[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, BROOKHAVEN NATIONAL LABORATORY]

Mass Spectra and Appearance Potentials of Ketene Monomer and Dimer; Relation to Structure of Dimer[1]

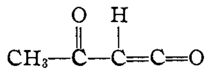
BY F. A. LONG AND LEWIS FRIEDMAN

RECEIVED JANUARY 23, 1953

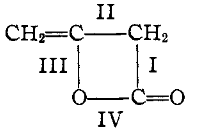
Mass spectra are given for ketene and ketene dimer. The spectrum of the latter indicates that in the vapor phase the structure is vinylaceto-β-lactone, the same as shown by the solid at low temperatures. Appearance potentials are given for the prominent ions from both species. The low value of the appearance potential of CH_2^+ from ketene, 13.8 v., can be explained by postulating that an energy coupling mechanism is involved in the formation of this ion.

Introduction

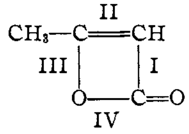
The structure of ketene dimer has been under investigation almost continually since its initial discovery. At various times the following structures have been seriously considered[2]



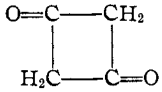
A



B



C



D

Recently several lines of evidence have tended to eliminate A and D and to suggest that the most likely structure is either B, vinylaceto-β-lactone or C, β-crotonolactone or perhaps a mixture of the two. Thus both the infrared spectra[3] and electron diffraction studies[4] are incompatible with A and D and favor B and C. The results of investigation of infrared spectra at various temperatures suggested to Miller and Koch that there is probably an equilibrium mixture of B and C.[5] The work of Roberts, Armstrong, Trimble and Burg[6] on reaction of ketene dimers containing carbonyl labeled C^{14} and also the fact that a non-zero dipole moment was observed,[7] tend to eliminate the symmetrical structure, D. Results which favor structure B have been reported by Blomquist and Baldwin,[8] Hurd and Blanchard,[9] and Johnson and Shiner.[10] Finally a very recent report on the X-ray studies of the crystalline solid at low temperatures[11] show that in this state the molecule is definitely vinylaceto-β-lactone (B).

This paper reports a study of the products obtained by electron bombardment of ketene and ketene dimer in a conventional analytical mass spectrometer and discusses the bearing of these dissociation patterns on molecular structure. The procedure somewhat resembles the pyrolysis approach as used by Williamson,[12] Hurd and Williams,[2c] and especially Rice and Roberts.[13] However the use of the mass spectrometer presents a distinctly different method of attack to this problem. Advantages of this method are that only primary products of the interaction of electrons with the molecules are obtained and that in some cases appearance potential data shed light on the mechanism of the dissociation process taking place in the mass spectrometer ion source.

Experimental

The relative intensities of the positive ions produced with 50 v. bombarding electrons were determined with a General Electric Analytical Mass Spectrometer. The abundance ratios were obtained by magnetic scanning with an ion accelerating potential of 2000 v. No temperature control of the ion source was maintained but the source temperature was estimated to be approximately 200°. Mass identification was straightforward in the spectrum of ketene; in the case of ketene dimer an internal standard, cyclohexane, was used to establish the identity of peaks in the region of mass 50 and higher.

Appearance potentials were determined in the conventional manner by varying the voltage on the ionizing electrons using a 10,000 ohm, 10 turn Helipot to divide the electron accelerating voltage supplied by the mass spectrometer emission regulator. Potentials were measured through a simple dividing network with a Rubicon Potentiometer. Corrections for contact potentials and instrument sensitivity were made by use of neon as a calibrating gas. The vanishing current method of appearance potential determination was used.[14]

Ketene was prepared from acetone in a conventional ketene generator.[15] Both before and after dimerization the products were purified by distillation. The purity of the monomer is established by its mass spectrum. The absence of acetone and methane is shown by the vanishingly low intensity of peaks at masses 43 and 16. Nearly all of the observed peak at 43 is C^{13} ketene. However a trace of ethylene is suggested by the peak of relatively low intensity at mass 27. The remaining impurity that might easily be found in ketene is diketene and the fact that no masses are observed between 30 and 40 or above 50 permits a conservative estimate of less than 3% as the maximum amount of diketene in the monomer.

Results and Discussion

The mass spectra of ketene and diketene are pre-

---

[1] Work supported in part by Atomic Energy Commission.

[2] (a) F. Chick and N. T. M. Wilsmore, *J. Chem. Soc.*, **93**, 946 (1908); (b) H. Staudinger and St. Bereza, *Ber.*, **42**, 4908 (1909); (c) C. D. Hurd and J. W. Williams, THIS JOURNAL, **58**, 962 (1936); (d) A. B. Boese, *Ind. Eng. Chem.*, **32**, 16 (1940).

[3] D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946).

[4] J. Bregman and S. H. Bauer, results reported in "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 127.

[5] F. A. Miller and S. D. Koch, THIS JOURNAL, **70**, 1890 (1948).

[6] J. D. Roberts, R. Armstrong, R. F. Trimble and M. Burg, *ibid.*, **71**, 842 (1949).

[7] P. F. Oesper and C. P. Smyth, *ibid.*, **64**, 768 (1942).

[8] A. T. Blomquist and F. H. Baldwin, *ibid.*, **70**, 29 (1948).

[9] C. D. Hurd and C. A. Blanchard, *ibid.*, **72**, 1461 (1950).

[10] V. J. Shiner and J. R. Johnson, *ibid.*, to be published.

[11] L. Katz and W. N. Lipscomb, *J. Org. Chem.*, **17**, 515 (1952); *Acta Cryst.*, **5**, 313 (1952).

[12] A. T. Williamson, THIS JOURNAL, **56**, 2216 (1934).

[13] F. O. Rice and R. Roberts, *ibid.*, **65**, 1677 (1943).

[14] T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 807 (1947).

[15] J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).

TABLE I

MASS SPECTRA FOR KETENE DIMER AND MONOMER

m/e	Relative intensity Monomer	Relative intensity Dimer	Fragments
12	7.3	1.3	C
13	10.2	3.7	CH
14	71.5	14.5	CH_2
15	0.9	4.9	CH_3; $C^{13}H_2$
24	2.6	0.4	C_2
25	4.5	2.7	C_2H
26	2.1	11.5	C_2H_2
27	1.1	9.8	C_2H_3
28	15.2	19.9	CO; C_2H_4
29	6.0	3.9	COH
36		1.0	C_3
37		6.1	C_3H
38		8.3	C_3H_2
39		16.9	C_3H_3
40	4.3	16.2	C_3H_4; C_2O
41	21.0	3.4	C_2HO
42	P 100.0	100.0	C_2H_2O
43	2.3	11.7	C_2H_3O
44		2.9	CO_2; C_2H_4O
56		19.2	$CH_2—CH_2—C=O$
57		1.1	
60		0.5	
69		0.5	
84		P 5.2	

sented in Table I which also gives probable formulas of the various ions. Intensities are normalized in the usual way to a value of 100 for the most intense peak in each spectrum. Table II gives appearance potentials for several of the prominent peaks for both species and Fig. 1 compares ionization efficiency curves for the ions of mass 42 from ketene and ketene dimer.

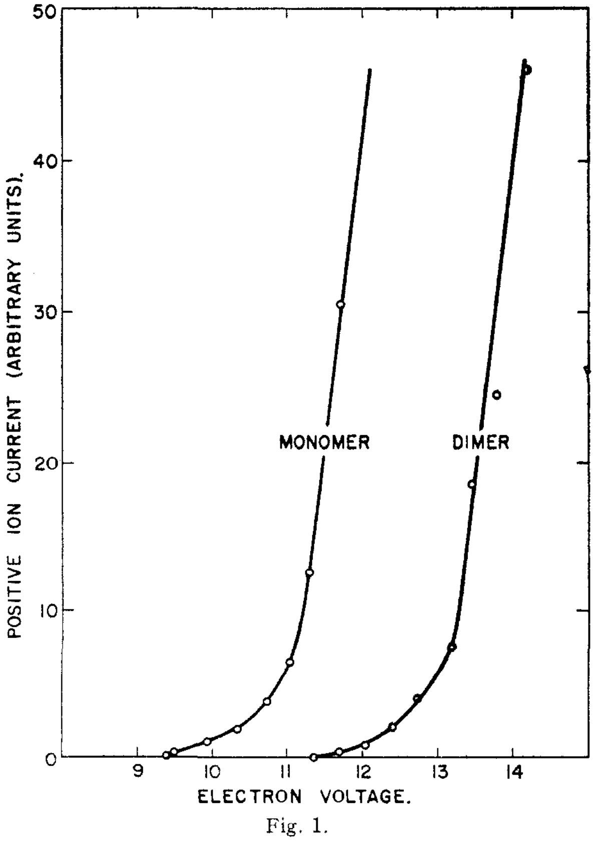


Fig. 1.

TABLE II

APPEARANCE POTENTIALS IN ELECTRON VOLTS

m/e	Ketene	Diketene
14	13.8 ± 0.3	15.5 ± 0.5
15		14.5 ± 0.5
26		15.0 ± 0.5
27		15.8 ± 0.5
28		10.3 ± 0.5
42	9.4 ± 0.3	11.3 ± 0.3
43		11.3 ± 0.3
56		9.8 ± 0.5
84		9.4 ± 0.3

The most intense peak for both spectra is at mass 42. Hence there is a possibility that the dimer is partially depolymerized in the ion source of the mass spectrometer to give ketene which then ionizes on electron impact. Fortunately this may be tested in the mass spectrometer itself by measuring the ionization efficiency curves of the mass 42 peaks from the two species, a technique which has recently been discussed by Honig[16] and by Stevenson and Wagner.[17] In order that this method be useful the appearance potential of the $C_2H_2O^+$ ion from the two species must differ by an amount greater than the Maxwellian energy spread of the ionizing electrons. As is evident from Fig. 1 the threshold to produce ions of mass 42 from ketene is approximately two volts less than the threshold for production of the same ions from diketene. Thus one can readily detect a few per cent. of monomer in the dimer merely by subjecting the latter to 11 v. ionizing electrons. No current of ions of mass 42 was detected in the ketene dimer spectrum with electrons of this energy and one can conclude that no appreciable preliminary dissociation of diketene occurs.

The mass spectrum of the monomer is uncomplicated. The most probable processes are the formation of the molecular ion at mass 42 and the production of CH_2^+ ions as a result of the rupture of the C–C bond. Relatively small yields of ions in the mass 24–26 range reflect the low probability of C–O bond rupture. Although some rearrangement is indicated by the small COH^+ peak at mass 29, the spectrum in general correlates well with the idea that in this fairly simple molecule ionization and dissociation occur with simple rupture of valence bonds and that the most probable processes are those which require the minimum amount of energy. Appearance potentials for the more abundant ions in the mass spectrum of ketene are discussed later.

The interpretation of the mass spectrum of the ketene dimer and discussion of its probable structure are greatly aided by the results from previous studies on the mass spectra of several common lactones.[18] The reason is that, as noted earlier, the only structures for the dimer which merit serious

---

[16] R. E. Honig, *Anal. Chem.*, **22**, 1474 (1950).

[17] D. P. Stevenson and C. D. Wagner, THIS JOURNAL, **72**, 5612 (1950).

[18] Lewis Friedman and F. A. Long, *ibid.*, **75**, 2832 (1953).

consideration are both β-lactones, vinylaceto-β-lactone (B) and β-crotonolactone (C); the latter has unsaturation in the lactone ring and the former has a saturated ring with a double bond to the side chain. The lactones studied previously include both saturated and unsaturated lactones and one of the former, β-propiolactone, is a four-membered ring. The major conclusions from the mass spectra of these lactones were: (a) that the most common processes are splits of alternate bonds in the lactone rings, (b) that rearrangements of the "radical" ions, which are formed by a split of two bonds, into ions with even numbers of electrons are fairly probable, (c) that with the saturated lactones, in contrast to the unsaturated, the major peaks are due to "radical" ions rather than to ions with even numbers of electrons even though the latter are generally more stable.

The most abundant ion in the mass spectrum of ketene dimer is due to $C_2H_2O^+$ at mass 42. Moderate ion yields are observed at masses 14, 28, 39, 40 and 56. The intensity of the parent ion at mass 84 is quite low which is consistent with the low stability of the molecule. The general spectrum is similar in many ways to that of β-propiolactone and it is evident that the general conclusions stated above for lactones hold for this species also. However the point of greater interest in this case is whether the results permit a choice between the structures B and C, vinylaceto-β-lactone and β-crotonolactone.

The large yield of $C_2H_2O^+$ at mass 42 and the small yields at masses 41 and 43 strongly favor structure B as against C. A large yield of mass 42 would be expected from structure B by a II–IV split since this same ion, produced by the same split, is the most prominent peak in the β-propiolactone spectrum. In contrast, structure C would be expected to give large yields at masses 41 and 43 and little at mass 42, particularly since the ion $C_2H_3O^+$ of mass 43 is known to be a stable ion and is a prominent peak in unsaturated lactones[18] as well as esters and ketones.[19] In fact the most likely explanation of the small peak at mass 43 which is observed for diketene is that it comes from the mass 42 fragment by rearrangement.

The yields for diketene of ions at masses 38, 39 and 40 indicate a moderate probability of a I–III split of the lactone ring. (The same split is observed with β-propiolactone where it leads to $C_2H_4^+$.) This split and the observed ion products would be expected from either structure B or C. Similarly the mass 56 peak and the mass 28 peak both indicate a split of the adjacent I–IV bonds and could arise from either structure B or C.

The large intensity of CH_2^+ ions of mass 14 compared to the smaller intensity of CH_3^+ at mass 15 argues for structure B rather than C. From structure B, the CH_2^+ ion can arise either from a split of the side chain bond or a split of the adjacent I–II bonds. The fact that a small yield of CH_3^+ is also obtained indicates some rearrangement to give this more stable "even electron" ion. Such rearrangements to give CH_3^+ are very common; for example they occur to a considerable extent with β-propiolactone.[18] In contrast, structure C would be expected to give a large yield of CH_3^+, by simple rupture of the side chain, and a much smaller yield of mass 14. On a somewhat similar basis the relatively high yield of $C_2H_2^+$ at mass 26 favors structure B rather than C.

In summary, several aspects of the mass spectrum of ketene dimer are in accord with the vinylaceto-β-lactone structure, B, and not with structure C and we conclude that in the vapor phase the large fraction of the material has the B structure. Although there is no compelling evidence that any of the material has structure C, the possibility of a small fraction present in this form cannot be eliminated.

Even though structures A and D have been eliminated on other grounds, it is of interest that the mass spectrum for diketene also indicates that they are not correct. This structure A would be expected to give large yields of stable ions at masses 43 and 15 contrary to observation. Structure D would be expected to yield a large peak at mass 42, as is observed, but the observed yields of $C_3H_4^+$ and $C_3H_3^+$ ions at masses 40 and 39 are clearly not consistent with structure D.

The appearance potentials of the ketene monomer and dimer are both 9.4 ± 0.3 electron volts. In view of Walsh's proposal[20] of a correlation between bond lengths of carbonyl groups and ionization potentials of molecules containing them, this similarity is quite surprising since the C═C bond length in diketene is 1.24 ± 0.06 Å.[11] whereas in ketene the value is 1.17 ± 0.02 Å.[21] The observed values of ionization potential and carbonyl bond length for diketene fit Walsh's correlation plot (Fig. 1, ref. 20a) excellently. However, the values for ketene itself fall very badly off the curve.

As is well known, ketene is anomalous in other respects also. For example, the dipole moment is considerably lower than expected from the results for other ketones.[22]

The appearance potential of the CH_2^+ ions from ketene monomer is 13.8 ± 0.2 v., much lower than the 19.2 v. required for the production of CH_2^+ ions from ethylene.[23] In both cases it can be assumed that the minimum energy required is the sum of the ionization potential of the CH_2 radical and the C═C bond energy. The best available value for the former is 11.9 ± 0.1 v.,[24] and the lowest estimated value for the latter is 4.3 v. The sum of these is still much larger than the observed appearance potential of CH_2 from ketene. The discrepancy can be resolved by considering the energy needed for the over-all process

$$H_2C{=}C{=}O = CH_2^+ + CO + e^-$$

i.e., one assumes that the energy gained in going from a ketonic C═O bond to carbon monoxide may

---

[19] A. P. Gifford, S. M. Rock and D. J. Comaford, *Anal. Chem.*, **21**, 1026 (1949).

[20] (a) A. D. Walsh, *Trans. Faraday Soc.*, **42**, 56 (1946); (b) *Quart. Rev.*, **2**, 73 (1948).

[21] J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

[22] N. B. Hannay and C. P. Smyth, THIS JOURNAL, **68**, 1357 (1946).

[23] P. Kusch, A. Hustrulid and J. T. Tate, *Phys. Rev.*, **52**, 843 (1937).

[24] (a) J. A. Hipple and A. Langer, *ibid.*, **69**, 691 (1946); (b) L. G. Smith, *ibid.*, **51**, 263 (1937).

be used to lower the energy required to produce the CH_2 ion. If this assumption is made and if consistent values are used for the heat of formation of carbon monoxide and for the C=C and C=O bond energies, then with the above value of 11.9 v. for the ionization potential of CH_2 we calculate for the appearance potential of CH_2^+ from ketene a value of 13.7 electron volts. This result is in excellent agreement with the observed value of 13.8 ± 0.2 v. and argues for the correctness of this energy coupling mechanism. A very similar mechanism of energy coupling has been postulated to explain the low value of the threshold energy for the photochemical dissociation of ketene.[25]

The possibility of such energy coupling mechanisms makes unambiguous interpretation of most appearance potentials of fragments from diketene very difficult. The relatively low value of the appearance potential of ions of mass 56 suggests an energy coupling mechanism of the type described above. In this case neither the structure nor the ionization potential of the product ion is known and so a quantitative treatment of the energetics of the formation of this ion is impossible at present. The difference between the appearance potentials of ketene ion from monomer and dimer is 1.9 ± 0.3 electron volts which corresponds to a heat of formation of dimer from monomer of 44 ± 7 kcal. Actually this value is only an upper limit since fragments from the diketene can conceivably be formed either with excess kinetic energy or in an excited state.

ITHACA, N. Y.
UPTON, LONG ISLAND, N. Y.

---

[25] R. G. W. Norrish, H. G. Crone and O. Saltmarsh, *J. Chem. Soc.*, 1533 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

An Electron Diffraction Study of Disulfur Decafluoride

BY R. B. HARVEY[1] AND S. H. BAUER

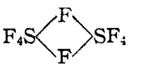
RECEIVED OCTOBER 4, 1952

An electron diffraction study has been carried out on the compound disulfur decafluoride. The compound was prepared by the passage of fluorine over sulfur as reported by other investigators. Electron diffraction photographs were taken with and without the use of a rotating sector, and the photographic intensity curve was inverted to a radial nuclear charge density distribution curve by IBM computing methods. Some information on the vibrational displacements of the atomic pairs in the molecule was obtained from the radial distribution curve. A molecular model was proposed in which two octahedral (SF_5) groups are joined by a sulfur–sulfur bond. The sulfur–fluorine distance is 1.56 ± 0.02 Å. and the sulfur–sulfur distance is 2.21 ± 0.03 Å. The (SF_5) groups exhibit hindered rotation about the sulfur–sulfur link as axis.

Introduction

Fluorine is the only halogen with which sulfur forms a saturated hexacoördinated molecule SF_6, a compound that is unique in its stability and chemical inertness. The compound disulfur decafluoride was prepared by Denbigh and Whytlaw-Gray[2] who measured many of its physical and chemical properties and, on a basis of the parachor and the general chemical similarity to SF_6, suggested that it contained a sulfur–sulfur bond linking two (SF_5) groups. Recently Hollies and McIntosh[3] prepared the compound again and made a careful determination of the properties, in particular the dielectric constant. They concluded that disulfur decafluoride is a highly stable, non-polar dielectric and they also suggested that a reasonable configuration might be two sulfur atoms linked together, each surrounded by five fluorine atoms, covalently linked.

Although these workers have both proposed a sulfur–sulfur link in the molecule, the possibility of a fluorine bridge between the sulfur atoms is not definitely excluded.



This structure is open to several objections; whereas it has been demonstrated that other halogen atoms form stable bridges of the type indicated, the existence of such a bridge involving fluorine atoms has not been demonstrated although some investigators have proposed it. In the above structure if each of the bonding fluorine atoms contributes 3 electrons toward bonding, each of the sulfur atoms would be left with an unpaired s-p-d hybridized electron; then the molecule should exhibit a magnetic moment.

In view of the evidence of the parachor and the dielectric constant as mentioned above, the low boiling point of disulfur decafluoride (29°), and its general inertness to chemicals, molecular configurations with less symmetry than those proposed above were discarded. An electron diffraction study on the vapor was carried out to obtain information on bond distances and to establish the correctness of the model first suggested.

Experimental Procedure

The S_2F_{10} used in this study was prepared by the passage of gaseous fluorine over solid sulfur as described by several authors.[2–5] The chief product is SF_6; the (SF_6 + S_2F_{10}) fraction can be separated from other products by virtue of its chemical inertness; and finally a low temperature distillation serves to separate the SF_6 from the S_2F_{10}. Redistillations at low temperature *in vacuo* were used to purify the S_2F_{10} fraction; vapor density measurements were used as a criterion of purity. Because of the high molecular weight of S_2F_{10} (254.1) the vapor density method was a sensitive measure for small amounts of SF_6 impurities.

---

[1] Suffield Experimental Station, Ralston, P. O., Alberta, Canada.

[2] K. G. Denbigh and R. Whytlaw-Gray, *J. Chem. Soc.*, 1346 (1934).

[3] N. R. S. Hollies and R. L. McIntosh, *Can. J. Chem.*, **29**, 494 (1951).

[4] D. M. Yost, "Inorganic Syntheses," Vol. I, John Wiley and Sons Inc., New York, N. Y., p. 121.

[5] W. C. Schumb, *Ind. Eng. Chem.*, **39**, 421 (1947).