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PHOTOCHEMISTRY OF SULPHUR-CONTAINING AMINO ACIDS.
FORMATION OF THIOPHENE DERIVATIVES

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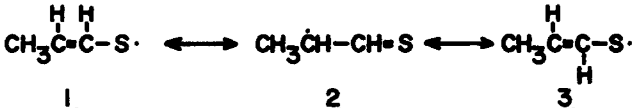
We have studied the formation mechanism of volatile products from S-containing amino acids (precursors of onion and garlic flavour) irradiated by γ-rays in oxygen-free aqueous solutions in terms of food irradiation.[1] Recently, a new *cis-trans* isomerization has been found from γ-radiolysis of S-(*cis*-prop-1-enyl)-L-cysteine(PeCS) and it has been elucidated that several *cis*- or *trans*-prop-1-enyl sulphides as the major products are produced *via* prop-1-enyl thiyl radicals as follows.[2]



$$CH_3\overset{H}{C}=\overset{H}{C}-S\cdot \longleftrightarrow CH_3\dot{C}H-CH=S \longleftrightarrow CH_3\overset{H}{C}=\underset{H}{C}-S\cdot$$

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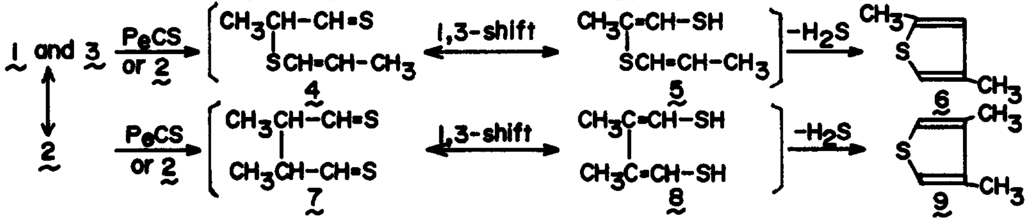
The major products from UV-photolysis of PeCS are remarkably different from γ-radiolysis in contrast to the case of S-*n*-propyl- or S-allyl-L-cysteine.[3] In the comparisons between UV and γ-ray, we wish to report on the identification and formation mechanism of the major products from UV-photolysis of PeCS,[4] one of S-compounds with biological interest. The oxygen-free neutral solution of PeCS(20 mM) dissolved in triply-distilled water was placed in stoppered quartz tubes and irradiated for 20 hr using a 50 W low pressure mercury lamp. 2,4-(ca.15%),3,4-(7%), and 2,5-Dimethylthiophenes(<1%) and 3-methylthiophene(5%) as thiophene derivatives and prop-1-enyl mercaptan(40%), di-prop-1-enyl sulphides(<1%) and *n*-propyl prop-1-enyl sulphides(<1%) as other S-compounds were characterized by the combined GC-MS and confirmed by comparing GLC and MS with those of reference compounds.[5] Alanine(large) and cystine(trace) etc. among the ninhydrin-positive products were identified by the two dimensional TLC. In the case of γ-irradiation (10^4—10^6rad), thiophene derivatives could not be detected even using the high sensitive GLC. From the results of ESR spectra(77°K) of PeCS irradiated in aqueous system, anisotropic $CH_3CH{=}CH{-}S\cdot$ radicals (g_1=2.00, g_2=2.02, g_3=2.05) were observed and the measured values agreed well with reference alkyl-thiyl radicals.[6] These evidences indicate that thiophene derivatives are produced *via* prop-1-enyl thiyl radicals. The yield of each of thiophene derivatives, H_2S, mercaptan, sulphides and alanine increased in parallel with irradiation time(0—20 hr), respectively and the proportion of the yields of these products in each time was approximately constant. Though there is such a possibility that each of dimethylthiophenes is produced by methyl scrambling on the thiophene ring or by the cyclization of di-prop-1-enyl sulphides from UV-irradiated PeCS, only the trace amount of 2,4-dimethylthiophene(6) was produced from 3,4-dimethylthiophene(9) or di-prop-1-enyl sulphides irradiated for 5-20 hr. Therefore, these facts indicate that each of dimethylthiophene is derived through the independent pathway. The reasonable mechanism for dimethylthiophene formation is suggested tentatively as follows.



Thiyl radicals(1 and 3) and alkyl radical(2) attack of PeCS to produce unstable 4 and 7, *via* 1,3-prototropic shift give 5 and 8 and the immediate elimination of H_2S leads to stable 6 and 9, respectively. Because of trace amounts in the yield, 2,5-dimethylthiophene might have been produced by methyl scrambling from 6. Moreover, 3-methylthiophene might be produced through the intermediate formed by 1,3-methyl shift of 4 and also through the methyl elimination of 6 or 9, though the yield of 3-methylthiophene from 6 or 9 was trace.

REFERENCES AND REMARKS

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