Acknowledgment. We are grateful to the National Research Council of Canada for financial support of this research (Grant No. N.R.C. A2267).

T. Money, J. L. Douglas
Department of Chemistry, University of British Columbia
Vancouver 8, British Columbia

A. I. Scott
Chemical Laboratory, University of Sussex
Brighton, England
Received November 29, 1965

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 $\geqslant$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.

Acknowledgments. Professor Philip E. Eaton of the University of Chicago generously furnished the cubane sample. The authors gratefully acknowledge the support of the Robert A. Welch Foundation, the National Aeronautical Space Administration, and the Petroleum Research Foundation of the American Chemical Society.

---

(1) B. D. Kybett, G. K. Johnson, C. K. Barker, and J. L. Margrave, *J. Phys. Chem.*, **69**, 3603 (1965).

(2) E. J. Prosen, W. H. Johnson, and F. D. Rossini, *J. Am. Chem. Soc.*, 72, 626 (1950).

(3) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(4) A. S. Pell and G. Pilcher, *Trans. Faraday Soc.*, **61**, 71 (1965).

(5) W. Weltner, *J. Am. Chem. Soc.*, **75**, 4224 (1953).

(6) H. G. Voorhies, C. F. Robinson, T. G. Hall, W. M. Brubaker, and C. E. Berry, "Advances in Mass Spectrometry," Vol. 1, J. D. Waldron, Ed., Pergamon Press, London, 1959, p. 44.

(7) J. L. Franklin, *J. Chem. Phys.*, **22**, 1304 (1954).

(8) Chercheur qualifie of the Belgium Fonds National de la Recherce Scientifique. On leave of absence from the University of Liege, Belgium.

B. D. Kybett, S. Carroll, P. Natalis[8]
D. W. Bonnell, J. L. Margrave, J. L. Franklin
Department of Chemistry, Rice University
Houston, Texas
Received November 23, 1965

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

---

(1) This research was supported by AEC Contract No. AT-(11-1)-34, Agreement No. 126, with the University of California, Irvine.

(2) Y.-N. Tang and F. S. Rowland, *J. Am. Chem. Soc.*, **87**, 1625 (1965).

(3) See, however, P. O. Gaspar and G. Hammond, Chapter 12 in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, for an analysis of the validity of these presumptions for CH_2.

$$\mathrm{T} + \mathrm{CH_2F_2} \longrightarrow \mathrm{CHTF_2} + \mathrm{H} \qquad (1)$$
$$(\mathrm{CH_2ClF}) \quad (\mathrm{CHTClF})$$

$$\mathrm{T} + \mathrm{CHF_3} \longrightarrow \mathrm{CHTF_2} + \mathrm{F} \qquad (2)$$

In each case, the monofluorocarbene is then formed by the elimination of HF (or HCl)[4] from the excited dihalomethane molecule. The monofluorocarbenes so formed are radioactively labeled as CTF and are subsequently traced through the radioactivity of the products.

The relative yields of the labeled dihalomethane molecules surviving without decomposition and of the cyclopropyl fluoride molecules under a variety of conditions are summarized in Table I.

Table I. Formation of Cyclopropyl Fluoride by Monofluorocarbene Addition to Olefins

Excited molecule	Gas pressure, cm Parent	C_2H_4	O_2	Relative yield[a]
$CHTF_2$	CH_2F_2, 54.0	22.9	—	45 ± 2[b]
$CHTF_2$	CH_2F_2, 52.3	23.8	4.1	45 ± 2[b]
CHTClF	CH_2ClF, 56.1	17.5	3.4	35 ± 2[b]
$CHTF_2$	CHF_3, 45.4	21.5	3.7	100 ± 8[b]
$CHTF_2$	CHF_3, 56.6	12.3	2.4	95 ± 8[b]
		trans-C_4H_8-2		
$CHTF_2$	CH_2F_2, 52.2	19.3	3.5	44 ± 1[c]

[a] Excited molecule = 100. [b] Cyclopropyl fluoride-*t*. [c] Dimethylcyclopropyl fluoride-*t*.

Additional experiments have been performed with various other substrates as possible reactants for the monofluorocarbene. Reactions with simple gaseous olefins lead to the corresponding substituted cyclopropyl fluorides in stereospecific reactions, without any substantial preference for *syn* or *anti* isomers. The products expected from the insertion of CTF into ethylene or ethane were not observed.[5]

No prior reports of the reactions of monofluorocarbene are in the literature. The formation of CHF has been suggested as occurring in the mercury-sensitized photolysis of $CF_2{=}CHF$, as indicated by subsequent reactions with various olefinic substrates.[6] In these systems, the corresponding cyclic products have not been observed, and the postulated mechanism involves the elimination of HF from an excited cyclic intermediate with the formation of the corresponding allene. Experiments with deuterated substrates further indicated that such dehydrofluorination must involve the loss of H and F atoms originally attached to the same carbon atom. Since our own experiments result in stabilized cyclopropyl fluoride molecules at gas pressures comparable to those used in the mercury-sensitized photolysis of $CF_2{=}CHF$, the absence of the cyclic products in the latter experiments implies a different intermediate from that found in our experiments—perhaps a difference in the electronic state involved. Since the allenes formed by the subsequent 1,1-dehydrofluorination of cyclic compounds would always be unlabeled with radioactivity in our experiments, our failure to observe these radioactive products is without significance.

The higher percentage decomposition of $CHTF_2^*$ formed by replacement of F in CHF_3 than of H in CH_2F_2 presumably indicates a greater average excitation energy in the former case. Similar results have been observed in comparison of CH_2TCl formed by T for CH_3 *vs.* T for H.[7]

Each system contained the halomethane parent molecule, ethylene, and He^3, and most also contained O_2. These irradiated systems are analyzed for their radioactive components by the usual techniques of radio gas chromatography,[2,8,9] utilizing a sufficient variety of separation columns to ensure isolation and identification of all of the radioactive components.

Acknowledgment. An authentic sample of cyclopropyl fluoride for calibration was kindly furnished to us by Professor A. F. Trotman-Dickenson. Dr. Hal Jackson kindly provided the samples of CH_2F_2 and CH_2ClF.

---

[4] Excited CHTClF can decompose either by elimination of HCl to form CTF, or of HF to form CTCl. Both pathways are observed. Alternative decomposition paths also exist for each molecule in which the radioactive atom is eliminated as TF or TCl, leaving a halocarbene without radioactivity. No product is measured by the radio gas chromatographic technique in these cases.

[5] G. L. Closs and J. J. Coyle have shown [*J. Am. Chem. Soc.*, **84**, 4350 (1962); **87**, 4270 (1965)] that addition to the double bond is strongly favored *vs.* the formation of insertion products by CHCl, and that the latter reactions, when they do occur, show a strong preference for occurrence at the weaker C–H bonds.

[6] R. J. Norstrom, O. P. Strausz, and H. E. Gunning, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 4–9, 1965.

[7] Y.-N. Tang and F. S. Rowland, *J. Am. Chem. Soc.*, **87**, 3304 (1965).

[8] See, for example, "Chemical Effects of Nuclear Transformations," Vol. 2, International Atomic Energy Agency, Vienna, 1961.

[9] J. K. Lee, E. K. C. Lee, B. Musgrave, Y. N. Tang, J. W. Root, and F. S. Rowland, *Anal. Chem.*, **34**, 741 (1962).

Y.-N. Tang, F. S. Rowland
Department of Chemistry
University of California, Irvine, California

Received December 4, 1965

Triphenylgermyl Hydroperoxide

Sir:

In a previous paper[1] the synthesis of silyl hydroperoxides has been described. We wish to report that the same preparative method has now yielded triphenylgermyl hydroperoxide. Although bisgermyl peroxides[2,3] and compounds containing a GeOOC structure[4] have been described, the corresponding hydroperoxides had not been investigated until the present work.

Triphenylbromogermane (2.0 g, 0.0052 mole) was dissolved in dry ether (200 ml), and 98% hydrogen peroxide (2 ml, 0.085 mole) was added. The mixture was stirred (2 min) and dry ammonia gas was bubbled through the solution for 30 sec. The reaction was then quenched by adding water (30 ml). The ether layer was separated, washed with water (two 10-ml portions), and then dried over magnesium sulfate. The ether was removed *in vacuo*, and the residue (1.25 g) was recrystallized twice from chloroform–hexane to give triphenylgermyl hydroperoxide (0.95 g, 54.5%), mp 135–136.5°. The compound does not decompose on melting, for if the molten mass is allowed to solidify, it remelts at 135–136.5°. The infrared spectrum of the hydroperoxide in carbon tetrachloride has a general qualitative similarity to the spectrum of triphenylsilyl

---

[1] R. L. Dannley and G. Jalics, *J. Org. Chem.*, **30**, 2417 (1965).

[2] A. G. Davies and C. D. Hall, *Chem. Ind.* (London), 1695 (1958).

[3] A. Rieche and J. Dahlmann, *Angew. Chem.*, **71**, 194 (1959); *Ann.*, **675**, 19 (1964).

[4] A. G. Davies and C. D. Hall, *J. Chem. Soc.*, 3835 (1959).