# Study of 2-Iodo-3-(phenylsulfinyl)-2-propen-1-ol and its Analogues by Self-chemical Ionization Mass Spectrometry

**ZHANG, Fang**[a](张芳) **GUO, Yin-Long***,[a](郭寅龙) **WEI, Qi**[b](魏琦)
**MA, Sheng-Ming***,[b](麻生明)

[a] *Department of Analytical Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

[b] *State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

**The self-chemical ionization (SCI) in quadrupole mass spectrometry was developed to determine the structure of (*E*)-2-iodo-3-(phenylsulfinyl)-2-propen-1-ol and its 6 analogues. Some techniques that increase the sample quantity and heating speed and shorten vaporization time to obtain high pressure in the ion source were applied to increase the chance of ion-molecule reactions. The structures of these compounds were identified by mass spectral data of $MH^+$ and some characteristic fragment ions. Compared with the mass spectra for 2-iodo-3-(phenylsulfinyl)-2-propen-1-ols obtained in electron impact ionization (EI), SCI showed more information, in particular, an improvement in amount of information at the high mass area. The absence of reagent gas makes the spectrum clean and simple.**

**Keywords** Self-chemical ionization, quadrupole mass spectrometry, sulfoxide, allylic alcohol

## Introduction

SCI is a kind of chemical ionization (CI) in which the reagent ions are fragment ions coming from the analyte neutral molecule.[1] In CI, reagent gas (*e.g.* methane, isobutane, ammonia, *etc.*) is ionized by interaction with electrons to form reagent ions. The ions react with analyte molecules to form analyte ions. This method (CI) has the advantage that the amount of energy transferred into the analyte molecule is significantly less than that required for the electron impact method, resulting in less fragmentation and a consequent improvement in the amount of information at the higher mass area.[2] In the absence of a reagent gas, CI can take place by reaction between the fragment ions of the analyte and analyte neutral molecules. Otherwise, when the sample is introduced, a mixed electron/chemical ionization spectrum is obtained. One of the interesting features of this spectrum is that a self-protonation process for some compounds may occur. This ion-molecule reaction is shown in Eq. (1):

$$XH^+ + M \longrightarrow MH^+ + X \qquad (1)$$

where $XH^+$ represents the fragment ion supplying $H^+$ from EI, *e.g.* $CH_5^+$, $C_2H_3^+$, $C_2H_5^+$, $C_3H_7^+$, $C_4H_5^+$, $C_4H_7^+$, and the sample molecule M accepts $H^+$ to form the protonated molecule $MH^+$. Ghaderl *et al.*[1] reported that SCI was observed in a Fourier transform mass spectrometer (FTMS), which used a trapped ion cell and an appropriate time delay between ion formation and ion detection. This method of chemical ionization is the most efficient for molecules which produce a large number of low-mass fragment ions serving as reagents. It was stated that SCI works well for long-chain aliphatics containing one or more functional groups and for molecules containing long hydrocarbon moieties such as fatty acid esters. From SCI/FTMS, we can observe the molecular ion peak[3] and confirm the structure of compounds,[4,5] and determine the accurate mass for the

* E-mail: ylguo@pub.sioc.ac.cn

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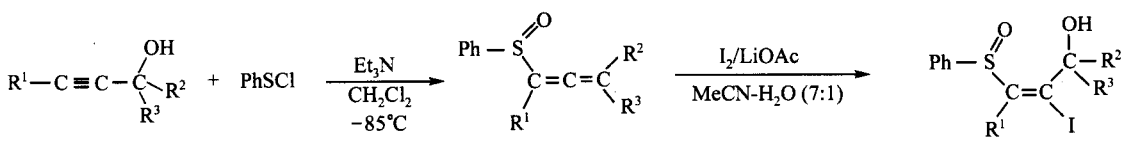
protonated molecular ion of 2, 4 (*erythro*/*threo*)-2-methyl-3-phenyl-2,3-propanediolamine compounds as well.[6] Compared with EI and CI, SCI has two advantages: (1) revealing molecular weight, (2) offering much structural information of unstable compounds. And in the absence of a reagent gas, the SCI mass spectrum is much cleaner and simpler than the conventional CI mass spectrum because the SCI has no background ions from a reagent gas. In quadrupole mass spectrometry, the residence time of ions is very short. High pressures resulting in the generation of more collision between the fragment ions and the sample molecules are necessary for a successful SCI in this short time. The sample quantity and heating speed are increased and vaporization time is shortened to obtain high pressure in the ion source. SCI in quadrupole mass spectrometry can be achieved. Guo *el al*.[7] applied this method to the study of Erythromycin Antibiotics. Here, we wish to report our recent study of 2-iodo-3-(phenylsulfinyl)-2-propen-1-ol and its analogues by mass spectrometry.

These seven 2-iodo-3-(phenylsulfinyl)-substituted alkenols are:

**A**, (*E*)-2-iodo-3-(phenylsulfinyl)-2-propen-1-ol; **B**, (*E*)-2-iodo-3-phenyl-3-(phenylsulfinyl)-2-propen-1-ol; **C**, (*E*)-2-iodo-3-(phenylsulfinyl)-2-hepten-1-ol; **D**, (*E*)-2-iodo-1-(phenylsulfinyl)-1-hepten-3-ol; **E**, (*E*)-2-iodo-4, 4-dimethyl-1-(phenylsulfinyl)-1-penten-3-ol; **F**, 1-[(*E*)-1′-iodo-2′-(phenylsulfinyl) ethenyl]-1-cyclohexanol; **G**, (*E*)-3-iodo-2-methyl-4-(phenylsulfinyl)-3-octen-2-ol.




| | $R^1$ | $R^2$ | | $R^3$ |
|---|---|---|---|---|
| **A** | H | H | | H |
| **B** | $C_6H_5$ | H | | H |
| **C** | *n*-$C_4H_9$ | H | | H |
| **D** | H | H | | *n*-$C_4H_9$ |
| **E** | H | H | | *t*-Bu |
| **F** | H | | | |
| **G** | *n*-$C_4H_9$ | $CH_3$ | $(CH_2)_5$ | $CH_3$ |

## Experimental

The instrumentation used in the study consisted of an HP 5989A mass spectrometer. The operation conditions for all SCI experiments were as follows: electron energy, 70 eV; filament emission current, 300 μA; source temperature, 300℃; mass range, 40—600 amu. During each experiment, the sample of about 1 μg was charged to a vial, then the vial was loaded into the end of the probe. Before being inserted into the ionization source, the probe was set aside out of the source for some minutes in order to let the low-boiling point impurities like $H_2O$ evaporate. Then the probe was inserted into the source. The tip of the probe was heated to about 320℃ rapidly. The operation conditions for EI were the same as those for all SCI experiments listed above.

All samples were synthesized by the halohydroxylation of 1,2-allenic sulfoxides with $I_2/H_2O$ and the structures were identified by X-ray diffraction study, MS, NMR, and IR spectra.[8]

## Results and discussion

Fig. 1 shows the spectra of 2-iodo-3-(phenylsulfinyl)-substituted alkenols obtained from SCI. All the spectra are displayed normally to the base peak. There are some particular ions in each spectrum, dominated by the $MH^+$ ion or $[M-17]^+$ ion, with the other peaks at

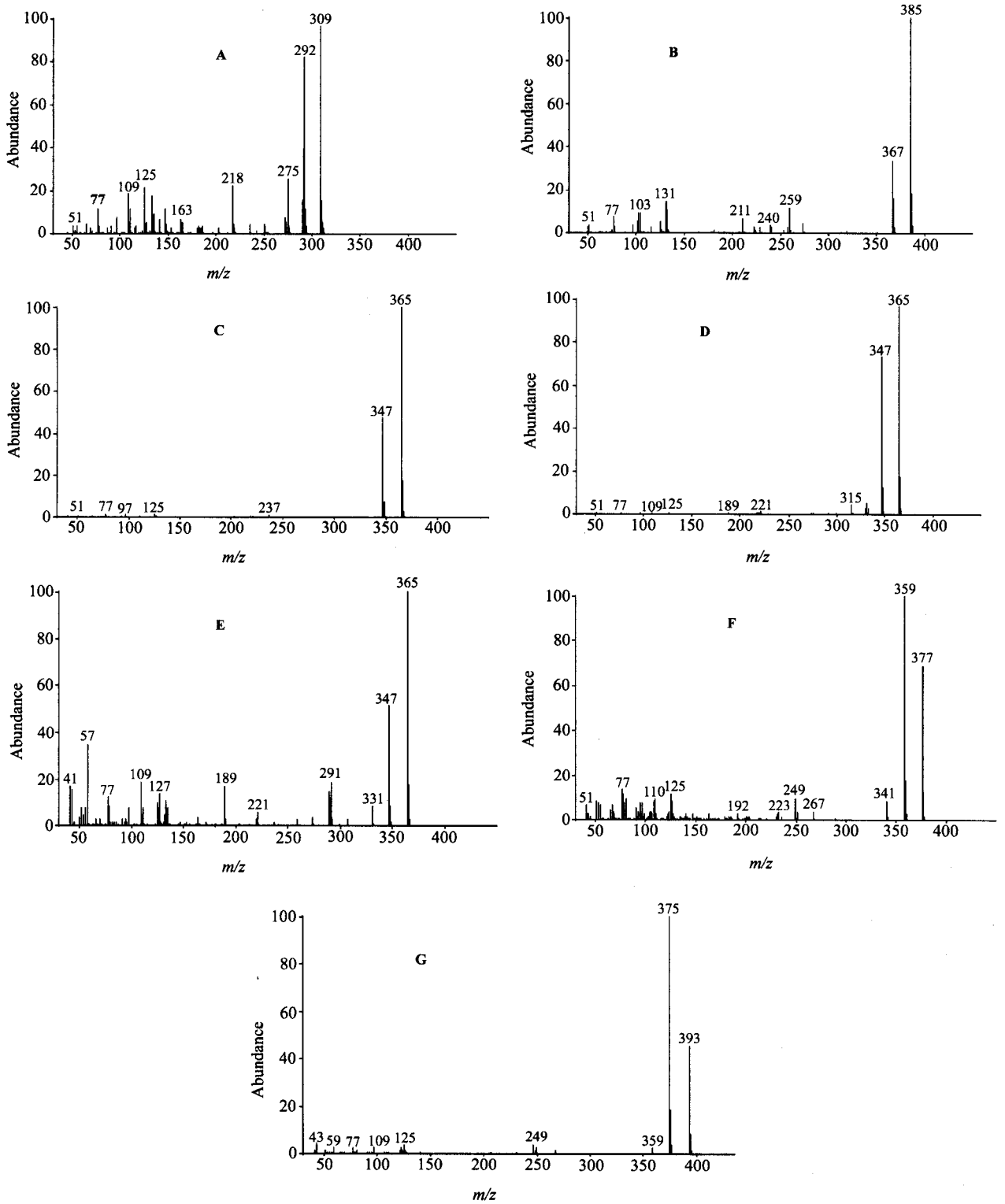
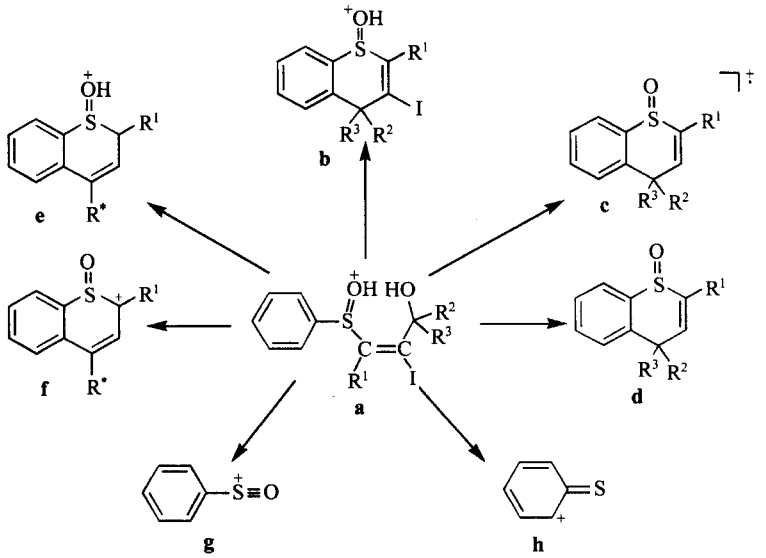



**Fig. 1** SCI mass spectra of samples A—G.

$m/z$ = 125 and 109 *etc*. The relative abundance of these ions are listed in Table 1. And the possible processes for the formation of the particular ionic product in SCI are as follows:



There are also some peaks in low mass range, *e.g.*, $m/z = 51$, 77, which may be generated from the aromatic structures, and $m/z = 41$, 55, 69, which may be generated from the alkene structure.

From the results presented above, SCI has some special ions compared to EI (see Fig. 2). The most evident difference, however, is the appearance of peaks at $MH^+$. With the existence of hydroxyl groups in these compounds, they tend to lose low-mass free radical like HO·, or $H_2O$ in electron impact ionization. The EI spectra of the same compounds show no molecular ions, while the corresponding molecular weight information can be obtained in the form of $MH^+$ ion for these compounds in SCI mode. And the other ions have some valuable inputs into the structural information. Furthermore, the low-mass peaks are shown in both EI and SCI, while high-mass peaks only appear in SCI. This phenomenon confirms the main advantage of SCI.

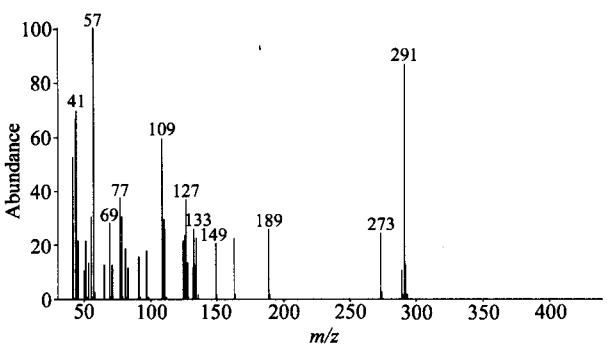



**Fig. 2** EI mass spectra of sample **E**: (*E*)-2-iodo-4,4-dimethyl-1-(phenylsulfinyl)-1-penten-3-ol.

The SCI process in quadrupole mass spectrometry contains two steps. When a sample is introduced into the ion source, the gasificated sample molecules interact with the electrons. And the ions formed by initial fragmentation have sufficient energy to fragment further. At this time the EI spectrum can be obtained. When the concentration of the sample molecules increases rapidly in the source, the number of molecule collision with ions is large enough to let ion-molecule reactions take place. A mixed electron impact/chemical ionization spectrum is obtained. The following requirements for a sample to be submitted to SCI are suggested:

1) Before vaporization, samples must be stable.

2) Samples must reach high gas pressure rapidly in ion source.

3) Fragment ions transferring $H^+$ can be self-produced by a sample molecule with electron impact.

4) There should be an acceptor site to $H^+$ in sample molecular structure, *e.g.* N, O or S.

5) There is a high possibility of the sample molecular collision with fragment ions.

SCI is a very useful mass spectrometry technique. Not only does it give us the molecular mass information based on quasimolecular ions, but also it provides us with the molecular structural information from particular ions. In the study of the compounds with unstable quasimolecular ions, fragment ion information can be only obtained by EI, or molecular mass information by fast atom bombardment (FAB), electrospray ionization (ESI), and CI, *etc*. While in SCI, no matrix, solvent, or reagent gas is applied, the spectrum is cleaner

with low noise. It shows that SCI is simple, quick and useful.

**Table 1** Main mass spectral data of γ-sulfinyl-β-iodo allyl alcohol analogues

| Compounds | MW | *m/z* (relative abundance) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | **a** | **b** | **c** | **d** | **e** | **f** | **g** | **h** |
| **A** | 308 | 309(100) | 291(40) | | | 165(6) | 163(7) | 125(21) | 109(18) |
| **B** | 384 | 385(100) | 367(33) | 241(3) | 240(4) | | | 125(6) | 109(1) |
| **C** | 364 | 365(100) | 347(48) | | | | | 125(2) | 109(1) |
| **D** | 364 | 365(100) | 347(68) | 221(1) | 220(1) | | 189(1) | 125(1) | 109(1) |
| **E** | 364 | 365(100) | 347(51) | 221(6) | 220(3) | 191(1) | 189(17) | 125(10) | 109(19) |
| **F** | 376 | 377(69) | 359(100) | 233(4) | 232(3) | | | 125(12) | 109(9) |
| **G** | 392 | 393(45) | 375(100) | 249(3) | 248(4) | | | 125(4) | 109(1) |

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