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ON THE MASS SPECTRUM OF CYCLOBUTANONE

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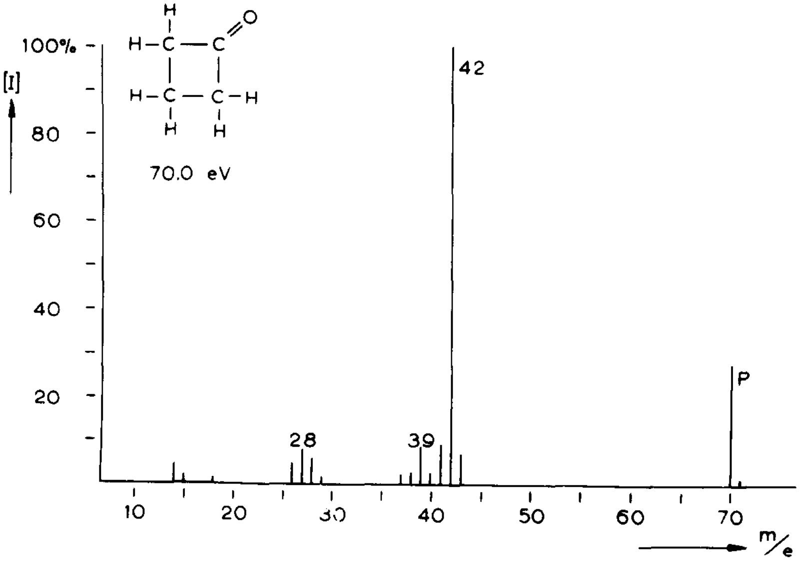
We have studied the mass spectrum of cyclobutanone (Fig I) with a single focussing mass spectrometer and have determined exact masses with an accuracy better than 1 : 10,000 in the m/e range 39 - 42. This was achieved by application of a suitable technique[1)] with the exact mass of argon (m/e = 39.962386) as a reference.Under the same conditions the exact masses in the same m/e range were determined for propene and ketene.In this way it was possible to get an estimate of the systematic error of this method.The mass spectra of



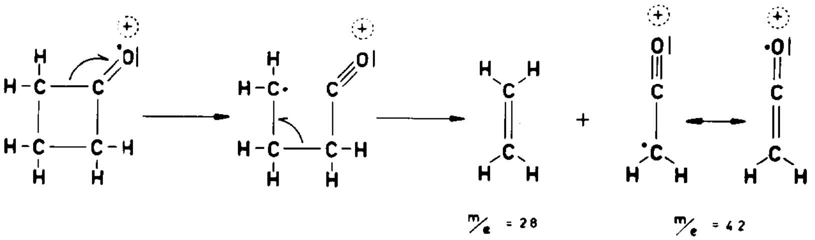
propene and ketene were comparable with published spectra[2]. The mass spectrum of cyclobutanone is shown in figure I. The experimental data are summarized in the table together with calculated exact masses[3] for the various ions.

Propene[a]	Cyclobutanone	Ketene
39.023 ± .002	39.026 ± .001	-
(39.023 = C_3H_3)[b]		
41.042 ± .002	41.041 ± .001	41.007 ± .003
(41.039 = C_3H_5)		(41.003 = C_2HO)
42.052 ± .002	42.018 ± .002	42.015 ± .002
(42.047 = C_3H_6)		(42.011 == C_2H_2O)

a) The mass scale used is the one based on ^{12}C = 12.000 a.m.u. as recommended by the I.U.P.A.C.[4]

b) Values between brackets are calculated[3].

It is evident that our values for the exact masses are slightly higher than the calculated values. With the values found for the ions at m/e = 41 and 42 from propene and ketene we could correct our values for the ions from cyclobutanone. But even apart from this correction it is clear that the value of 41.041 a.m.u. for the ion at m/e = 41 from cyclobutanone corresponds with the value of 41.042 a.m.u. from propene. That means that the ion at m/e = 41 from cyclobutanone is free from oxygen and corresponds with C_3H_5. Similarly it follows that the composition of the ion at m/e = 42 from cyclobuta-



none is predomenantly C_2H_2O⁵⁾.Therefore the most important reaction leading to this fragment involves the elimination of ethylene.That both fragments originate from one process is shown by the diffuse peak found at m/e = 25.26 ± .02.For the reaction $70^+ \longrightarrow 42^+ + C_2H_4$ we calculated a diffuse peak at m/e = 25.20.The reaction is analogous to the one proposed for the decomposition of cyclobutanole⁶⁾. Part of the ethylene molecules are charged and decompose to acetylene ions.The calculated diffuse peak for the metastable transition should arise at m/e = 24.14 and was found at m/e = 24.16 ± .02.

These experiments were performed on an A.E.I.-MS2H Mass Spectrometer with assistance of Messrs W.J.Rooselaar,J.A.M.Spitteler and J.D.van Wageningen.

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