

STABILITY AND RING DEFORMATION VIBRATION OF CYCLOPROPENIUM IONS

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Stability of the highly strained cyclopropenium ion has been evaluated in terms of pK_R^+ value determined by the equilibrium between cyclopropenium ion and cyclopropenol. In spite of its convenience, this method can not be applied to the unstable cyclopropenium ions in aqueous solution such as trichloro- and tribromoderivatives.¹ Some special devices are required to obtain the pK_R^+ value²⁻⁴ for such carbonium ions. We have found out an interesting relationship between pK_R^+ and the frequencies of the skeletal deformation modes of cyclopropenium ions. The molecular symmetry of trisubstituted cyclopropenium ions (C_3X_3 , $X = C_6H_5$, $N(CH_3)_2$)^{5,6} can be approximated to the D_{3h} point group from the X-ray structural analyses.^{7,8} Three skeletal vibrations of the cyclopropenium ring are classified into two normal vibrations; the A_1' (Raman active) and E' (Raman and infrared active) species. The observed frequencies of totally symmetric deformation (A_1') and degenerated deformation (E') modes are listed in Table 1.

Table 1. $\nu_{(C-C)}$ of $C_3X_3^+$ (cm^{-1})

X	A'	E'	reference
NMe ₂	1985	1553	(13)
CH ₃	1880	1490	(9)
C ₆ H ₅	1845	1411	(11)
Cl	1791	1312	(11)

It is noted that the frequency of the A_1' mode increases with that of the E' mode. The quite stable trimethylcyclopropenium ion shows a Raman line at 1880 cm^{-1} and an infrared absorption at 1490 cm^{-1} which are assigned to the A_1' and E' mode vibrations of the C_3^+ ring by the normal coordinate analysis, respectively.⁹ These frequencies¹ for $C_3Cl_3^+$ have been observed at relatively lower frequency region ($1791\text{ cm}^{-1}(A_1')$ and $1312\text{ cm}^{-1}(E')$). The lowest frequency of the E' mode among cyclopropenium ions has been reported as 1276 cm^{-1} for relatively unstable $C_3H_3^+$ ion ($pK_R^+ = -7.4$).⁴ The frequency shifts of both ring deformations due to the substituents are extremely large as is seen in Table 1. Their shifts are possibly due to the mass effect and the electronic effect of the substituent. If the mass effect of the substituent attached to the C_3^+ core is predominant, the frequency shift to shorter wavelength will be in the following order, $H < CH_3$, $N(CH_3)_2 < Cl$. However, the frequency of the E' mode of $C_3H_3^+$ shows the lowest frequency among them. Therefore, it is most likely that the C_3^+ ring deformation vibrations are rather sensitive to the electronic effect of the substituent.

The normal coordinate analysis (GVFF) of the $C_3(C_6H_5)_3^+$ ion in the simplified model has suggested that Raman active line at 1845 cm^{-1} is mainly due to the C_3^+ ring deformation (80 %) and weakly coupled with the $C_3^+-C \angle$ stretching vibration (20 %) based on the potential energy distributions.¹⁰ On the other hand, the ir active band at 1411 cm^{-1} has been assigned to the C_3^+ ring deformation (41 %) and the $C_3^+-C \angle$ stretching vibration (51 %). In order to discuss on the substituent effect, the Raman frequency is considered to be preferable parameter because of its high contribution of the C_3^+ ring deformation mode. Unfortunately, the Raman spectra of the cyclopropenium ions are less available than their ir spectra at the present time.

Higher frequency of the A_1' mode of the $C_3(N(CH_3)_2)_3^+$ ion than that of the $C_3(C_6H_5)_3^+$ ion is probably related to the difference in the C-C bond length of the C_3^+ core. According to the X-ray crystallographic study, the C-C bond length of the former ion is about 0.01 \AA shorter than that of the later ion. If this difference is significant as has been mentioned by Sundaralingam,¹⁸ the slight change in the C-C bond length of the C_3^+ core may cause relatively large change in the vibrational spectra.

Although the substituent effect on the cyclopropenium ring must be interpreted in terms of the force constants for quantitative comparison, empirical relationship between pK_{R^+} and $\nu(C_3^+)_{E'}$ is available to estimate the stability of the trisubstituted cyclopropenium ions. If the pK_{R^+} values^{4,11,12} are

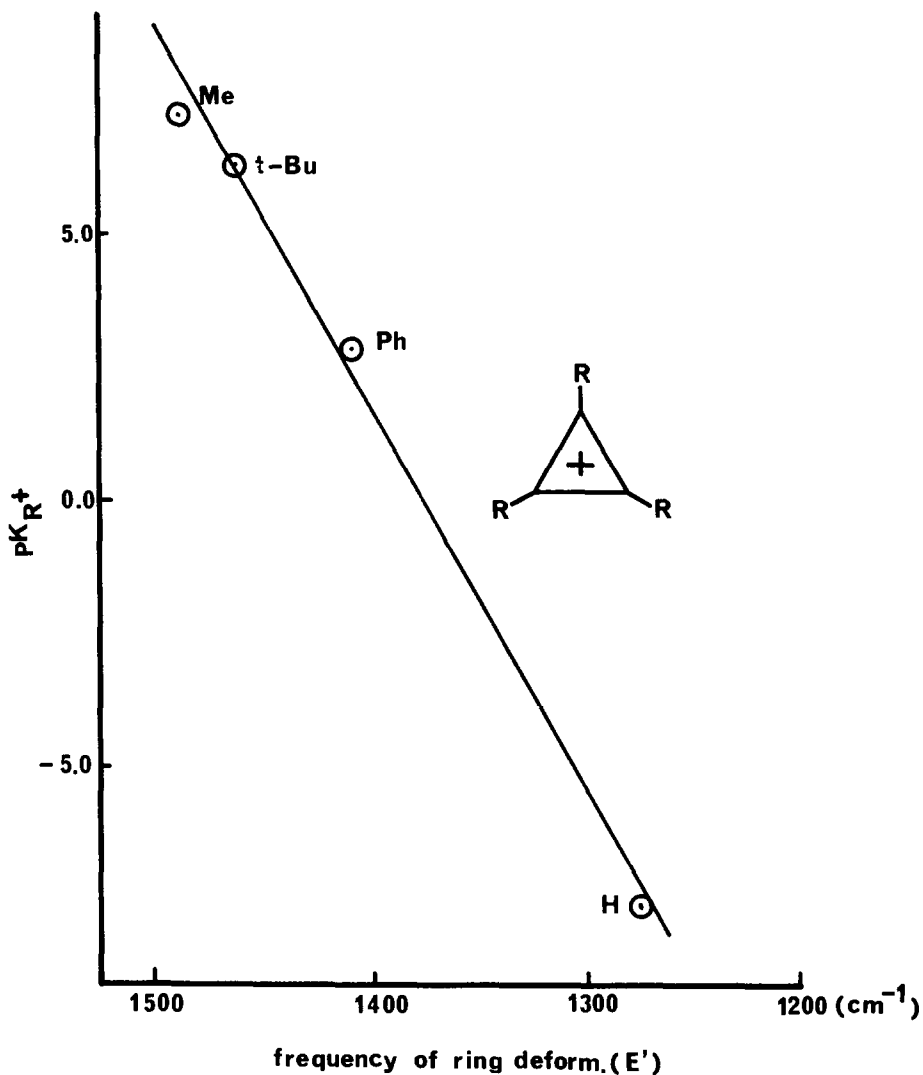


Figure 1. Plot of pK_{R^+} versus ring deformation vibration (E').

plotted against the frequencies of E' mode, an approximate linear relationship between them is obtained as shown in Figure 1. For example, the pK_R^+ of trichlorocyclopropenium ion is estimated as -5, and that of triaminocyclopropenium ion¹³ can be evaluated as 13 by the extrapolation.

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