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Measurement of Gas Phase Reactions Using Automated Headspace Gaschromatography

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The kinetics of the gas phase-conversion of 0,0-dimethylmaleic ester into 0,0-dimethyl fumaric ester, catalyzed by piperidine, were measured in the gas phase at 95 °C. Headspace-sample flasks served as the reaction vessels for the gaseous components and an automated headspace gaschromatograph as the sampling and analyzing system. The method was applied to investigate the thermal decomposition of *DFP* and sarin to propene in the range of 148 to 189 °C.

(Keywords: Headspace gaschromatography; Gas reactions; 0,0-*Dimethyl maleic ester;* 0,0-*Dimethyl fumaric ester; DFP; Sarin)*

Messung der Kinetik von Gasphasenreaktionen unter Verwendung der automatischen Dampfraumanalyse

Die Piperidin-katalysierte Isomerisierung von 0,0-Dimethylmaleinsäureester zum Fumarsäureester wurde in der Gasphase bei 95° durchgeführt. Als Reaktionsgefäße dienten Probenflaschen, wie sie für die automatische Dampfraumanalyse (HSGC) zur Verwendung kommen. Mit Hilfe der HSGC-Analyse wurde die Kinetik der Reaktion untersucht. Dieses Verfahren wurde sodann angewandt, um die thermolytische Zersetzung von *DFP* und Sarin zu Propen zwischen 148 und 189 °C zu studieren.

Introduction

Automated Headspace-Gaschromatography (HSGC) is a well established analytical method for determining volatile components in solid or liquid matrices. The decisive advantage of this technique is brought about by its automatization and on-line coupling of sampling and analysis: gas phase aliquots are withdrawn from the headspace (HS) of a closed vessel and injected into the gaschromatograph (GC). The calibration of the system is done by HS-analysis of vessels containing known amounts of the substance to be determined. Hence the signal given by the GC-detector essentially represents a gas concentration.

Consequently, the HSGC-technique should offer an access to measuring time dependent gas concentrations too, which means in other words, the investigation of reaction kinetics in the HS-vessel. For a first approach, we decided to confine our experiments on pure gas phase reactions. As a model reaction we chose the gas phase-conversion of 0,0-dimethyl maleate into 0,0-dimethyl fumarate, catalyzed by piperidine. This reaction is described in the literature [4] to proceed with high yield and velocity in the liquid phase. However no reports could be found about the efficiency of this catalyst in the gas phase. After establishing the experimental technique, the procedure could be tried to measure the thermolysis of the highly toxic compounds 0,0-diisopropylphosphorylfluoride (*DFP*) and 0-isopropylmethylphosphonylfluoride (sarin). Knowledge of this reaction is required in connection with the search for efficient detoxification measures.

In the literature, only few informations are available about the thermal breakdown of these substances: *Franke* [5] mentions that sarin at 300–400 °C decomposed "essentially into methylphosphonylfluoride and propene". This would be consistent with the finding that the thermolysis of diaryloxy alkoxy phosphoryl esters leads almost completely to the corresponding alkenes [6]. *Medema* et al. [7] studied the catalytic effectiveness of various oxides upon the decomposition of *DFP* and sarin at temperatures up to 65 °C. But no data about the thermolysis in absence of catalysts are given here, presumably because of the low rate of this reaction at low temperatures.

Experimental

Equipment

For the experiments described in this paper the HSGC-arrangement HS 6/F 22 (Bodenseewerk Perkin-Elmer, Überlingen, Federal Republic of Germany) was used. This system works as follows:

The sample is enclosed in a septum-sealed vial of 9.192 ml internal volume which is transferred into a thermostated magazine, situated near to the injector block of the GC. A needle, connected to the gas flow system at the injector, is introduced through the septum into the headspace of the vial, so that the back pressure of the GC-column is built up also in the flask. Next, for a short time, e.g. precisely 5 s, the carrier gas flow is interrupted by closing a magnetic valve, so that a certain portion of the gas phase can escape out of the vial. After this sampling interval, the valve opens again and the carrier gas flushes the sample onto the GC-column and to the detector.

In order to study the possible influence of the glass wall of the HS-flask upon the reaction, both the regular and silanized flasks were used. Silanization of the

HS-flasks was achieved by 15 min treatment with a mixture of dimethylchlorosilane (10 ml), hexamethyldisilazane (1 ml), abs. pyridine (10 ml) and abs. toluene (80 ml).

Chemicals

0,0-Dimethyl maleic ester (*M*) was purchased from Fluka (Buchs, CH), 0,0-dimethyl fumaric ester (*F*), piperidine, toluene and the alkanes from Merck (Darmstadt). *M* contained 1.2% *F* (GC-analysis). Propene was taken from a certified 0.102% (*v*/*v*)-mixture in nitrogen (Messer Griesheim, FGR) by means of a gas syringe under controlled pressure and temperature conditions. *DFP* was of 93%, sarin of 80% purity, as determined by titration according to *Beach* and *Sass* [8].

HSGC-Conditions

Conversion of 0,0-dimethylmaleate (*M*) to 0,0-dimethylfumarate (*F*) in presence of piperidine; column: Chromosorb W/SP 2340 (10%), 100/120 mesh; 2.2 mm × 3.3 m, 150 °C; N_2 3 bar (pressure controlled), 28 ml/min; FID: 250 °C, H_2 2.3 bar, air 3.8 bar; injector 120 °C; pressurization 1 min, injection time 5 s; 30 s after injection needle removed out of HS-flask; RT: *F* 5.2 min, *M* 9.4 min; piperidine was eluted together with the solvent toluene.

Thermolysis of *DFP* and sarin; column: Chromosorb G/DC 550 (4%) 80/100 mesh, 3.6 m × 3 mm, 50 °C (2 min) → 150 °C (8 min), 30 °C/min; N_2 2 bar (pressure controlled); FID: 200 °C H_2 2.3 bar (60 ml/min) air 3.8 bar (500 ml/min) Injector: 180 °C; pressurization 1 min, injection time 5 s. RT: Propene 1.3 min, *i*-octane (solvent) 4.3 min, *n*-decane (internal standard for *DFP* expts.) 8.7 min, *DFP* 9.8 min; *n*-dodecance (internal standard for sarin expts.) 14.8 min, sarin 8.0 min.

Selection of Septum, "Septum Constant"

A series of HS-flasks was filled with identical amounts of substance, either in its pure form or in solution, as planned for the main experiment. The amounts of solute and solvent have to be kept low enough, so that both will be completely vapourized at the test temperature. The test temperature should be in the same range as applied later in the main experiment. The contents of the flasks were analyzed after different storage times in the thermostated magazine. The detector signals, plotted on a logarithmic scale versus storage time (linear), yielded in each case a linear decrease. This indicates, that the loss of substance through the septum followed a first order time course, which can be characterized by a "septum constant" in the dimension of $\min^{-1}$. Those septa which showed the lowest loss of substance were chosen for the main experiments.

Calibration

A series of HS-flasks was filled with different amounts of test substance or its solution, so that complete vapourization was guaranteed, sealed with the selected type of septum and analyzed at test temperatures as planned for the main experiment.

The plots of the detector signals vs. the flask contents yielded straight lines in each case.

Isomerization of 0,0-*Dimethyl Maleic Ester*

Preliminary tests: A series of HS-flasks was filled with 2 μl toluene containing 41.7 μg *M* and 28.4 μg *F*, closed with butyl rubber/PTFE septa and stored for different times at 95 °C before analysis. The reason for this experiment was to find out, whether (i) *M* could be converted into *F* even in absence of piperidine (which did not occur) and (ii) there would be any other mutual interference between *M* and *F* (which was not the case). A second series of HS-flasks was filled with 9.6 μg *F* in 2 μl toluene, sealed and heated 95 °C. Next, 72.2 μg piperidine in 2 μl toluene were introduced through the septum into the hot flask. After being stored at 95 °C for different time intervals, the flask contents were analyzed. Obviously no reaction between *F* and piperidine took place, because the time dependent disappearance of *F* from the flask corresponded exactly to the "septum constant".

Main Experiment

A series of HS-flasks was filled with 43.5 μg *M* in 2 μl toluene, sealed with butylrubber/PTFE-septa and heated to 95 °C. At "time zero" 26 μg piperdine in 2 μl toluene were injected through the septum into the hot flask. After storage at 95 °C for different time intervals the flask contents were analyzed. From each flask two detector signals were obtained, representing the actual concentrations in *M* and *F*, respectively. By automatic integration they were converted into peak areas. Furthermore, the sum of the peak areas for each *M* and *F* pair, ΣMF, was calculated. This together with the finding, that the detector response to *M* and *F* was identical, provided a valuable means of control and additional information about the course of the reaction.

After conversion from peak areas into mass units, according to the calibration curve, the results yielded straight lines in a semilogarithmic plot vs. time. The reaction rate constants were calculated by linear regression. The experiments were carried out in both regular and silanized HS-flasks.

Thermolysis of DFP

A series of HS-flasks (dried over P_2O_5 in vacuo overnight) was filled with 18.3 μg (99.6 nmol) *DFP* in 2 μl iso-octane, containing 20.9 μg *n*-decane as an internal standard. The flasks were sealed with silicone/PTFE-septa, thermostated at 148, 168 or 189 °C, respectively, and analyzed after different storage times. It took about 5 min to reach the temperature equilibrium in the HS-flasks, so that "time zero" was set at 5 min after introduction into the thermostating magazine. Each flask yielded as the detector signals peak areas for *DFP*, propene and *n*-decane (as an internal standard providing a control for the dosage). After conversion of the *DFP*-results into molar units the semilogarithmic plots vs. reaction time gave straight lines. The experiments were carried out in regular and silanized HS-flasks.

Thermolysis of Sarin

The experiments were performed in the same way as with *DFP* at 168, 178.5 and 189 °C using each 8.38 μg (59.8 nmol) sarin in 2 μl iso-octane, containing 7.49 μg *n*-dodecane as internal standard. In this series only silanized HS-flasks were used. As with *DFP*, the semilogarithmic plots of the results vs. time were linear.

As a safety precaution in the experiments with *DFP* and sarin a fume hood was arranged above the HS 6 magazine. After analysis, the flasks were deflated by piercing a canula with a charcoal tube mounted on its outlet. The final decontamination of the HS-flasks was effected by injection of sodium hypochlorite solution.

General Kinetic Treatment

The conversion of 0,0-dimethyl maleic ester as well as the thermolysis of *DFP* and sarin follow a general reaction scheme $A \rightarrow B$, where B represents the reaction products 0,0-dimethyl fumaric ester or propene, respectively. Linearity of the log A_t/t-plots (as in fact obtained from the measured A-values after different time intervals) shows that the overall reaction follows first order kinetics:

$$A_t = A_0 \cdot e^{-k_A t} \tag{1}$$

with the concentrations A_0 at time zero and A_t after reaction time t and k_A as the (pseudo) first order rate constant. The disappearance of A during the reaction time is caused not only by conversion into B but additionly by passage into or through the septum. The latter process is measured separately (and proved to be of first order, too). If we denote the portion lost through the septum as AS, then the reaction scheme becomes $AS \leftarrow A \rightarrow B$ and eq. (1) has to be extended on account of this parallel reaction:

$$A_t = A_0 \cdot e^{-(k_R + k_{AS})t} \tag{2}$$

with k_{AS} = "septum constant" and k_R = rate constant of the conversion $A \rightarrow B$; $k_R = k_A — k_{AS}$. The material balance at time t is

$$A_t = A_0 — (AS_t + B_{Rt})$$

with B_{Rt} = product formed up to time t.

The concentration of A which is actually available for the reaction, is given by

$$A_{0Rt} = A_0 \cdot e^{-k_{AS} t} \tag{3}$$

The concentration of the product formed up to time t is

$$B_{Rt} = A_0 \cdot e^{-k_{AS} t} \cdot (1 — e^{-k_R t}) \tag{4}$$

Not only A but also B disappears into or through the septum: $AS \leftarrow A \rightarrow B \rightarrow BS$.

The portion of B lost through the septum by this consecutive first order process is given by eq. (5).

$$BS_t = A_{0RT} \quad 1 + \frac{k_{BS} \cdot e^{-k_R t} — k_R \cdot e^{-k_{BS} t}}{k_R — k_{BS}} \tag{5}$$

The material balance regarding the product at time t is $B_t = B_{Rt} — B_{St}$ with B_t = the concentration product as to be measured. Combining eqs. (3), (4), and (5) and rearranging yields

$$B_t = A_0 k_R \cdot e^{-k_{AS} t} \; \frac{e^{-k_{BS} t} — e^{-k_R t}}{k_R — k_{BS}} \tag{6}$$

The measured values for A_t as resulting from the HSGC-analysis should be described by eq. (2), those for B_t by eq. (6). All terms in these equations are experimentally accessible: A_0 and k_A result from the semilogarithmic plot of the measured A_t-values versus time, k_{AS} and k_{BS} from separate determinations (in case of the maleic ester-conversion) and $k_R = k_A — k_{AS}$. This provides a control for the proper function of the experimental procedure: The terms A_0, k_R, k_{AS} and k_{BS}, inserted in eq. (2) and (6) should yield A_t and B_t values which are in agreement with the measured results.

Results and Discussion

"Septum Constant" and Calibration

The rate constants for the passage of 0,0-dimethyl maleic ester (*M*), 0,0-dimethyl fumaric ester (*F*), propene (*P*), *n*-decane and *n*-dodecane into or through the septa are given in Table 1. These data were calculated by linear regression of plots as shown in Fig. 1, yielding correlation coefficients throughout better than 0.95. For the evaluation of the main experiment, as the septum constant for *M* an *F*, $k_S = 0.45 \cdot 10^{-3}\,\mathrm{min}^{-1}$ was used.

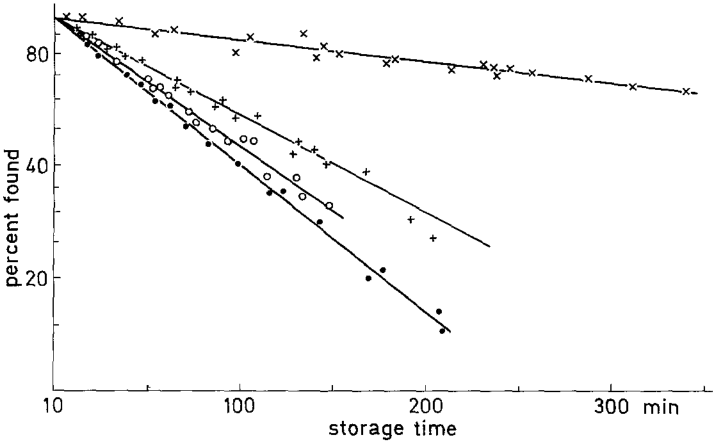

Fig. 1. Passage into or through the silicone/PTFE-septum of the headspace flask at higher temperatures: propene, 168 °C (×); *n*-decane, 168 °C (+), 189 °C (○), *n*-dodecane, 189 °C (·)

The time dependence of the septum passage has been measured in our laboratory with numerous other substances as a routine control experiment in HSGC; in all cases studied up to now, it proceeded in a first order time course.

The calibration experiments with *M* and *F* resulted in identical response factors of the FID for both substances.

A calibration in the usual way for *DFP* and sarin at flask temperatures between 150 and 190 °C would have been falsified by the rapid thermolysis and septum passage. Therefore the "F_0"-values, as resulting from linear regression to time zero, were used for a "one point calibration" of the detector. The linearity of the detector response to the amount of organophosphate was established separately. This mode of calibration was decidingly facilitated by use of the internal standards in the stock solutions.

Table 1. *Rate constants k_S for the passage through the septum*

Substance	Temp. °C	k_S $10^3\,\mathrm{min}^{-1}$	Septum
0,0-dimethyl maleic ester (*M*)	95	0.44	butyl rubber/PTFE
0,0-dimethyl fumaric ester (*F*)	95	0.45	butyl rubber/PTFE
propene (*P*)	148	0.90	silicone/PTFE
	168	1.43	silicone/PTFE
	178.5	1.61	silicone/PTFE
	189	1.98	silicone/PTFE
n-decane	148	4.68	silicone/PTFE
	168	6.13	silicone/PTFE
	189	8.07	silicone/PTFE
n-dodecane	168	8.93	silicone/PTFE
	178.5	9.31	silicone/PTFE
	189	9.66	silicone/PTFE

Isomerisation of 0,0-*Dimethyl Maleic Ester* (*M*)

The experimental results are presented in Fig. 2. There was no significant difference between the results from regular and silanized HS-flasks, so that they could be comprised for the following evaluations. The analysis of each HS-flask yielded three informations: (i) the actual concentration in M, (ii) that in F and (iii) the sum of $M + F = \Sigma$.

Σ is an additional meaningful value because of the identical detector response for M and F. Hence, linear regression of the $\log \Sigma/t$ data should give $k_\Sigma = k_S = 0.45 \cdot 10^{-3}\,\mathrm{min}^{-1}$. Instead of this, $k_\Sigma = 1.89 \cdot 10^{-3}\,\mathrm{min}^{-1}$ was found. $k_\Sigma - k_S = k_a = 1.44 \cdot 10^{-3}$ represents the rate constant of a side reaction (a) occurring in the gas phase, which presumably leads to the corresponding amide(s) MA (the preliminary test with F + piperidine has shown, that F does not react).

The linear regression of the Σ-data yielded $\Sigma_0 = 42.1\,\mu\mathrm{g}\,M$. Originally introduced into the flask were $M_{00} = 43.5\,\mu\mathrm{g}$. $43.5 - 42.1 = 1.5\,\mu\mathrm{g}$ disappeared, probably again to form MA; this reaction (b) must have occurred on the droplets of the piperidine solution just after injection, before complete vapourization was achieved.

During this short time interval obviously a further reaction takes place on or in the droplets: the conversion of M into F. The contribution of this side effect (c) can be read from the difference $\Sigma_0 - M_0 = 42.1 - 37.3 = 4.8\,\mu\mathrm{g}$ (M_0 resulted from linear regression of the $\log M/t$-data).

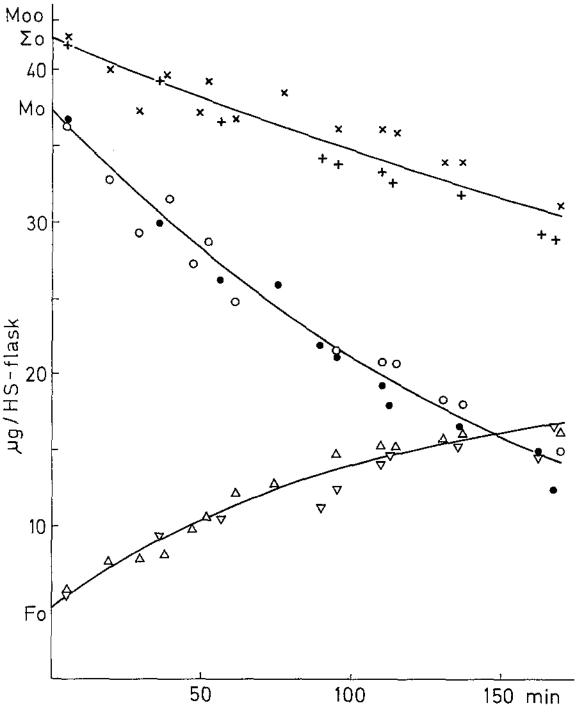

Fig. 2. Piperidine-catalyzed gasphase-conversion of 0,0-dimethyl maleic ester (M) to 0,0-dimethyl fumaric ester (F) at 95 °C in the headspace flask (9.192 cm^3). Disappearance of M in regular (·) and silanized (○) flasks, measured amounts of F in regular (·) and silanized (○) flasks, $M + F = \Sigma$ as measured (see text) in regular (+) and silanized (×) flasks. $M_{00} = 43.5$ µg M originally introduced, $\Sigma_0 = 42.1$ µg $M + F$ at time zero (see text), $M_0 = 37.3$ µg/flask and $F_0 = 4.8$ µg/flask as starting concentrations of the gasphase reaction

Consequently these 4.8 µg F were set as the starting concentration F_0 for the gas phase reaction.

On account of the three mentioned side effects the general reaction scheme from above has to be modified in the following way

$$\begin{tikzcd}
 & MA & & \\
MS & M \arrow[l, "k_S"'] \arrow[u, "a", "k_a"'] \arrow[r, "k_R", "c"'] \arrow[d, "b"'] & F \arrow[r, "k_S"] & FS \\
 & MA & &
\end{tikzcd}$$

Reactions b and c are regarded to be already completed when the gas phase reaction begins. Only reaction a contributes to the disappearence of M during the gas phase reaction. In order to facilitate the calculation reaction a is assumed to be of first order (although this might be incorrect). Thus all three reactions contributing to the gas phase consumption of M can be handled as first order parallel reactions. The overall rate constant k_M is then

$$k_M = k_R + k_S + k_a$$

with $k_a = 1.44 \cdot 10^{-3}\,\mathrm{min}^{-1}$, $k_S = 0.45 \cdot 10^{-3}\,\mathrm{min}^{-1}$, $k_M = 5.68 \cdot 10^{-3}\,\mathrm{min}^{-1}$ (from linear regression of the log M/t-data), k_R results to be $3.79 \cdot 10^{-3}\,\mathrm{min}^{-1}$.

Accordingly, eq. (1) has to be formulated

$$M_t = M_0 \cdot \mathrm{e}^{-k_M t} \qquad (7)$$

where $M_0 = 37.3\,\mu\mathrm{g}$/HS-flask.

In applying eq. (6) we have to account for the fact that at time zero the process starts with $F_0 = 4.8\,\mu\mathrm{g}$/HS-flask, which will be diminished also by passage through the septum. Correspondingly, eq. (6) has to be extended to

$$F_t = M_0 \cdot k_R \cdot \mathrm{e}^{-k_S t}\,\frac{\mathrm{e}^{-k_S t} - \mathrm{e}^{-k_R t}}{k_R - k_S} + F_0 \cdot \mathrm{e}^{-k_S t} \qquad (8)$$

In order to check the consistency of the proposed mechanism and the kinetic calculations with the measured values, the above given data for M_0, F_0, k_M, k_R and k_S were inserted into eqs. (7) and (8); the resulting M_t and F_t were used to draw the lines in Fig. 2. The good agreement with the experimental results, especially regarding the F_t-values, confirms at the same time the proper function and reliability of the method.

Thermolysis of Sarin

As an example, the experimental results for the run at 189 °C are shown in Fig. 3. In these series only silanized HS-flasks were used.

To set up a reaction scheme, we assumed that only one reaction would take place giving propene as the only volatile product:

$$(\mathrm{H_3C})_2\mathrm{CHOP(O)(CH_3)F} \rightarrow \mathrm{H_3C{-}CH{=}CH_2} + \ldots$$

This assumption is based on the information from literature, that the thermal decomposition of sarin gave propene at least as the main product [5].

In fact, the gaschromatograms yielded no other peaks than those for the solvent iso-octane, sarin, propene and the internal standard *n*-dodecane.

Thus the tentative reaction scheme is

$$FS \xleftarrow{k_{FS}} F \xrightarrow{k_R} P \xrightarrow{k_{PS}} PS$$

with F = sarin, FS = sarin passed into or through the septum, P = propene, PS = propene passed into or through the septum, and the respective (first order) rate constants.

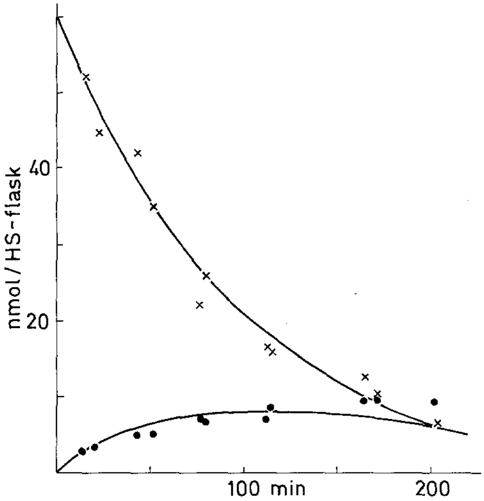

Fig. 3. Thermolysis of sarin vapour in silanized headspace flasks at 189 °C; sarin (×), propene (·)

From the descending concentration values for $F(=F_t)$ the starting concentration F_0 and the overall rate constant $K_F = k_R + k_{FS}$ were calculated by linear regression (see Table 2). The septum passage of propene was determined separately. For sarin, the septum passage and decomposition could not be measured separately. The evaluation of the data for k_{FS} and k_R given in Table 2 was therefore done by a "best fit" approximation using eq. (9) [which is analogous to eq. (4)]:

$$P_t = F_0 \cdot k_R \cdot \mathrm{e}^{-k_{FS}t} \; \frac{\mathrm{e}^{-k_{PS}t} - \mathrm{e}^{-k_R t}}{k_R - k_{PS}} \qquad (9)$$

A typical example for the range of variability in the best fit procedure and the accuracy of the approximated result is presented in Fig. 4 for *DFP*.

The lines drawn in Fig. 3 resulted from calculation, inserting the values of Table 2 into eqs. (9) and (10):

$$F_t = F_0 \cdot \mathrm{e}^{-k_F t} \qquad (10)$$

Table 2. *Thermolysis of sarin in silianized HS-flasks;* starting concentration $F_0 = 59.8$ nmol/HS-flask, activation energy $E_A = 119$ kJ/mol

Temp. °C	$k_F \cdot 10^3$ min^{-1}	$k_{FS} \cdot 10^3$ min^{-1}	$k_R \cdot 10^3$ min^{-1}	$k_{PS} \cdot 10^3$ min^{-1}
168	6.4	5.6	0.8	1.4
178.5	8.3	6.7	1.6	1.6
189	10.4	6.9	3.5	2.0

Table 3. *Thermolysis of DFP;* starting concentration $F_0 = 99.6$ nmol/HS-flask; activation energy $E_A = 120$ kJ/mol

HS-flasks	Temp. °C	$k_F \cdot 10^3$ min^{-1}	$k_{FS} \cdot 10^3$ min^{-1}	$k_R \cdot 10^3$ min^{-1}	$k_{PS} \cdot 10^3$ min^{-1}
silanized	148	3.7	3.4	0.3	0.9
	168	5.7	4.2	1.5	1.4
	189	9.5	4.3	5.2	2.0
regular	148	5.0	3.4	1.6	0.9
	168	8.3	4.2	4.1	1.4
	189	13.6	4.3	9.3	2.0

The calculated results from eq. (9) do not fit satisfactory in the course of the experimental data: the proposed reaction to propene is obviously not the only pathway of break down. The estimated k_R represents a minimum value, the true decomposition rate of sarin may be somewhat higher (and k_{FS} smaller, respectively).

The *Arrhenius* plots in Fig. 5 present the temperature dependence of k_F and k_R for both organophosphates. The activation energies for the descomposition were calculated from the slopes of the log k_R/T^{-1} plots.

Thermolysis of DFP

Because *DFP* contains two isopropyl residues, the reaction scheme was assumed to be

$$FS \xleftarrow{k_{FS}} F \xrightarrow{k_R} 2\,P \xrightarrow{k_{PS}} 2\,PS$$

with $F = DFP$ and $FS = DFP$ passed into septum. Eq. (9) has therefore to be modified to

$$P_t = 2\,F_0 k_R \cdot e^{-k_{FS}t}\,\frac{e^{-k_{PS}t} - e^{-k_R t}}{k_R - k_{PS}} \qquad (11)$$

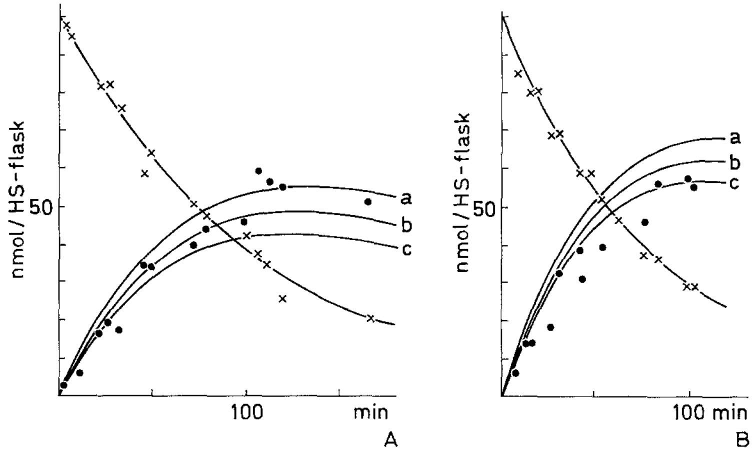

Fig. 4. Thermolysis of *DFP* vapour in silanized (A) and regular (B) headspace flasks at 189 °C; *DFP* (×), propene (·). The curves a, b, c are the best fit results using $10^3 \cdot k_{FS}$ (min^{-1}) = 3.8 (a), 4.3 (b), 4.8 (c) (see text)

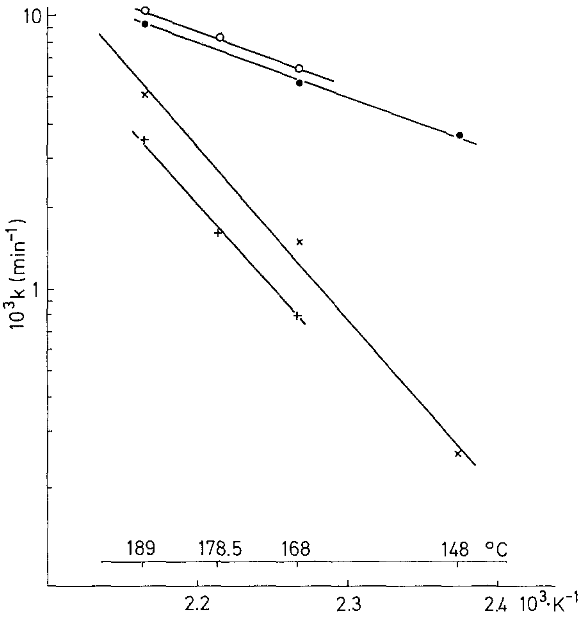

Fig. 5. Thermolysis of *DFP* and sarin in silanized headspace flasks; *Arrhenius* plots for *DFP*: k_F (·), k_R (×), and sarin: k_F (○), k_R (+)

For the evaluation of the results given in Table 3 the same procedure was applied as with sarin.

Furthermore Table 3 contains the results obtained in regular HS-flasks. The rate constants k_{FS} and k_{PS} must be the same as in silanized flasks and are therefore taken as such from that series of experiments. The measured k_F-values, and consequently also the k_R, are significantly higher than in the silanized flasks.

In Fig. 4 the results of the "best fits" are presented for the experiments at 189 °C. Due to the high scattering in the P_t-data, only an estimation of the range of the k_R-value can be given. The figures for k_R in Table 3 correspond to the curves b. The best achievable fit for the regular flask-series (part B of Fig. 4) is much worse than that in part A. The tendency of deviation indicates, that the additional decomposition reaction occurring on the glass walls does not produce propene.

The fact that indeed 2 moles propene are liberated from one mole *DFP*, was checked by insertion of of F_0, k_F, k_{PS} and k_{FS} (from the silanized flask-series) into eq. (9), i.e. omitting the factor 2 in eq. (11). Then the "best fit" lead to the nonsense-result, that the "septum constant" at 189 °C had to be by 2/3 smaller then that at 168 °C.

References

[1] *Hachenberg H, Schmidt AP* (1977) Gas-chromatographic headspace analysis. Heyden, London Philadelphia Rheine

[2] *Kolb B* (1980) Applied headspace chromatography. Heyden, London Philadelphia Rheine

[3] *Joffe BV, Vitenberg AG* (1984) Head-space analysis and related methods in gas chromatography. Wiley, New York

[4] *Clemo B, Graham J* (1930) J Chem Soc 215

[5] *Franke S* (1967) Lehrbuch der Militärchemie. Deutscher Akademie Verlag, Berlin, Bd 1. p 400

[6] *Eto M* (1977) Organophosphorus pesticides, organic and biological chemistry. CRC-Press, Cleveland/Ohio, p 700

[7] *Kuipers AET, van Bokhoven JJGM, Medema J* (1976) J Catalysis 43: 154, 181

[8] *Beach LK, Sass S* (1961) Anal Chem 33: 901

[9] *Schoene K, Steinhanses J* (1981) Fresenius Z Anal Chem 309: 198

[10] *Schoene K, Steinhanses J* (1984) Fresenius Z Anal Chem 319: 903

[11] *Frost AA, Pearson RG* (1964) Kinetik und Mechanismen homogener chemischer Reaktionen. Verlag Chemie, Weinheim/Bergstr, p 148 ff