Kinetics and Mechanism of the Cycloaddition of Diphenylketene and Dihydropyran[1]

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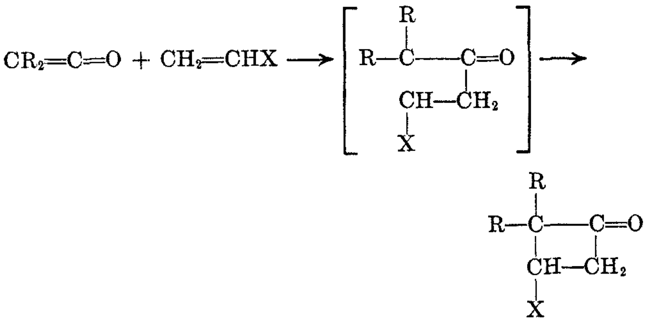
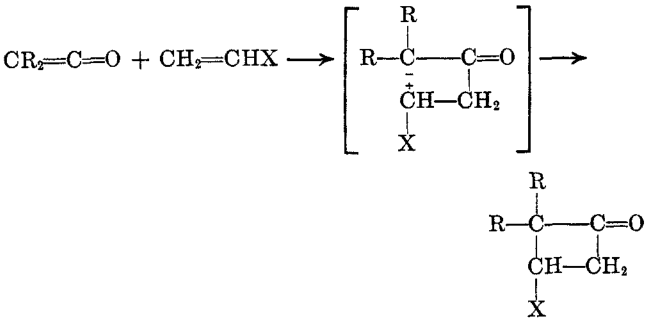
The question of whether the cycloaddition of ketenes and olefinic compounds proceeds by a diradical, ionic, or concerted mechanism has been investigated. The kinetics of the cycloaddition of diphenylketene and dihydropyran in THF were studied at various temperatures. The reaction was found to be second order with $\Delta H^* = 9.0 \pm 0.1$ kcal/mole and $\Delta S^* = -43.5$ eu. The rates of this reaction were measured in several solvents and the solvent effect was found to be quite small. These results are discussed and interpreted to suggest a near-concerted mechanism with some charge separation in the transition state.

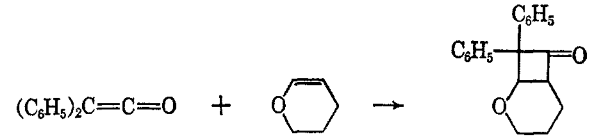
There are numerous examples of cycloaddition reactions of ketenes and olefins to form substituted cyclobutanones reported in the literature. However, no work can be found which concerns the kinetics and mechanism of this general reaction of ketenes. Roberts has discussed two plausible mechanisms which involve a diradical intermediate and a zwitterionic species as shown below.[3]





The ease of cycloaddition of ketenes to the strongly nucleophilic enamines supports the ionic mechanism.[4] A considerable solvent effect has been reported for the cycloaddition of dimethylketene and cyclopentadiene which certainly indicates an ionic process.[5] Isotope effect studies on the cycloaddition of diphenylketene and cyclohexene indicate that the transition state is not symmetrical (*i.e.*, the bonds are not equally formed).[6] It is the purpose of this paper to present kinetic evidence which might be used to further elucidate the true mechanism for the cycloaddition of ketenes.

The cycloaddition of diphenylketene and dihydropyran to produce 8,8-diphenyl-2-oxabicyclo[4.0.2]octan-7-one was selected for study.[7] This reaction is convenient for kinetic study since it proceeds cleanly and in high yield at moderate rates. Also, diphenylketene does not undergo dimerization at the temperature range studied in contrast to many other ketenes.



The rate of disappearance of dihydropyran was followed by vpc. The yield of cycloadduct was consistently 85-90%. The rates were followed to about 75% completion at which point scattering of data occurred. The rates of reaction in THF were determined at temperatures of 30, 40, 50, and 60°. A treatment of these rate data indicated that the reaction was first order in diphenylketene and first order in dihydropyran. These data are presented in Figure 1. The second-order rate constants at the various temperatures are given in Table I. The heat of activation (ΔH^*) for the reaction was found to be 9.1 ± 0.1 kcal/mole from an Eyring plot as shown in Figure 2. This value was obtained by least-squares regression analyses.

TABLE I
SECOND-ORDER RATE CONSTANTS

Temp, °C	$k \times 10^5$ l. mole^{-1} sec^{-1}
30	1.65 ± 0.07
40	2.35 ± 0.05
50	4.55 ± 0.14
60	6.62 ± 0.24

The entropy of activation (ΔS^*) of -43.5 eu was calculated using the average rate constant 2.35×10^{-5} l./mole sec at 40° and ΔH^* of 9.1 kcal/mole.

The reaction was also run employing cumene as the solvent. This material is an excellent hydrogen donor and dicumyl, the main reaction product of the cumyl radicals, if produced, is conveniently handled. However, this experiment yielded no dicumyl, but the cycloadduct was isolated in 93% yield.

The rates of reaction of diphenylketene and dihydropyran were determined in several different solvents. These rates are recorded in Table II.

Results and Discussion

Dihydropyran would be expected to give the same substituted cyclobutanone regardless of whether an

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[1] Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[2] To whom communications concerning this paper should be addressed.

[3] J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 26 (1962).

[4] R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963).

[5] J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *ibid.*, **30**, 4175 (1965).

[6] T. J. Katz and R. Dessau, *J. Am. Chem. Soc.*, **85**, 2172 (1963).

[7] C. D. Hurd and R. D. Kimbrough, Jr., *ibid.*, **82**, 1373 (1960).

Table II

The Effect of Solvent on the Second-Order Rate Constants for the Reaction of Diphenylketene and Dihydropyran at 40°

Solvent	$k \times 10^5$ l. mole^{-1} sec^{-1}
Toluene	3.42 ± 0.04
THF	2.35 ± 0.05
n-Butyronitrile	1.56 ± 0.15
DMF	0.94 ± 0.05

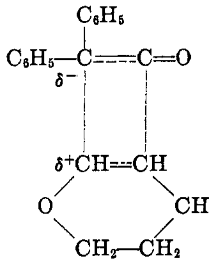
ionic, a concerted with charge separation, or diradical mechanism was operative. This is due to the fact that the olefin is nucleophilic with the alkoxy substituent being capable of stabilizing either the diradical or polar intermediate or a transition state with charge separation.

The large negative activation entropy reflects a high degree of orientation in the transition state; *e.g.*, the steric configuration must be highly ordered.

The solvent effect on the second-order rate constant is quite small as shown in Table II. Since the rate increases with decreasing polarity of the solvent, the transition state is probably only weakly polarized and the kinetic advantages of a polar solvent are thus obscured. Evidently the transition state is less polar than the reactants. This would seem to indicate a highly ordered transition state with relatively little charge separation.

If a diradical intermediate were produced in this reaction, the utilization of a good hydrogen donor as solvent, such as cumene, might be expected to yield some coupled product unless the diradical were extremely short lived. The fact that no dicumyl could be detected does not completely eliminate the diradical mechanism but is suggestive of some other process.

Roberts has suggested the use of electrophilic olefins for cycloaddition study.[3] The orientation of products would be expected to be different depending on the type of mechanism involved. To our knowledge, no cycloadducts involving electrophilic olefins have been reported, the problem being that diphenyl- and dialkylketenes undergo cycloaddition with unactivated olefins with difficulty and simply will not form cycloadducts with electrophilic olefins under the normal conditions.[5,8] This in itself is very indicative of a polar process since, of the several possible polar intermediate structures that can be written, none would appear to be stabilized when an electron-withdrawing substituent is attached to the olefin. Contrasting this to the following transition state, it seems very reasonable that this cycloaddition reaction proceeds by a near-concerted process whereby electron-releasing substituents in the olefin stabilize the charge separation.



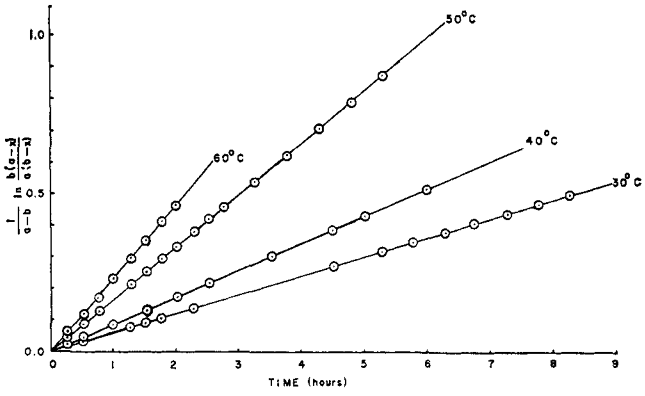


Figure 1.

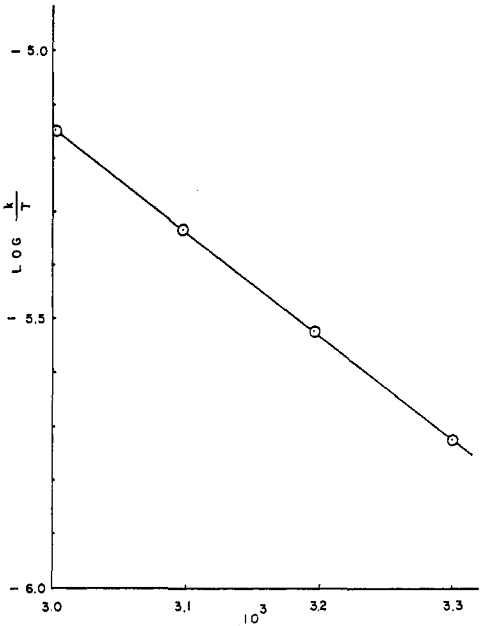


Figure 2.

In conclusion, the kinetic data described make a biradical intermediate highly improbable. The small solvent effects suggest that a discrete dipolar intermediate is not formed. Our interpretation of the data leads to the conclusion that this is a one-step, concerted process with some charge separation in the transition state. The kinetic results, low activation energy, high negative entropy of activation, and small solvent effects, correspond to the kinetic data reported for the Diels–Alder reaction.[9] Consequently, it would appear that for this system, the same type of mechanism is involved as for many Diels–Alder reactions. As suggested in a recent review, virtually all Diels–Alder reactions may be satisfactorily interpreted as proceeding by a multicenter mechanism analogous to what we have described above for our system.

It was indicated earlier that there is some evidence in the literature which suggests that at least some cycloadditions of ketenes proceed by a truly ionic process. Also, we have recently reported on the cycloaddition of methylchloroketene and cyclopentadiene and presented some evidence which suggests a stepwise process for this system.[10] Therefore, a general mecha-

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(8) W. T. Brady and O. Hurst, unpublished results. Numerous attempts to prepare a cycloadduct of diphenylketene and acrylonitrile were unsuccessful.

(9) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964.

(10) W. T. Brady and B. M. Holifield, *Tetrahedron Letters*, in press.

nism for all ketene cycloadditions is probably not likely but rather the process is dependent upon the substrates involved.

Experimental Section

Diphenylketene was prepared by the dehydrochlorination of diphenylacetyl chloride with triethylamine.[11,12] The ketene was vacuum distilled prior to each kinetic run. Benzene, heptane, cumene, and THF were distilled from lithium aluminum hydride under a nitrogen atmosphere through a 30-plate Oldershaw column.

Apparatus.—A constant-temperature water bath was heated with an immersion heating element coupled to a Fisher proportional temperature controller that afforded a temperature control of ±0.02°. The rate of disappearance of dihydropyran was followed by vpc. An Aerograph AP-40 operating with a thermal conductivity detector was used with 10 ft × 0.25 in. columns packed with 15% Ucon and 2% Oronite on 30–60 mesh white Chromosorb. An oven temperature of 95° was employed. *n*-Heptane was used as an internal standard. Least-squares rate constants and activation parameters were calculated on an IBM 1620 computer.

Cycloaddition in Cumene.—To a solution of 4.57 g (0.0645 mole) of dihydropyran, 12 ml of cumene, and 2.5 ml of *n*-heptane, 3.77 g (0.0195 mole) of diphenylketene was added. The reaction was undisturbed for 24 hr. Obtained was 5.0 g of 8,8-diphenyl-2-oxabicyclo[4.0.2]octan-7-one which corresponds to a 93% yield, mp 154–156° (lit.[3] mp 154–155°). The nmr spectrum (Varian A-60) in $CDCl_3$ with internal TMS standard showed the following: multiplet at 7.75 (aromatic protons), doublet centered at 5.25 (methinyl hydrogen adjacent to ether linkage), multiplet centered at 3.95 (methinyl hydrogen adjacent to carbonyl), a multiplet centered at 3.5 (methylene adjacent to ether linkage), and a multiplet centered at 1.6 ppm (remaining two methylenes). These protons were in the ratio 10:1:1:2:4.

Solvent Effects.—The solvents employed in this study were DMF, *n*-butyronitrile, THF, and toluene. All of the solvents were refluxed and distilled from lithium aluminum hydride under a nitrogen atmosphere through a 30-plate Oldershaw column. The description of a typical run follows. A solution of 4.56 g (0.0545 mole) of dihydropyran, 2.5 ml of *n*-heptane, and 12.5 ml of dry tetrahydrofuran was placed in a 30-ml reaction vessel equipped with a rubber septum. The vessel was placed in a constant-temperature bath at 40 ± 0.02° and the contents were allowed to equilibrate. A 5.68-g (0.0293 mole) portion of diphenylketene was then added through a hypodermic syringe and the rate of disappearance of dihydropyran was followed by vpc.

Registry No.—Diphenylketene, 525-06-4; dihydropyran, 110-87-2.

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(11) H. Staudinger, *Ber.*, **44**, 1619 (1911).

(12) In a private communication, Dr. J. C. Martin (Tennessee Eastman Co., Kingsport, Tenn.) suggested a modified procedure which employs benzene as a solvent. This was found to definitely be an improvement for obtaining pure diphenylketene.

The Anodic Oxidation of 3,3-Diphenylacrylic Acid and Diphenylacetylene

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The anodic oxidation of 3,3-diphenylacrylic acid in acetic acid at a carbon anode yields without rearrangement 4-phenylcoumarin, 2,2-diphenylvinyl acetate, and diphenylacetaldehyde, and with rearrangement benzil and related compounds which are also obtained from diphenylacetylene. A mechanism is proposed which involves the oxidation–rearrangement sequence 2,2-diphenylvinyl radical → 2,2-diphenylvinylcarbonium ion → 1,2-diphenylvinylcarbonium ion. Anodic oxidation of diphenylacetylene under the same conditions yields mainly benzoin acetate and a keto diacetate which is readily hydrolyzed or pyrolyzed to benzil.

We have reported previously[1] on the anodic oxidation of aliphatic carboxylic acids at carbon anodes. Olefins and esters were obtained *via* carbonium ion intermediates. The products were similar to those obtained by diazotization of the corresponding amines, also a carbonium ion process. Now we wish to report a similar study of an α,β-unsaturated acid, 3,3-diphenylacrylic acid. Again, data from the diazotization of the corresponding amine are available for comparison.

Diazotization of 2,2-diphenylvinylamine with nitrosyl chloride yielded diphenylacetylene and *cis*- and *trans*-α-chlorostilbene. These products were explained by means of a phenyl migration in a vinylcarbonium ion.[2] With isoamyl nitrite as the diazotizing agent, the only product was diphenylacetylene.

We expected diphenylacetylene from the electrolytic oxidation of 3,3-diphenylacrylic acid by an oxidation sequence analogous to that of the aliphatic acids. Because aromatic[3] and olefinic[4] hydrocarbons are acetoxylated under the electrolysis conditions used, the acetoxylation of diphenylacetylene was also studied.

Results

The principal products of the anodic oxidation of 3,3-diphenylacrylic acid are summarized in Table I, and those of diphenylacetylene and related compounds are listed in Table II. Carbon anodes were used in all experiments; acetic acid was the usual solvent. None of the expected diphenylacetylene was detected among the products of 3,3-diphenylacrylic acid, but compounds which are derived from diphenylacetylene under the same conditions were found.

Benzoin and benzoin acetate are primary products of the electrochemical reactions of both diphenylacetylene and the acid; that is, they are observed spectroscopically in the product mixture obtained by dilution of the electrolyte with water. Benzil is a secondary product. It is not detected spectroscopically in this mixture, but is readily formed from some component of it by hydrolysis or by pyrolysis on the gas chromatograph. In this discussion the term benzil is used to include any compounds which are detected as benzil on the gas chromatograph.

A sample of a benzil precursor was isolated by column chromatography from a diphenylacetylene product mixture. Of the acetates and keto acetates derivable from diphenylacetylene, the elemental analysis of

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(1) W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **86**, 4686 (1964).

(2) D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *ibid.*, **87**, 863 (1965).

(3) S. D. Ross, M. Finkelstein, and R. C. Peterson, *ibid.*, **86**, 4139 (1964).

(4) F. D. Mango and W. A. Bonner, *J. Org. Chem.*, **29**, 1367 (1964).