

# "Kinetic NMR-Titration": Including Chemical Shift Information in the Kinetic Analysis of Supramolecular Reaction Systems such as Organic Replicators

Insa Stahl, Günter von Kiedrowski\*

Ruhr-Universität Bochum, Lehrstuhl für Organische Chemie I, Universitätsstrasse 150, 44780 Bochum, Germany

kiedro@rub.de

## Supporting Information

### Example SimFit command file (input file)

```
*****
* S158K1_B, 1H-NMR-Kinetik, 1 + 2b (X = Br), T = 323K, c = 15 mmol/l, C2D2C14
*****

define (1, a, e, 1) scale (3, 1)
define (2, c, p, 3) scale (3, 1)
define (3, d, nmr, 8) scale (3, 1) *definition of chemical shift as an observable
define (4, e, nmr, 4) scale (3, 1)

select (a, c, d, e)
read (S158K1_B_NMR_neu_2.txt) *data file
choose (exp1)
reaction ( A + B --> C) constant (1, 4.15087E-5, 0)
reaction ( A + B --> AB) constant (2, 1.00000E+6, 0)
*association reactions were assumed to be diffusion controlled; exemplary
calculations using 1.0E+8 and 1.0E+10 as rate constants for the association led to
comparable results for the equilibrium constants
reaction ( AB --> A + B) constant (3, 3.7315E+3,1, 1.00000E+0, 100)
reaction ( A + C --> AC) constant (4, 1.00000E+6, 0)
reaction ( AC --> A + C) constant (5, 3.7315E+3,1, 1.00000E+0, 100)
reaction ( B + C --> BC) constant (6, 1.00000E+6, 0)
reaction ( BC --> B + C) constant (7, 3.7315E+3,1, 1.00000E+0, 100)
reaction ( AB + B --> BC) constant (8, 4.15087E-5, 0)
reaction ( AB + A --> AC) constant (9, 4.15087E-5, 0)
reaction (AC + B --> ABC) constant (10, 1.00000E+6, 0)
reaction (ABC --> AC + B) constant (11, 3.7315E+3,1, 1.00000E+0, 100)
reaction (BC + A --> ABC) constant (12, 1.00000E+6, 0)
reaction (ABC --> BC + A) constant (13, 3.7315E+3,1, 1.00000E+0, 100)
reaction ( ABC --> C2) constant (14, 9.5705E-4,2, 1.00000E+0, 100)
reaction ( 2 C --> C2) constant (15, 1.00000E+6, 0)
reaction ( C2 --> 2 C) constant (16, 1.2721E+1,3, 1.00000E+0, 100)
*rate constants werde pre-optimized in preceded analyses
reaction (compile)
reaction (show)
assign (obs, a = A + AB + AC + ABC)
assign (obs, c = C + AC + BC + ABC + 2 C2)
assign (obs, d = C + 2 C2 + AC + BC + ABC)
assign (obs, e = A + AB + AC + ABC)
assign (spec, A = a)
assign (spec, B = # 1.49000E-2)
```

```
assign (spec, c = # 0.00000E+0)
```

```
czero (4, a, 1, 1, 1.05)
```

```
*chemical shift iteration for the species according to the reaction model
```

```
delta (d, c, 8.2597E+0, 5.00000E+0, 7.00000E+0, 9.00000E+0)
```

```
delta (d, AC, 8.2597E+0, 5.00000E+0, 7.00000E+0, 9.00000E+0)
```

```
delta (d, BC, 8.0161E+0, 7.00000E+0, 7.00000E+0, 9.00000E+0)
```

```
delta (d,ABC, 8.2631E+0, 8.00000E+0, 7.00000E+0, 9.00000E+0)
```

```
delta (d, C2, 8.2968E+0, 6.00000E+0, 7.00000E+0, 9.00000E+0)
```

```
delta (e, A, 8.0135E+0, 9.00000E+0, 7.00000E+0, 9.00000E+0)
```

```
delta (e, AB, 8.2635E+0, 1.00000E+1, 7.00000E+0, 9.00000E+0)
```

```
delta (e, AC, 8.2635E+0, 1.00000E+1, 7.00000E+0, 9.00000E+0)
```

```
delta (e,ABC, 8.1735E+0, 1.10000E+1, 7.00000E+0, 9.00000E+0)
```

```
time (h)
```

```
conc (mM)
```

```
win (0,70,10,0,-1,16,2,0)
```

```
nmrwin (0,70,10,0,8.05,8.30,0.1,0) *set
```

```
dim (11)
```

```
int (stiff, 1e-7, 32, 0.05, 500, 1500)
```

```
plot (spec)
```

```
simplex (plot)
```

```
opar (1e+8)
```

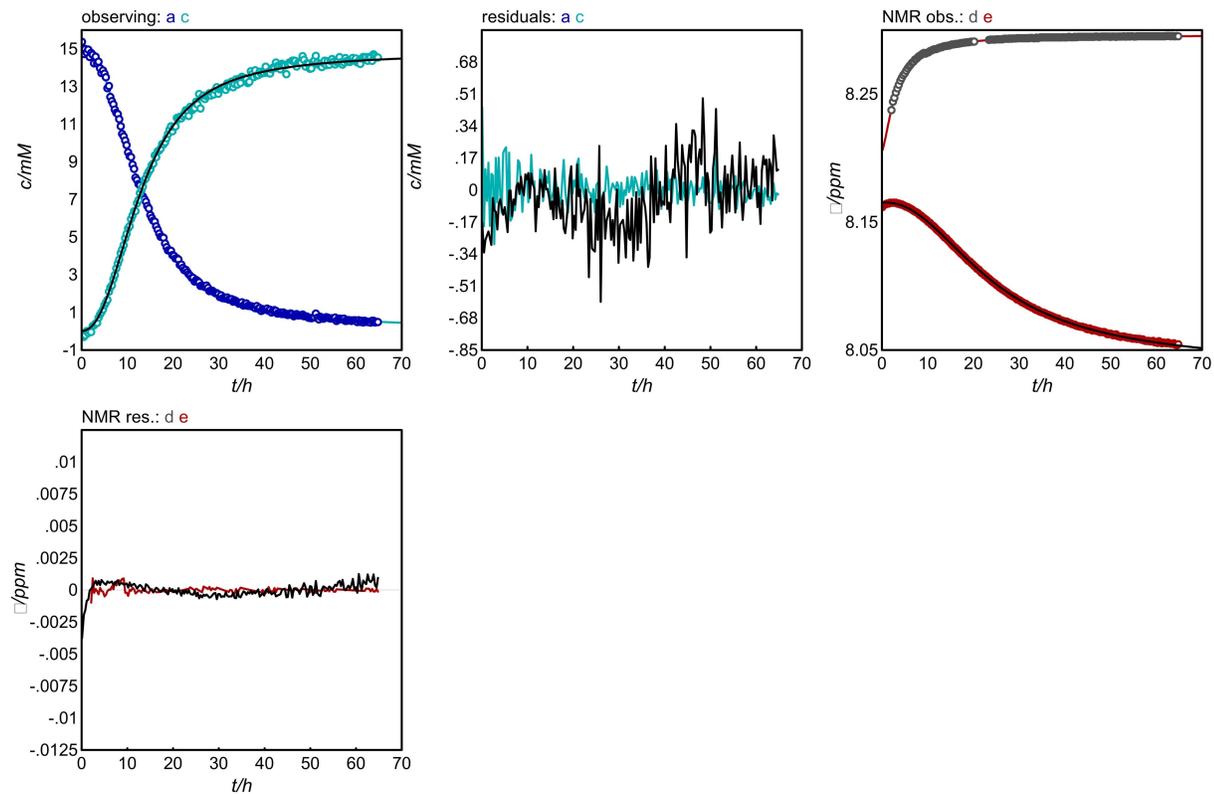
```
newton (plot)
```

```
plot (spec)
```

```
plot (resi)
```

```
make
```

## SimFit plot results



## SimFit command file (text result file)

```
*****  
* SimFit (PB/DLL6) 32-bit (10-Feb-2003) (C) 1989-2001 G. v. Kiedrowski *  
*****
```

This version of SimFit comes with 2 GB variable space.

SF32.INI is currently set to:

63 species,63 reactions,24 iteratable rate constants,  
32 observables,2 files,10 experiments/file,256 reaction times/experiment.

DEFINE (1,a,e,1)

SCALE (3,1)

a: K1 \* FE

DEFINE (2,c,p,3)

SCALE (3,1)

c: K1 \* FE

DEFINE (3,d,nmr,8)

SCALE (3,1)

d: K1 \* FE

DEFINE (4,e,nmr,4)

SCALE (3,1)

e: K1 \* FE

SELECT (a,c,d,e)

READ (s158k1\_b\_nmr\_neu\_2.txt)

The following observables found in s158k1\_b\_nmr\_neu\_2.txt are DEFINED:

a

c

d

e

Unit of time is not defined in data file.

SimFit assumes minutes as unit of time.

CHOOSE (exp1)

REACTION (a + b --> c)

CONSTANT (1,4.15087e-5,0)

REACTION (a + b --> ab)

CONSTANT (2,1.00000e+6,0)

REACTION (ab --> a + b)

CONSTANT (3,3.7315e+3,1,1.00000e+0,100)

REACTION (a + c --> ac)

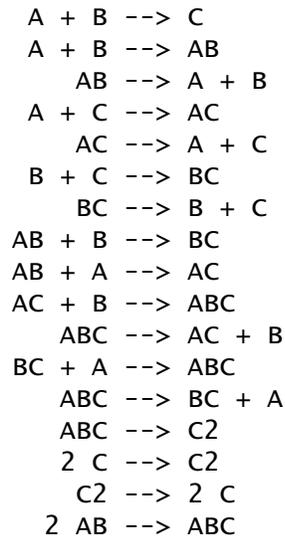
CONSTANT (4,1.00000e+6,0)

```

REACTION (ac --> a + c)
CONSTANT (5,3.7315e+3,1,1.00000e+0,100)
REACTION (b + c --> bc)
CONSTANT (6,1.00000e+6,0)
REACTION (bc --> b + c)
CONSTANT (7,3.7315e+3,1,1.00000e+0,100)
REACTION (ab + b --> bc)
CONSTANT (8,4.15087e-5,0)
REACTION (ab + a --> ac)
CONSTANT (9,4.15087e-5,0)
REACTION (ac + b --> abc)
CONSTANT (10,1.00000e+6,0)
REACTION (abc --> ac + b)
CONSTANT (11,3.7315e+3,1,1.00000e+0,100)
REACTION (bc + a --> abc)
CONSTANT (12,1.00000e+6,0)
REACTION (abc --> bc + a)
CONSTANT (13,3.7315e+3,1,1.00000e+0,100)
REACTION (abc --> c2)
CONSTANT (14,9.5705e-4,2,1.00000e+0,100)
REACTION (2 c --> c2)
CONSTANT (15,1.00000e+6,0)
REACTION (c2 --> 2 c)
CONSTANT (16,1.2721e+1,3,1.00000e+0,100)
REACTION (2 ab --> abc)
CONSTANT (17,4.15087e-5,0)
REACTION (compile)
REACTION (show)
-----
DGLCODER                Version 11.03.93
-----

```

Reactions:



Species found: A B C AB AC BC ABC C2

Rate equations:

$$\begin{aligned}
 d[A]/dt &= -k_1 \cdot [A] \cdot [B] - k_2 \cdot [A] \cdot [B] + k_3 \cdot [AB] - k_4 \cdot [A] \cdot [C] + k_5 \cdot [AC] - \\
 &k_9 \cdot [A] \cdot [AB] - k_{12} \cdot [A] \cdot [BC] + k_{13} \cdot [ABC] \\
 d[B]/dt &= -k_1 \cdot [A] \cdot [B] - k_2 \cdot [A] \cdot [B] + k_3 \cdot [AB] - k_6 \cdot [B] \cdot [C] + k_7 \cdot [BC] - \\
 &k_8 \cdot [B] \cdot [AB] - k_{10} \cdot [B] \cdot [AC] + k_{11} \cdot [ABC] \\
 d[C]/dt &= +k_1 \cdot [A] \cdot [B] - k_4 \cdot [A] \cdot [C] + k_5 \cdot [AC] - k_6 \cdot [B] \cdot [C] + k_7 \cdot [BC] - \\
 &2 \cdot k_{15} \cdot [C]^2 + 2 \cdot k_{16} \cdot [C_2] \\
 d[AB]/dt &= +k_2 \cdot [A] \cdot [B] - k_3 \cdot [AB] - k_8 \cdot [B] \cdot [AB] - k_9 \cdot [A] \cdot [AB] - 2 \cdot k_{17} \cdot [AB]^2 \\
 d[AC]/dt &= +k_4 \cdot [A] \cdot [C] - k_5 \cdot [AC] + k_9 \cdot [A] \cdot [AB] - k_{10} \cdot [B] \cdot [AC] + k_{11} \cdot [ABC] \\
 d[BC]/dt &= +k_6 \cdot [B] \cdot [C] - k_7 \cdot [BC] + k_8 \cdot [B] \cdot [AB] - k_{12} \cdot [A] \cdot [BC] + k_{13} \cdot [ABC] \\
 d[ABC]/dt &= +k_{10} \cdot [B] \cdot [AC] - k_{11} \cdot [ABC] + k_{12} \cdot [A] \cdot [BC] - k_{13} \cdot [ABC] - k_{14} \cdot [ABC] + \\
 &k_{17} \cdot [AB]^2 \\
 d[C_2]/dt &= +k_{14} \cdot [ABC] + k_{15} \cdot [C]^2 - k_{16} \cdot [C_2]
 \end{aligned}$$

Jacobian matrix: NJacobi& = 44 JacobiList& = 115

$$\begin{aligned}
 d(d[A]/dt)/d[A] &= -k_1 \cdot [B] - k_2 \cdot [B] - k_4 \cdot [C] - k_9 \cdot [AB] - k_{12} \cdot [BC] \\
 d(d[A]/dt)/d[B] &= -k_1 \cdot [A] - k_2 \cdot [A] \\
 d(d[A]/dt)/d[C] &= -k_4 \cdot [A] \\
 d(d[A]/dt)/d[AB] &= +k_3 - k_9 \cdot [A] \\
 d(d[A]/dt)/d[AC] &= +k_5 \\
 d(d[A]/dt)/d[BC] &= -k_{12} \cdot [A] \\
 d(d[A]/dt)/d[ABC] &= +k_{13} \\
 d(d[B]/dt)/d[A] &= -k_1 \cdot [B] - k_2 \cdot [B] \\
 d(d[B]/dt)/d[B] &= -k_1 \cdot [A] - k_2 \cdot [A] - k_6 \cdot [C] - k_8 \cdot [AB] - k_{10} \cdot [AC] \\
 d(d[B]/dt)/d[C] &= -k_6 \cdot [B] \\
 d(d[B]/dt)/d[AB] &= +k_3 - k_8 \cdot [B] \\
 d(d[B]/dt)/d[AC] &= -k_{10} \cdot [B] \\
 d(d[B]/dt)/d[BC] &= +k_7 \\
 d(d[B]/dt)/d[ABC] &= +k_{11} \\
 d(d[C]/dt)/d[A] &= +k_1 \cdot [B] - k_4 \cdot [C] \\
 d(d[C]/dt)/d[B] &= +k_1 \cdot [A] - k_6 \cdot [C] \\
 d(d[C]/dt)/d[C] &= -k_4 \cdot [A] - k_6 \cdot [B] +-4k_{15} \cdot [C] \\
 d(d[C]/dt)/d[AC] &= +k_5 \\
 d(d[C]/dt)/d[BC] &= +k_7 \\
 d(d[C]/dt)/d[C_2] &= +2 \cdot k_{16} \\
 d(d[AB]/dt)/d[A] &= +k_2 \cdot [B] - k_9 \cdot [AB] \\
 d(d[AB]/dt)/d[B] &= +k_2 \cdot [A] - k_8 \cdot [AB] \\
 d(d[AB]/dt)/d[AB] &= -k_3 - k_8 \cdot [B] - k_9 \cdot [A] +-4k_{17} \cdot [AB]
 \end{aligned}$$

$$\begin{aligned}
d(d[AC]/dt)/d[A] &= + k4 \cdot [C] + k9 \cdot [AB] \\
d(d[AC]/dt)/d[B] &= - k10 \cdot [AC] \\
d(d[AC]/dt)/d[C] &= + k4 \cdot [A] \\
d(d[AC]/dt)/d[AB] &= + k9 \cdot [A] \\
d(d[AC]/dt)/d[AC] &= - k5 - k10 \cdot [B] \\
d(d[AC]/dt)/d[ABC] &= + k11 \\
d(d[BC]/dt)/d[A] &= - k12 \cdot [BC] \\
d(d[BC]/dt)/d[B] &= + k6 \cdot [C] + k8 \cdot [AB] \\
d(d[BC]/dt)/d[C] &= + k6 \cdot [B] \\
d(d[BC]/dt)/d[AB] &= + k8 \cdot [B] \\
d(d[BC]/dt)/d[BC] &= - k7 - k12 \cdot [A] \\
d(d[BC]/dt)/d[ABC] &= + k13 \\
d(d[ABC]/dt)/d[A] &= + k12 \cdot [BC] \\
d(d[ABC]/dt)/d[B] &= + k10 \cdot [AC] \\
d(d[ABC]/dt)/d[AB] &= + 2 \cdot k17 \cdot [AB] \\
d(d[ABC]/dt)/d[AC] &= + k10 \cdot [B] \\
d(d[ABC]/dt)/d[BC] &= + k12 \cdot [A] \\
d(d[ABC]/dt)/d[ABC] &= - k11 - k13 - k14 \\
d(d[C2]/dt)/d[C] &= + 2 \cdot k15 \cdot [C] \\
d(d[C2]/dt)/d[ABC] &= + k14 \\
d(d[C2]/dt)/d[C2] &= - k16
\end{aligned}$$

ASSIGN (obs,a = a + ab + ac + abc)

ASSIGN (obs,c = c + ac + bc + abc + 2 c2)

ASSIGN (obs,d = c + 2 c2 + ac + bc + abc)

ASSIGN (obs,e = a + ab + ac + abc)

ASSIGN (spec,a = a)

ASSIGN (spec,b = # 1.49000e-2)

ASSIGN (spec,c = # 0.00000e+0)

CZERO (4,a,1,1,1.05)

DELTA (d,c,8.2597e+0,5.00000e+0,7.00000e+0,9.00000e+0)

DELTA (d,ac,8.2597e+0,5.00000e+0,7.00000e+0,9.00000e+0)

DELTA (d,bc,8.0161e+0,7.00000e+0,7.00000e+0,9.00000e+0)

DELTA (d,abc,8.2631e+0,8.00000e+0,7.00000e+0,9.00000e+0)

DELTA (d,c2,8.2968e+0,6.00000e+0,7.00000e+0,9.00000e+0)

DELTA (e,a,8.0135e+0,9.00000e+0,7.00000e+0,9.00000e+0)

DELTA (e,ab,8.2635e+0,1.00000e+1,7.00000e+0,9.00000e+0)

DELTA (e,ac,8.2635e+0,1.00000e+1,7.00000e+0,9.00000e+0)

DELTA (e,abc,8.1735e+0,1.10000e+1,7.00000e+0,9.00000e+0)

TIME (h)

CONC (mm)

WIN (0,70,10,0,-1,16,2,0)

NMRWIN (0,70,10,0,8.05,8.30,0.1,0)

DIM (11)

INT (stiff,1e-7,32,0.05,500,1500)

PLOT (spec)

SIMPLEX (plot)

k1_____	k2_____	k3_____	k4_____	k5_____	k6_____	k7_____
k8_____	k9_____	k10_____	k11_____	R.M.S. [%]		
initial values:						
3.7315E+3	9.5705E-4	1.2721E+1	1.5370E-2	8.2597E+0	8.2968E+0	8.0161E+0
8.2631E+0	8.0135E+0	8.2635E+0	8.1735E+0	8.5788		
3.9122E+3	9.8316E-4	1.3337E+1	1.5485E-2	8.2334E+0	8.2968E+0	8.0785E+0
8.1882E+0	8.0150E+0	8.2678E+0	8.3675E+0	8.2863		
3.9289E+3	9.8528E-4	1.3331E+1	1.5162E-2	8.2739E+0	8.2972E+0	8.0932E+0
8.1784E+0	8.0157E+0	8.2695E+0	8.4040E+0	5.3682		
4.0129E+3	9.5366E-4	1.3260E+1	1.5210E-2	8.2612E+0	8.2986E+0	8.0535E+0
8.2533E+0	8.0151E+0	8.2646E+0	8.3194E+0	4.8380		
3.7971E+3	9.4845E-4	1.3544E+1	1.5122E-2	8.2636E+0	8.2964E+0	8.0514E+0
8.2273E+0	8.0144E+0	8.2630E+0	8.3860E+0	3.5345		
3.9491E+3	9.5658E-4	1.3542E+1	1.4988E-2	8.2427E+0	8.2966E+0	8.0261E+0
8.2696E+0	8.0135E+0	8.2613E+0	8.2668E+0	2.9070		
3.8898E+3	9.6925E-4	1.3561E+1	1.5041E-2	8.2691E+0	8.2967E+0	8.0559E+0
8.2523E+0	8.0147E+0	8.2645E+0	8.2857E+0	2.5051		
3.8956E+3	9.6475E-4	1.3597E+1	1.4985E-2	8.2698E+0	8.2970E+0	8.0492E+0
8.2288E+0	8.0144E+0	8.2641E+0	8.2773E+0	2.4927		
3.7798E+3	9.7600E-4	1.3678E+1	1.4938E-2	8.2569E+0	8.2959E+0	8.0510E+0
8.2457E+0	8.0137E+0	8.2608E+0	8.2734E+0	2.0748		
3.8822E+3	9.6459E-4	1.3535E+1	1.4958E-2	8.2637E+0	8.2963E+0	8.0434E+0
8.2540E+0	8.0139E+0	8.2625E+0	8.2789E+0	2.0225		
3.8029E+3	9.6816E-4	1.3618E+1	1.4933E-2	8.2604E+0	8.2972E+0	8.0448E+0
8.2623E+0	8.0142E+0	8.2624E+0	8.2720E+0	1.9508		
3.8566E+3	9.6101E-4	1.3587E+1	1.4965E-2	8.2611E+0	8.2962E+0	8.0337E+0
8.2676E+0	8.0135E+0	8.2613E+0	8.2499E+0	1.8185		
3.8581E+3	9.7683E-4	1.3608E+1	1.4891E-2	8.2598E+0	8.2964E+0	8.0362E+0
8.2680E+0	8.0136E+0	8.2619E+0	8.2224E+0	1.5750		
3.8108E+3	9.7223E-4	1.3630E+1	1.4950E-2	8.2600E+0	8.2962E+0	8.0461E+0
8.2506E+0	8.0138E+0	8.2616E+0	8.2724E+0	1.5508		

3.8033E+3	9.7076E-4	1.3611E+1	1.4904E-2	8.2607E+0	8.2963E+0	8.0348E+0
8.2581E+0	8.0135E+0	8.2612E+0	8.2554E+0	1.4789		
3.8073E+3	9.7248E-4	1.3605E+1	1.4944E-2	8.2662E+0	8.2964E+0	8.0443E+0
8.2528E+0	8.0140E+0	8.2624E+0	8.2682E+0	1.4719		
3.8239E+3	9.6967E-4	1.3605E+1	1.4943E-2	8.2619E+0	8.2966E+0	8.0414E+0
8.2577E+0	8.0139E+0	8.2622E+0	8.2671E+0	1.4472		
3.8364E+3	9.6934E-4	1.3600E+1	1.4951E-2	8.2629E+0	8.2965E+0	8.0413E+0
8.2535E+0	8.0139E+0	8.2623E+0	8.2669E+0	1.4402		
3.8397E+3	9.7362E-4	1.3610E+1	1.4915E-2	8.2609E+0	8.2964E+0	8.0380E+0
8.2623E+0	8.0137E+0	8.2619E+0	8.2436E+0	1.4251		
3.8175E+3	9.7183E-4	1.3636E+1	1.4913E-2	8.2615E+0	8.2964E+0	8.0375E+0
8.2592E+0	8.0138E+0	8.2617E+0	8.2604E+0	1.4123		
3.8120E+3	9.7217E-4	1.3617E+1	1.4937E-2	8.2617E+0	8.2964E+0	8.0394E+0
8.2567E+0	8.0138E+0	8.2619E+0	8.2608E+0	1.4088		
3.8121E+3	9.7119E-4	1.3612E+1	1.4920E-2	8.2615E+0	8.2963E+0	8.0376E+0
8.2571E+0	8.0136E+0	8.2616E+0	8.2600E+0	1.4054		
3.8155E+3	9.7416E-4	1.3625E+1	1.4917E-2	8.2615E+0	8.2964E+0	8.0398E+0
8.2561E+0	8.0138E+0	8.2617E+0	8.2525E+0	1.3828		
3.8174E+3	9.7329E-4	1.3614E+1	1.4926E-2	8.2623E+0	8.2965E+0	8.0416E+0
8.2565E+0	8.0138E+0	8.2620E+0	8.2582E+0	1.3818		
3.8206E+3	9.7198E-4	1.3612E+1	1.4931E-2	8.2619E+0	8.2965E+0	8.0403E+0
8.2569E+0	8.0138E+0	8.2620E+0	8.2608E+0	1.3795		
3.8207E+3	9.7302E-4	1.3612E+1	1.4920E-2	8.2624E+0	8.2965E+0	8.0388E+0
8.2580E+0	8.0138E+0	8.2620E+0	8.2556E+0	1.3727		
3.8190E+3	9.7376E-4	1.3615E+1	1.4916E-2	8.2617E+0	8.2965E+0	8.0403E+0
8.2562E+0	8.0138E+0	8.2619E+0	8.2552E+0	1.3645		
3.8175E+3	9.7334E-4	1.3617E+1	1.4920E-2	8.2614E+0	8.2965E+0	8.0388E+0
8.2561E+0	8.0138E+0	8.2619E+0	8.2563E+0	1.3593		
3.8192E+3	9.7364E-4	1.3611E+1	1.4921E-2	8.2617E+0	8.2966E+0	8.0400E+0
8.2563E+0	8.0138E+0	8.2620E+0	8.2560E+0	1.3579		
3.8214E+3	9.7352E-4	1.3609E+1	1.4924E-2	8.2621E+0	8.2965E+0	8.0402E+0
8.2556E+0	8.0138E+0	8.2621E+0	8.2560E+0	1.3559		
3.8187E+3	9.7491E-4	1.3611E+1	1.4919E-2	8.2614E+0	8.2966E+0	8.0415E+0
8.2539E+0	8.0138E+0	8.2620E+0	8.2527E+0	1.3496		
3.8217E+3	9.7411E-4	1.3605E+1	1.4916E-2	8.2615E+0	8.2966E+0	8.0386E+0
8.2556E+0	8.0138E+0	8.2620E+0	8.2497E+0	1.3448		
3.8274E+3	9.7390E-4	1.3601E+1	1.4921E-2	8.2613E+0	8.2966E+0	8.0392E+0
8.2558E+0	8.0138E+0	8.2622E+0	8.2508E+0	1.3415		
3.8278E+3	9.7389E-4	1.3600E+1	1.4926E-2	8.2611E+0	8.2966E+0	8.0395E+0
8.2536E+0	8.0138E+0	8.2622E+0	8.2522E+0	1.3375		

3.8241E+3	9.7472E-4	1.3597E+1	1.4924E-2	8.2613E+0	8.2967E+0	8.0402E+0
8.2535E+0	8.0138E+0	8.2622E+0	8.2503E+0	1.3362		
3.8274E+3	9.7445E-4	1.3596E+1	1.4919E-2	8.2614E+0	8.2967E+0	8.0381E+0
8.2547E+0	8.0138E+0	8.2622E+0	8.2484E+0	1.3334		
3.8371E+3	9.7495E-4	1.3589E+1	1.4918E-2	8.2612E+0	8.2967E+0	8.0389E+0
8.2544E+0	8.0138E+0	8.2623E+0	8.2416E+0	1.3294		
3.8322E+3	9.7454E-4	1.3595E+1	1.4923E-2	8.2610E+0	8.2967E+0	8.0389E+0
8.2541E+0	8.0139E+0	8.2623E+0	8.2488E+0	1.3293		
3.8343E+3	9.7488E-4	1.3588E+1	1.4923E-2	8.2609E+0	8.2967E+0	8.0388E+0
8.2531E+0	8.0138E+0	8.2624E+0	8.2449E+0	1.3288		
3.8395E+3	9.7551E-4	1.3583E+1	1.4921E-2	8.2608E+0	8.2968E+0	8.0386E+0
8.2538E+0	8.0139E+0	8.2625E+0	8.2392E+0	1.3258		
3.8299E+3	9.7593E-4	1.3596E+1	1.4922E-2	8.2617E+0	8.2967E+0	8.0406E+0
8.2527E+0	8.0139E+0	8.2624E+0	8.2452E+0	1.3251		
3.8370E+3	9.7518E-4	1.3590E+1	1.4924E-2	8.2612E+0	8.2967E+0	8.0396E+0
8.2541E+0	8.0139E+0	8.2624E+0	8.2433E+0	1.3242		
3.8463E+3	9.7527E-4	1.3580E+1	1.4929E-2	8.2611E+0	8.2967E+0	8.0393E+0
8.2531E+0	8.0139E+0	8.2626E+0	8.2393E+0	1.3229		
3.8381E+3	9.7563E-4	1.3589E+1	1.4918E-2	8.2615E+0	8.2967E+0	8.0382E+0
8.2545E+0	8.0139E+0	8.2624E+0	8.2402E+0	1.3208		
3.8399E+3	9.7567E-4	1.3586E+1	1.4927E-2	8.2609E+0	8.2967E+0	8.0392E+0
8.2528E+0	8.0139E+0	8.2626E+0	8.2423E+0	1.3193		
3.8495E+3	9.7651E-4	1.3584E+1	1.4922E-2	8.2614E+0	8.2967E+0	8.0395E+0
8.2545E+0	8.0139E+0	8.2627E+0	8.2344E+0	1.3157		
3.8410E+3	9.7702E-4	1.3584E+1	1.4924E-2	8.2620E+0	8.2967E+0	8.0407E+0
8.2531E+0	8.0139E+0	8.2627E+0	8.2383E+0	1.3122		
3.8494E+3	9.7688E-4	1.3579E+1	1.4926E-2	8.2619E+0	8.2967E+0	8.0392E+0
8.2524E+0	8.0140E+0	8.2628E+0	8.2358E+0	1.3027		
3.8500E+3	9.7771E-4	1.3582E+1	1.4933E-2	8.2625E+0	8.2966E+0	8.0420E+0
8.2518E+0	8.0140E+0	8.2630E+0	8.2367E+0	1.3024		
3.8647E+3	9.7887E-4	1.3573E+1	1.4934E-2	8.2632E+0	8.2966E+0	8.0409E+0
8.2529E+0	8.0141E+0	8.2633E+0	8.2280E+0	1.2965		
3.8643E+3	9.8074E-4	1.3576E+1	1.4921E-2	8.2627E+0	8.2966E+0	8.0423E+0
8.2509E+0	8.0141E+0	8.2632E+0	8.2234E+0	1.2885		
3.8725E+3	9.8016E-4	1.3573E+1	1.4935E-2	8.2635E+0	8.2966E+0	8.0409E+0
8.2509E+0	8.0142E+0	8.2636E+0	8.2237E+0	1.2802		
3.8894E+3	9.8301E-4	1.3556E+1	1.4938E-2	8.2643E+0	8.2965E+0	8.0425E+0
8.2491E+0	8.0143E+0	8.2641E+0	8.2097E+0	1.2754		

3.8811E+3	9.8345E-4	1.3566E+1	1.4936E-2	8.2644E+0	8.2965E+0	8.0433E+0
8.2483E+0	8.0143E+0	8.2641E+0	8.2194E+0	1.2694		
3.8884E+3	9.8608E-4	1.3557E+1	1.4928E-2	8.2645E+0	8.2966E+0	8.0447E+0
8.2449E+0	8.0144E+0	8.2643E+0	8.2066E+0	1.2571		
3.9083E+3	9.8848E-4	1.3544E+1	1.4940E-2	8.2661E+0	8.2964E+0	8.0458E+0
8.2439E+0	8.0145E+0	8.2650E+0	8.1984E+0	1.2528		
3.8973E+3	9.8848E-4	1.3547E+1	1.4934E-2	8.2653E+0	8.2965E+0	8.0441E+0
8.2433E+0	8.0145E+0	8.2648E+0	8.1984E+0	1.2457		
3.9061E+3	9.9027E-4	1.3551E+1	1.4935E-2	8.2662E+0	8.2964E+0	8.0471E+0
8.2421E+0	8.0146E+0	8.2650E+0	8.1952E+0	1.2454		
3.9066E+3	9.9010E-4	1.3544E+1	1.4941E-2	8.2659E+0	8.2965E+0	8.0469E+0
8.2407E+0	8.0146E+0	8.2651E+0	8.1963E+0	1.2451		
3.9053E+3	9.8988E-4	1.3551E+1	1.4935E-2	8.2661E+0	8.2964E+0	8.0463E+0
8.2417E+0	8.0146E+0	8.2650E+0	8.1971E+0	1.2451		
3.9089E+3	9.9155E-4	1.3547E+1	1.4941E-2	8.2667E+0	8.2964E+0	8.0474E+0
8.2401E+0	8.0147E+0	8.2653E+0	8.1935E+0	1.2430		
3.9021E+3	9.8980E-4	1.3548E+1	1.4940E-2	8.2661E+0	8.2964E+0	8.0466E+0
8.2417E+0	8.0146E+0	8.2650E+0	8.1972E+0	1.2428		
3.9059E+3	9.9015E-4	1.3548E+1	1.4939E-2	8.2663E+0	8.2964E+0	8.0466E+0
8.2415E+0	8.0146E+0	8.2651E+0	8.1957E+0	1.2427		
3.9012E+3	9.8975E-4	1.3551E+1	1.4937E-2	8.2661E+0	8.2964E+0	8.0466E+0
8.2418E+0	8.0146E+0	8.2650E+0	8.1980E+0	1.2427		
3.9026E+3	9.9010E-4	1.3551E+1	1.4937E-2	8.2661E+0	8.2964E+0	8.0466E+0
8.2414E+0	8.0146E+0	8.2650E+0	8.1967E+0	1.2426		
3.9047E+3	9.9013E-4	1.3548E+1	1.4939E-2	8.2661E+0	8.2964E+0	8.0467E+0
8.2413E+0	8.0146E+0	8.2651E+0	8.1963E+0	1.2426		
3.9046E+3	9.9057E-4	1.3547E+1	1.4938E-2	8.2662E+0	8.2964E+0	8.0468E+0
8.2411E+0	8.0146E+0	8.2651E+0	8.1950E+0	1.2425		
3.9063E+3	9.9084E-4	1.3548E+1	1.4939E-2	8.2664E+0	8.2964E+0	8.0470E+0
8.2408E+0	8.0146E+0	8.2652E+0	8.1949E+0	1.2423		
3.9037E+3	9.9014E-4	1.3549E+1	1.4939E-2	8.2662E+0	8.2964E+0	8.0468E+0
8.2413E+0	8.0146E+0	8.2651E+0	8.1971E+0	1.2423		
3.9048E+3	9.9053E-4	1.3548E+1	1.4939E-2	8.2663E+0	8.2964E+0	8.0469E+0
8.2409E+0	8.0146E+0	8.2651E+0	8.1954E+0	1.2422		
3.9043E+3	9.9031E-4	1.3549E+1	1.4939E-2	8.2663E+0	8.2964E+0	8.0469E+0
8.2412E+0	8.0146E+0	8.2651E+0	8.1964E+0	1.2422		
3.9033E+3	9.9022E-4	1.3548E+1	1.4939E-2	8.2662E+0	8.2964E+0	8.0465E+0
8.2413E+0	8.0146E+0	8.2651E+0	8.1963E+0	1.2421		

sum squares = 1.7932E-4

Minmax constraint was active.

OPAR (1e+8)

NEWTON (plot)

k1_____	k2_____	k3_____	k4_____	k5_____	k6_____	k7_____			
k8_____	k9_____	k10_____	k11_____	R.M.S. [%]					

Initial values:-----

3.9033E+3	9.9022E-4	1.3548E+1	1.4939E-2	8.2662E+0	8.2964E+0	8.0465E+0			
8.2413E+0	8.0146E+0	8.2651E+0	8.1963E+0	1.2421					
±0.0000E+0									
±0.0000E+0	±0.0000E+0	±0.0000E+0	±0.0000E+0						

-----

3.9033E+3	9.9130E-4	1.3548E+1	1.4939E-2	8.2712E+0	8.2963E+0	8.0361E+0			
8.2428E+0	8.0146E+0	8.2650E+0	8.2019E+0	1.2412					
±3.4145E+0	±4.2980E-5	±1.7804E-2	±6.4758E-5	±3.7391E-1	±8.1877E-3	±2.8812E-1			
±4.8418E-2	±8.0427E-4	±5.5243E-3	±1.8867E-1						

3.9033E+3	9.9033E-4	1.3548E+1	1.4939E-2	8.2684E+0	8.2964E+0	8.0365E+0			
8.2457E+0	8.0146E+0	8.2650E+0	8.1992E+0	1.2408					
±1.6768E+0	±1.1218E-4	±1.0896E-2	±4.1417E-5	±3.4214E-1	±8.8846E-3	±3.3118E-1			
±3.6743E-1	±5.7653E-3	±9.8577E-3	±3.4853E-1						

3.9033E+3	9.9071E-4	1.3548E+1	1.4935E-2	8.2498E+0	8.2969E+0	8.0393E+0			
8.2639E+0	8.0144E+0	8.2651E+0	8.2007E+0	1.2385					
±3.4952E+0	±3.3925E-6	±9.5354E-3	±9.2221E-5	±3.5179E-1	±8.8772E-3	±2.8821E-1			
±3.1784E-1	±2.8271E-3	±4.0814E-3	±9.7279E-2						

3.9033E+3	9.9071E-4	1.3548E+1	1.4935E-2	8.2498E+0	8.2969E+0	8.0393E+0			
8.2639E+0	8.0144E+0	8.2651E+0	8.2007E+0	1.2385					
±2.2144E+0	±2.6026E-5	±1.7397E-2	±8.1379E-5	±4.4235E-1	±1.0413E-2	±1.2134E-1			
±1.9155E-1	±1.3202E-3	±4.0704E-3	±1.1149E-1						

sum squares = 1.7829E-4

Covariance Matrix:

___k10_	___k11_	___k1___	___k2___	___k3___	___k4___	___k5___	___k6___	___k7___	___k8___	___k9___	
k1	1.000	0.133	-0.432	-1.242	0.036	-0.031	-0.095	-0.044	-2.081		
0.276	0.080										
k2	0.133	1.000	-0.203	-0.142	0.017	-0.006	-0.358	0.093	0.524	-	
0.261	0.486										
k3	-0.432	-0.203	1.000	0.316	-0.068	0.065	0.221	0.076	0.409	-	
0.024	-0.095										
k4	-1.242	-0.142	0.316	-1.000	0.028	-0.021	-0.077	-0.026	-1.843		
0.259	-0.024										
k5	0.036	0.017	-0.068	0.028	-1.000	1.014	2.315	1.480	0.060	-	
0.011	0.007										
k6	-0.031	-0.006	0.065	-0.021	1.014	-1.000	-2.729	-1.338	-0.041		
0.006	-0.002										
k7	-0.095	-0.358	0.221	-0.077	2.315	-2.729	1.000	-6.166	-0.409		
0.123	-0.169										
k8	-0.044	0.093	0.076	-0.026	1.480	-1.338	-6.166	-1.000	0.028	-	
0.022	0.047										
k9	-2.081	0.524	0.409	-1.843	0.060	-0.041	-0.409	0.028	-1.000	-	
0.026	-0.227										

```

    k10   0.276  -0.261  -0.024   0.259  -0.011   0.006   0.123  -0.022  -0.026
1.000  -0.709
    k11   0.080   0.486  -0.095  -0.024   0.007  -0.002  -0.169   0.047  -0.227  -
0.709   1.000

```

PLOT (spec)

PLOT (resi)

MAKE ()

```

*****
*
* Cmd file rebuild from internal data generated from
* file SimFit runs:
* on date 07-14-2006 (mm-dd-yyyy) at time 08:01:23
*
*****
define (1,a, e,1) scale (3, 1.00000E+0)
define (2,c, p,3) scale (3, 1.00000E+0)
define (3,d,nmr,8) scale (3, 1.00000E+0)
define (4,e,nmr,4) scale (3, 1.00000E+0)
select (a,c,d,e)
read (s158k1_b_nmr_neu_2.txt)
choose (exp1)
reaction ( A + B --> C) constant (1, 4.15087E-5, 0)
reaction ( A + B --> AB) constant (2, 1.00000E+6, 0)
reaction ( AB --> A + B) constant (3, 3.90335E+3,1, 1.00000E+0, 3.73150E+1,
3.73150E+5)
reaction ( A + C --> AC) constant (4, 1.00000E+6, 0)
reaction ( AC --> A + C) constant (5, 3.90335E+3,1, 1.00000E+0, 3.73150E+1,
3.73150E+5)
reaction ( B + C --> BC) constant (6, 1.00000E+6, 0)
reaction ( BC --> B + C) constant (7, 3.90335E+3,1, 1.00000E+0, 3.73150E+1,
3.73150E+5)
reaction ( AB + B --> BC) constant (8, 4.15087E-5, 0)
reaction ( AB + A --> AC) constant (9, 4.15087E-5, 0)
reaction (AC + B --> ABC) constant (10, 1.00000E+6, 0)
reaction (ABC --> AC + B) constant (11, 3.90335E+3,1, 1.00000E+0, 3.73150E+1,
3.73150E+5)
reaction (BC + A --> ABC) constant (12, 1.00000E+6, 0)
reaction (ABC --> BC + A) constant (13, 3.90335E+3,1, 1.00000E+0, 3.73150E+1,
3.73150E+5)
reaction ( ABC --> C2) constant (14, 9.90714E-4,2, 1.00000E+0, 9.57050E-6,
9.57050E-2)
reaction ( 2 C --> C2) constant (15, 1.00000E+6, 0)
reaction ( C2 --> 2 C) constant (16, 1.35481E+1,3, 1.00000E+0, 1.27210E-1,
1.27210E+3)
reaction ( 2 AB --> ABC) constant (17, 4.15087E-5, 0)
reaction (compile)
reaction (show)
assign (obs, a = A + AB + AC + ABC)
assign (obs, c = C + AC + BC + ABC + 2 C2)
assign (obs, d = C + 2 C2 + AC + BC + ABC)
assign (obs, e = A + AB + AC + ABC)
assign (spec, A = a)
assign (spec, B = # 1.49000E-2)
assign (spec, C = # 0.00000E+0)

```

```

delta (d, C, 8.24976E+0, 5.00000E+0, 7.00000E+0, 9.00000E+0)
delta (d, AC, 8.24976E+0, 5.00000E+0, 7.00000E+0, 9.00000E+0)
delta (d, BC, 8.03930E+0, 7.00000E+0, 7.00000E+0, 9.00000E+0)
delta (d,ABC, 8.26386E+0, 8.00000E+0, 7.00000E+0, 9.00000E+0)
delta (d, C2, 8.29691E+0, 6.00000E+0, 7.00000E+0, 9.00000E+0)
delta (e, A, 8.01443E+0, 9.00000E+0, 7.00000E+0, 9.00000E+0)
delta (e, AB, 8.26510E+0, 1.00000E+1, 7.00000E+0, 9.00000E+0)
delta (e, AC, 8.26510E+0, 1.00000E+1, 7.00000E+0, 9.00000E+0)
delta (e,ABC, 8.20066E+0, 1.10000E+1, 7.00000E+0, 9.00000E+0)
* The initial concentration of observable a in experiment 1
* of file s158k1_b_nmr_neu_2.txt was assumed to be 1.49346062475697E-2 mol/l and
was forced
* to be between 1.46380952380952E-2 and .0161385 mol/l.
Czero (4,a,1,1, 1.46381E-2, 1.61385E-2, 1.49346E-2)
time (h)
conc (mM)
win (0,70,10,0,-1,16,2,0)
nmrwin (0,70,10,0,8.05,8.3,.1,0)
dim (11)
integ (stiff, .0000001, 32, .05, 500, 1500)
plot

```

## Excel macro for transformation of NMR-data into SimFit data files

```

Sub IntegraleZeit()

Dim yh$(300)
Dim errdat(20)
roota$ = "N:\Users\Insa\Nopub\InsaLaptop\NMR-Kinetik\auswert\"
roote$ = "011.asi" *files created by WinNMR (Bruker) containing integrals
rootf$ = "001.aqs" *files created by WinNMR (Bruker) containing time information
startzeit = 0.27 *time delay in h before running the first experiment
yalt = 0
lastexp = 210 *last NMR-experiment number
errdat(1) = 0 *number of defective or missing NMR-experiment to be excepted
errdat(2) = 0 *0 = no excepted experiment

If lastexp > 99 Then
last2 = lastexp
last1 = 99
Else
last1 = lastexp
End If

For c = 1 To 26
yh$(c) = Chr$(c + 64) & "1"
Next c
For d = 1 To 8
For c = 1 To 26
yh$(c + (d * 26)) = Chr$(d + 64) & Chr$(c + 64) & "1"
Next c
Next d

For a = 10 To last1

```

```

For eri = 1 To 20
If a = errdat(eri) Then a = a + 1
Next eri

root$ = roota$ & "0" & a & roote$
asi$ = "0" & a & roote$
    Workbooks.OpenText FileName:=root$, Origin:=xlWindows, _
        StartRow:=7, DataType:=xlFixedWidth, FieldInfo:=Array(Array(0, 9), Array(41
-
        , 1), Array(52, 9))
    Range("A3:A22").Select
    Selection.Copy
    Windows("Dummy_aktuell_Nopub.xls").Activate
    Range(yh$(a - 9)).Select
    ActiveSheet.Paste
    Windows(asi$).Activate
    ActiveWorkbook.Close
Next a
If lastexp > 99 Then
For a = 100 To last2

For eri = 1 To 20
If a = errdat(eri) Then a = a + 1
Next eri

root$ = roota$ & a & roote$
asi$ = a & roote$
    Workbooks.OpenText FileName:=root$, Origin:=xlWindows, _
        StartRow:=7, DataType:=xlFixedWidth, FieldInfo:=Array(Array(0, 9), Array(41
-
        , 1), Array(52, 9))
    Range("A3:A22").Select
    Selection.Copy
    Windows("Dummy_aktuell_Nopub.xls").Activate
    Range(yh$(a - 9)).Select
    ActiveSheet.Paste
    Windows(asi$).Activate
    ActiveWorkbook.Close
Next a
End If
Range("A1:GS22").Select
    Selection.Copy
    Workbooks.Add
    Range("C3").Select
    Selection.PasteSpecial Paste:=xlAll, Operation:=xlNone, SkipBlanks:=False _
        , Transpose:=True
    ActiveWorkbook.SaveAs FileName:= _
        "N:\Users\Insa\Nopub\InsaLaptop\NMR-Kinetik\auswert\Ergebnisse.xls",
FileFormat:= _
        xlNormal, Password:="", WriteResPassword:="", ReadOnlyRecommended:=False _
        , CreateBackup:=False
    Windows("Dummy_aktuell_Nopub.xls").Activate
    Selection.ClearContents

For a = 10 To lastexp

```

```

    For eri = 1 To 20
If a = errdat(eri) Then a = a + 1
Next eri

If a > 99 Then
root$ = roota$ & a & rootf$
Else
root$ = roota$ & "0" & a & rootf$
End If
b$ = "A" & (a - 9)

    Workbooks.OpenText FileName:=root$, Origin:=xlWindows, _
        StartRow:=6, DataType:=xlFixedWidth, FieldInfo:=Array(Array(0, 9), Array(14
-
        , 1), Array(22, 9))
    Range("A1").Select
    Selection.Copy
    ActiveWorkbook.Close
    Range(b$).Select
    ActiveSheet.Paste

Next a

Columns("A:A").Select
Selection.NumberFormat = "0.00"

x0 = Range("A1")
For a = 1 To (lastexp - 9)

    For eri = 1 To 20
If a = (errdat(eri) - 9) Then a = a + 1
Next eri

b$ = "A" & a
x = Range(b$)
y = (x - x0) * 24 + startzeit
10 If y < yalt Then y = (y + 24)
If y < yalt Then GoTo 10
yalt = y
Range(b$).Select
ActiveCell.FormulaR1C1 = y
Next a

    Range("A1:A201").Select
    Application.CutCopyMode = False
    Selection.Copy
    Windows("Ergebnisse.xls").Activate
    Range("A3").Select
    ActiveSheet.Paste
    Windows("Dummy_aktuell_Nopub.xls").Activate
    Application.CutCopyMode = False
    Selection.ClearContents

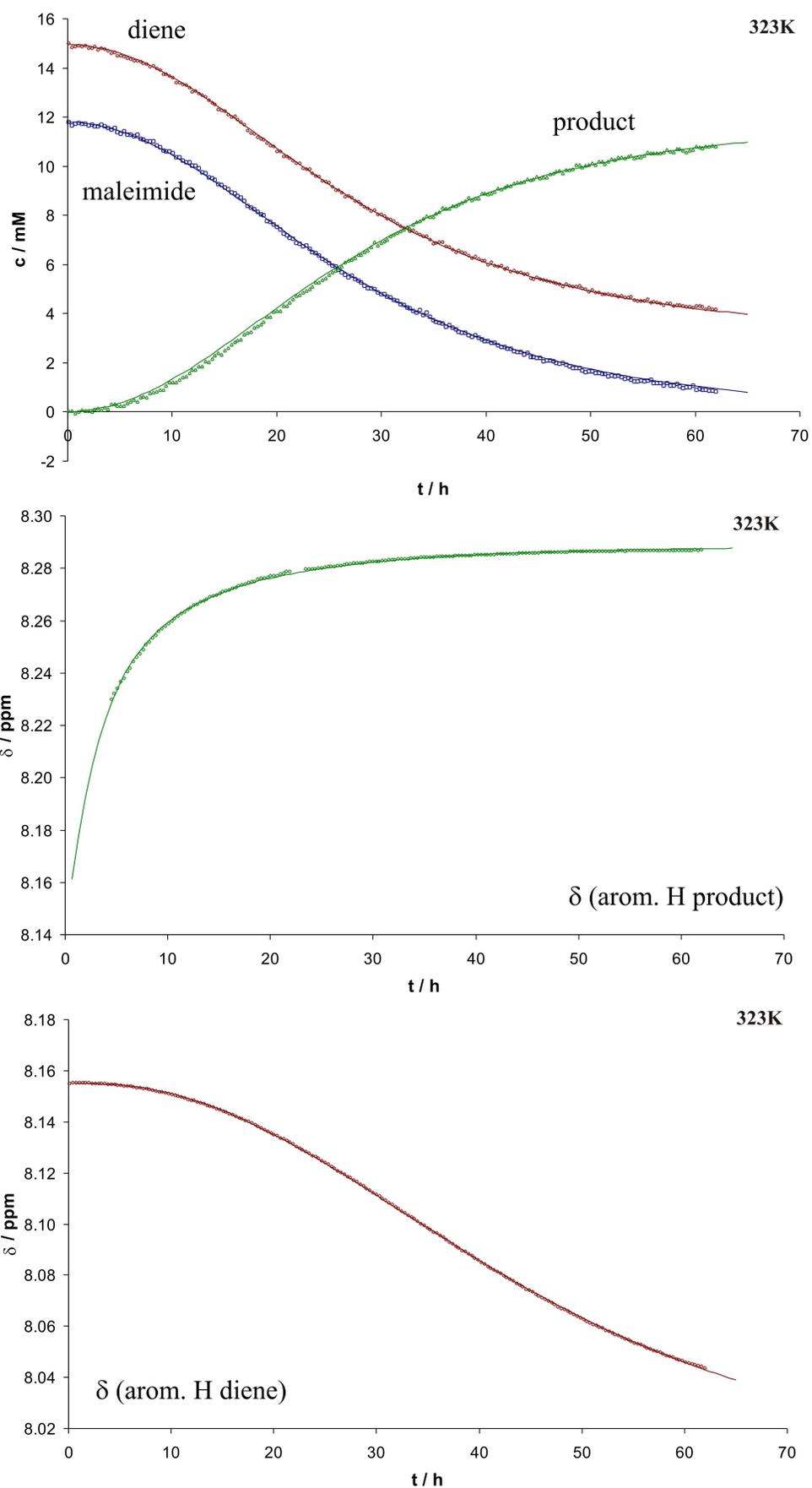
End Sub

```

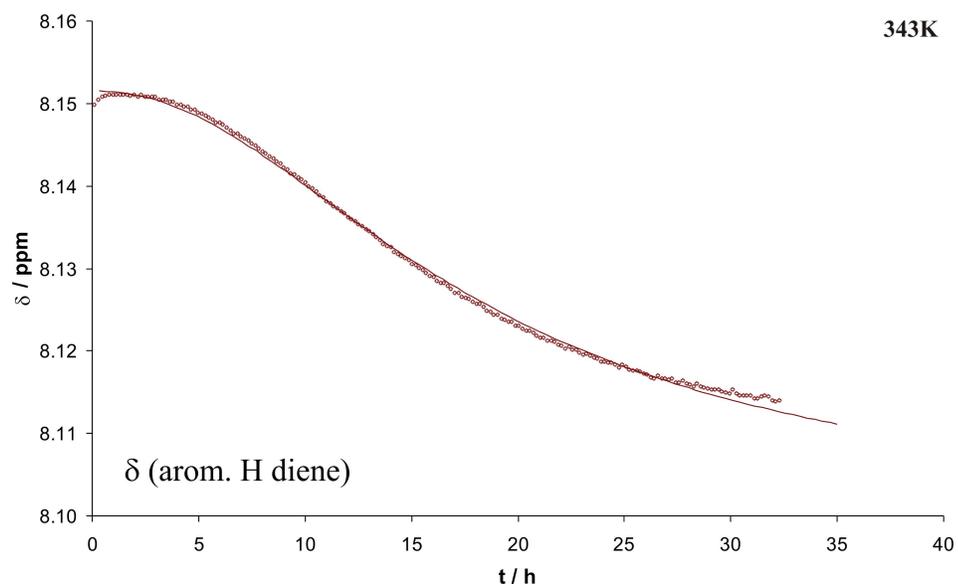
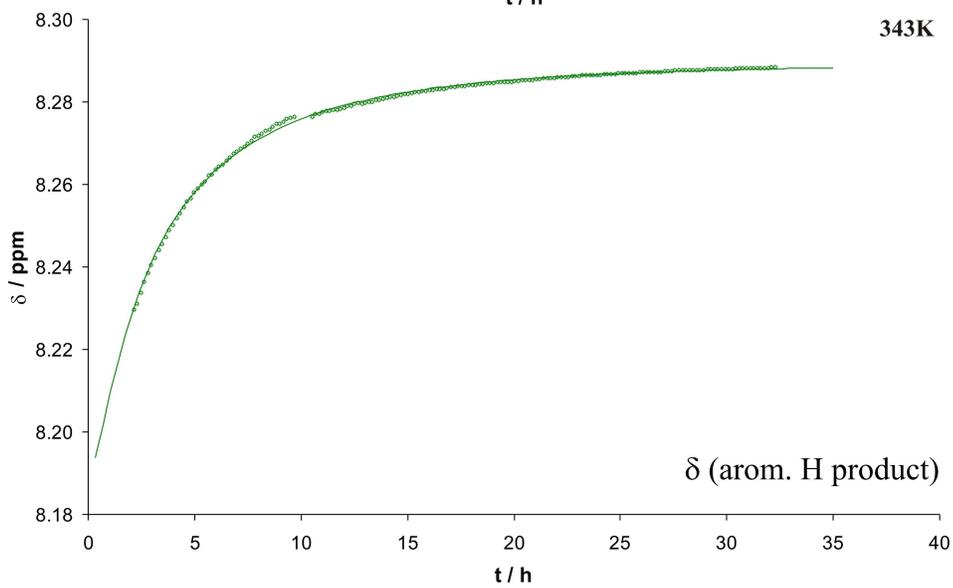
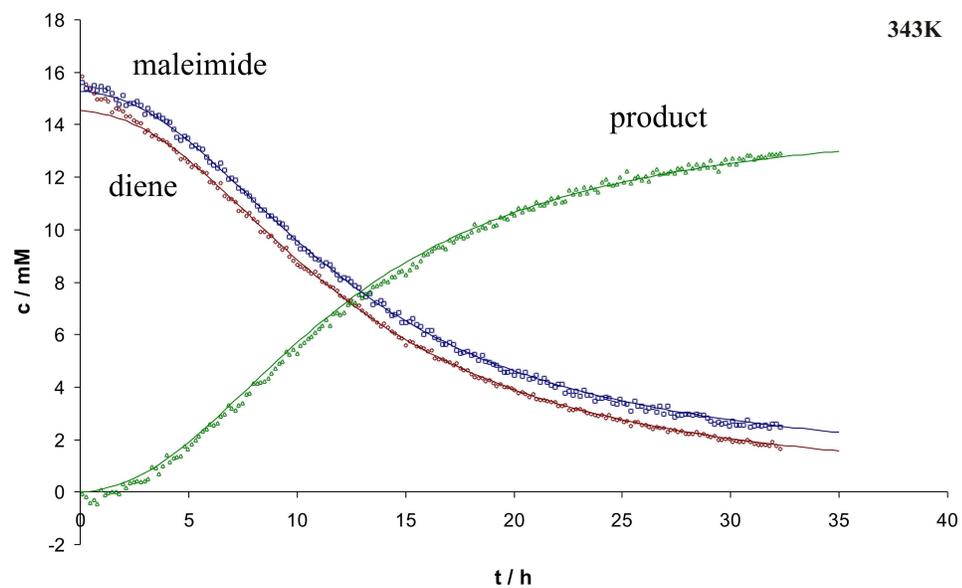
## Concentration-time and chemical shift-time profiles for the reaction of 1 with 2a

( $c = 15 \text{ mM}$  for both precursors,  $\text{C}_2\text{D}_2\text{Cl}_4$ ; continuous lines represent theoretical curves)

**T = 323 K**



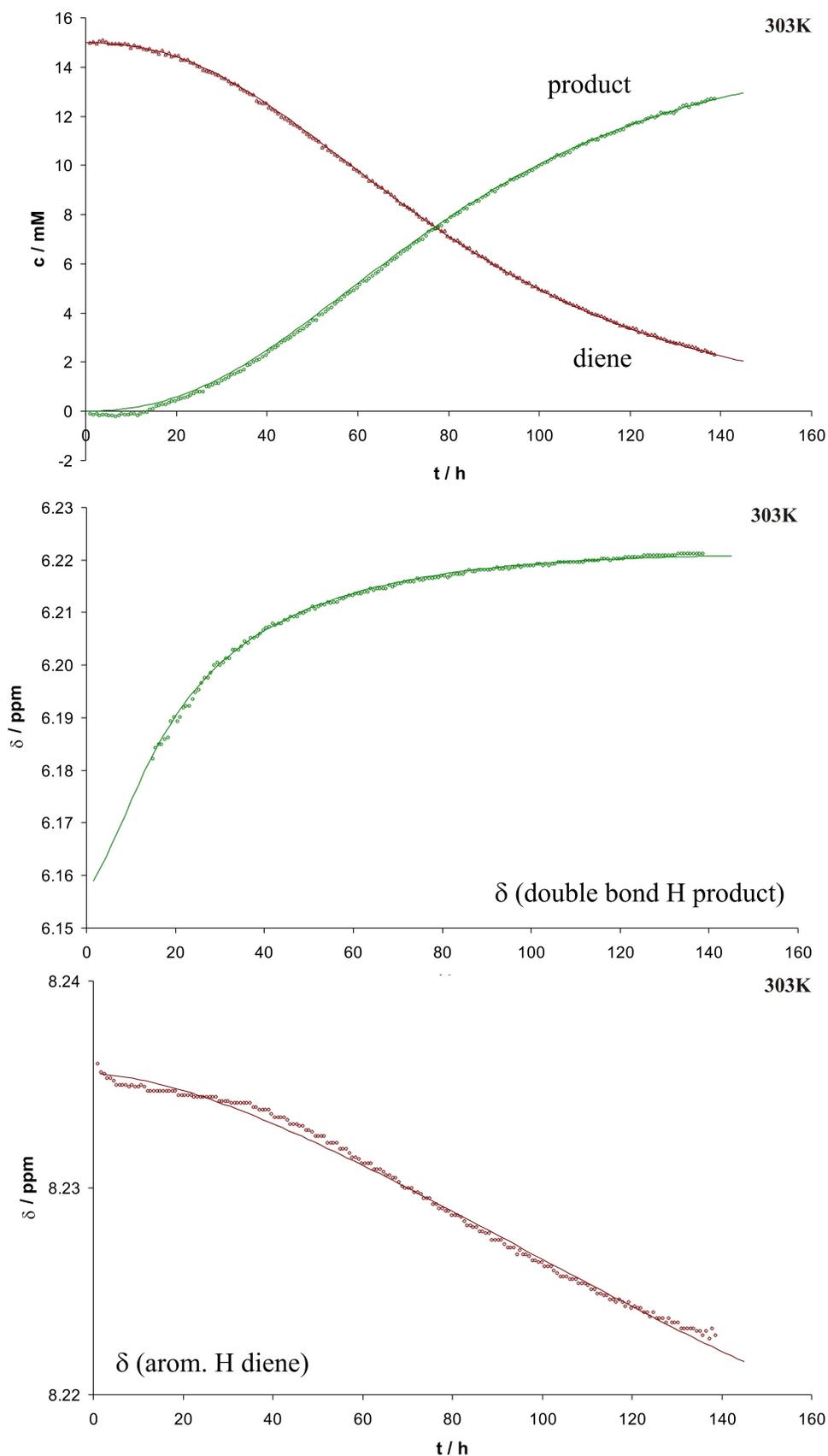
T = 343 K



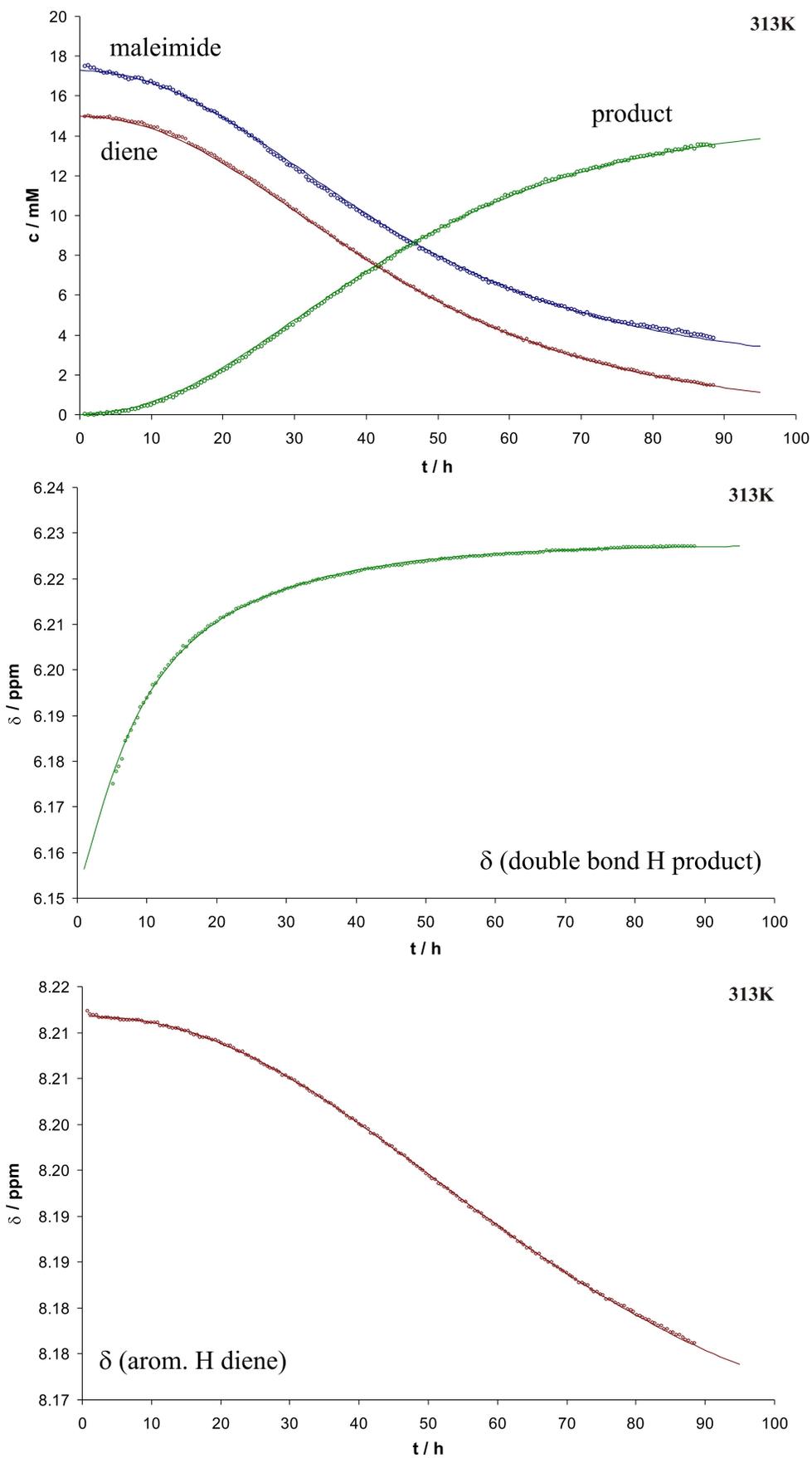
## Concentration-time and chemical shift-time profiles for the reaction of 1 with 2b

( $c = 15 \text{ mM}$  for both precursors,  $\text{C}_2\text{D}_2\text{Cl}_4$ ; continuous lines represent theoretical curves)

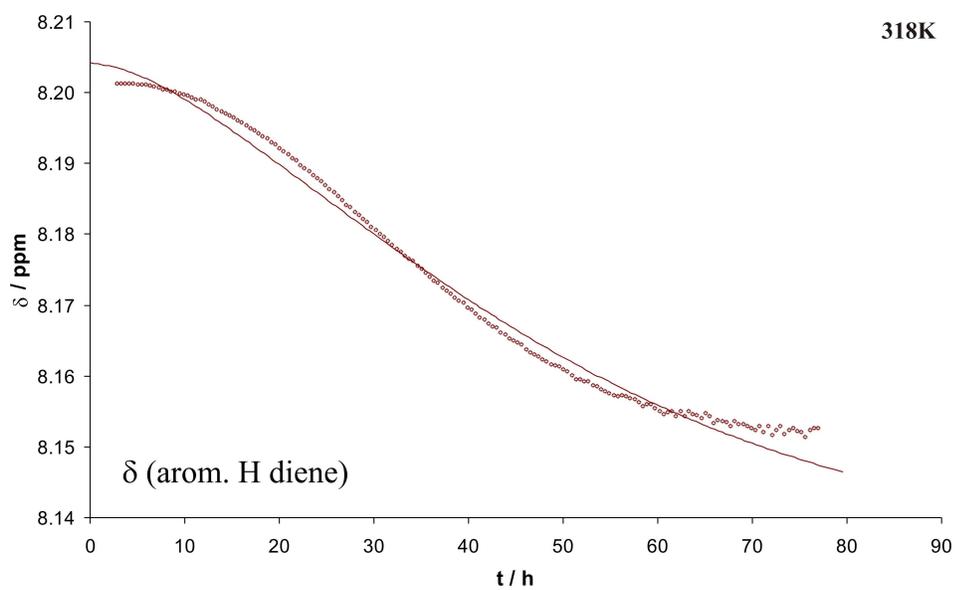
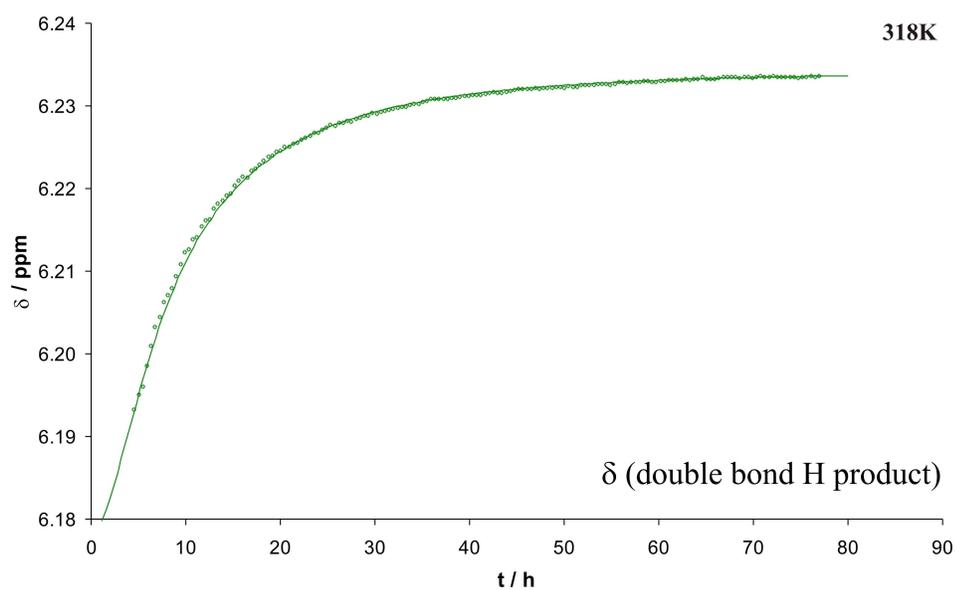
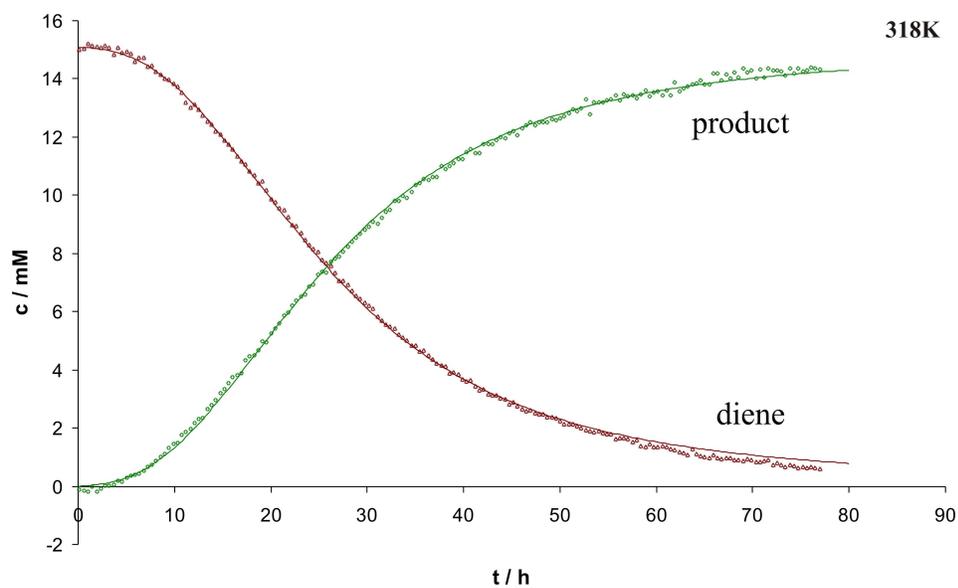
$T = 303 \text{ K}$



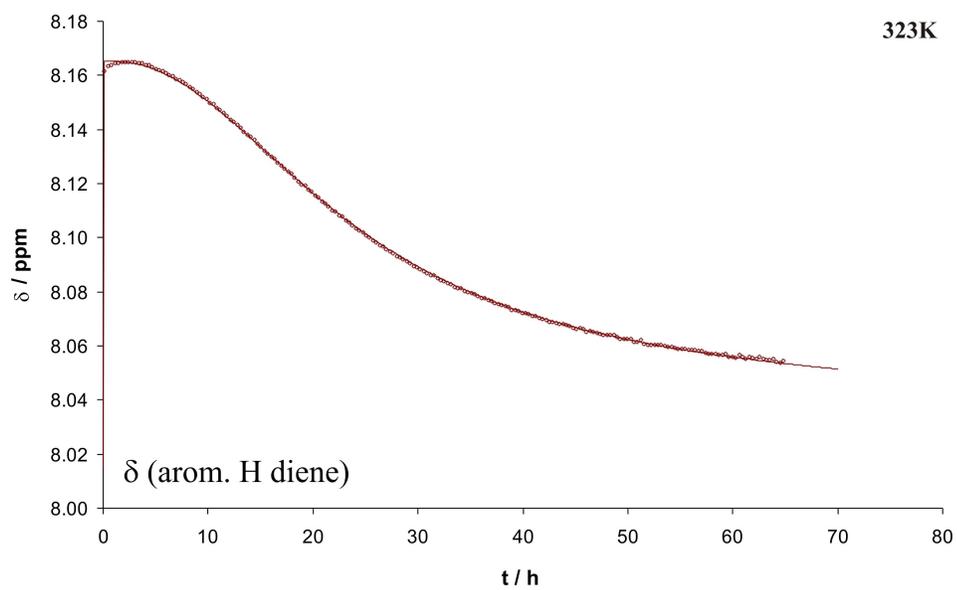
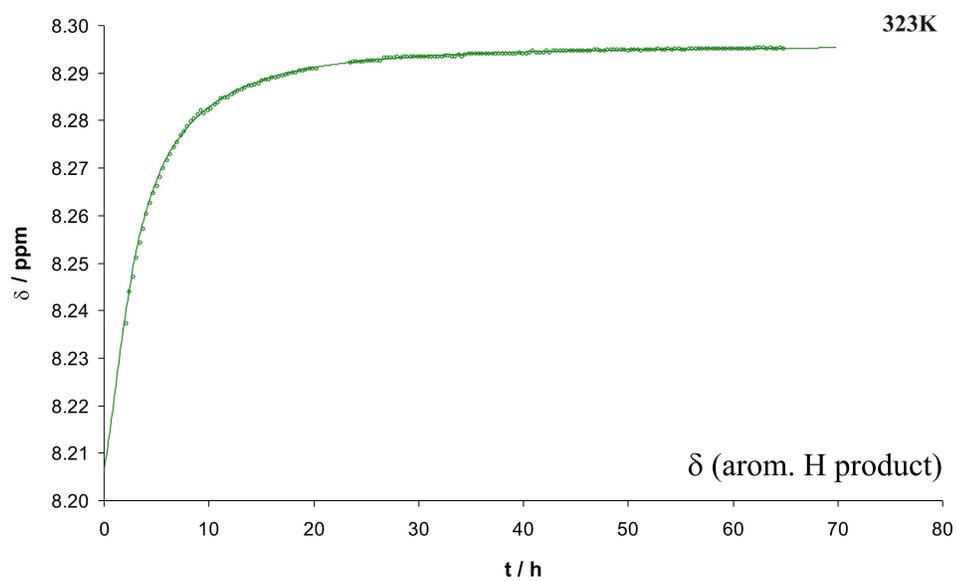
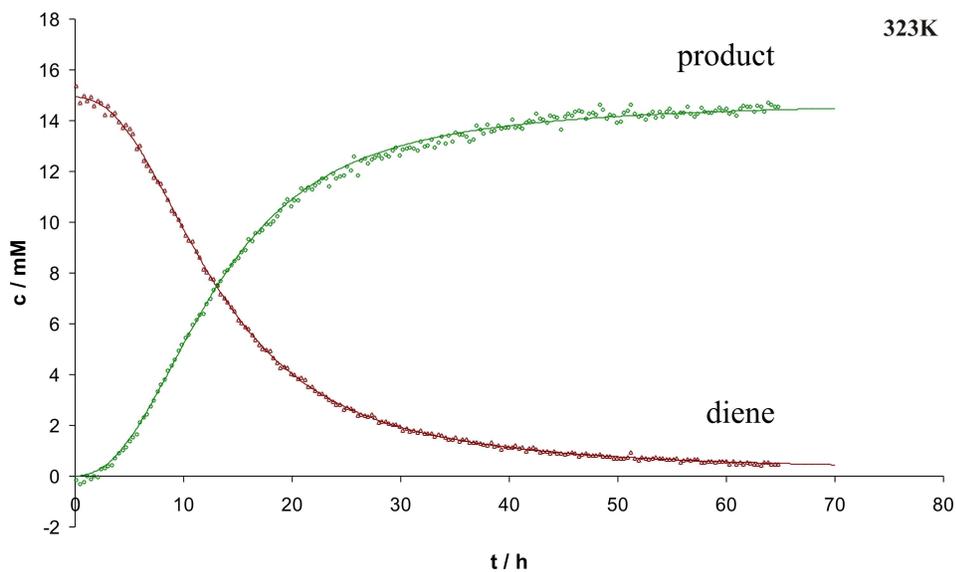
T = 313 K



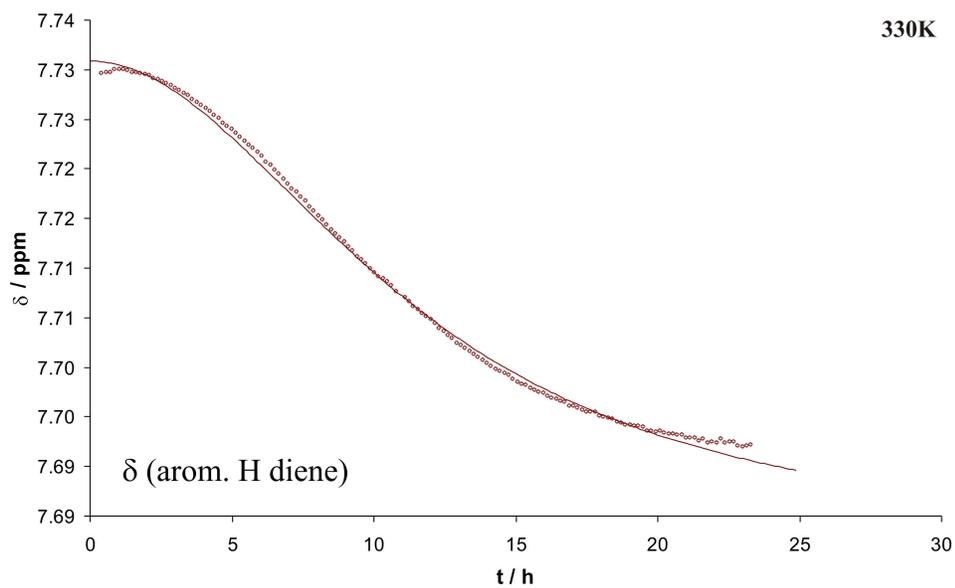
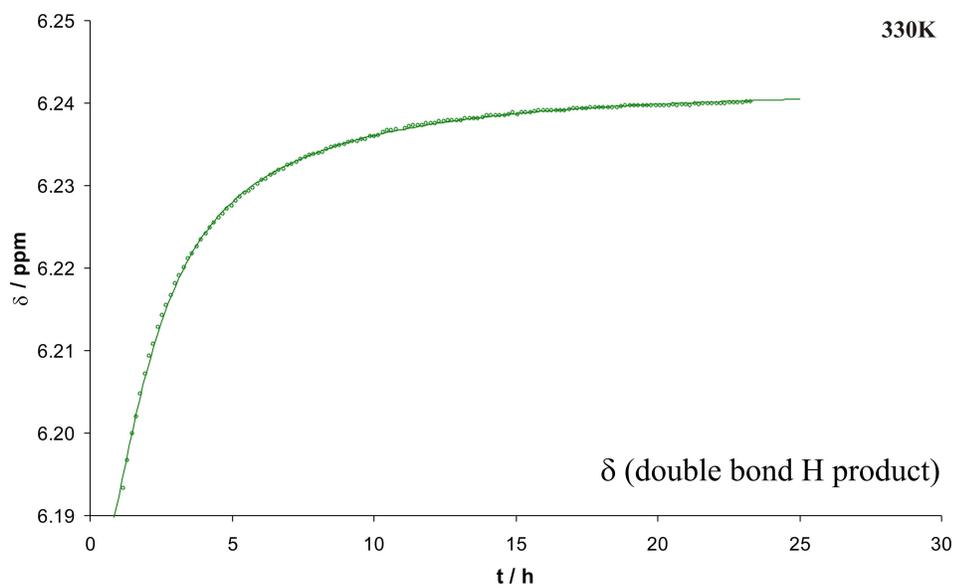
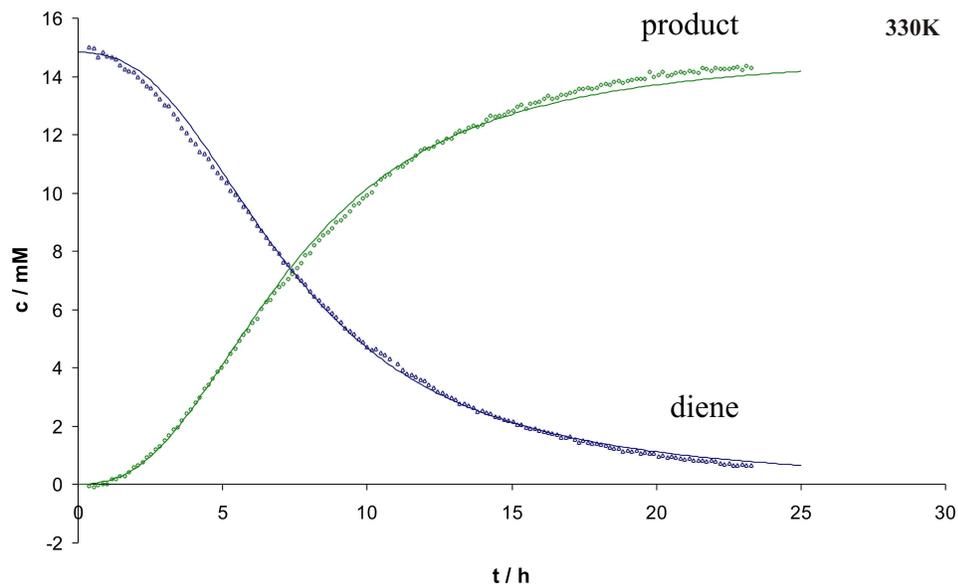
T = 318 K



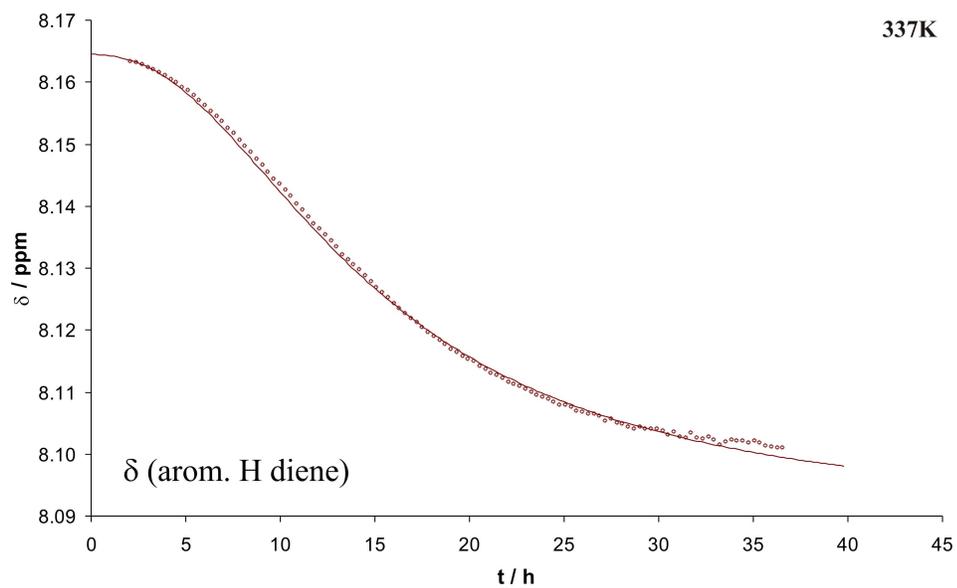
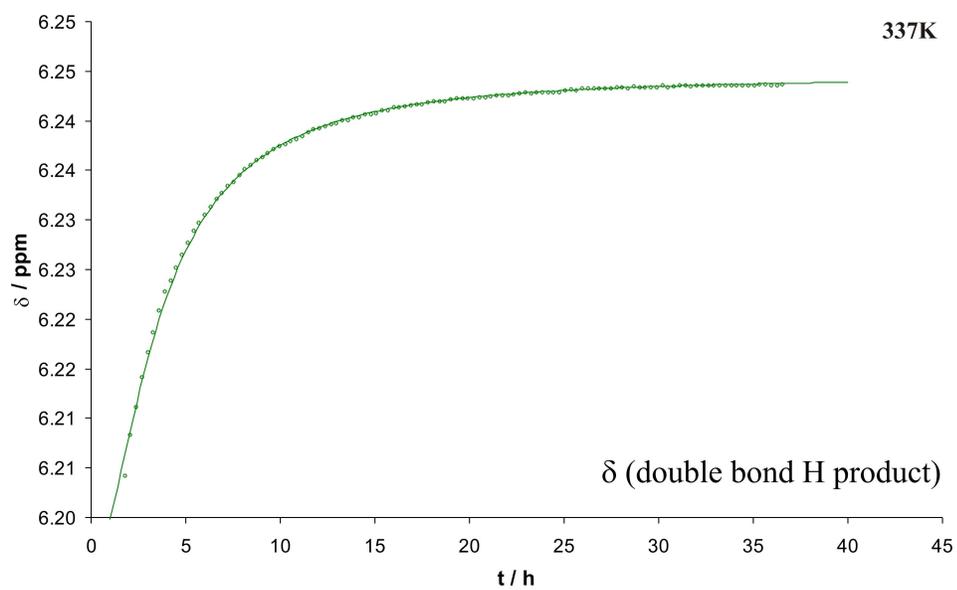
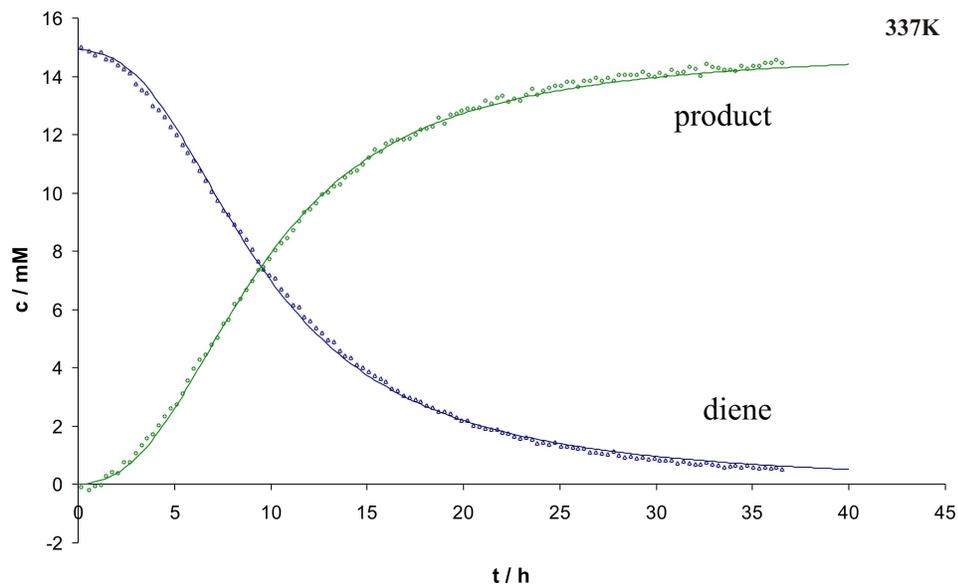
T = 323 K



T = 330 K



T = 337 K



T = 343 K

