Kinetics for The Chemistry, Biology, Medicine and Agriculture

G.E. Zaikov

N.M. Emanuel Institute of Biochemical Physics,

Russian Academy of Sciences

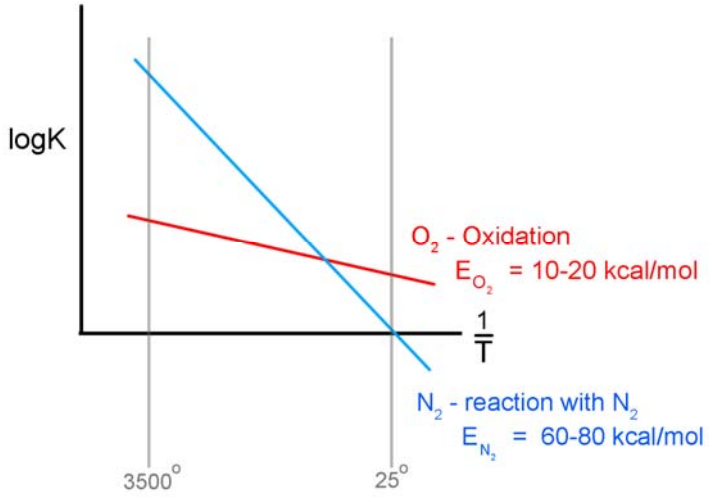
4, Kosygin st., Moscow 119991, Russia

GEZAIKOV@yahoo.com

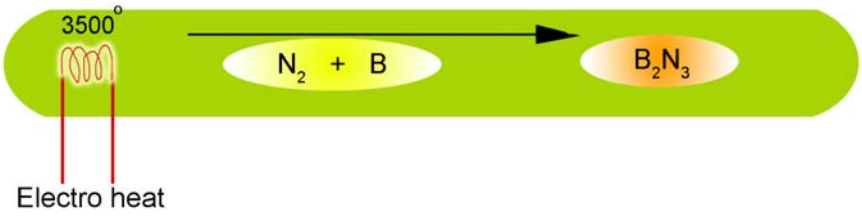
I Chemistry

1. Making of artificial diamonds from compounds having no carbon (A.G Merzhanov)

$$4B + 3N_2 \rightarrow 2B_2N_3$$

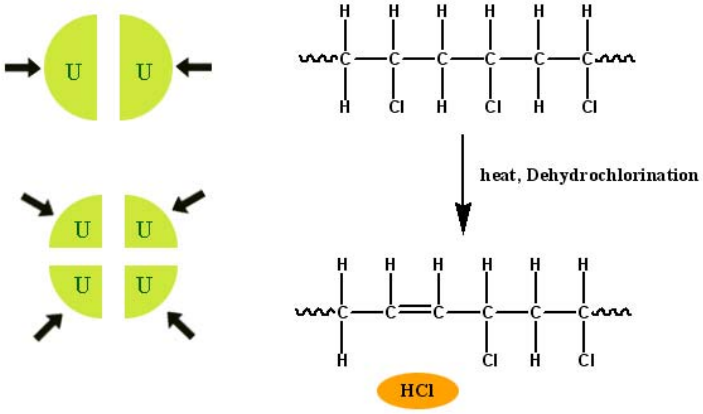


Self propagated high temperature synthesis



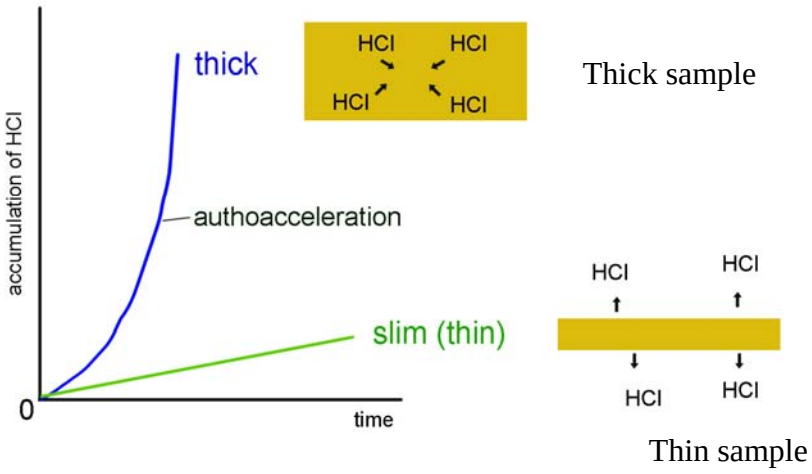
Artificial production of diamond from carbon was predicted by O.I. Leipunskii in 1939, Institute of chemical physics – very high pressure and very high temperature.

2. PVC-Degradation is imitation of atomic bomb mechanism action (V.S. Pudov)



Kiryl Shchelkin

HCl is catalysis of dehydrochlorination

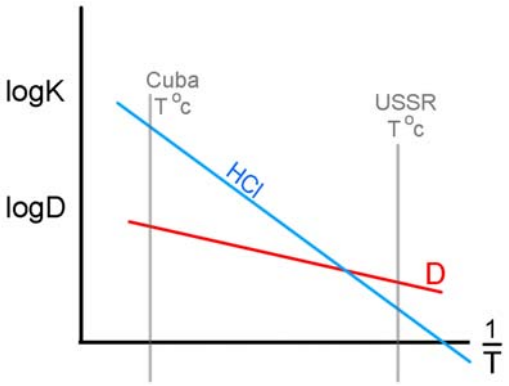


Criterium (critical phenomena) is ratio between speed of diffusion of HCl and rate of dehydrochlorination

E_D = 10 kcal/mol

E_{HCl} = 20 kcal/mol

Degradation of sole of shoes



3. Combusion in oxygen! (S.M. Lomakin, G.E. Zaikov)

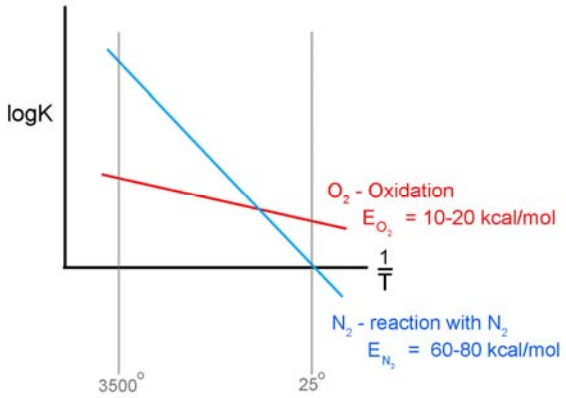
LOI = Oxygen index

Combusion in nitrogen!

LOI is not informative for high temperature!

→ World Trade Center (NYC)

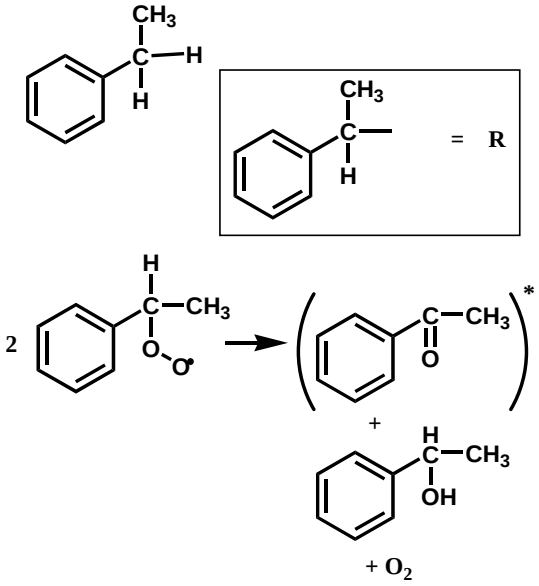
→ Russian submarine (Kursk)



4. Development of highly sensitive methods of investigation of chemical reactions

4A. Chemiluminescence (V.Ya Shlyapintokh, R.F. Vasiliev, O.N. Karpukuin)

Mechanism of oxidation of organic compounds



$$R\text{-}H + O_2 \xrightarrow{K_0} R^{\bullet} + {}^{\bullet}O_2H$$

$$R^{\bullet} + O_2 \xrightarrow{K_1} RO_2^{\bullet}$$

$$RO_2^{\bullet} + RH \xrightarrow{K_2} ROOH + R^{\bullet}$$

$$R^{\bullet} + R^{\bullet} \xrightarrow{K_3} R\text{-}R$$

$$R^{\bullet} + RO_2^{\bullet} \xrightarrow{K_4} ROOR$$

$$RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{K_5} \text{ketone} + O_2 + \text{alcohol}$$

$$ROOH \xrightarrow{K_6} RO^{\bullet} + {}^{\bullet}OH$$

$$K_1 >> K_2$$

$$[R^{\bullet}] << [RO_2^{\bullet}]$$

Ketone is in exiting condition

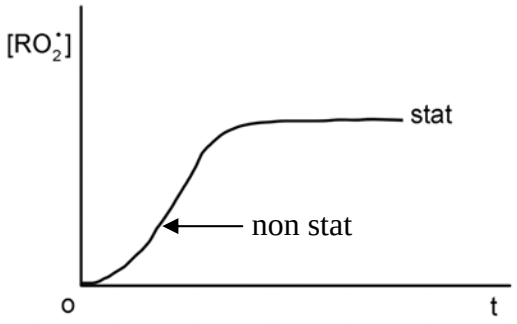
---------- $R_1\text{-}CO\text{-}R_2$*

hν → Chemiluminescence

---------- $R_1\text{-}CO\text{-}R_2$ + hν

$$\frac{dR^{\bullet}}{dt} = W_i - K_1[O_2][R^{\bullet}] + K_2[RO_2^{\bullet}][RH]$$

$$\frac{d[RO_2^{\bullet}]}{dt} = K_1[R^{\bullet}][O_2] - K_2[RO_2^{\bullet}][RH] - K_6[RO_2^{\bullet}]^2$$



$$\frac{d[R^{\bullet}]}{dt} = \frac{d[RO_2^{\bullet}]}{dt} = 0$$

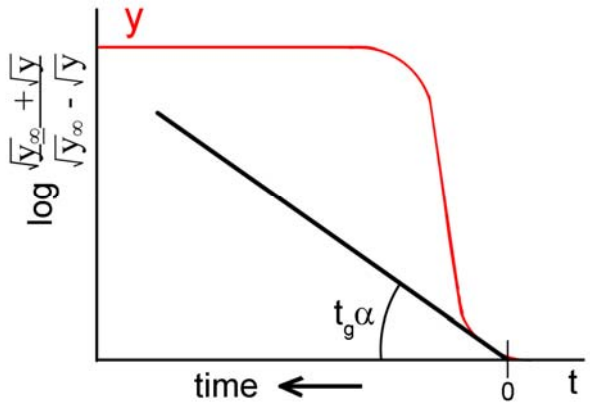
$$W_i = K_6[RO_2^{\bullet}]^2 \; ; \; [RO_2^{\bullet}]_{stat} = \frac{\sqrt{W_i}}{\sqrt{K_6}}$$

$$\frac{d[RO_2^{\bullet}]}{dt} = W_i - K_6[RO_2^{\bullet}]^2$$

$$\ln\frac{[RO_2^{\bullet}]_{\infty} + [RO_2^{\bullet}]}{[RO_2^{\bullet}]_{\infty} - [RO_2^{\bullet}]} = 2t\sqrt{K_6 \cdot W_i}$$

$$W_i = K_6[RO_2^{\bullet}]^2 \sim y_i \qquad \frac{y_1}{y_2} = \frac{[RO_2^{\bullet}]_1^2}{[RO_2^{\bullet}]_2^2}$$

$$\ln\frac{\sqrt{y_{\infty}} + \sqrt{y}}{\sqrt{y_{\infty}} - \sqrt{y}} = 2t\sqrt{K_6 \cdot W_i}$$



$$t_g\alpha = \frac{2}{2.3}\sqrt{K_6 \cdot W_i}$$

$$K_6 = \frac{(t_g\alpha)^2 \cdot 1325}{W_i}$$

$$W = \frac{K_2}{K_6}[RH]\sqrt{W_i}$$

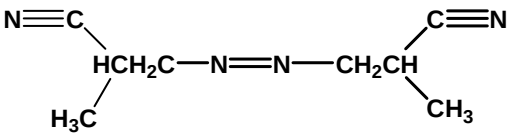
$$\frac{d\,(y/y_0)}{dt} = \frac{0.22\,K_7}{\sqrt{2 \cdot K_6 \cdot W_i}}$$

$$RO_2^{\bullet} + InH \xrightarrow{K_7} ROOH + In^{\bullet}$$

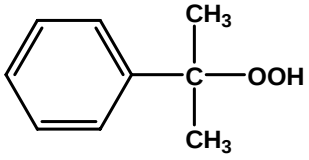
$$R_1\text{-}N{=}N\text{-}R_1 \xrightarrow{W_i} R_1^{\bullet} + N{=}N + R_1^{\bullet}$$

$$R_1^{\bullet} + RH \rightarrow R^{\bullet} + R_1H$$

Azo-isobutironitile



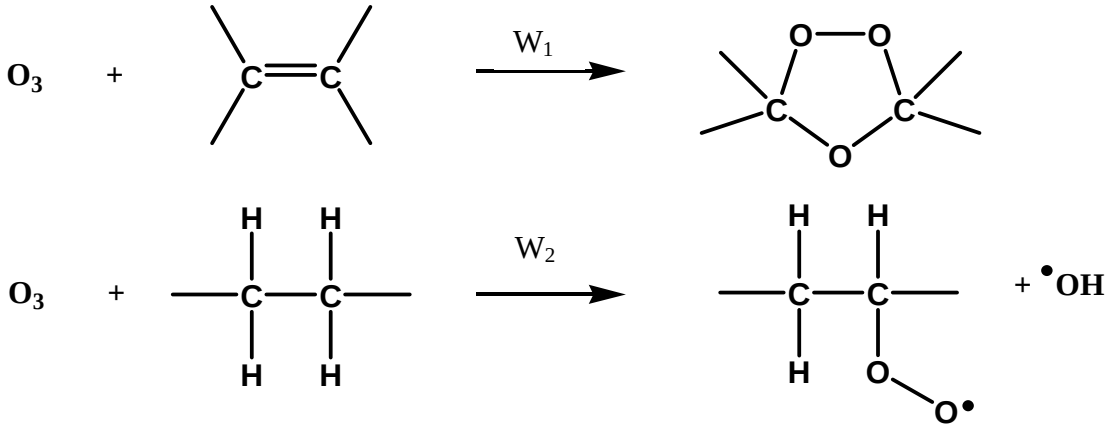
" initiator "



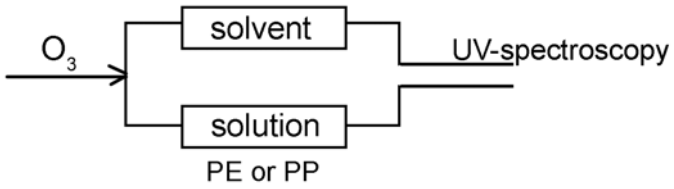
Cumene hydroperoxide

4B Analysis of Reaction products (K.S. Minsker, S.D. Razumovskii)

Determination of double bonds (one double bond in a carbon chain polymer and it location against 50,000 single bonds)



W_1 / W_2 = 100,000 one double bond will destroy one molecule of ozone



Location of double bond

A ----------=---------- C ----------=--=--=---------

B =---------- D =--=--=----------

Molecular weight (by viscosity)

Combination of ozone method and method of measurement of molecular weight will give us information about amount and location of double bonds (single double bond or polyene sequence)

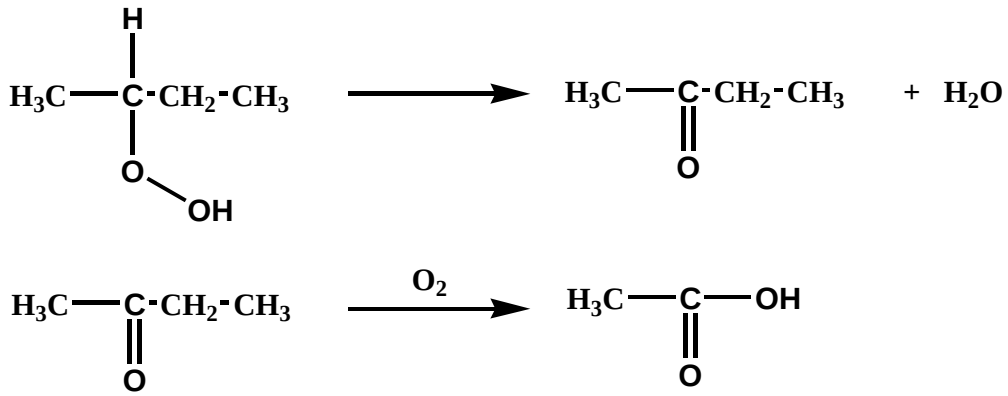
5. Multitonnage chemical production design

5A Oxidation of n-butane (R-H) (N.M. Emanuel, E.A. Blumberg, G.E. Zaikov, etc.)

$R\text{-}H + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet}$

$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$

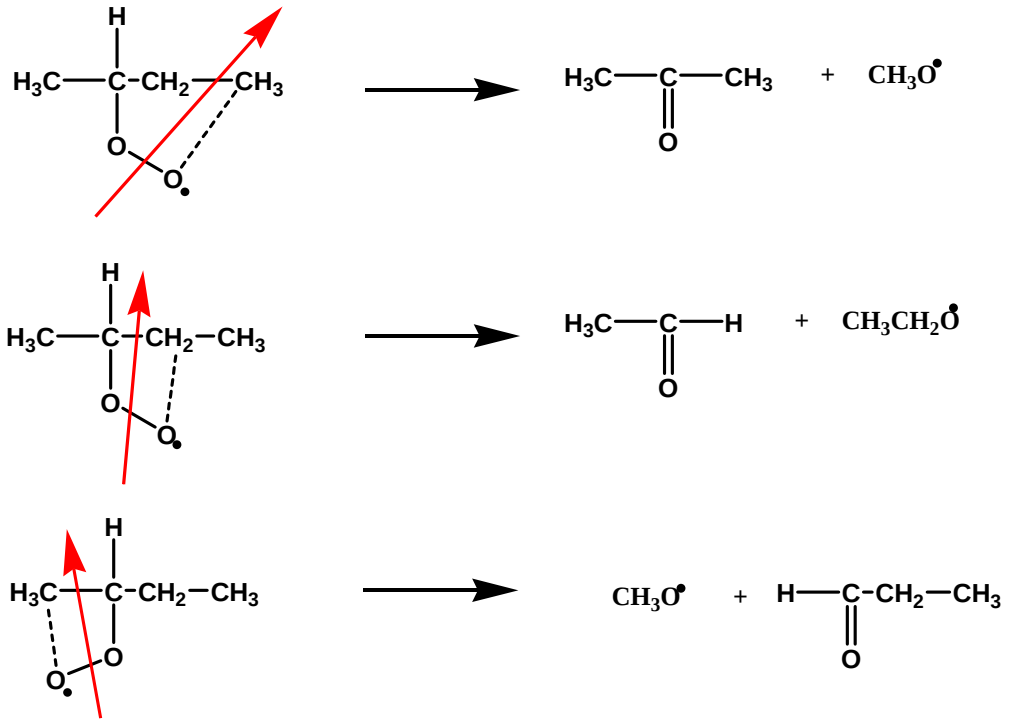
$RO_2^{\bullet} + RH \rightarrow ROOH \rightarrow$ Liquid phase



“Two main products”

In gas phase

Concentration of n-butane in gas phase in 100-1000 times less than in Liquid phase



“Many products”

Oxidation of n-butane in liquid phase (145-150 ^{o}C, 50 atm) – Critical condition of n-butane is 152.5^{o}C

Production of 10,000 T/year Acetic acid and 10,000 T/year methyl ethyl ketone.

5B Oxidation of CH_2=CH-CH_3 in solution to CH_2-CH-CH_3 with France compound Rohn-Poulenk (San-Fone, Dessine, Lyon) (N.M. Emanuel, E.A. Blumberg, etc.)

5C Stabilization of polymers (polyorganosiloxanes) in conditions when temperature is 1000 ^{o}C (G.P. Gladyshev)

Phenols – only till 150 ^{o}C

Amines – only till 200-220 ^{o}C

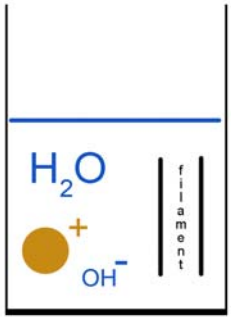
S- and P-organic compounds ~ 250 ^{o}C

Atomic dispersion metals-powder (Fe, Co, Ni, Cu, etc.) can react with O_2 faster than O_2 can reacts with polymers (diffusion control reaction). Stabilizers for Sputnics (shuttes!)

Additives – salts of organic acids. If temperature is elevating salts will give the atomic dispersion metals by pyrolysis of salts in the presence of reduction systems.

6. Degradation as a method of modification (G.E. Zaikov, Yu.V. Moiseev, S.D. Razumovskii)

6A Triacetal cellulose (Fibers, Filaments)

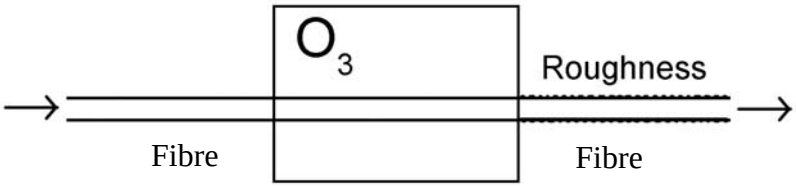


High cation!

Regenerated cellulose on the surface (cotton, fiber)

Triacetate cellulose inside (keep good mechanical properties)

6B Artificial silk from polyethylene therphtalate (PETPh)



6C Tape for tape recorder from PETPh

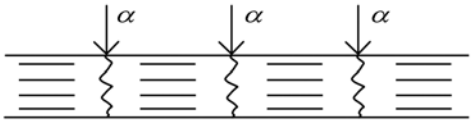
The same applications as **6B**

6D Hydrophilic surface on the hydrophobic polymer materials

PP + O_2 , combustion, O_3

PE + O_2 , combustion, O_3

6E Membranes

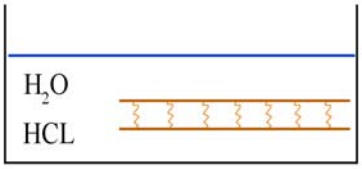


in amorphic phase

$D_{am} = 10^{-15}$ cm^2/sec

in crystalline phase

$D_{cr} = 10^{-21}$-10^{-22} cm^2/sec



Radiation of PET by α-particle

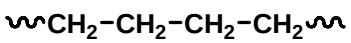
Degradation is occured along of track of α-particles.

Hydrolysis is going along of track of α-particles.

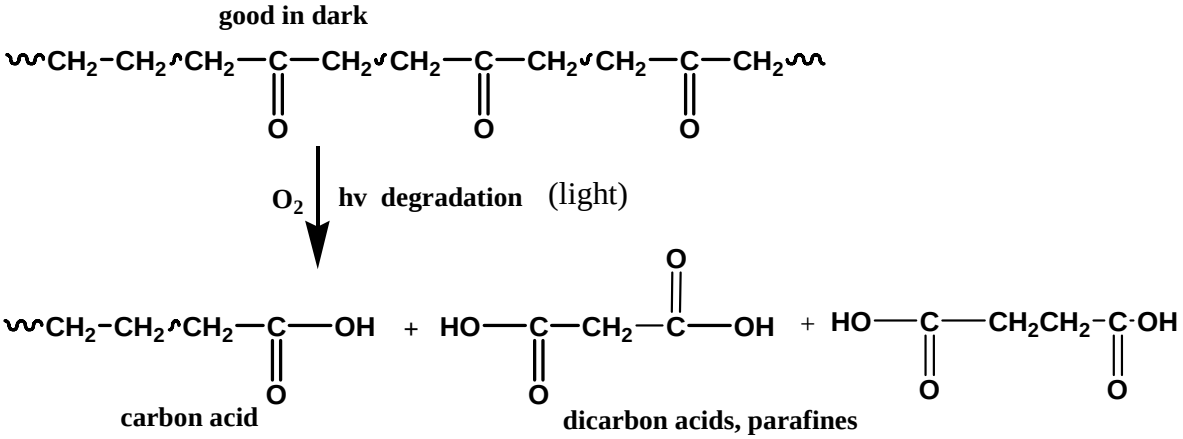
Size of tunnel depends on time of hydrolysis

6F Restricted life-spent of polymers - action of light (James Edwin Guillett, Toronto university, Canada and Tsutomo Kagia, Kyoto university, Japan)

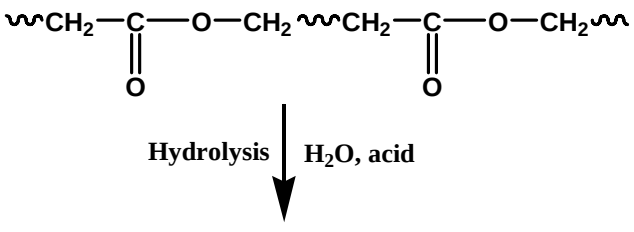
$6F_1$



50 - 100 years



$6F_2$ Action of water – Hydrolysis (G.E. Zaikov, Institute of Chemical Physics, Moscow, USSR)



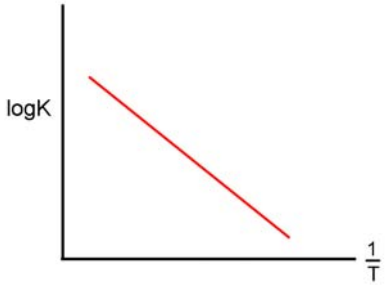
$6F_3$ initiator + inhibitor (Yu.A. Shlyapnikov, Institute of Chemical Physics, Moscow, USSR)

When inhibitor will be over, initiator will destroy polymer very fast.

6E Chemistry again (Appendix)

Prognosis of life spent of polymer materials (G.E. Zaikov)

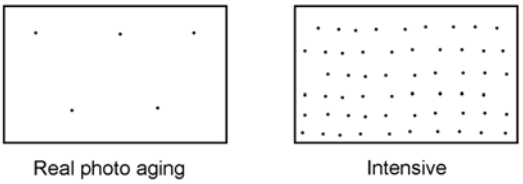
1. For thermo oxidative degradation, scientist would like to use Arrenius law.



To make experiment in high temperature region and transfer results to low temperature. Arrenius is correct only for one reaction (absolute rate constant) but, thermooxidative degradation is 100 or 1000 reactions with different energy of activation.

We can not use strait line for prognosis because we will have curve in reality.

2. For photodegradation, scientist would like to increase of intensity of light. It is not correct. (G.E. Zaikov)



For intensive photodegradation-no propagation but just termination. We have another products of photodegradations.

For real photoaging we have **long** propagation of chain reaction and only after that-termination, but for intensive photodegradation- **no propagation** but only termination

3. Purification of smoked sausage from soot (cancerogenic compounds) by action of ozone. Ozone can react with soot in 1000-10000 times faster than with meat. (S.D. Razumovskii)

4. Recycling of polymers

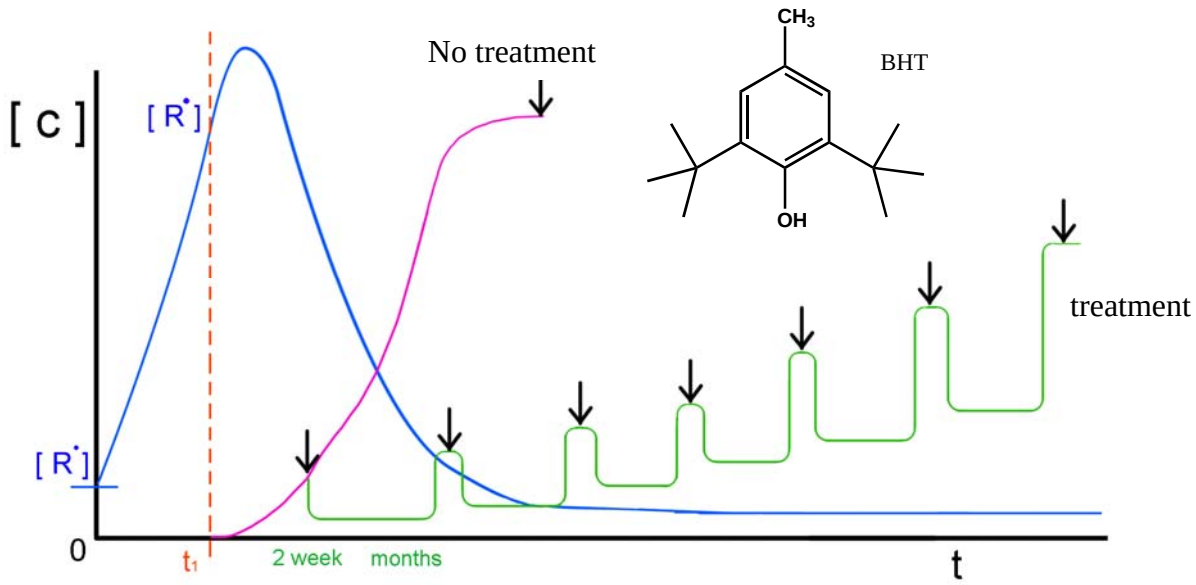
   - Heterochain polymers (polyamide, polyesters, polyacetals, cellulose, derivative of cellulose, etc.) by hydrolysis – till monomers
   - Carbon chain polymers (polyolefins) by pyrolysis – till gas products (fuel)
   - Second using of polymers

II Biology- Medicine (Nikolai M. Emanuel)

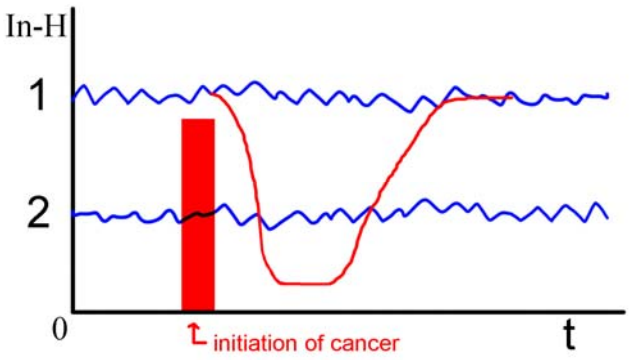
1. Cancer and anticancer drugs (antitumor preparation)

- Radical reactions in living body (oxidation).

- Many illness are radical reactions (cancer, aging of body, radiation of body, action of light on the eyes, AIDS, Altsheimer)



- Anticancer drugs as vitamin E



Tocopheroles

Vitamin E

Phenols

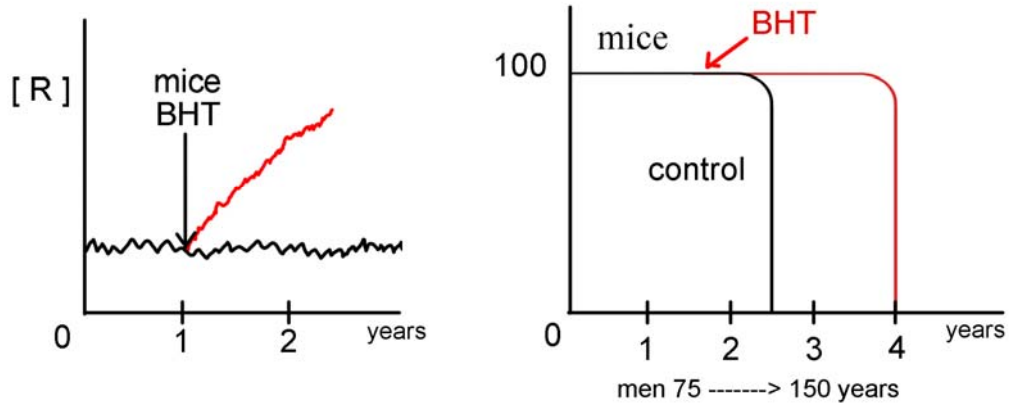
Amines

S-organic compounds

P-organic compounds

- Nitrozomethylurea (non-radical chemical drug)

2. Gerontology



3. Stress

1. Every minute noisy bell
2. Every minute pain by electric discharge

I In 24 hours ulcer of stomach

II In 48 hours – cancer of stomach

<u>Stress! Remove stress!</u>

Vodka is very good antistress preparate but side effect is very bad (degradation of liver, kidnies, brain and social life!) – opinion of G.E. Zaikov

1. **Plato (Ancient Greece)**

- November 7, Symposium in honor of 81st Birthday of Plato (Removed stress)
- Passed away during of his symposium

2. **Aristotilus (Ancient Greece)**

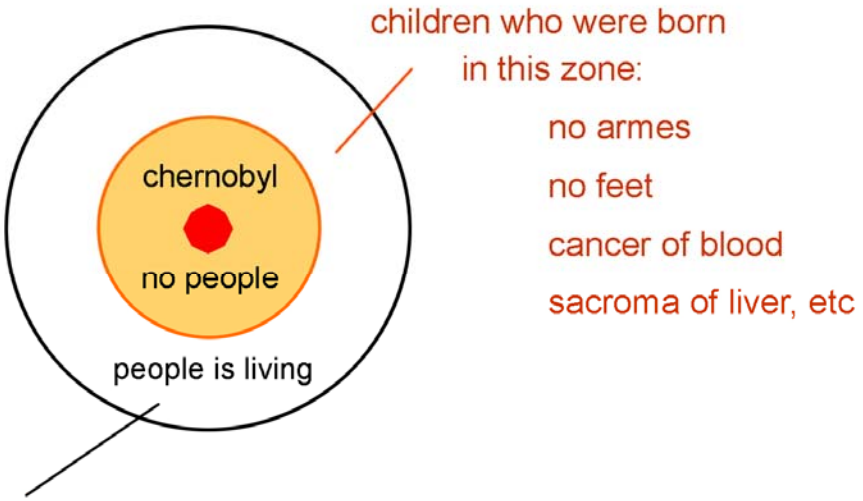
- Rock (cliff) – Ponte Negro in EGE sea: High tide-Low tide-stress!
- Jumped from the rock to EGE sea and passed away (suicide!)

4. Radiation damage (E.B. Burlakova)

Chernobyl nuclear power plant

1 Chernobyl = 500 Hiroshima bombs

By radiation (no shock wave)

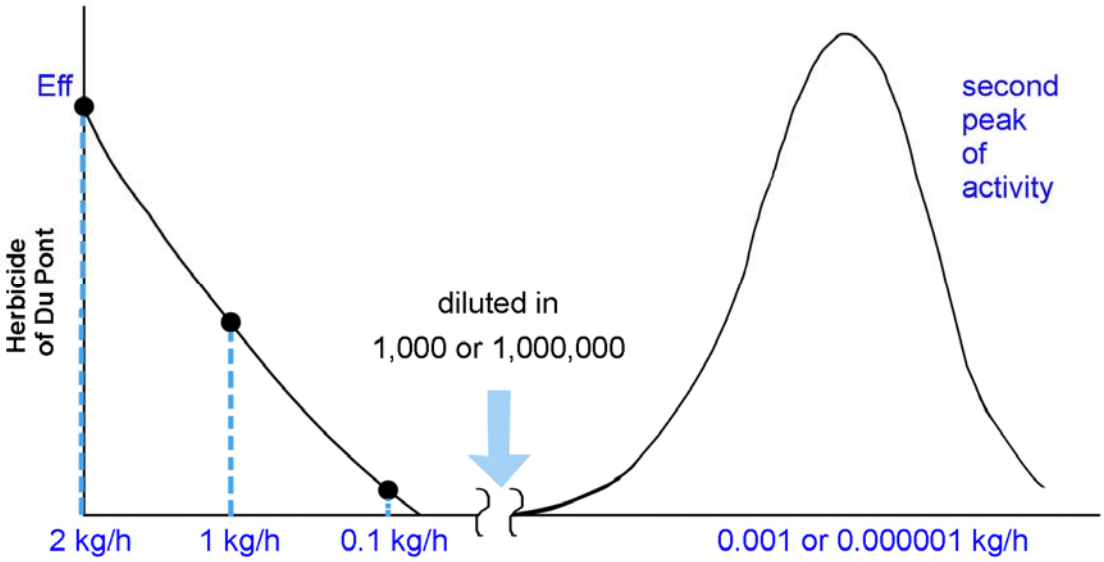


level of radiation is below at critical level (as scientists expected)

III Agriculture (E.B. Burlakova, Institute of Biochemical Physics, Moscow, USSR)

1. Effect of super low dozes of regulators of Growth (pesticides)

The same effect as in **homeopaty**



2. Chemical compounds could be toxic in low concentration again

We should rewrite chemistry of toxicity

Acknowledgement

Wissawat Sakulsaknimitr

Is thanked for preparation all these pictures!