New Steric Effect Parameters. A Simple Method of Estimation

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Earlier Charton has proposed steric effect parameters ν and ν' to correlate the rates of esterification and S_N2 reactions.[1,2] Very recently we have demonstrated that the rates of imine-forming eliminations can be correlated with ν values.[3-5] However, the ν' values are known for only limited number of substituents.

In this paper we wish to report a simple method of estimation of ν values and new ν' values for sec-Bu and neo-pentyl groups. We found that the ν and ν' parameters can be correlated with two straight lines as depicted in Figure 1. When the hydrogen atoms of the CH_3 group is successively replaced CH_3 groups (Me, Et, *i*-Pr, *t*-Bu) both ν and ν' values increase linearly with a slope of 0.81 ($r = 0.999$). Similiarly, when a Me group of the CH_3CH_2 substituent is replaced by Et and *i*-Pr groups (Et, *n*-Pr, *i*-Bu), the data fit on a straight line with a slope of 2.43 ($r = 0.999$)[6]. The excellent linearity between the ν and ν' values for the structually related alkyl groups is striking. However, the smaller slope of the former is not surprising because the steric effect increases more dramatically in the former series and the susceptibility of the S_N2 reaction to the substrate steric effect is greater than that for the esterification.

The ν' values for alkyl substituents of known ν value can be estimated utilizing the linear relationship. The ν value of neo-pentyl group is 1.34.[1] Since this group can be considered as a derivative of CH_3 group in which a hydrogen atom is replaced by a *t*-Bu group, it is reasonable to expect that the relationship between ν and ν' values of this group would fit on the straight line with a slope of 2.43. Utilizing the ν value and the straight line we can estimate the ν' value of neo-pentyl group to be 0.71. Similiaryl, a sec-Bu group can be viewed as a derivative of $CH(CH_3)_2$ in which a CH_3 group is replaced by a CH_3CH_2 group. Therefore, the ν and ν' values for $CH(CH_3)_2$ and $CH(CH_2CH_3)(CH_3)$ are expected to be correlated by a straight line with a slope of 2.43. Based upon this assumption and ν value of 1.51, the ν' value for sec-Bu is estimated to be 0.73.

In order to check the validity of this estimation we have determined the ψ' values for MeONa-promoted eliminations from *N*-chlorobenzylalkylamines [$PhCH_2N(Cl)R$]. The $|\psi'|$ value calculated with the data for R=Me, Et, *i*-Pr, *i*-Bu, sec-Bu, *t*-Bu, and neo-pentyl alkyl substituents is 2.08 ($r = 0.985$).[7] This is in excellent agreement with $|\psi'| = 2.09$ ($r = 0.989$) calculated without the data for R = sec-Bu and neo-pentyl substituents. This result strongly suggest that the ν' values of alkyl substituents of known ν values can be estimated utilizing the linear relationship depicted in Figure 1. Estimations and validation of ν values of other alkyl substituents are in progress in our laboratory.

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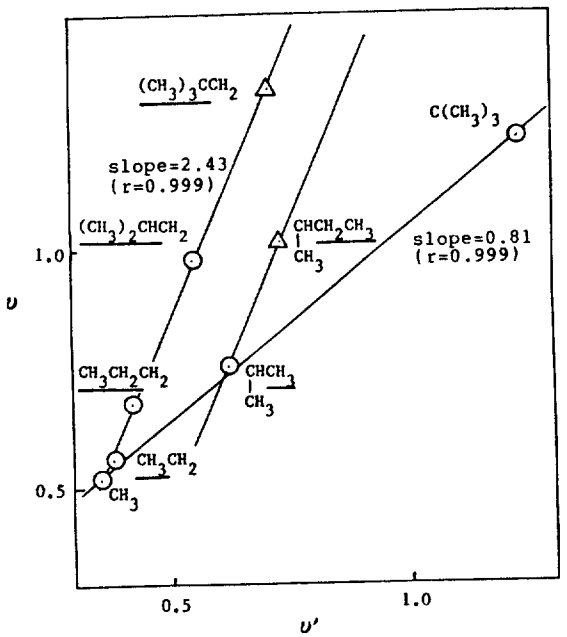

Figure 1. Correlation of ν and ν' values for alkyl substituents. Literature data(⊙) are correlated by two straight lines. The ν values of sec-Bu and neo-pentyl groups (△) are indicated on appropriate straight lines (see text).

References

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6. Although the data for CH_3 group appear to fit on the straight line with a slope of 2.43, it is excluded from the series. Otherwise, CH_3CH_2, $(CH_3)_2CH$, and $(CH_3CH_2)(CH_3)CH$ must also be considered as a series because these can be regarded as derivatives of CH_3CH_2 in which one hydrogen atom at *C*-1 is replaced by Me and Et. This would predict that the data for sec-Bu would fit on the first straight line with a slope of 0.81. This is not reasonable because sec-Bu is structurally related to *i*-Pr but not to Et, Me, or *t*-Bu in the series. Furthermore, the ν' value estimated this way gave very poor correlation in the Chartons plot of imine-forming elimination reactions ($|\psi'| = 1.99$, $r = 0.919$).
7. The k_2 values determined by previous method[3] are $(2.58 \pm 0.11) \times 10^{-3} M^{-1}s^{-1}$ for R = *i*-Bu and $(1.24 \pm 0.03) \times 10^{-3}$ for R = neo-pentyl, respectively. These values and the k_2 values for other alkyl substituents published earlier[3] are used in the calculation.