

THE RATE OF ACID HYDROLYSIS
OF N-ALKYL ACETATES AND OF THEIR $\omega(\text{CH}_3)_3\text{M}$
(M = C, Si, AND Ge)-SUBSTITUTED DERIVATIVES*

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Received February 4th, 1974

Rates of acid hydrolysis of n-alkyl acetates $\text{CH}_3(\text{CH}_2)_n\text{OCOCH}_3$ ($n = 3-8$), their tert-butyl derivatives $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OCOCH}_3$ ($n = 1-4$), trimethylsilyl derivatives $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OCOCH}_3$ ($n = 1-6$), and trimethylgermyl derivatives $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OCOCH}_3$ ($n = 1-4$) were measured. Kinetic data were interpreted in terms of the predominant role of the steric effect of alkoxy groups and of the electron-donating effect of $(\text{CH}_3)_3\text{MCH}_2$ (M = Si, Ge)-groups.

Intramolecular interaction of the functional group with the $(\text{CH}_3)_3\text{M}$ -group in compounds of the type $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OX}$ (M = Si, Ge) may change properties of the functional group and then differentiate these compounds from analogous carbon derivatives $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OX}$. Depending on the distance between these potentially interacting centres, these interactions are known as α - or β -effect and $(p \rightarrow d)_\sigma$ coordination ($n > 2$). From a kinetic study of alkaline hydrolysis of compounds $\text{R}(\text{CH}_2)_n\text{OCOCH}_3$ (R = CH_3 , $(\text{CH}_3)_3\text{M}$; M = C, Si, and Ge) it followed that a weak $(p \rightarrow d)_\sigma$ coordination of the type $o \rightarrow \text{M}$ probably takes place in the ground state of the compounds $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OCOCH}_3$ (M = Si, Ge; $n > 2$) (ref.¹).

The rate of acid hydrolysis of the above compounds is not so sensitive indicative means for detecting $(p \rightarrow d)_\sigma$ coordination as the rate of their alkaline hydrolysis (cf.¹), but comparison of trends in reaction rates of acid and alkaline hydrolysis of series $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OCOCH}_3$ (M = C, Si, and Ge; $n = 1-3$) may provide further information about the importance of the α -effect in the compounds $(\text{CH}_3)_3\text{MCH}_2\text{OCOCH}_3$ (M = Si, Ge) on their interaction with electrophilic or nucleophilic species.

EXPERIMENTAL

Rates of acid hydrolysis of the acetates were determined by titrimetric method. A 100 ml - reaction flask was charged with 20 ml of 0.1M solution of the appropriate acetate in 70% aqueous dioxane and 20 ml of 0.1M solution of *p*-toluene sulphonic acid in 70% dioxane were added.

* Part CXXIV in the series Organosilicon Compounds. Part CXXIII: This Journal 39, 2630 (1974). Part XIX in the series Organogermanium Compounds; Part XVIII: This Journal 39, 2630 (1974).

The contents of the sealed reaction flask were shaken and the flask was placed in a temperature controlled bath maintained at 65°C. At fixed time intervals 5 ml-samples of the reaction mixture were removed and placed into a titration flask containing 50 ml of water, by which procedure they were also cooled. The hydrolysis was thus stopped and the samples were titrated by 0.05M-NaOH on phenolphthalein. Under conditions chosen the over-all reaction order was degenerated and rate constants k could be calculated from the expression derived from an integrated equation for pseudo-first order reaction (Eq. (1)) where a is the initial molar amount of a given acetate, x is its molar amount reacted in time t , and b is the molar amount of *p*-toluenesulphonic acid. The rate constant k ($1 \text{ mol}^{-1} \text{ s}^{-1}$) was taken as an average of at least 14 values. With all acetates the confidence interval

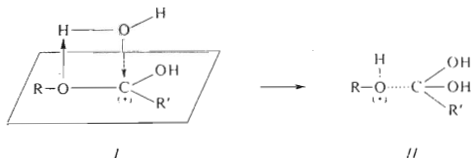
$$k = (1/tb) \ln [a/(a - b)] \quad (1)$$

did not exceed 6%, with the exception of ethyl acetate (9.52%). Preparation of all acetates was reported earlier¹.

RESULTS AND DISCUSSION

The rate-determining step of acid hydrolysis of primary alkyl esters is assumed to be formation of a complex by nucleophilic attack of water molecule on the protonated form of the ester^{2,3}. The ability of the oxygen of alkoxy group RO- to transfer electronic effect of substituent R on the reaction center is in acid hydrolysis by far weaker compared to alkaline hydrolysis⁴.

This fact was explained under the assumption that polar effect facilitating protonisation of the alkoxy group operate in the opposite way in the subsequent cleavage of alcohol molecule from a complex³, despite of the fact that neither protonisation of the alkoxy oxygen of the ester, nor decomposition of the complex proceed in the rate-determining step. Another explanation takes into account a possible compensation of the opposite effects exerted by substituent R on the alkoxy oxygen and the carbonyl carbon, both atoms being regarded as equivalent centers in transition state formation⁴. Comparatively higher electronegativity of the sp^2 hybridised oxygen as well as the ability of esters to form complexes with Lewis acids *via* the carbonyl oxygen favour, however, protonisation on the carbonyl oxygen. Protonated form of the ester⁵ can form a complex with water molecule by two synchronous interactions which lead to a four-membered cyclic transition state: by nucleophilic



attack of the oxygen of increasingly labilised water molecule on the carbonyl carbon and by nucleophilic attack of the alkoxy oxygen on the proton having been released from the water molecule (structure I).

The latter concept, which renders it possible to account for relatively lower transmission of polar effects of substituent R of the alkoxy group through oxygen in acid hydrolysis also by assuming opposite influencing of both reaction centers, will be adopted in interpreting the rates of acid hydrolysis of the acetates $R(\text{CH}_2)_n\text{OCOCH}_3$ ($R = \text{CH}_3, (\text{CH}_3)_3\text{M}; \text{M} = \text{C}, \text{Si}, \text{and Ge}$) (Fig. 1). The rates of acid hydrolysis of *n*-alkyl acetates $\text{CH}_3(\text{CH}_2)_n\text{OCOCH}_3$ ($n = 1-8$) show a similar dependence on the number of methylene groups as the rates of their alkaline hydrolysis¹; as *n* increases, the rate first fastly and then slowly decreases. This decrease can be ascribed to increasingly more effective enveloping of the reaction center by the alkoxy group. The rate of acid hydrolysis of the compounds $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OCOCH}_3$ decreases from 2,2-dimethylpropyl acetate to 3,3-dimethylbutyl acetate and then it remains constant even for $n = 3$ or 4. The rate of hydrolysis of all these compounds is lower than the rate of hydrolysis of respective members of the series $\text{CH}_3(\text{CH}_2)_n\text{OCOCH}_3$. OCOCH_3 , and the reactivity difference between these two series can be explained (similarly as in the case of their alkaline hydrolysis¹) by comparatively greater steric effect of the $(\text{CH}_3)_3\text{C}$ group whose influence becomes gradually less important as *n* increases. The faster rate of acid hydrolysis of the first member of the series $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OCOCH}_3$ is surprising when compared to the trend found for alkaline hydrolysis of the same series¹. This increase can be caused either by diminishing steric effect of the $(\text{CH}_3)_3\text{C}$ group in the protonated form of this compound due to repulsion between positively charged carbonyl carbon and quaternary carbon, the latter becoming partially electron deficient as a result of the $-I$ effect of the methyl

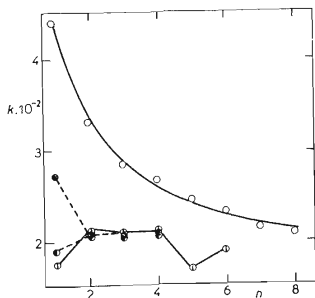


FIG. 1

Dependence of Rate Constants of Acid Hydrolysis of the Acetates $R(\text{CH}_2)_n\text{OCOCH}_3$ ($R = \text{CH}_3, (\text{CH}_3)_3\text{M}; \text{M} = \text{C}, \text{Si}, \text{and Ge}$) at 65°C on *n*

○ $\text{CH}_3(\text{CH}_2)_n\text{OCOCH}_3$, ● $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OCOCH}_3$, ● $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OCOCH}_3$, ⊙ $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OCOCH}_3$.

groups (cf.^{6,7}) and of the polarity of the $O \leftarrow CH_2$ bond, or (and more likely) by relatively lower energy barrier toward complex decomposition (structure II), since the $(CH_3)_3CCH_2$ group is stronger electron acceptor than the $(CH_3)_3C(CH_2)_n-$ ($n > 1$) groups. Hydrolytic rates in series $(CH_3)_3M(CH_2)_nOCOCH_3$ ($M = Si, Ge$) increase from $n = 1$ to $n = 2$ and remain further constant, with the exception of the compounds $(CH_3)_3Si(CH_2)_nOCOCH_3$ ($n = 5, 6$). A similar rate acceleration as in the series $(CH_3)_3C(CH_2)_nOCOCH_3$ is not observed in the series $(CH_3)_3M(CH_2)_n.OCOCH_3$ ($M = Si, Ge$) when going from $n = 2$ to $n = 1$, but, on the contrary, the rate decreases. This fact can be explained either by strong electron-donating ability of $(CH_3)_3MCH_2$ groups, which is the reason why these groups cannot diminish the steric effect of $(CH_3)_3M$ groups in protonated forms of the compounds $(CH_3)_3MCH_2OCOCH_3$, unlike the $(CH_3)_3CCH_2$ group in protonated forms of their carbon analogues, or (and more likely) by an increased energy barrier toward decomposition of complex II. It is not yet clear whether the lower reaction rate observed with compounds containing 5 or 6 methylene groups can be ascribed to a more difficult protonisation of the ester group which was already assumed¹ to weakly interact in these cases with silicon.

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Translated by J. Hetflejš.