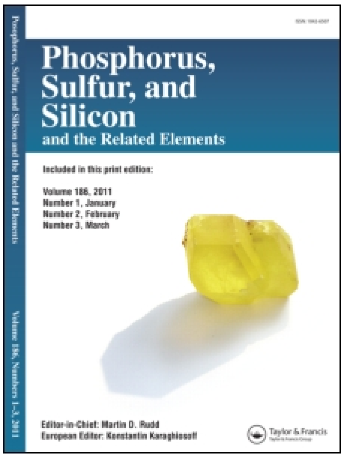


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Gas-Phase Thermal Decomposition Mechanism of the Important Movpe Precursor t-Bu$_2$Se

Douglas F. Foster; Nigel L. Pickett; Janet E. Hails; David J. Cole-Hamilton

To cite this Article Foster, Douglas F. , Pickett, Nigel L. , Hails, Janet E. and Cole-Hamilton, David J.(1998) 'Gas-Phase Thermal Decomposition Mechanism of the Important Movpe Precursor t-Bu$_2$Se', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 427 — 430

To link to this Article: DOI: 10.1080/10426509808545970

URL: http://dx.doi.org/10.1080/10426509808545970

Advanced Materials: Invited Lectures

Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 427–430
Reprints available directly from the publisher
Photocopying permitted by license only

GAS-PHASE THERMAL DECOMPOSITION MECHANISM OF THE IMPORTANT MOVPE PRECURSOR t-Bu_2Se

DOUGLAS F FOSTER[a], NIGEL L PICKETT[a], JANET E HAILS[b], and DAVID J COLE-HAMILTON[a]
[a]School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, UK; [b]Defence Establishment Research Agency, St Andrews Road, Great Malvern, Worcs WR14 3PS, UK

Quantitative GCMS analysis of the decomposition products formed during the gas-phase thermal decomposition of deuterated t-Bu_2Se in inert, He, or reducing, H_2, ambients reveals the principle mode of decomposition to involve homolytic Se-C bond cleavage reactions.

Keywords: MOVPE; ditertiarybutylselenide; decomposition mechanism

INTRODUCTION

Both t-Bu_2Se[1] and t-BuSeH[2] have been proposed as suitable sources of Se in the 'Metalorganic Vapour Phase Epitaxy' (MOVPE) growth of the ternary compound semiconductor, ZnS_xSe_{1-x}; one of two systems competing in the race to develop 'blue' laser devices for use in data storage systems. The required high p-type, N atom, doping of this system is difficult due to the tendency to form inactive N-H bonds. Whether the source of the H atoms is the H_2 carrier gas employed in the growth process, or active H atoms contained within precursors such as t-BuSeH is open to question. This has nevertheless led to a preference for the use of t-Bu_2Se; but might not t-Bu_2Se itself decompose through a mechanism involving the intermediate formation of t-BuSeH?

Ditertiarybutylselenide

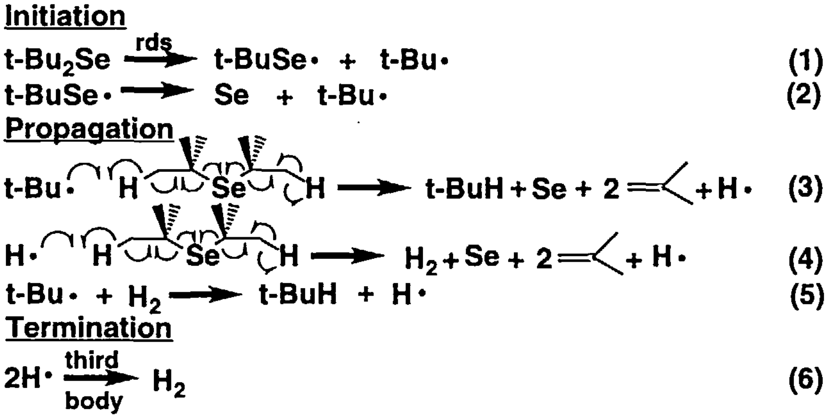
In agreement with previous reports on the gas-phase thermal decomposition of t-Bu_2Se[3, 4], we have observed that when a dilute gas stream of t-Bu_2Se (300-600 ppm) is passed through a heated quartz tube, the hydrocarbon product from the decomposition is almost exclusively composed of isobutene and isobutane. We have also found that both the ratio of isobutene to isobutane (5.6:1 in He and 5.8:1 in H_2) and the temperature at which 50% t-Bu_2Se decomposition occurs (420°C in He and 400°C in H_2) are virtually independent of the nature of the carrier gas. It has been suggested that these observations are explained by a decomposition mechanism for t-Bu_2Se which involves an initial ß-H abstraction to afford isobutene and the intermediate t-BuSeH. The selenol then undergoing a second ß-H abstraction to afford H_2Se and more isobutene or, in a less competitive reaction, reductive elimination to afford Se and the observed isobutane[3, 4].

The proposed intermediate, t-BuSeH, has not been observed in even trace amounts during any of our t-Bu_2Se decomposition studies; nor was it unambiguously observed in the earlier studies[3, 4]. In addition, although we observed traces of H_2Se during t-Bu_2Se decomposition in H_2, none was observed in a He ambient, again in agreement with observations made in the earlier studies. In other studies we have shown that t-BuSeH and H_2Se are sufficiently stable under the conditions of the experiments reported here that they would not decompose completely if formed from t-Bu_2Se[5]. This then rules out the ß-H abstraction pathway for t-Bu_2Se.

The intricacies of the selenide decomposition have been further probed by monitoring the decomposition of the fully deuterated selenide, d_{18}-t-Bu_2Se. In He, as expected, the decomposition profile mirrors that of d_0-t-Bu_2Se, with $(CD_3)_2CCD_2$ and $(CD_3)_3CD$ the only hydrocarbon products. However, in H_2, although the ratio of isobutene to isobutane mirrors that found for d_0-t-Bu_2Se, the isobutane is found to be largely

$(CD_3)_3CH$, rather than the expected $(CD_3)_3CD$ (in a 2.6:1 ratio at 50% and 1.4:1 ratio at 100% decomposition). In addition, traces of H_2Se (no D incorporation) are observed. Clearly, when H_2 is used as the carrier gas it becomes involved in hydrocarbon forming steps without effecting either the rate determining step of selenide decomposition or the relative rates of production of isobutene and isobutane.

All these experimental observations are explained by a radical mechanism initiated by homolytic Se-C bond cleavage and whose **essential** features are depicted in Scheme 1.



SCHEME 1 Proposed mechanism for $t\text{-}Bu_2Se$ decomposition

Reactions involving the disproportionation of the t-Bu• radicals to afford equimolar ratios of isobutene and isobutane, or bimolecular combinations of t-Bu• with H• to form isobutane, will be negligible under the conditions of extreme dilution employed in these studies. Instead, the t-Bu• radical abstracts H• from intact $t\text{-}Bu_2Se$, in the cascade reaction of Eq. (3). The larger amounts of isobutene than expected from this reaction alone can be explained if the H• produced in Eq. (3) also abstracts H• from $t\text{-}Bu_2Se$ in the cascade reaction of Eq. (4) - a self propagating cycle (regeneration of H•) resulting in the formation of a single hydrocarbon product, isobutene. The cycle is terminated by 'third body' dimerisation of H• to form H_2, Eq. (6). The formation of $(CD_3)_3CH$ during the decomposition of the fully deuterated selenide, d_{18}-t-Bu_2Se, in H_2 can be explained if reaction of t-Bu• radicals with the large excess of H_2, Eq. (5), competes with H• abstraction from t-Bu_2Se, Eq. (3). This will not lead to an increase in the proportion of isobutane as the H• produced in Eq. (5) is able to initiate the formation of isobutene, Eq. (4). This mechanism is supported by observations made during codecomposition studies on a 1:1 mixture of d_0 and d_{18}-t-Bu_2Se in He. When partial decomposition has occurred (rate decomposition $d_0 > d_{18}$), there is no formation of the crossover species, d_9-t-Bu_2Se, and the hydrocarbon products are the expected d_0/d_8-isobutenes (enriched in d_0) and the isobutanes $(CH_3)_3CH$, $(CH_3)_3CD$, $(CD_3)_3CH$ and $(CD_3)_3CD$ which form in the ratio 2.29:1:2.86:1.2. These observations being consistent with the significant isotope effect expected for the hydrogen abstraction reactions of Eq. (3) and (4).

In conclusion, the mechanism proposed in Scheme 1 does not lead to the formation of Se-H bonds, thus affording some support for the preferred use of t-Bu_2Se, over t-BuSeH, as a precursor in MOVPE.

Acknowledgements

This authors are grateful to the EPSRC and the DERA for support and to Dr N. Maung for helpful discussions.

References

[1.] W. Kuhn, A. Naumov, H. Stanzl, S. Bauer, K. Wolf, H. P. Wagner, W. Gebhardt, U. W. Pohl, A. Krost, W. Richter, U. Dumichen and K. H. Thiele, *J. Crystal Growth*, **123**, 605 (1992).

[2.] K. Nishimura, Y. Nagao and K. Sakai, *Japan. J. Appl. Phys.*, **32**, L428 (1993).

[3.] W. S. Kuhn, R. Helbing, B. Qu'Hen and O. Gorochov, *J. Crystal Growth*, **146**, 580 (1995).

[4.] G. H. Fan, N. Maung, T. L. Ng, P. F. Heelis, J. O. Williams, A. C. Wright, D. F. Foster and D. J. Cole-Hamilton, *J. Crystal Growth*, **170**, 485 (1997).

[5.] N. L. Pickett, D. J. Cole-Hamilton and D. F. Foster, unpublished results.