ORGANOGERMANIUM COMPOUNDS. IX.*

DETERMINATION OF RELATIVE BASICITY
OF SOME HEXAALKYLDIGERMOXANES**

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The present work is a continuation of our previous studies[1-5] in which infrared spectroscopy was employed in the determination of relative basicity of oxygen and nitrogen atoms in model series of organosilicon and -germanium compounds with the aim to examine a tendency of formation of $(p \to d)\,\pi$ dative bonds between the Group IV elements and the oxygen or nitrogen atoms.

The object of this work was to determine the relative basicities of the oxygen atoms in a series of hexaalkyldigermoxanes $[(CH_3)_3Ge]_2O$ (*I*), $[(C_2H_5)_3Ge]_2O$ (*II*), $[(n\text{-}C_3H_7)_3Ge]_2O$ (*III*) and $[(n\text{-}C_4H_9)_3Ge]_2O$ (*IV*) in terms of the strength of hydrogen bonds between studied compounds as proton acceptors and hydrogen (deuterium) of a series of proton donors. As proton donors we employed the following compounds: phenol, 2,6-xylenol, methanol, pyrrole, phenyl-acetylene, and deuteriochloroform. In addition to the differences in wavenumbers ($\Delta \nu$) of infrared absorption bands of the X—H bond of the non-associated proton donor (where X = O, N, C) and of the bond X—H...O of the complex, we made an attempt to estimate quantitatively temperature dependence of the spectra of the ternary mixtures pyrrole–hexaalkyldigermoxane–carbon tetrachloride.

EXPERIMENTAL

Preparation of compounds[6]. Hexamethyldigermoxane was prepared by the reaction of methylmagnesium chloride (3·2 mol) with germanium tetrachloride (1 mol), followed by hydrolysis of the reaction mixture with and aqueous sodium hydroxide solution. The other hexa-n-alkyldigermoxanes were prepared by aluminium chloride-catalyzed redistribution of tetraalkylgermane with germanium tetrachloride an subsequent hydrolysis of the reaction mixture with an aqueous sodium hydroxide solution. The starting tetraalkylgermanes were obtained by the reaction of an appropriate alkylmagnesium bromide (4·5 mol) with germanium tetrachloride (1 mol). Physical constants of prepared compounds were in accordance with the literature data[7]. The purity of the compounds was checked by gas–liquid chromatography and by infrared spectroscopy.

Infrared spectra. The IR spectra of hydrogen bonds of studied compounds were taken on a Zeiss Model UR 20 double beam spectrophotometer in the $3700-2200\ cm^{-1}$ region. The transmittance and frequency scales[8] of the instrument were calibrated in the usual way. The wavenumber of absorption band maxima were expressed as average values of three measurements. The accuracy of the determination of the position of absorption band maximum of non-associated proton donor was $\pm 2\ cm^{-1}$. The accuracy of the determination of the position of the

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*   Part VIII: This Journal *35*, 1870 (1970).

**   Presented in part on the 2nd International Symposium on Organosilicon Compounds, Bordeaux, July 1968.

associated band maximum is lowered due to a large half-width of the band and depends on the type of a proton donor.

For the measurements of hydrogen bonds in the region of LiF prism we used NaCl cells of 0·1 cm thickness. Spectral grade carbon tetrachloride was used as the solvent. The spectra of hydrogen bonds of the system 0·0015M pyrrole–0·2M hexaalkyldigermoxane–carbon tetrachloride in dependence on temperature (6—45°C) were measured using a temperature-controlled LiF cell of thickness 1 cm. Experimental arrangement and the method of calculation of the enthalpy of association, $-\Delta H$, were taken over from ref.[9].

RESULTS

The obtained wavenumbers and their shifts, $\Delta\nu$, are given in Table I. In Fig. 1 are shown summarily the spectra of hydrogen bonds of all proton donors used with 1M hexaethyldigermoxane in carbon tetrachloride. The spectra of the other hexaalkyldigermoxanes show similar patterns. From Fig. 1 it follows that not all proton donors are equally suited for the determination of relative basicities. So, for instance, the determination of the absorption band maximum of the associated complex between hexaalkyldigermoxanes and phenol (curve 2) is hampered by a diffusion band of relatively low intensity in the vicinity of the ν_{C-H} bands, the absorption of which overlaps with the low-frequency branch of the former band. The intensity of the associated band of 2,6-xylenol is due to steric screening of the hydroxyl group markedly reduced, relative to phenol (curve 6). The intensity of the associated band of phenylacetylene is so low that even if it no doubt indicates the presence of a hydrogen bond between a weakly acid hydrogen of the "C-acid" and the oxygen atom of hexaalkyldigermoxane, its absorption maximum can be only roughly estimated. For comparison of relative basicities of model compounds studied pyrrole[2] proved to be the most suitable proton donor (curve 3). We made use of this compound also in the determination of temperature dependences. The absorption band of stretching frequency $\nu(\text{N-H})$ (3 500 cm^{-1}) of pyrrole itself is sufficiently intense even at its very low concentrations in an inert solvent. (Molar absorptivity of this band decreases with increasing temperature.)

The concentration of hexaalkyldigermoxanes in the measurements in ternary mixtures were chosen so that both absorption band of the complex and that of free proton donor could be simultaneously recorded. The effect of proton acceptor concentration upon the $\Delta\nu$ values was
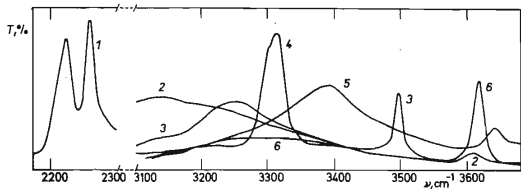

Fig. 1

IR Spectra of Hydrogen Bonds of Hexaethyldigermoxane with Various Proton Donors in Carbon Tetrachloride

1 Deuteriochloroform, *2* phenol, *3* pyrrole, *4* phenylacetylene, *5* methanol, *6* 2,6-xylenol.

Table I

Wavenumbers and Their Shifts Δv (cm^{-1}) for Studied Hexaalkyldigermoxanes

Base	Conc.	0·02M Phenol			0·04M 2,6-Xylenol		
		$v_{assoc.}$	v_{free}	Δv	$v_{assoc.}$	v_{free}	Δv
I	1M	3 190	3 613	423	3 312	3 625	313
II	1M	3 135	3 612	477	3 292	3 626	334
	in sub.	—	—	—	—	—	—
III	0·2M	3 130	3 612	492	—	—	—
	1M	—	—	—	3 292	3 625	333
	1·5M	—	—	—	—	—	—
	in sub.	3 140	3 613	473	3 290	3 619	329
IV	1M	3 135	3 614	479	3 282	3 628	346
	in sub.	—	—	—	—	—	—

examined with hexa-n-propyldigermoxane for its 0·2M, 1M, and 1·5M solutions in carbon tetrachloride and in the absence of the solvent. A more pronounced effect of the proton acceptor concentration was observed only for methanol. In this case the Δv value for binary systems methanol–hexaalkyldigermoxane was lower than that for the ternary system methanol–hexaalkyldigermoxane–carbon tetrachloride (Table I). With increasing temperature (6—45°C) the wavenumber of the v(N—H) non-associated band increases by 3 cm^{-1}, while the increase in wavenumber of the (N—H) associated band amounts to 20 cm^{-1}. The intensity of by far broader band of stretching vibration of the associated N—H bond is slightly decreased (by approx. 1%). It seems that the expected increase in maximal absorption of the v(N—H$_{non-assoc}$) band is compensated by temperature change of absorbance of free pyrrole, which operates in the opposite direction.

DISCUSSION

From comparison of the measured (Table I) and reported[11] values it is obvious that the basicity of germoxane oxygen is markedly higher than that of siloxane oxygen. This is further illustrated by diagram of frequency shifts with phenol and pyrrole for the methylderivatives of type [(CH$_3$)$_3$.M]$_2$O (M = C, Si, Ge), which shows that the maximal Δv values are displayed by hexamethyldigermoxane (see Fig. 2). The Δv values for di-tert-butyl ether, tert-butoxytrimethylsiloxane and hexamethyldisiloxane plotted in Fig. 2 were taken over from ref.[1]. If we add the Δv value of hydrogen bond between trimethylethoxygermane[2] and pyrrole (215 cm^{-1}) we can state that the relative basicity of the oxygen atom decreases in the sequence Ge—O—Ge > C—O—Ge > > C—O—C > C—O—Si > Si—O—Si.

Table I
(Continued)

0·05M Methanol			0·03M Pyrrole			0·09M Phenylacetylene			2·5M Deuteriochloroform		
ν_{assoc}	ν_{free}	$\Delta\nu$	ν_{assoc}	ν_{free}	$\Delta\nu$	ν_{assoc}	ν_{free}	$\Delta\nu$	ν_{assoc}	ν_{free}	$\Delta\nu$
3 409	3 646	237[a]	3 262	3 495	233[a]	3 230	3 314	84	2 223	2 255	32
3 388	3 646	258	3 246	3 496	250	3 210	3 313	103	2 219	2 255	36
3 398	3 646	248	3 253	3 500	247	3 213	3 320	107	—	—	—
3 385	3 645	260	3 243	3 495	252	—	—	—	—	—	—
3 385	3 645	260	3 245	3 496	251	3 213	3 313	100	2 218	2 255	37
3 392	3 649	257	3 251	3 499	248	3 230	3 318	88	2 221	2 256	35
3 396	3 646	250	3 250	3 500	250	3 223	3 320	97	2 219	2 255	36
3 384	3 647	263[b]	3 241	3 497	256[b]	3 218	3 315	97	2 218	2 256	38
3 395	3 646	251	3 244	3 499	255	3 221	3 321	100	—	—	—

[a] Reported[10] 274 cm^{-1} and 300 cm^{-1}, resp. [b] Reported[10] 285 cm^{-1} and 320 cm^{-1}, resp.

In view of a small difference between the inductive effects of analogical trialkylsilyl and trialkylgermyl groups a significant increase in the basicity of the germoxane oxygen can be atributed to a less pronounced ($p \rightarrow d$) π nature of the germanium to oxygen bond in hexaalkylgermoxanes, as compared with the silicon to oxygen bond in hexaalkylsiloxanes. From Fig. 2 it is further obvious that the basicity of the oxygen atom in hexamethyldigermoxane is higher than that in the corresponding tert-butyl ether[1]. This can be accounted for by the higher electropositivity of the germanium atom over the carbon atom[12].

The high basicity of the oxygen atom in germoxanes manifests itself in that all the hexaalkyldigermoxanes studied from hydrogen bonds also with weakly acid deuteriochloroform (Fig. 1, curve 1), contrarily to analogical organosilicon compounds. The formation of the hydrogen bond here is further facilitated by easier steric accessibility of the oxygen atom in digermoxanes, in contrast to analogical disiloxanes, which is due to the smaller Ge—O—Ge bond angle relative to that of the Si—O—Si bond[13].

Fig. 2

The $\Delta\nu$ Values for the Methyl Derivatives $((CH_3)_3M)_2O$ (M = C, Si, Ge)

1 Phenol, 2 pyrrole.
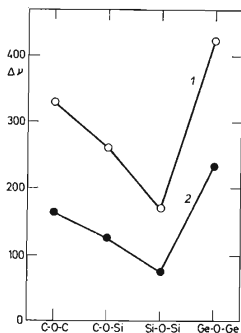
If we compare the relative basicities of the alkyldigermoxanes prepared by us with those of analogical alkyldisiloxanes[11], we find that in both series the basicities gradually decrease on going from the butyl derivative to the methyl derivative. This is likely due to $+I$ effect of the alkyl group, the highest difference being between the methyl and the ethyl derivatives[12], quite in accordance with expectation. The differences between the ethyl, propyl and butyl derivatives lie within the limits of accuracy of the reading of absorption band maximum of the associated form, however, systematic changes determined on the basis of the measurements of hexaalkyldigermoxanes with a series of proton donors confirm the increase in relative basicity in the sequence hexamethyldigermoxane < hexaethyldigermoxane < hexapropyldigermoxane ≦ hexabutyldigermoxane.

The results of thermodynamic calculations based on the measurement of temperature dependences, too, do not allow to differentiate between the small changes in basicity of individual hexaalkyldigermoxanes. On the basis of the discussed experiments it can only be stated that the magnitude of the association constant speaks for the lowest tendency of the complex formation in the case of the hexamethylderivative — in harmony with its lowest relative basicity — and that the value of the enthalpy of complex formation for hexaalkyldigermoxanes amounts to approx. 4 kcal/mol.

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Translated by J. Hetflejš.