Ionization Potentials of Cyclopropylethylenes

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Summary It has been shown that ethylenes substituted by cyclopropyl group(s) have extremely low ionization potentials.

CYCLOPROPYLETHYLENE gives a smooth 2 + 2 cycloaddition with tetracyanoethylene[1] thus indicating that it is an electron-rich olefin. Therefore, the ionization potentials of several ethylenes substituted by cyclopropyl group(s) were determined by photoionization using a 0·5 m Seya–Namioka type vacuum u.v. monochromator in the photon energy range 7—11 eV.[2]†

As expected, the cyclopropylethylenes exhibited lower ionization potentials than those of the methyl substituted analogues (Table). 1,2-Dicyclopropylethylenes have ionization potentials of 7·70—7·72 eV, which is even lower than that of hexa-1,3,5-triene (8·23 eV).[3] Tricyclopropylethylene (7·35 eV) is an alkene of extremely low ionization potential.[4] The unusually low ionization potentials observed here could be due to the ability of the cyclopropyl group to stabilize an adjacent electron deficient centre.[5] A cation radical produced by loss of an electron from cyclopropylethylene is therefore much more stable than that derived from a simple alkene.

Ionization potentials of cyclopropylethylenes and alkenes

Cyclopropylethylene	I.P. (eV)[a]	Alkene	I.P. (eV)[a,b]
1,1-Dicyclopropyl	8·08[c]	Isobutene	9·23
cis-1,2-Dicyclopropyl	7·70	*cis*-But-2-ene	9·13
trans-1,2-Dicyclopropyl	7·72[d]	*trans*-But-2-ene	9·13
Tricyclopropyl	7·48	2-Methylbut-2-ene	8·67
1,1-Dicyclopropyl-2,2-dimethyl	7·82[e]	2,3-Dimethylbut-2-ene	8·30

[a] Photoionization method. [b] Ref. 4. [c] Photoelectron method (P.E.) gave 8·08 eV. [d] P.E., 7·74 eV. [e] P.E., 7·80 e.V.

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† Some data were duplicated by a photoelectron method (see Table) by K. Kimura, S. Katsumata, and Y. Achiba (Institute of Applied Electricity, Hokkaido University) with a Japan Spectroscopic Co. PE-1 Photoelectron Spectrometer.

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