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Thermodynamic Properties of Cubane

Sir:

The heat of formation of solid cubane (C_8H_8) has been determined by combustion with oxygen in a conventional bomb calorimeter.[1] Five determinations yielded an average value for $\Delta E_c°$ of -1156.0 kcal/mole, and, after allowance for a small amount of carbon adhering to the bomb wall, one calculates $\Delta H_f°_{298} = 129.5 \pm 0.8$ kcal/mole. The vapor pressure has been determined over the range 239 to 262°K by the Knudsen effusion method and is given by the equation

$$\log P_{\text{mm}} = (-4.19 \pm 0.097)(10^3/T) + (14.0 \pm 0.8)$$

Thus, at 298°K $\Delta H°_{\text{sub}} = 19.2 \pm 0.4$ kcal/mole and $\Delta H_f°_{[\text{cubane(gas)}]} = 148.7 \pm 1.0$ kcal/mole. By comparison, the heat of formation of an isomeric gas C_8H_8 (cyclooctatetraene) is $+71.1 \pm 0.1$ kcal/mole at 298°K.[2]

Franklin's[3] method of group equivalents assigns a value of -8.7 kcal/mole to eight $\gt$CH groups. This combined with the measured heat of formation gives a total strain energy of 157 kcal/mole for cubane. This strain energy distributed over the six cyclobutane faces of the cube gives 26.2 kcal/mole of strain energy per cube face, in close agreement with the value of 26.0 kcal/mole for the strain energy in cyclobutane.[4] Weltner[5] predicted that cubane (tricyclooctane) should be 80 kcal less stable than cyclooctatetraene which is almost exactly the case.

Mass spectra of cubane have been obtained with 50-v electrons at 100 and 25° on a Consolidated Electrodynamics Corporation Type 21-701 mass spectrometer.[6] The spectra at the two temperatures were in good agreement and thus showed that no significant amount of decomposition occurred in the instrument. Appearance potentials were determined for the principal ions, and these together with relative abundances are given in Table I. The ionization potential agrees quite well with the value computed by the group orbital method[7] employing parameters obtained from paraffin and cycloparaffin hydrocarbons.

The appearance potentials of the fragment ions suggest that in all cases the ion has probably rearranged to an open-chain structure. The appearance potential for $C_6H_6^+$ agrees very closely with the ionization potential of benzene; nevertheless, we think this is fortuitous. The agreement of the 25 and 100° spectra shows little decomposition, and the relative intensities of the 78 and 77 ions and the appearance potential of $C_6H_5^+$ are quite different from those in benzene. Thus the 78 peak is probably a fragment ion of cubane.

Table I. Relative Abundances and Appearance Potentials of Principal Ions from Cubane

Mass no.	Formula	Rel abundance[a]	Appearance potential, ev
39	$C_3H_3^+$	75.6	11.14 ± 0.18
50	$C_4H_2^+$	30.9	16.85 ± 0.08
51	$C_4H_3^+$	48.0	16.74 ± 0.21
52	$C_4H_4^+$	43.8	13.78 ± 0.08
63	$C_5H_3^+$	13.2	14.59 ± 0.24
77	$C_6H_5^+$	32.1	12.21 ± 0.10
78	$C_6H_6^+$	89.1	9.15 ± 0.10
102	$C_8H_6^+$	9.0	10.26 ± 0.21
103	$C_8H_7^+$	100.0	9.50 ± 0.11
104	$C_8H_8^+$	16.5	8.74 ± 0.15

[a] At 25° (% of base peak; electron energy 50 v).

A more detailed paper will be published in the near future.

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The Formation of Monofluorocarbene by the Gas-Phase Decomposition of Dihalomethane Molecules Excited during Atomic Exchange Reactions[1]

Sir:

We have formed monofluorocarbene in the gas phase through dehydrohalogenation of excited dihalomethane molecules, in analogy with earlier experiments producing monochlorocarbene,[2] and have detected it through the observation of cyclopropyl fluoride in the presence of ethylene. The reactions have been carried out in the presence of substantial concentrations of O_2 and therefore presumably involve monofluorocarbene in the singlet electronic state.[3]

The excited dihalomethane molecules have been formed through these substitution reactions

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