SHORT COMMUNICATIONS

An Attempt to Estimate the Relative Stability of Tri(hetero)substituted Carbonium Ions*

Takeshi Nakai, Kazuhisa Hiratani and Makoto Okawara

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

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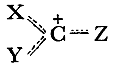
In connection with our study on the structures and ambident reactivities of tri(hetero)carbonium ions containing α-alkylthio groups,[1,2] we attempted to estimate the relative stability of tri(hetero)carbonium ions from their electronic spectra and simple HMO calculations. A series of tri(hetero)-carbonium ions shown below were prepared as perchlorates and iodides.[3]



I, X, Y, Z=SMe; II, X, Y=SMe, Z=NMe$_2$ III, X, Y=NMe$_2$, Z=SMe; IV, X, Y, Z=NMe$_2$

In the electronic spectra we observed a well-defined trend, *viz.*, a strong shift of the absorption maxima to shorter wavelengths was observed with the progressive replacement of SMe in (I) by NMe$_2$.[4] This trend led us to postulate that *there is a linear correlation between the relative stability of the carbonium ion and the transition energy* ($1/\lambda_{max}$). In order to prove this hypothesis we made some attempts described below.

Firstly, it is expected that the stabilizing effect of α-heterosubstituents on carbonium ions concerned might be estimated *relatively* in terms of the Brown-Okamoto's substituent constants ($\sigma_p{}^+$), on the assumption that the additivity rule holds for the series. The observed frequencies of absorption maxima gave a definitely linear correlation with $\sum\sigma_p{}^+$ [5] (Fig. 1), providing a positive criterion for the above hypothesis.

Another criterion for the hypothesis was obtained

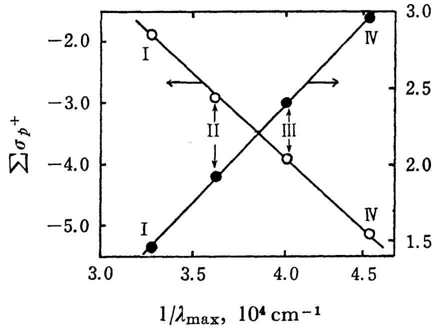


Fig 1. Plots of $1/\lambda_{max}$ (solvent, water) *vs.* $\sum\sigma_p{}^+$ (○) and DE (●).

from simple HMO calculations. In our calculations,[6] the values assumed for the Coulomb integral and resonance integral are as follows: $\alpha_{\ddot{S}}=\alpha+\beta$, $\alpha_{\ddot{N}}=\alpha+1.5\beta$; $\beta_{C-S}=0.6\beta$, $\beta_{C-N}=1.2\beta$[7] Using these parameters, we calculated the energies of the molecular orbitals, the transition energies (ΔE) and the delocalization energies (DE) in the usual manner. A linear correlation between ΔE and $1/\lambda_{max}$ was obtained. Furthermore, a definitely linear correlation of DE with $1/\lambda_{max}$ was obtained (Fig. 1). This correlation provides the second positive criterion.

We suggested that the rates of reactions of various bis(alkylthio)-dialkylaminocarbonium ions with hydroxide ion depend upon the relative stability of the carbonium ions.[2] The logarithms of the rate constants gave a nearly linear correlation with $1/\lambda_{max}$ for the open-chain and cyclic[8] carbonium ions. This may provide a third positive criterion. The relationship between the relative stability and the reactivity of tri(hetero)-carbonium ions will be discussed in full elsewhere.

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1) T. Nakai and M. Okawara, *Tetrahedron Lett.*, **1967**, 3835; This Bulletin, **43**, 1864 (1970).

2) T. Nakai, K. Hiratani and M. Okawara, 19th Symposium on Organic Reaction Mechanisms, Yamagata, 1968, Abstracts, p. 140, and our previous results cited therein.

3) All carbonium salts gave correct data of elementary analyses and NMR properties in $(CD_3)_2SO$.

4) In all cases, ε_{max} were about 10^4. The values of $\lambda_{max}^{H_2O}$ were dependent slightly upon the nature of the counter anion (± 1 mμ).

5) $\sigma_{p-SMe}^{+}=-0.604$ and $\sigma_{p-NMe_2}^{+}=-1.70$: H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1959).

6) The non-orthogonality integral and the auxiliary inductive parameters for the central carbon atoms were neglected.

7) M. J. Janssen, *Rec. Trav. Chim. Pays-Bas*, **79**, 1066 (1960).

8) For example, 2-dimethylamino-1,3-dithiolanylium ion and 2-methylthio-3-methyl-4,5-dihydrothiazolium ion.