Electronic Supplementary Information

Thermal decay of TEMPO in acidic media via an N-oxoammonium salt intermediate

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1. Kinetic modelling of TEMPO disproportionation in acid

TEMPO disproportionation in inorganic acids at low temperature (*e.g.* below 50ºC) has been studied by Golubev *et al.* in the 1970s[1] and revised recently[2]. Adequate kinetic data were generated in their study. However, a kinetic model of this reaction was not built. Thus, by using the reported kinetic constants, a full kinetic model was built to predict TEMPO disproportionation reaction using the following procedure:-

The reaction was assumed to involve four steps.

1. Protonation of TEMPO: fast equilibrium
2. Relatively slow disproportionation
3. Comproportionation of TEMPOH and oxoammonium salt
4. Protonation of TEMPOH.

Hence the reaction is described by the following equations.

$$\begin{array}{ll}
\mathrm{T + H \rightleftharpoons TH} & \mathrm{Ka_1} \\
\mathrm{(T + H \underset{\mathit{k}_{-1}}{\overset{\mathit{k}_1}{\rightleftharpoons}} TH)} & \\
\mathrm{T + TH \longrightarrow TOH + T{=}O} & \mathrm{k_2} \\
\mathrm{TOH + T{=}O \longrightarrow T + TH} & \mathrm{k_{-2}} \\
\mathrm{TOH + H \rightleftharpoons TOH} & \mathrm{Ka_3}
\end{array}$$

Here, Ka_1 and Ka_3 are acid dissociation constants of TEMPO (T) and TEMPOH (TOH), respectively. TH^+, $T{=}O^+$, TOH_2^+ represents protonated TEMPO, *N*-oxoammonium cation and protonated TEMPOH, respectively.

In order to build a kinetic model it was assumed that under the reaction conditions, the amount of protonated TEMPO and unprotonated TEMPOH in the reaction mixture is negligible. Thus the concentration equations of reagents can be written as:

$$d[T]/dt = -2k_2\,[T]_t\,[TH^+]_t + k_{-2}[TOH]_t[T{=}O^+]_t$$

$$[TH^+]_t=[T]_t[H^+]/Ka_1$$

$$d[T{=}O^+]/dt=k_2[T]_t[TH^+]_t - k_{-2}[TOH]_t[T{=}O^+]_t$$

$$d[TOH_2^+]/\,dt=k_2[T]_t[TH^+]_t - k_{-2}[TOH]_t[T{=}O^+]_t$$

$$[TOH]= [T]_tKa_3/[H^+]$$

Temperature dependence of k_{-2} and k_2/k_{-1} was reported in Golubev's study[1]:

$$\lg k_2/Ka_1=13.70-19500/4.575T$$

$$\lg k_{-2}=17.77-21900/4.575T$$

Here, the units for rate constants, dissociation constant temperature (T) are $M^{-1}\cdot s^{-1}$, M and K respectively. Therefore the concentration equations are modified to the following equations:

$$d[T]/dt = -2k_2 [T]_t{}^2[H^+] + k_{-2}[TOH]_t[T{=}O^+]_t$$

$$[TH^+]_t=[T]_t[H^+]/Ka_1$$

$$d[T{=}O^+]/dt=k_2[T]_t{}^2[H^+] - k_{-2}[TOH]_t[T{=}O^+]_t$$

$$d[TOH_2{}^+]/ dt= k_2[T]_t{}^2[H^+] - k_{-2}[TOH]_t[T{=}O^+]_t$$

$$[TOH]= [T]_tKa_3/[H^+]$$

A user-friendly kinetic model of TEMPO disproportionation was thus built by applying the equations in an Excel spreadsheet. Reaction parameters including initial concentrations of TEMPO and acid, reaction temperature and reaction time scale can be modified by the user. TEMPO decay and oxoammonium cation/TEMPOH formation are plotted. One can adjust the reaction parameters to predict the reaction rate at the desired conditions. The simulated kinetic curves at some typical conditions are shown in Figure 1.

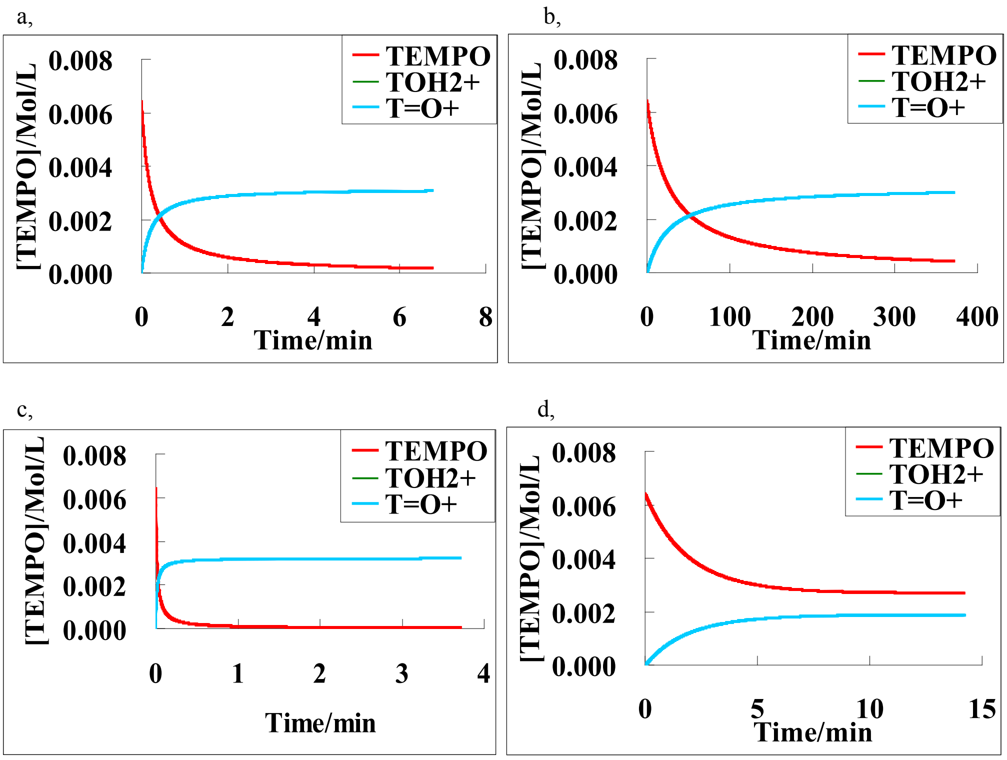


Figure 1. *Simulated TEMPO, oxoammonium salt and protonated hydroxylamine evolution in acid under different reaction conditions: a, 6.4×10^{-3}M TEMPO in 0.1M H_2SO_4 at 25℃. b, 6.4×10^{-3}M TEMPO in 1M H_2SO_4 at 25℃.. c, 6.4×10^{-3}M TEMPO in 1M H_2SO_4 at 80℃. d, 6.4×10^{-3}M TEMPO in 0.005M H_2SO_4 at 80℃.*

2. Fitting of TEMPO decay in acid experimental data to the kinetic model.

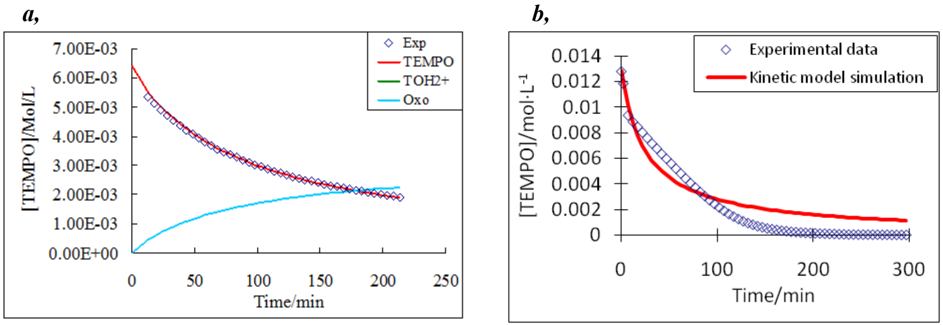


Figure 2. *Fitting of 6.41×10^{-3} M TEMPO in 0.1M H_2SO_4 at 15℃ to the kinetic model. b, Fitting of 1.28×10^{-2} M TEMPO in 0.1M H_2SO_4 at 80℃ to the kinetic model.*

3. Comproportionation of TEMPOH and oxoammonium salt at different pH.

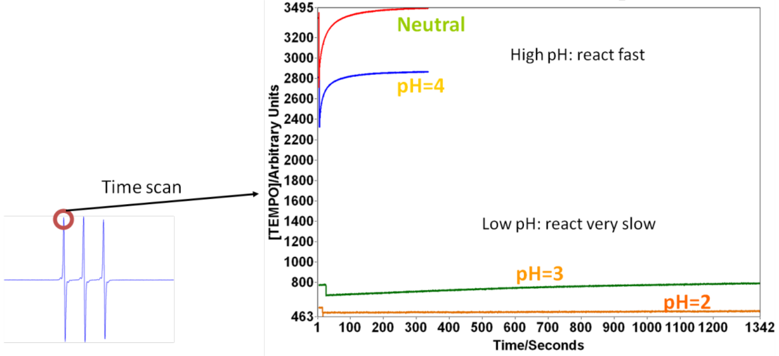


Figure 3. *TEMPO formation vs. time in comproportionation reaction of* 2×10^{-3} *M TEMPOH and* 2×10^{-3} *M oxoammonium salt at different pH.*

4. NMR spectra of the reaction product of TEMPO decay and oxoammonium salt decomposition in H_2SO_4 at 80 °C.

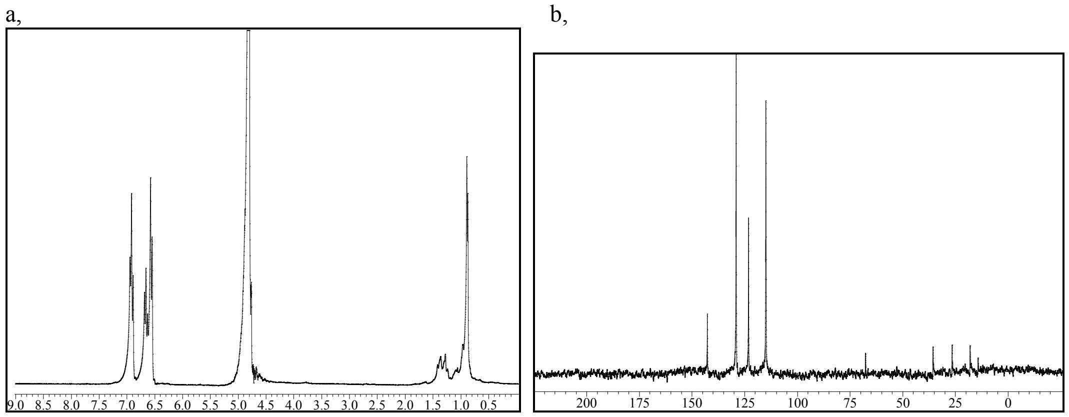


Figure 4. *NMR spectra of 1% (w/w) TEMPO in 1M* H_2SO_4 *heated at 80 °C for 24 hours. The reaction mixture was reduced by* $PhNHNH_2$ *prior to monitoring by NMR spectroscopy. a,* ^1H*. b,* ^{13}C*.*

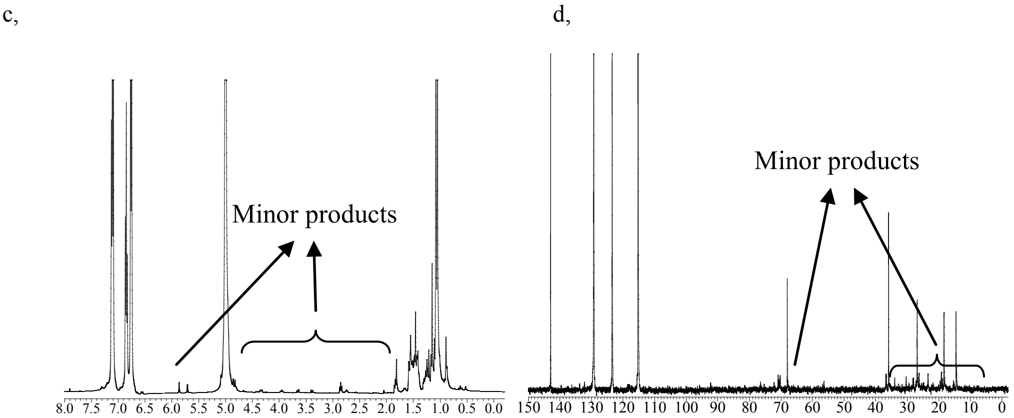


Figure 5. *NMR spectra of reaction mixture of 4% oxoammonium chloride in 1 M* H_2SO_4 *in* D_2O *at 80 °C. The reaction mixture was reduced by* $PhNHNH_2$ *prior to monitoring by NMR spectroscopy. c,* ^1H *NMR spectrum of the reaction product after heating for 2 hrs. d,* ^{13}C *NMR spectrum of the reaction product after heating for 2 hrs.*

5. Mass spectra of the reaction product of TEMPO decay and oxoammonium salt decomposition in H_2SO_4 at 80 °C.

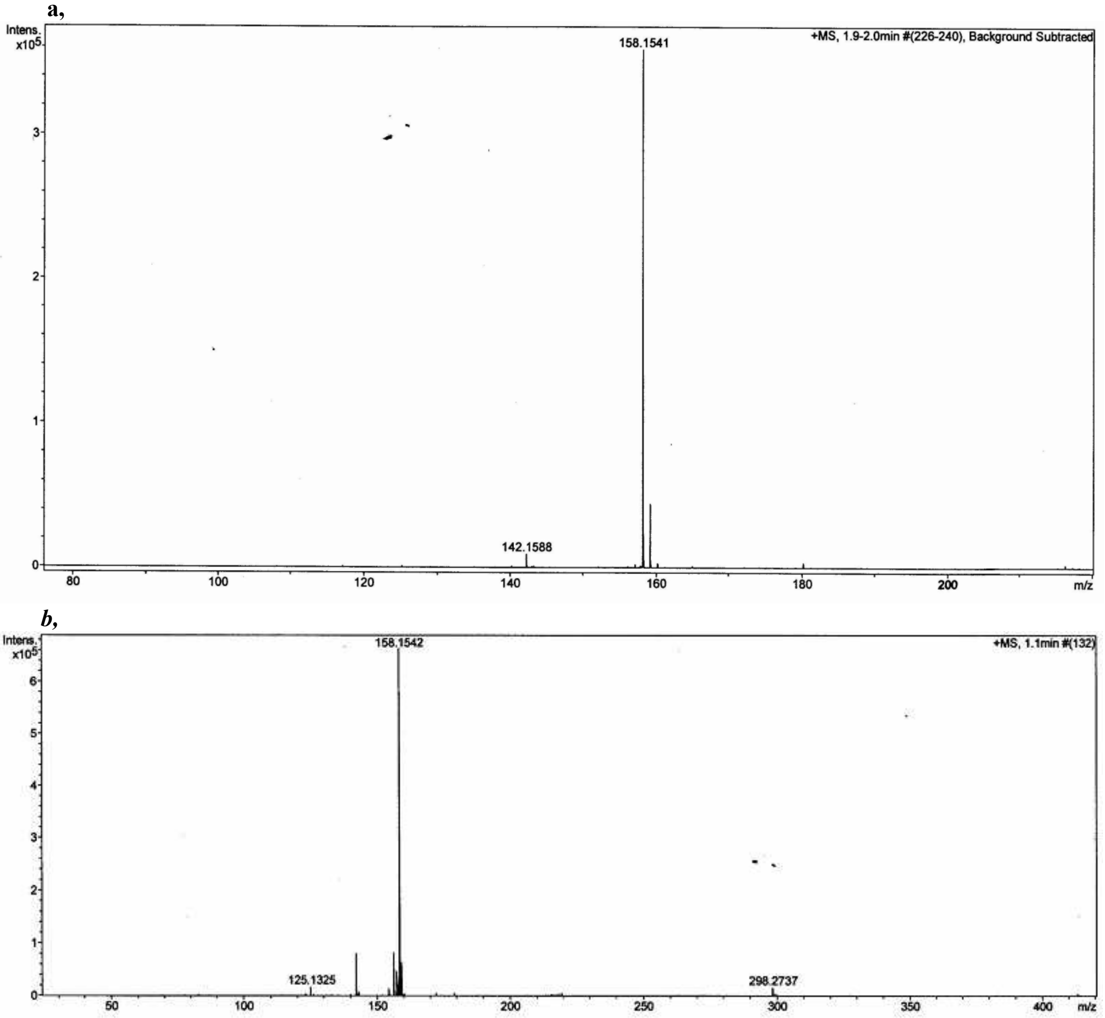


Figure 6. *Mass spectra (electrospray, positive mode) of TEMPO/oxoammonium chloride in 0.5 M* H_2SO_4 *after heating for 1 hour. a, 3% (w/w) TEMPO in 0.5M* H_2SO_4*. B, 4% (w/w) oxoammonium chloride in 0.5M* H_2SO_4*.*

6. Titration curve of TEMPOH in H2SO4 by NaOH.

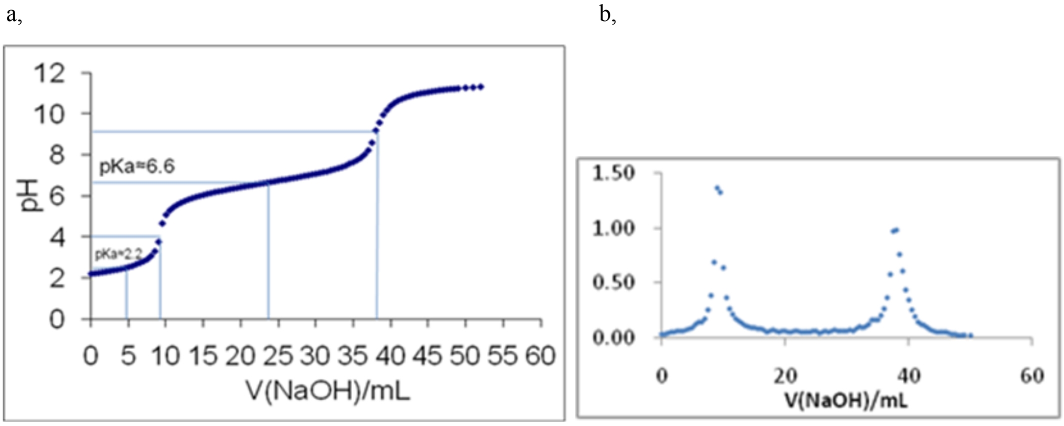
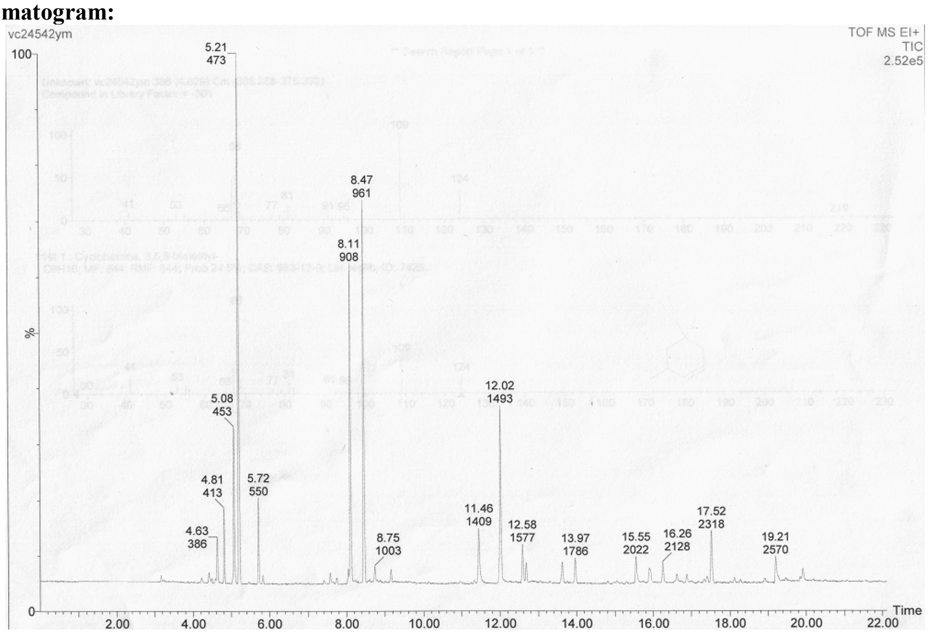


Figure 7. *Titration curve of a solution of* 0.61×10^{-3} *mol TEMPOH in 20mL 0.02 M* H_2SO_4 *titrated with 0.0203 M NaOH (aq). a, titration curved. b, 1st-derivative of the titration curve.*

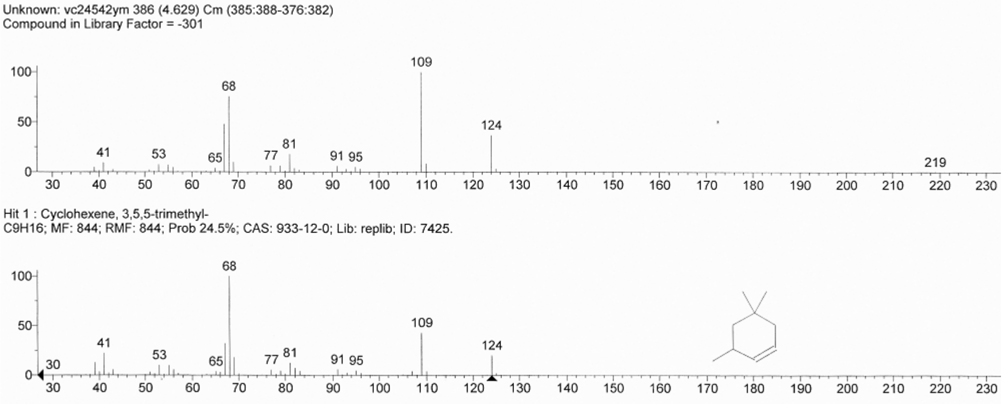
7. GC-MS analysis of the organic phase product

GC chromatogram:

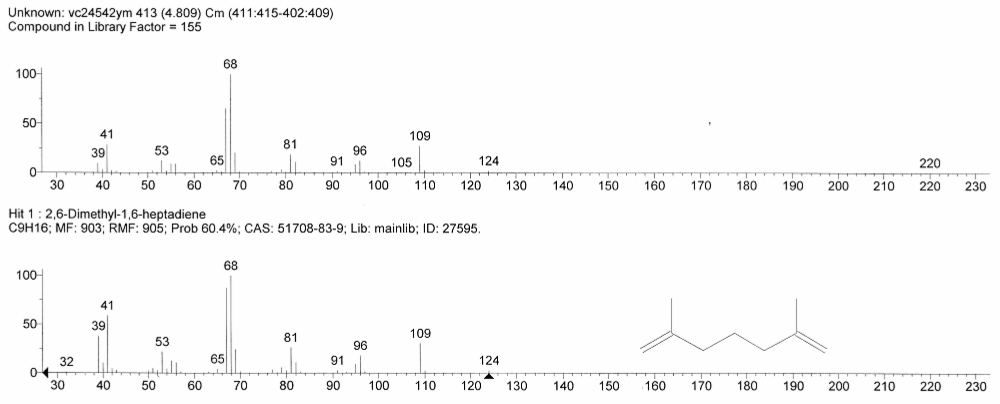


Mass spectra of components at different retention times.

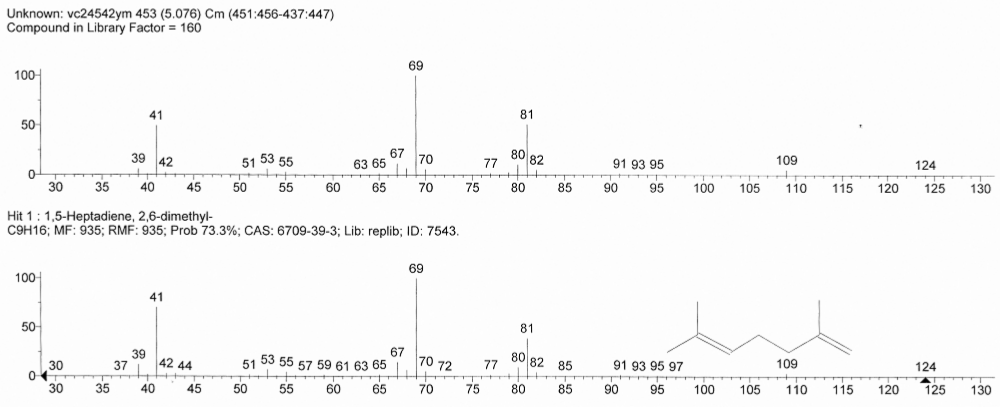
(1) Retention time = 4.63 min



(2) Retention time = 4.81 min

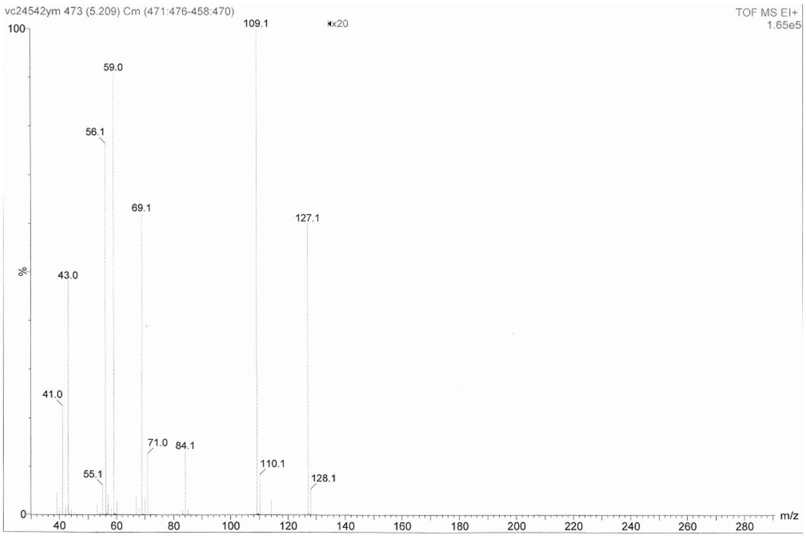


(3) Retention time = 5.08 min

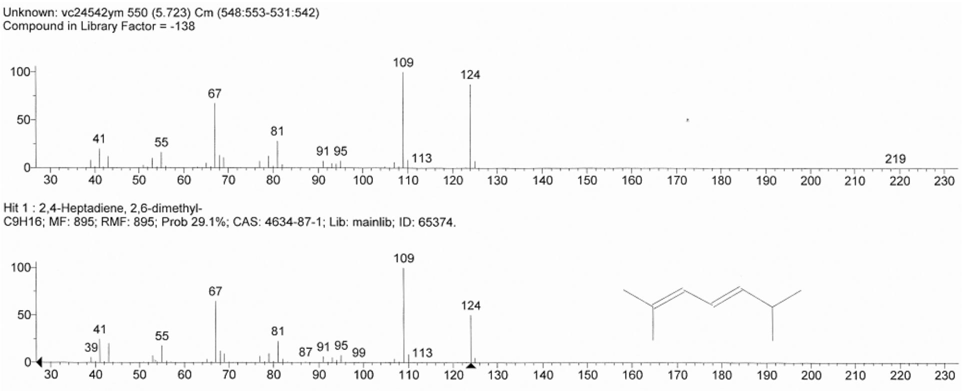

Unknown: vc24542ym 453 (5.076) Cm (451:456-437:447)
Compound in Library Factor = 160

Hit 1 : 1,5-Heptadiene, 2,6-dimethyl-
C9H16; MF: 935; RMF: 935; Prob 73.3%; CAS: 6709-39-3; Lib: replib; ID: 7543.

(4) Retention time = 5.21min

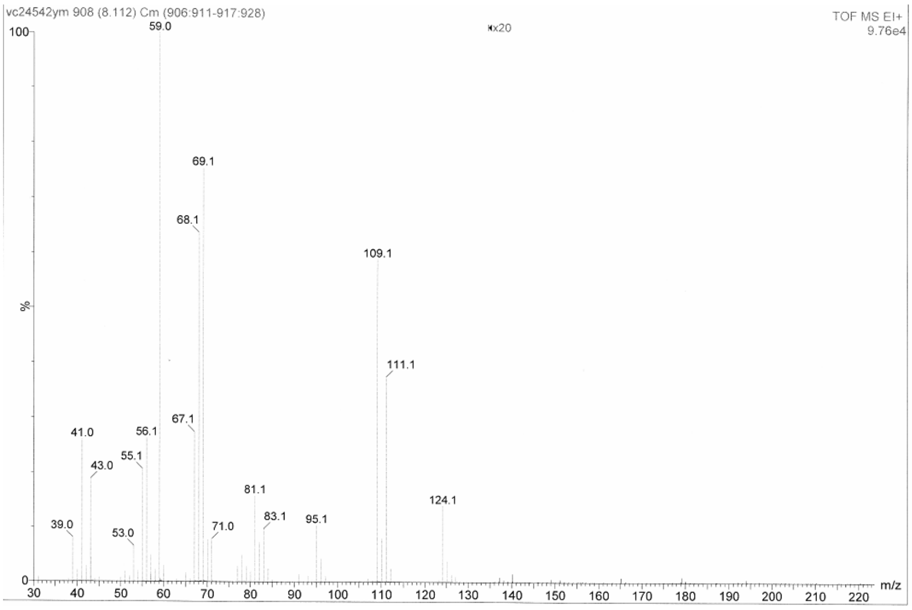


(5) Retention time = 5.72min

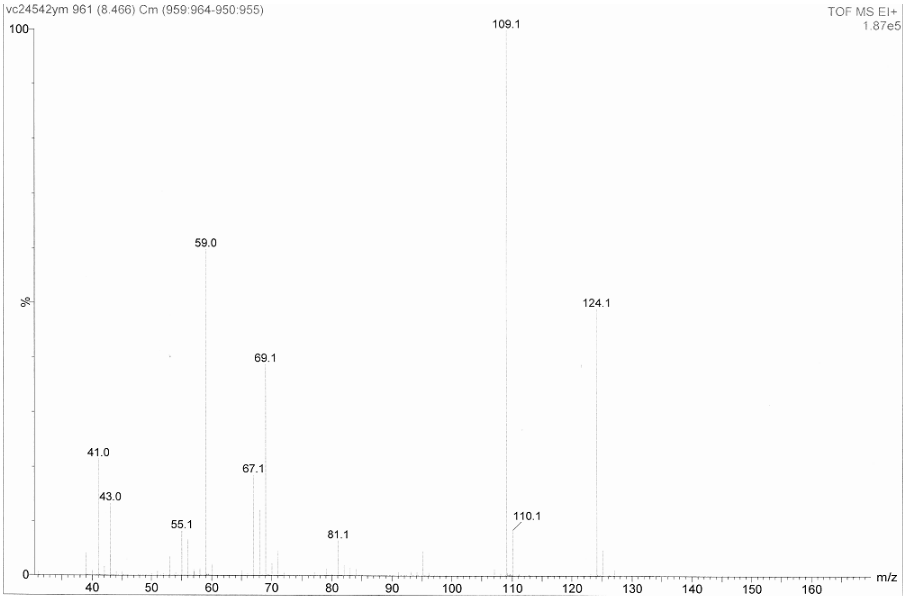

Unknown: vc24542ym 550 (5.723) Cm (548:553-531:542)
Compound in Library Factor = -138

Hit 1 : 2,4-Heptadiene, 2,6-dimethyl-
C9H16; MF: 895; RMF: 895; Prob 29.1%; CAS: 4634-87-1; Lib: mainlib; ID: 65374.

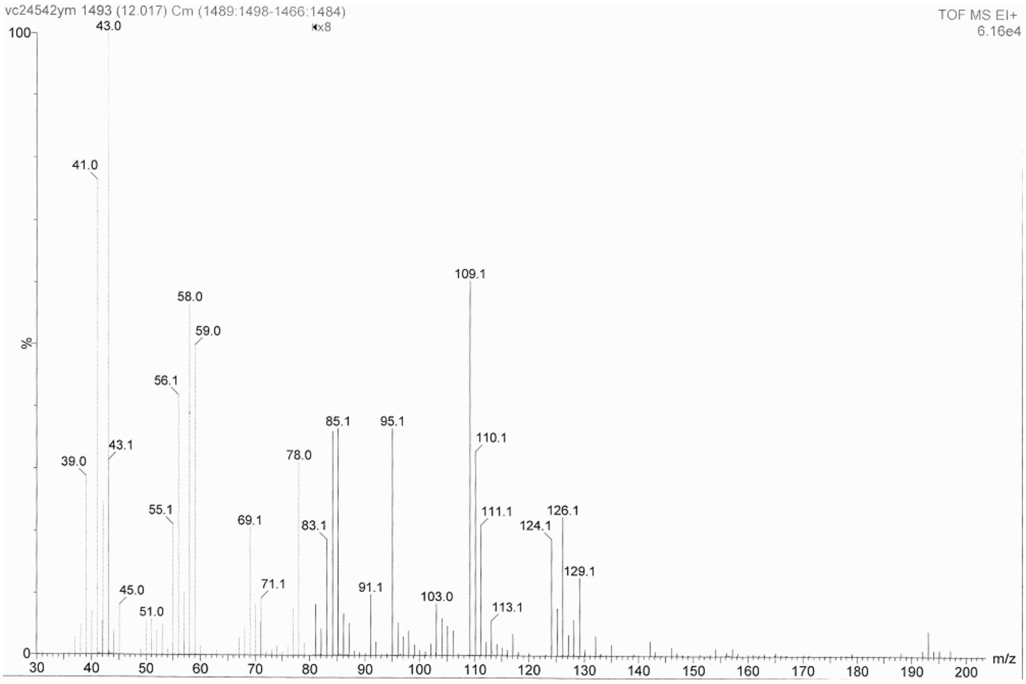
(6) Retention time = 8.11min



(7) Retention time = 8.47min



(8) Retention time = 12.017min



References:

1. V. A. Golubev, V. D. Sen, I. V. Kulyk and A. L. Aleksandrov, *B. Acad. Sci. USSR Ch.*, 1975, **24**, 2119-2126.
2. V. D. Sen and V. a. Golubev, *J. Phys. Org. Chem.*, 2009, **22**, 138-143.