[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Structure of Ketene Dimer[1]

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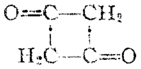
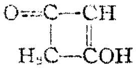
Five structures for diketene are still under active discussion. These include 1,3-cyclobutanedione (I),[3] its mono-enol form (II),[4] β-crotonolactone (III),[5] vinylaceto-β-lactone (IV),[6] and acetylketene (V).[7] The Raman spectrum of diketene has been obtained by Angus, Leckie, LeFèvre, LeFèvre and Wassermann[4] and more recently and accurately by Kohlrausch and Skrabal.[8] The latter authors alone have seriously attempted to draw structural conclusions from the data, and they considered only structure I and its two possible enol forms. For this reason it was decided to re-examine diketene by means of the Raman effect and to compare its spectrum with the spectra of compounds whose structures resemble the various proposed formulas. These related compounds include 2,2,4,4-tetramethyl-1,3-cyclobutanedione, β-butyrolactone, vinyl acetate and dehydroacetic acid. The spectrum of diketene does not resemble that of any of the compounds examined, nor that of any of the compounds whose spectra are available to us. However, the characteristic features of the spectrum do not seem to support structures I, II and III. Neither IV nor V can be eliminated by the Raman spectrum alone.


I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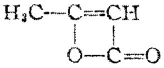
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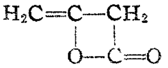
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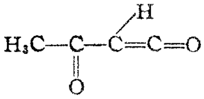
V

Experimental

A sample of diketene was furnished by Dr. C. D. Hurd; the compound was also prepared several times in this Laboratory by the method given in "Organic Syntheses."[9] When a nichrome wire was used in the pyrolysis lamp much carbonization occurred. The Raman spectrum showed that the product contained a considerable quantity of acetic anhydride. Substitution of platinum for nichrome wire eliminated the carbonization, and this product was fractionated in an efficient column. The sample isolated, b. p. 124.5° at 745 mm., n^{20}_D 1.4368, gave no trace of line at 2940 cm.$^{-1}$, which is the position of the strongest Raman frequency of acetic anhydride.

2,2,4,4-Tetramethyl-1,3-cyclobutanedione was first prepared by the method of Staudinger[10] by dropping α-bromoisobutyryl bromide on zinc.

α-Bromoisobutyryl bromide was prepared by the action of phosphorus tribromide on α-bromoisobutyric acid at 190°. The product was distilled directly from the reaction mixture. After fractionation the yield of material boiling at 160–161° was 30%. An ether solution of α-bromoisobutyryl bromide was dropped onto a large excess of mossy zinc mixed with thirty-mesh zinc and zinc dust. The acid bromide was added at such a rate that the heat of reaction caused the ether–dimethylketene solution to distil from the mixture. The solution was allowed to stand and the dimethylketene slowly polymerized. After several weeks the ether was taken off under vacuum, and the dione was steam-distilled from the residue. A very poor yield of product, melting at 114–115° in a sealed tube, was obtained.

The dione was also prepared by the pyrolysis of carefully dried N-isobutyryl phthalimide by the procedure of Hurd and Dull.[11] Three separate attempts employing different conditions of pyrolysis failed to yield more than a trace of the dione which each time was contaminated by considerable phthalic anhydride.

The dione was prepared in good yield from dimethylmalonic anhydride by the method of Staudinger.[12] Ethyl methylmalonate was prepared by the procedure given in "Organic Syntheses,"[13] and ethyl dimethylmalonate was prepared therefrom by similar reactions. The ester was saponified with alcoholic sodium hydroxide, and the dimethylmalonic acid was recrystallized from water. The acid, m. p. 187°, was converted by the action of acetic anhydride to dimethylmalonic anhydride, which decomposed when heated to 110°. The anhydride was pyrolyzed by the method of Staudinger,[12] and a 60% yield of 2,2,4,4-tetramethyl-1,3-cyclobutanedione was obtained. The product was purified by steam-distillation; m. p. 114–115° in a sealed tube.

β-Butyrolactone, b. p. 54.5 55.5° at 100 mm., was made available by Dr. F. O. Rice.

Dehydroacetic acid was Eastman Kodak Co. material and was purified by distillation under reduced pressure. No accurate boiling point was obtained.

Vinyl acetate was Eastman Kodak Co. material and boiled at 73.0° at atmospheric pressure.

The method of obtaining the Raman spectra has been described earlier.[14,15] Dehydroacetic acid was examined in chloroform solution and the spectrum of 2,2,4,4-tetramethyl-1,3-cyclobutanedione was obtained using both chloroform and carbon tetrachloride solution. The spectrum did not vary noticeably with the solvent.

Discussion

The spectra of the various compounds examined are listed in Table I. The data for β-

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[1] Presented at the Cleveland meeting of the American Chemical Society, April, 1944.

[2] Abstract of a portion of the thesis presented by Harvey J. Taufen to the Graduate Faculty of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1944. Present address: Tennessee Eastman Co., Oak Ridge, Tenn.

[3] Rice and Roberts, THIS JOURNAL, **65**, 1677 (1943).

[4] Angus, Leckie, LeFèvre, LeFèvre and Wassermann, *J. Chem. Soc.*, 1751 (1935).

[5] Calvin, Magel and Hurd, THIS JOURNAL, **63**, 2174 (1941).

[6] Boese, *Ind. Eng. Chem.*, **32**, 16 (1940).

[7] Hurd and Williams, THIS JOURNAL, **58**, 962 (1936).

[8] Kohlrausch and Skrabal, *Proc. Indian Acad. Sci.*, **8A**, 424 (1938).

[9] Drake, "Organic Syntheses," Vol. 21, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 64.

[10] Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, p. 140.

[11] Hurd and Dull, THIS JOURNAL, **54**, 2432 (1932).

[12] Staudinger, *Helv. Chim. Acta*, **8**, 306 (1924).

[13] Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 279.

[14] Cleveland, Murray, Coley and Komarewsky, *J. Chem. Phys.*, **10**, 18 (1942).

[15] Taufen, Murray and Cleveland, THIS JOURNAL, **65**, 1130 (1943).

TABLE I

RAMAN SPECTRA OF DIKETENE AND SOME RELATED COMPOUNDS

Diketene		2,2,4,4-Tetramethyl-1,3-cyclobutanedione[a]		Vinyl acetate		β-Butyrolactone		Dehydroacetic acid[a]		Ketene[b]	
$\Delta\nu$	I[c]	$\Delta\nu$	I[c]	$\Delta\nu$	I	$\Delta\nu$	I[c]	$\Delta\nu$	I[c]	$\Delta\nu$	I[c]
154	44	162	50								
		294	20								
324	8					332	5				
				405	24						
444	15			462	10	434	16				
504	7					516	28	500	16	510	1b
531	20										
		585	23							599	$^1/_2$b
		633	53	636	17			620	36		
670	100										
				702	2	711	80	707	10	715	$^1/_2$b
803	3									801	$^1/_2$b
840	6			846	10	825	49				
870	9			875	7			926	20		
951	3	965	10	977	11	967	46	971	5		
986	10							996	5	998	1
1017	4	1049	10			1022	13	1027	9		
						1063	13				
1104	1					1105	26				
				1139	7	1128	w			1130	6b
				1217	6					1198	1
				1295	80	1280	w	1272	31		
1374	20			1371	11	1360	w			1344	2
				1387	11			1390	7	1386	1b
		1441	26			1422	w	1429	w		
		1465	28			1457	29	1463	w		
								1560	56		
								1615	56		
				1646	100			1646	100		
1689	10b							1710	w		
1760	w										
1791	w	1806	w	1758	20						
						1818	25				
1859	20	1855	19								
1896	14									1895	$^1/_2$
										2049	$^1/_2$b
		2863	31			2870	10				
		2904	50								
		2933	70	2939	60	2935	60	2926	27		
2958	61	2971	100			2963	100			2952	5
				2993	4	2984	73				
3019	43			3043	17	3017	25			3015	
3072	w			3093	3						
3127	15			3125	8						

[a] Dissolved in chloroform; spectrum incomplete. [b] Data reported by Kopper.[16] [c] Lines broader than usual are designated b. Lines with intensity too weak to measure on the densitometer are designated w.

butyrolactone, 2,2,4,4-tetramethyl-1,3-cyclobutanedione and dehydroacetic acid are reported for the first time. Kohlrausch and Skrabal[8] have previously reported the spectrum of some unknown material which they took to be 2,2,4,4-tetramethyl-1,3-cyclobutanedione. These investigators prepared their material by the procedure of Staudinger.[12] We have prepared the tetramethyldione by this method and also by Staudinger's earlier procedure.[10] The spectra of these two samples were identical, very different from the report of Kohlrausch and Skrabal, and in better agreement with expectations for this compound. The two lines at 1806 and 1855 cm.$^{-1}$ representing the carbonyl group are especially noteworthy. Acyclic, unconjugated ketones exhibit a line very close to 1720 cm.$^{-1}$ which is characteristic of the carbonyl group. On the other hand, if the carbonyl group is exocyclic to a strained ring the frequency is considerably higher, as in the present case. Although there are two carbonyl groups in the dione, only one Raman line in the 1700 cm.$^{-1}$ region would ordinarily be expected, since both groups are structurally identical. Instead, the tetramethylcyclobutanedione shows two such lines. Examination of the spectra of compounds containing carbonyl groups where the C=O vibration is usually above 1800 cm.$^{-1}$, *e. g.*, anhydrides and acid chlorides, shows that a doublet quite often is present. A logical explanation of this phenomenon is Fermi resonance, which apparently can occur when the carbonyl frequency falls in the higher regions but not in general when the usual ketonic frequency near 1720 cm.$^{-1}$ is present.

In both β-butyrolactone and vinyl acetate the carbonyl frequency is higher than that ordinarily observed in ester linkages. In β-butyrolactone this is caused by the position of the carbon–oxygen double bond exocyclic to the four-membered ring. In vinyl acetate the enhancement of the frequency is probably caused by interaction of the vinyl group with the electrons on the "ether" type oxygen. This reduces the customary interaction of these electrons with the carbonyl group. This in turn reduces the contribution within the carbonyl group of the resonance form which has only a single bond between the carbon and oxygen atoms. The corresponding increase in "double bond character" is then reflected by the increase in the frequency of the Raman line. The ester carbonyl frequency is also high for some other compounds of this type. For example, in phenyl acetate and phenyl butyrate the frequency is observed above 1750 cm.$^{-1}$, whereas the usual frequency for an ester such as butyl butyrate is near 1735 cm.$^{-1}$.

By means of the Raman spectrum it was found that diketene, as ordinarily prepared, may contain a considerable quantity of acetic anhydride which cannot be separated by a cursory distillation. It would appear that the results of previous investigations should be re-examined with this point in mind. It is felt that the acetic anhydride is formed by the reaction of water with the ketene produced in the pyrolysis. The origin of the water is uncertain. It may be a product of the carbonization or it may be present in the original acetone. The amount of anhydride formed seems hardly in accord with the latter view.

The spectrum of diketene does not resemble that of any of the compounds examined. Among the characteristic features are the small number of Raman lines above 2700 cm.$^{-1}$ and the high frequencies of those lines which are observed. Lines in this region are generally associated with carbon–hydrogen valence vibrations, and most aliphatic compounds with as many hydrogen atoms as diketene have some lines between 2700 and 2940 cm.$^{-1}$.

The spectrum of diketene possesses three strong Raman lines in the frequency region generally associated with carbon–oxygen double bonds. These are at 1689, 1859, and 1896 cm.$^{-1}$. Two other lines of very low intensity were observed at 1760 and 1791 cm.$^{-1}$.

The 1,3-cyclobutanedione structure accounts for the lines at 1859 and 1896 cm.$^{-1}$ since the tetramethyl-substituted homolog has two frequencies in a region not too far distant from these two lines. Against this structure is the complete lack of an explanation for the 1689 cm.$^{-1}$ band which is conspicuously absent in the tetramethylcyclobutanedione. Then, too, Kohlrausch and Skrabal have pointed out that the total number of Raman lines observed is too great for a molecule as highly symmetrical as is the dione.[8]

The mono-enol form (II) is more consistent with the dipole moment data than is form I. Such a structure would give rise to an intense Raman line characteristic of the olefinic double bond. This frequency should be lower than the observed 1689 cm.$^{-1}$, both because of the conjugation between the olefinic and carbonyl bonds and because of its presence within a strained ring. No line corresponding to this vibration is found in the spectrum of diketene. Furthermore, this form does not afford any explanation for the line at 1689 cm.$^{-1}$.

β-Crotonolactone (III) is another structure containing an olefinic double bond within a strained ring. The same arguments apply as before. No line is observed for the olefinic bond and no group is present to which can be assigned the line at 1689 cm.$^{-1}$.

The spectroscopic evidence for structure IV is somewhat more favorable than for those thus far considered. This structure could account for the high frequencies of the lines at 1859 and 1896 cm.$^{-1}$. First, the ester carbonyl is exocyclic to a strained ring. This grouping in β-butyrolactone increases the frequency from 1735 cm.$^{-1}$, that of an ordinary ester, to 1818 cm.$^{-1}$. Second, the presence of the vinyl group should raise the frequency still higher, an effect analogous to that discussed under vinyl acetate. Assignment of the 1689 cm.$^{-1}$ band to the exocyclic methylene group would be reasonable except for the diffuse nature of the band. Usually olefinic bands in the Raman effect are sharp as compared to the line in question, which is only moderately intense and spreads over thirty wave numbers on the spectrogram.

There remains the acetylketene formula (V). If conjugation of the acetyl carbonyl with the ketene group is assumed, the line at 1689 cm.$^{-1}$ falls very close to the predicted value. It is more difficult to predict where frequencies arising from a substituted ketene linkage should be observed. In the first place, knowledge of the usual value of carbonyl and olefinic Raman frequencies is of no help in predicting the frequencies of the ketene group itself, as the symmetry and types of vibration of the groups are so different. Secondly, the only monomeric ketene so far examined by the Raman effect is ketene itself[16]; the color and

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(16) Kopper, *Z. physik. Chem.*, **B34**, 396 (1936).

rapid polymerization of other ketenes have prevented observation of their spectra. In ketene no Raman lines were found in the general range where olefinic frequencies are expected, but above this were lines at 1895 and 2049 cm.$^{-1}$. The two lines of diketene at 1859 and 1896 cm.$^{-1}$ could therefore very conceivably arise from the substituted ketene linkage. There is no evidence that this is actually the case, as acetylketene would be the only known member of its homologous series. At any rate, the authors feel that the Raman spectrum of diketene does not contradict the acetylketene structure.

The spectrum of diketene agrees well with the observations of Kohlrausch and Skrabal. Those investigators did not observe, however, the two weak lines at 1760 and 1791 cm.$^{-1}$ and reported a weak line at 3213 cm.$^{-1}$ which was not found in the present work. The weak lines at 1760 and 1791 cm.$^{-1}$ are probably not caused by a small amount of an impurity, because the intensity of these lines, relative to the intensity of the stronger lines of diketene, did not vary in different fractions when the product was distilled through a 15-plate column. Lines as weak as these two are of little value for the type of structure determination employed here, and their presence is difficult to explain with any of the proposed structures.

Acknowledgment.—The authors wish to express their thanks to Dr. C. D. Hurd and to Dr. F. O. Rice for supplying samples of ketene dimer and β-butyrolactone, respectively.

Summary

1. Raman spectra are reported for diketene, 2,2,4,4-tetramethyl-1,3-cyclobutanedione, β-butyrolactone, vinyl acetate, and dehydroacetic acid. The spectrum of diketene does not resemble that of any of the compounds whose spectra are available.

2. Of the currently discussed structures for diketene it is possible by its Raman spectrum to exclude all except vinylaceto-β-lactone and acetylketene. No definite choice between these two formulas has been made.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Molecular State of Acetic Acid Vapor

BY H. L. RITTER AND J. H. SIMONS

The phenomenon of association of carboxylic acids in the vapor phase is a familiar one, and the specific linkage through which the association is effected is usually called the hydrogen bond. It has been assumed that dimerization represents the full tendency toward polymerization of these structures, Hammett having mentioned the failure of such compounds to undergo further association.[1] MacDougall's work on propionic acid vapor,[2] however, shows definite evidence of higher order polymerization. His earlier work on acetic acid[3] shows the same evidence, although it is too slight to permit of precision calculations of the concentration of higher order polymer. The data of Ramsay and Young[4] on the density of acetic acid vapor are too sparse for the same calculations.

The present study represents an attempt to procure data on the vapor density of acetic acid over a sufficiently wide range of temperature and pressure and of sufficient precision to determine whether or not acetic acid vapor contains a polymer of higher order than the second and, if so, to establish the identity of this polymer. The equilibrium constants for the polymerization reactions have been calculated as well as the heats of association.

Purification of Material.—Reagent grade acetic acid was fractionally crystallized in an apparatus, a diagram of which is shown in Fig. 1a. About 100 cc. of material was placed in bulb A. It was frozen, allowed to melt all except the last few crystals, and then 90% refrozen with a swirling motion of the container. The 10% liquid was removed by filtration using a vacuum, and the process repeated eleven times. The melting point rose from 15.05° to a final value of 16.56° (cor.),[5] as shown in Fig. 1b. This corresponds to 0.06 mole per cent. impurities, or 0.02 per cent. if water is the sole contaminant. The transfer to sample vials was made by means of a sealed glass manifold system, and contact with foreign gases or water was avoided.

Vapor Pressure.—MacDougall[3] has corroborated the low temperature values given by the "International Critical Tables"[6] and the normal boiling point is accurately known. As this constitutes corroboration of both ends of the vapor pressure curve in which we are interested, the data in these Tables were accepted as correct.

Liquid Density.—Available data on the liquid density of acetic acid as a function of temperature[4,7] are discordant and appear unreliable. Accordingly, and inasmuch as the available data do not cover the wide range of temperature we

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[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 35.

[2] F. H. MacDougall, THIS JOURNAL, **63**, 3420 (1941).

[3] F. H. MacDougall, *ibid.*, **58**, 2585–2591 (1936).

[4] Ramsay and Young, *J. Chem. Soc.*, **49**, 790 (1886).

[5] True melting point assumed to be 16.60°. See W. R. Bousfield and T. M. Lowry, *J. Chem. Soc.*, **99**, 1437 (1911).

[6] "International Critical Tables," Vol. III, p. 217.

[7] D. Tyrer, *J. Chem. Soc.*, **105**, 2534 (1914).