Mechanisms of Photochemical Reactions in Solution. XXXVII.[1] Solvent Effects in the Photolysis of Tetramethyloxetanone

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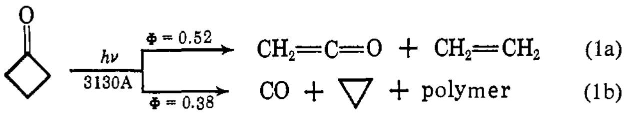
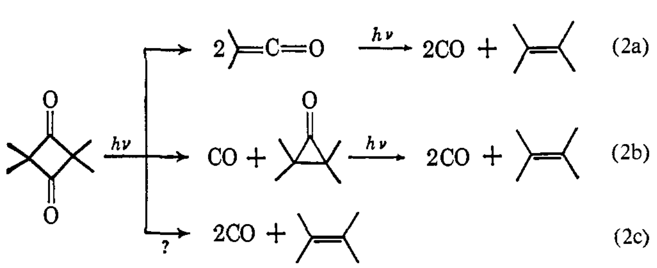
Abstract: Irradiation of tetramethyloxetanone with 3130-A light results in two competing modes of decomposition: (a) cleavage to acetone and dimethylketene; and (b) decarbonylation to yield tetramethylethylene oxide and other products. In polar solvents path a occurs to the virtual exclusion of path b, while in nonpolar solvents the paths are about equally important. The quantum yield for disappearance of tetramethyloxetanone is 1.0 in all solvents, even in the presence of high concentrations of typical triplet quenchers. Consequently, it is inferred that decomposition occurs from the lowest vibrational levels of the first excited singlet state, and that solvent polarity influences reactivity of the excited states.

Irradiation of cyclic ketones in the vapor phase results in very efficient decarbonylation. However, in solution, intramolecular rearrangements become dominant,[5] probably because of the efficiency of vibrational deactivation.

Cyclobutanone has been studied only in the vapor phase, where photocleavage (path a) to ketene and ethylene competes with decarbonylation (path b).[6] It might be expected that the increased strain present in the four-membered ring would facilitate decomposition, so that it would occur with an appreciable quantum yield even in solution.

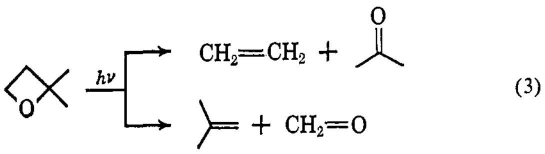


Considerable attention has been devoted to the photochemistry of 1,3-cyclobutanediones[7-10] which undergo facile cleavage and decarbonylation in solution.

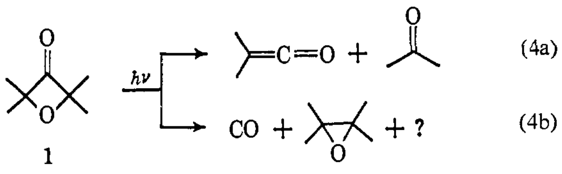


In attempts to determine the relative proportions of the different primary processes operative in the 1,3-diones, photolyses have been carried out in different solvents that can trap the dimethylketene and tetramethylcyclopropanone. However, unambiguous conclusions cannot be reached due to the lack of knowledge about possible solvent effects on competing modes of photodecomposition.

Cleavage by path a resembles the well-studied thermolysis of four-membered rings. Oxetanes are another group of compounds that undergo this reaction photochemically.[11]



We wish to report observations concerning the photochemistry of tetramethyloxetanone (**1**) and especially on the solvent dependence of the competition between paths a and b.



Results and Discussion

Rate of Decomposition. Solutions containing 0.25 *M* tetramethyloxetanone in cyclohexane, cyclopentene, piperylene, isoprene, 3-methyl-3-pentanol, 2-pentanol, 2-propanol, and ethanol were irradiated simultaneously. The rates of disappearance of **1** were identical in all of the samples. Added naphthalene and oxygen do not decrease the rate. The quantum yield in 2-propanol was found to be 1.0 using 3130-A light. No traces of dimers could be found among the reaction products formed in piperylene and isoprene. Consequently, we conclude that the photodecomposition occurs before the oxetanone can cross to a triplet state. No emis-

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[1] Part XXXVI: G. S. Hammond, H. Gotthardt, L. M. Coyne, M. Axelrod, D. Raynor, and K. Mislow, *J. Am. Chem. Soc.*, **87**, 4959 (1965).

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[10] I. Haller and R. Srinivasan, *ibid.*, **87**, 1144 (1965).

[11] J. D. Margerum, J. N. Pitts, Jr., J. G. Rutgers, and S. Searles, *ibid.*, **81**, 1549 (1959).

sion results from irradiation of tetramethyloxetanone dissolved in glasses at 77°K. No attempt was made to measure the extent of photolytic decomposition at the low temperature. Attempts to sensitize formation of the triplet failed. Photoreduction of propiophenone (E_T = 74.6 kcal) in 2-pentanol proceeds with the same quantum yield in the presence of tetramethyloxetanone as in its absence, and no disappearance of oxetanone or appearance of acetone could be detected by vpc analysis. It is remotely possible that the lack of emission and of quenching effects could occur if the triplet state decomposes exceedingly fast (with a rate constant of at least 10^{11} sec^{-1}). However, we feel that any reaction that *could* occur so fast in an excited triplet state most likely would occur at least as fast in the first-formed excited singlet.

Product Yields. Although variation in the solvent does not affect the quantum yield for photodecomposition, the results in Table I show that the distribution of products does change. In the very polar solvents, yields of acetone are almost quantitative and the alcohols trap dimethylketene as isobutyrate esters. The yields of esters approach, but never equal, those of acetone, due perhaps to traces of water in the more polar solvents. In the tertiary alcohol, the very small yield of ester suggests some unknown fate for the dimethylketene.

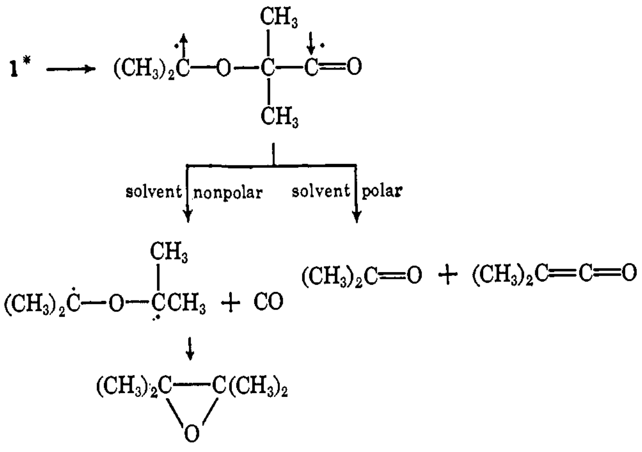
Table I. Solvent Dependence of Acetone Yields in Photolysis of Tetramethyloxetanone[a]

Solvent	Acetone yield,[b] %	Alkyl isobutyrate yield,[b] %
CH_3CN	96	. . .
EtOH	95	90
i-PrOH	92	77
i-PrOH[c]	78	61
i-PrOH[d]	53	50
2-Pentanol	84	80
3-Methyl-3-pentanol	69	2
Cyclohexane	61	. . .
n-Hexane	55	. . .
Piperylene	50	. . .

[a] 0.25 *M* solutions; 3130-A irradiation. [b] Relative to amount of oxetanone reacted, as determined by vpc, at 20–30% conversion. [c] Not degassed. [d] Containing 0.2 *M* piperylene.

As the solvent becomes less polar, the acetone yields drop until they account for little more than half the reaction in inert solvents. Obviously some other reaction is becoming competitive with path a. Some decarbonylation to tetramethylethylene oxide occurs. Carbon monoxide was identified as product of a reaction run to high conversion in Freon 113 ($CF_2ClCFCl_2$), by its characteristic retention time on a molecular sieves vpc column. Small peaks with the correct retention time for tetramethylethylene oxide occur in the vapor chromatograms of products formed in 2-pentanol, in 3-methyl-3-pentanol, and in all the inert solvents. Two fairly sizeable peaks representing as yet unknown products appear in the vpc traces with retention times characteristic of 80–100° boiling points. Identification of tetramethylethylene oxide was provided by the presence of a sharp singlet resonance at δ 1.24 in the nmr spectrum of the reaction products in Freon 113. However, the oxide amounts to only 5–10% of the total yield, leaving at least 30% mass balance missing. Unfortunately, nmr analysis offers no help in deciding what these products may be. Besides the oxide resonance at δ 1.24 and the oxetanone resonance at δ 1.38, the only other nmr signals are a large singlet at δ 2.10 corresponding to acetone, another large singlet at δ 1.55 probably corresponding to dimethylketene, an unresolvable multiplet underneath the oxetanone peak, and a small doublet centered at δ 1.16 suggestive of an isopropoxy group or an isobutyryl group. No resonance in the vinyl region could be seen.

Solvents are known to affect rates of competing reactions of excited states in a few instances, most notably in the rearrangements of dienones.[12] In these cases, however, actual protonation of excited states seems to be involved.[13] With tetramethyloxetanone it would appear that the fate of the excited singlet is influenced simply by solvent polarity. The effect could reflect competition between two fundamentally different paths but it seems somewhat implausible that there should be two totally independent reaction paths having such exceptionally high specific rates. We prefer the view that a single process, bond stretching culminating in bond fission, leads to both sets of reaction products. If an intermediate biradical is formed from an excited singlet state in an adiabatic process, the intermediate should be spin paired when it is first formed. Perhaps it is such an intermediate that partitions itself between two paths with solvent-dependent, relative rates. Although the following mechanism is entirely speculative, it is representative of the kind of competition that we have in mind.



Analogous behavior has been found in the alkoxy radical system, where polar solvents enhance cleavage to acetone.[14]

Although it is possible that the alcohols react with the excited state of the oxetanone to yield acetone and an ester, the low yields of ester in alcohols together with the high yield of acetone in acetonitrile do not support this possibility. In addition, we suspect that no bimolecular reaction, even one involving the solvent, could have the very high rate which must characterize these processes.

(12) For a review, see O. L. Chapman, *Advan. Photochem.*, **1**, 330 (1963).

(13) For example, see P. J. Kropp and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 2456 (1963).

(14) C. Walling and P. Wagner, *ibid.*, **86**, 3368 (1964).

The multiplicity of products which accompanies the lowering of acetone yields is not unusual, for photodecarbonylations of all cyclic ketones result in extensive bond breaking and shifting in the carbon fragment.[5] It is somewhat surprising that the ether oxygen atom has so little effect on the ratio of decomposition paths. At 3130 A both the oxetanone in inert solvents and cyclobutanone in the vapor phase[6] yield 55–60% acetone.

It has been reported that inclusion of ethylene in systems in which cyclobutanone and cyclopentanone are photolyzed results in C_5 and C_6 products, presumably by trapping of 1,3- and 1,4-biradicals, respectively.[15] We find that oxygen and dienes in alcohols lower the yields of path a products. This implies that some relatively long-lived intermediate, which cannot revert to the ground state of the original molecule, is formed.

Experimental Section

Tetramethyloxetanone was prepared as described.[16] Steam distillation of 2,5-dimethyl-2,5-dihydroxy-3-hexyne from mercuric sulfate yields 2,2,5,5-tetramethyltetrahydro-3-furanone.[17] Treatment of this ketone with bromine yields the 4,4-dibromo derivative,[17] which upon refluxing with dilute bicarbonate[16] and then concentrated potassium hydroxide yields 3-hydroxy-2,2,4,4-tetramethyl-3-oxetanecarboxylic acid. Oxidative decarboxylation with lead tetraacetate in refluxing chloroform then produces the tetramethyloxetanone, which is obtained pure by distillation, bp 115–119°, mp 48°. Vapor phase chromatographic analysis indicated both the purity of the compound and its stability to the analytical conditions.

Solvents were redistilled commercial materials, except for 3-methyl-3-pentanol, which was prepared by reaction of methylmagnesium iodide with 3-pentanone.

Rates in Different Solvents. Solutions 0.25 *M* in tetramethyloxetanone and 0.15 *M* in chlorobenzene or *m*-dichlorobenzene were prepared, and 3.0 ml of each was placed into each of three 13-mm Pyrex tubes, in which they were degassed and sealed. In a given experiment all tubes were placed on a rotating turntable with an unfiltered 450-w Hanovia Type L lamp in the middle and one sample from each set was removed after 12, 24, and 48 hr. The amount of the oxetanone destroyed was determined by vpc analysis using 5 ft × 0.25 in. columns packed with 25% Carbowax 20M on 42–60 firebrick, programming up from 100° at 8°/min. For a given time of irradiation the amount of oxetanone that disappeared varied by only 10–15% among the various solvents.

Quantum Yield. Degassed and sealed 13-mm Pyrex tubes, two per sample, each containing 3.4 ml of sample, were subjected to exactly equal amounts of absorbed light in a quantum yield merry-go-round fitted with an $NiSO_4$–$CoSO_4$ solution filter such that the only source lines transmitted were 3025 and 3130 A. Samples of 2-hexanone, which decomposes with a quantum yield of 0.5,[18] were irradiated in parallel with samples of the oxetanone. The rate of disappearance of **1** was twice that of 2-hexanone.

Product Yields. These were determined by vpc analysis with the Carbowax 20M column (Ucon Polar for acetonitrile) from samples irradiated both in the rate runs and in smaller tubes. Usual conversions were 20–30%. Carbon monoxide was detected by running a sample in Freon 113 to large conversion and then opening the tube so that the vapors above the solution could be sucked into an airtight syringe. Vpc analysis using a 10-ft column packed with molecular sieves yielded a large peak with a retention time of 45 min, identical with that of carbon monoxide. No other peaks besides nitrogen and oxygen appeared.

Identification of Products. A 20% solution of tetramethyloxetanone in Freon 113 was degassed and sealed in an nmr tube. Products were followed at different conversions. From 2 to 50% reaction, the only new peaks were assigned as follows: acetone at δ 2.10, (probably) dimethylketene at δ 1.55, tetramethylethylene oxide at δ 1.24. A small doublet centered at δ 1.16, and an unresolved multiplet under the oxetanone at δ 1.38 were not assignable to any reference compounds tested.

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(17) H. Richert, *Ann. Chim.*, [8] 30, 485 (1913).

(18) N. C. Yang, private communication.