Results

The determined amounts of the products at 150° C in percent values are shown in Table 1. Table 2 contains the first order reaction rate constants from 130 to 170° C and Table 3 shows the calculated Arrhenius parameters.

Discussion

The main pathways of the thermal decay of DBP in the gas phase are as follows [5]:

 $(CH_3)_3 - C - O - O - C(CH_3)_3 \rightarrow 2 (CH_3)_3 CO'$ (1)

$$(CH_3)_3CO' \rightarrow CH'_3 + (CH_3)_2CO$$
(2)

 $2 \operatorname{CH}_{3}^{\cdot} \to \operatorname{C}_{2} \operatorname{H}_{6} \tag{3}$

In the gas phase the overall rate of the degradation will be governed by reaction (1). Relay et al. have investigated the DBP decomposition in detail [6]. The agreement or our results with theirs is quite good:

$$E = 39.1 \pm 0.5 \text{ Kcal/mole}$$
 $A = 3.2 \cdot 10^{16} \text{ s}^{-1}$.

Therefore, we might assume that by applying the above described procedure we in fact obtain the rate constant of the reaction in the gas phase, because the partition of DBP and its degradation products at temperatures of 130° to 170° C lies far to the side of the gaseous state.

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Received June 11, 1987

Fresenius Z Anal Chem (1987) 329:487-489 © Springer-Verlag 1987

GC-determination of chlorophenoxy acetic herbicides (MCPA and 2,4-D) in water and soil. Reinvestigation of the technique

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GC-Bestimmung von Chlorphenoxyessigsäure-Herbiciden (MCPA und 2,4-D) in Wasser und Boden. Neubearbeitung des Verfahrens

GC procedure for the determination of MCPA and 2,4-D herbicides in water and soil was published in 1985 [1]. The procedure was carried out on a 160 cm long chromatographic column filled with 1.5% OV-17 + 1.95% QF-1 on Gas-Chrom Q (80-100 mesh) at 185°C. When this technique was applied to water and sediment samples from Miedwie lake (north-west Poland) as well was for samples of other origin including rural tap water, a residue of MCPA and 2,4-D was found in almost all samples. A maximum concentration of the herbicides was found during spring time, what was in agreement with the

application time of these herbicides in the field and confirming their migration into surface water.

Anyhow, the results were doubtful and therefore reinvestigation of the technique was necessary. By increasing the length of the column up to 360 cm as well as using a capillary column of 530 μ m with OV-17 the results were unchanged. However, when using another column of 185 cm length filled with 3% Silar 10 CP on Gas Chrom Q (100–120 mesh) the results were quite different and the peaks of the investigated herbicides were not detected in many samples. The following analysis on Hewlett Packard GC/MS Model 5992 B confirmed in many samples the presence of some organic acids which are not herbicides and normally overlapped MCPA and 2,4-D peaks. We, therefore, suggest to employ for the GC determination of MCPA and 2,4-D only a 3% Silar 10 CP column instead of that proposed previously.

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Received June 10, 1986; revised June 19, 1987

Fresenius Z Anal Chem (1987) 329:489 © Springer-Verlag 1987

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