

Concentration Dependence of VOC Decomposition by Dielectric Barrier Discharges

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A comparative study of the decomposition of Volatile Organic Compounds (VOCs: Vinyl Chloride (VC), Ethyl Acetate (EA), Toluene (T), Acetone (A)) in dielectric barrier discharges (DBD) in zero and humidified air at atmospheric pressure was performed. Small scale tubular-flow with pulse excitation and large scale planar-flow with sinusoidal excitation were used to determine the removal efficiency in dependence on inlet concentration S_0 and air humidity. According to the destruction law $S=S_0 \exp(-E/\beta)$, where E is the plasma energy density, linear functions were found for the β -parameters with respect to S_0 containing an absolute term β_0 . By modeling the reaction kinetics it was possible to discriminate active species responsible for the decomposition. Ozone was confirmed to be involved in VC decomposition in zero air whereas OH radicals were best suited to explain the absolute efficiency of EA and toluene destruction in humid air. Their decomposition in zero air however, as well as the degradation of acetone cannot be explained in a similar way.

KEY WORDS: Non-thermal plasma; dielectric barrier discharge; VOC decomposition; oxidative removal.

1. INTRODUCTION

Atmospheric pressure non-thermal discharges have been studied for many years as a promising tool for treatment of polluted air, water and soil. Plasma chemical processes can be highly effectively in promoting oxidation or reduction, enhancing molecular dissociation or in producing free radicals to simulate chemical reactions.

With a view to broader industrial application improving of removal efficiency remains a primary task. But this is only possible on the basis of a detailed knowledge about the ongoing plasma-chemical processes. Unfortunately reaction chains are well known only for a few pollutants. In many cases already the primary decomposition reactions are not understood.

This work is a comparative study of the concentration dependence of removal efficiency in DBDs of different scale. In most cases we started our

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measurements in a larger test system medium flows with variable humidity. In some cases we completed these studies in a small scale DBD allowing ready dry (zero) air flows.

The experimental data could be fitted to a "first order" kinetic law. In this way the characteristic removal energies $\beta(S_0)^{(1)}$ were deduced. By modeling the β -functions the average production and lifetime parameters of the active species, which are involved in the removal process, could be obtained. So we were able to distinguish between different decomposition reactions and could get a feeling for the relative importance and absolute concentrations of OH and other radicals.

2. DESCRIPTION OF THE EXPERIMENTS

Experimental Set-Up

Two non-thermal plasma reactors of different scale were used. The small scale reactor consisted of a cylindrical glass barrier of 400 mm length with an inner diameter of 23 mm. An outer metallic mesh served as ground electrode and a stainless steel tube of 21 mm diameter as hv-electrode leaving a gap of approximately 1 mm. This reactor was excited by 20 kV pulses with 45 μ s rise time and a repetition rate of 1–100 pps, delivering a single pulse energy of 50–60 mJ.

The large scale reactor consisted of planar dielectric barriers of $210 \times 370 \text{ mm}^2$ forming a single discharge module with 3,151 of active volume. The barriers were made from a high-temperature composite material. Metallic plates between the barriers build up multiple discharge gaps of 2 mm. The discharge was excited by a frequency inverter with sinusoidal voltages of 50 . . . 400 . . . 600 . . Hz and up to 15 kV amplitude. One discharge module could treat an air flow of up to $150 \text{ m}^3/\text{hr}$.

Power Measurement

In the small reactor the pulse energy was determined using the voltage-charge Lissajous figure. The electric signals were recorded with an oscilloscope (Tektronix TDS 520C) and the area of the Lissajous figure, representing the energy dissipated during one period, was obtained by numerical processing.

Power measurements in the large reactor were based on voltage-current recording by a hv-probe (Tektronix P6015 A) and a Rogowski coil with 20 MHz bandwidth (Stangenes Industries 2–0.1 W). To obtain the average power the signals were numerically multiplied and averaged.

Organic and Water Vapour Admixtures

In the small reactor synthetic gas flows of 120 NI/hr were prepared by means of mass flow controllers from zero air (21% O₂ in N₂) and premixed VOC test gas bottles. The synthetic air could be humidified by bubbling it through water.

In the large system outdoor air of normal humidity was used. Water vapor and VOCs were added by means of mass flow controlled vaporization and temperature controlled saturation of appropriate zero air flows.

Gas Analysis

VOC concentrations were measured on line by a fast process gas chromatograph with PID detector (IUT). Vinyl chloride was analyzed by means of a mass spectrometer with atmospheric pressure inlet system (Balzers QMG 421). Gas samples could pass a high-temperature furnace in order to verify the carbon balance by means of non-dispersive IR absorption measurements of CO₂ (Rosemount NGA 2000) upstream and downstream to the plasma reactors. Ozone concentrations were measured using a UV-absorption based ozone detector (Anseros Ozomat GM).

3. KINETIC MODEL AND VOC REMOVAL EQUATION

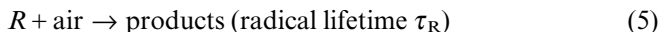
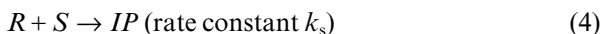
At relatively low VOC decomposition the removal law almost displayed an exponential behavior in dependence on plasma energy density E (plasma power per unit). If S_0 and S denote the initial and final hydrocarbon concentrations respectively then

$$S = S_0 \exp(-E/\beta) \quad (1)$$

with a characteristic parameter β depending linear on S_0 with a nonzero value of $S_0 \rightarrow 0$

$$\beta = \beta_0 + \beta_1 S_0 \quad (2)$$

Such a behavior can be obtained from a very general kinetic model [1] which takes into account radical production, radical-pollutant interaction and radical scavenging by "air" molecules.



The corresponding rate equations for S and R are

$$dS/dT = -k_s SR, \quad dR/dt = Q(E) - R/\tau_R - k_s SR - kRIP \quad (6)$$

where Q is the radical source term ($Q = G_R E/\tau$), G_R is the average production efficiency (G -value), τ is the residence time, and t is time ($t = x/v$, x -reactor coordinate, v -flow velocity).

In case of low decomposition $1 - S/S_0 \ll 1$ and short living radicals ($\tau_R \ll \tau$) these equations can be solved analytically. In this case the final concentration is an exponential function of energy density and the β -parameters depend linearly on the initial concentration of hydrocarbons:

$$S(E) = S_0 \exp(-E/\beta), \quad \beta = (k_s \tau_R G_R)^{-1} + S_0/G_R, \quad \beta = \beta_0 + S_0/G_R \quad (7)$$

In our case the residence times of the different gas flows always exceed 100 ms which is much longer than typical lifetimes of short living radicals (see Table I). Furthermore, a more detailed analysis shows,⁽²⁾ that in a first approximation relationship (7) is not severely restricted to the assumption of low decomposition. Therefore, the experimental data were fitted to Eqs. (7) in order to obtain the radical production efficiency G_R and the lifetime τ_R of the pollutant attacking species.

Table I

Substance	$\beta(S_0)$ - function	β_0 (Wh/m ³)	G_R (ppm/(Wh/m ³))	k_s (10 ⁻¹³ cm ³ /s)	τ_R (μ s)
EA in dry air 12-122 ppm	linear	15.1	2.86	19.4 (OH)	
EA in humid air 12-126 ppm	linear	20.1	4.77	19.4 (OH)	219
EA in zero air 5-30 ppm 30-120 ppm	nonlinear	~13 ~87	~0.3 ~0.9		
EA in humid zero air 12-100 ppm	linear	17	3.1	19.4 (OH)	402
Toluene in dry air 12-94 ppm	linear	12.3	3.1	60.3 (OH)	487
Toluene in humid air 12-88 ppm	linear	12.3	2.87	60.3 (OH)	192
Toluene in zero air 10-25 ppm 25-195 ppm	nonlinear	~48 ~112	~0.4 ~3.8		
Toluene in humid zero air 39-146 ppm	?	~36			
Acetone in dry air 17-146 ppm	linear	~44	~2.5	1.9 (OH)	1937
Acetone in humid air 15 ppm	74.3				
VC in zero air 49-495 ppm	linear	27.6	23		
VC in humid zero air 49-185 ppm 185-495 ppm	nonlinear	~11 ~41	~5.9 ~105		

4. EXPERIMENTAL RESULTS

The removal of vinyl chloride (VC), ethyl acetate (EA), toluene (T) and acetone (Ace) was measured using the two different discharge reactors. The results are shown in Figs. 1–6 and summarized in Table I. The table contains the β -functions, G-values, OH-rate constants and radical lifetimes.

VC (Fig. 1) was treated in the small reactor in the concentration range of 50–500 ppm. In zero air a well pronounced linear relationship $\beta(S_0)$ was found. As a consequence of a relatively large radical production efficiency of $23 \text{ ppm}/(\text{Wh}/\text{m}^3)^2$ the concentration dependence was the weakest among all compounds of this study

$$\beta_{\text{VC}} = 27.6 + S_0/23 \tag{8}$$

In humid zero air (~20 mbar H₂O) the $\beta(S_0)$ -function could be fitted by two linear parts

$$\beta_{\text{VC}} = 10.9 + S_0/5.9, \quad S_0 = 50\text{--}185 \text{ ppm} \tag{9}$$

$$\beta_{\text{VC}} = 41 + S_0/105, \quad S_0 = 185\text{--}500 \text{ ppm} \tag{10}$$

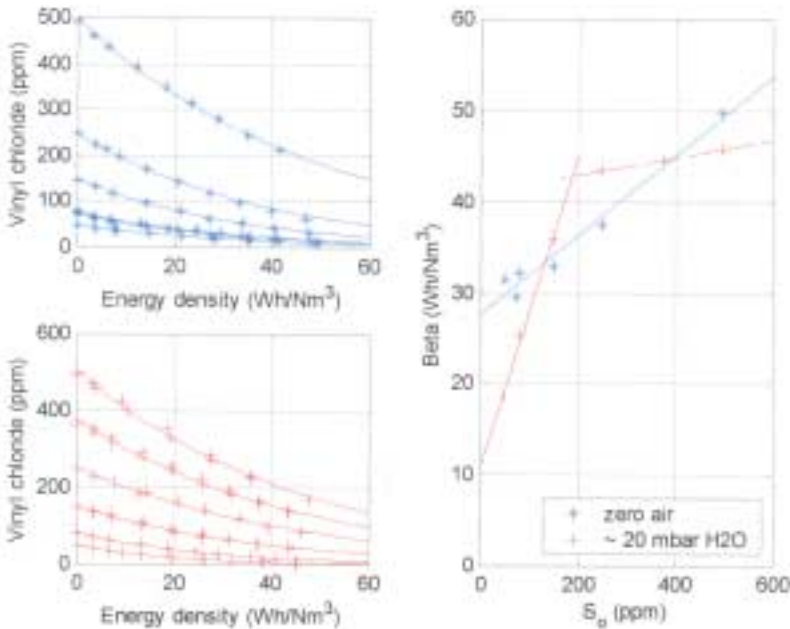


Fig. 1. Decomposition of VC in 120 NI/hr synthetic air.

²1 ppm/(Wh/Nm³) = 0.1196 molecule/100 eV.

EA decomposition (Fig. 2) was studied in both reactors and in the concentration range of 5–120 ppm. In the small reactor the following relationships could be deduced

$$\beta_{EA} = 13.9 + S_0/0.3, \quad S_0 = 5\text{--}30 \text{ ppm, zero air} \quad (11)$$

$$\beta_{EA} = 87.1 + S_0/0.9, \quad S_0 = 30\text{--}120 \text{ ppm, zero air} \quad (12)$$

$$\beta_{EA} = 17 + S_0/3.1, \quad S_0 = 12\text{--}100 \text{ ppm, } \sim 20 \text{ mbar H}_2\text{O} \quad (13)$$

The last $\beta(S_0)$ -function is very similar to those obtained in the large reactor (Fig. 3).

$$\beta_{EA} = 15.1 + S_0/2.86, \quad S_0 = 12\text{--}100 \text{ ppm, } \sim 8.5 \text{ mbar H}_2\text{O} \quad (14)$$

$$\beta_{EA} = 20.1 + S_0/4.77, \quad S_0 = 12\text{--}100 \text{ ppm, } \sim 28 \text{ mbar H}_2\text{O} \quad (15)$$

In these measurements the air flow was varied between 30 and 92 m³/hr. No dependence of removal efficiency on flow rate was noticed. Moreover, EA was not decomposed when a typical amount of ozone was added to the flow at the reactor inlet flange instead of applying a discharge.

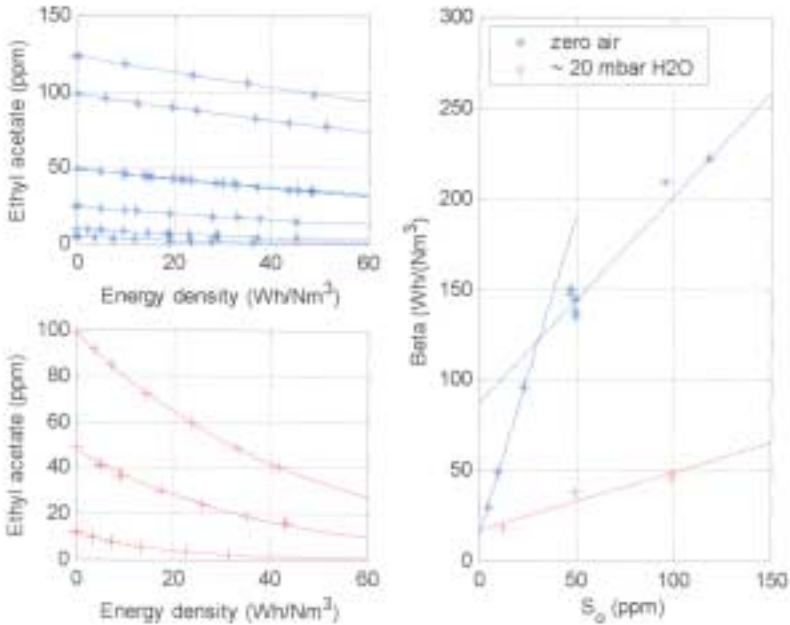


Fig. 2. Decomposition of ethyl acetate in 120 NI/hr synthetic air.

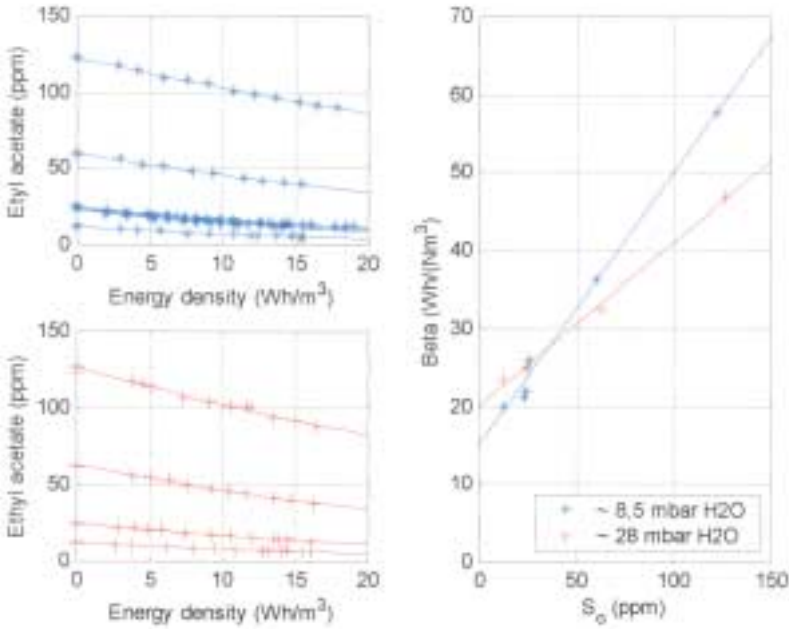


Fig. 3. Decomposition of ethyl acetate in 30–92 m³/hr dry (upper figure) and 30 m³/hr humid air (lower figure).

Toluene (10–194 ppm) degradation behaves very similar to that of ethyl acetate (Figs. 4–5. In zero air, again a twofold-linear behavior of the $\beta(S_0)$ -function was observed together with a strong water vapor influence

$$\beta_T = 48 + S_0/0.4, \quad S_0 = 10\text{--}195 \text{ ppm, zero air} \quad (16)$$

$$\beta_T = 112 + S_0/3.7, \quad S_0 = 39\text{--}146 \text{ ppm, zero air} \quad (17)$$

In the large reactor (18–31 m³/hr) the difference between dry and humid air was less pronounced so that the data could be fitted to a unique $\beta(S_0)$ -function

$$\beta_T = 12.4 + S_0/3, \quad S_0 = 12\text{--}94 \text{ ppm, } 7.5\text{--}30 \text{ mbar H}_2\text{O} \quad (18)$$

Again, no dependence of removal efficiency on flow rate was observed.

Acetone decomposition (Fig. 6) was studied in an air flow of 29 m³/hr in the large reactor. Again, the $\beta(S_0)$ -function is linear in a first approximation in the concentration range from 17 to 146 ppm

$$\beta_A = 44 + S_0/2.5, \quad S_0 = 17\text{--}146 \text{ ppm, } \sim 7 \text{ mbar H}_2\text{O} \quad (19)$$

Gas analysis problems avoided the evaluation of the water vapor influence in this case.

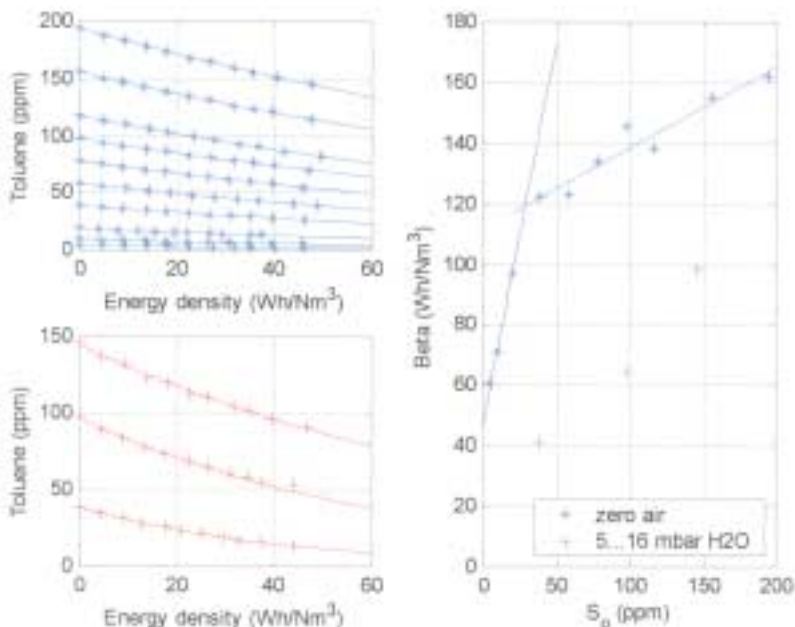


Fig. 4. Decomposition of toluene in 120 NI/hr synthetic air.

In addition ozone concentrations measurements were carried out at typical discharge conditions. One example is shown in Fig. 7. A low plasma power ozone production in zero and laboratory air was always proportional to plasma energy density. In the small reactor a production rate of 30–35 ppm/(Wh/Nm³) was measured in zero air. It decreased down to ~10 ppm/(Wh/Nm³) at a water vapor pressure of ~20 mbar. In the large reactor G_{O_3} was 25–35 ppm/(Wh/m³) in air (< 8 mbar H₂O) and decreased down to 16 ppm/(Wh/m₃) at 37 mbar water vapor.

5. DISCUSSION

As can be seen from the table the radical production efficiencies, as obtained from the experimental data, can be divided into three groups:

- small values < 1 ppm/(Wh/m³) in zero air,
- medium values in the range of 2–5 ppm/(Wh/m³) in laboratory air,
- large values > 10 ppm/(Wh/m³) in the case of VC treatment.

We believe that these groups represent the different primary decomposition reactions of the organic compounds. The third group is surely related

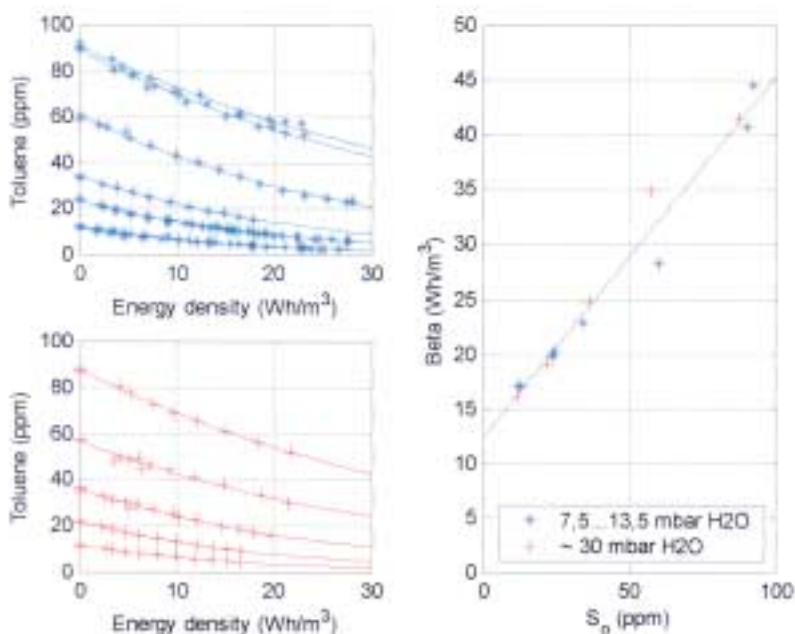


Fig. 5. Decomposition of toluene in 18–30 m³/hr dry (upper figure) and 18–31 m³/hr humid air (lower figure).

to ozone treatment because VC in zero air is largely decomposed by ozone. So, it is not surprising that the G -value of 23 ppm/(Wh/Nm³) is close to that of ozone synthesis. The same result can be found for other organic molecules with a double-bond (ethylene, for example). If treated in zero air they all display a weak dependence of the removal efficiency on input concentration.

In the presence of water vapor the removal process of VC is more confusing. At low concentrations VC is probably attacked by both OH radicals and ozone. At higher concentrations these processes get certainly enhanced by chlorine species.⁽³⁾

Ethyl acetate, toluene and acetone are not decomposed by ozone.⁽⁴⁾ For EA this was verified explicitly. EA and toluene in zero air belong to the first group, where the pollutant molecules are attacked by species with extremely low G -values (< 1 ppm/(Wh/Nm³)). This excludes atomic oxygen to be involved in the degradation process in agreement with the results of Krasnoporov *et al.*⁽⁵⁾ In fact, because of the ozone synthesis reaction



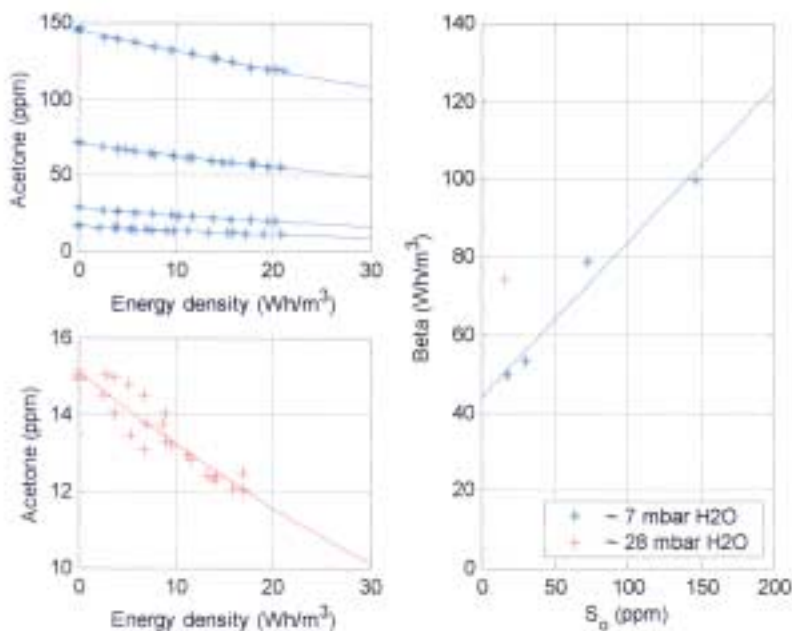


Fig. 6. Decomposition of acetone in $29 \text{ m}^3/\text{hr}$ dry (upper figure) and $28 \text{ m}^3/\text{hr}$ humid air (lower figure).

G_{O} must be almost equal to G_{O_3} . Moreover, according to the rate constant of reaction (20) the lifetime of atomic oxygen in zero air is in the order of $10\text{--}20 \mu\text{s}$. But given the rate constants^(6,7) of the $\text{O} + \text{EA} \rightarrow$ and $\text{O} + \text{T} \rightarrow$ reactions, milliseconds are necessary rather than microseconds in order to explain the $\beta(S_0)$ -functions in zero air. We believe that excited nitrogen species are involved in the reactions typical for the first group. This hypothesis was raised up by Fitzsimmons *et al.*⁽⁸⁾ in order to explain dischloromethane degradation. It will be proofed by treatment of EA in poor nitrogen in future.

When treated in humid air, ethyl acetate and toluene belong to the second group. Its degradation seriously depends on water vapor concentration. For EA the G -value increases from 2.86 to 3.1 and 4.77 ppm/(Wh/m³) at ~ 8.5 , 20 and 28 mbar H₂O respectively. For toluene a broad humidity range can be fitted by one G -value. Consequently, this behavior was attributed to the presence of OH radicals. Taking into account the rate constants^(9,10) for $\text{OH} + \text{EA} \rightarrow$ and $\text{OH} + \text{T} \rightarrow$ reactions, lifetimes of OH radicals were deduced from Eq. (7) to be in the range of $200\text{--}500 \mu\text{s}$ (see the table). Similar G -values and lifetimes were reported by Hilbert *et al.*,⁽¹¹⁾

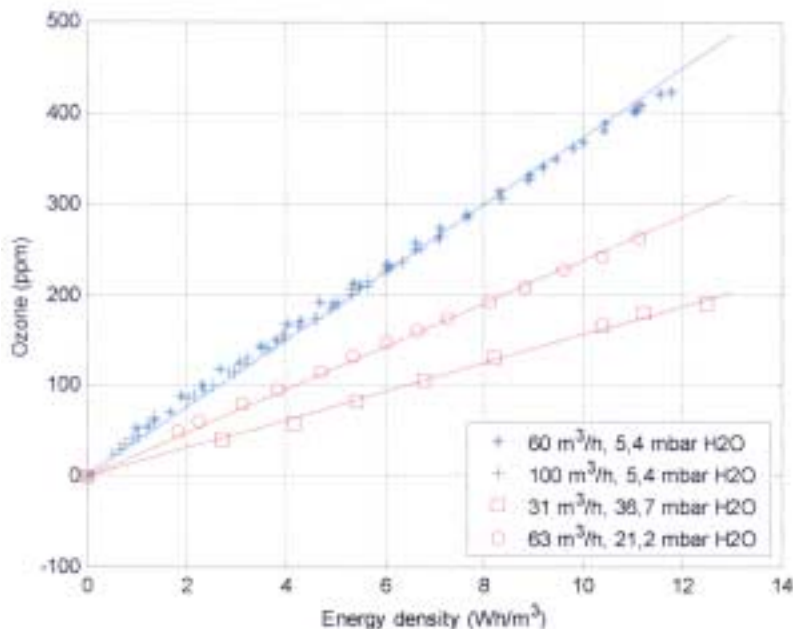


Fig. 7. Ozone synthesis in the large reactor vs. energy density at different conditions.

who studied OH radicals in a DBD in wet air by resonant absorption spectroscopy.

The decomposition of acetone is not understood at all. Its β -function looks very similar to those of EA and toluene but the rate constant for $\text{OH} + \text{A} \rightarrow$ reactions is one order of magnitude smaller.⁽¹²⁾ This leads to an unbelievable high OH radical lifetime of nearly 2 ms.

6. SUMMARY

By measuring the concentration dependence of the β -parameters it is possible to determine average radical production efficiency G_R and their lifetime τ_R . Three groups with low, medium and large G -values could be distinguished.

Ozone treatment manifests itself in a small slope of the $\beta(S_0)$ -function (high G -value).

OH radicals are very likely, if the radical production efficiency is in the range of 2–5 ppm/(Wh/m³). The removal of ethyl acetate and toluene in humid air can be analytically modeled very well; OH radical lifetimes in the range of 100–500 μs are obtained.

Degradation of ethyl acetate and toluene in zero air is probably based on two different reactions. Atomic oxygen can be ruled out by its high G -value and small lifetime. Excited nitrogen species are thought to be involved.

The $\beta(S_0)$ -function of acetone in laboratory air is very similar to those of ethyl acetate and toluene but it cannot be explained on the basis of an OH radical decomposition process.

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