Ionization Potentials of Cyclobutadiene

By S. D. WORLEY*

(*Space Physics Division, NASA Manned Spacecraft Center, Houston, Texas* 77058)

Summary The photoelectron spectra of the iron tricarbonyl complexes of *cis*-buta-1,3-diene and cyclobutadiene in conjunction with appropriate SCF MO calculations indicate that the first and second ionization potentials of cyclobutadiene are *ca.* 8·5 and 11·7 ev, respectively.

INDEPENDENT conflicting measurements of the first ionization potential (I_1) of cyclobutadiene (A) have been reported recently.[1,2] Li and McGee[1] produced a stable C_4H_4 isomer (thought to be A) from the pyrolysis of cyclobutadieneiron tricarbonyl (B). The subsequent electron-impact measurement of I_1 for the compound was 9·55 ev. Hedaya *et al.*[2] have reported an electron-impact value† of 8·2 to 8·6 ev for I_1 of the C_4H_4 isomer (A), which was generated by the flash vacuum pyrolysis of photo-α-pyrone. Hedaya *et al.*[3] have also investigated the flash vacuum pyrolysis of (*B*). No evidence of (A) was found; the only C_4H_4 thermal product of (B) was vinylacetylene.

Dewar and Worley[4,5] measured the low-resolution photoelectron spectra of several iron tricarbonyl complexes, including (B) and *cis*-buta-1,3-dieneiron tricarbonyl (C). The important regions of the spectra of these two complexes and of *trans*-buta-1,3-diene are shown in the Figure. The ionization potentials that correspond to the first several breaks in the spectra are listed in the Table. The Table also contains adiabatic first ionization potentials[6] and π-orbital energies[7] for (A) and for the two isomers of butadiene calculated by π semiempirical SCF MO procedures. In addition, the predicted values of I_1 and the second ionization potential (I_2) for (A) and *cis*-buta-1,3-diene are given.

The estimate of I_1 for (A) (8·5 ev) has been described elsewhere[4] in detail. Because I_1 for *cis*-buta-1,3-diene might be as low as 9·07 ev,[8] a lower limit for the estimate is 8·36 ev. The range for I_1 (8·36 to 8·5 ev) is well within the spread (8·2 to 8·6 ev) reported by Hedaya *et al.*,[2] thereby supporting their results. The two determinations are probably of similar accuracy because of the theoretical assumptions made by Dewar and Worley[4] and because of the error that is inherent in the electron-impact method (used by Hedaya *et al.*[2]).

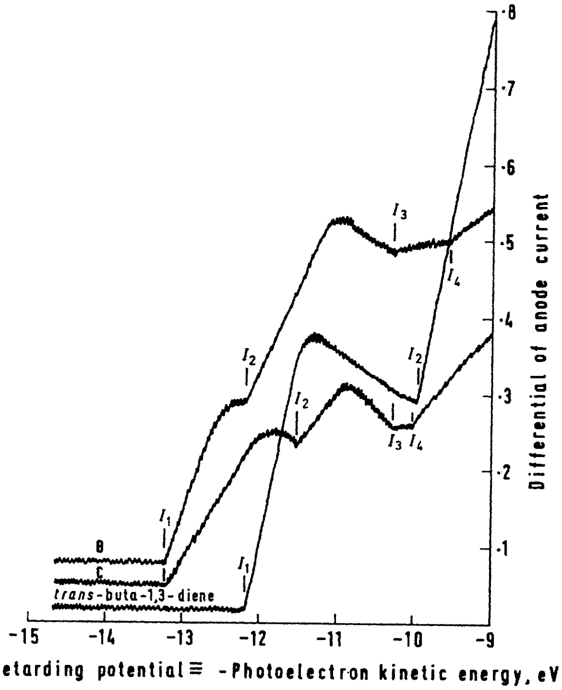

FIGURE. *Photoelectron spectra excited by the* 584 Å (21.22 ev) *resonance line of helium.*

Dewar and Worley[4] have pointed out that the perturbing influence of iron tricarbonyl on the second π-orbital of (B)

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† The 0·4 ev range reflects the difficulty of choosing the "break" in an electron-impact ion current–electron energy curve. Hedaya reports that 8·2 ev is the best electron-impact value (ref. 2).

and of (C) should be very small. Arguments analogous to those used in estimating I_1 of (A) give an I_2 for (A) of 11·66 ev, which is in excellent accord with the value (11·62 ev) obtained from the direct SCF MO calculation.

Observed and calculated ionization potentials[a]

Compound		Observed	Calculated (π)[b]	Calculated (π)[c]
Cyclobutadieneiron tricarbonyl (B)	..	8·04, 9·02, 10·89, 11·64		
cis-Buta-1,3-dieneiron tricarbonyl (C)	..	8·04, 9·73, 10·92, 11·23		
trans-Buta-1,3-diene..	..	9·07, 11·27	8·83	9·16, 11·20
cis-Buta-1,3-diene	..	9·21,[d] 11.25[e]	8·97	9·19, 11·18
Cyclobutadiene (A)	..	8·50,[e] 11·66[f]	8·51	8·66, 11·62

[a] All values are given in ev.

[b] Adiabatic I_1 calculated by the half-electron method.[6]

[c] Ionization potentials estimated from Koopmans' theorem.[7]

[d] Estimated value.[8]

[e] Estimated value.[4]

[f] Estimated value (this communication).

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