaOH)

[1]"Polymer Handbook", Eds. Brandrup, J; Immergut, E.H.; Grulke, E.A., 4th Edition, John Wiley, New York, 1999, II/2-69; **Aldrich Catalog No.** Z412473.

[2]Amines can significantly increase the decomposition rates of peroxides, e.g., addition of *N,N*-dimethyl aniline to benzoyl peroxide causes the latter to decompose rapidly at room temperature.

[3]Persulfate decomposition is pH dependent.