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RADIATION CHEMISTRY AND THE ENVIRONMENT

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Abstract

The rather strong and many-sided pollution of the environment (atmosphere, water ressources, soil) as a consequence of human activities is summarized. The solution of the arised problems by application of radiation chemistry methods and the utilization of modern environmentally "clean" and economical technologies, founded on electron beam processing, are mentioned.

Some basic environmental problems and their solution are briefly discussed; i) Removal of CO_2 from flue gases and its radiation induced utilization. ii) Principals for degradation of aqueous pollutants by electron beam processing in the presence of ozone (synergistic effect).

The radiation chemistry as a modern and manifold discipline with very broad applications can also essentially contribute in the conservation of the environment.

1.General remarks

As a consequence of the growing of the world population and the strong development of various industries as well as the increasing traffic on the roads, the seas and in the air, rather heavy pollution of the global environment is occuring.

A very essential contribution in this respect is the usage of fossil energy sources (coal, oil, natural gas) and this will not change for the next 50-60 years. The search for replacement of fossil fuels by alternative energy sources (solar energy, hydrogen as energy carrier, nuclear and fusion energy etc.) are still not yet satisfactory. A survey of the negative consequences of the human activities is given in Scheme 1.

The consequences of the environmental pollution are manifold:

- **Health hazard for the population:** respiratory deseases, cancer, allergies etc.
- **Environmental impact on a local scale:** polluted soil, drinking water, agriculture products and hence animal deseases, pollution of rivers and oceans resulting in plankton killing and reduction of fishes etc.
- **Environmental impact on a global scale:** acid rain, CO_2-greenhouse effect resulting in global warming etc.

Scheme I:

Human activity = pollution in:

Air | **Water** | **Soil**

- **Pollutants in air: CO_2, CO, NO_x, SO_2/SO_3 etc.,** resulting from combustion of fossil fuels (coal, oil, natural gas)
  CO_2 → world warming (climate change)
  CO → chemical & biological problems
  NO_x, SO_2/SO_3 → acid rain

- **Pollutants in water: biologically resistant compounds, chlorinated substances etc.** from chemical, pharmaceutical and other industries, dyestuffs from dyehouses etc.

- **Pollutants in soil: various chemicals, solids etc.** originating from chemical and other industries; application of pesticides and other chemicals in agriculture, household waste etc.

In the frame of this symposium it will be demonstrated that **radiation technology helps to solve environmental problems. Its main principals and advantages are:**

- **No radioactivity is produced during the treatment procedure**
- **No waste**
- **Safe for operating personnel**
- **Environmentally safe**
- **Safe for general public**
- **Economically competitive**
- **Higher efficiency**

In addition to this it has to be mentioned that **new "clean technologies" for the production of goods based on radiation processing are developed which cause no or very small load for the environment.** They are unique, operating at room temperature and covering a broad spectrum of industrial applications as quoted in scheme II.

Scheme II:

NEW CLEAN TECHNOLOGIES BASED ON RADIATION CHEMISTRY

- **Polymerisation and polymer modification of plastics at room temperature e.g. crosslinking, grafting, surface coating etc. under irradiation**
- **Electron-beam curing of special coatings on surfaces of plastic films, paper, videotypes, floppy discs, metalized surfaces, ceramics, wood panels, silicon release etc. at room temperature**
- **Production of various new high-quality materials e.g. wood-polymer composites, wire and cable insulation, heat-shrinkable films and tubes etc.**
- **Curing of pigment paints, containing very small amounts of solvent at room temperature (strong reduction of solvent losses and hence, very low environmental pollution)**
- **Radiation-induced synthesis as well as addition of oxygen-, halogen-, sulfur-, nitrogen-, phosphorus- and silane-compounds to organic substances at room temperature**
- **Sterilization of medical supplies, pharmaceutics, cosmetics etc.**
- **Production of artificial implantates with "biologically friendly" surface**
- **Radiation treatment of food (disinfection and killing of pathogenic microorganisms, extension of shelf life, delay of maturation, sprout inhibition, grain disinfection etc.)**

As mentioned above, there are a number of radiation chemistry methods for solving environmental problems. They are compiled in scheme III. Some of them e.g. the radiation-induced conversion of NO_x and SO_2/SO_3 contained in flue gases are already applied in industrial scale. This subject matter will be discussed in more detail by other authors in the frame of this symposium. Other methods, e.g. the utilization of CO_2 and CO as well as the degradation of biologically resistant pollutants in drinking water and industrial wastewater are more specific in respect to the given situation (origin, content of total pollutants etc.) are still under development. They will be treated briefly in this lecture. It should be noted that the degradation mechanisms of some water pollutants by electron beam processing are rather well understood. In such case there are no obstructions for an industrial usage of the method.

Scheme III:

RADIATION CHEMISTRY METHODS FOR SOLVING ENVIRONMENTAL PROBLEMS

- Conversion of NO_x and SO_2/SO_3 in combustion gases into fertilizer in the presence of ammonia
- CO_2 and CO utilization - formation of valuable products
- Disinfection as well as decomposition of pollutants in drinking water
- Degradation of biologically resistant harmful substances in wastewaters from industry etc.
- Disinfection of sludge and conversion into fertilizer
- Disinfection of hospital wastes
- Recycling of biologically undegradable plastics and rubber waste

2. Radiolysis of water

The water radiolysis is nowadays fairly well understood. the primary reactions of water radiolysis and the G-values *) of the primary products are given below.

Primary reactions:

$$H_2O \rightsquigarrow H_2O^* \longrightarrow H + OH \quad (1a)$$

$$\hookrightarrow H_2O^+ + e^- \longrightarrow e^-_{th}\,;\; e^-_{th} + n\,H_2O \longrightarrow e^-_{aq} \quad (1b)$$

Gross reaction of water radiolysis (the G-values at pH=7 are given in brackets):

$$H_2O \rightsquigarrow e^-_{aq},\ H,\ OH,\ H_2,\ H_2O_2,\ H^+,\ OH^-_{aq} \quad (2)$$

$$(G)\quad (2.7)\ (0.6)\ (2.8)\ (0.45)\ (0.7)\ (3.2)\ (0.5)$$

For further details concerning the reactions, absorption spectra etc. of the primary products of water radiolysis see e.g. /1,2/.

3. Radiation-induced CO_2 and CO transformation into organic compounds

The fossil fuels are representing the major energy sources in the world and as a consequence of this fact enormous amounts of CO_2 and CO etc. are discharged in the atmosphere. Hence, CO_2 content in the air is constantly increasing and as a result of this a global climate change is observed. This has been now recognized and several strategies were suggested for its removal. The most frequent proposal is based on CO_2 separation from flue gases by selective absorption in recyclable solvents (e.g. monomethanolamine) followed by stripping, liquefaction and finally discarging into deep ocean (3000-5000 m) /3-6/. However, the water levels at these depths are not absolutely stationary. Vulcanos, hot water sources and earth quakes can effect a mixing up of the sea water with the dissolved CO_2 causing a pH-change. As a

*) G-value = number of changed molecules per 100 eV (1.60×10^{-17} J) absorbed energy. For conversion into SI-units: multiply the G-value by 0.10364 to obtain G(x) in $\mu mol.J^{-1}$.

consquence of this, the very sensitive marine life can be destroyed. Hence, this method seems not to be recomendable for CO_2 removal, apart from the enormous financial requirements.

The most appropriate pathway is to utilize CO_2 and CO in a suitable manner. It has been shown for the first time /7/ that aqueous CO_2 can be transformed in simple organic compounds under ionizing as well as UV-irradiation /8-10/. Competition reactions, pK-value of the transients, substrate concentration and the absorbed dose are the major factors influencing the CO_2 conversion. In the presence of Fe^{2+} and SO_4^{2-} ions an additional amount of e^-_{aq} is formed leading to higher product yields /11,12/. For more information in this respect see /10, 13 and ref. therein/.

The major reactions involved in the radiation-induced CO_2 reduction and conversion into a number of simple organic substances are compiled in Scheme IV.

Scheme IV:

Radiation-induced CO_2-transformation

$$H_2O \rightsquigarrow \underset{(2.7)}{e^-_{aq}}, \underset{(0.6)}{H}, \underset{(2.8)}{OH}, \underset{(0.45)}{H_2}, \underset{(0.72)}{H_2O_2}, \underset{(3.2)}{H^+_{aq}}, \underset{(0,5)}{OH^-_{aq}}$$

$$CO_2 + e^-_{aq} \rightarrow \dot{C}OO^- \quad (k{=}1\times10^{10}\,M^{-1}s^{-1})$$

$$CO_2 + H \rightarrow \dot{C}OOH \ (HCO\dot{O}) \quad (k{=}8\times10^{6}\,M^{-1}s^{-1})$$

$$H^+ + e^-_{aq} \rightarrow H \quad (k{=}2.3\times10^{10}\,M^{-1}s^{-1})$$

$$\dot{C}OOH \rightleftharpoons H^+ + \dot{C}O_2^- \quad (pK = 1.4)$$

$$2\,\dot{C}O_2^- \rightarrow (COO^-)_2 \quad \text{(oxalate)} \quad (2k = 2\times10^{9}\,M^{-1}s^{-1})$$

$$2\,\dot{C}OOH \rightarrow (COOH)_2 \quad \text{(oxalic acid)}$$
$$\quad\quad \rightarrow CO_2 + HCOOH \quad \text{(formic acid)}$$

$$2\,HCO\dot{O} \rightarrow CO_2 + HCOOH$$

$$H{-}C({=}O){-}\dot{O} + OH \rightarrow H\dot{C}O + H_2O$$

$$HO{-}\dot{C}{=}O + OH \rightarrow CO_2 + H\dot{O}_2$$

$$2\,H\dot{C}O \rightarrow CO + HCHO \quad \text{(aldehyde)}$$
$$\quad\quad \rightarrow (HCO)_2 \quad \text{(glyoxal)}$$

$$HCHO + \dot{C}OOH \rightarrow \dot{C}H_2OH + CO_2$$

$$2\,\dot{C}H_2OH \rightarrow (CH_2OH)_2 \quad \text{(glycol)}$$
$$\quad\quad \rightarrow HCOH + CH_3OH \quad \text{(methanol)} \quad (2k = 2\times10^{9}\,M^{-1}s^{-1})$$

$$\dot{C}H_2OH + \dot{C}OO^- \rightarrow HOH_2C{-}COO^- \quad \text{(glyoxalic acid)}$$

4. Radiation- induced carboxylation of organic compounds

It has been demonstrated that aqueous CO_2 can be incorporated as carboxylic group in various organic compounds under the influence of ionizing radiation and UV-light / 8, 10, 12, 13 and ref. therein/. This pathway for CO_2 utilization makes it possible to produce value-added products. For illustration two examples are presented in this respect: carboxylation of phenol to salicylic acid and the formation of malonic acid from monochloroacetate and CO_2 or CO and formiate, respectively.

4.1. Formation of salicylic acid from phenol and CO_2

Fig.1 shows the formation of salicylic acid as a function of phenol concentration. The product yield is passing a maximum at 2×10^{-2} mol.dm $^{-3}$ phenol, because of competition reactions, which are discussed in more detail elsewhere / 14, 15/. The major reaction steps of the salicylic acid formation are also given for the sake of completeness.

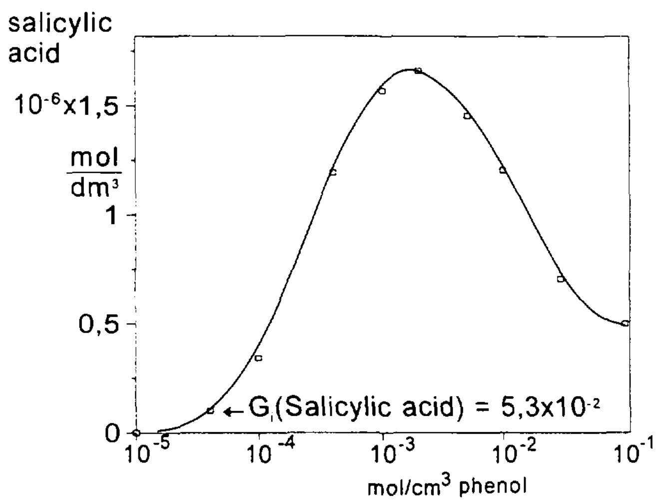
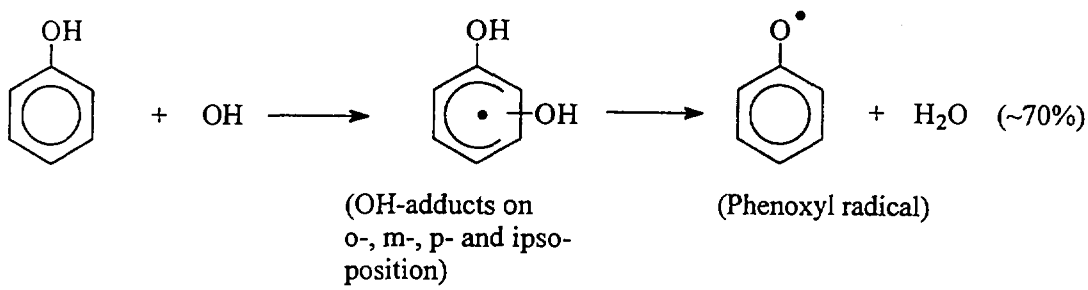


Fig.1: Radiation induced formation of salicylic acid from phenol and CO_2: $[CO_2]$ = 3.5×10^{-2} mol.dm^{-3}; [phenol] = 10^{-5} to 10^{-1} mol.dm^{-3}; absorbed dose: 3 kGy

Major reactions for the salicylic acid formation from phenol and CO_2 :



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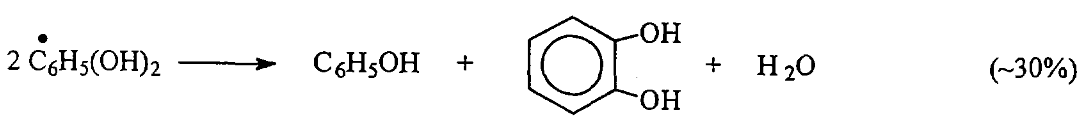

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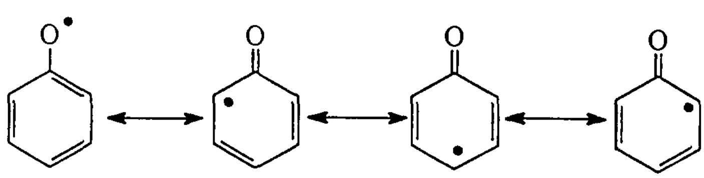
Mesomeric structures of the phenoxyl radical:



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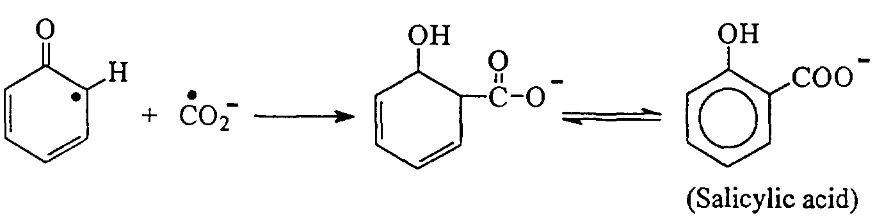


(6)

The yield of salicylic acid can be increased under given optimal conditions /13/.

4.2. Formation of malonic acid from monochloroacetate ion in the presence of CO_2, CO and/or formiate

First, it might be mentioned that the desired COO^- transients for the carboxylation process can be formed by the following set of reactions (see also scheme IV) /14/:

$$CO_2 + e^-_{aq} \longrightarrow \dot{C}OO^- \quad (7)$$

$$CO_2 + H \longrightarrow \dot{C}OOH \quad (8)$$

$$CO + e^-_{aq} \longrightarrow \dot{C}O^-_{aq} \equiv HCOOH^{\bullet -} \quad (k = 1x10^9\ dm^3.mol^{-1}.s^{-1}) \quad (9)$$

$$HCOOH^{\bullet -} + OH^- \longrightarrow HCOO^- + e^-_{aq} \quad \text{(chain reaction)} \quad (10)$$

$$CO + OH \longrightarrow \dot{C}OOH \quad (k = 8.3x10^8\ dm^3.mol^{-1}.s^{-1}) \quad (11)$$

$$HCOO^- + OH \longrightarrow \dot{C}OO^- + H_2O \quad (k_{OH} = 2.7x10^9\ dm^3.mol^{-1}.s^{-1}) \quad (12)$$

$$HCOO^- + H \longrightarrow \dot{C}OO^- + H_2 \quad (k_H = 2.5x10^9\ dm^3.mol^{-1}.s^{-1}) \quad (13)$$

Monochloroacetate is used as a model compound in order to study the involvement of the above reactions in the carboxylation process. As an example in this respect the formation of malonic acid is presented in Fig.2 as a function of pH and absorbed dose (insert Fig.2). A rather high yield of malonic acid has been observed, $G_i = 675$, which is of practical interest.

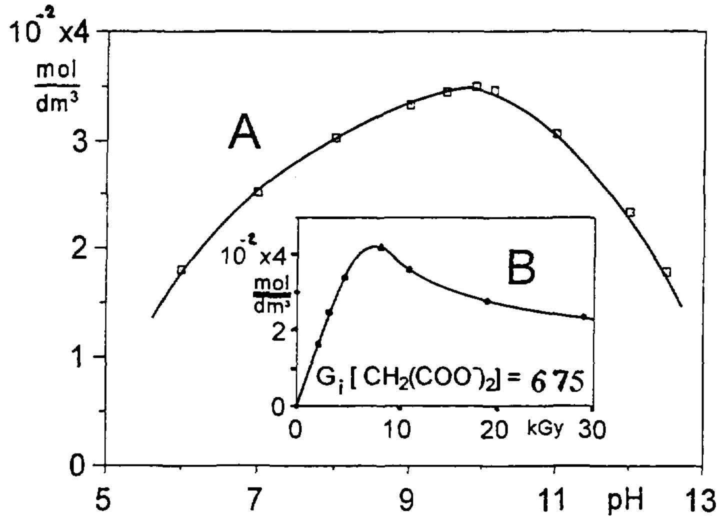


Fig.2: (A) pH-dependance of malonic acid formation (dose: 4.8 kGy)
(B) Malonic acid yield as a function of dose
Solution: $5x10^{-2}$ mol.dm^{-3} $ClCH_2COO^-$, $1x10^{-2}$ mol.dm^{-3} $HCOO^-$ and $1x10^{-3}$ mol.dm^{-3} CO; pH = 9.9; dose rate: 0.32 kGy.min^{-1}

The product yield is passing through a maximum at pH~10, whereas an optimal absorbed dose of about 8 kGy was found (see insert, Fig.2). The yield of malonic acid depends in the first place on the concentration of both radicals, COO^- and CH_2COO^-:

$$ClCH_2COO^- + e^-_{aq} \longrightarrow Cl^- + \dot{C}H_2COO^- \quad (14)$$

$$\dot{C}H_2COO^- + \dot{C}OO^- \longrightarrow CH_2(COO^-)_2 \text{ (malonic acid)} \quad (15)$$

A more detailed discussion on this subject matter is presented elsewhere /16/.

It should be mentioned that several possibilities for CO_2 utilization, such as catalytic processes /17/, photoelectrochemical reduction /18, 19/ etc. have been reported.

5. Radiation-induced degradation of aqueous pollutants

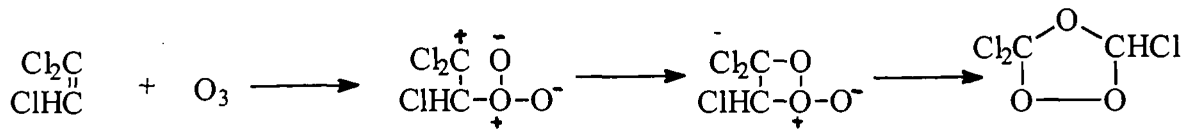
The global water resources became rather polluted in the last decades. The supply of drinking water in some regions of the world makes problems. This is the sequence of lack of responsibility of industrial enterprises as well as of the corresponding governmental authorities. There are a number of methods for water purifiction which are comprised in scheme V.

Scheme V:

	Method		Method
1	Radiation-induced oxidation of pollutants using: electrons, γ-rays, x-rays; synergistic effect in the presence of O_3/O_2, eventually H_2O_2 as additive	5	Photocatalytic treatment: UV/VIS light using TiO_2, ZnO etc. as catalyst
		6	Thermal oxidation of pollutants, used for liquid industrial wastes
2	Biological process for biodegradable pollutants, used for wastewater treatment	7	Fenton processes: H_2O_2/Fe^{2+} or $H_2O_2/O_3/Fe^{2+}$ (acid media)
3	Ozone treatment: O_3 or O_3/H_2O_2		
4	Photoinduced oxidation by UV (185 & 254 nm) or UV/O_3, UV/H_2O_2 and $UV/O_3/H_2O_2$ resp. using e.g. low pressure HG-lamp	8	Foto-Fenton process: $UV/H_2O_2/Fe^{2+}$ or $UV/H_2O_2/O_3/Fe^{2+}$ (acid media)
		9	Ultrasonic treatment (sonolysis of water)
		10	Electrochemical oxidation

It should be stressed that the most efficient method for degradation of biologically resistant water pollutants in industrial scale is the electron beam processing of water in the presence of ozone (synergistic effect). More details on this subject matter are discussed elsewhere /e.g. 2, 20-22/.

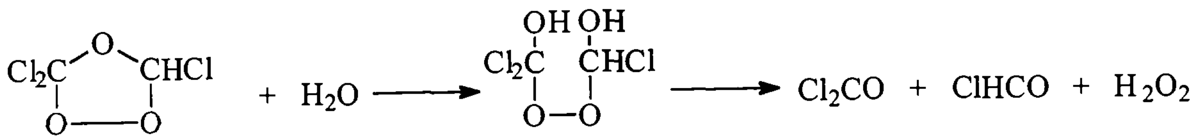
In the present contribution only brief remarks are given, considering the synergistic action of ozone and radiation on trichloroethylene ($Cl_2C=CHCl$), as a representative of chlorinated olefines and phenol (C_6H_5OH) as an example for aromatic pollutants.



(16)

(complex forms) (ozonide)

The ozonide undergoes hydrolysis, whereby two carbonyl compounds (phosgen and aldehyde) as well as H_2O_2 are formed:

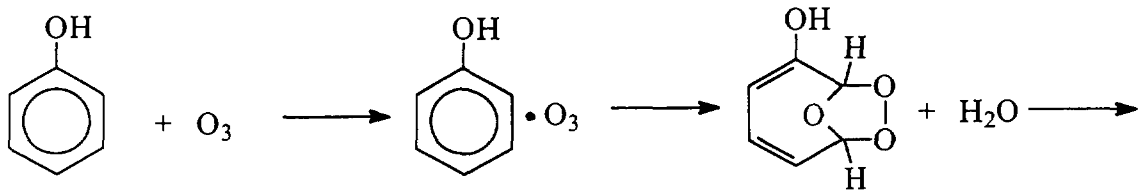


(17)

Subsequently phosgen is hydrolyzing according to reaction (18) and the resulting halogenated aldehyde is unstable and can likewise undergo a hydrolysis.

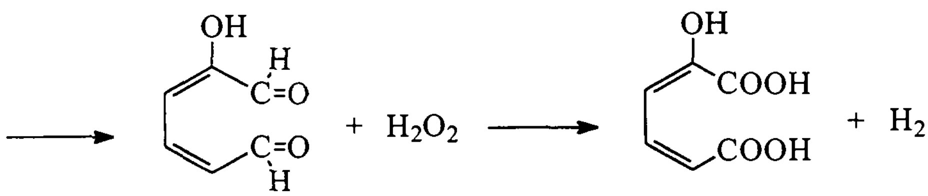
$$Cl_2CO + H_2O \longrightarrow CO_2 + H^+ + Cl^- \quad (18)$$

$$ClHCO + H_2O \longrightarrow HCOOH + H^+ + Cl^- \quad (19)$$



(20)

(complex) (ozonide) (hydrolysis)



(21)

(Muconic aldehyde) (Hydroxy muconic acid)

Since the modern electron accelerators are very reliable and have a very high conversion factor (η) e.g. for 2-3 MeV-machines $\eta \sim 80\%$ (100 kW electricity results into ~ 80 kW electron beam power) the method is very economical. The photochemical and photocatalytic methods (see scheme V) are rather promising and lot of efforts have been made in the last years in this respect.

6.Conclusion

- As a consequence of the human activities, the air, water ressources and soil became rather polluted in the last decades.
- The radiation chemistry methods can solve most of the environmental problems. In addition to this a number of new clean technologies based on radiation chemistry are developed.

- CO_2 and CO resulting from the combustion of fossil fuels can be utilized by irradiation-induced incorporation into cheeper organic starting materials to produce value-added products.
- Biologically resistant water pollutants can be decomposed successfully and economically by electron beam processing.

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