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Generation, low-temperature stabilization, structure and reactivity of intermediates with low-coordinated carbon, silicon and germanium atoms

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Abstract- The mechanisms of thermal and photochemical transformations of organic and organometallic compounds with the formation of various reactive intermediates, as well as their spectral and structural parametres have been studied by low-temperature IR matrix technique.

INTRODUCTION

Direct investigation of mechanisms of chemical reactions involving reactive intermediates, as well as of compounds containing unusual chemical bonds by various techniques is an important task of physical organic chemistry.

The main difficulties associated with the direct spectroscopic detection and investigation of unstable species are the high reactivity and short lifetime of these species under normal conditions. One possible method for direct studies of unstable intermediates is based on their isolation in inert gas matrices at low temperature, usually below 20K. The matrix isolation technique enables to increase the life time of these species almost indefinitely. The combined application of this method with suitable detection procedure such as ESR, UV, and IR spectroscopy has proved extremely fruitful.

We shall discuss here our results concerning the application of low-temperature matrix IR-spectroscopy to thermal and photochemical studies of reactions of organic and organometallic compounds leading to formation of reactive intermediates such as free radicals, carbenes, their silicon and germanium analogues, and compounds having double-bonded silicon and germanium atoms. Pyrolytic mass-spectrometry has been also used for the investigation of some thermal reactions and for optimization of their conditions.

In some cases the structural parameters of the unstable species determined by the high resolution matrix IR spectroscopy have been further supported by gas phase electron diffraction data of these species and/or by X-ray difraction analysis of their molecular complexes.

These investigations have been started in the late 60s in our laboratory in the Institute of Organic Chemistry (USSR Academy of Sciences) by Dr. A.K. Maltsev (1933 - 1986). His contribution to this study is enormous. Other major contributions are due to the work of R.G.Mikhaelyan, V.A.Svyatkin, N.D.Kagramanov, V.A.Korolev, E.G.Baskir, P.S.Zuev, V.N.Khabashesku, Z.A.Kerzina and S.E.Boganov.

The mass-spectrometric investigations have been carried out in cooperation with Dr. J.Tamas and coworkers from the Central Research Institute of Chemistry of the Hungarian Academy of Sciences, Budapest. High-temperature electron diffraction studies of unstable species have been conducted by Prof. I.Hargittai and his colleagues at the Department of Structural Studies of the Hungarian Academy of Sciences, Budapest. The X-ray analysis has been perfomed by Prof. Yu.T.Struchkov and his colleagues at the Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, Moscow.

TRIHALOMETHYL RADICALS, DIHALOCARBENES AND THEIR SILICON AND GERMANIUM ANALOGUES

Based on trapping experiments we have shown that the trihalomethyl mercury derivatives $RHgCHal_3$ are convenient precursors of carbenes in the gas phase (ref. 1-6).

Low temperature matrix stabilization (matrix temperature 8-10K) of the vacuum pyrolysis (200-600°C) products of compounds $RHgCCl_3$ (R = Ph,CCl_3,Cl) has indicated the presence of dichlorocarbene CCl_2 (ν_1 720, ν_3 746 cm^{-1}) and trichloromethyl radical CCl_3 (ν_3 898 cm^{-1}) (ref. 1,2). At 200-500°C the relative intensity ratio of $\nu_3(CCl_2)/\nu_3(CCl_3)$ for the studied $RHgCCl_3$ varied from 1.1 to 4.0 depending on the substituent R. It increased when the pyrolysis temperature was reduced. These results suggest that carbene CCl_2 and radical CCl_3 are formed simultaneously and independently, and that the formation of CCl_2 is preferable. These conclusions have been supported by pyrolytic mass-spectrometry (ref. 3).

$$RHgCCl_3 \xrightarrow{\Delta} \begin{cases} CCl_2 + RHgCl \\ CCl_3 + [RHg] \end{cases}$$
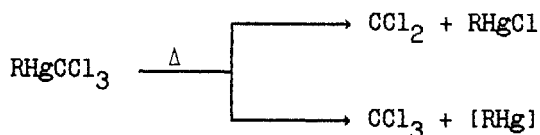
R = Ph, CCl_3, Cl

Vacuum pyrolysis (250-450°C) of $PhHgCCl_2Br$ in the gas phase is even more selective in regard to formation of dichlorocarbene (ref. 4). Bromochlorocarbene is formed predominantly along with small amounts of $CClBr_2$ radical upon the vacuum pyrolysis of $PhHgCClBr_2$ (ref. 4).

The observed splitting of the bands, due to ^{35}Cl and ^{37}Cl isotopes, and their intensities are in accordance with the number and the natural abundance of the Cl atoms in the studied intermediates. Based on the isotopic splitting the bond angles in these species have been calculated (see Table 1).

According to the matrix IR spectra the preferable formation of dichlorocarbene has been also observed under vacuum pyrolysis (500-1000°C, 10^{-2}-10^{-3}torr) of trichloromethyltrichlorosilane and trichloromethyltrichlorogermane. The CCl_3 radical was formed in substantially lower amounts (ref.8, 9).

$$Cl_3MCCl_3 \xrightarrow{\Delta} \begin{cases} CCl_2 + MCl_4 \\ CCl_3 + [MCl_3] \end{cases}$$

M = Si, Ge
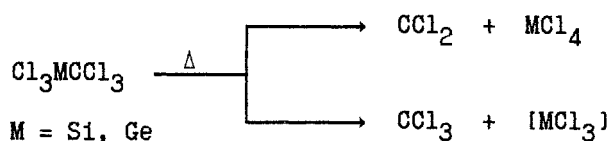
Vacuum pyrolysis (600-1100°C, 10^{-3}-10^{-4}torr) of hexachlorodisilane proceeds selectively with the formation of only $SiCl_2$ and $SiCl_4$(ref. 8, 10).

The preferable formation of dihalocarbenes (but not the trihalomethyl radicals) upon thermolysis of trihalomethyl mercury, silicon and germanium derivatives seems. to be a result of intermolecular coordination, of $R_nM{-}CX_2$ type, and of thermodynamic preference (M = Hg, Si, Ge) type, and of thermodynamic preference of the carbene-forming pathway.

High resolution matrix IR spectra of dichlorosilylene $SiCl_2$ (ref. 8) and of dichlorogermylene $GeCl_2$ (ref. 11), obtained by thermal depolymerization of $(GeCl_2)_x$ in vacuum, display complex patterns due to many combinations of chlorine isotopes (^{35}Cl,^{37}Cl) as well as Si (^{28}Si,^{29}Si,^{30}Si) and Ge (^{70}Ge,^{72}Ge,^{73}Ge,^{74}Ge,^{76}Ge) isotopes.

Table 1. **Matrix IR Spectra and Structural Data of the Perhalogenated Intermediates formed in Pyrolysis Reactions (ref.4, 6 - 8)**

Intermediate	Vibration frequencies, cm^{-1}	Bond angle,°
CCl_2	$C^{35}Cl_2$: 719.5 (ν_1),745.8 (ν_3) $C^{35}Cl^{37}Cl$: 717.0 (ν_1),744.0 (ν_3) $C^{37}Cl_2$: 714.9 (ν_1),741.7 (ν_3)	106
$CClBr$	$C^{35}ClBr$: 743.9 (ν_3) $C^{37}ClBr$: 739.5 (ν_3) 611.4[a]	
CF_3	$1084(\nu_1),702(\nu_2),1205(\nu_2+\nu_4),1249(\nu_3)$	17.8[b]
CCl_3	$C^{35}Cl_3$: 897.8 (ν_3) $C^{35}Cl_2^{37}Cl$: 896.4 (ν_3) $C^{35}Cl^{37}Cl_2$: 895.2 (ν_3) $C^{37}Cl_3$: 893.9 (ν_3)	15.5[b]
CCl_2Br	$C^{35}Cl_2Br$: 888.3 (ν_3) $C^{35}Cl^{37}ClBr$: 886.4 (ν_3) 835.1[a] $C^{37}Cl_2Br$: 884.3 (ν_3)	
$CClBr_2$	$C^{35}ClBr_2$: 856.5 (ν_3) $C^{37}ClBr_2$: 853.0 (ν_3) 782.8[a]	

[a] C-Br stretch
[b] Angle between C-X bond and the plane of the three halogen atoms.

Table 2. **Bond angles** α **in** MX_2 **molecules**

MX_2	α,°, from IR matrix spectra (ref.6,8,11)	α,°, from electron diffraction (ref.12-14)
CCl_2	106 ± 5	109.2 [a]
$SiCl_2$ [b]	102 ± 5	102.8 ± 0.6
$SiBr_2$		102.7 ± 0.3
$GeCl_2$ [c]	99 ± 4	100.3 ± 0.4
$GeBr_2$		101.2 ± 0.9

[a] From the millimeter- and submillimeter-wave spectrum (ref. 15).
[b] MW spectral data give a value of 101.25° (ref. 16).
[c] The α values of 94.6° and 97.7° have been obtained by X-ray diffraction of $C_4H_9O_2 \cdot GeCl_2$ and $Ph_3P \cdot GeCl_2$ molecular complexes, respectively (ref. 17-18).

The comparison of the experimentally obtained and the calculated frequencies allowed to determine the force constants and bond angles of these species (see Tables 2,3).

The bond angles in the dichlorides $SiCl_2$ (ref. 12) and $GeCl_2$ (ref. 13) which were determined by direct electron diffraction studies of these unstable species are close to those from the IR-matrix technique (Table 2).

Both the bond angle (from 106 to 99°) and force constant (from 2.99 to 2.08 mdyne/Å) values decrease in the following order : $CCl_2 > SiCl_2 > GeCl_2$ (see Tables 2, 3).

The force constants values $F_{(M-Cl)}$ in MCl_2 are appreciably smaller compared to those in the corresponding MCl_4. Thus, this fact excludes for MCl_2 species a significant contribution of resonance structures of the type $Cl-M=Cl$ resulting from a possible interaction of the lone pairs on the chlorine atoms with a vacant p-orbital of the central M atom.

Table 3. Bond lengths and M-Cl bond force constants
in MCl_2 and MCl_4 species (ref. 8, 12-14)

M	MCl_2		MCl_4	
	$F_{(M-Cl)}$, mdyne/$\overset{o}{A}$	r_{M-Cl}, $\overset{o}{A}$	$F_{(M-Cl)}$, mdyne/$\overset{o}{A}$	r_{M-Cl}, $\overset{o}{A}$
C	2.99	1.7157[a]	3.59	1.766
Si	2.29	2.083	3.37	2.020
Ge	2.08	2.186	2.79	2.113
Sn	2.1	2.347	3.63	2.2808

[a] From millimeter- and submillimeter-wave spectrum (ref. 15).

This conclusion is in accordance with direct electron diffraction studies of MCl_2 and MBr_2 (M = Si, Ge) (ref. 12-14) which show that the bond lengths in MCl_2 are usually longer compared with those in the corresponding MCl_4 (see Table 3).

In contrast to carbenes of the AX_2 type which contain three atoms generation of carbenes with a more complex structure under vacuum pyrolysis may be accompanied by intramolecular rearrangements. Thus, the matrix isolation study of the vacuum pyrolysis products of $Me_3SiCH=N_2$ (730°C, 10^{-4}torr) and bis(trifluoromethyl) diazirine 1 (350 - 500°C, 10^{-3}torr) show that the carbenes Me_3SiCH and $(CF_3)_2C$ formed under these conditions isomerise completely into silene $Me_2Si=CHMe$ (ref. 19) and an olefin $CF_3CF=CF_2$ (ref. 20), respectively. These compounds were identified by their matrix IR spectra. The carbene-olefin isomerization under these conditions is faster than $10^{-6}- 10^{-5}$sec.

ARYL- AND TRIFLUOROMETHYLHALOGEN CARBENES: GENERATION AND REACTIONS IN LOW-TEMPERATURE MATRICES

Another, more traditional approach to the stabilization of carbenes and the investigation of their spectral properties deals with direct generation of carbenes in low-temperature matrices, e.g. by the photolysis of diazo-compounds or ketenes.

Thus, the UV-irradiation (λ> 200 nm, 12K) of Ar matrix, containing 0.1% diazirine 1, gave bis(trifluoromethyl)carbene (IR bands at 1380, 1344, 1197, 1157, 965, 671 cm^{-1}) and a small amount of $(CF_3)_2C=N_2$ (ref. 20).
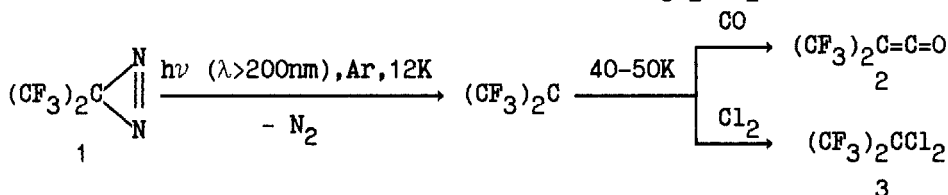
During photolysis of 1 in Ar matrix doped with 4% CO, bands belonging to the ketene 2 were observed along with those of the carbene. Upon further warming to 40-45K the carbene bands disappeared and were replaced by bands of the ketene 2, indicating a direct interaction of carbene $(CF_3)_2C$ with CO.

Photolysis of 1 in a matrix doped with 3% Cl_2 yielded $(CF_3)_2C$ and $(CF_3)_2CCl_2$ 3. Upon warming to 40-45K the intensities of the carbene bands are decreased simultaneously with the increase of the intensities of the bands of 3. The photolysis of diazirines 4 in Ar matrix was studied in a similar way (ref. 21).

X=Cl, Br, CF_3
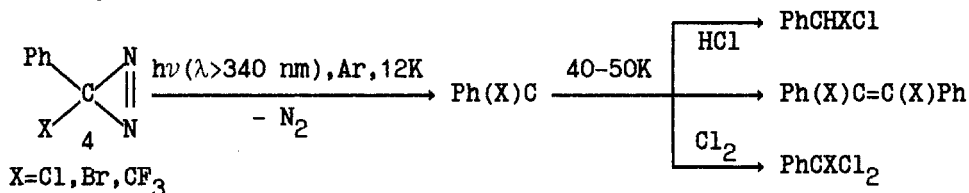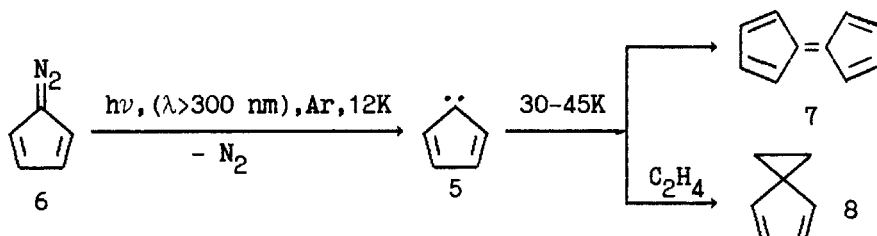
We were succesful in carrying out a direct IR monitoring of the [1+2]-cycloaddition reaction of cyclopentadienylidene 5 to ethylene in Ar matrix which gave a corresponding cyclopropane 8 (ref. 22, 23). UV irradiation ($\lambda > 300$ nm) of diazocyclopentadiene 6 at 12K led to carbene 5 (bands at 1341, 1335, 1100, 1074, 700, 573 cm^{-1}). The use of a harder matrix (Ar + 10-15% N_2O) enabled us to prevent completely the formation of fulvalene 7 during the photolysis. After the complete photolytic decomposition of 6 into 5 at 12K in Ar matrix doped by 2% ethylene the matrix temperature was raised up to 40-50K. An increase of cyclopropane 8 concentration and a simultaneous disappearance of carbene 5 bands were observed.

UNSATURATED ORGANIC RADICALS OF ALLYL, PROPARGYL AND BENZYL TYPES

Unsaturated conjugated organic radicals are another group of unstable molecules studied by matrix IR spectroscopy, pyrolysis mass-spectrometry and electron diffraction.

The free <u>allyl radical</u>, C_3H_5, was obtained by vacuum pyrolysis (600-1000°C, 10^{-3}-10^{-5} torr) of various allyl compounds (ref. 24-27).

Stabilization of C_3H_5 radical in Ar matrix at 12K enabled us to determine for the first time (ref. 24) seventeen IR bands of this radical (3107, 3051, 3040, 3019, 1602, 1477, 1463, 1389, 1317, 1284, 1242, 1182, 983, 973, 809, 801, 510 cm^{-1}). A year later (in 1983) a similar matrix IR spectrum of the allyl radical was published by G.Maier, H.Bock and coworkers (ref. 27). In 1984 we obtained the matrix IR spectrum of C_3D_5 radical which display eleven bands (2285, 2214, 2209, 1263, 1062, 1018, 1007, 767, 762, 650, 646 cm^{-1}) (ref. 25). Assignment of the bands in the IR spectrum was carried out and valence force field was calculated . This analysis showed that the stretching frequencies of all the C-H bonds are in the region of ethylenic CH stretches (>3000 cm^{-1}). The vibrational frequencies and the force constant of the carbon frame in C_3H_5 radical (ν^{as}_{CCC} 1284 cm^{-1}, ν^{s}_{CCC} 1242 cm^{-1}, F_{CCC} 5.8 mdyne/Å) lie between the corresponding values for a double C=C bond ($\nu_{C=C}$ 1640 cm^{-1}, $F_{C=C}$ 9.0 mdyne/Å) and a single C-C bond (ν_{C-C} 920 cm^{-1}, F_{C-C} 4.5 mdyne/Å).

Later, we have succeeded in determination of the molecular structure of the free allyl radical from high-temperature electron diffraction, augmented by mass spectrometry studies (ref. 28). The structural parameters obtained for the allyl radical were : r_{C-C} 1.428 Å, r_{C-H} 1.69 Å, α (CCC) 124.6°, α (CCH) 120.9°. This was the first electron diffraction study of an unstable organic molecule.

Comparison of IR and ED data for the C_3H_5 radical with IR and X-ray data of π-allyl metal complexes shows that the formation of such complexes results in an increase of the ν^{as}_{CCC} frequency from 1284 cm^{-1} to 1380 or 1480 cm^{-1} and in shortening of the C-C bond from 1.428 Å to 1.380 Å. These changes may be explained by the transfer of electron density from the metal atom to a nonbonding orbital of the π-allyl system rather than to an antibonding orbital.

<u>Perfluoroallyl radical</u>, C_3F_5, was obtained by vacuum pyrolysis (850-950°C, 10^{-4} torr) of 1,5-perfluorohexadiene or of 3-Iodopentafluoropropylene and was studied by pyrolytic mass spectrometry (ref. 29) and by IR spectroscopy in an Ar matrix (ref. 30).

Ionization potential of C_3F_5 radical is 8.44 eV (cf. $IP_{C_3H_5}$ 8.13 eV) (ref. 29). Five bands were registered in matrix IR spectrum of C_3F_5 radical (ref. 30): 1498, 1350, 1215, 1008, 579 cm^{-1}. A normal coordinate analysis has been carried out and force constants were calculated. Comparison of the antisymmetric stretching frequency of the carbon skeleton (ν^{as}_{CCC} 1498 cm^{-1}) of C_3F_5 and the force constant of its C-C bonds (F_{CCC} 5.0 mdyne/Å) together with the corresponding values in C_3H_5 radical (1284 cm^{-1} and 5.8 mdyne/Å) and the frequency and the force constant values in perfluoropropylene (1795 cm^{-1} and 7.8 mdyne/Å) shows a substantial weakening of the C-C bonds in the C_3F_5 radical compared with perfluoropropylene, and an insignificant weakening compared with the allyl radical (ref. 31).

Propargyl radical was produced by vacuum pyrolysis (900-1050°C, 10^{-4}-10^{-5} torr) of propargyl iodide or of dipropargyl oxalate (ref. 32) and it was frozen into Ar matrix at 12K. We have observed twelve bands in the matrix IR spectrum of the C_3H_3 radical (only three bands were recorded earlier (ref. 33) for this radical): 3307, 3111, 3026, 2080, 1440, 1369, 1061, 1017, 686, 618, 532, 482 cm^{-1}.

Based on the experimental IR spectrum a normal coordinate analysis has been carried out and a valence force field was calculated. Stretching frequencies of the carbon skeleton ($\nu_{C\equiv C}$ 2080 cm^{-1} and ν_{C-C} 1017 cm^{-1}), as well as calculated values of the force constants ($F_{C\equiv C}$ 15.05 mdyne/Å, F_{C-C} 6.53 mdyne/Å) show a weakening of the triple bond and strengthening of the C-C bond in the propargyl radical due to electron density delocalization in the conjugated system (cf. for methylacetylene HC≡CCH$_3$: $\nu_{C\equiv C}$ 2142 cm^{-1}, $F_{C\equiv C}$ 15.8 mdyne/Å; ν_{C-C} 931 cm^{-1}, F_{C-C} 5.12 mdyne/Å).

Vacuum pyrolysis of iodoacetonitrile proceeds similarly to that of propargyl iodide and leads to the corresponding cyanomethyl radical, C_2H_2N, which was studied by low-energy mass spectrometry in the gas phase and by IR spectroscopy in Ar matrix (ref. 34).

Contrary to the author, who observed only one IR band of this radical (664 cm^{-1}) (ref. 35), we have succeeded in detection of seven bands: 3142, 3044, 2087, 1431, 1025, 1021, 664 cm^{-1}. The bands at 2087 and 1021 cm^{-1} were assigned to the stretchings of the C≡N bond ($\nu_{C\equiv N}$) and C-C bond (ν_{C-C}), respectively. These frequencies and the calculated values of the force constants ($F_{C\equiv N}$ 15.09 mdyne/Å, F_{C-C} 6.82 mdyne/Å) show (as well as in the propargyl radical) a weakening of the C≡N and strengthening of C-C bonds caused by delocalization of electron density (cf. for acetonitrile N≡C-CH$_3$: $\nu_{C\equiv N}$ 2267 cm^{-1}, $F_{C\equiv N}$ 17.5 mdyne/Å; ν_{C-C} 918 cm^{-1}, F_{C-C} 5.14 mdyne/Å). This conclusion is indirectly supported by the high values of the stretching frequencies of the CH bonds ($\nu^{as}_{CH_2}$ 3142 cm^{-1} and $\nu^{s}_{CH_2}$ 3044 cm^{-1}) which are lying in the region of the C-H stretchings in ethylene.

Benzyl radical, $C_6H_5CH_2$, and its deuterated analogues ($C_6H_5CD_2$, $C_6D_5CH_2$) were obtained by vacuum thermolysis of dibenzyl derivatives or by pyrolysis of the corresponding benzyl bromides (ref. 31).

The following frequencies were recorded in the matrix IR spectra of benzyl radicals:

$C_6H_5CH_2$: 3111, 3069, 1469, 1466, 1409, 1305, 1264, 1015, 948, 882, 862, 710, 667, 466 cm^{-1};

$C_6H_5CD_2$: 1468, 1440, 1289, 1030, 880, 752, 668 cm^{-1};

$C_6D_5CH_2$: 1410, 1201, 821, 811, 759, 711, 519 cm^{-1}.

Perfluorobenzyl radical has been obtained similarly by vacuum pyrolysis of perfluorobenzyl iodide or of perfluorodibenzyl (ref. 31, 36) The matrix IR spectrum of $C_6F_5CF_2$ radical contained the following bands: 1597, 1501, 1485, 1312, 1267, 892 cm^{-1}. Based both on the determined isotopic shifts and the comparison of the radical IR spectrum with the spectra of various substituted benzenes we have assigned the bands of the normal modes and calculated the force field of the benzyl radical.

The increase of the exocyclic C-C bond stretching frequency from 1208 cm^{-1} in toluene to 1264 cm^{-1} in the benzyl radical and the simultaneous decrease of the C-C ring bond stretching frequencies (from 1494 and 1460 cm^{-1} to 1469 and 1446 cm^{-1}, respectively) result from electron density delocalization in the benzyl system. Furthermore, the force constant value for the C-C bond in the $C_6H_5CH_2$ radical (5.5 mdyne/Å) is between the values for ordinary C-C bond (4.5 mdyne/Å) and double C=C bond (9.0 mdyne/Å) and is close to the corresponding force constant in the allyl radical (5.8 mdyne/Å).

Compared with perfluorotoluene the stretching vibration frequency of the exocyclic C-C bond in perfluorobenzyl radical increase (from 1237 to 1267 cm^{-1}) whereas the stretchings of benzene ring decrease (from 1657, 1525 and 1510 to 1597, 1501 and 1485 cm^{-1}).

Finally, the cyclopentadienyl radical, C_5H_5, was obtained by vacuum pyrolysis (970°C, 10^{-5} torr) of bis (cyclopentadienyl)nickel and it was frozen into Ar matrix at 12K (ref. 37). Only three bands (3079, 1383, 661 cm^{-1}) of the four possible ones for this highly symmetric molecule (D_{5h}) have been found in the IR spectrum. The band at 1383 cm^{-1} belongs to a stretching of the C-C bond in C_5H_5. Comparison of this band with the corresponding band in the IR spectra of the cyclopentadienyl ligand of π-complexes (1410–1435 cm^{-1}) and of free cyclopentadienyl anion (1455 cm^{-1}) leads to the conclusion that contrary to olefinic systems, the C-C bond stretchings increase in the order: C_5H_5 radical – C_5H_5 ligand – $C_5H_5^-$ anion due to increase in the aromaticity of the cyclopentadienyl system.

UNSTABLE COMPOUNDS WITH SILICON AND GERMANIUM DOUBLE BONDED ATOMS (SILENES, SILANONES, GERMANONES, GERMATHIONES)

Compounds containing silicon and germanium double bonded atoms are the nearest analogs of olefins, ketones and thioketones. However, most of them are very unstable and highly reactive species.
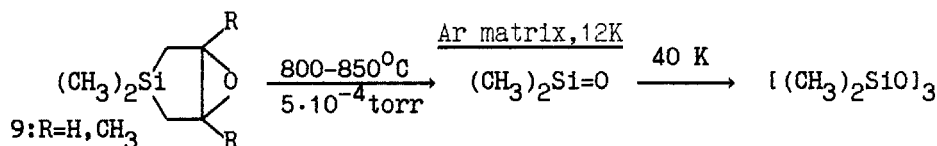
The first successful stabilization of a silene, $(CH_3)_2Si=CH_2$, in an Ar matrix has been achieved by us in experiments on the vacuum pyrolysis of 1,1-dimethylsilacyclobutane (ref. 38).

The IR spectra of this silene and some deuterated analogs were recorded and their full assignment was performed (ref. 38-42). The bands at 642.9, 817.5, 825.2, 1003.5, 1251.0, 1259.0 cm^{-1} were assigned to $(CH_3)_2Si=CH_2$. The band at 1003.5 cm^{-1} was specifically assigned to the

silicon-carbon double bond stretching vibration. The force constant for the
Si=C bond turned out to be 5.6 mdyne/Å. The value is considerably higher
than 3.06 mdyne/Å for a silicon-carbon single bond and is close to that of
well studied phosphonium ylides, called "salt-free ylides" (5.59 mdyne/Å).
This similarity between Si=C and P=C rather than between Si=C and C=C
reflects a certain polarity of the silicon-carbon double bond. According to
Siebert's rule the calculated order of the Si=C bond is 1.62.

Silene $Me_2Si=CHMe$ as one of the products of vacuum pyrolysis of
trimethylsilyldiazomethane (ref. 19) was stabilized in an Ar matrix. The
observed frequencies were in a good agreement with the frequencies assigned
to this silene which was generated directly by photolysis of
trimethylsilyldiazomethane in a solid Ar matrix (ref. 43).

The first inorganic silanones, $Cl_2Si=O$ and $F_2Si=O$, were obtained by
UV irradiation of Ar matrices containing silicon monoxide and halogenes
(ref. 44). We performed IR-detection of the first organic silanone,
$Me_2Si=O$, as one of the products of vacuum pyrolysis of the
6-oxa-3-silabicyclo[3.1.0]hexanes 9 (ref. 45). The bands at 1244, 1240,

$$(CH_3)_2Si \underset{\substack{R \\ R}}{\overset{}{\diamond}} O \xrightarrow[5\cdot10^{-4}\text{torr}]{800-850^\circ C} \overset{\text{Ar matrix,12K}}{(CH_3)_2Si=O} \xrightarrow{40\ K} [(CH_3)_2SiO]_3$$

9: R=H, CH_3

1210, 822, 798, 770, 657 cm^{-1}in the matrix IR spectra were assigned to this
intermediate, and a full assignment to various vibration modes was made on
the basis of IR spectra of isotopically labeled species (ref. 45-47).
Slightly later, $Me_2Si=O$ was produced in inert matrices by cophotolysis of
Me_2SiH_2 and Me_3SiH with O_3. The obtained frequencies of $Me_2Si=O$ are in good
agreement with our data (ref. 48).

In each experiment we also observed an unstable dimer $(Me_2SiO)_2$ besides
other products of pyrolysis. The presence of $(Me_2SiO)_2$ was confirmed by mass
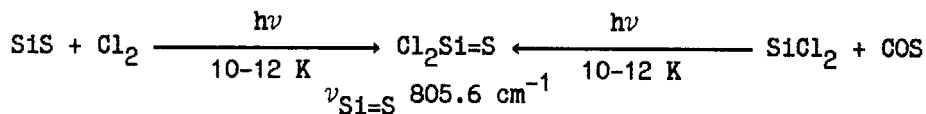spectroscopic study (ref. 49).

The calculated force constant for the Si=O bond in $Me_2Si=O$ is 8.32
mdyne/Å. It agrees with similar parameters for $X_2Si=O$ (X=Cl,F) (ref. 44)
being equal to 9 mdyne/Å, whereas the force constant of the Si-O single bond
is roughly 5.3 mdyne/Å. The calculated order of Si=O bond is 1.45.

For studying the influence of substituents on the spectral behavior and
on the thermal and kinetic stability of silanones, we stabilized two new
organic silanones - dimethylsilicate and silabenzophenone, which were
obtained in the vacuum pyrolysis of the corresponding epoxides 10 (ref. 50).

$$R_2Si \diamond O \xrightarrow{\Delta} \overset{\text{Ar matrix,12K}}{R_2Si=O} \xrightarrow{40\ K} (R_2SiO)_3$$
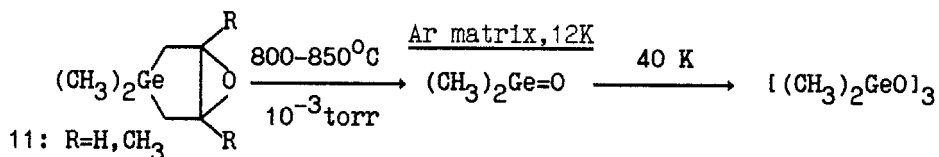
10: R=CH_3O, Ph
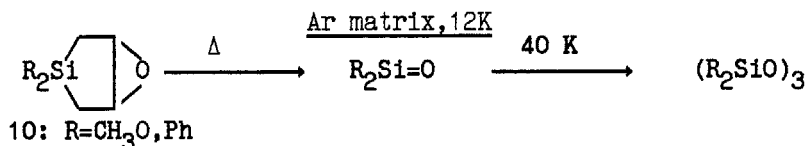
We have found out, that among the studied silanones silabenzophenone
seems to be the most thermally stable, while dimethyl silicate is the
kinetically most stable.

Recently the first <u>silathione</u>, $Cl_2Si=S$, has been stabilized in an Ar matrix (ref. 51):

$$SiS + Cl_2 \xrightarrow[\text{10-12 K}]{h\nu} Cl_2Si=S \xleftarrow[\text{10-12 K}]{h\nu} SiCl_2 + COS$$

$$\nu_{Si=S} \ 805.6 \ cm^{-1}$$

Ten years ago the first inorganic <u>germanone</u>, $F_2Ge=O$, was produced by reaction of GeO with F_2 in an Ar matrix under photolysis ($\nu_{Ge=O}$ was found to be 989.9 cm^{-1}) (ref. 52). Recently three new inorganic germanones were characterized (ref. 53).

The first organic germanone $Me_2Ge=O$ was succesfully detected by us upon vacuum pyrolysis of the 6-oxa-3-germabicyclo[3.1.0]hexanes 11 (ref. 54).

$$(CH_3)_2Ge \xrightarrow[10^{-3}\text{torr}]{800-850^{o}C} (CH_3)_2Ge=O \xrightarrow[]{\text{Ar matrix,12K}\ \ 40\ K} [(CH_3)_2GeO]_3$$

11: R=H,CH_3

Seven bands at 1241, 1231, 972, 796, 606, 524 and 465 cm^{-1} were assigned to $Me_2Ge=O$. The force constant for the Ge=O bond has been calculated to be 7.2 mdyne/Å (cf. $F_{Ge=O}$ in Ge=O is 7.34 mdyne/Å (ref. 55)). The calculated order of the Ge=O bond is 1.75 and its frequency is 972 cm^{-1}.

By using epoxysilacyclopentanes and epoxygermacyclopentanes as suitable precursors of Si=O and Ge=O containing species, we have attempted to generate in the gas phase the monomeric SiO_2 and GeO_2, earlier produced by reactions in inert matrices at 10-20K (ref. 56,57).

Monomeric SiO_2 has been stabilized in Ar matrix (band at 1419 cm^{-1}), but we failed to detect GeO_2, although the band of monomeric GeO at 976 cm^{-1} was found in the matrix IR spectra of the pyrolysis products.

Recently the first germathione, $Me_2Ge=S$, has been obtained independently by J.Michl et al. (ref. 58) and by us (ref. 59,60) in an Ar matrix. It was generated by vacuum pyrolysis of $(Me_2GeS)_3$ or by matrix reaction of Me_2Ge with atomic sulphur. The IR bands assigned to $Me_2Ge=S$ by both groups are basically in agreement. As follows from the force field calculations , the Ge=S stretching vibration is non-characteristic due to a strong mixing with the symmetrical Ge-C vibration , which results in splitting into two frequencies at 606 and 518 cm^{-1}, with the greatest contribution of the Ge=S stretching mode into the latter frequency. Mass spectrometric study of the pyrolysis of $(Me_2GeS)_3$ has been resulted in the determination of ionization energy of $Me_2Ge=S$ (8.63 ± 0.1 eV), practically coinciding with that obtained earlier by PES (8.60 eV) (ref. 61).

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