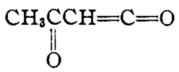
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CATHOLIC UNIVERSITY]

The Structure of Diketene[1]

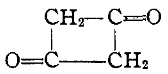
BY FRANCIS OWEN RICE AND RALPH ROBERTS

1. Introduction

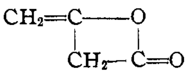
The structure of diketene has been under discussion by chemists ever since its discovery in 1908 by Chick and Wilsmore.[2] Three fundamentally different structures have been proposed


$CH_3C(=O)CH{=}C{=}O$

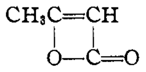
IA



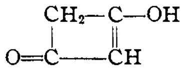
IIA



III



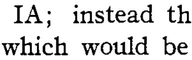
IB



IIB

All of these are still under active discussion and while quite a number of other structures having the formula $C_4H_4O_2$ can be written, we shall consider in this paper only those mentioned above.

The first structure IA was originally proposed by Chick and Wilsmore.[2] They verified the composition by combustion analysis and determined the molecular weight by the freezing point lowering in solution and by a modified Victor Meyer determination. On the basis of the formation of various reaction products such as those formed with water, alcohol or aniline, Chick and Wilsmore concluded that the results were best explained by addition at the double bond adjoining one of the carbonyl groups; hydrogen goes to the α carbon atom and the rest of the reactant adds at the other side of the double bond.

In the following year Staudinger and St. Bereza[3] proposed the cyclobutanedione structure, IIA, or its tautomeric enol form, IIB, for diketene. This proposal was based on the analogy of the reactions of diketene with those of the dimer of a substituted ketene, this dimer clearly being a substituted cyclobutanedione. The cyclobutanedione structure was accepted by Chick and Wilsmore[4] upon discovering that the addition of bromine did not give  $CH_3C(=O)CHBrC(Br){=}O$ as they expected from formula IA; instead they obtained $CH_2BrCOCH_2COBr$ which would be expected if one of the single bonds of the cyclobutanedione opened and a bromine atom added to each of the two free valences.

Hurd and his co-workers[5a,b,c,d] concluded that the differences in properties between the substituted cyclobutanediones and diketene make the cyclobutanedione formula untenable. Hurd and Roe[5b] and also Hurd and Abernethy[5c] proposed a new structure formed by resonance between acetylketene IA and β-crotonolactone IB. More recently Calvin, Magel and Hurd[5d] have concluded on the basis of absorption spectra measurements that the β-crotonolactone formula is the most probable but that it can transform easily into the isomeric acetylketene form. Since these two structures are so different spacially, it seems unlikely that fusion into an intermediate form could be important and it seems better, therefore, to regard IA and IB as two isomeric forms in equilibrium which require a small activation energy to interchange.

Boese[6] holds that the acetylketene structure is untenable because it fails to account for the almost quantitative thermal decomposition of the dimer into ketene. The cyclobutanedione structure was also considered untenable on the basis of considerations advanced by Hurd and Williams. For these reasons Boese favors formula III (proposed by A. L. Wilson[5]), vinylaceto-β-lactone, for the ketene dimer.

In this paper we shall present evidence based mainly on the gaseous thermal decomposition of diketene, that it has the formula IIA, namely, cyclobutanedione-1,3 proposed by Staudinger and St. Bereza shortly after its discovery. We shall discuss the various aspects of the problem in the following sections and shall point out that the Staudinger formula is the only one that is compatible with the results of pyrolysis. In view of the present uncertainty of the chemical evidence based on reactions in condensed systems, we have advanced some reasons why the reactions of diketene in solution and at catalyst surfaces may not

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[1] Taken from the thesis presented by Ralph Roberts for the degree of Doctor of Philosophy in the Catholic University. Original manuscript received April 2, 1942.

[2] Chick and Wilsmore, *J. Chem. Soc.*, **93**, 946 (1908).

[3] Staudinger and St. Bereza, *Ber.*, **42**, 4908 (1909).

[4] Chick and Wilsmore, *J. Chem. Soc.*, **97**, 1978 (1910).

[5] (a) Hurd and Williams, THIS JOURNAL, **58**, 962 (1936); (b) Hurd and Roe, *ibid.*, **61**, 3355 (1939); (c) Hurd and Abernethy, *ibid.*, **62**, 1147 (1940); (d) Calvin, Magel and Hurd, *ibid.*, **63**, 2174 (1941).

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

be inconsistent with the cyclobutanedione formula.

On the other hand, this formula is not consistent with the high dipole moment, 3.53, recently found by Hurdis and Smyth[6a] for diketene in the vapor state. We are unable to offer any explanation for this discrepancy since our own results are just as clear-cut in favor of the cyclobutanedione formula as the dipole moment measurements are against it. Although the high dipole moment appears to eliminate the Staudinger formula, the measurement does not permit one to distinguish unequivocally between the other proposed formulas and we must, therefore, regard the question as still unsettled.

(2) **Keto–Enol Forms.**—In view of the long controversy over the formulas of such compounds as acetoacetic ester, it is curious that no one seems to have made a thorough examination of the ketene dimer in order to find out whether it is a single substance or a mixture of perhaps keto-enol isomers. The methods for doing this have now been thoroughly developed and involve working at as low a temperature as possible and taking every precaution to ensure the absence of catalysts, especially bases. We have examined the pure dimer of ketene by freezing methods and by the so-called aseptic distillation[7] and all our evidence indicates that the dimer is essentially a single substance and is not a mixture of two easily interconvertible forms.

Experimental

Some carefully distilled diketene was placed in a Pyrex test-tube which had been thoroughly cleaned and flamed according to a procedure previously described.[7] The dimer was cooled slowly with constant stirring until it was almost completely frozen. It was then removed from the freezing bath and allowed to warm up slowly. From time to time a small amount was removed and the refractive index measured. Although this diminished by a few units in the fourth place, we do not consider the difference significant. In a second experiment we distilled the dimer in an all-Pyrex apparatus under aseptic conditions but the different fractions of distillate all had the normal refractive index. We had previously tested the apparatus using acetoacetic ester and had found that the enolic form could be obtained easily.

These experiments are not of course conclusive since there might be two forms not easily separated or having nearly identical refractive indices, furthermore these experiments refer only to the pure liquid.

(3) **Reactions in Condensed Systems.**—Chemical evidence for the formula of diketene can be obtained from its thermal decomposition in the vapor state, its reactions in solution or in the liquid condition and its hydrogenation at a catalytic surface. We shall consider the gaseous decomposition in a succeeding section and will make in this section some observations of a general character on the nature of reactions in condensed systems and apply these observations to the point in question. It is a curious fact that none of the formulas proposed for diketene is really satisfactory for explaining the various reactions in solutions and at surfaces.

Chemists have been interested for a long time in the mechanism of organic reactions and it is now recognized that formal mechanisms which represent an organic molecule as breaking into two parts such as a hydrogen atom and a residual radical, which then add to an unsaturated point in a second molecule, are not correct. If we consider an organic substrate such as ketene dimer reacting in a condensed system we must realize that the strong microscopic fields of the solvent and other reactants which are always in contact with the substrate cause distortion of the molecule and result in the extreme case in formation of a positive or negative ion.

The classical experiment of Kurt Meyer[8] in which he acidified an alkaline solution of malonic ester illustrates the curious structural changes that sometimes occur. After acidifying, the solution was divided into two parts and bromine was added to one part immediately and to the other part after a few minutes. There was extensive reaction when the bromine was added immediately but no reaction after a few minutes.

The product formed by a reaction in solution permits us to draw inferences regarding the distorted substrate molecule which actually reacts to give the final product; this distortion may be so great that actually a different structure, present perhaps in small quantity, is the actual reactant; in such examples inferences concerning the structure of the substrate may be very misleading.

Fortunately this difficulty is not too trouble-

(6a) Hurdis and Smyth, THIS JOURNAL, **65**, 94 (1943).

(7) Rice and Sullivan, *ibid.*, **50**, 3048 (1928).

(8) Meyer, *Ber.*, **45**, 2864 (1912).

some in the case of most organic reactions; however, in the case of a compound such as diketene, in which resonance almost certainly plays a large part in determining its structure, there must be a profound modification of this factor caused by the presence of electron pair donors and acceptors. Correspondingly, inferences concerning the structure of the original diketene molecule must have a large element of uncertainty.

The same situation exists with reactions at metallic surfaces. It is now well known through the use of deuterium, that an interchange occurs at metallic surfaces[9] even in a temperature range below that at which reaction occurs. In the case of a compound like diketene it seems only reasonable to conclude that addition of hydrogen is preceded by separation into a hydrogen atom and a residual radical both adsorbed on the catalyst surface; the stablest configuration for this residual radical may be very different from that of diketene and so here again we are prevented from drawing unequivocal conclusions regarding the structure of diketene, based on the product of hydrogenation.

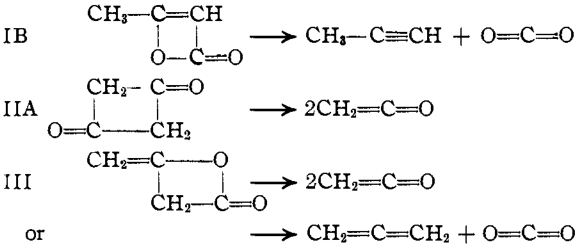
It would seem, therefore, that reactions in condensed systems must be used with great caution for determining the structure of molecules, especially if resonance is present to an appreciable degree.

(4) Pyrolysis in the Vapor State.—The products of the thermal decomposition in the vapor state of diketene may be used for drawing inferences concerning its structure and the objections that may be urged against such conclusions are not nearly so weighty as those discussed in the previous section. A principle known as the principle of least motion has been suggested[10] in order to serve as a guide for deciding the mechanism of homogeneous gas reactions. This principle states that that reaction is favored which involves least motion of the atoms of the substrate molecule and least rearrangement of the electronic system; the application of the principle has been already discussed in detail.

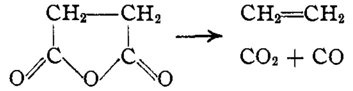
In our first experiments we decomposed diketene at low pressures in a flowing system according to the Paneth technique[11] and passed the gases over a tellurium mirror. There were no radicals formed that attacked tellurium since the mirror was quite unaffected although extensive decomposition had occurred.

Of the various formulas listed in section (1) of this paper, we believe this experiment rules out acetylketene, IA. Our experience in this Laboratory indicates that if diketene really has the structure represented by acetylketene, it should decompose through a radical chain reaction and the radicals could be detected by the Paneth technique.[12] This reasoning would also apply to formula IIB so that we believe that diketene does not exist in greater part as the enolic form of cyclobutanedione.

The absence of mirror removal is consistent with diketene having any of the other three formulas and further evidence must be secured by examining the products of the reaction. According to the principle of least motion, these reactions would be expected



Before discussing our results, we would like to mention that we have applied this principle successfully to a number of thermal decompositions; as an example, we may quote succinic anhydride, which gave, under our conditions, almost the theoretical yields of ethylene, carbon monoxide and carbon dioxide



Maleic anhydride gives similarly acetylene, carbon monoxide and carbon dioxide.

We examined the products of decomposition of diketene very carefully and showed that within experimental error they consisted only of ketene; in particular methylacetylene, allene or carbon dioxide were absent even in traces. This appears

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[9] Twelfth Report Committee on Catalysis, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 32.

[10] Rice and Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939).

[11] Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929); Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932).

[12] A referee to whom this paper was submitted made the following statement: "The experiments on the non-removal of tellurium mirrors do not prove the absence of radicals, merely the absence of established kinds of radicals (CH_3CH_2). The experiment has nothing to say about unknown radicals such as CH═C═O, and it should not be interred that it does." However, we still believe that our experiment rules out acetylketene which should certainly give CH_3 as a decomposition product.

to eliminate[13] formula IB leaving only IIA and III as possibilities. Formula III appears to be unlikely because of thermodynamic considerations; naturally the principle of least motion applies only when the energy differences involved in two competing reactions are not very different.

A calculation of the heats of formation from the elements in their standard states, of ketene and allene and carbon dioxide gives

$$4C(s) + 2H_2 + O_2 \longrightarrow 2CH_2{=}C{=}O + 29.6 \text{ kcal.}$$
$$4C(s) + 2H_2 + O_2 \longrightarrow CH_2{=}C{=}CH_2 + CO_2 + 49.7 \text{ kcal.}$$

We would expect therefore that if diketene really has the formula III, it would decompose into allene and carbon dioxide. The complete absence of carbon dioxide together with the other results leads us to the conclusion that diketene is cyclobutanedione as represented by the formula IIA.

Experimental.—In order to determine whether the decomposition of diketene is molecular or free radical in nature, the effect of the intermediate decomposition products of diketene on tellurium mirrors was studied. The ketene dimer[14] was purified by distillation through a Vigreux column at 30 mm. and the middle fraction was used. The apparatus used was similar to that shown in Fig. 2 of a previous paper[11] except that two bulbs were connected at the inlet end, one containing the ketene dimer and one containing diacetyl. We used diacetyl because it readily produces radicals at the rather low temperature at which diketene decomposes and served as a test that our apparatus was working correctly and that the metallic mirrors were not being deactivated by either the diketene or its decomposition products. We used tellurium mirrors throughout this work and measured the pressure with a dibutyl phthalate manometer.

Our method was first to pump out the apparatus and bring the main furnace up to about 700°. By means of the smaller furnace, a tellurium mirror was placed near the exit end of the main furnace and the stopcock connected with the diketene container was opened. The temperature of the diketene was adjusted so that it exerted a pressure of a few mm. of dibutyl phthalate in the furnace. After a few minutes the diketene container was closed off and a test was made with diacetyl. The results are shown in Table I.

TABLE I

TEST FOR FREE RADICALS IN THE THERMAL DECOMPOSITION OF DIKETONE

	Diketene			Diacetyl (same mirror)	
Temp., °C.	Press., mm.	Exposure time, min.	Result	Press., mm.	Time of removal, sec.
700	0.45	6	No change	0.45	55
715	0.4	7	No change	0.4	25
750	0.5	5	Slight change	0.4	10

After having established that diketene decomposed molecularly, we built an apparatus shown in Fig. 1 to enable us to determine the products of decomposition. The bulb B, containing a known weight of dimer, could be connected through stopcock S to a regulated pressure source so that the liquid dimer could be forced through the very fine capillary tube T into the furnace F. This was electrically heated and fitted with a manometer and thermocouple well. The gases from the furnace passed into two traps B_2 and B_3 cooled with liquid air and these in turn led to a pumping system consisting of a steel mercury vapor pump and an ordinary rotatory pump in which the oil was replaced by glycerol. This pump was arranged so that any permanent gases would be collected over aqueous zinc sulfate. No permanent gases were found in any of the runs. Before a run was started, 50 cc. of absolute alcohol was placed in the vessel B_4, which was then cooled by liquid air and exhausted. On completion of a run, B_4 could be connected to the apparatus by means of the three-way stopcock S_2, and the volatile contents (ketene) of traps B_2 and B_3 distilled into it. The vessel B_4 was then warmed up

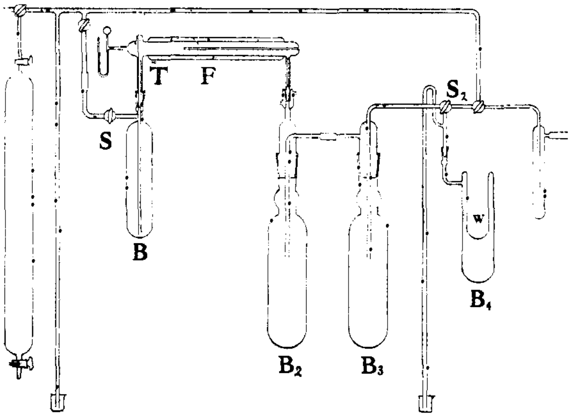

Fig. 1.

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[13] A referee to whom this paper was submitted made the following statement: "It seems an unwarranted assumption to state that IB must decompose to methylacetylene plus carbon dioxide, when it has been pointed out in reference 4d that the change of IB to IA is a very easy thermal one." We believe, however, that our experiments with tellurium mirrors had already eliminated formula IA, acetylketene.

[14] We wish to thank the Carbide & Carbon Co. for the gift of a sample.

from liquid air temperature by placing it in dry-ice. As the ketene and alcohol react the heat of the reaction may cause it to get out of control; if this occurs liquid air can be placed in the well W to avoid loss of products. The contents of the trap were distilled and the ethyl acetate content determined by saponification with standard alkali. Our method was checked by a number of blank runs in which we proved that the dimer does not react, under our conditions, with ethyl alcohol to form a volatile ester. In all experiments a weight balance was obtained by comparing the weight of dimer taken with the weight recovered plus the ketene formed. The two weights checked within experimental error and no methane, ethylene or carbon monoxide was found in any of the runs. The experimental results are shown in Table II.

TABLE II

THE THERMAL DECOMPOSITION OF DIKETENE

	I	II	III	IV
Moles diketene used	0.798	0.604	0.478	0.534
Moles diketene recovered	.750	.524	.323	.237
Moles ketene produced	.082	.140	.301	.568
Pressure ±1.0 mm.	9.0	8.7	10.0	9.7
Duration of run, seconds	1650	1280	1110	1340
Contact time, sec.	0.036	0.033	0.039	0.039
Temp., °C. ±8°	410	460	505	548
Decomposed, %	5.14	11.6	31.3	53.2

Summary

1. Pure liquid diketene has been examined by the method of aseptic distillation and found to consist of a single substance.

2. In the vapor state, diketene decomposes quantitatively into ketene. No substances such as methylacetylene, allene or carbon dioxide are formed even in traces. A test for free radicals, using tellurium mirrors, was negative.

3. On the basis of the principle of least motion, we have concluded that the cyclobutanedione formula is the only one that is consistent with our vapor state experiments.

4. Reactions of diketene in condensed systems do not seem to be conclusive in determining its structure. Possibly distortion of the highly resonating diketene molecules by the microscopic fields of the solvent may actually change the structure from that present in the gas phase.

5. The high dipole moment, 3.53, of gaseous diketene appears to rule out the cyclobutanedione formula in spite of the evidence from our vapor state experiments.

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[CONTRIBUTION FROM THE DIVISIONS OF ANIMAL HUSBANDRY AND CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Absorption of Oxygen by Glutathione in Alkaline Solutions. II. Kinetics of the Reaction at *p*H 13

BY M. B. YOUNG AND H. A. YOUNG

It has been shown[1] that, in the presence of a copper salt as catalyst and at a *p*H of 13, the quantity of oxygen absorbed in the reaction between glutathione and oxygen indicates that the product formed is primarily the salt of the sulfinic acid. A continuation of the discussion of the factors influencing the rate of this reaction and the presentation of the rate law and a possible mechanism follow.

Experimental

The experiments were carried out in the Warburg apparatus at 37°. The procedure was similar to that of previous experiments[1] except that it proved more convenient to place 4 cc. of the sodium hydroxide–copper sulfate mixture in the main compartment of the Warburg flask and 1 cc. of glutathione solution in the side arm. Upon mixing, the fine suspension of copper hydroxide dissolved immediately in the glutathione. As before, the oxygen absorption was measured at constant volume. Since only about 5% of the total available oxygen was used during the course of any one experiment, the oxygen pressure remained essentially constant.

The reaction was studied at *p*H 13 to 13.3 with glutathione concentration varying from 0.00110 to 0.00440 molar, copper sulfate concentration 0 to 20×10^{-6} molar and oxygen pressure 0.2 to 1.0 atm.

Experimental Results

The type of absorption curve is shown in Fig. 1. In all cases, except at $CuSO_4 = 0$ molar, the

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(1) M. B. Young and H. A. Young, THIS JOURNAL, 64, 2282 (1942).