THE OXYGEN BASICITY STRENGTHENING EFFECT IN PEROXIDES*

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The hydrogen-bonding ability of peroxides $R_3MOOM'R'_3$ having M = C, Si and Ge with phenol in CCl_4 is analyzed. The oxygen basicity of the $R_3MOOM'R'_3$ with M = C and Si is indicated to be increased over the ability of the electronic effect of R_3C- and R_3Si- groups probably due to the interaction between lone electron pairs located at the oxygen atoms.

In spite of a great body of data[1-3] on the peroxides $R_3MOOM'R'_3$ having substituted alkyl, silyl or germyl groups (M = C, Si, Ge) attached to the oxygens, the information concerning their physical properties is scanty[4-10]. Besides the low stability[4] of the bond between the oxygen atoms, these compounds appear to have almost covalent character of the O—M and the O—O bonds and show[7-10] only a small variation of the O—O bond parameters with substitution at the atom M. The last fact is also consonant with the hydrogen-bonding ability of the peroxides. The studies[8-10] on this property revealed the decrease of the oxygen basicity in $R_3MOOM'R'_3$ compounds with increasing electronwithdrawing action of R and R' substituents and the operation of the $\mathrm{Si} \underline{\leftarrow} \mathrm{O}$ backbonding. However, some conclusions drawn[10] appear apparently inconsistent with the results of our recent studies[11-14] on the oxygen basicity of ether-like compounds. Herein we present an analysis and new interpretation of the oxygen basicity data on peroxides different from that reported earlier[10].

RESULTS AND DISCUSSION

The oxygen basicity of peroxides $R_3MOOM'R'_3$, measured[8-10] as the wavenumber shift $\Delta\nu(OH)$ of phenol due to its interaction with these compounds in CCl_4, is for all $(CH_3)_3COOMR_3$ (M = C, Si, Ge) compounds lower than that for $(CH_3)_3COMR_3$ compounds (Table I). This fact together with the basicity order $(CH_3)_3COOC(CH_3)_3 \sim \sim (CH_3)_3COOSi(CH_3)_3 < (CH_3)_3COOGe(C_2H_5)_3$ indicates that (*1*) electron-withdrawing effect of $(CH_3)_3MO$-group is greater than that of $(CH_3)_3M$-group and (*2*) the M atom electronegativity and the $\mathrm{O} \underline{\rightarrow} \mathrm{Si}$ back-bonding, known to control

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properties of $(CH_3)_3COMR_3$ systems are also in operation in the peroxides $R_3MOOM'R'_3$. The difference in the $\Delta\nu(OH)$ values between $R_3MOOM'R'_3$ and $R_3MOM'R'_3$ however declines when going from carbon to silicon compounds – it approaches zero for M and M′ = Si. The strikingly comparable oxygen basicity for bis(trimethylsilyl) peroxide and hexamethyldisiloxane (taking into account some, but with regard to steric effect of *t*-butyl group in $(CH_3)_3COC(CH_3)_3$, smaller steric effect of $(CH_3)_3Si$-group) would then indicate either some basicity lowering

TABLE I

$\Delta\nu(OH)$ Data[a] for $R_3MO_nM'R'_3$ Compounds

R_3M	R'_3M'	n = 1	n = 2	$\Delta\,\Delta\nu(OH)$
$(CH_3)_3C$	$(CH_3)_3C$	321	206	115
$(CH_3)_3C$	$(CH_3)_3Si$	265	210	55
$(CH_3)_3C$	$(C_2H_5)_3Ge$	$>400^b$	302	98
$(CH_3)_3Si$	$(CH_3)_3Si$	169	172	−3

[a] $\Delta\nu(OH)$ of phenol due to its interaction with $R_3MO_nM'R'_3$ in CCl_4, in cm^{-1}, taken from refs[8–10,15–17]. [b] The value 400 cm^{-1} corresponds to $\Delta\nu^{pyrrol}$ with $(CH_3)_3GeOC_2H_5$ (215 cm^{-1}, ref.[18]) and was obtained by the equation $\Delta\nu^{phenol} = 1{\cdot}76\,\Delta\nu^{pyrrol} + 21{\cdot}0$ (see ref.[14]).

TABLE II

Experimental[a] and Calculated[b] $\Delta\nu(OH)$ Data for $R_3MOOM'R'_3$ Compounds

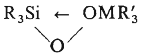
Compound	$\Delta\nu(OH)$		
	exp.	calc.[c]	calc.[d]
$(CH_3)_3COOC(CH_3)_3$	206	92 ± 28	—
$(CH_3)_3COOSi(CH_3)_3$	210	117 ± 10	76 ± 27
$(CH_3)_3COOSi(C_6H_5)_3$	140	—	36 ± 31
$(CH_3)_3SiOOSi(CH_3)_3$	172	106 ± 10	—
$(CH_3)_3SiOOSi(C_6H_5)_3$	153	—	76 ± 12
$(CH_3)_3COOGe(C_2H_5)_3$	302	—	271 ± 7

[a] Refs[8–10]. [b] Calculated from the developed $\sigma^*_{R_3MO}$ parameters and the known[11,21] $\Delta\nu(OH)$ *vs* σ^*_X relationship for the X—$OM(CH_3)_3$ (M = C and Si) compounds. [c] Acquired from the σ^* of the left-sided R_3MO group. [d] Acquired from the σ^* of the right-sided R_3MO group.

interaction in hexamethyldisiloxane, or some basicity strengthening effect in bis(trimethylsilyl)peroxide. The following analysis of the oxygen basicity in peroxides was made in order to answer this question.

The electronic effect parameter of R_3MO-groups (R_3MO, σ^*: $(CH_3)_3CO$, 1·56; $(CH_3)_3SiO$, 1·68; $(C_6H_5)_3SiO$, 1·99; $(C_2H_5)_3GeO$, 0·15) was obtained from that of R_3M-groups[14,19] ($(CH_3)_3C$, $\sigma^* = -0{\cdot}30$; $(CH_3)_3Si$, $\sigma^* = -0{\cdot}15$; $(C_6H_5)_3Si$, $\sigma^* = 0{\cdot}45$; $(C_2H_5)_3Ge$, $\sigma^* = -1{\cdot}50$*) attached to oxygen on the basis of the interrelation[20] between σ^*_{RO} and σ^*_R. Thereafter, the oxygen basicity of R_3MO—$OC(CH_3)_3$ and R_3MO—$OSi(CH_3)_3$ was calculated from the known[11,21] $\Delta\nu$(OH) *vs* σ^*_X relationship for the X—$OC(CH_3)_3$ and X—$OSi(CH_3)_3$ sets on the basis of the parameter $\sigma^*_{R_3MO}$.

The results gathered in Table II invalidate the operation of an intramolecular coordination bond in peroxides (structure *I*) suggested earlier[10] and indicate that the calculated oxygen basicity in the peroxide with GeOOC grouping



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matches well with the experimental value. Those $\Delta\nu$(OH) values calculated for the peroxides with COOC, COOSi, and SiOOSi groupings are much greater than their experimental counterparts. It thus turns out that some oxygen basicity strengthening effect has to be operative in peroxides $R_3MOOM'R'_3$ with M = C and Si. It obviously originates from the interaction between lone pairs of electrons localized at the oxygens that, by increasing the HOMO energy, makes the peroxide more apt to interact with soft acid by which the dissociating phenol obviously is.

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* Assumed identical with σ^* for $(n\text{-}C_3H_7)_3Ge$ that was obtained from $\Delta\nu$ pyrrol for $(n\text{-}C_3H_7)_3GeOC_2H_5$ (226 cm^{-1}, ref.[18]) and using the equation interrelating $\Delta\nu^{phenol}$ with $\Delta\nu^{pyrrol}$ (ref.[14]), and the relationship $\Delta\nu^{phenol}$ *vs* σ^*_X for X—OC_2H_5 (ref.[11]).

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