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Spectroscopy and kinetics of germylene and digermene reactions photogenerated in the condensed phase

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Abstract. The state of the art in the spectroscopic identification and kinetic analysis of condensed-phase reactions of bivalent germanium derivatives and their dimers is considered. Considerable attention is drawn to the comparison of results obtained by laser flash photolysis and spin chemistry methods. The bibliography includes 95 references.

I. Introduction

At present, the most important direction in chemistry and photochemistry of organometallic derivatives is devoted to the establishment of their reaction mechanisms. The wide use of modern physical research methods [optical, EPR and NMR spectroscopies, Chemically Induced Dynamic Nuclear Polarisation (CIDNP), flash photolysis, time-resolved luminescence, photolysis in cryogenic matrices] made it possible to identify short-lived species in many reactions of organosilicon and organogermanium derivatives. Keen attention of chemists to organometallic compounds containing the 14th Group elements is largely explained by their use in high technologies, first of all, in integrated microelectronics.

Laser flash photolysis and the methods of spin chemistry, namely, photochemically induced dynamic nuclear polarisation and the magnetic effect, play the decisive role in studying reactions that involve short-lived intermediates. The use of photogeneration makes it possible to produce transient species in high concentrations, record their optical spectra and study the kinetics of their growth and decay.

The literature contains numerous publications devoted to the identification of transient species formed in the condensed-phase photolysis of different silicon and germanium compounds. Among these species, mention should be made of carbene anologues, namely, organylsilylenes and -germylenes, silyl and germyl free radicals and short-lived derivatives of tricoordinate silicon and germanium, namely, substituted silenes and germenes. Thus information on heavy analogues of carbenes can be found in a monograph [1] devoted to the carbene chemistry; results on the synthesis, structure, spectroscopy and reactivity of germylenes and stannylenes are summarised in several reviews [2–8] and recently published collections [9, 10] of reviews. However, despite the abundance of reference literature on this issue, no comparative analysis of the kinetic data obtained by different spectroscopic techniques and by different authors was carried out.

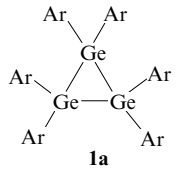
From our viewpoint, a real assessment of the further development in this field of chemistry requires comparison of the results obtained by laser flash photolysis and CIDNP. Thus, to date, based on the results of spin chemistry methods, the detailed schemes of processes that occur in solutions, involving germylenes and digermenes and including their interconversions, were constructed and the mechanisms for the formation of germanium-containing biradicals were proposed. Note that, although the involvement of the latter in elementary steps was often postulated based on the analysis of reaction products, their presence has never been proved by physical methods with the exception of CIDNP. This is why it seems useful to compare the CIDNP data that contain information on the structure of paramagnetic intermediates (free radicals, carbene analogues, biradicals) as the precursors of products formed, on the one hand, with the kinetic data on the fomation and decay of short-lived germanium derivatives obtained in laser flash photolysis techniques, on the other hand.

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II. Germylene precursors

In this Section, we describe the organogermanium derivatives that generate diorganylgermylenes under radiation. Cyclic germanium compounds such as $(R^1R^2Ge)_n$ are the efficient sources of germylenes.[1,11–20] In 1982, the first cyclotrigermane, hexakis(2,6-dimethylphenyl)cyclotrigermane (**1a**) was isolated and described.[16] To date, other cyclic tri- and polygermanes were synthesised.



1a

Ar = 2,6-$Me_2C_6H_3$.

The ring may also include atoms of other elements, *e.g.*, silicon or carbon.[21]

Linear germanes with alkyl and aryl substituents, the analogues of linear hydrocarbons, can also serve as germylene precursors.[22,23] The largest group of precursors is formed by germanes of the $R^1R^2GeX_2$ type, where R^1, R^2 are alkyl or aryl groups and X is a weakly bound heteroatomic substituent.[3,24–28]

$$R^1R^2GeX_2 \xrightarrow{h\nu} R^1R^2Ge + X{-}X,$$

R^1, R^2 = Alk, Ar; X = $SiMe_3$, SePh, N_3, *etc.*

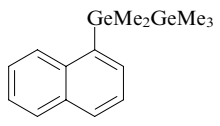
The possibility of generation of germylenes from such compounds is often determined by the fact that a heteronuclear bond Ge–E (E = Si, Se, N) is less stable than a homonuclear bond E–E.

Stable digermenes with bulky substituents can serve as efficient sources of germylenes. Digermenes with small substituents are short-lived species and are usually cyclised into cyclotetragermanes.

The formation of a germylene from tetraaryldigermene preliminarily synthesised by the photodecomposition of the corresponding trigermane was described.[17]

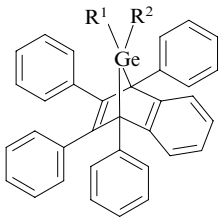
$$(2,6\text{-}Et_2C_6H_3)_2Ge{=}Ge(C_6H_3Et_2\text{-}2,6)_2 \xrightarrow{h\nu} 2\,(2,6\text{-}Et_2C_6H_3)_2Ge.$$

Aryl-substituted digermanes and silylgermanes $R^1R^2_2Ge-GeR^2_3$, $R^1R^2_2Ge-GeR^1R^2_2$ and $R^1R^2_2Ge-SiR^2_3$ (R^1, R^2 = Ar) were synthesised and studied by laser flash photolysis and matrix-isolation methods.[29–32] It was demonstrated that this kind of compounds are germylene precursors. Germanium-containing naphthalenes were distinguished as a separate class of precursors with properties similar to those of phenyl-substituted digermanes. Thus for photochemical reactions of 1-(pentamethyldigermanyl)naphthalene (PMDGN) (**2**), the transient species were identified and the composition of final products was determined using the methods of flash and steady-state photolyses.[33]



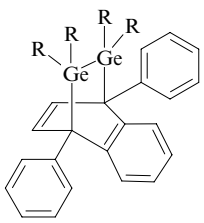
2

Among the most convenient and frequently used germylene sources, a special place belongs to bicyclic compounds that contain germanium atom(s) in their bridges, namely, 7,7-dialkyl(diaryl or alkylaryl)-7-germanorbornadienes **3a–e** (see Refs 24, 25 and 34) and 7,8-digermabicyclo[2.2.2]octadienes **4a**,**b**. The latter serve as precursors of both germylenes and digermenes.



3a–e

R^1 = R^2 = Me (**a**), Et (**b**), Bu^n (**c**), Ph (**d**); R^1 = Me, R^2 = Ph (**e**).

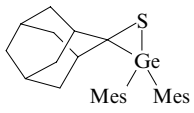


4a,**b**

R = Me (**a**), Et (**b**).

Photolysis of 7,7,8,8-tetramethyl-1,4-diphenyl-1,3-benzo-7,8-digermabicyclo[2.2.2]octa-2,5-diene (**4a**) was described for the first time by the authors of Ref. 35. Light-initiated reactions of these compounds were explored[36,37] by flash photolysis, matrix isolation and CIDNP methods.

The literature also contains a description of the photodecomposition of thiagermiranes, for example, compound **5**, to afford the corresponding germylene and digermene.[38]



5

Mes = 2,4,6-$Me_3C_6H_2$.

Thus, the precursors of reactive transient species of bivalent germanium are rather diverse. The wide choice of molecules with the desired and convenient spectroscopic and photochemical parameters makes it possible to carry out different pulse and steady-state experiments on the determination of properties of primary short-lived products.

III. Generation of transient species in the photolysis of germanium-containing compounds in low-temperature matrices

In chemistry and photochemistry of germanium-containing compounds, the identification of optical spectral bands of germylenes and other transient species faces an essential problem associated with the strong dependence of the absorption band peak position (λ_{max}) on the experimental conditions. Moreover, both the method of species generation and the precursor type, on the one hand, and the solvent nature and temperature, on the other hand, are significant. According to modern concepts,[4] one of the main reasons for this effect could be a trend of germylenes towards complexation with Lewis acids and bases. The detection of active species involves either their stabilisation in low-temperature matrices or the use of methods with short detection times (time-resolved methods). Below, we consider the results of studies of short-lived germanium-containing intermediates that appear in the photolysis of different precursors in low-temperature matrices.

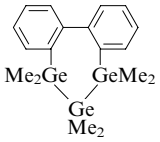
The first matrix-frozen germanium-containing compound subjected to the photolysis was $(2,6\text{-}Et_2C_6H_3)_2Ge(SiMe_3)_2$.[17] The germylene formation was deduced solely from the analysis of final products obtained after the matrix was annealed.

Upon the photolysis (the excitation wavelength λ = 254 nm) of 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-germanorborna-2,5-diene (Me_2GNB) (**3a**) in 3-methylpentane (3-MP) glasses at 77 K, the optical spectra displayed absorp-

tion bands with maxima at 420 and 317 nm.[24,25] The first band, which decayed above the matrix melting point, was assigned to dimethylgermylene (Me_2Ge). The second band, which remained in the spectrum after the sample was annealed, was attributed to 1,2,3,4-tetraphenylnaphthalene (TPN) (**6**).

Photolysis of bis(trimethylsilyl)germane $R_2Ge(SiMe_3)_2$ derivatives (R = 2,6-$Me_2C_6H_3$, 2,6-$Et_2C_6H_3$, 2,4,6-$Me_3C_6H_2$) in 3-MP glasses made it possible to record optical spectra for a series of substituted germylenes.[25] Table 1 shows spectral characteristics of germylenes formed from different precursors. It is evident that the absorption maxima of observed bands fall in a range of 400 – 570 nm. (The nature of an electronic transition corresponding to germylene absorption bands is discussed below). It is noteworthy that the extinction coefficients of bands in low-temperature matrix spectra were not determined due to the absence of internal standards; the quantum yields of germylenes described in the cited studies were also absent.

Table 1. Positions of absorption maxima for diorganylgermylenes in a 3-methylpentane matrix ($T = 77$ K).

Germylene	Precursor	λ_{max}/nm	Ref.
Me_2Ge	$Me_2Ge(N_3)_2$	405	28
	$PhMe_2GeSiMe_3$	418	29
	3a	420	24, 25
	$Me_2Ge(SePh)_2$	420	27
	$Me_2Ge(GePhMe_2)_2$	422	12, 22, 23
		430	21
	cyclo-Ge_6Me_{12}	430	11, 12
	$Me(Me_2Ge)_5Me$	436	12
	cyclo-Ge_5Me_{10}	506	19
Et_2Ge	**3b**	440	25
Bu^n_2Ge	**3c**	440	25
PhMeGe	**3e**	440	25
	$PhMeGe(GeMe_3)_2$	456	22
Ph_2Ge	**3d**	466	25
	$Ph_2Ge(SiMe_3)_2$	466	25
	$Ph_2Ge(GeMe_3)_2$	462	22
$(4\text{-}MeC_6H_4)_2Ge$	$(4\text{-}MeC_6H_4)_2Ge(SiMe_3)_2$	471	25
$MesBu^tGe$	$MesBu^tGe(SiMe_3)_2$	508	25
$(2,6\text{-}Me_2C_6H_3)_2Ge$	$(2,6\text{-}Me_2C_6H_3)_2Ge(SiMe_3)_2$	543	25
$(2,6\text{-}Et_2C_6H_3)_2Ge$	$(2,6\text{-}Et_2C_6H_3)_2Ge(SiMe_3)_2$	544	25
Mes_2Ge	$Mes_2Ge(SiMe_3)_2$	550	25
$(2,4,6\text{-}Pr^i_3C_6H_2)_2Ge$	$(2,4,6\text{-}Pr^i_3C_6H_2)_2Ge(SiMe_3)_2$	558	25

In 'soft' matrices,† germylene molecules even those containing substituents move and gradually undergo dimerisation to digermenes. At liquid nitrogen temperature, this proceeds over tens and hundreds of minutes. Dimerised products exhibit absorption bands at shorter wavelengths. Thus digermene $(Mes_2Ge)_2$ has an absorption band with the maximum at 406 nm, whereas the corresponding germylene (Mes_2Ge) absorbs at 550 nm (see Table 1). In 'soft' 3-MP – IP matrices, several germylene complexes with organic molecules were synthesised.[25] As a rule, complexation substantially shifts the optical absorption bands to shorter wavelengths.

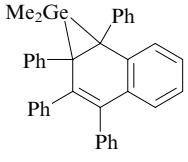
Photolysis of Me_2GNB (**3a**) in a low-temperature toluene-d_8 matrix was observed[39] to give rise to an optical absorption band with the maximum at 420 nm, the same as for many other germanium-containing compounds (see Table 1). However, the authors of this study assigned this band not to a germylene but rather to a biradical $TPN^{\bullet} - {}^{\bullet}GeMe_2$ that appears on the cleavage of merely one Ge – C bond. This assumption was based on the absence of noticeable decomposition of germanorbornadiene upon the annealing of the irradiated matrix. According to the authors, on heating of the matrix, the homolysis of the second Ge – C bond proceeds much slower than the recombination of the first one. At higher temperatures, the rate constant for the second-bond homolysis may increase to the greater extent than the recombination rate constant. For this reason, in contrast to photolysis in matrices, photolysis in solutions leads to the decomposition of germanorbornadiene **3a**.

The data in Table 1 demonstrate that the position of the absorption band maximum (405 – 506 nm) in spectra of Me_2Ge formed in low-temperature matrices from different precursors varies over a wide range. One of the reasons for the band shift could be the different geometry of matrix-isolated germylenes. As is seen from Table 1, the absorption band maxima of germylenes with bulk substituents are shifted up to ~560 nm. As shown below, in such germylenes, the C – Ge – C angle is substantially larger due to the repulsion of substituents, which results in the long wavelength shift of the band. Apparently, in low-temperature matrices, too, Me_2Ge species generated from different precursors also have different C – Ge – C angles.

IV. Laser flash photolysis of germanium-containing compounds in solutions. Optical spectra of germylenes

Matrix isolation allows one to determine the spectroscopic parameters of reactive species but does not provide any kinetic information on their formation. The time resolution of an order of magnitude of 10 ns, which is typical of laser flash photolysis, offers a possibility for measuring rate constants for the fastest bimolecular reactions. At present, this method is widely used in photochemistry of germanium-containing compounds for studying transient species; this allowed optical spectra to be recorded and different reaction channels to be studied for many germylenes.

One of the earliest studies[39] was devoted to the lamp flash photolysis of Me_2GNB (**3a**) solutions with 5 μs time resolution. Two absorption bands of transient species with maxima at 380 and 460 nm were observed. Experiments with the addition of dimethylgermylene acceptors into the solution have shown that this species is responsible for the first band. A comparison of absorbances at 380 nm (recorded immediately after the flash) and 320 nm (in 50 ms), *i.e.*, corresponding to the absorption range of TPN (**6**), the second stable product of norbornadiene decomposition, made it possible to determine the extinction coefficient of the dimethylgermylene band ($\varepsilon^{380} = 1300$ litre mol^{-1} cm^{-1}). The second band with the maximum at 460 nm in the original spectrum was assigned to germabenzonorcaradiene **7**, the product of the subsequent recovery of the broken Ge – C bond.



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A later publication[34] described the results of laser flash photolysis (248 nm) of compound **3a** in methylcyclohexane

† At 77 K, the viscosity of 3-MP mixtures with isopentane (IP) is in the range of $10^{12} - 10^7$ Ps (g s^{-1} cm^{-1}),[25] which allows one to call them 'soft'.

with 10 ns time resolution. It was found that upon a laser pulse, two wide bands with maxima at 330 and 490 nm appeared, which were assigned to the triplet–triplet (T–T) absorption of a TPN (**6**) molecule. The same bands appeared when the solutions of tetraphenylnaphthalene itself were subjected to flash photolysis. In both cases, the spectral bands decayed upon the addition of oxygen into the reaction mixture; moreover, these reactions were characterised by similarly high rate constants (1.5×10^9 litre mol^{-1} s^{-1}). Note that such rate constants are typical of quenching of triplet states of molecules. Thus, no absorption that could have been assigned to dimethylgermylene was observed. This contradicts both the results of flash photolysis [39] and the data on the photolysis of Me_2GNB (**3a**) in low-temperature matrices [26] (see Table 1).

It was assumed [34] that, upon the germylene elimination, an excited **3a** molecule transforms into an excited TPN (**6**) molecule as a result of dissociation. The transient Me_2Ge was not detected because its lifetime is shorter than several hundreds of nanoseconds. The high quantum yield ($\varphi \sim 0.4$) of the conversion

$$^1(Me_2GNB)^* \longrightarrow {}^1(TPN)^*$$

points to the fast (on the picosecond time scale) homolytic cleavage of two Ge–C bonds. In this case, the luminescence with a lifetime of 3 ns observed on the excitation of Me_2GNB (**3a**) can only be attributed to singlet-state ^{1}(TPN)* luminescence. It should be noted that this explanation is inconsistent with the CIDNP effects observed on the photolysis of compound **3a**, which will be discussed in Section XIII.

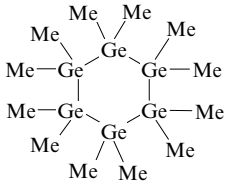
An attempt to obtain a spectrum of Ph_2Ge germylene on the flash photolysis (248 nm) of 7,7-diphenyl-7-germanorbornadiene **3d** in hexane was unsuccessful.[40] Strong T–T absorption of tetraphenylnaphthalene **6**, which was present in the reaction mixture as an impurity (5%), prevented the detection of the weak germylene signal.

Photodissociation of many other compounds to generate germylenes occurred without any complications associated with the formation of excited triplet molecules, in contrast to the case of compounds **3a**,**e**. Thus laser flash photolysis of aryl-substituted linear trigermanes $R^1_3Ge-GeR^2R^3-GeR^1_3$ (R^1-R^3 = Me, Ph) led to the appearance of two absorption bands with maxima in the ranges of 320–330 and 420–450 nm in the spectra recorded after the pulse.[22, 23] Both bands decayed with second-order kinetics. The use of double-pulse excitation made it possible to prove that germylene forms upon extrusion from an excited molecule

$$R^1_3Ge-GeR^2R^3-GeR^1_3 \xrightarrow{h\nu} (R^1_3Ge)_2 + R^2R^3Ge.$$

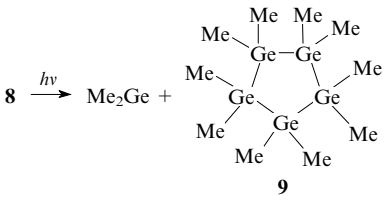
The analysis of kinetic data has shown that germylenes possess long-wavelength absorption bands in the range of 420–450 nm. Short-wavelength bands (320–330 nm) might be associated with digermanes $(R^1_3Ge)_2$; however, these species have absorption bands in the range of 370–380 nm (see Section XI). Presumably,[22, 23] the homolytic cleavage of the Ge–Ge bond to form digermyl radicals that absorb in the range of 320–330 nm (see Section X) can occur simultaneously with the germylene extrusion. According to the results of laser flash photolysis, the positions of germylene absorption bands (420–450 nm) are well consistent with the results on the trigermane photolysis in low-temperature matrices,[21, 22] which demonstrated similar bands (see Table 1).

Laser flash photolysis (266 nm) of dodecamethylcyclohexagermane (**8**) in cyclohexane [11] led to the appearance of an absorption band with the maximum at 450 nm in the optical spectrum.



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The decay of this band according to the second-order kinetics (the effective rate constant $k/\varepsilon = 2.7 \times 10^7$ cm s^{-1}, where k is the reaction rate constant and ε is the extinction coefficient of the band) was accompanied by the appearance of a new band at 370 nm. The first band belongs to dimethylgermylene and the second one belongs to its dimerisation product, namely, digermene $(Me_2Ge)_2$. Photolysis of compound **8** in a low-temperature 3-MP matrix also resulted in the appearance of a germylene (identified by a band at 430 nm, see Table 1). Apparently, the shift of the band maximum to shorter wavelengths by 20 nm is explained by the changes in the reaction temperature and the solvent nature. Presumably,[11] dimethylgermylene is generated from the excited state of the parent molecule without the formation of transient germyl radicals.



9

On excitation (266 nm) of decamethylcyclopentagermane (**9**) in cyclohexane, [19] an absorption band with the maximum at 490 nm appeared in the spectrum immediately after the laser pulse and then decayed at a rate corresponding to the second-order kinetics ($k/\varepsilon = 3.5 \times 10^7$ cm s^{-1}). As it decayed, a new band with the maximum at 370 nm grew and then also decayed by the second-order kinetics ($k/\varepsilon = 4.8\ 10^6$ cm s^{-1}). The former band belonged to dimethylgermylene and the latter corresponded to its dimerisation product $(Me_2Ge)_2$. Photolysis of compound **9** in a 3-MP matrix led to the appearance of a band with the maximum at 506 nm, which was also assigned to germylene. Thus, for unknown reasons, spectra of germylenes formed from cyclopolygermanes **8** (Ref. 11) and **9** (Ref. 19) in cyclohexane solutions demonstrated absorption bands shifted with respect to one another by 40 nm. Moreover, for the germylene formed from compound **9**, the absorption band maximum in the low-temperature matrix shifted to long wavelengths.

Of considerable interest are experiments [33] on subjecting a solution of 1-(pentamethyldigermanyl)naphthalene (**2**) in cyclohexane to laser flash photolysis (308 and 337 nm). Two absorption bands with maxima at 440 and 400 nm appeared in the spectrum immediately after the flash, and a new band at 460 nm appeared in 10 μs. The band at 440 nm assigned to dimethylgermylene decayed with second-order kinetics ($k/\varepsilon = 2.5 \times 10^7$ cm s^{-1}), which suggests the formation of a digermene $(Me_2Ge)_2$. The latter is presumably responsible for the band with the maximum at 400 nm. A comparison of the time of germylene appearance with the compound **2** fluorescence lifetime made it possible to conclude that dimethylgermylene forms from the parent molecule in the excited singlet state. The subsequent appearance of an additional band at 460 nm was explained by the T–T absorption of the parent molecule **2**. However, the 10 μs delay in the appearance of the triplet state ^{T}(PMDGN), which forms from the same excited singlet state ^{S}(PMDGN) as dimethylgermylene, still remains unexplained.

A spectrum recorded on the laser flash photolysis (248 and 266 nm) of a solution of dimethylphenyl(trimethylsilyl)germane ($PhMe_2Ge-SiMe_3$) in cyclohexane demonstrated a broad absorption band with the maximum at 425 nm, which was explained by the appearance of dimethylgermylene.[29]

$$PhMe_2GeSiMe_3 \xrightarrow{h\nu} Me_2Ge + PhSiMe_3.$$

A similar intense absorption band with the maximum at 420 nm (together with two weaker bands at 330 and 490 nm and an additional shoulder in the vicinity of 380 nm) was observed upon a laser flash impact (308 nm) on a solution of dimethylbis(phenylseleno)germane [$Me_2Ge(SePh)_2$] in cyclohexane.[27] To identify the absorption bands, $Me_2Ge(SePh)_2$ was photolysed in 3-MP (77 K) and Ar (21 K) matrices. Upon irradiation (254 nm) of these matrices, similar spectra that contained the same bands as in flash photolysis experiments were observed. A band at 330 nm was assigned to a diphenyl diselenide molecule and the absorption at 490 nm was attributed to the radical PhSe$^{\bullet}$ formed from this molecule.

$$Me_2Ge(SePh)_2 \xrightarrow{h\nu} Me_2Ge + PhSeSePh,$$

$$PhSeSePh \xrightarrow{h\nu} 2\,PhSe^{\bullet}.$$

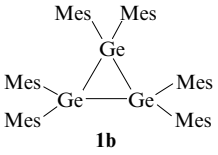
Thus, the remaining band (420 nm) might belong to dimethylgermylene. EPR spectra of irradiated matrices showed that the shoulder at 380 nm is related to the appearance of the radical PhSe$^{\bullet}$.

Germylene Mes_2Ge represents a transient species that formed on the laser flash photolysis (248 nm) of dimesitylbis(trimethylsilyl)germane [$Mes_2Ge(SiMe_3)_2$] in hexane.[13] After a flash, absorption bands at 550 and 320 nm were observed. A band at 550 nm decayed according to the second-order kinetics over *ca.* 10 μs with the simultaneous formation of a new band with the maximum at 405 nm. These spectral and kinetic transformations were explained by the following reaction sequence:

$$Mes_2Ge(SiMe_3)_2 \xrightarrow{h\nu} Mes_2Ge + Me_3SiSiMe_3,$$

$$2\,Mes_2Ge \longrightarrow Mes_2Ge{=}GeMes_2.$$

According to the data on the photolysis of organylgermanes in low-temperature matrices (see Table 1), the band at 550 nm was assigned to germylene Mes_2Ge and the band at 405 nm was assigned to digermene $Mes_2Ge{=}GeMes_2$. A band similar to the former was observed on the photolysis of hexamesitylcyclotrigermane (cyclo-Ge_3Mes_6, **1b**).[13] The absorbance in a band at 405 nm that appeared immediately after the pulse increased in the process. These data are well described by the following reaction scheme:



1b

$$\xrightarrow{h\nu} Mes_2Ge + Mes_2Ge{=}GeMes_2,$$

$$2\,Mes_2Ge \longrightarrow Mes_2Ge{=}GeMes_2.$$

Flash photolysis (266 nm) of phenyl-substituted digermanes $(Ph_nMe_{3-n}Ge)_2$, where $n = 1-3$, in tetrahydrofuran[30] also led to the appearance of two absorption bands in the optical spectrum, namely, in ranges of 440–470 and 315–330 nm. The long-wavelength absorption bands of germylenes decayed with quasi-first-order kinetics, presumably, in their reaction with THF (for $n = 2$ and 3, the rate constants were 1.1×10^5 and 2.0×10^5 s^{-1}, respectively). The short-wavelength band assigned to germyl radicals $Ph_nMe_{3-n}Ge^{\bullet}$ decayed with second-order kinetics with the observed rate constants (k_{obs}) in the range of $(1.9-4.3) \times 10^5$ s^{-1}.

The absorption band of germylene Ph_2Ge with the maximum at 445 nm was observed on the flash photolysis (266 nm) of a bis(trimethylsilyl)diphenylgermane [$Ph_2Ge(SiMe_3)_2$] solution in cyclohexane.[41] The absorption decayed with second-order kinetics ($k_{obs} = 3.7 \times 10^5$ s^{-1}) and was accompanied by growth of a new band at 320 nm. The latter corresponds to diphenyldigermene ($Ph_2Ge{=}GePh_2$) and also decayed with second-order kinetics ($k_{obs} = 1.5 \times 10^5$ s^{-1}).

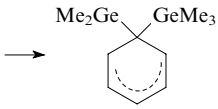
$$Ph_2Ge(SiMe_3)_2 \xrightarrow{h\nu} Ph_2Ge + Me_3SiSiMe_3,$$

$$2\,Ph_2Ge \longrightarrow Ph_2Ge{=}GePh_2,$$

$$2\,Ph_2Ge{=}GePh_2 \longrightarrow \text{cyclo-}Ge_4Ph_8.$$

Studies of solutions of digermane $PhMe_2GeGeMe_3$ in cyclohexane revealed the appearance of two absorption bands with maxima at 430 and 320 nm 200 ns after a flash (266 nm).[31] Presumably, the long wavelength band belongs to a dimethylgermylene formed in the following reactions:

$$PhMe_2GeGeMe_3 \xrightarrow{h\nu} [PhMe_2Ge^{\bullet} + {}^{\bullet}GeMe_3]_{cell} \longrightarrow$$



$$\longrightarrow GeMe_2 + PhGeMe_3.$$

This dimethylgermylene decayed with second order kinetics ($k/\varepsilon = 3.2 \times 10^7$ cm s^{-1}). The short-wavelength band at 320 nm corresponds to the germyl radical $PhMe_2Ge^{\bullet}$, which also dimerises ($k/\varepsilon = 7.0 \times 10^7$ cm s^{-1}).

Table 2 shows the positions of absorption band maxima for diorganylgermylenes revealed by the laser flash photolysis. The large number of molecular precursors used and the regular appearance of transient absorption bands in the range of 420–550 nm, and also the detection of similar bands on the photolysis of the same precursors in low-temperature matrices (see Table 1) allows one to conclude that these bands indeed belong to germylenes. However, it should be noted that even in the same solvent, the position of a band maximum might considerably shift when a germylene was generated from different precursors. In matrices, the absorption band maxima for Me_2Ge were located in a narrower interval, 420–440 nm (see Table 1); the exception is the data of a study[19] in which a band with the maximum at 506 nm was assigned to dimethylgermylene.

The position of absorption bands in solutions of germylene Me_2Ge (see Table 2) formed from different precursors varies in the interval of 420–470 nm. In this case, too, the position of the dimethylgermylene absorption band maximum (490 nm) given in Ref. 19 does not fit into this interval. Insofar as the majority of studies used cyclohexane as the solvent (see Table 2), the shift of the absorption band of germylenes generated from different precursors cannot be explained by the solvent effect.

A recently published comprehensive review[44] on gas-phase reactions of germylenes and dimethylstannylene points to a wide scatter of absorption band maxima assigned to dimethylgermylene. Presumably, this suggests that intermediates may have different structures including donor–acceptor complexes of this species.

It should be noted that in recent experiments on the flash photolysis with the better time resolution and the higher sensitivity (experiments with digital signal build-up), the absorption band maxima of germylenes were shifted in the long-wavelength direction. It cannot be ruled out that in earlier

Table 2. Positions of absorption maxima for diorganylgermylenes in solutions observed on laser flash photolysis.

Germylene	Precursor	Solvent	λ_{ex} /nm [a]	λ_{max} /nm	Ref.
Me_2Ge	**3a**	hexane	UV [b]	380	4, 39
	3a	methylcyclohexane	248	–	34
	$Me_2Ge(SePh)_2$	cyclohexane	308	420	27
	$PhMe_2GeGeMe_2GeMe_2Ph$	"	266	420	22, 23
	$PhMe_2GeSiMe_3$	"	248	425	29
	$PhMe_2GeGeMe_3$	"	266	430	31
	$(PhMe_2Ge)_2$	THF	266	440	30
	2	cyclohexane	308	440	33
	8	"	266	450	11
	9	"	266	490	19
	10a [c]	hexane	248	470	40
Et_2Ge	$(Et_2Ge)_n$ (see [d])	cyclohexane	266	430	14
Bu^n_2Ge	$(Bu^n_2Ge)_n$	"	266	450	14
PhMeGe	$(PhMeGe)_n$	"	266	440	14
	$Me_3GeGePhMeGeMe_3$	"	266	440	22, 23
	10b [c]	hexane	248	490	42
	$(Ph_2MeGe)_2$	THF	266	450	31
Ph_2Ge	$Ph_2Ge(SiMe_3)_2$	cyclohexane	266	445	41
	$Me_3GeGePh_2GeMe_3$	"	266	450	22, 23
	$(Ph_2Ge)_2$	THF	266	470	30
	10c [c]	hexane	248	500	43
$(n\text{-}C_6H_{13})_2Ge$	$[(n\text{-}C_6H_{13})_2Ge]_n$	cyclohexane	266	460	14
Mes_2Ge	$Mes_2Ge(SiMe_3)_2$	hexane	248	550	13
	cyclo-Ge_3Mes_6	"	248	550	13
	cyclo-Ge_3Mes_6	"	248	560	43

[a] λ_{ex} is the radiation wavelength used for the precursor excitation; [b] measurements by lamp flash photolysis with time resolution of 5 μs; [c] compounds **10**:  [$R^3 = R^4 = Me$: $R^1 = Ph$, $R^2 = H$ (**a**); $R^1 = R^2 = Me$: $R^3 = Ph$, $R^4 = Me$ (**b**); $R^3 = R^4 = Ph$ (**c**)]; [d] from hereon, the formula $(R_2Ge)_n$ designates germanium-containing polymers ($\bar{M}_w \sim 10^3$).

studies, the shorter wavelength bands that belonged to digermenes were assigned to germylenes due to insufficient resolution times and high recombination rates of intermediates. In the gas phase, the kinetics of reactions of dimethylgermylene formed from different precursors was studied by the absorption in a range of 450–510 nm.[44] The spectra represented a broad band with the maximum at 476.5 nm, which corresponds to the longest-wavelength absorption band observed for germylene in the liquid phase (see Table 2).

In solutions, germylenes are almost always formed in a cage that contains the solvent and the residual precursor. Hence, the formation of germylene complexes with such residues may be assumed as the additional reason for the absorption band shift for germylenes generated from different precursors.

In most cases, germylenes are dimerised to form digermenes. The value $k/\varepsilon \sim (1-5) \times 10^7$ cm s^{-1} shows that the recombination occurs with a high rate constant. The rate constant for bimolecular recombination (k) is unknown because the extinction coefficient of the germylene band was determined in none of the cited studies. As was mentioned above, the value $\varepsilon^{380} = 1300$ litre mol^{-1} cm^{-1} shown in Ref. 39 corresponds to a band with the maximum at 380 nm, which was revealed by the lamp flash photolysis method (time resolution > 5 μs). The position of this band strongly differs from those for germylenes synthesised in later studies by laser flash photolysis. It is only in the past three years that the attempts were undertaken to determine the extinction coefficients of Me_2Ge and Ph_2Ge species. For dimethygermylene, $\lambda_{max} = 470$ nm, $\varepsilon = 730$ litre mol^{-1} cm^{-1} (Ref. 40) and for diphenylgermylene, $\lambda_{max} = 500$ nm, $\varepsilon = 1850$ litre mol^{-1} cm^{-1} (Ref. 43). Therefore, assuming the extinction coefficient equal to 10^3 litre mol^{-1} cm^{-1}, the dimerisation of germylenes proceeds with a rate constant in a range of $(1-5) \times 10^{10}$ litre mol^{-1} cm^{-1}. This range virtually coincides with the diffusion rate constant of a bimolecular reaction in hexane [2.1×0^{10} litre mol^{-1} cm^{-1} (Ref. 40)].

V. Fluorescence of germylenes

Photolysis of germanium-containing compounds in low-temperature matrices allows one to obtain not only optical absorption spectra, but also luminescence spectra of transient species. Luminescence of dimethylgermylene was first observed upon photolysis of dodecamethylcyclohexagermane (**8**) in a 3-MP matrix.[11] The spectrum represented a broad band with the maximum at 650 nm and was the mirror image of the dimethylgermylene absorption band with the Stokes shift of 7870 cm^{-1}. The fluorescence lifetime was 1–2 ns. Assuming that both the absorption and the fluorescence were due to the transitions between the ground (S_0) and the first excited (S_1) singlet states, the positions of band maxima allow one to determine the energy of the 0–0 transition (2.4 eV). The large Stokes shift was attributed to a considerable increase in the C–Ge–C angle in the first excited singlet state as compared with the ground state.

Fluorescence spectra of certain germylenes synthesised from different molecular precursors can be found in Ref. 12. All germylenes demonstrated an emission band with the maximum in the range of 620–650 nm (Table 3) and a considerable Stokes shift. Fluorescence excitation spectra coincided with the absorption spectra of these species. The energy of the 0–0 transition of germylenes was 2.04–2.43 eV.

Table 3. Fluorescence maxima and the Stokes shift for diorganylgermylenes in 3-MP matrices ($T = 77$ K).

Germylene	Precursor	λ_{max}/nm	Stokes shift/cm^{-1}	Ref.
Me_2Ge	**8**	650	7870	11
	$Me(Me_2Ge)_5Me$	628	7012	12
	$Me_2Ge(GePhMe_2)_2$	623	7645	12
	3a	620	7909	12
PhMeGe	$PhMeGe(GeMe_3)_2$	645	6426	12
Ph_2Ge	$Ph_2Ge(GeMe_3)_2$	651	6285	12

VI. Electronic structure of germylenes and the nature of their optical absorption band

Whereas carbenes are characterised by the triplet ground state,[45,46] the calculations by different quantum chemical methods have shown that the germylene ground state is singlet (Table 4). This was also confirmed by the absence of signals in the EPR spectra of matrices frozen at 77 and 10 K and containing a germylene accumulated on irradiation.[11] The singlet–triplet splitting in germylenes X_2Ge substantially depends on the nature of substituent X (X = H, Me, F, Cl, Br) and lies in the range of 84–355 kJ mol^{-1} ($\sim$1–4 eV).[45] As regards energy, the excited singlet state is higher than the ground state by > 188–209 kJ mol^{-1}.[46] On germylene excitation, the Ge–X bond distance changes insignificantly; however, the X–Ge–X angle between the bonds substantially increases. The results of quantum chemical calculations of the structure and electronic state energies for carbene heavy analogues including germylenes were comprehensively surveyed in several studies.[8,9] The calculations showed a slight decrease in the E–X bond distance (E = C, Si, Ge) and a substantial increase in the X–E–X angle upon the transition of all carbenes and their analogues into the excited states.

Table 4. Calculated energies (E/kJ mol^{-1}), bond lengths (r_e/Å) and angles between X–Ge–X bonds (q_e/deg) for the ground ($^1A_1$) and electronically excited ($^3B_1$, $^1B_1$) electronic states of germylenes.

Germylene	Parameter	Electronic state			Ref.
		$^1A_1$	$^3B_1$	$^1B_1$	
H_2Ge	E	0	43.5–123.1	182.9–199.3	47–55
	r_e	1.595 ± 0.018	1.543 ± 0.018	1.548 ± 0.005	
	q_e	92.3 ± 1.0	119.1 ± 0.5	122.7 ± 0.6	
Me_2Ge	E	0	57.3–128.3	213.1	45, 47,
	r_e	2.022 ± 0.005	2.004 ± 0.004	2.021	53, 56
	q_e	97.1 ± 1.6	118.0 ± 0.5	122.0	
Ph_2Ge	E	0	–	–	57
	r_e	2.006	–	–	
	q_e	101.6	–	–	

The optical absorption bands of germylenes shown in Tables 1 and 2 are attributed to the electronic transition from the binding $2a_1$ orbital of a germylene X_2Ge (a linear combination of the 4s and $4p_z$ orbitals of the germanium atom with the σ orbitals of the substituent X) to the non-bonding $1b_1$ orbital, which is the $4p_y$ orbital of the Ge atom. Presumably, germylenes are characterised by the C_{2v} symmetry group. In this group, the $^1A_1 \rightarrow {}^1B_1$ transition between the terms is permitted as regards the symmetry; however, the orbitals lie in different planes, which decreases their overlap and reduces the transition intensity. Apparently, for this reason the molar extinction coefficient of the germylene band does not substantially exceed 10^3 litre mol^{-1} cm^{-1}.

VII. Spectroscopy of germylene complexes

The presence of a vacant antibonding $4p_y$ orbital of the germanium atom in germylenes makes possible the formation of donor–acceptor complexes of these species with different molecules. Spectroscopic studies of such complexes are often carried out in low-temperature matrices. The UV irradiation of a matrix containing a germanium precursor and a potential complexing agent leads to the accumulation of a germylene. Subsequent annealing and refreezing of the matrix makes it possible to obtain a germylene complex and record its spectrum. This procedure allowed the optical absorption bands of germylene complexes with organic molecules including those containing heteroatoms to be observed.[26]

For instance, in the spectrum of a 3-MP–IP matrix in the presence of triethylamine, the absorption band of dimesitylgermylene (Mes_2Ge) with the maximum at 550 nm decayed upon annealing and a new band at 414 nm was formed.

Table 5 shows the positions of maxima of new bands that appeared upon the matrix refreezing and belong to germylene complexes. As is seen, the binding of a germylene into a complex shifts the absorption band to shorter wavelengths. Absorption bands of germylene complexes with molecules containing P, N, S and O atoms lie in the range of 306–376 nm. Apparently, this is explained by the interaction of the vacant $4p_y$ orbital of the germylene atom with orbitals of heteroatoms of organic molecules, which changes the energy of the corresponding n–π transition.[3,25]

The studied germylene–heteroatomic compound complexes were unstable and dissociated as the matrix temperature increased so that germylenes either dimerised to digermenes with the absorption bands in approximately the same spectrum range or were inserted into different bonds. Thus for a 3-MP–IP matrix, a band of the $Bu^n_3P \cdot Ge(C_6H_2Pr^i_3\text{-}2,4,6)_2$ complex at 334 nm was preserved at 153 K[25] but gradually decayed at 173 K with the appearance of the corresponding digermene signal. At 194 K, the lifetime of such a complex was 48 s. The germylene complex with dimethyl sulfide was stable only at 133 K. Certain complexes of this kind decomposed as the matrix melted. As was first observed in Ref. 12, a slight short-wavelength shift ($\sim$10 nm) of the germylene absorption band accompanies the formation of a germylene complex with aromatic molecules containing π-systems, namely, benzene and naphthalene (see Table 5).

At 77 K, the 3-MP–IP matrix is so 'soft' that germylenes can diffuse in it. Upon the addition of ethanol into this matrix, the storage of an irradiated sample in it is accompanied by the decay of the germylene absorption band even at 77 K and the growth of a new absorption band with the maximum at 320–367 nm, which belongs to a germylene complex with ethanol (see Table 5).

An argon matrix containing germane (GeH_4) and ozone was studied at 14–18 K.[58] The analysis of numerous bands in the IR spectrum that appeared on irradiation in different spectral ranges allowed the identification of certain species including germylene complexes with a water molecule. Presumably, the complex was formed in the reaction

$$GeH_4 + O_3 \xrightarrow{h\nu} H_2Ge \cdot OH_2 + O_2.$$

The IR spectrum of the complex $H_2Ge \cdot OH_2$ demonstrated absorption bands with frequencies of 1586, 3597, 3687 cm^{-1}, which are close to the vibrational frequencies of a free water molecule in an argon matrix (the matrix contained no water before excitation). Moreover, the H_2Ge fragment of this complex exhibited a triplet signal (1777, 1794, 1814 cm^{-1}) and a low-frequency line (898 cm^{-1}) that corresponded to vibrations of H–Ge–H bonds. A frequency of 1794 cm^{-1} is close to the double frequency of 898 cm^{-1} being its overtone.

Table 5. Absorption maxima for germylene complexes with complexing molecules in low-temperature (T = 77 K) matrices.

Complexing agent	λ_{max}/nm					Ref.
	Me_2Ge	Ph_2Ge	Mes_2Ge	$(2,6\text{-}Et_2C_6H_3)_2Ge$	$(2,4,6\text{-}Pr^i_3C_6H_2)_2Ge$	
3-MP Matrix						
3-MP	420	466	550	544	558	25, 26
Bu^n_3P	–	–	306	314	334	25, 26
1-Azabicyclo[2.2.2]octane	–	334	349	356	363	25, 26
Me_2S	–	326	348	357	357	25, 26
Thiophene	–	332	352	359	366	25, 26
2-Methyltetrahydrofuran	–	325	360	369	376	25, 26
cyclo-$C_6H_{11}Cl$	341	374	495	508	544	25, 26
PhCl	392	403	538	532	553	25, 26
Et_3N	–	–	414	–	445	25, 26
EtOH	–	320	333	332	–	25, 26
Bu^tOH	–	332	363	367	–	25, 26
$CH_2{=}CHCH_2Cl$	–	–	530	–	–	25, 26
$(CH_2{=}CHCH_2)_2S$	–	–	380	–	–	25, 26
Matrix 3-MP – IP (4 : 1)						
3-MP – IP	436	–	–	–	–	12
PhH	422	–	–	–	–	12
Haphthalene	422.5	–	–	–	–	12

Note. Precursors: for Me_2Ge, Me_2GeNB (**3a**) [25, 26] and $Me(GeMe_2)_5Me$;[12] for Ph_2Ge, Ph_2GeNB (**3d**); for the rest germylenes, $R_2Ge(SiMe_3)_2$.

Moreover, the flash photolysis method allows one to detect germylene complexes with different molecules also in solutions. An optical spectrum of a dimethylgermylene complex with triphenylphosphine represented a broad band with the maximum at 370 nm and the extinction coefficient of 7.5×10^3 litre mol^{-1} cm^{-1}.[4, 59]

$$Me_2Ge + PPh_3 \longrightarrow Me_2Ge \cdot PPh_3. \quad (1)$$

The use of a competitive reaction of dimethylgermylene with CCl_4 made it possible to determine the rate constant of reaction (1), $k = 6.5 \times 10^8$ litre mol^{-1} s^{-1}. The $Me_2Ge \cdot PPh_3$ complex disappeared with the second-order kinetics presumably to form digermene (or a digermene complex with triphenylphosphine) with the rate constant $2k = 1.5 \times 10^9$ litre mol^{-1} s^{-1}. However, from our viewpoint, these results should be checked, because the earlier studies on the lamp flash photolysis of germanorbornadiene with the same time resolution (5 μs) [39] failed to correctly identify the transient absorption band at 380 nm.

An absorption band with the maximum at 325 nm was assigned to complexes $R_2Ge \cdot NBu^nH_2$ (R = Me, Ph).[43] Complexes $PhMeGe \cdot NR^1_2R^2$ ($NR^1_2R^2 = NH_2Bu^n$ and NEt_3) were characterised by bands at 330 nm.[42] The absorption of germylene (PhMeGe) complexes with molecules that contain double bonds [isoprene, 2,3-dimethylbuta-1,3-diene (DMB), 4,4-dimethylpent-1-ene] was shifted to shorter wavelengths ($\lambda_{max} \sim 275$ nm).[42] A comparison of these data with the position of absorption bands of complexes in low-temperature matrices (see Table 5) shows that in solutions, the spectrum substantially (by ~100 nm) shifts to shorter wavelengths. Provided the interpretation of the absorption band is correct, this shift may be associated with the different geometries of complexes in solutions and low-temperature matrices.

Thus, germylenes efficiently form complexes with organic molecules. In spectra of these complexes, the light absorption bands are substantially shifted as compared with germylene signals. For this reason, in the studies of optical spectra and kinetics of germylene reactions, the potent complexing agents should be removed from the solution. Data on germylene complexes are shown in a review.[9]

VIII. Vibrational spectra of germylenes

On irradiation of germane (GeH_4) isolated in an argon matrix at 4 K with visible and UV light the IR spectrum demonstrated lines that belonged to different photolysis products.[60] Among numerous signals, the lines of germylenes H_2Ge and D_2Ge with frequencies of 1887, 1864, 920 cm^{-1} and 1329, 1325, 662 cm^{-1}, respectively, were identified. These frequencies correspond to two stretching and one vibrations of Ge – H(D) bonds.

An IR spectrum of dimethylgermylene was recorded in a cryogenic (12 K) argon matrix under UV irradiation (254 or 248 nm) of diazidodimethylgermane $[Me_2Ge(N_3)_2]$.[28] The preliminary irradiation of $Me_2Ge(N_3)_2$ in hydrocarbon matrices at 77 K in the presence of molecules-scavengers of germylenes and the analysis of trapping products showed that diazide is the source of Me_2Ge. In an argon matrix, the majority of bands observed in the IR range belonged to methyl group vibrations; however, in the 600 – 500 cm^{-1} range, bands corresponding to vibrations of Ge – C bonds were observed (Table 6).

Table 6. Vibrational frequencies (ν/cm^{-1}) of argon matrix-isolated Me_2Ge at 12 K and stable $[(Me_3Si)_2CH]_2Ge$ germylene in crystalline state.

Germylene	Vibration	Experiment		Calculation	
		ν	Ref.	ν	Ref.
Me_2Ge	ν(Ge – C)	541	28	560	47
	ν(Ge – C)	527	28	497	47
	δ(C – Ge – C)			288	47
$[(Me_3Si)_2CH]_2Ge$	ν(Ge – C)	643	61	–	–
	ν(Ge – C)	613	61	–	–

Quantum chemical calculations of vibrational frequencies of Ge – C bonds were carried out [47, 50, 62 – 64] for the ground and excited states of two germylenes, namely, H_2Ge and Me_2Ge (Table 7). It was shown [28, 60] that all frequencies calculated for the ground states of these species are well consistent with those measured in an argon matrix. Modern laser spectroscopic

Table 7. Calculated and experimental vibrational frequencies (ν /cm^{-1}) for ground and electronically excited states of germylene and dimethylgermylene.

Species	Method	Term	ν_1	ν_2	ν_3	Ref.
Calculation						
H_2Ge	CF-CI	$^1A_1$	1857	923	1866	50
	CI	$^1A_1$	1887	958	2036	47
		$^3B_1$	1855	924	2063	
		$^1B_1$	1864	860	2011	
	CASSCF	$^1A_1$	1840	913	1840	64
		$^3B_1$	1998	801	2054	
		$^1B_1$	1809	783	1909	
Me_2Ge	SCF	$^1A_1$	560	288	497	47
		$^3B_1$	576	203	611	
		$^1B_1$	554	194	607	
Experiment						
H_2Ge	VUV photolysis in Ar matrix [a]	$^1A_1$	1887	920	1864	60
	LOS	$^1A_1$	1856	916	–	65
	Jet-cooled LIF	$^1B_1$	1798	783	–	64

[a] VUV is Vacuum Ultra Violet.

techniques, namely, Jet-cooled Laser Induced Fluorescence (Jet-cooled LIF) [64] and Laser Optogalvanic Spectroscopy (LOS),[65] made it possible to experimentally determine the vibrational frequencies of H_2Ge in the ground [65] and singlet excited [64] states (see Table 7). These results well agree with those obtained by the theoretical CFCI (Corrected Full Configuration Interaction) [50] and CI (Configuration Interaction) [47] methods and also with the recent quantum-chemical calculations using the CASSCF (Complete Active Space Self-Consistent Field) method.[64] The bending vibrational frequency of the C–Ge–C fragment was twice lower than the stretching vibrational frequency of the Ge–C bond (see Table 7), which is often observed in vibrational spectroscopy. Detailed information on vibrational frequencies of germylenes and their complexes can be found in a review.[9]

IX. Germylene reactions

As was noted above, in the absence of scavenging molecules, germylenes disappear in a second-order reaction, *i.e.*, dimerise to form digermenes. A parameter k_{rec}/ε, where k_{rec} is the rate constant for bimolecular recombination, usually lies in the range of $(1-3)\times10^7$ cm s^{-1} (Table 8). Although the exact extinction coefficient of the germylene band was not measured experimentally, it, as noted above, cannot substantially exceed 10^3 litre mol^{-1} cm^{-1}, because the recombination constant would otherwise exceed the diffusion rate constant.

Germylenes that contain bulky groups as substituents recombinate with substantially lower rate constants as compared with dimethylgermylene. For example, k_{rec}/ε decreases by more than an order of magnitude (see Table 8) when the methyl group is replaced by an ethyl group and by two orders of magnitude for the butyl group substitution. Thus, the steric factor substantially affects the recombination rate.

Sometimes, germylenes disappear in a first-order reaction. Thus the absorption band of diisopropylgermylene (Pr^i_2Ge) with the maximum at 560 nm decays with first-order kinetics over 56 ns.[15] Presumably, Pr^i_2Ge isomerises to 2-germapropene $H_2C{=}CMeGeH_2Pr^i$ so quickly that the dimerisation has no time to compete with this reaction. It was found [31,33] that germylenes PhMeGe (the absorption band maximum at 450 nm) and Ph_2Ge (470 nm) disappear over *ca.* 5–10 μs in a first-order reaction (see Table 8) presumably with the solvent, namely, tetrahydrofuran. However, the same germylenes were dimerised in cyclohexane.[22,23]

Laser flash photolysis studies have demonstrated that germylenes quickly react with oxygen. For Me_2Ge, the rate constant for this reaction in cyclohexane lies in the range of

Table 8. Observed rate constants (k_{rec}/ε) for the germylene loss in recombination reactions (T = 293 K).

Germylene	Precursor	Solvent	λ_{max} /nm	k_{rec}/ε /cm s^{-1}	Ref.
Me_2Ge	$(PhMe_2Ge)_2GeMe_2$	cyclohexane	420	2.5×10^7	22, 23
	8	"	450	2.7×10^7	11
	9	"	490	3.5×10^7	19
	2	"	440	2.5×10^7	33
	$PhMe_2GeSiMe_3$	"	430	1.0×10^7	31
	$PhMe_2GeGeMe_3$	"	430	3.2×10^7	31
	$(PhMe_2Ge)_2$	THF	440	–	30, 32
	10a	hexane	470	5.0×10^7	40
	10d [a]	"	480	7.5×10^7	43
Et_2Ge	$(Et_2Ge)_n$	cyclohexane	430	1.1×10^6 (460 nm) [b]	14
Pr^i_2Ge	cyclo-$Ge_4Pr^i_8$	hexane	560	1.8×10^7 (see [c])	15
Bu^n_2Ge	$(Bu^n_2Ge)_n$	cyclohexane	450	2.4×10^5	14
$(n\text{-}C_6H_{13})_2Ge$	$[(n\text{-}C_6H_{13})_2Ge]_n$	"	460	1.5×10^5 (450 nm) [b]	14
PhMeGe	$PhMeGe(GeMe_3)_2$	"	440	2.2×10^7	22, 23
	$(PhMeGe)_n$	"	440	4.1×10^5 (450 nm) [b]	14
	$(Ph_2MeGe)_2$	THF	450	1.1×10^5 (see [c])	30, 32
Ph_2Ge	$Ph_2Ge(GeMe_3)_2$	cyclohexane	450	3.0×10^6	22, 23
	$(Ph_3Ge)_2$	THF	470	2.0×10^5 (see [c])	30, 32
	$Ph_2Ge(SiMe_3)_2$	cyclohexane	445	~270 [d]	41
	10c	hexane	500	6.0×10^6	66
Mes_2Ge	cyclo-Ge_3Mes_6	"	550	1.1×10^5 (see [c])	13

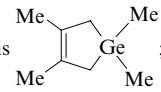
[a] Compound **10d** is  ; [b] wavelength of kinetic measurements is shown; in the other cases, λ_{max}; [c] the first-order reaction rate constant is shown, in s^{-1}; [d] the half-time of transformation (loss) is shown ($\tau_{1/2}$), in μs.

Table 9. Rate constants for germylene reactions with oxygen ($T = 293$ K).

Germylene	Precursor	Solvent	k / litre mol^{-1} s^{-1}	Ref.
Me_2Ge	$Me_2HGeGeMe_3$	see [a]	2.7×10^7	44
	3a	hexane	2.0×10^7	4, 39
	8	cyclohexane	9.7×10^8	11
	$PhMe_2GeSiMe_3$	"	2.0×10^9	29
	$PhMe_2GeSiMe_3$	"	2.1×10^9	31
	$PhMe_2GeSiMe_3$	"	1.7×10^9	31
	9	"	1.6×10^9	19
	$(PhMe_2Ge)_2$	THF	–	30, 32
	10a	hexane	9×10^7	40
PhMeGe	$(Ph_2MeGe)_2$	THF	2.3×10^8	30, 32
	10b	hexane	6×10^7	42
Ph_2Ge	$Ph_2Ge(SiMe_3)_2$	cyclohexane	1.0×10^8	41
	$(Ph_3Ge)_2$	THF	1.8×10^8	30, 32
	10c	hexane	2.7×10^7	66
Mes_2Ge	cyclo-Ge_3Mes_6	"	7.3×10^6	13

[a] In the gas phase.

$(1-2) \times 10^9$ litre mol^{-1} s^{-1} for different precursors (Table 9). These values are 10–20 times lower than the diffusion rate constant of the bimolecular reaction in cyclohexane, which is due to the steric effect and the spin prohibitions for the singlet germylene reaction with a triplet oxygen molecule. The steric effect is pronounced for germylenes with bulky substituents, *e.g.*, Ph_2Ge and Mes_2Ge, which react with oxygen, correspondingly, one- and two-orders-of-magnitude more slowly than dimethylgermylene. Note that the one-order-of-magnitude smaller rate constant obtained for Me_2Ge [4, 39] most probably belongs to the digermene reaction (see Section X).

In a solvent more polar than cyclohexane, namely, tetrahydrofuran, the rate constant decreased by an order of magnitude which was apparently associated with the formation of a $Me_2Ge \cdot THF$ complex that reacted with the oxygen molecule. In the gas phase, the rate constant for the dimethylgermylene reaction with oxygen (4.5×10^{14} cm^3 mol^{-1} s^{-1} = 2.7×10^7 litre mol^{-1} s^{-1}) [44] was two-orders-of-magnitude lower than the constants measured earlier in cyclohexane (see Table 9).

In recently published studies [40, 42, 66] on the laser flash photolysis of solutions of germanium-containing compounds, the rate constants for reactions of germylenes Me_2Ge, PhMeGe and Ph_2Ge with oxygen were determined. These constants turned out to be one-order-of-magnitude smaller (see Table 9) than those measured earlier (*e.g.*, see Refs 11, 19, 30–33, 41). These data additionally demonstrated the effect of complexation on the germylene reactivity. The structure of these complexes can be different in each particular case. It is noteworthy that high rate constants were obtained for reactions in cyclohexane, whereas lower rate constants were found in hexane. Probably, in hexane, oxygen forms complexes with solvent molecules, which lessens its diffusion mobility and, correspondingly, reactivity. Moreover, the presence of uncon-

Table 10. Rate constants for germylene reactions with unsaturated compounds ($T = 293$ K).

Germylene	Precursor	Solvent	Reactant	k /litre mol^{-1} s^{-1}	Ref.
Me_2Ge	$Me_2HGeGeMe_3$	see [a]	buta-1,3-diene	6.6×10^9	44
	$Me_2HGeGeMe_3$	see [a]	3,3-dimethylbut-1-ene	5.9×10^9	44
	$Me_2Ge(GePhMe_2)_2$	cyclohexane	DMB	2.4×10^7	22, 23
	9	"	DMB	2.2×10^7	11
	$PhMe_2GeSiMe_3$	"	DMB	1.7×10^7	29
	$PhMe_2GeSiMe_3$	"	DMB	4.1×10^7	31
	$PhMe_2GeSiMe_3$	"	buta-1,3-diene	1.24×10^7	29
	$PhMe_2GeSiMe_3$	"	but-1-ene	$< 10^5$	29
	$PhMe_2GeSiMe_3$	"	isoprene	1.63×10^7	29
	$PhMe_2GeSiMe_3$	"	*cis*-piperylene	9.2×10^6	29
	$PhMe_2GeSiMe_3$	"	*trans*-piperylene	2.9×10^6	29
	$PhMe_2GeSiMe_3$	"	*cis*,*cis*-hexa-2,4-diene	1.2×10^6	29
	$PhMe_2GeSiMe_3$	"	*cis*,*trans*-hexa-2,4-diene	3.5×10^6	29
	$PhMe_2GeSiMe_3$	"	*trans*,*trans*-hexa-2,4-diene	$< 5 \times 10^5$	29
	$PhMe_2GeSiMe_3$	"	hex-1-ene	$< 10^4$	29
	$PhMe_2GeSiMe_3$	"	hex-1-ine	3.0×10^4	29
	$PhMe_2GeSiMe_3$	"	prop-1-ine	$< 10^5$	29
	$PhMe_2GeGeMe_3$	cyclohexane	DMB	2.1×10^7	31
	$(PhMe_2Ge)_2$	THF	DMB	–	30, 32
	10d	hexane	DMB	12.5×10^9	40
	3a	"	**11** [b]	5.0×10^8	4, 39
	3a	"	styrene	7×10^7	4, 39
Et_2Ge	$(Et_2Ge)_n$	cyclohexane	DMB	8.4×10^7	14
Bu^n_2Ge	$(Bu^n_2Ge)_n$	"	DMB	3.1×10^7	14
$(n\text{-}C_6H_{13})_2Ge$	$[(n\text{-}C_6H_{13})_2Ge]_n$	"	DMB	4.0×10^7	14
PhMeGe	$(PhMeGe)_n$	"	DMB	22.0×10^7	14
	$(Ph_2MeGe)_2$	THF	DMB	4.5×10^6	30, 32
	$PhMeGe(GeMe_3)_2$	cyclohexane	DMB	2.2×10^6	22, 23
	10b	hexane	DMB	4×10^9	42
Ph_2Ge	$(Ph_3Ge)_2$	THF	DMB	1.0×10^6	30, 32
	$Ph_2Ge(GeMe_3)_2$	cyclohexane	DMB	0.72×0^6	22, 23
	$Ph_2Ge(SiMe_3)_2$	"	DMB	2.75×10^4	41
	10c	hexane	isoprene	5.5×10^9	64

[a] In the gas phase. [b] 3,3,6,6-Tetramethyl-1-thiacyclohept-4-yne (**11**).

Table 11. Rate constants of germylene reactions with carbon tetrachloride in cyclohexane ($T = 293$ K).

Germylene	Precursor	Solvent	k / litre mol^{-1} s^{-1}	Ref.
Me_2Ge	**3a**	hexane	0.12×10^8	4, 39
	$Me_2Ge(GePhMe_2)_2$	cyclo-hexane	no reaction	22, 23
	8	"	4.9×10^8	11
	$PhMe_2GeSiMe_3$	"	3.2×10^8	29
	10d	hexane	8×10^7	40
Et_2Ge	$(Et_2Ge)_n$	cyclo-hexane	10×10^8	14
Bu^n_2Ge	$(Bu^n_2Ge)_n$	"	9.2×10^8	14
$(n\text{-}C_6H_{13})_2Ge$	$[(n\text{-}C_6H_{13})_2Ge]_n$	"	13×10^8	14
PhMeGe	$(PhMeGe)_n$	"	1.6×10^8	14
	$Me_2Ge(GePhMe_2)_2$	"	0.65×10^8	22, 23
	10b	hexane	1.7×10^7	42
Ph_2Ge	$Ph_2Ge(GeMe_3)_2$	cyclo-hexane	1.5×10^8	22, 23
	10c	hexane	4.8×10^6	66

trolled impurities in cyclohexane, which bind germylenes and accelerate their loss, is also possible.

One of the tests for the presence of a germylene in photochemical processes included its addition to the double bond of 2,3-dimethylbuta-1,3-diene to form the corresponding germacyclopentene. The rate constants for this reaction with Me_2Ge measured on flash photolysis of different molecular precursors lie in a range of $(1.7-4.1) \times 10^7$ litre mol^{-1} s^{-1} (Table 10).

Due to the fast reaction of Me_2Ge with the solvent, the rate constant of its reaction with DMB in tetrahydrofuran was not measured. In cyclohexane, the rate constant of the reaction of germylenes Et_2Ge and PhMeGe with DMB increased 2- and 5-fold, respectively, as compared with rate constants for Me_2Ge (see Table 10). It should be noted that the rate constants for the reaction of PhMeGe with DMB measured in Refs 22 and 23 were exactly one-order-of-magnitude smaller than that found in Ref. 14 (both experiments were carried out in cyclohexane but used different precursors). For the reaction of Ph_2Ge with DMB in cyclohexane, the data on the rate constant considerably differed from one another, for instance, by a factor of 26 (see Refs 22, 23 and 41). Gas-phase measurements have shown[44] that in the limit (at high pressures), the rate constant for the addition of Me_2Ge to the doubl bonds of buta-1,3-diene and 3,3-dimethylbut-1-ene approaches the diffusion limit (1.1×10^{11} cm^3 mol^{-1} s^{-1} = 6.6×10^9 cm^3 mol^{-1} s^{-1}) and exceeds the rate constant typical of this reaction in cyclohexane by two orders of magnitude (see Table 10). The rate constants for the germylene addition to unsaturated compounds found in recent studies[40, 42, 66] exceed the earlier data by two orders of magnitude (see Table 10). Probably, the authors of earlier works observed reactions of digermenes rather than germylenes. Thus, the development of instrumentation and methods for the detection of reactions in the liquid phase and also the use of new precursors bring the germylene rate constants measured in solutions closer to those measured in the gas phase.

Carbon tetrachloride is an efficient germylene scavenger. The rate constants for the germylene reaction with CCl_4 are $(1-10) \times 10^8$ litre mol^{-1} s^{-1} (Table 11). Studies of ^{1}H and ^{13}C NMR spectra of the reaction products have shown[27] that germylene inserts into a CCl_4 molecule at a C—Cl bond.

$$Me_2Ge + CCl_4 \longrightarrow Cl_3CGeMe_2Cl.$$

For this reaction, the data on rate constants also vary depending on the precursor nature. However, the scatter (for the same germylene) is substantially weaker as compared with

Table 12. Rate constants for germylene reactions with some organic molecules ($T = 293$ K).

Germylene	Precursor	Solvent	Reagent	k /litre mol^{-1} s^{-1}	Ref.
Me_2Ge	$PhMe_2GeSiMe_3$	cyclohexane	DMSO	$< 10^7$	29
	$PhMe_2GeSiMe_3$	"	THF	$< 10^4$	29
	$PhMe_2GeSiMe_3$	"	Et_3SiH	$< 10^4$	29
	$PhMe_2GeSiMe_3$	"	EtOH	1.86×10^4	29
	$PhMe_2GeSiMe_3$	"	EtOH	no reaction	31
	$PhMe_2GeGeMe_3$	"	EtOH	the same	31
	$Me_2Ge(GePhMe_2)_2$	"	Et_3SiH	4.2×10^6	22, 23
	$Me_2Ge(GePhMe_2)_2$	"	EtOH	no reaction	22, 23
	$(PhMe_2Ge)_2$	THF	EtOH	the same	32
	3a	hexane	Me_3SnCl	3.5×10^8	4, 39
	3a	"	**3a**	1.2×10^7	4, 39
	3a	"	MeOH	3×10^7	4, 39
PhMeGe	$PhMeGe(GeMe_3)_2$	cyclohexane	Et_3SiH	4.1×10^6	22
	$PhMeGe(GeMe_3)_2$	"	Et_3SiH	6.5×10^7	23
	$PhMeGe(GeMe_3)_2$	"	EtOH	no reaction	22, 23
Ph_2Ge	$Ph_2Ge(SiMe_3)_2$	"	$EtMe_2SiH$	1.0×10^4	41
	$Ph_2Ge(SiMe_3)_2$	"	MeOH	no reaction	41
	$Ph_2Ge(SiMe_3)_2$	"	Me_2EtBr	1.0×10^4	41
	$Ph_2Ge(SiMe_3)_2$	"	Bu^tBr	6.4×10^5	41
	$Ph_2Ge(SiMe_3)_2$	"	MeSSMe	5.0×10^6	41
	$Ph_2Ge(SiMe_3)_2$	"	Me_2EtBr	1.0×10^4	41
	$Ph_2Ge(GeMe_3)_2$	"	Et_3SiH	6.6×10^5	22, 23
	$Ph_2Ge(GeMe_3)_2$	"	EtOH	no reaction	22, 23
	10c	hexane	MeOH	6.1×10^9	66
	10c	"	Bu^tOH	4.8×10^9	66
	$(Ph_3Ge)_2$	cyclohexane	EtOH	no reaction	32
Mes_2Ge	cyclo-Ge_3Mes_6	hexane	Et_3SiH	1.1×10^5	13
	cyclo-Ge_3Mes_6	"	EtOH	no reaction	13
	cyclo-Ge_3Mes_6	"	1-bromohexane	5.4×10^5	13

germylene reactions with DMB (see Tables 10 and 11). In the gas phase, the rate constant of the reaction of Me_2Ge with CCl_4 was not measured,[44] because the radiation (193 nm) used in the majority of studies was absorbed by carbon tetrachloride.

Reactions of insertion into H–X bonds (X = C, N, O, F, Si, P, S, Cl) are typical of carbenes, silylenes and germylenes. According to quantum chemical calculations,[45, 56, 67–69] the activation energies of such reactions are substantially higher for dimethylgermylene as compared with carbenes and silylenes. Nonetheless, such processes involving germylenes often proceed with high rate constants (Table 12).

X. Optical spectra, vibrational frequencies and kinetics of digermene decay

As was noted above, the annealing of low-temperature matrices containing an accumulated germylene and the flash photogeneration of germylenes in solutions lead in many cases to dimerisation of these species to form digermenes. Table 13 shows the position of absorption bands for certain digermenes formed from different precursors. The data obtained at 293 K pertain to laser flash photolysis experiments. A temperature of 77 K corresponds to experiments that involved annealing and refreezing of irradiated matrices. It is evident that digermene absorption bands are shifted to shorter wavelengths as compared with germylene bands (see Tables 1 and 2). Note that the extinction coefficients of digermene bands also remained unknown. The only extinction coefficient value was determined[43] for the $Ph_2Ge{=}GePh_2$ band with the maximum at 440 nm to be 5970 litre mol^{-1} cm^{-1}.

On the photolysis (254 nm) of dimethyldiazidogermane [$Me_2Ge(N_3)_2$] in an argon matrix at 12–18 K, the IR spectrum of dimethylgermylene was recorded[29] (see Table 6). Matrix heating to 36 K led to changes in the spectrum, namely, the disappearance of Me_2Ge lines and the appearance of new signals assigned by the authors to tetramethyldigermene (Table 14). Similar results were obtained on the thermolysis of compound **3a** in the crystalline state with the isolation of gaseous products in argon or nitrogen matrices at 5 K.[70]

In certain cases, the digermene absorption decayed with second-order kinetics, which implies the formation of cyclotetragermanes.[11] For this process, only the effective rate constant k/ε was determined (Table 15). Insofar as the changes in the absorbances at 450 (germylene) and 370 nm (digermene) were comparable,[11] the extinction coeffcients of these species are close to one another and apparently equal to $\sim 10^3$ litre mol^{-1} cm^{-1}. Then, the rate constant for digermene dimerisation is approximately $k \sim 3.9 \times 10^6 \varepsilon \sim 4 \times 10^9$ litre mol^{-1} cm^{-1}, *i.e.*, fairly close to the diffusion limit. A constant that was found[37] for the $Me_2Ge{=}GeMe_2$ dimerisation in cyclohexane with compound **4a** used as the precursor turned out to be nearly six times smaller. Lower recombination rate constants were also found for digermenes containing more bulky substituents (Et and Ph groups) (see Table 15). Note that a digermene with mesityl groups[13] disappeared with quasi-first-order kinetics ($\tau \sim 300$ μs) by a yet unclear mechanism.

Thus, the performed analysis shows that the dimerisation of, first, germylenes and, then, digermenes may lead to the formation of cyclic germanes. On steady-state photolysis of germanium organic derivatives, the formed germylenes and digermanes may react with cyclic products as the latter are accumulated, which ultimately leads to the appearance of germanium-containing polymers in solutions.

Table 14. Calculated and experimental vibrational frequencies (cm^{-1}) of Ge–C and Ge–Ge bonds of tetramethyldigermene[70] recorded in argon (Ar) and nitrogen (N_2) matrices at 5 K.

Vibration	Raman spectra			IR Spectra		
	experiment		calculation	experiment		calculation
	Ar	N_2		Ar	Ar[a]	
ν(Ge–C)	591	589	588	598	594	593
	580	580	576	568	569	564
ν(Ge–Ge)	404	405	401	–	–	–
δ(C–Ge–C)	235	234	232	–	–	–
	200	198	206			

[a] According to data of Ref. 28.

Table 13. Spectroscopic characetristics of digermenes in solutions (T = 293 K) and low-temperature 3-MP matrices (T = 77 K).

Digermene	Precursor	Solvent	λ_{max}/nm	Ref.
Solutions				
$Me_2Ge{=}GeMe_2$	**8**	cyclohexane	370	11
	4a	"	380	37
$Et_2Ge{=}GeEt_2$	**4b**	"	380	37
$Pr^i_2Ge{=}GePr^i_2$	cyclo-$Ge_4Pr^i_8$	"	390	15
$Ph_2Ge{=}GePh_2$	$Ph_2Ge(SiMe_3)_2$	"	320	41
	10c	hexane	440	43
$Mes_2Ge{=}GeMes_2$	cyclo-Ge_3Mes_6	"	405	13
	$Mes_2Ge(SiMe_3)_2$	"	405	13
(2,6-$Me_2C_6H_3)_2Ge{=}Ge(C_6H_3Me_2$-2,6)$_2$	cyclo-$Ge_3(C_6H_3Me_2$-2,6)$_6$	cyclohexane[a]	~ 410	16
Matrices				
$Me_2Ge{=}GeMe_2$	**4a**	–	370	37
$Et_2Ge{=}GeEt_2$	**4b**	–	380	37
$Pr^i_2Ge{=}GePr^i_2$	cyclo-$Ge_4Pr^i_8$	–	390	15
$MesBu^tGe{=}GeMesBu^t$	$MesBu^tGe(SiMe_3)_2$	–	378	25
(2,6-$Me_2C_6H_3)_2Ge{=}Ge(C_6H_3Me_2$-2,6)$_2$	(2,6-$Me_2C_6H_3)_2Ge(SiMe_3)_2$	–	406	25
(2,6-$Et_2C_6H_3)_2Ge{=}Ge(C_6H_3Et_2$-2,6)$_2$	(2,6-$Et_2C_6H_3)_2Ge(SiMe_3)_2$	–	400	25
$Mes_2Ge{=}GeMes_2$	$Mes_2Ge(SiMe_3)_2$	–	406	25
$Mes_2Ge{=}GeMes_2$	**15**	–	406	38
(2,4,6-$Pr^i_3C_6H_2)_2Ge{=}Ge(C_6H_2Pr^i_3$-2,4,6)$_2$	(2,4,6-$Pr^i_3C_6H_2)_2Ge(SiMe_3)_2$	–	416	25

[a] Deuterated cyclohexane was used.

Table 15. Effective rate constants for second-order reactions (k/ε) of digermene loss (T = 293 K).

Digermene	Precursor	λ_{max}/nm	Solvent	k/ε/cm s^{-1}	Ref.
$Me_2Ge{=}GeMe_2$	**8**	370	cyclohexane	3.9×10^6	11
	9	370	"	4.8×10^6	19
	4a	380	"	6.5×10^5	37
$Et_2Ge{=}GeEt_2$	**4b**	380	"	4.2×10^5	37
$Ph_2Ge{=}GePh_2$	$Ph_2Ge(SiMe_3)_2$	320	"	$\sim8.0\times10^4$	41
	10c	440	hexane	$\sim2.5\times10^4$ (see [a])	43
$Mes_2Ge{=}GeMes_2$	cyclo-Ge_3Mes_6	405	cyclohexane	3.4×10^3 (see [b])	13

[a] Reaction of the first and second orders, k_{eff} is shown in s^{-1}; [b] first-order reaction, k is shown in s^{-1}.

In addition to their loss in polymerisation, digermenes may disappear in competitive reactions with other molecules. Table 16 shows the rate constants for some of these processes. As seen, oxygen molecules are efficient scavengers of digermenes. However, literature provides the rate constant values for this reaction that differ by three orders of magnitude (see Table 16). Note that germylenes react with oxygen and carbon tetrachloride at the rates nearly one-order-of-magnitude higher than digermenes. The reaction of a digermene with 2,3-dimethylbuta-1,3-diene is two-orders-of-magnitude slower than a similar reaction involving a germylene (compare the data in Tables 12 and 16). The rate constant for a digermene reaction with triethylsilane is also substantially lower as compared with a germylene. At the same time, the reactions of methyl-substituted digermenes with alcohols feature the opposite trend. Whereas germylenes do not virtually react with alcohols, the rate constants for digermenes approach $\sim5\times10^7$ mo litre^{-1} s^{-1}. Nonetheless, it can be concluded that by and large, digermenes exhibit considerably lower reactivity as compared with germylenes.

XI. Optical spectra of germyl radicals

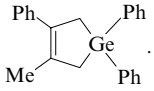
In addition to the heterolytic cleavage of the Ge–C bond on the photolysis and thermolysis of germanium-containing compounds, the homolytic processes to form germyl radicals may also occur. It was shown [22] that the photolysis of tetramethylphenyldigermane $PhMe_2GeGeHMe_2$ in a low-temperature 3-MP matrix leads to the appearance of an absorption band with the maximum at 320 nm, which was assigned to a digermyl radical. The band decayed with the matrix melting.

Laser flash photolysis of solutions of peraryltrigermanes $R^1_3Ge-GeR^2R^3-GeR^1_3$ (R^1-R^3 = Ar) also demonstrated [22,23] absorption bands with maxima in the range of 320–330 nm, which were attributed to the formation of aryl-substituted digermyl radicals. Extinction coefficients of these bands were not determined. It was shown that the species responsible for this absorption did not react with 2,3-dimethybuta-1,3-diene but reacted with carbon tetrachloride with high rate constants [$k = (1.3-7.2)\times10^8$ litre mol^{-1} cm^{-1}].

Solutions of polygermanes $(R_2Ge)_n$ in cyclohexane were subjected to laser flash photolysis.[14] In addition to germylene absorption (430–460 nm), the spectrum showed bands in the

Table 16. Rate constants for digermene reactions (T = 293 K) in solutions.

Digermene	Precursor	Solvent	Reagent	k/litre mol^{-1} s^{-1}	Ref.
$Me_2Ge{=}GeMe_2$	cyclo-Ge_4Me_8	cyclohexane	O_2	2.3×10^5	13
	8	"	O_2	2.8×10^8	11
	4a	"	O_2	4.0×10^8	37
	10e	hexane	O_2	5.0×10^7	40
	8	cyclohexane	CCl_4	$<10^7$	11
	4a	"	CCl_4	1.2×10^7	37
	10c	hexane	CCl_4	2.3×10^7	40
	4a	cyclohexane	DMB	5.3×10^5	37
	4a	"	EtOH	4.9×10^7	37
	4a	"	EtOD	4.8×10^7	37
	4a	"	Pr^{i}OH	2.0×10^7	37
	4a	"	Bu^{t}OH	2.0×10^7	37
	10e	hexane	MeOH	2.7×10^6	71
	10e	cyclohexane	Bu^{t}OH	5.2×10^5	71
$Et_2Ge{=}GeEt_2$	**4b**	"	O_2	3.3×10^8	37
	4b	"	CCl_4	3.7×10^7	37
	4b	"	DMB	1.7×10^5	37
	4b	"	EtOH	9.4×10^7	37
$Ph_2Ge{=}GePh_2$	**10c**	hexane	O_2	4.8×10^6	40
	10c	"	CCl_4	2.0×10^6	40
	$Ph_2Ge(SiMe_3)_2$	cyclohexane	MeOH	7.1×10^3	41
	10c	hexane	MeOH	1.9×10^7	71
	10c	"	Bu^{t}OH	2.1×10^6	71
$Mes_2Ge{=}GeMes_2$	cyclo-Ge_3Mes_6	cyclohexane	O_2	2.3×10^5	13

[a] Compound **10e** is 

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vicinity of 350–370 nm, which were assigned to polygermyl radicals $(R_2Ge)_m^{\bullet}$. The latter decayed as a result of recombination with effective rate constants in a range $k/\varepsilon = 2.3\times10^4 - 5.1\times10^5$ litre mol^{-1} cm^{-1}. It should be noted that the identification of bands assigned to germyl radicals was complicated by the fact that digermenes exhibit absorption bands in the same spectral range (see Table 13) and disappear in a second-order reaction with very close k/ε parameters (see Table 15).

Laser flash photolysis of aryl-substituted digermanes $(Ph_nMe_{3-n}Ge)_2$ (n = 1, 2) led to the formation of germylenes (absorption band maxima in the range of 440–470 nm) and germyl radicals $Ph_nMe_{3-n}Ge^{\bullet}$ (315–330 nm).[30] The radicals disappeared through recombination with observed rate constants $k_{obs} = (1.9-4.3)\times10^5$ s^{-1}. The flash photolysis of a $PhMe_2GeGeMe_3$ solution made it possible to record[31] the optical spectrum of a germyl radical $PhMe_2Ge^{\bullet}$, which represented a band with the maximum at 320 nm. The radical dimerised with $k/\varepsilon = 7.0\times10^7$ cm s^{-1}.

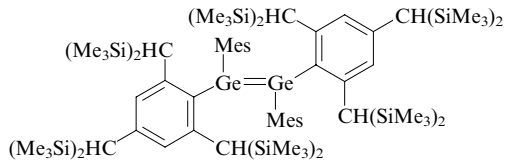
Thus, the available data on the laser flash photolysis of germanium-containing compounds show that germyl and digermyl radicals absorb in a range of 315–330 nm and disappear in recombination reactions with effective rate constants of the order of magnitude of 10^4-10^8 litre mol^{-1} s^{-1}.

XII. Stable germylenes

Diorganylgermylenes R_2Ge are usually short-lived reactive species; however, the introduction, into the precursor molecules, of bulky groups R (see Ref. 57) or ligands that are n or π donors able to transfer the electron density to the vacant orbital of the central germanium atom allows one to synthesise long-lived carbene analogues. At present, nearly 30 stable germylenes are known.[72] A comprehensive review[73] devoted to stable germanium analogues of carbenes, imines and thiones was published.

In certain cases, it is possible to isolate germylenes in the crystalline form and study their structure. Crystals of stable germylene $[(Me_3Si)_2CH]_2Ge$ were isolated and its solution in hexane was prepared.[61] A spectrum of this solution demonstrated three light absorption bands with maxima at 414, 302 and 227 nm and extinction coefficients of 970, 1450 and 19 600 litre mol^{-1} cm^{-1}, respectively. The position of the long-wavelength band (414 nm) well agrees with the absorption maxima of unstable germylenes synthesised using laser flash photolysis (see Table 2). The extinction coefficient ($\varepsilon \sim 10^3$ litre mol^{-1} cm^{-1}) assessed based on the recombination parameter for unstable germylenes $2k_{rec}/\varepsilon$ was also close to the analogous characteristic of the long-wavelength band for $[(Me_3Si)_2CH]_2Ge$.

A sterically hindered stable digermene **12** was synthesised.[74, 75]



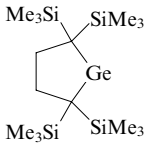
12

Repulsion of bulky groups led to a substantial increase in the Ge–Ge distance (2.416 Å) in this compound. In solution, as the temperature increased, digermene **12** reversibly dissociated to form two molecules of stable germylene {2,4,6-[$(Me_3Si)_2CH]_3C_6H_2$}MesGe. Compound **12** exhibited an absorption band with the maximum at 439 nm ($\varepsilon = 2\times10^4$ litre mol^{-1} cm^{-1}), while germylene {2,4,6-[$(Me_3Si)_2CH]_3C_6H_2$}MesGe had a band at 575 nm ($\varepsilon = 1.6\times10^3$ litre mol^{-1} cm^{-1}). Thermodynamic parameters of the reversible dissociation were ΔH = 61.5 kJ mol^{-1} and ΔS = 177.5 J mol^{-1} K^{-1}. The energy of the Ge–Ge bond (61.5 kJ mol^{-1}) was considerably lower‡ due to the bond stretching as a result of repulsion of bulky substituents.

The extinction coefficient of the long-wavelength band of MesBu^{t}Ge germylene was also consistent with the estimates for unstable germylenes. The band itself was shifted to longer wavelengths similarly to the absorption bands of unstable germylenes containing bulky subtituents.

A stable germylene $(2,4,6\text{-}Bu^t_3C_6H_2)_2Ge$ could be stored at −30 °C for several months.[77] At room temperature, it decomposed in several weeks to evolve 1,3,5-tri(*tert*-butyl)benzene. X-Ray diffraction analysis has shown that the spatial positions of two aryl groups were different and the Ge–C bond distance was 2.053 Å. The C–Ge–C angle was close to 108°, which substantially exceeded the estimates of 91–93° calculated for Me_2Ge (see Table 4). Despite its distorted geometry, germylene $(2,4,6\text{-}Bu^t_3C_6H_2)_2Ge$ in solution exhibited an absorption band with the maximum at 430 nm, the position of which virtually coincided with that of the Me_2Ge band (see Tables 1, 2). A still wider C–Ge–C angle (111.3°) was observed for stable germylene $(Me_3Si)_3CGeCH(SiMe_3)_2$ (Ref. 78) with Ge–C bond lengths equal to 2.012 and 2.067 Å. Unfortunately, the optical spectrum of this germylene was not presented in the study.[78] Note that in germylene $(2,6\text{-}Mes_2C_6H_3)_2Ge$ the C–Ge–C angle was equal to 114.4° and the Ge–C bond distance was 2.033 Å.[79]

A stable cyclic dialkylgermylene, namely, 2,2,5,5-tetrakis-(trimethylsilyl)-1-germacyclopentane-1,1-diyl (**13**), which is a monomer in the solid state with the averaged Ge–C bond length of 2.015 Å and the C–Ge–C angle of 91°, was described.[80]



13

The absorption spectrum revealed a long-wavelength band of germylene **13** at 450 nm with a small extinction coefficient. Its unstable analogue, 1-germacyclopent-3-ene-1,1-diyl in an argon matrix at 12 K demonstrated a broad absorption band with the maximum in the range of 400–410 nm; the Ge–C bond length was 2.017 Å and the C–Ge–C angle was 88.1° (Ref. 81). Table 17 shows the optical spectral parameters for certain stable germylenes. It is noteworthy that a stable germylene $(Bu^t_2N)_2Ge$ exhibits a long-wavelength absorption band with the maximum at 445 nm, the Ge–N bond length of 1.88 Å and the N–Ge–N angle of 111.4° (Ref. 80).

In a recent study,[43] the extinction coefficients of long wavelength spectral bands of different short-lived germylenes were determined (see Table 17). As seen, the coefficients $\varepsilon \sim 1000-2000$ litre mol^{-1} cm^{-1} fall in the same range as those of stable germylenes.

‡ According to quantum chemical calculations,[76] for an unsubstituted digermene ($H_2Ge{=}GeH_2$) the Ge–Ge bond energy is substantially higher (125.6–188.4 kJ mol^{-1}).

Table 17. Positions of maxima and extinction coefficients of bands in germylene spectra ($T = 293$ K).

Germylene	Solvent	λ_{max} / nm	ε / mol litre^{-1} cm^{-1}	Ref.
Stable germylenes				
$[2,4,6\text{-}(CF_3)_3C_6H_2]_2Ge$	hexane	374	1300	72
$MesBu^tGe$	"	575	1600	74, 75
$[(Me_3Si)_2CH]_2Ge$	"	414	970	61, 82
	"	312	1450	61, 82
	"	227	19600	61, 82
$(2,4,6\text{-}Bu^t_3C_6H_2)_2Ge$	hexane, THF	430	520	77
$(2,6\text{-}Mes_2C_6H_3)_2Ge$	Et_2O	578		79
$(2,4,6\text{-}Pr^i_3C_6H_2)Bu^tGe$	hexane, THF	580		83
13	"	450	320	80
	"	280	1300	80
$(Bu^t_2N)_2Ge$	cyclo-	445	420	84
	hexane	310	shoulder	84
	"	227	7000	84
Unstable germylenes				
Ph_2Ge	hexane	500	1650	43
Mes_2Ge	"	550	1440	43

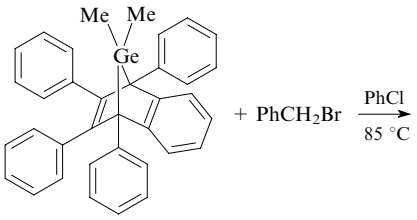
XIII. Comparison of the data obtained by chemically induced dynamic nuclear polarisation and laser flash photolysis methods

The analysis of chemically induced dynamic nuclear polarisation effects in thermal and photochemical reactions provides valuable information on the processes involving short-lived (with lifetimes varying from nano- to microsecond scales) radicals and biradicals. CIDNP measurements allow one to find the multiplicities of radical pairs, their precursors and also the reactive states of carbenes and their analogues, *viz.*, silylenes and germylenes.[85] Note that the nanosecond laser photolysis with the time resolusion of an order of magnitude of 10 ns provides no way for the observation of intermediates with lifetimes of several nanoseconds.

Unfortunately, the literature contains no results of photochemical studies of germanium-containing compounds carried out in the pico- and nanosecond time resolution ranges. Apparently, this is associated with the low extinction coefficients of spectral bands of both the parent compounds and the transient species. Moreover, the studies on the photodissociation of germanium derivatives never used the time-resolved IR spectroscopy in the picosecond range. Hence, at present, CIDNP is the only method that allows one to acquire information on the processes involving species with lifetimes of nanoseconds. To date, the literature contains only one review[86] devoted to the application of spin chemistry methods to studies of short-lived intermediates of photochemical reactions of germanorbornadienes and digermabicyclooctadienes.

CIDNP effects were observed[87,88] on the thermal decomposition of Me_2GeNB (**3a**). After heating (85 °C) of a chlorobenzene solution of this compound in the presence of benzyl bromide, two germanium-containing products were isolated.

It was assumed that the reaction produces a primary radical pair $\{PhCH_2^{\bullet}\cdots{}^{\bullet}GeMe_2Br\}$ the recombination of which affords a polarised molecule $PhCH_2GeMe_2Br$. Elimination of the bromine atom from $PhCH_2Br$ by the radical $^{\bullet}GeMe_2Br$ results in the extrusion of a second germanium-containing product, Me_2GeBr_2, to the solution bulk. The analysis of CIDNP signs points to the singlet state of the radical pair and, hence, the



3a

$\longrightarrow PhCH_2GeMe_2Br + Me_2GeBr_2 + ...$

singlet ground state of the germylene, which is well consistent with quantum chemical calculations (see Table 4). Note that no CIDNP effects were observed for parent compound **3a** that could be associated with the synchronous cleavage of both Ge–C bonds during the thermal decomposition.

The NMR method was used[89,90] to study the thermolysis of germanorbornadienes containing different substituents at the germanium atom and in the organic fragment. The authors of a study[89] assumed that the thermolysis includes two steps with the initial formation of a transient $TPN^{\bullet}\cdots{}^{\bullet}GeR_2$ biradical. Insofar as the authors[89,90] did not study CIDNP effects, their conclusion on the involvement of a biradical in the reaction stemmed from enhanced thermal stability of germanorbornadienes with methyl substituents in the naphthalene fragment.

CIDNP effects were also observed[91] in the photochemical decomposition of compound **3a**. The presence of CIDNP signals for methyl protons of the parent norbornadiene allowed the authors to assume the step-wise cleavage of Ge–C bands to form a transient biradical. According to the proposed scheme, a singlet biradical produces the parent norborndiene, whereas the triplet state serves as the source of the other products, namely, 1,2,3,4-tetraphenylnaphthalene (**6**) and dimetylgermylene. 3,3,6,6-Tetramethyl-1-thiacyclohept-4-yne (**11**) served as the dimethylgermylene scavenger. Based on the analysis of CIDNP signs for the dimethylgermylene adduct to the C≡C triple bond in compound **11**, it was concluded that germylene reacts in the triplet state. This was the first study that demonstrated the involvement of triplet dimethylgermylene in a chemical reaction.

Similar results were obtained with CCl_4 molecules used as the dimethylgermylene scavengers.[86] Photolysis of compound **3a** in a solution containing CCl_4 and C_6D_6 (in a ratio of 1 : 1 or 1 : 3) generated signals from polarised Me_2GeCl_2 and $Me_2ClGeCCl_3$ molecules that were formed from the primary radical pair $ClMe_2Ge^{\bullet}\cdots{}^{\bullet}CCl_3$, as follows from NMR spectra recorded during the irradiation. The analysis of CIDNP signs showed that the radical pair was formed in the triplet dimethylgermylene reaction with carbon tetrachloride.

However, a later study[34] revealed no CIDNP effects for Me_2GNB (**3a**) and TPN (**6**), which allowed its authors to assume a single-step mechanism for the dimethylgermylene generation. In the latter study, an attempt was undertaken to detect transient species in the decomposition of compound **3a** in experiments with laser flash photolysis. It was shown that the excitation of a **3a** molecule leads to the formation of TPN (**6**) in the triplet excited state. Presumably, singlet germanorbornadiene **3a** undergoes one-step dissociation, which is accompanied by the cleavage of both Ge–C bonds over a picosecond time interval. A single TPN (**6**) molecule is formed and quickly converted into the triplet state ($S_1 \rightarrow T_1$). Unfortunately, in the latter study,[34] no attempt was undertaken to measure the extinction coefficient for triplet–triplet transition band; hence, the relative yield of triplet TPN (**6**) was not determined. Therefore, there is a probability that the formation of TPN in the S_1 state followed by its transition into the

triplet state is not the main channel in the dissociation of Me_2GNB (**3a**).

A thorough analysis of the kinetics of transient absorption changes on the laser flash photolysis of compound **3a** in hexane was accomplished.[92] A laser flash generated two transient species, which disappeared with substantially different rates. An absorption band in the range of 400–550 nm (λ_{max} = 480 nm), which decayed over 300 ns, was assigned to germylene Me_2Ge. Another wide band, which decayed much more slowly (over several microseconds), was assigned to the triplet–triplet absorption of TPN (**6**). This conclusion was substantiated by the measurements of the T–T absorption at the laser flash photolysis of a TPN solution in hexane.

Photodecomposition of germanorbornadiene **3a** may produce TPN (**6**) molecules in the ground (S_0), and excited triplet (T_1) and singlet (S_1) states. The determination of relative yields (γ) of these states requires the knowledge of the extinction coefficient for T–T absorption and the quantum yield of intersystem crossing (φ_T for the $S_1 \rightarrow T_1$ process). To determine the extinction coefficient, the T–T energy transfer from a tetraphenylnaphthalene molecule to anthracene was considered and $\varepsilon_{TPN}^{421} = 12\,700$ litre mol^{-1} cm^{-1} was obtained.[92] Measurements of the laser flash intensity on the photolysis of TPN solutions (excitation to the S_1 state) and the found ε_{TPN} value made it possible to determine the quantum yield of intersystem crossing $\varphi_T = 0.13$. Note that the $S_1 \rightarrow S_0$ fluorescence quantum yield (φ_F) for TPN was found to be 0.09.[34] The use of these parameters and the kinetic curves measured on the flash photolysis of compound **3a** allowed the following yields of S_0 and T_1 states of TPN to be estimated: $\gamma_{S0} = 0.66$ and $\gamma_{T1} = 0.34$.[92]

The value $\gamma_{S0} = 0.66$ can be governed by both the TPN formation immediately in the ground state and the relaxation of the excited S_1 state ($S_1 \rightarrow S_0$). A parameter $\gamma_{T1} = 0.34$ may also be due to both the direct formation of the triplet state and the intersystem crossing ($S_1 \rightarrow T_1$). According to the analysis, the direct triplet TNP yield on the photodissociation of compound **3a** falls in the range of 0.24–0.34. Thus, the formation of solely S_1 state as was proposed in Ref. 34 cannot provide the appearance of a considerable amount of triplet TNP molecules due to the low quantum yield of the intersystem crossing. A triplet TPN molecule cannot be formed in the photodissociation of a triplet molecule Me_2GNB (**3a**). It was shown[34] that the latter mechanism is unlikely because the sensitised photolysis (benzophenone and 9*H*-xanthen-2-one as triplet sensitisers) generated no transient absorption attributable to the triplet state of germanorbornadiene **3a**.

In the photodissociation of compound **3a** from the S_1 state, the appearance of a triplet TPN molecule can only be explained by the formation of a ^{S}(TPN$^{\bullet}\cdots{}^{\bullet}$GeMe$_2$) biradical with one Ge–C bond cleaved, which can transform from the initial singlet state to the triplet state ^{T}(TPN$^{\bullet}\cdots{}^{\bullet}$GeMe$_2$). In this case, upon the biradical decomposition (the cleavage of the second Ge–C bond), one of components (Me_2Ge or TPN) may find itself in the triplet state. The formation of triplet germylene was confirmed by the analysis of signs of ^{1}H CIDNP effects on the photolysis of compound **3a** in the presence of electron acceptors.[90,91,93] Unfortunately, the CIDNP method gives no way for making quantitative estimates; hence, the relative yield of ^{T}(Me_2Ge) species remains uncertain, although it is known to vary from 0% to 66%. The lower limit (0%) is reached in the dissociation of the triplet state ^{T}(TPN$^{\bullet}\cdots{}^{\bullet}$GeMe$_2$) to form the triplet state for only TPN. This is much unlikely because CIDNP confirms the existence of dimethylgermylene in the triplet state.[86,91,93] The upper limit of the triplet Me_2Ge yield is restricted by $\gamma_{Me2Ge} = 1 - \gamma_{T1} = 0.66$.

Thus, in aggregate, the results of laser flash photolysis and CIDNP studies show that the photodissociation of dimethylgermanorborbadiene **3a** and the formation of dimethylgermylene may involve several competitive reactions. The primary process is the excitation of the molecule Me_2GNB (**3a**) into the first singlet excited state.

$$^{S_0}(Me_2GNB) \xrightarrow{h\nu} {}^{S_1}(Me_2GNB). \qquad (2)$$

Insofar as the quantum yield of the photodissociation of compound **3a** is substantially lower than unity ($\varphi \sim 0.4$[34]) and fluorescence is virtually absent, the non-radiative relaxation into the ground state plays a considerable role for this molecule. From the excited state, ^{S_1}(Me_2GNB) can dissociate with the cleavage of two Ge–C bonds to form TPN and dimethylgermylene. In turn, TPN can be in either ground or excited singlet states.

$$^{S_1}(Me_2GNB) \longrightarrow \begin{cases} {}^{S_0}(TPN) + {}^{S}(GeMe_2), \\ {}^{S_1}(TPN) + {}^{S}(GeMe_2). \end{cases} \qquad (3)$$

The long-wavelength absorption band of compound **3a** lies in the vicinity of ~275 nm, which corresponds to the absorbed quantum energy of ~4.5 eV. The efficient thermal decomposition of Me_2GNB at approximately 100 °C showed[87,88] that the energy of the first Ge–C bond cleavage is 1.0–1.2 eV[94] (after this process, the break of the second bond consumes far less energy). Hence, the balance energy of ~3.3–3.5 eV is indeed insufficient for the formation of an excited ^{S_1}(TPN) molecule, because the maximum of the long-wavelength absorption band of TPN is located at 300 nm [therefore, the energy of ^{S_1}(TPN) $\geqslant$ 4.1 eV].

In the singlet-state dissociation, the appearance of one component (TPN or Me_2Ge) in the triplet state is forbidden in accordance with the total spin conservation law. Though this law does not forbid the simultaneous formation of two species in the triplet state

$$^{S_1}(Me_2GNB) \longrightarrow {}^{T_1}(TPN) + {}^{T}(GeMe_2), \qquad (4)$$

the probability of such a process is far lower (1 : 9) as compared with the appearance of singlet species. Moreover, in the former case, a problem of energy deficiency also exists, because the stored energy of 3.2–3.5 eV is obviously insufficient for the appearance of ^{T_1}(TPN) (with the energy of 2.8–3.0 eV) and ^{T}($GeMe_2$) (1.2 eV[45,53]).

Above, we considered processes in which the photodissociation of Me_2GNB (**3a**) occurred in a single elementary event that included the cleavage of both Ge–C bonds. A reaction with products in singlet states would be more probable. The assumption on the elementary event means that the time lag between the cleavages of the first and second Ge–C bond is much shorter than the time resolution of the experimental method so that the short lifetime of the biradical (the cleavage of the first bond)

$$^{S_1}(Me_2GNB) \rightleftharpoons {}^{S}(TPN^{\bullet}\cdots{}^{\bullet}GeMe_2) \qquad (5)$$

does not induce any substantial changes in the yields and electronic states of final products. However, measurements of CIDNP effects[86,91,93] suggest that the biradical lifetime is sufficient for the transition into the triplet state

$$^{S}(TPN^{\bullet}\cdots{}^{\bullet}GeMe_2) \rightleftharpoons {}^{T}(TPN^{\bullet}\cdots{}^{\bullet}GeMe_2). \qquad (6)$$

From this state, the biradical can dissociate to produce one component in the triplet state.

$$^{T}(TPN^{\bullet}\cdots{}^{\bullet}GeMe_2) \begin{cases} \rightarrow {}^{T_1}(TPN) + {}^{S}(GeMe_2), \\ \rightarrow {}^{S_0}(TPN) + {}^{T}(GeMe_2). \end{cases} \quad (7)$$

The S – T transition time of a biradical is determined by the intensity of hyperfine interaction (HFI) in radical centres, the difference of *g*-factors and the magnetic field intensity. For parameters characteristic of many radical pairs, the time of transition into the triplet state usually lies in a range of 1 – 10 ns. The nanosecond laser flash photolysis has the resolution time of 5 – 10 ns; hence, the optical spectrum of a biradical in both triplet and singlet states is yet unavailable.

The final product, TPN (**6**) in different electronic states, can appear in at least five of reactions shown above [see reactions (3), (4) and (7)]. The relative share of each channel remains unknown and only the value $\gamma_{T_1} = 0.34$ shows that the triplet biradical dissociation can contribute about 1/3 of the overall photoreaction yield. The use of the CIDNP method for the detection of reactions (4) and (7) provided evidence for the presence of $^{T}(GeMe_2)$ species; however, the individual contribution of each product can be determined only after the determination of its relative yield. Disagreement on the photodissociation mechanism of Me_2GNB that exists in the literature [34, 91, 93] can be due to the fact that each channel makes a substantial contribution into the overall yield of photoreaction products. The absence of quantitative measurements of yields led to different conclusions on the mechanism of phototransformations of dimethylgermanorbornadiene **3a**. The comprehensive quantitative characterisation of all processes will be possible only after the determination of the relative yield of dimethylgermylene in the triplet state.

Similar problems arise in the studies on the photochemistry of 7,7,8,8-tetramethyl-1,4-diphenyl-1,3-benzo-7,8-digemabicyclo[2.2.2]octa-1,5-diene (**4a**). This compound was studied by laser flash photolysis [37] and CIDNP [36] methods. After a laser pulse (in 300 ns), two absorption bands with maxima at 380 and 430 nm were observed in spectra of a cyclohexane solution of compound **4a**. The band at 430 nm, which decayed over 3 μs, was assigned [37] to the T – T absorption of diphenylnaphthalene [^{T}(DPN), $\varepsilon^{430} = 3.2 \times 10^4$ litre mol^{-1} cm^{-1} (Ref. 95)]. The band at 380 nm, which was assigned to a digermene $Me_2Ge{=}GeMe_2$ (see Table 13), decayed with second-order kinetics ($k/\varepsilon = 6.5 \times 10^5$ cm s^{-1}).

Studying the CIDNP effects for methyl-group protons of the parent molecule **4a** and protons of the final product (DPN) made it possible to assume [36] that the cleavage of one Ge – C bond to form a singlet biradical $DPN{-}Me_2Ge^{\bullet}\cdots{}^{\bullet}GeMe_2$ is the primary process. The biradical reversible transition into the triplet state and the recovery of the broken bond led to the appearance of CIDNP for protons in parent compound **4a**. Two possible channels were discussed [36] for the triplet radical transformation. The first channel was the dissociation of the remaining Ge – C bond to form a digermene and a triplet DPN molecule. The second channel was the dissociation of the Ge – Ge bond to form dimethylgermylene and a triplet biradical ($DPN^{\bullet}\cdots{}^{\bullet}GeMe_2$). The latter could either pass into the singlet state and form a Ge – C bond with the remaining germanium atom (to afford germanorbornadiene) or dissociate to yield the triplet DPN and the second dimethylgermylene species. The analysis of CIDNP effects and the kinetic behaviour of the transient absorption gave no way for making the ultimate choice between these two mechanisms of the triplet 1,6-biradical transformation; however, its involvement in the formation of CIDNP signals is beyond any doubt.

Thus, to be completed, the description of photodissociation of compound **4a** [36, 37] requires the quantitative analysis of the relative yield of diphenylnaphthalene in the triplet and singlet states to be carried out. This information would be helpful in the determination of contributions of different photodissociation channels for molecule **4a** (biradical dissociation from singlet and triplet states, dissociation without transient biradical formation with simultaneous cleavage of both Ge – C bonds to form a digermene). Insofar as the laser radiation used in Refs 36 and 37 was of different wavelengths (266 and 308 nm, respectively), it cannot be ruled out that the photolysis mechanisms were different. For example, on the excitation of compound **4a** with light with a wavelength of 266 nm, a single photoreaction channel was realised (the digermene $Me_2Ge{=}GeMe_2$ formation that involved no biradical),[37] whereas on the photolysis at longer wavelengths, only one Ge – C bond was cleaved to generate a biradical.[36]

XIV. Conclusion

The analysis of literature data shows that the light absorption spectrum of dimethylgermylene has a band in the range of 420 – 490 nm. For this species in the gas phase, the band maximum lied at 480 nm. Apparently, the absorption observed at shorter wavelengths (405 – 420 nm) belongs to the donor – acceptor germylene complexes. Bands in the range of 370 – 380 nm are caused by the fast formation of digermenes due to the germylene dimerisation. The absorption of germylenes containing bulky substituents or groups with π-systems is shifted to longer wavelengths (450 – 550 nm), which is most probably due to widening of the C – Ge – C angle. The shift of germylene absorption bands in the spectra of low-temperature matrices as compared with the solution spectra can be explained by the effects of temperature, the solvent nature and the germylene geometry.

Germylenes usually disappear in dimerisation reactions to form digermenes. Determination of the recombination rate constants requires the knowledge of extinction coefficients of bands in spectra of unstable germylenes. To date, these parameters were measured only for two germylenes, namely, Ph_2Ge and Mes_2Ge. The determination of the mentioned values for other germylenes is the burning problem of photochemistry of germanium-containing compounds. Digermenes also disappear in second-order reactions to form cyclic and eventually polymeric structures. Absorption bands of digermenes are shifted to shorter wavelengths by 40 – 50 nm as compared with germylene bands. For digermenes, the data on the extinction coefficients of bands are also absent. The wide scatter (sometimes up to 2 – 3 orders of magnitude) of literature data on the reaction rate constants for germylenes synthesised from different precursors presents an important problem. Most probably, the scatter is due to the incorrect assignment of transient absorption bands. Thus the bands earlier assigned to germylenes actually belong to digermenes or germanium-containing radicals. Moreover, this might also be due to the formation of germylene transition complexes with the decomposition products of germanium-containing compounds that appear simultaneously with germylenes.

The majority of studies on the photochemistry of germanium organic derivatives assumed that in the excited states of these molecules, the heterolytic break of Ge – C bonds occurs to form germylenes. However, presumably, in some cases, the competitive homolytic cleavage of a Ge – Ge bond takes place to form germyl radicals. The relative probability of these channels in photoreactions of germanium-containing compounds remains unknown, because for radicals with absorption bands located at still shorter wavelengths, the extinction coefficients are also unknown. The quantum yields of different transient species cannot be determined for the same reason.

The use of the CIDNP method that provides information on the short-lived species unobservable by even the laser flash photolysis method with the nanosecond time resolution is a very interesting trend in photochemistry. A more detailed photolysis mechanism with the formation of transient birad-

icals was first proposed in CIDNP studies of germanium-containing compounds. However, no studies were published to date that contain information on the quantitative relationship between the CIDNP data and the results of laser flash photolysis of germanium derivatives. For this purpose, the resolution time of the laser flash photolysis must be shifted in the pico- and femtosecond ranges. To detect short-lived transient biradicals, it seems promising to use nanosecond photolysis of cooled solutions and low-temperature matrices.

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