

## Interactions of free electrons with molecules of TCDDs in a controlled way

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### Introduction

It is known that metabolism rate of isomers of tetra-chloro-dibenzo-*p*-dioxins (TCDD) in organisms of animals is different [1,2]. We have attempted to connect these differences with an electron structure of TCDD-molecules. One of the methods that allow to discover a correlation of biologic properties of the active compounds with their molecular structure is method of the negative ion mass spectrometry in the resonant electron capture mode [3].

### Material and Methods

Experiments with 1,2,3,4- and 2,3,7,8-TCDD have been conducted on the magnet sector type mass spectrometer MI-1201 modified for registration of negative ions with possibility of recording their effective yield curves (EYC), i.e., ion currents as a function of electron energy [4]. The monokinetic electron beam was generated by a trochoidal monochromator and, in operation, an electron energy distribution (FWHM) was ranged from 0.08 to 0.4 eV depending on signal intensity. Energy scale was calibrated by maxima of EYC of  $\text{SF}_6^- / \text{SF}_6^-$  ( $\approx 0$  eV) and  $\text{NH}_2^- / \text{NH}_3^-$  ( $\approx 5.65$  eV). The molecular beam was obtained by heating the solid probe to 80 – 90 °C (1,2,3,4-TCDD) and 130 – 140 °C (2,3,7,8-TCDD) in the direct inlet system. The ionization chamber temperature  $T_{ic}$  was varied from 50 up to 350 °C.

### Results and Discussion

The mass spectrum of 1,2,3,4-TCDD represents ions  $\text{M}^-$ ,  $\text{Cl}^-$ ,  $(\text{M-H})^-$ ,  $(\text{M-Cl})^-$ ,  $(\text{M-Cl-2H})^-$ ,  $(\text{M-2Cl})^-$ . In mass spectrum of 2,3,7,8-TCDD additionally to these cited above ions the rearrangement ions  $(\text{M-HCl})^-$  and cluster ions  $\text{Cl}_2\text{H}^-$  were observed.  $\text{M}^-$  ions are formed in

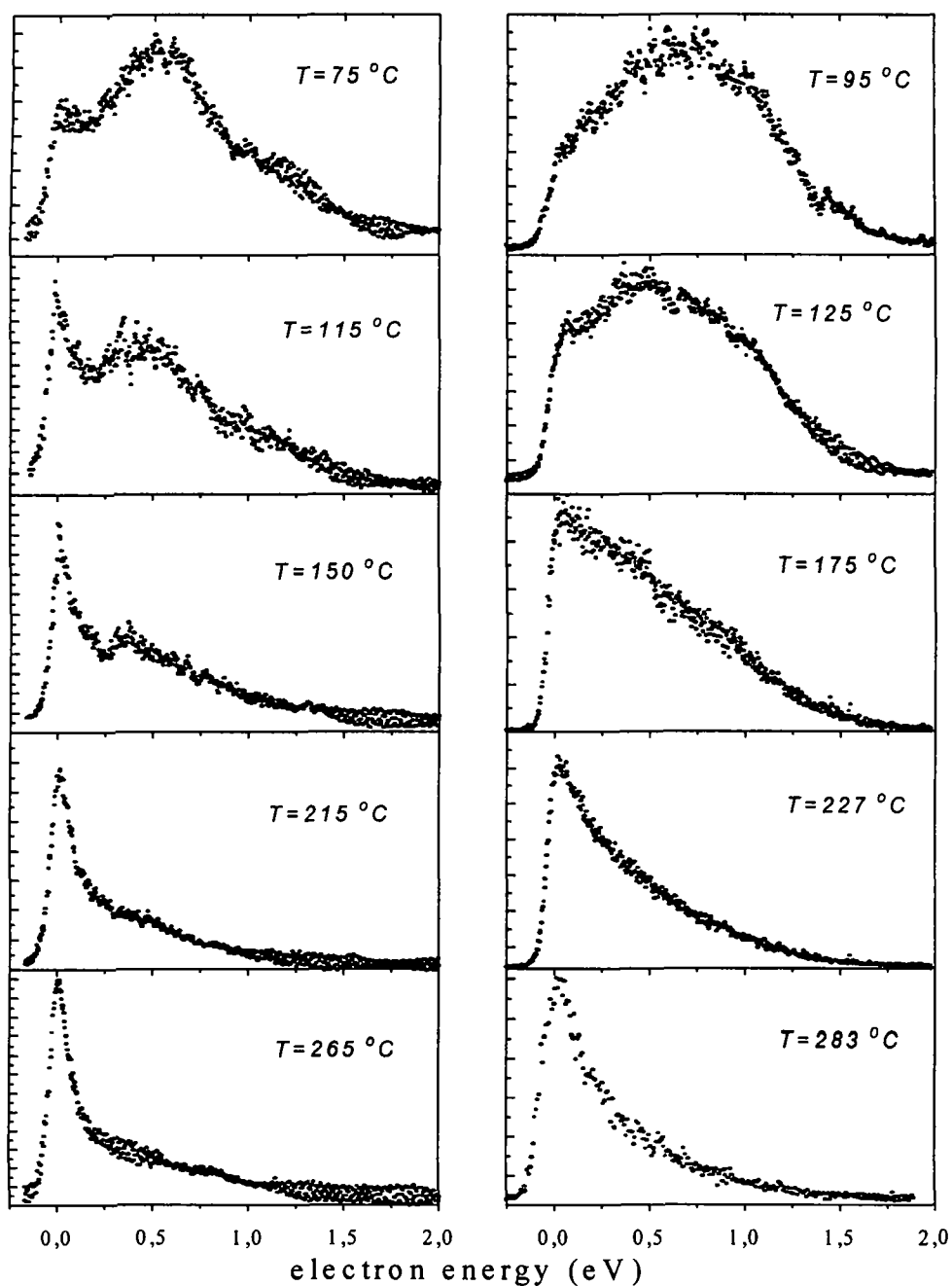


Fig. 1. Effective yield curves of Cl<sup>-</sup> ions in the energy region 0–2 eV at different temperature of ionization chamber from 1,2,3,4-TCDD (left) and 2,3,7,8-TCDD (right).

the thermal energy region and their curves are identical to that of  $SF_6^-$ . The mean lifetime of  $M^-$  with respect to electron autodetachment ( $\tau_a$ ) at  $T_{ic} \approx 50^\circ C$  is 30  $\mu s$  for both isomers. As temperature  $T_{ic}$  rises to 350  $^\circ C$ ,  $\tau_a$  is decreased by factor of 1.5 – 2. The temperature dependence on negative ion mass spectra has been revealed. It is in appearance of additional maximum in the EYC of fragment ions and in increasing their relative intensity at rising  $T_{ic}$ . Fig. 1 demonstrates this temperature dependence on the example of  $Cl^-$  at energy range 0 – 2 eV. On the background of a wide peak with maximum at  $\approx 0.5$  eV in the EYC of  $Cl^-$  from 1,2,3,4-TCDD the schedule at thermal energy is emerged at  $T_{ic} = 75^\circ C$ . As temperature rises, this schedule convert to the sharp peak and its relative intensity is enhanced more than by order of magnitude. Analogous dynamics was also fixed for EYC of  $Cl^-$  from 2,3,7,8-TCDD (Fig. 1). The phenomenon under observation is, perhaps, caused by the "hot band" effect [5]. It should be noted that with increasing the temperature, relative intensity of  $M^-$  ions is dramatically decreased at the thermal energy. Such degradation of  $M^-$  ions is associated with dissociation rather than with electron autodetachment. The ratio of  $Cl_s^-/M_s^-$  for different temperatures are shown in the table 1, where  $Cl_s^-$  and  $M_s^-$  are the relative intensities of chlorine and molecular ions summed over the all isotopes' peaks of mass spectra at the thermal energy. Values of  $\ln[1+Cl_s^-/M_s^-]$  which are proportional to the  $M^- \rightarrow Cl^-$  dissociation rate constant are shown too. Data of the table are

Table 1

T, $^\circ C$	1,2,3,4-TCDD				2,3,7,8-TCDD			
	55	160	250	350	40	140	240	340
$Cl_s^-/M_s^-$	0.238	3.45	37.7	392	0.147	0.944	12.9	168
$\ln[1+Cl_s^-/M_s^-]$	0.213	1.49	3.66	5.97	0.137	0.665	2.63	5.13
$1/kT, eV^{-1}$	35.4	26.8	22.2	18.6	37.1	28.1	22.6	18.9
$\ln[\ln(1+Cl_s^-/M_s^-)]$	-1.544	0.401	1.296	1.787	-1.986	-0.408	0.967	1.64

plotted in the Fig. 2(a) and one can see that over the all temperature range dissociation  $M^-/(1,2,3,4-TCDD)$  proceeds more effectively than that for 2,3,7,8-TCDD. It is more suitable to plot  $\ln[\ln(1+Cl^-/M^-)]$  as a function of  $1/kT$  (Fig 2(b)) that is straight line. From this Fig. it is easy to find the ratio of the dissociation rate constants for any temperature. For example, at

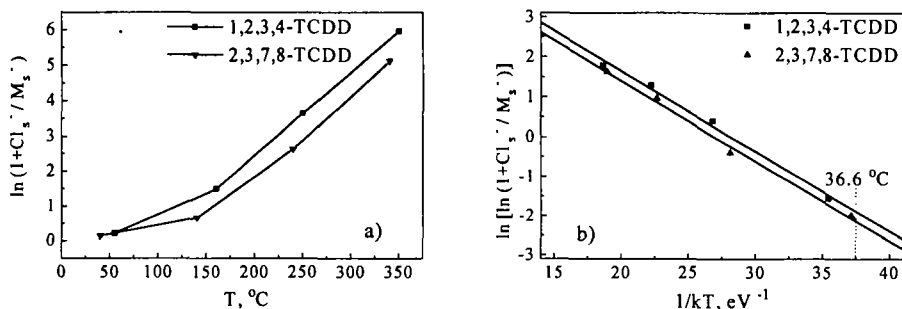


Fig. 2. Plot of  $\ln(1+Cl^-/M^-)$  as a function of ionization chamber temperature (a) and  $\ln[\ln(1+Cl^-/M^-)]$  as a function of  $1/kT$ .

T=36.6 °C (temperature of the human organism) the value of  $\ln[1+Cl^-/M^-]$  ratio for 1,2,3,4- and 2,3,7,8-TCDD is *ca.* 1.5. It shows that degradation of  $M^-$  from the former isomer at this temperature range proceeds more effectively than for the later. Analogous conclusion may be done from analysis of  $Cl^-$  ions' EYC plotted on the Fig. 1. The ion yield from 1,2,3,4-TCDD in the thermal energy region is higher than that from 2,3,7,8-TCDD, assuming approximately equal effective yield of these ions in the epithermal energy region (0.25 – 1.0 eV) for both compounds.

From cited above one can conjecture that the decay of 1,2,3,4-TCDD molecules has to occur quickly than that of 2,3,7,8-TCDD in organism, *i.e.*, rate of metabolism for the former is higher than for the latter. Unfortunately, based on results of these mass spectral experiments only with two compounds, it is impossible to connect a degradation dynamics of molecular ions (and, hence, metabolism of molecules of chlorodioxins in living organism) with their electron structure and structure of molecules. The progress in this direct we see in study of other compounds of this class of molecules.

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