TABLE V

Compound	Relative methyl affinities	E_{S-T}, cm.$^{-1}$	Ref.
Benzene	1	29,400	*a, b*
Diphenyl ether	2.5	28,200	*b*
Pyridine	3	26,050	*b*
Diphenyl	5	22,800	*b*
Benzophenone	11	24,100	*a*
Naphthalene	22	21,300	*a, b*
Phenanthrene	27	21,600	*a*
Quinoline	29	21,700	*a*
Stilbene	183 (*trans*)	21,700 (*cis*)	*b*
Chrysene	57.5	19,800	*a*
Pyrene	125	16,800	*a*
Benzanthracene	468	16,500	*a*
Anthracene	820	14,700	*a*

[a] D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949). [b] R. V. Nauman, Thesis, Berkeley.

fers to the *trans*-isomers while the phosphorescence was measured for the *cis*-isomer. Consequently, the discrepancy may result from the difference in the properties of the isomers.[23] All these results show definitely that the suggested model for the reaction is plausible, and the assumptions introduced are justified at least in the first approximation. The above discussed correlation implies that one might predict the reactivity of an aromatic molecule toward radicals from the observed singlet–triplet excitation energy, or *vice versa*.

Finally, we wish to mention that this type of investigation can be extended to many classes of compounds, and indeed the above method has been applied recently in determining the reactivities of methyl radicals toward vinyl monomers, quinones, substituted aromatics and other compounds. These results will be published later.

In conclusion, we would like to thank the National Science Foundation for financial support of this investigation.

[23] Indeed it is reported that the *cis* isomer is much less reactive than the *trans*, see, *e.g.*, Marvel and Anderson, THIS JOURNAL, **76**, 5434 (1954).

SYRACUSE, N. Y.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

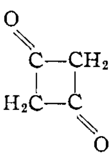
An Electron Diffraction Study of Ketene Dimer, Methylketene Dimer and β-Propiolactone[1]

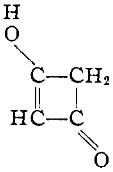
BY JUDITH BREGMAN AND S. H. BAUER

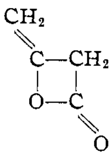
RECEIVED NOVEMBER 4, 1954

The results of electron diffraction studies of the structures of β-propiolactone, and the dimers of ketene, and monomethyl ketene in the gas phase are reported. Procedures for the reduction of diffraction intensity data obtained with a rotating sector are described. A comparison is made of the structural parameters found with those in related straight-chain and small ring molecules.

The structure of diketene has been of interest due to its great reactivity. This reactivity has meant, however, that by following standard organic methods it has not been possible to reject any of the following five configurations conclusively.[2]


I
diketone


II
mono-enol of I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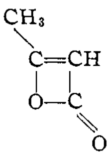
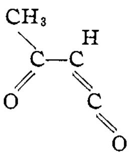
vinylaceto-β-lactone


IV
β-crotonolactone


V
acetylketene

Measurements of the dipole moment and other additive physical properties eliminated only the symmetric configuration I.[3] The absorption spectra of the liquid phase[4] have been interpreted as consistent with one or another of the lactone configurations, III and IV, or possibly requiring a mixture of them. Recent studies of the exchange of H by D on treating diketene with CH_3OD[5] support the presence of III alone in the liquid phase. Mass spectrograph studies[6] indicate that the configuration in the vapor is predominantly, if not entirely, III. A determination of the crystal structure by X-ray diffraction[7] also reported the configuration to be III; the angles and distances agree with those

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[1] A preliminary report on the structure of diketene was presented at the American Chemical Society Meeting in April 1946, "An Electron Diffraction Study of Ketene and Dimethylketene Dimers" by S. H. Bauer, J. Bregman and F. W. Wrightson. Some of this material was presented at the American Society for X-Ray and Electron Diffraction meeting in June 1949, "An Electron Diffraction Investigation of the Structures of Beta-propiolactone and Ketene Dimers," Judith Bregman and S. H. Bauer, and some at the American Crystallographic Association meeting in April 1950, "The Reduction of Electron Diffraction Photographs and the Computation of Radial Distributions from Scattering Data," K. P. Coffin, Judith Bregman and S. H. Bauer.

[2] P. F. Gross, Thesis, Cornell University, 1936; A. B. Boise, Jr., *Ind. Eng. Chem.*, **32**, 16 (1940); C. D. Hurd and J. L. Abernethy, THIS JOURNAL, **62**, 1147 (1940); F. O. Rice and R. Roberts, *ibid.*, **65**, 1677 (1943); J. T. Fitzpatrick, *ibid.*, **69**, 2236 (1947); A. T. Blomquist and F. H. Baldwin, *ibid.*, **70**, 29 (1948); C. D. Hurd and C. A. Blanchard, *ibid.*, **72**, 1461 (1950).

[3] F. Chik and N. T. M. Wilsmore, *J. Chem. Soc.*, **93**, 946 (1908); **97**, 1978 (1910); W. R. Angus, A. H. Leckie, G. L. LeFevre, R. J. W. LeFevre and A. Wasserman, *ibid.*, 1751 (1935); C. D. Hurd and J. W. Williams, THIS JOURNAL, **58**, 962 (1936); P. F. Oesper and C. P. Smyth, *ibid.*, **64**, 768 (1942); E. C. Hurdis and C. P. Smyth, *ibid.*, **65**, 89 (1943); J. D. Roberts, R. Armstrong, R. F. Trimble, Jr., and M. Burg, *ibid.*, **71**, 843 (1949).

[4] G. C. Lardy, *J. chim. phys.*, **21**, 281, 353 (1924); M. Calvin, T. T. Magel and C. D. Hurd, THIS JOURNAL, **63**, 2174 (1941); H. J. Taufen and M. J. Murray, *ibid.*, **67**, 754 (1945); D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946); F. A. Miller and S. D. Koch, Jr., THIS JOURNAL, **70**, 1890 (1948); R. C. Lord, Jr., R. S. McDonald and R. J. Slowinski, unpublished work, see J. D. Roberts, *et al.*, ref. 3.

[5] J. R. Johnson and V. I. Shiner, Jr., THIS JOURNAL, **75**, 1350 (1953).

[6] F. A. Long and Lewis Friedman, *ibid.*, **75**, 2837 (1953).

[7] W. Lipscomb and L. Katz, *Acta Cryst.*, **5**, 313 (1952).

TABLE I

Compound	Sample temp., °C.	M.p., °C. lit.	M.p., °C. before run	After run	Obsd. $n^{20}{}_D$ Lit.	Before run	After run
Dimethyl ketene dimer	100	114–116	114–115	113–115 114–115			
β-Propiolactone	100	−33.4	−33	−32	1.4110 (24°)	1.4108 1.4109	1.4108
Diketene	60–75	−7	− 7	− 7	1.4368	1.4369	1.4367
Methyl ketene dimer	75–90	.....	−52	−52	1.4322[a]	1.4351	1.4351
	60–75		−11		1.4290[b] 1.4280[c]		

[a] J. D. Roberts, *et al.*, ref. 3. [b] C. M. Hill, ref. 8. [c] J. C. Sauer, ref. 8.

found in this investigation and will be discussed later. The electron diffraction study was begun when only the dipole and some of the spectroscopic evidence were available.

At least two products of direct dimerization of methylketene have been reported,[8] a solid (with m.p. 140°) and a liquid (b.p. 50–52° at 9 mm.). An acidic dimer, which is generally assumed to be identical with the solid, can be prepared from dimethyl α,α'-dimethylacetone carboxylate.[9] Woodward[10] has shown this compound to be the monoenol of the cyclic β-diketone (configuration of type II, but with two hydrogen atoms not on the same carbon atom replaced by methyl groups). The liquid dimer, although easily prepared by the same type of reaction as that yielding the dimer of dimethylketene, has properties similar to diketene and markedly different from those of dimethylketene dimer. It was this dimer that was studied by electron diffraction. The chemical evidence[8] permits consideration of five configurations homologous to those for diketene. Configurations of type I, II, and V can be eliminated as in the case of diketene: I by the large dipole moment, II and V by the Raman and infrared spectra which were found consistent with either lactone and may require a mixture of them.[3,4]

The configuration of β-propiolactone is known from chemical evidence.[11] It was included in this investigation to provide diffraction patterns for comparison with those of diketene. In addition, the values of the parameters in the four-membered strained ring are of interest.

Dimethylketene dimer is known to have a configuration I, excluded for ketene dimer, and had previously been studied by electron diffraction.[12] Photographs of this compound were taken for comparison with those of diketene and to aid in developing a method for handling microphotometer traces of sector pictures.

Experimental

The earliest diffraction patterns of diketene were obtained without the use of a sector.[13] From these it was apparent that the diffraction pattern contained complicated features whose estimation by the visual method was not sufficiently reliable for quantitative comparisons. Therefore, sector pictures, from which a more objective estimate of the diffraction pattern may be obtained, were taken of all four compounds. Samples of the three lower molecular weight materials were vacuum fractionated and stored *in vacuo* at Dry Ice temperatures. Dimethylketene dimer was vacuum sublimed in the presence of anhydrite. Portions used for the electron diffraction studies were transferred under high vacuum to holders which fitted onto the camera. Physical constants obtained on these samples are given in Table I. Measurements after runs were made on material sublimed from the residues in the sample holders. The methylketene dimer was not pure, as evidenced by the two melting points of one cut and a decrease of index of refraction in successive cuts in the vacuum fractionation (from 1.4359 to 1.4341). It seems probable that the impurity was propionic anhydride (see below). It is interesting to note that the refractive indices reported in previous studies, as well as those of possible impurities resulting from the preparation used,[14] are all lower than those observed in this investigation.

The electron diffraction photographs were obtained with the camera and high temperature nozzle described by Hastings and Bauer.[15] The camera conditions were as follows

	Nozzle plate distance, cm.	Wave length, Å.	Film	Max. *s* obtained
Sector	19.12	0.0691	Microfile	12–14
Non-sector	19.20	.0539	Eastman commercial	27–30

Analysis of the Data.—Visual estimates of the intensity and position of the maxima and minima were made from both sector and non-sector pictures. Microphotometer traces of the sector pictures were also obtained and treated as described below.

The usual comparison of the observed intensity curves with computed curves for various models were made, both with the visual data and the reduced microphotometer trace. These intensity curves were computed according to the equation

$$I(\mathrm{s}) = 1 + \frac{\Sigma_{\mathrm{ij}} f_{\mathrm{i}} f_{\mathrm{j}} e^{-\alpha_{\mathrm{ij}}^2 \mathrm{s}^2}}{\Sigma_{\mathrm{ij}}(f_{\mathrm{i}}^2 + g_{\mathrm{i}})} \frac{\sin sr_{\mathrm{ij}}}{sr_{\mathrm{ij}}}$$

(where the symbols have their usual meanings) to be comparable with the sector data. Most of the calculations with variable coefficients were made with I.B.M. machines, using the method of progressive digiting.[16] The microphotometer data allowed a quantitative comparison of computed and observed relative intensities. This comparison, the "specific contrast," defined as $[I(\mathrm{s})/I_{\mathrm{bg}}]_{\mathrm{obs}}/[I(\mathrm{s})/I_{\mathrm{bg}}]_{\mathrm{calc}}$ and computed at the observed maxima and minima, provides another criterion by which postulated models may be judged.

Two radial distribution curves were calculated for each of the four compounds, from the visual data, and from the

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(8) C. M. Hill, Thesis, Cornell University, 1941; J. C. Sauer, THIS JOURNAL, **69**, 2444 (1947); H. Staudinger and H. W. Klever, *Ber.*, **44**, 533 (1911).

(9) G. Schroeter and C. Stassen, *ibid.*, **40**, 1604 (1907).

(10) R. B. Woodward and Gilbert Small, Jr., THIS JOURNAL, **72**, 1297 (1950).

(11) T. L. Gresham, L. E. Jansen, F. W. Shaver, *et al.*, *ibid.*, **70**, 998 and ff. (1948).

(12) W. N. Lipscomb and V. Schomaker, *J. Chem. Phys.*, **14**, 475 (1946).

(13) The work of Dr. Frances M. Wrightson, who obtained the first diffraction patterns and made the approximate calculations, is gratefully acknowledged.

(14) The dimer was prepared from propionyl chloride (m.p. −94°, $n^{20}{}_D$ 1.4051) and triethylamine (m.p. −114.8°, $n^{20}{}_D$ 1.4003). Methylketene formed and dimerized. Had moisture been present, propionic acid (m.p. −22°, $n^{20}{}_D$ 1.3874) and propionic anhydride (m.p. −45°, $n^{20}{}_D$ 1.4038) might also have formed.

(15) J. M. Hastings and S. H. Bauer, *J. Chem. Phys.*, **18**, 13 (1950).

(16) This procedure and the relatively small card file needed will be described in a forthcoming publication (JB).

microphotometered sector data extended with visual data from non-sector photographs. The calculations were made using punched card machines according to the equation

$$rD_{\mathrm{m}}^{*}(r) = \sum_{q_{\mathrm{i}}=1}^{n} q_{\mathrm{i}} e^{-b^2 q_{\mathrm{i}}^2}\, i(q_{\mathrm{i}}) \sin\left(\frac{\pi}{10} q_{\mathrm{i}} r\right)$$

where $s = \pi q_{\mathrm{i}}/10$, b^2 was chosen so that $e^{-b^2 q_{\mathrm{i}}^2} \cong 0.1$ at $q_{\mathrm{i}} = q_{\max}$, $n \cong 100$, and $i(q_{\mathrm{i}})$ is directly proportional to the observed intensities, except for small q_{i} where the intensity curves were "drawn-in" from preliminary calculations of $I(s)$.

The microphotometer traces of the sector photographs must be corrected to take out extraneous contributions to the scattering, and for variation of the atomic scattering function with angle, before they can be used in calculations as a measure of the molecular scattering. This process, drawing in a background on the microphotometer trace, itself yields structural information. The background can be positioned using the theoretical intensity curves as follows: the microphotometer densities at those s values for which the molecular contribution to the scattering is zero (the "cross-over points" where the atomic and molecular curves intersect) would lie on a straight line if the diffraction experiment were ideally conducted. Each theoretical model provides a set of such points which can be marked on the photometer record. Even if no set lies on a straight line, those sets of points given by fairly satisfactory models scatter about a line whose curvature changes slowly compared to the molecular oscillations. This curve may be considered to be a "reasonable background." In addition, the better the model, the closer the cross-over points lie to the background. Thus variations in parameters can be followed quantitatively. The positions of cross-over points on the microphotometer trace for two configurations of diketene are shown in Fig. 1. The points from intensity curves for models with the lactone configuration, curve A, lie much closer to a reasonable background than do points from models based on a straight-chain configuration, curve B.

A similar procedure is possible using the maxima and minima of the photometer trace. The heights of the maxima and minima of the computed intensity curves can be reduced so that they all have the same value at one peak. Then for each model, at the positions of the computed maxima, multiples of these reduced heights can be marked on the graph of the photometer data, measuring downward from the microphotometer trace. Correspondingly, at the positions of the computed minima, multiples of the reduced depth can be marked on the graph, measuring upward from the trace. For accurate data and the correct structures, the points corresponding to some multiple should lie on a straight line. Experimentally they do not. However, the requirements that the background should curve only slowly and that the multiples which fall on it should change slowly with s, allow a "reasonable background" to be drawn. And the better the model, the more nearly will this background lie on points of a constant multiple. Variation in this multiple measures the same effect as variation in the specific contrast. Curves C and D of Fig. 1, show cross-over points and maxima–minima multiples for two models, marked on the microphotometer trace of the dimethylketene dimer sector photographs.

Results

Dimethylketene Dimer.—Our results are in good agreement with those of Lipscomb and Schomaker,[12] but have one interesting new feature. A high-resolution microphotometer trace of the sector patterns showed the ring near $s = 4$ as a maximum, although our visual interpretation and the Leeds and Northrup microphotometer both indicated a shoulder (Fig. 2). The radial distribution curve analysis (Fig. 3) follows Lipscomb and Schomaker's. The point of interest for comparison with the diketene results is the small peak at $r = 2.19$ Å. which corresponds to the two diagonals in a four carbon ring (2.20 Å.) plus the twelve non-bonded C–H (2.17 Å.).

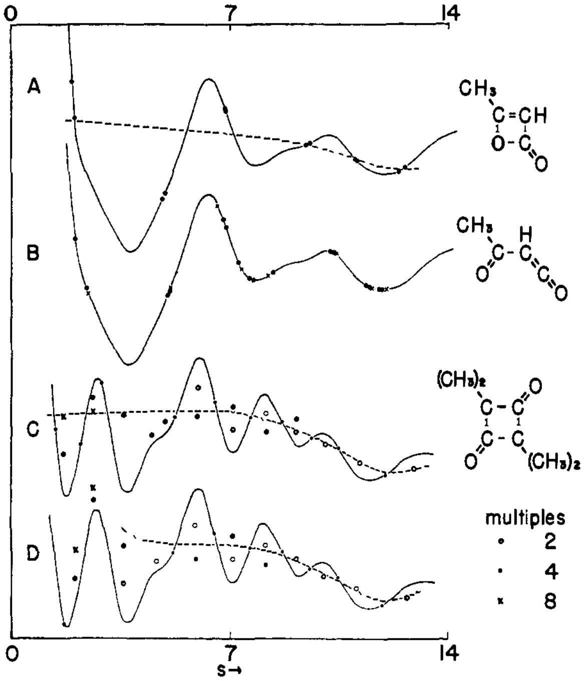


Fig. 1.—Microphotometer trace background analysis: A and B, cross-over points from intensity curves for models based on two configurations of diketene; C and D, cross-over and maxima–minima points from intensity curves for dimethylketene dimer, model A (Lipscomb and Schomaker): C–C = 1.56 Å., C–CH$_3$ = 1.54 Å., C=O = 1.22 Å.; ∠C–CO–C = 90°, ∠CH$_3$–C–CH$_3$ = 109° 28′; α_{ij}^2(bonded) = 0.0015, α_{ij}^2(unbonded) = 0.0022 except: C, α_{ij}^2 = 0.0061 for heavy atom distances above 3 Å.; α_{ij}^2 = 0.0043 for hydrogen distances above 2.2 Å. D, all hydrogen distances above 2.2 Å. omitted.

Correlation of the visual and microphotometer intensity curves with calculated curves yields new results only as regards details affecting the intensity curves near $s = 4$. Lipscomb and Schomaker omitted the long hydrogen distances (above 3 Å.) in their calculations. Inclusion of these terms converts the shoulder on the computed curves at $s = 4.5$ to a maximum. The need for these hydrogen distances is also indicated by the microphotometer trace, both from the calculation of contrast (Table II), and from the background analysis; compare

TABLE II

DIMETHYLKETENE DIMER: MICROPHOTOMETER DATA

s		Relative height, visual	Dev. from unit background, mpr.	Specific contrast	
Max.	Min.			mpr./D	mpr./C
	1.7	25	−0.180	2.00	1.18
2.7		30	.064	<0	1.07
	3.6	35	− .204	0.88	0.68
6.0		40	.128	.59	.56
	7.0	25	− .076	.54	.54
8.0		20	.070	.55	.55
	9.0	14	− .036	.35	.45
10.0		14	.028	.36	.48
	11.0	20	− .038	.38	.43
12.9		14	.046	.68	.56
Av. s = 3.6–11.0				.52	.53
Av. dev.				.12	.06

curves C and D, Fig. 1. The intensity data for dimethylketene dimer, and one of the better computed curves are shown in Fig. 2.

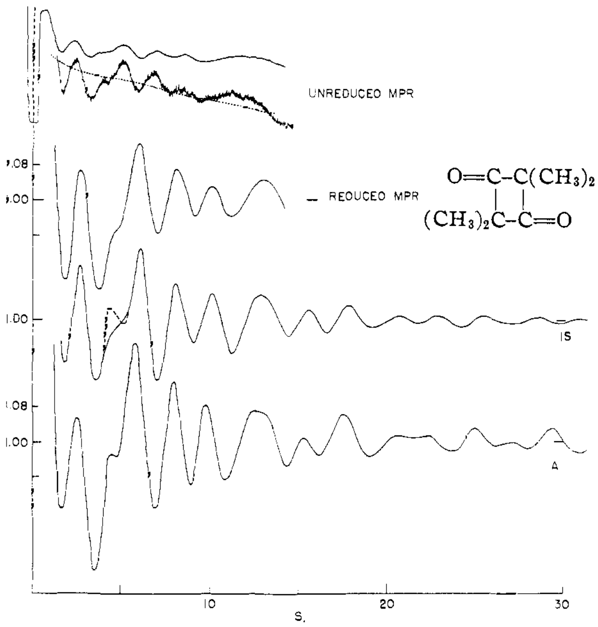


Fig. 2.—Unreduced microphotometer traces: obtained using Leeds and Northrup microphotometer (upper curve) and Eastman Kodak Co. high resolution microphotometer (lower curve). Reduced microphotometer data: I/I_{bg}, average of several traces obtained on Leeds and Northrup microphotometer. Visual data, average of sector and nonsector pictures. A, theoretical intensity curve for model A. See legend Fig. 1, curve C for the parameters.

β-Propiolactone.—The bonded distances for this lactone can be found from the first two maxima of the radial distribution curve (Fig. 3). Assuming C–H = 1.09 Å., the peak at 1.16 Å. (mpr. 1.14 Å.) yields C=O = 1.18 ± 0.02 Å. Assuming C–C = 1.54 Å., the peak at 1.49 Å. (mpr. 1.48 Å.) yields C–O = 1.45 ± 0.02 Å. If the lactone existed in the enol form the first peak would either contain only the four C–H distances at 1.09 Å., or these and the C=C distance near 1.33 Å. The latter combination would give a peak near 1.23 Å. Neither of these possibilities agrees with the observed peak at 1.16 Å. If the C=C distance were in the second peak (as it is for diketene) this maximum would appear below 1.46 Å. instead of at 1.49 Å. Therefore, the enol configuration is very unlikely.

The secondary distances produce a complicated peak with a maximum at r = 2.12 Å. (mpr. 2.10 Å.) and a shoulder on the side of large r (a composite of two cross-ring distances near 2.10 Å., eight nonbonded C–H and O–H distances near 2.15 Å., and two non-ring distances near 2.45 Å.) which confirms the ring structure. The peak corresponding to the longer distances is poorly resolved, reflecting both the inequality of the contributing distances and the larger vibration possible for the ketone oxygen against the ring than between ring atoms. Assuming that the location of the maximum itself is due only to the ring diagonal distances, it is in satisfactory agreement with the models containing C–O around 1.45 Å. For the final model, K, the computed peak position is 2.12 Å. Using the parameters for this model and assuming an 0.02 Å. uncertainty in the diagonal length, this maximum requires that the lactone ring be planar to within 20°. The next two radial distribution peaks correspond nicely to the longer distances in the final molecule: the 3.15 Å. peak (mpr. 3.21 Å.) to a C–O distance at 3.20 Å. plus two O–H distances near 3.05 Å., the shoulder on the inside of this peak to two C–H distances near 2.85 Å. and the peak at 3.85 Å. to more O–H distances near 3.86 Å.

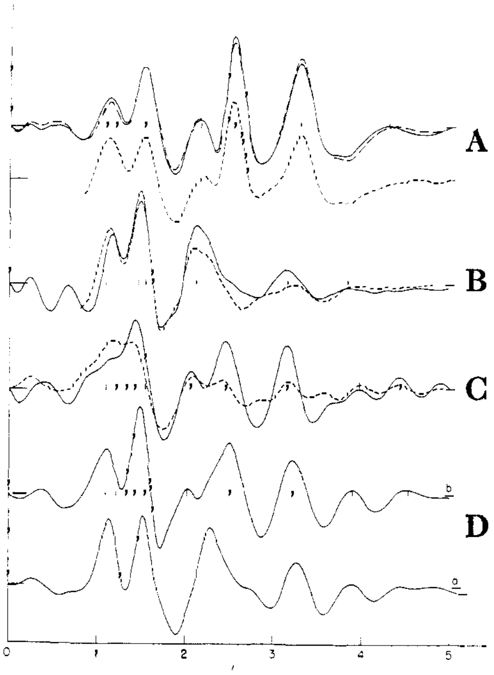
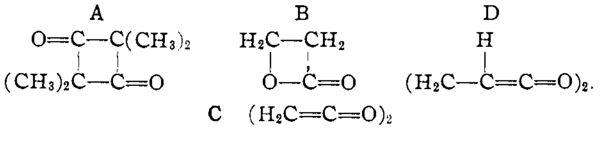


Fig. 3.—Radial distribution curves: solid lines, inversion of visual data; dotted lines, inversion of microphotometer data extended with visual data; dashed lines, inversion of visual data for dimethylketene dimer including a maximum near s = 4.5. The short lines under the peaks below r = 2 Å. indicate the distances contributing to these peaks. The lines under peaks above r = 2 Å. mark the positions of the observed maxima.



A $\begin{array}{l}O{=}C{-}C(CH_3)_2 \\ \;\;|\quad\;\,| \\ (CH_3)_2C{-}C{=}O\end{array}$ B $\begin{array}{l}H_2C{-}CH_2 \\ \;\;|\quad\;\,| \\ \;\;O{-}C{=}O\end{array}$ D $\begin{array}{l}\quad\;\;H \\ \quad\;\;| \\ (H_2C{-}C{=}C{=}O)_2\end{array}$

C $(H_2C{=}C{=}O)_2$

The intensity curves of Fig. 4 were computed for equal C–O distances, equal C–C distances, coplanar heavy atoms and C_{2v} local symmetry for CH_2, with ∠H–C–H = 120°, C–H = 1.09 Å., and C–C = 1.54 Å. The parameters varied were the distances C–O and C=O, and the angles C–O–C and C—C=O. The features sensitive to changes in structure are the shoulder at s = 9, the wide minimum at s = 16, and the doublet at s = 22. The only satisfactory model is K. The long C–O is required by the position of the outer rings, ∠C–O–C = 89° by the shoulder at s = 9, and the unsymmetric location of C=O by the minimum at s = 16. No attempt was made from the electron diffraction data alone to determine on which side of the bisector of the ring corner angle the ketone oxygen lies. The positions studied in detail, ∠C–C–O = 133–149°, overlap those found by Lipscomb and Katz[7] for crystalline diketene. Excluding the possibility that ∠O—C=O is larger than ∠C—C=O, ∠C—C=O = 143 ± 3.5°.

Intensity curves for the enol form of the lactone probably would not be satisfactory since this configuration would have a smaller ring than the lactone, and the data require a larger ring than was expected. No intensity curves were computed. The s_c/s_0 comparison and the specific contrast of the microphotometer data are given in Table III for K and G. G was eliminated visually by the positions of peaks beyond s = 20. However, a comparison of the microphotometer results for G and K discriminates between the two models although such data are available only for s less than 12. The size of the molecule is determined by the $<s_c/s_0>_{av}$. and the radial distribution data. The latter require that (C–O + C–C)/2 = 1.49 ± 0.01 Å., the former that C–C/C–O = 1.54/1.47.

TABLE III

β-PROPIOLACTONE: INTENSITY CURVE DATA

Max.	Min.	s_0 Visual	s_0 M.p.r.	s_c/s_0 Vis./K	s_c/s_0 mpr./K	s_c/s_0 mpr./G
0			1.15			
	0	3.34	2.70	1.15_5[a]	1.00_0	1.01_1
1		3.49				
	1	4.79				
2		6.35	6.36	0.94_5[a]	0.94_3[a]	0.94_0[a]
	2	7.63	7.77	0.99_3	0.97_5	0.98_3
3		8.71	9.59		0.99_1	1.04_4
3^1		9.90				
	3	11.24	11.22	0.98_2	0.98_3	1.02_9
4		12.61		1.04_1[a]		
	4	15.78		0.96_8		
5		18.09		0.98_6		
	5	20.20		0.99_1		
6		22.08		0.99_0		
	6	24.12		1.00_0		
7		25.32		1.04_9[a]		
	7	27.00		1.05_0[a]		
8		28.43				
Av.				0.98_7	0.98_7	1.01_7
Av. dev.				0.008	0.008	0.020

Max.	Min.	Relative height, visual	Dev. from unit background, mpr.	Specific contrast mpr./K	Specific contrast mpr./G
	0	35	−0.150	0.77	0.76
2		35	.125	.98	0.93
	2	25	− .066	.76	0.73
3		12	.036	.76	1.35
	3	9	− .034	.68	1.12
Av.				.79	0.98
Av. dev.				.08	0.21

[a] Omitted in computation of average.

The microphotometer trace analysis made while drawing in the background is consistent with the above conclusions although it did not unambiguously eliminate any structures.

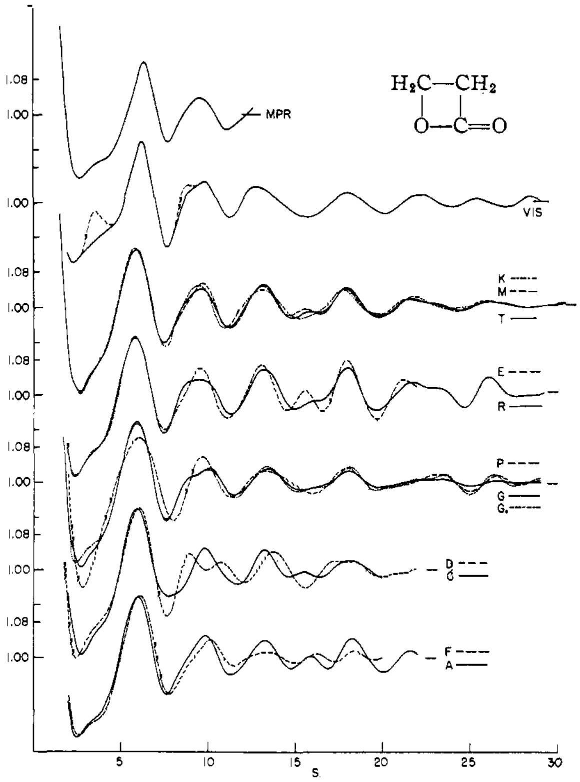
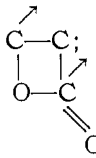


Fig. 4.—β-Propiolactone, parameters for models investigated.

Curve	∠C–O–C, degrees	C–O, Å	C=C, Å	∠C—C=O, degrees
C	100	1.42	1.21	133 (bisects
A	92	1.42	1.21	133 exterior
G	89	1.42	1.21	133 angle)
D	85	1.42	1.21	133 (bisects
E	92	1.47	1.21	133 exterior
T	89	1.47	1.21	133 angle)
R	87	1.47	1.21	133 (bisects
F	92	1.37	1.21	133 exterior
M	89	1.47	1.24	133 angle)
K	89	1.47	1.21	145
G_a	like G—using Z_i instead of f_i			
P	like G_a—but omitting secondary distances from the ketone oxygen.			

The bond angles and bond distances found for β-propiolactone, within the simplifying assumptions made earlier, are C–C = 1.53 Å., C–O = 1.45 Å., C=O = 1.19 Å., ∠C–O–C = 89°, and ∠C—C=O = 143°. The limits of error, not permitting simultaneous variation of parameters, would be 0.03 Å. for the distances, and 3° for the angles. However, neither the radial distribution nor the intensity curve analyses resolve the ring distances, so that if simultaneous variations of these distances are not excluded larger limits (up to 0.10 Å.) are required. One simultaneous variation requiring large limits on the parameters is

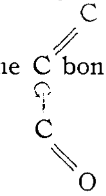


; decreasing the C–C and increasing the C–O distances while changing the others little or not at all. Increments of more than 0.04 Å. in the distances themselves would lead to a C–O bond longer than the C–C bond. Such a structure, although still consistent with the diffraction pattern, is highly improbable in view of our knowledge at these distances in other molecules.

Diketene.—Diffraction patterns were obtained at three different times over several years, with samples of diketene from different sources, the sample temperature varying from about 25 to 75°. No evidence for two distinct types of diffraction patterns, as found by Schomaker and Lipscomb[17] appear among the three sets of non-sector and two sets of sector photographs. One of their patterns agrees well with the one obtained in this investigation.

The first radial distribution peak at r = 1.16 Å. (mpr.) is consistent with C–H = 1.09 Å. and C=O = 1.19 Å. The location of the second peak (1.44 Å.) and its lack of sharper resolution from the first compared to the β-propiolactone curve are consistent with the presence of C=C as well as C–C and C–C distances in diketene. The component distances cannot be resolved uniquely but either C–O or C–C or both must be shorter than in β-propiolactone, or C=C must be less than 1.30 Å. The 2.05 Å. peak (mpr. 2.08 Å.) can be identified with the diagonals in a small four-membered ring and its presence definitely eliminates the chain configuration. Its position eliminates a diketone configuration (computed position 2.20 Å.) and requires slightly short ring distances in either the enol configuration (*e.g.*, computed position 2.08 Å. if C–C = 1.52 Å. and C=C = 1.33 Å.) or the vinyllactone configuration (*e.g.*, computed position 2.08 Å. if C—C = 1.52 Å. and C–O = 1.41 Å.). The crotonolactone configuration can be eliminated since long ring distances would be required (*e.g.*, computed position 2.05 Å. if C–C = 1.56 Å., C–O = 1.46 Å., and C=C = 1.33 Å.) and these are precluded by the 1.44 Å. peak. The peak at r = 2.45 Å. (mpr. 2.42 Å.), corresponds to four secondary non-ring distances and four non-bonded hydrogen interactions in a vinyllactone configuration. It is best fitted (computed position 2.44 Å.) by a ring with slightly short distances, and the unsymmetrically located side-chains found by Lipscomb and Katz in crystalline diketene.[7] With symmetrically located side-chains and the same ring, the computed position is 2.46 Å. The enol configuration, computed position 2.55 Å., is eliminated. The 3.15 Å. peak, (mpr. 3.17 Å.) is consistent with smaller vinyllactone rings (computed position near 3.18 Å.), as is the 4.4 Å. peak, although the differences between rings for the latter peak are not large. The remaining small peaks are consistent with non-bonded hydrogen distances in a vinyllactone configuration. The radial distribution results eliminate all configurations except the vinyllactone, require that some of the bond distances be shorter than normal single bond distances, and that the side chain positions be unsymmetric. A satisfactory set of distances is C–C = 1.52 Å., C–O = 1.41 Å., C=C = 1.31 Å., and C=O = 1.19 Å. These distances are in general consistent with the microphotometer radial distribution curve when it differs from the curve based on visual data only. The differences (0.02–0.03 Å.) are largely due to the shape of the peak at s = 10, in the intensity curves, the shoulder of which was greatly exaggerated in the visual estimation (see Fig. 5). The values obtained from the microphotometer distribution curve are more reliable. The same type of exaggeration may be present in the visual estimation of the next peak (compare visual and calculated curves Fig. 5). The shifts in radial distribution peak positions caused by it are probably smaller than the shifts observed for the s = 10 peak. The distances reported by Lipscomb and Katz for crystalline diketene (Table VI) do not agree as well as the above values. Their long C=O distances and small ring distances would predict radial distribution peaks at 1.18, 1.42 and 2.04 Å. rather than at the observed 1.16, 1.44 and 2.05 Å. (mpr. 2.08 Å.).

Intensity curves shown in Fig. 5 were calculated for the five postulated models. Different configurations due to hindered rotation as well as variations of some of the parameters were considered. The sensitive features are the small shoulders or maxima near s = 3, and 4.5, the large shoulder at s = 8, the broad peak at s = 14, the wide minimum at s = 20, and the doublet at s = 23. The dashed part of the "visual" curve indicates the appearance of the sector photographs; elsewhere the estimates from sector and non-sector pictures were alike.

The diketone curve, G and an enol curve, F, are both unsatisfactory. No attempt was made to distort the enol configuration to yield acceptable curves. For the chain models, curves H through N, are also hopeless, the changes resulting from different rotations about the  bond. Lengthening C=O and C=C while shortening one of the C–C (J and K), or making the chain more nearly linear (L) or more like a lactone ring (by decreasing ∠O=C—C and ∠C—C=O) are all inadequate. Sufficiently large distortions of this last type would ultimately lead to acceptable models, but the resultant configuration would have to be described as that of a lactone.

Intensity curves for vinyllactone configurations agree satisfactorily with the diffraction pattern. The model is required to have ∠C–O–C near 90°. The parameters for B, corrected for a 1% size factor, are close to those found from the radial distribution curves. No models were considered with the side chains unsymmetrically located, as found in β-propiolactone and crystalline diketene. It is likely that such models would decrease discrepancies between B and the observed curves. The crotonolactone model, IV, curve E, is not as satisfactory as are those for the vinyllactone. Some variations of parameters would improve the curve. However, good agreement would not be expected, according to the radial distribution results, until the molecule was distorted into what might better be called a vinyllactone configuration. The suggestion from spectroscopic work[4] that diketene may be an equilibrium mixture of vinyl- and crotonolac-

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[17] V. Schomaker, private communication.

tone configurations was not investigated in detail. The radial distribution results do not encourage it.

The specific contrast of the microphotometer data and the scale factor, $<s_c/s_0>_{av}$ for both the visual and photometer data are given in Table IV for model B. The structural information obtained from drawing a background onto the microphotometer trace is consistent with, though not as complete as that from the correlation and radial distribution analyses. All the chain models may be rejected. All the unsymmetric rings are acceptable; for the vinyllactone rings the background passes through maxima-minima points of constant multiple. However, the differences among the rings are smaller than the differences between them and the "reasonable" background position finally chosen.

TABLE IV

DIKETENE: INTENSITY CURVE DATA

Max.	Min.	s_0 Visual	s_0 Mpr.	s_c/s_0 B/vis.	s_c/s_0 B/mpr.
	0	2.24			
1		2.88			
	1	3.83	4.01	0.935[a]	0.893[a]
2		4.45			
	2	5.13			
3		6.20	6.30	0.960[a]	0.944[a]
	3	7.46	7.80	1.013	0.969
4		8.53		1.028	
	4	9.43		0.972	
5		10.36	10.18	0.980	0.998
	5	11.47	11.87	1.041	1.007
6		13.26		0.995	
	6	13.86			
7		14.31			
8		16.22		0.965	
9		18.28		0.993	
	9	20.47			
10		22.51			
11		23.52		1.005	
	11	24.41		1.018	
12		26.49		1.002	
Av.				1.00	0.99
Av. dev.				0.02	0.015

Max.	Min.	Relative height, visual	Dev. from unit background, mpr.	Specific contrast, mpr./B
	1	35	−0.108	0.50
3		35	.104	.62
	3	26	− .030	.39
5		17.5	.030	.68
	5	21	− .020	.63
Av.				.56
Av. dev.				.10

[a] Omitted in computation of average.

Electron diffraction results lead to the conclusion that diketene in the vapor state has the vinyllactone configuration, III, although the possibility of a mixture of III with a small amount of the crotonolactone configuration, IV, cannot be excluded by this method. Assuming no mixture, the satisfactory model has distances and angles similar to those found in the β-propiolactone; only the C–O distance differs appreciably. An acceptable set of parameters are C=O = 1.19 Å., C=C = 1.31 Å., C–O = 1.41 Å., C–C = 1.52 Å., ∠C–O–C = 89°.

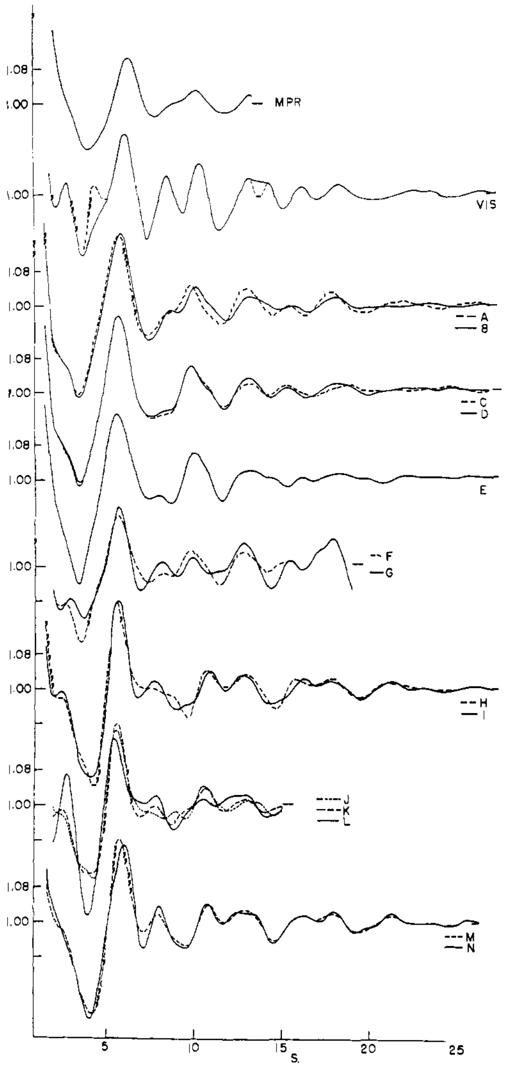
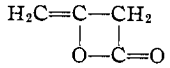
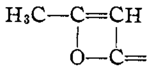


Fig. 5.—Diketene, models investigated. Parameters for all curves unless otherwise specified: Rings planar. HCH plane ⊥ to ring. Other groups attached to the ring lie in its plane and bisect the exterior angle. C–C = 1.54 Å., C–O = 1.42 Å., C–H = 1.09 Å., C=C = 1.33 Å., C=O = 1.21 Å., O–H = 0.97 Å. ∠HCH = 109° 28' in -CH_3 groups, ∠HCH = 120° in CH_2 groups. A, C–O = 1.47 Å., ∠COC = 89°; B, ∠COC = 89°; C, H_2C–CO = 1.56 Å., C–O = 1.40 Å., C=C = 1.36 Å., C=O = 1.23 Å., ∠COC = 97°; D, ∠COC = 97°; E, ∠COC = 90°; F, ∠CCC = 86°; G, ∠CCC = 90°; H, as drawn (*cis*), with ∠H_3C–C–C = 110°, ∠O=C—C = 125°, ∠CCH = 120°, ∠C—C=C = 120°; I, CH_3CO rotated through 180° from position in H (*trans*); J, angles as in H. OC–C = 1.48 Å., C=C = 1.37 Å., O=CCH_3 = 1.28 Å., O=CCH = 1.24 Å.; K, *trans* to J; L, (*cis*) ∠H_3C–C–C = 110°, ∠O=C—C = 130°, ∠C—C=C = 130°, ∠CCH = 115°; M, CH_3CO group rotated 90° from position in H; N, equal weights of H + I + M.

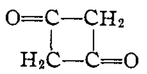
A, B,



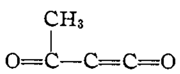
E,



F, G,



H, I,



$$O{=}C(CH_3){-}C{=}C{=}O$$

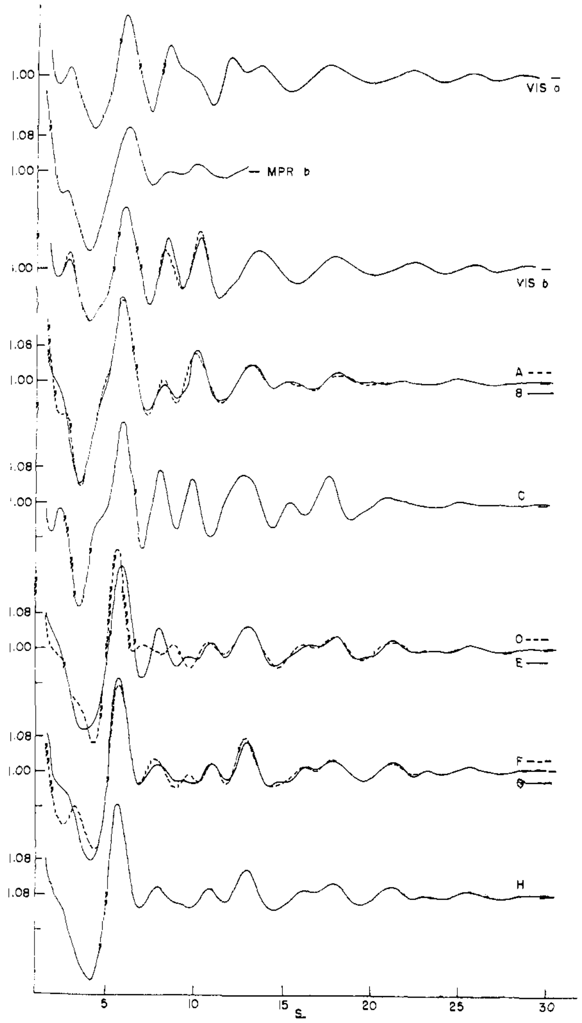
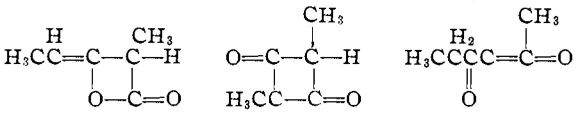


Fig. 6.—Methylketene dimer, models investigated. The parameters for all curves unless otherwise specified are: rings planar. CH_3–C(ring)–H plane ⊥ to ring. Other side-chains coplanar with the ring and bisect the exterior angle. C–C = 1.54 Å., C–O = 1.42 Å., C═C = 1.33 Å., C═O = 1.21 Å., C–H = 1.09 Å. ∠HCH– 109° 28′ in –CH_3 groups, ∠CH_3–C–H = 109° 28′ adjacent to ring, ∠CH_3–C–H = 120° adjacent to C═C. Both –CH_3 groups are not attached to the same carbon. B, as drawn. ∠COC = 97°, C–O = 1.40 Å., C═C = 1.36 Å., C═O = 1.23 Å.; A, like B except 180° rotation around C═C; C, ∠CCC = 90°, CH_3 groups *cis* to each other; D, as drawn except 60° rotation of CH_3CH_2. ∠C–CO–C = 110°, ∠O═C—C = 125°, ∠C—C═C = 120°, ∠OC–CC–CH_3 = 120°, ∠OC–CH_2–CH_3 = 109° 28′; E, like D except 90° rotation of CH_3CCO; G, like D except 180° rotation of CH_3CCO; F, like G except 120° rotation of CH_3CH_2 so both CH_3 groups coplanar with chain; H, free rotation: equal weights of D + E + G.

A, B C D, E



The side-chain angles were not investigated in detail. Those found by Lipscomb and Katz in the crystal, ∠C—C═O = 145°, ∠C═C—C = 136°, are in satisfactory agreement with the electron diffraction data. The limits of error, excluding simultaneous variation of parameters, are 0.04 Å. and 4°. If this restriction is removed, the limits must be larger, although considerations similar to those given earlier again apply.

Methylketene Dimer.—Two types of diffraction patterns, differing in the range s = 4–19, were apparent in the non-sector pictures of methylketene dimer (Fig. 6). Only one type, b, was found on the sector photographs. The effect may be due to the impurity (possibly propionic anhydride) believed to have been present. It was found after completing the photographs that the beam shutter was defective. Since it was not always open when intended, it may have allowed the scattering due to one compound to be selectively recorded in each picture, due to a difference in volatility of the two.

Both patterns were used to compute radial distribution curves, Fig. 3. Pattern a yielded a curve with peaks at r = 1.14, 1.53, 2.29, 3.28 and 3.90 Å., which cannot be interpreted as representing the distances in any of the possible methylketene dimer configurations. The C═C and C–O distances are missing; the 2.29 Å. peak is unexplained. This curve is consistent with an acid or acid anhydride structure which has no C═C bonds: the O–O distance is expected to be near 2.30 Å. Propionic anhydride, a possible impurity in the preparation used, melts at −45°, and its presence would account for the lower of the two observed melting points.

The analysis of the distribution curve from pattern b is straightforward in terms of some of the possible configurations for methylketene dimer. The peak at 1.10 Å. corresponds to the primary distances C–H and C═O. It occurs at a smaller value of r than expected, possibly due to the large oscillations below r = 1 Å. The next maximum at r = 1.48 Å., represents the [C═O + C–O + C–C] distances. It occurs at a larger value of r than the corresponding peak for diketene, but there are twice as many C–C bonds in the methyl dimer as in diketene. The small peak at 2.03 Å. corresponds to the diagonals in a small four-membered ring. The secondary non-ring distances contribute to the peak at 2.50 Å. The larger distances contribute to a peak at 3.22 Å. (similar to diketene and β-propiolactone and unlike the dimethyl dimer) and to peaks at 3.88 and 4.5 Å. All the postulated configurations would have distances near r = 3.90 Å. One of the lactone rings, B has one near 4.50 Å. Therefore, according to the radial distribution results from pattern b, the dimer cannot have either a symmetric diketone ring or the chain configuration, but can have that of a substituted four-membered lactone ring.

Intensity curves were computed for three of the five postulated models; II and IV were omitted. No attempt was made to distinguish between these and III, the vinyllactone. For any one model, variations of the parameters were not investigated, though different configurations due to restricted rotation were. The angles and distances for the various models are given with Fig. 6, with the intensity curves. The critical features of the pattern for structure determination are a shoulder at s = 4.5, the relative heights of the two peaks between s = 8 and 10.5, the width of the maximum at s = 13.5, and of the minima at s = 16 and 20.

Both patterns were compared with calculated intensity curves. Type a differs from all the computed curves, as was anticipated from the radial distribution analysis. Type b is similar in appearance to the diffraction pattern observed for diketene and β-propiolactone and could be correlated with the computed curves.[18]

The cyclic diketone, curve C, is not acceptable. The sector curve is helpful here since estimation of the relative peak heights in the doublet is difficult on non-sector plates. All of the chain models, curves D through H, can be rejected. The variations in intensity curves, considering different positions of the groups in the molecule, assuming hindered rotation or free rotation, are small compared to the discrepancies between them and the observed intensity curve. The vinyllactone curves, A and B, agree adequately with the observed diffraction pattern. The maxima at s = 16 and 20 would probably be removed or decreased if a model with the ketone oxygen unsymmetrically located were considered (compare curves T and K, Fig. 4). The contrast of the microphotometer data and the scale factor for B are given in Table V. A close check is not expected since no attempt was made to refine parameters in this large and unsymmetric molecule.

TABLE V

METHYLKETENE DIMER: INTENSITY CURVE DATA

		s_0		s_0/s_0	
Max.	Min.	Visual	Mpr.	B/vis.	B/mpr.
	0	(2.10)	2.38		
1		2.78	2.65		
	1	3.94	3.90	0.873^a	0.881^a
2		4.86			
	2	5.34			
3		6.10	6.20	0.958	0.942
	3	7.33	7.48	.982	.962
4		8.26	8.40	.985	.967
	4	9.22	9.05	.958	.963
5		10.18	10.00	.982	1.000
	5	11.29	11.35	1.003	0.998
6		11.90			
	6	12.83			
7		13.50		0.978	
	7	15.55			
8		17.64		1.017	
	8	19.98			
9		22.42		0.962	
	9	23.76		0.991	
10		25.66		0.962	
	10	26.74		1.003	
11		28.72		1.03^a	
Av.				0.98	0.97
Av. dev.				0.015	0.02

Max.	Min.	Relative height, visual	Dev. from unit background, mpr.	Specific contrast, mpr./B
	1	30	−0.180	0.78
3		35	.140	.73
	3	20	− .032	.50
4		10	(− .004)	
	4	12	− .008	.20
5		21	.016	.24
	5	17	− .016	.36
Av.				.47
Av. dev.				.20

[a] Omitted in computation of average.

The acceptable models, determined while drawing the microphotometer trace background, agree with the results of the visual correlation procedure. According to the three methods of analysis of pattern b the liquid form of methylketene dimer has a substituted four-membered lactone ring configuration, rather than that of a 1,3-cyclic diketone or a chain. The parameters are probably similar to those in diketene.

Discussion

The visual appearance of the diffraction patterns and the microphotometer tracings agree most closely for dimethylketene dimer, a symmetric molecule. For the other three molecules, all unsymmetric, these data differed where the visual estimation of the pattern is known to be less reliable; the photometer data were found to be consistent with the over-all best models. The microphotometer results allowed a quantitative comparison of intensities as well as s_0 values, even on unsymmetric peaks, to be made.

The confirmation by structural measurements that the liquid form of methylketene dimer has the ketene dimer configuration rather than that of the dimethyl dimer is interesting since all three dimers can be prepared by the direct dimerization of the appropriate monomeric ketenes. No other forms of the ketene or dimethyl dimers have been prepared to date. The mono-enol of the symmetric diketone form of the methyl dimer is known. Steric effects[10] apparently determine which configuration of the disubstituted dimer can result from the direct dimerization. In addition, the possibility of an enol form is excluded. Neither of these restrictions applies to the smaller molecules. The question of their configurations involves not only steric effects but energetic considerations among the various strained ring possibilities. Evidently the dienol ring is too highly strained, despite the possibility for a conjugated closed ring system. It is not immediately apparent why diketene should occur only as a lactone, and methylketene dimer both as a lactone and the mono-enol of the diketone, or why neither occurs as a diketone.

The structural results reported by Lipscomb and Katz for crystalline diketene are given in Table VI with the electron diffraction results for diketene and β-propiolactone. In the crystal, the molecule is planar and has the vinyllactone configuration, III. The angles reported by the two experiments are in excellent agreement. Within the uncertainties, the distances also agree: the over-all size of the molecule is the same within 1.5%.

It is informative to compare the parameters found for the lactones with those found for similar linear molecules (Table VI). Divinyl ether[19] con-

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(18) Both patterns were compared with the two obtained by Lipscomb and Schomaker for diketene.[17] Pattern b is similar to the one of theirs that is like the diketene pattern. Pattern a differs from b, in the same s range as their two differ.

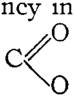
(19) L. L. Barricelli and O. Bastiansen, *Acta Chem. Scand.*, **3**, 301 (1949).

TABLE VI

COMPARISON OF STRUCTURAL PARAMETERS

	X-Ray	Electron diffraction, Å.			
	Diketene, Å.	Diketene	β-Propiolactone	Methyl acetate	Divinyl ether
C=C	1.35	1.31			1.35
C=O	1.24	1.19	1.19	1.22	
Methoxy C–O	1.39	1.41	1.45	1.46	1.42
Carboxy C–O	1.40	1.41	1.45	1.36	
C-C of C—C=C	1.48	1.52	1.53		
C-C of C—C=O	1.46	1.52	1.53	1.52	
∠C=C—O	130°	130°[a]			123°
∠C=C—C	136°	136°[a]			
∠O-CC-C	94°	95°	94°		
∠C-O-C	89°	89°	89°	113°	107°
∠O-CO-C	94½°	95°	94°	116°	
∠C-C-C	83°	81°	83°		
∠O—C=O	121°	121°[a]	123°	124°	
∠C—C=O	145°	145°[a]	143°	(120°)	
Limits of error	±0.06 Å.	±0.04 Å.	±0.03 Å.	0.03–0.04 Å.	
	±2°	±4°	±3°	3–4°	
Configuration	*trans* Planar	*trans* Assumed planar	*trans* Assumed planar	*cis*, non-planar, av. angle C–O–C plane to O=C—O plane 25°, limiting values 0 and 35°	Non-planar, both vinyl groups rotated 20° around C–O in same direction

[a] Assumed value from X-ray results.

tains a doubly unsaturated system, as does diketene. It is not planar, and the distances are those found in simpler molecules. The esters, methyl formate and methyl acetate[20] are also non-planar. In addition they both have *cis* configurations, while the planar lactone may be considered an extreme *trans* configuration. The two C–O in each ester are unequal. The angles in the esters at the carboxy carbons are somewhat different from the 120° expected for strictly trigonal hybridization, consistent with the shortened carboxy C–O but opposite to the effect found in the β-lactones. Apparently the strain of the planar four-membered ring configuration in the lactones predominates over the tendency in the unstrained molecule for conjugation in 

In view of the structural differences between linear esters and lactones, it is interesting to compare the mechanisms of similar reactions (recognizing, of course, that reacting molecules in solution differ from molecules in the gas phase). The kinetics of hydrolysis of aliphatic esters, β-, and γ-lactones have been investigated in detail.[21] γ-Lactones, are less strained than β-lactones, and react similarly to aliphatic esters. The cleavage occurs at the short carboxy C–O both in acid- and base-catalyzed hydrolysis. In acid solution, the process was found to be bimolecular, the proton reacting directly with the molecule. The mechanism for the β-lactones is different. In the acid- and base-catalyzed hydrolysis, the cleavage also occurs at the (now long) carboxy C–O. However, for acid catalysis, the process is the unimolecular opening of the strained ring; the addition of the reagent occurs later.

The deviations from "normal" bond angles and distances shown by diketene and related molecules are part of the more general problem of the structures of small strained ring molecules. The parameters of three- and four-membered hydrocarbon and oxygen-containing rings whose structures are known are listed in Table VII, with the unique features of the structures indicated in the last column. Qualitative attempts to explain them may delineate the problems to be solved. In the three-membered rings, the abnormalities in bond distances seem to be uniformly toward shorter internuclear distances; in four-membered rings the effect is generally toward longer distances. The shortening in the former has been attributed to the presence of "bent bonds"[22] in which the line of maximum bonding electron density is outside the direct line joining the nuclei. The lengthening in four-membered hydrocarbon rings has been attributed to repulsions of the non-bonded ring atoms.[23] However, the lengthening of the ring distances cannot be attributed to hydrogen repulsions since such an effect would, in trimethylene oxide, probably result in increased C–C distances instead of the observed increased C–O distances. The evidence concerning planarity of four-membered rings is not clearcut. Persubstituted rings are reported to be puckered, tetrasubstituted ones planar, and C_4H_8 is either non-planar or has a large amplitude out-of-plane vibration. The oxygen-containing rings are planar at least in the mean. When the two sides of the ring contiguous with a side chain are not identical, the chain lies about 10° off the bisector of the corner. The ring corner angle in four-carbon rings, contiguous with an unsaturated side-chain, is about

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[21] P. D. Bartlett and G. Small, Jr., *ibid.*, **72**, 4867 (1950); S. C. Datta, J. N. E. Day and C. K. Ingold, *J. Chem. Soc.*, 939 (1939); F. A. Long and F. Dunkle, private communication; F. A. Long and L. Friedman, THIS JOURNAL, **72**, 3692 (1950); F. A. Long and M. Purchase, *ibid.*, **72**, 3267 (1950).

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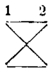
TABLE VII

PARAMETERS OF THREE- AND FOUR-MEMBERED RINGS[23]

Compound	Distances, Å. C=C	C–C	C–O	Angles	Unique features
Cyclopropane		1.525		∠H–C–H = 118 ± 2°	C–C short
		1.515 ± 0.02		∠C–C–H = 116 ± 2°	
Spiropentane  1 2		1.51 ± .04 C_1–C_2		∠C_2–C_3–C_1 = 61.5 + 2°	C–C short
		1.48 ± .03 C_1–C_3		∠H–C–H = 120 ± 8°	
Cyclopropene	1.286 ± 0.04	1.525 ± .02		∠C=C—M = 152 ± 12°	C=C short
Ethylene oxide		1.472	1.436	∠H–C–H = 116° 41′	C–C short
				∠C–O–C = 61° 24′	
				∠H_2–C–C = 159° 25′	
Cyclobutane		1.568 ± .02		Non-planar ring on average	C–C long
				∠H–C–H = 114 ± 8°	
Tetraphenylcyclobutane		1.555 ± .02		Ring planar	C–C long
		1.585 ± .02			
Per-substituted cyclobutanes		1.59 – 1.60		Non-planar rings	C–C long
Methylenecyclobutane	1.34 ± 0.02	1.55 ± 0.02		∠C–CCH_2–C = 92.5 ± 4°	C–C long
		1.56 ± .03			∠s at C=C
1-Methylcyclobutene	1.34 ± 0.03	1.54 ± .03		∠C=C—C = 93.5 ± 3°	∠s at C=C
				∠CH_3–C–C = 125 ± 4°	
Methylcyclobutane		1.56 ± .03 ring		Ring may be non-planar	C–C long
		1.54 ± .06 chain		∠C–C–CH_3 = 118°	
Dimethyl ketene dimer		1.56 ± .05 ring		∠C–CO–C = 93.5 ± 6°	C–C long
		1.54 ± .05 chain		∠CH_3–C–CH_3 = 111 ± 6°	∠s at C=O
Trimethylene oxide		1.54 ± .03	1.46 ± 0.03	∠C–O–C = 94.5 ± 3°	C–O long
				∠C–C–O = 88.5 ± 3°	
β-Propiolactone			See Table VI		C–O long
					∠s at C=O
Diketene			See Table VI		∠s at C=O

93°, whereas for a planar unsubstituted ring it is 90°.

Accumulated evidence points to considerable delocalization of the electrons in the planar strained rings. With the bonding orbitals becoming more alike, greater dimension symmetry in the ring results. In both ethylene oxide and trimethylene oxide the ratio of distance C–O/C–C is closer to unity than it is for linear molecules, although in the former the C–C is short, and in the latter the C–O is long. In addition, unsaturated side-chains seem to interact with the four-membered rings appreciably. The lengthening of C–C in saturated four-carbon rings is least in the cases of dimethylketene dimer and methylene cyclobutane. One may argue that in the three member rings, the necessity for "bent bonds" leads to a short C–C, with the C–O remaining nearly normal; were one to measure along the bonding orbital axes, the CO would also be longer than 1.42 Å. On the other hand, in trimethylene oxide, delocalization permits the effects of non-bonding repulsion to be absorbed in lengthening the C–C.

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ITHACA, N. Y.