Mechanism of Thermolysis of Diketene in the Gas Phase

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The mechanism of diketene thermolysis is investigated by isotopic double-labeling experiments and the thermolysis of cyclobutane-1,3-dione. The results of these experiments suggest that the thermolysis reaction is concerted. An activation energy of 50 kcal/mol was obtained for the thermolysis of diketene. This leads to an estimate of 31 kcal/mol as an activation energy for the dimerization of ketene in the gas phase. The heats of combustion (ΔH_c) and sublimation of cyclobutane-1,3-dione were measured and values of -450.7 ± 0.5 and 17.6 ± 0.5 kcal/mol were calculated. A comparison of $\Delta H_c^{25}(g)$ for diketene and cyclobutane-1,3-dione suggests that both compounds are thermodynamically accessible from dimerization of ketene in the gas phase.

The dimerization reaction of ketenes has been an area of considerable interest for over half a century. Initial attention was focused on the structure of ketene dimers[2,3] and more recent attention has been concerned with the mechanism of the reaction.[4,5] Orbital symmetry considerations of Woodward and Hoffman have stimulated the most recent interest in these $(2 + 2)$ cycloaddition reactions.[6]

We became interested in the dimerization of ketene to diketene for a variety of reasons. First, despite the commercial importance of both ketene and diketene, very little concerning the mechanism of this reaction has been reported; the work of Rice and Greenberg appears to be the only mechanistic study reported which relates to this reaction.[4] In addition, regiospecific head-to-tail dimerization of ketene is anomalous in comparison to the cyclobutane-1,3-diones which are obtained in the dimerization reaction of other ketoketenes.[2] Finally we have recently reported some calculations using a semiempirical molecular orbital method to calculate potential energy surfaces for ketene dimerization.[7] The results of these calculations suggested the concerted ($_\pi 2_s + _\pi 2_s$) cycloaddition pathway to be preferred. The course of this reaction was governed by both electronic factors as well as by nuclear repulsion. In addition, a barrier of only 6 kcal (using configuration interaction) was calculated for the dimerization reaction. This report summarizes our efforts to obtain experimental verification of these calculations.

Rice and Greenberg found an activation energy of only 11 kcal for the rate of disappearance of ketene in acetone. The rough parallelism between the rate of reaction and the dielectric constant of the solvent has been interpreted by some workers as evidence of an ionic mechanism.[2a] Similar experimental results have been obtained for the dimerization of dimethylketene although the results in this case were interpreted to involve a cycloaddition reaction with unequal bond formation and partial charge separation.[5a] To avoid the ambiguities brought about by the solvent, we decided to examine the dimerization reaction in the gas phase. However, as described in the Experimental Section, the dimerization of ketene at pressures below 1 atm could not be accomplished.
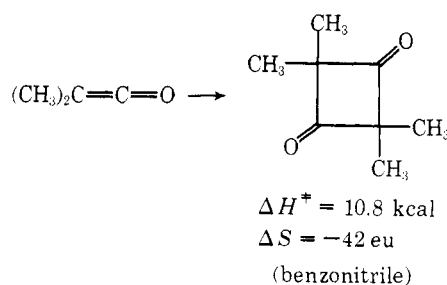
The thermolysis of diketene in a flow system at 500 °C has been reported to produce ketene quantitatively.[3a] Failing to achieve gas-phase dimerization of ketene, the thermolysis of diketene was investigated next. We were specifically interested in determining whether this thermolysis reaction was a homogeneous unimolecular process, and if so, in measuring the activation parameters for this process. To the extent that it is possible, we were also interested in determining whether this reaction is concerted as suggested by our calculations.

The thermolysis of diketene has recently been shown to be a homogeneous unimolecular process by demonstrating that the intermolecular secondary deuterium isotope effect is pressure dependent, decreasing with decreasing pressure. In addition, a kinetic isotope effect k_H/k_D of 1.04 (140 mm, 420 °C) was obtained, suggesting that carbon–carbon bond
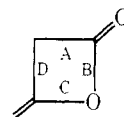
breaking is a rate-determining factor in the thermolysis of diketene.[9] The sole product of the pyrolysis is ketene, and this suggests that bonds B or D are broken sequentially or concertedly. The rapid and reversible formation of diradical intermediates involving rate-determining bond cleavage at A, B, or C was effectively eliminated on the basis of the following experiment.
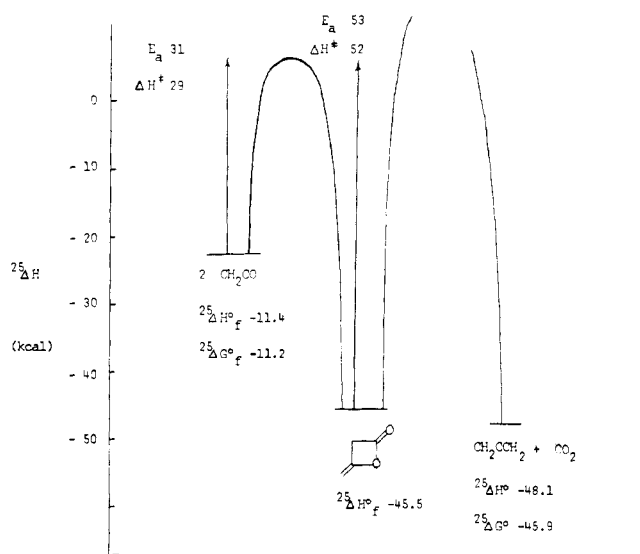

$$(CH_3)_2C = C = O \longrightarrow$$

$$\Delta H^{\ddagger} = 10.8 \text{ kcal}$$
$$\Delta S = -42 \text{ eu}$$

(benzonitrile)

Figure 1. Enthalpy differences between diketene and possible thermolysis products.[20]

Table I. Heats of Combustion of Diketene and Cyclobutane-1,3-dione

	Diketene[a]		Cyclobutane-1,3-dione[b]
ΔH_c^{25}	−457.11	ΔH_c^{25}(s)	−450.7 ± 0.5
ΔH_v^{25}	10.25	ΔH_s^{25}	+17.6 ± 0.5
ΔH_c^{25}(g)	−467.36	ΔH_c^{25}(g)	−468.3 ± 1.0

[a] M. Mansson. Y. Nakasi, and S. Sunner, *Acta Chem. Scand.,* **22,** 171 (1968). [b] Cyclobutane-1,3-dione exists as the dione tautomer in the solid phase and in solvents of moderate to low polarity.[19] Similar behavior would be expected in the gas phase.

Diketene was prepared from a mixture of ^{18}O-labeled ketene and D_2 labeled ketene. Approximately equal amounts of ketene-[18]O (26.6% [18]O) and ketene-d_2 (98.5%) were allowed to dimerize in a sealed tube. The diketene isolated was pyrolyzed at 380 °C in a nitrogen stream. Mass analysis of the product did not reveal any ketene doubly labeled with [18]O and deuterium, thus ruling out all of the scrambling processes summarized in the equations below, *both in the dimerization and subsequent thermolysis reactions.*
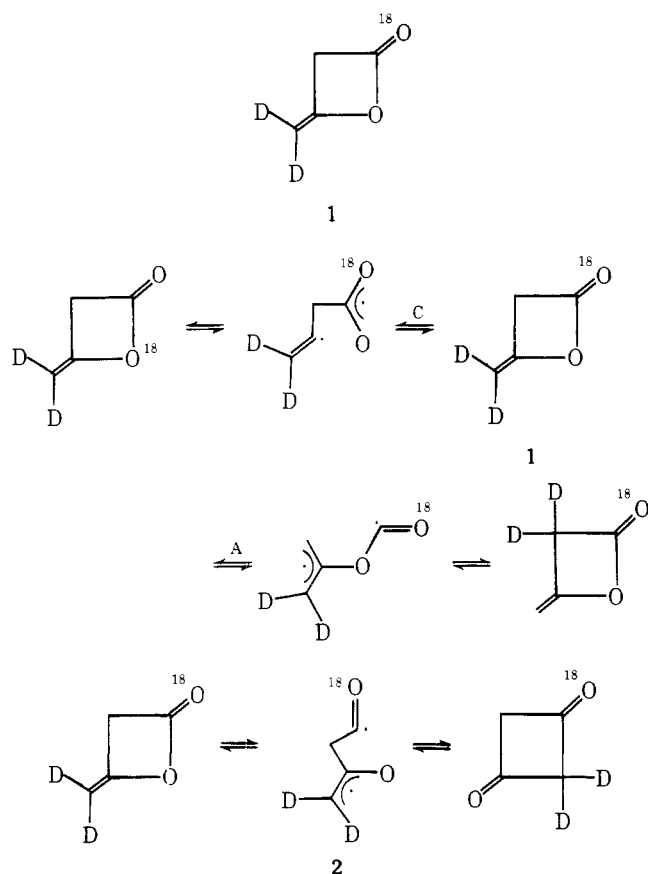
The labeling experiment mentioned above does not conclusively eliminate rapid cleavage of bond B as a possibility. However, it does require that a substantial barrier be present to prevent the isomerization to cyclobutane-1,3-dione. Evidence that cyclobutane-1,3-dione is thermodynamically accessable from diketene was obtained by determining the heat of combustion of cyclobutane-1,3-dione at 25 °C. The results are listed in Table I along with the known heats of combustion of diketene. The results within experimental error indicate similar ground-state stabilities.

Thermolysis of cyclobutane-1,3-dione in a flow system using a nitrogen carrier (140 mm) at 400 °C affords a 53% yield of ketene. No diketene could be detected. Thermolysis of diketene under similar conditions affords ketene in 83%, the
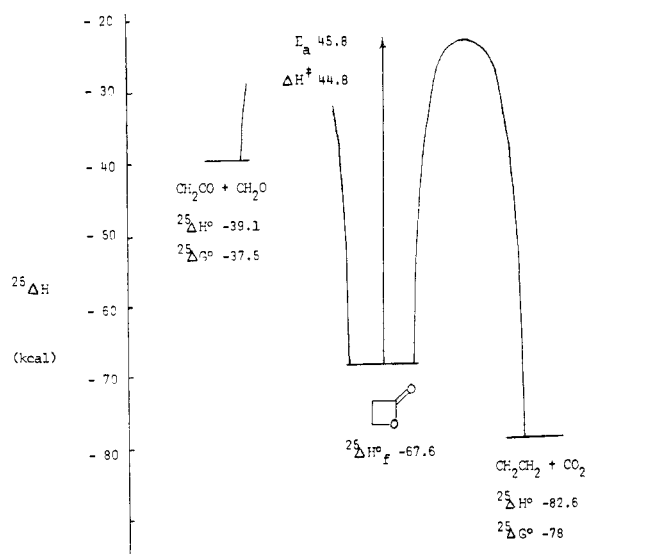

Figure 2. Enthalpy differences between propiolactone and possible thermolysis products.[20,24]

remainder being starting material. Failure to observe isomerization of diketene and cyclobutane-1,3-dione in either direction leads to the conclusion that there is no common intermediate in the thermolysis of cyclobutane-1,3-dione and diketene. Thus either both reactions are concerted or one is concerted and the other occurs in a stepwise fashion through a diradical intermediate, **2,** which is not capable of surmounting the barrier to lead to isomerization. The simplest explanation is that both reactions are concerted.[17]

If it is assumed that the entropies of both isomers are comparable ($\Delta S°$), the similar ground-state stabilities ($\Delta G°$) and yields of ketene at 400 °C suggest that the barriers to thermolysis of both, $\Delta G^{\ddagger}$, must also be similar in magnitude. This leads to an interesting conclusion regarding the regioselectivity of the gas-phase dimerization of ketene (presumable at pressures above 1 atm). Both diketene and cyclobutane-1,3-dione should be accessible from direct dimerization of ketene, similar to what is observed in the low-temperature (liquid phase) dimerization of aldoketenes.[12]

The activation energy for thermolysis of diketene was obtained in a flow system by competitive co-thermolysis of acetic-d_6 anhydride and diketene at 294–417 °C using N_2 (42, 142 mm) as a carrier gas. The results are given in Table III. An activation energy of approximately 50 kcal was obtained. (For further discussion see Experimental Section.) Combining this with the heats of formation of ketene and diketene (Table I) leads to an estimate of the activation enthalpy for the dimerization reaction in the gas phase of approximately 30 kcal. This number is considerably larger than the 6-kcal barrier calculated for this reaction.[7]

It is immediately evident from examination of Figure 1 that the regiospecific thermolysis of diketene to ketene must be the result of kinetic control. Even at 350 °C, the formation of allene and carbon dioxide is thermodynamically preferred by 21 kcal/mol ($\Delta\Delta G°$). The thermolysis of β-propiolactone which cleaves thermally to carbon dioxide and ethylene provides an interesting comparison to the diketene thermolysis (Figure 2). The free-energy difference between the products resulting from thermodynamic control and kinetic control, $\Delta\Delta G°$, in β-propiolactone (40.5 kcal/mol) is larger than the similar $\Delta\Delta G°$ for diketene (23.5 kcal/mol) by 17 kcal at 25 °C. This additional difference in free energy is presumably the cause for the change in the orientation of cleavage. It would be interesting to determine whether this is also accompanied by a change in mechanism.

Table II. Calculation of the ^{18}O, d Label in Diketene

A. Distribution of Label in Reacting Ketenes[a]

Fraction of ketene (K)	[diketene-$^{16}O_2$/total diketene]$^{1/2}$	$[0.09]^{1/2}$	0.3
Fraction of ketene-^{18}O (K_{18})	[ketene-^{18}O/ketene-^{16}O] $\times K$	$[0.266/(1 - 0.266)][0.3]$	0.109
Fraction of ketene-d_2 (K_2)	$[1 - K - K_{18}]$	$[1 - 0.409]$	0.509

B. Distribution of Label in Diketene[b]

			Calcd	Found
m/e 74	Diketene	$[K]^2$		0.09
m/e 76	Diketene-^{18}O	$2[K_{18}][K]$	0.065	0.41
	Diketene-d_2	$2[K_2][K]$	0.355	
m/e 78	Diketene-$^{18}O_2$	$[K_{18}]^2$	0.011	0.50
	Diketene-$^{18}O,d_2$	$2[K_{18}][K_2]$	0.129	
	Diketene-d_4	$[K_2]^2$	0.345	

[a] Based on the unlabeled diketene content and ^{18}O, D_2 content in ketene: ketene-^{18}O, ^{18}O content, 26.6%; ketene-d_2, deuterium content, 98%; mass spectrum of diketene-^{18}O, -d_2, m/e 74, 9.0; 76, 41.2; 78, 49.7. [b] Assuming a statistical distribution with no isotope effect.

Table III. Co-thermolysis of Acetic-d_6 Anhydride (AA) with Diketene (DK)[a]

Run	Temp, °C	Total mmol of reactants	Fraction reacted	Initial ratio of reactants DK^0/AA^0	mmol of ketenes isolated[b] (m/e 74/76)	Ketene/ ketene-d_2	k_{AA}/k_{DK}	K_{DK}[b]
1	760	0.431	1.0	2.78	0.750	5.56		
2	690	0.398	0.80	2.78	0.556	4.78	1.6	2.2
3	654	0.403	0.35	2.78	0.243	1.96	4.6	0.2
4	621	0.438	0.12	2.78	0.088	0.50	15.2	1.7×10^{-2}
5	597	0.449	0.05	2.78	0.039	0.28	22.7	4.0×10^{-3}
6	567	0.444	0.012	2.78	0.0097	0.23	24.9	8.6×10^{-4}
7	727	0.706	1.0	2.27	0.706	4.54		
8	664	0.358	0.72	2.27	0.437	3.75	1.54	2.5
9	652	0.336	0.51	2.27	0.296	2.88	3.01	0.92
10	618	0.361	0.20	2.27	0.122	0.750	9.05	7.71×10^{-2}
11	595	0.367	0.097	2.27	0.0602	0.321	17.9	1.41×10^{-2}
12	569	0.264	0.026	2.27	0.0117	0.206	23.8	3.04×10^{-3}

[a] Conditions used in thermolysis: (runs 1–6) carrier gas N_2 (42 ± 1 mm), flow (measured at the exhaust of pump) 0.27 ± 0.02 mL/s; (runs 7–12) carrier gas N_2 (142 ± 1 mm), flow 0.34 ± 0.02 mL/s. [b] Ketene analyzed as methyl acetate.

The thermolysis of diketene to the kinetically controlled product, ketene, in a concerted manner is a good indication that orbital topology does play an important factor in the reaction. Yet to be determined is whether the reaction is best described as a $(_\pi 2_a + _\pi 2_s)$ or $(_\pi 2_s + _\pi 2_s)$ cycloaddition.

Experimental Section

Thermolysis of Ketene and Diketene in a Static System. The experiments performed in a static system were performed in an untreated 3 L Pyrex bulb suspended in an air bath maintained at ±5 °C. The products were identified by comparison of their infrared spectra to authentic samples. During the course of these studies a carbonaceous material was deposited on the surface of the bulb. In addition a tarry liquid was also formed from which an undetermined amount of 4-acetoxy-6-methyl-2-pyrone could be isolated. Typically, several hundred millimeters of ketene were pyrolyzed at 250 °C for 24 h. The products were condensed in liquid nitrogen and analyzed. In addition to the unreacted ketene, acetic anhydride, and acetic acid which were transferred to the trap, a white crystalline material was deposited during evacuation along the cooler portions of the tube connecting the 3-L flask. This material was identified as 4-acetoxy-6-methyl-2-pyrone: mp 45–46 °C; λ_{max} (KBr) 5.55, 5.65, 6.0, 6.2, 6.3, and 8.3 μm; NMR (CDCl$_3$, Me$_4$Si) 2.28, 2.32 (6 H), 6.0, 6.05 ppm (1.96 H); m/e 168; calcd for C$_8$H$_8$O$_4$, 168.[10] The acetic acid, acetic anhydride are most likely the result of surface promoted processes leading to the carbonaceous deposit and release of water. The thermal homogeneous decomposition of ketene at higher temperatures is known to give mixtures of gases including carbon monoxide, ethylene, and methane.[8]

Preparation of 4-Acetoxy-6-methyl-2-pyrone. 4-Hydroxy-6-methyl-2-pyrone (3.32 g), acetic anhydride (4 mL), and a few drops of sulfuric acid were warmed to 75 °C for 1 h. Upon cooling, ether was added and the solution was washed with water. Evaporation of the ether afforded a solid (2.41 g) which was sublimed and then recrystallized from cyclohexane–ethyl acetate (2:1) (1.44 g), mp 45–6 °C, the infrared and NMR spectra were identical to that obtained above. There was no depression of the mp upon admixture.

Preparation of Ketene-^{18}O. Acetone-^{18}O was prepared by hydrolyzing 2-methoxypropene[13] (22.6 mmol) with H$_2$^{18}O (22.6 mmol) and a crystal of p-toluenesulfonic acid (hydrate). After stirring for approximately 2 h the methanol was derivatized with phenyl isocyanate (2.74 g, 2.3 mmol). The mixture was allowed to stand overnight at room temperature. After cooling to −20 °C, the acetone was removed by bulb-to-bulb distillation: yield 17.6 mmol; 78.5%.

Ketene-^{18}O was prepared by the pyrolysis of acetone under conditions of low conversion by passing the acetone through a heated quartz tube at 500 °C using nitrogen gas (1 atm) as a carrier. After three passes, 5.04 mmol of ketene-^{18}O was obtained. Ketene-^{18}O (.59 mmol) was converted to methyl acetate and analyzed by mass spectrometry for the ^{18}O content. Analysis of the parents indicated that 26.6% of the ketene was labeled with ^{18}O.

Codimerization of Ketene-^{18}O with Ketene-d_2. Ketene-d_2 (∼99.5% isotopic purity, prepared from thermolysis of acetic-d_6 anhydride (Aldrich Chem. Co.) in an evacuated hot tube (500 °C, 4.78 mmol)) and ketene-^{18}O (4.808 mmol) were combined and sealed in a glass tube. The tube was cooled to −78 °C and then allowed to warm slowly to 0 °C. The tube was opened, the contents were transferred, and the diketene was isolated by bulb-to-bulb distillation on a vacuum line. The diketene had the following analysis: m/e 74 (9.0), 76 (41.2), 78 (49.7). Since the ketene-^{18}O was known to be impure (methane and other impurities), the composition of the reacting ketenes was determined by using the isotopic distribution of both diketene and ketene-^{18}O (26.6% ketene-^{18}O). This in turn was then used to calculate the isotopic composition of the diketenes. This is shown in Table II. The calculated results are very close to the experimental values. Of all the isotopically labeled diketenes, only diketene-$^{18}O,d_2$,
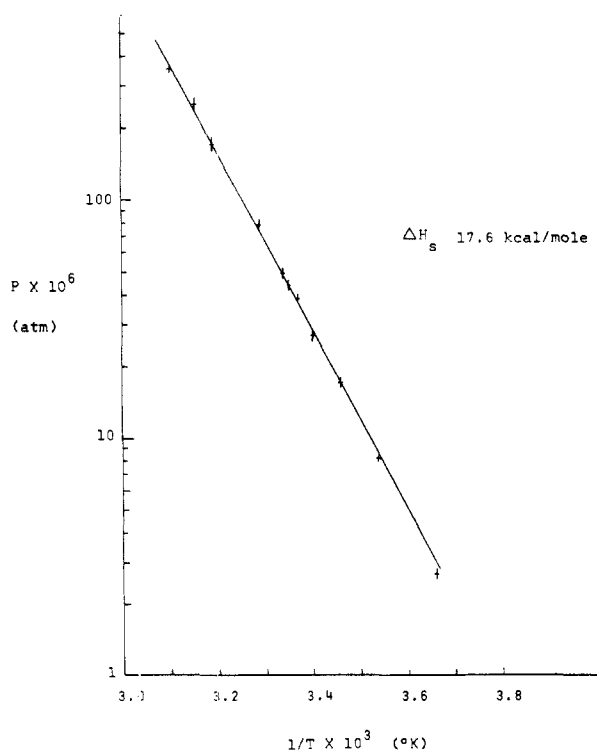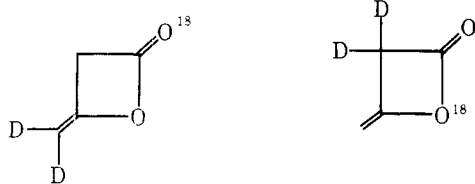
Figure 3. Vapor pressure–temperature relationship for cyclobutane-1,3-dione. Each entry determined in triplicate.

amounting to 12.9% of the total, is of interest. This material consists of a mixture of the following:

Thermolysis of Diketenes-$^{18}O,d_2$. The diketenes (0.44 mmol) were thermolyzed at 380 °C. The ketene and diketene were trapped and separated as previously described.[9] The ketene (0.632 mmol, 72%) was derivatized with methanol and analyzed. The following results were obtained: m/e 74 (28.89), 76 (71.02), 78 (0.08). Calcd for no exchange and ignoring isotope effects: m/e 74 (30), 76 (70). Calcd assuming complete scrambling, no isotope effects: m/e 74 (30), 76 (63.6), 78 (6.5).

As an upper limit, the amount of scrambling which can be accounted for by the experimental data is 1.2% (0.08/6.5). Mass analysis of the diketene at m/e 42, 44, 46 (ketene fragmet) of both starting material and residue from thermolysis (0.1 mmol) did not reveal any changes in the m/e 44/46 ratio. Thermolysis of diketene to 90% completion gave essentially the same results.

Heat of Combustion of Cyclobutane-1,3-dione. The heats of combustion were determined in a Parr Oxygen Bomb calorimeter. The energy equivalent of the calorimeter was determined by combustion of benzoic acid (AR grade). The reagents used were pelleted and fuse wire, 2.3 cal/cm. was purchased from Parr Instrument Co., Molene, Ill. Calculations were according to Manual 130 "Oxygen Bomb Calorimetry and Combustion Methods", Parr Instrument Co. The results were corrected for formation of nitric acid and for the heat of combustion of the fuse.

The heat of sublimation of cyclobutane-1,3-dione was determined by measuring vapor pressure as a function of temperature by a method previously described.[15] Concentrations of cyclobutane-1,3-dione were determined by ultraviolet spectroscopy (ethanol). The results of these measurements are given in Figure 3. The combined results of both the heats of combustion and sublimation are given in Table I. Errors reported are average deviations.

Measurement of the Activation Energy for Thermolysis of Diketene. The activation energy for thermolysis of diketene (DK) was determined by competition with the thermolysis of acetic-d_6 anhydride (AA) in flow system. The temperature dependence on the

rate of thermolysis of acetic anhydride is given by $k = 10 \exp(-32194/TR)$ s^{-1} over the temperature range 197–370 °C.[16] No correction for the kinetic isotope effect was included. In the calculation of the activation energy of diketene, it was necessary to extrapolate to 417 °C. The results of these experiments are given in Table III. The products, ketene (k) and ketene-d_2 (k$_{d_2}$), were derivatized with methanol and analyzed as methyl acetate. Although a temperature gradient of about 25 °C existed in the tube, the temperature at each point of the tube was maintained to ±2 °C. The rate constants for thermolysis of diketene were calculated from the following equation.

$$\frac{\ln\left[DK°/(DK° - (1/2)K)\right]}{\ln\left[AA°/(AA° - K_{d_2})\right]} = \frac{k_{DK}}{k_{AA}}$$

The initial concentrations of reactants were determined by analysis of the amount and composition of the ketenes obtained from complete thermolysis (runs 1 and 7).

Competitive thermolyses of acetic-d_6 anhydride with diketene were performed at two pressures, approximately 40 and 140 mm. A plot of $\ln k$ vs. y_I gave rise to two sets of data from which activation energies of 50.2 and 53 kcal/mol were calculated (correlation coefficient: 0.9924, 0.996, respectively). *Differences in the intercepts are probably due to the fact that even at 40 mm, diketene is still in the falloff region.* Although activation energies in the low-pressure region are known to decrease anywhere from 5 to 10 kcal/mol, the differences in this instance should probably be attributed to experimental error.[22,23]

Cyclobutane-1,3-dione. Cyclobutane-1,3-dione was prepared according to the procedure of Wasserman-Piper and Dehmlow.[19] We have found that in the preparation of 3-ethoxy-2-cyclobutenone, a more convenient manner of purifying this material is to molecularly distill the dark liquid at low temperatures. The cyclobutenone obtained on the cold finger (−10 °C) was obtained in approximately 50–70% yield; mp 25 °C (lit. 26–27.5 °C). Hydrolysis as reported gave cyclobutane-1,3-dione, mp 116–120 °C (lit. 119–120 °C).

Thermolysis of Cyclobutane-1,3-dione. Thermolysis experiments with cyclobutane-1,3-dione were performed in the same flow apparatus as the diketene thermolysis at 140 mm (N$_2$). The vapor pressure of cyclobutane-1,3-dione is quite low at room temperature (~20 μm). It is improbable that the thermolysis of cyclobutane-1,3-dione occurs by anything other than a first-order process. Consistent with this conclusion was the observation that the fractional conversion to ketene was not affected when the pot temperature was increased above room temperature (~35 °C) and the time required for transfer *was significantly reduced.* If the thermolysis of cyclobutane-1,3-dione was conducted in the absence of a carrier gas, considerably less ketene was obtained and significant amounts of decomposition on the surface of the quartz tube were observed. No unreacted starting material was recovered nor was any diketene detected in both the high- and low-pressure experiments. The effect of carrier gas on the decomposition of cyclobutane-1,3-dione suggests that the thermolysis reaction to give ketene is a homogeneous process. The yield of ketene may be considerably higher at these temperatures in the absence of the surface-promoted process. Characterization of the tarry residue or other products was not attempted. Characterization of the products was conducted by infrared spectroscopy in the gas phase.

Registry No.—Cyclobutane-1,3-dione, 15506-53-3; propiolactone, 57-57-8; diketene, 674-82-8; 2-methyl-1-propen-1-one, 598-26-5; ketene, 463-51-4; 4-acetoxy-6-methyl-2-pyrone, 22073-80-9; 4-hydroxy-6-methyl-2-pyrone, 675-10-5.

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(10) We currently believe that gas-phase polymerization of ketene (including dimerization) will occur at ketene pressures in excess of 1 atm. 4-Acetoxy-6-methyl-2-pyrone is probably formed from low-level concentrations of diketene present. A possible mechanism for its formation is shown below. This mechanism is similar to the one postulated for the dimerization of diketene to dehydroacetic acid.
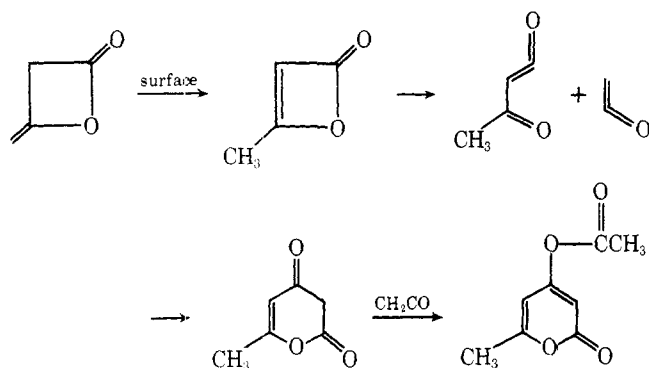
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(17) We specifically ignored a potential energy surface such as shown below for the thermolysis of diketene. The small size of the molecule (ten atoms) decreases the likelihood that the system could sustain an intermediate in such a situation. The large internal energy necessary to overcome the initial

barrier would most likely transform the intermediate directly to product.[18] Should the lifetime of intermediate be increased by collisional deactivation, scrambling of label would be possible by way of the following 1,3-dioxetane intermediate providing no significant barrier separates the diradical and the dioxetane. Our experimental results are also incapable of discriminating between the concerted process and a situation in which transition state and intermediate are essentially isoergic (as calculated for tetramethylene[25]) and lifetimes are short compared to bond rotations.
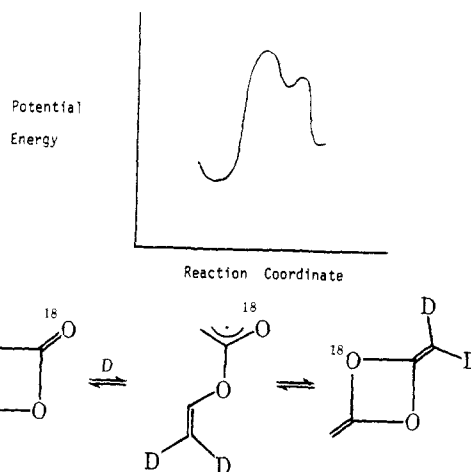
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Bridged Polycyclic Compounds. 86. Multiple Mechanisms in the Reactions of Some Bridged Alcohols with Triphenylphosphine and Carbon Tetrachloride[1]

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Reactions of several isomeric benzobicyclooctadienyl alcohols and dibenzobicyclononatrienyl alcohols with triphenylphosphine–carbon tetrachloride reagent demonstrate that these alcohol to chloride transformations are much more complex than originally proposed. Products from these and from deuterium-labeled alcohols show that direct displacements, Wagner–Meerwein rearrangement displacements, and allylic rearrangement displacements all occur. The reactions are rationalized as involving competitions between S_N2, S_N1, and S_Ni' or S_N2' processes.

Since the discovery[2] of the use of triarylphosphine dihalides in the ready conversion of alcohols to alkyl halides without rearrangement,[2,3b] and with clean inversion of configuration in the reaction of menthol to give neomenthyl halides, there has been considerable use of these reagents.[3] A mixture of triphenylphosphine and carbon tetrachloride was found[4] to cause transformations analogous to triphenylphosphine

dichloride, under rather mild conditions. Although the initial papers[2] describing the use of the dichloride reported clean stereochemistry and thus the intervention of a direct displacement mechanism in the attack of chloride ion on the ROPPh₃Cl intermediate,[2,3c] later work suggested alternative mechanistic possibilities. Thus, the lack of inversion (and loss of optical activity) in treatment[3e] of (+)-*exo*-norborneol with