Mass Spectrum and Ionization Potential of Condensed Cyclobutadiene

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Summary Cyclobutadiene has been produced as a stable compound from the pyrolysis and subsequent cryoquench of cyclobutadieneirontricarbonyl, and its mass spectrum and ionization potential have been measured at very low temperatures and compared with similar measurements on the other C_4H_4 isomers.

CYCLOBUTADIENE is an extremely reactive intermediate[1] that has been directly, but not definitively, observed in only one experiment which was based on kinetic mass spectrometry in flash-photolysed cyclobutadieneiron tricarbonyl (CIT).[2] We now report the mass spectrum, ionization potential, and the indefinite existence of condensed cyclobutadiene at very low temperatures from the pyrolysis and rapid cryo-quench of CIT. These new data, though very compelling, are however still not completely definitive, but it seems clear that any absolute identification and characterization of reagent cyclobutadiene will demand the techniques of cryochemistry.

The apparatus consists of a pyrolysis furnace mounted inside a cryogenically-cooled inlet system attached to a Bendix time-of-flight mass spectrometer.[3] The pyrolysis was conducted at low pressures and short contact times, and the products travelled only a few mm. from the furnace exhaust port before being quenched.

Each pyrolysis lasted two hours with inlet pressures of CIT of 10^{-2} to 10^{-1} torr (indicated at a distance of 93 cm. from the furnace) and with furnace temperatures of 320° to 380°. During controlled warm-up, the quenched products vaporized and travelled less than 8 cm. with no additional warming before controlled energy electron bombardment in the source. The principal products of pyrolysis and the approximate temperatures at which they evolved from the composite product are shown in Table 1; most of these species were also observed in the earlier flash photolysis of CIT.[2] At $-105°$ a large peak at *m/e* 52, $C_4H_4^+$, and a small peak at *m/e* 54, $C_4H_6^+$, were observed. Continuous pumping at $-110°$ for 6 hours failed to remove C_4H_6 completely. The C_4H_6 was identified as buta-1,3-diene and the mass spectrum of C_4H_6 reported here (see Table 2) was obtained by subtracting the mass spectrum of buta-1,3-diene from the observed total mass spectrum at $-105°$.

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Both isomers of cyclobutadiene, butatriene and vinyl acetylene, were also studied. Each of the three isomers exhibited different mass spectrometric patterns and different ionization potentials as shown in Tables 2 and 3. To avoid possible misinterpretation from temperature effects, the ionization potentials of cyclobutadiene, vinylacetylene, and butatriene were determined at −100°, −108°, and −90°, respectively using the linear extrapolation method with ionization efficiency curves recorded directly from the electrometer with an X–Y plotter. These ionization potentials were also calculated using a semi-empirical SCF treatment recently developed by Dewar and Klopman.[4] The experimental and theoretical results are summarized in Table 3.

TABLE 1

Pyrolysis products and their appearance temperatures

Compound	Temperature	Relative quantity
CO	−196°	large
C_2H_2	−155°	medium
CO_2	−145°	small
C_4H_6	−120°	small
C_4H_4	−105°	large
C_6H_6	− 90°	large
C_8H_8	− 80°	medium

TABLE 2

Mass spectra of C_4H_4 *isomers at* 70 ev.

m/e	C_4H_4 from pyrolysis of CIT	Butatriene		Vinylacetylene	
52	100%	100%	(100%)[a]	100%	(100%)[b]
51	59	70	(72—80)	56	(50·2)
50	51	51	(54)	49	(41)
49	17	26	(24)	19	(13)
48	1	8	(—)	8	(2·8)
39	5	1	(—)	1	(0·85)
26	26	18	(21·2)	12	(11)

[a] Measured with a magnetic mass spectrometer (CEC, Model 21-103), W. M. Schubert, T. H. Libbicoet, and W. A. Lanka, *J. Amer. Chem. Soc.*, 1954, **76**, 1929. An additional peak at *m/e* 53 of 14·7—22·2 per cent is evidently produced by reaction in the inlet.

[b] Measured with a magnetic mass spectrometer (CEC, Model 21-101), Selected Mass Spectra Data, API Research Project 44.

TABLE 3

Experimental and theoretical ionization potentials for C_4H_4 *isomers*

Isomer	Experiment, ev	Theory, ev[a]
Cyclobutadiene	9·55	8·91
Vinylacetylene	9·9 (9.9[b])	9·42
Butatriene	9·25	8·99

[a] Computational theory and technique from ref. 5.

[b] Ref. 6, p. 261.

The ionization potentials at *m/e* 78, and 104, were also determined from the low temperature evolved gases. The observed I.P. of C_8H_8 was 9·1 ev, and since the value for cyclo-octatetraene is 8·6 ev,[5] the $I(C_8H_8)$ observed here is postulated as cyclobutadiene dimer. The associated mass spectrum and ionization potential at *m/e* 78 are in agreement with that of benzene. The formation of benzene in the pyrolysis can occur by the reaction of cyclobutadiene and acetylene or by the polymerization of acetylene at these pyrolysis temperatures. Benzene was in fact observed upon passing pure acetylene through the furnace at 380°.[6] The reaction of cyclobutadiene and acetylene to form Dewar benzene and then benzene itself has been suggested by Pettit.[7]

From these comparisons of the mass spectra and ionization potentials of the C_4H_4 species, and from the formation of benzene and cyclobutadiene dimer, we conclude that cyclobutadiene was produced from the pyrolysis of CIT and quenched as a reactive compound which is probably isolable below about −90°.

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[5] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, 1957, p. 268.

[6] Formation of benzene in the pyrolysis of acetylene is well known; see for example, G. M. Badger, G. E. Lewis, and I. M. Napier, *J. Chem. Soc.*, 1960, **87**, 2825.

[7] L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 3253.