Molecular Structure and Photochemical Reactivity. VI. Photochemistry of γ-Butyrolactone in the Liquid Phase[1]

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Abstract: The photolysis of γ-butyrolactone was investigated in the liquid phase with the 2537-Å line of a mercury resonance lamp. The major products were allyl formate, succinaldehyde, cyclopropane, and carbon dioxide with quantum yields at 25° of 0.23, 0.06, 0.013, and 0.015, respectively. From product-quenching data, it is suggested that triplet–triplet energy transfer from γ-butyrolactone to *cis*-butene, *trans*-butene, cyclohexene, and biacetyl occurs at a diffusion-controlled rate and that the allyl formate and cyclopropane originate from one state, probably a triplet, but that succinaldehyde originates from a different state. Added isopropyl alcohol quenched the formation of allyl formate and cyclopropane, but acetonitrile as a solvent had no effect on their yields over the concentration range of 0.3–16.0 *M*. An increase in temperature from 25 to 98° increased the yields of succinaldehyde and cyclopropane and decreased the yield of allyl formate, but the sum of the quantum yields of these products remained relatively constant.

While the photochemistry of aliphatic esters[3] and cyclic ketones[3b,4] has been investigated in some detail, the photochemistry of the simple cyclic esters (lactones), except for a brief report of the photolysis of β-propiolactone[5] and a preliminary report by us on the photolysis of γ-butyrolactone,[6] has not been described. It is well known that cyclic ketones (C_5–C_7) undergo an isomerization reaction to an unsaturated aldehyde in solution, and decarbonylation and isomerization in the vapor phase, and it was of interest to see if the lactones undergo analogous reactions. Furthermore, since the singlet states of esters and lactones[7] lie at appreciably higher energies than those of ketones, we felt that their triplet states would also be higher and, in contrast to the ketones,[8] energy transfer to simple monoolefins could occur at diffusion-controlled rates in solution. Finally, it was interesting to examine the nature of the excited states responsible for the observed products. Thus, in this paper we wish to report our study of γ-butyrolactone photochemistry, including a discussion of the effects of solvents, temperature, concentration, and quenchers. Energy-transfer processes are also considered.

Results

Products. The following products are produced on irradiation of γ-butyrolactone with the 2537-Å line of a mercury resonance lamp; allyl formate, succinaldehyde, cyclopropane, carbon dioxide, and small amounts of ethylene, propylene, and carbon monoxide. Their quantum yields are presented in Table I. The yields of the major products were determined as functions of time of irradiation in order to show that the products are formed directly from the lactone and not from secondary photolysis (Figure 1). To ensure that all measurements were carried out in the linear portion of the yield *vs.* time curve, the conversion was limited to 0.01%. When this was substantially exceeded, acetaldehyde and cyclopropanol were detected. These were shown to be products of the secondary photodecomposition of succinaldehyde. Thus, irradiation of succinaldehyde isolated from the irradiated lactone, and succinaldehyde synthesized by an independent nonphotochemical method, yielded these two products. The photochemistry of succinaldehyde will be discussed in another publication.

Quenching Experiments with Olefins and Biacetyl. A Stern–Volmer plot for quenching of allyl formate and cyclopropane with cyclohexene and of succinaldehyde with pentene-2 is presented in Figure 2, and a Stern–Volmer plot for quenching of allyl formate with biacetyl is presented in Figure 3. The plots in Figures 2 and 3 are for experiments carried out with the 2537-Å mercury resonance line. Figure 4 presents a Stern–Volmer plot for quenching of allyl formate and succinaldehyde with biacetyl when the exciting light was the 2380-Å line of mercury. Φ^0 is the quantum yield in the absence of quencher, and Φ is the quantum yield with quencher present. Two points representing the Φ^0/Φ quantity for the quenching of allyl formate by single concentrations of *cis*-butene and *trans*-butene are also included in Figure 2.

cis-Butene isomerized to *trans*-butene with a quantum yield of 0.37 ± 0.07 when the *cis*-butene concentration was 0.51 *M*. No additional products were detected.

When the 2537-Å line was used as the exciting light and with biacetyl as a quencher, it was necessary to correct for the light it absorbed. In order to do this readily, it is necessary that Beer's law be obeyed in the concentration range of the experiments. This was confirmed in the concentration range 0–0.07 *M*. The highest concentration of biacetyl used in the quenching experiments was somewhat higher than this (0.15 *M*), but it seems reasonable to make this limited extrapolation. In the experiments with the 2380-Å line, this correction is negligible (<4%).

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[1] Presented in part at the International Conference on Photochemistry, Aug 25–28, 1965, Tokyo, Japan.

[2] This paper is taken from the Ph.D. dissertation of R. S., University of California, Riverside, Calif.

[3] (a) P. Ausloos, *Can. J. Chem.*, **36**, 383 (1958); R. Borkowski and P. Ausloos, *J. Am. Chem. Soc.*, **83**, 1053 (1961); P. Ausloos and R. E. Rebbert, *J. Phys. Chem.*, **67**, 163 (1963); (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966.

[4] R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963).

[5] R. H. Linnell and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **72**, 3863 (1950).

[6] J. N. Pitts, Jr., R. Simonaitis, and J. M. Vernon, *Tetrahedron Letters*, **36**, 3209 (1965).

[7] W. D. Closson and P. Haug, *J. Am. Chem. Soc.*, **86**, 2384 (1964).

[8] R. Borkman and D. R. Kearns, *ibid.*, **88**, 3467 (1966).

Table I. γ-Butyrolactone Photodecomposition Product Quantum Yields and Product Quenching Constants at 25°

		K					
						Biacetyl	
	Φ	Cyclohexene	*trans*-Butene	*cis*-Butene	Pentene-2	2537 Å	2380 Å
Allyl formate	0.23	4.5 ± 0.6	4.0 ± 0.6	4.0 ± 0.6		4.0 ± 1.0	4.0 ± 1.0
Succinaldehyde	0.06			0.5 ± 0.5	0.5 ± 0.5		1.0 ± 0.5
Cyclopropane	0.013	4.6 ± 0.6					
CO_2	0.015						
CO	0.01						
Ethylene	0.005						
Propylene	0.001						

Table I lists the quenching constants K. These are defined as $k_q\tau$ and are obtained from the slopes of the Stern–Volmer plots. The quantity k_q is the bimolecular quenching rate constant, while τ is the excited-state lifetime, equal to the reciprocal sum of all rate constants for deactivation of the excited state. It is evident that, within experimental error, the quenching constants for allyl formate and cyclopropane for all quenchers and for both wavelengths are equal, but that the quenching constant for succinaldehyde is considerably smaller.

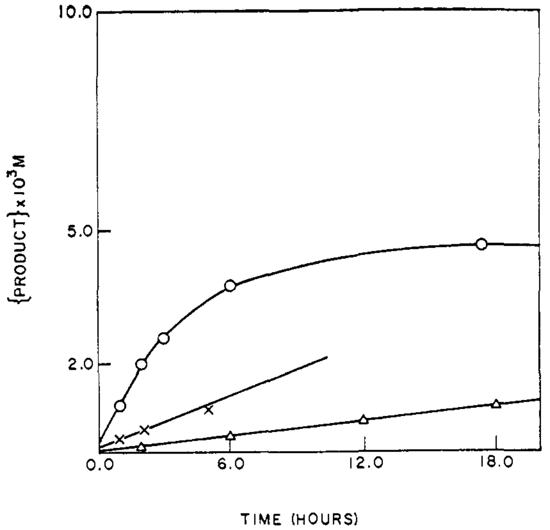

Figure 1. Product yield as a function of irradiation time: O, allyl formate; X, succinaldehyde; Δ, cyclopropane.

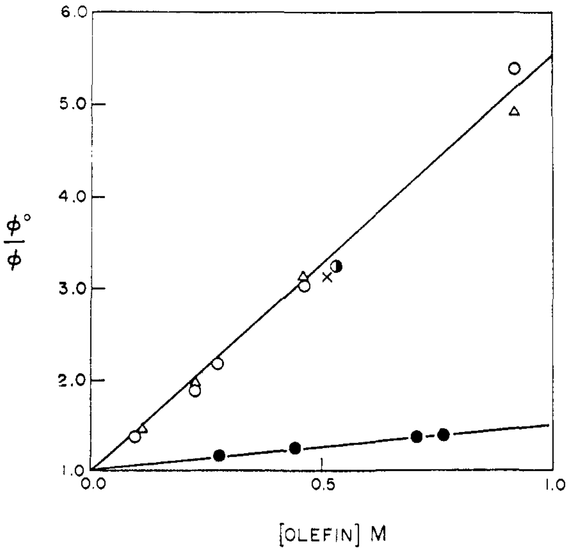

Figure 2. Stern–Volmer plot for product quenching with olefins: O, allyl formate; Δ, cyclopropane–cyclohexane; ●, succinaldehyde–pentene-2; ◑, allyl formate–*trans*-butene; X, allyl formate–*cis*-butene.

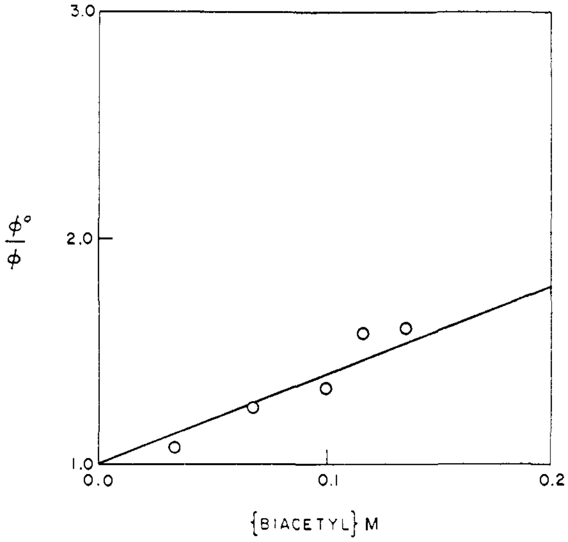

Figure 3. Stern–Volmer plot for quenching of succinaldehyde with biacetyl (exciting light 2537 Å).

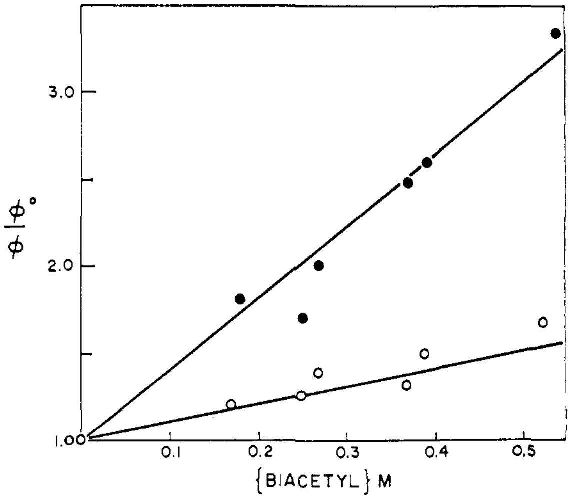

Figure 4. Stern–Volmer plot for allyl formate and succinaldehyde quenching with biacetyl (exciting light 2380 Å): ●, allyl formate; O, succinaldehyde.

Concentration and Solvent Dependence of Quantum Yields. The quantum yields of allyl formate and cyclopropane were determined in acetonitrile over the concentration range 2–100% and with added isopropyl alcohol up to 10%. The data for acetonitrile as solvent are presented in Table II. It is evident that the quantum yields of allyl formate and cyclopropane are independent of concentration.

Table II. Concentration Dependence of Product Quantum Yields in Acetonitrile

[γ-Butyrolactone], *M*	$\Phi_{\text{allyl formate}}$	$\Phi_{\text{cyclopropane}}$
16.0	0.23	0.013
6.40	0.26	0.014
1.60	0.25	0.013
0.80	0.25	0.014
0.32	0.24	0.013

The effect of concentration on the other products was not investigated. In the presence of added isopropyl alcohol, the quantum yields of allyl formate and cyclopropane are reduced, and Figure 4 shows a Stern–Volmer plot for quenching of allyl formate and cyclopropane with isopropyl alcohol.

Temperature Dependence of Quantum Yields in Neat γ-Butyrolactone. The effect of temperature on the quantum yields of allyl formate, succinaldehyde, and cyclopropane is shown in Table III. It is evident that the quantum yield of allyl formate decreases and the quantum yield of succinaldehyde increases with temperature but that the sum of the three quantum yields is relatively constant over the range studied.

Table III. Temperature Dependence of Quantum Yields

Temp, °C	$\Phi_{\text{allyl formate}}$	$\Phi_{\text{succinaldehyde}}$	$\Phi_{\text{cyclopropane}}$	$\Sigma\Phi$
24	0.23	0.06	0.013	0.30
39	0.22	0.08	0.016	0.32
56	0.21	0.09	0.017	0.32
74	0.19	0.09	0.018	0.30
98	0.16	0.14	0.018	0.32

Oxygen Effect. The quantum yields of allyl formate, succinaldehyde, and cyclopropane were the same in air-saturated or degassed neat butyrolactone. When butyrolactone was saturated with pure oxygen, the quantum yields of allyl formate, succinaldehyde, and cyclopropane decreased by about 5–10%.

The Photolysis of α-Methyl-γ-butyrolactone. A preliminary examination of the products from the photolysis of α-methyl-γ-butyrolactone under the same conditions as that for α-butyrolactone revealed the formation of the following products: *cis-* and *trans-*crotyl formate, α-methylsuccinaldehyde, methylcyclopropane, and small amounts of propylene and the butenes.

Discussion

The Absorption Spectrum and the Lowest Excited States. The presence of the electron-donating heteroatom α to the carbonyl group in esters and lactones increases the energy of their singlet states by about 25 kcal. Thus, their first absorption maxima in ethanol fall at about 2100 Å and, according to Closson, are of the n–π* type.[7] If the singlet–triplet state splitting in esters is of the same order as in ketones and aldehydes, the lowest triplet state of aliphatic esters could be as high as 105 kcal compared to about 78 kcal for aliphatic ketones.[9] Excitation with the 2537-Å line thus leads to the n–π* singlet state.

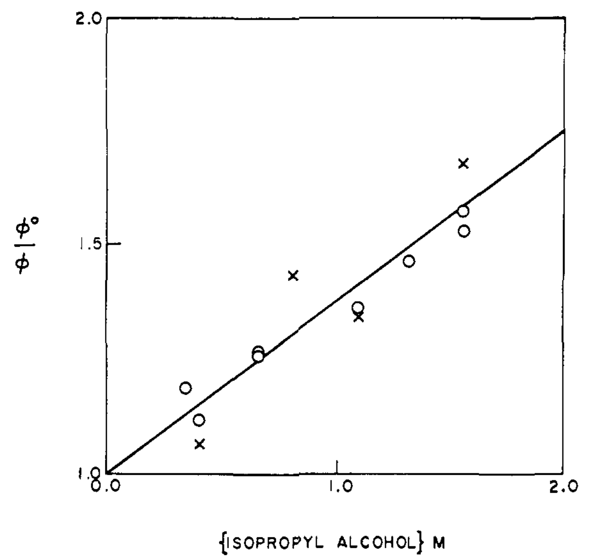

Figure 5. Stern–Volmer plot for isopropyl alcohol as quencher: O, cyclopropane; ×, allyl formate.

The nature of the lowest triplet state is also probably of the n–π* configuration for the following reasons. Ketones having the n–π* configuration are known to undergo efficient intramolecular and intermolecular photoreduction, whereas those having the π–π* configuration are generally unreactive toward photoreduction.[3b,10] Alicyclic esters also are known to undergo both intramolecular and intermolecular photoreduction.[3a] Although no rates for photoreduction of esters have yet been published, we can estimate the rate constant for the quenching step of excited γ-butyrolactone by isopropyl alcohol from the lifetime and the slope of the plot in Figure 5 to be about 3×10^8 mole $l.^{-1}$ sec^{-1}. We have not yet definitely established that product quenching is due to competing photoreduction since the reduction products have not been identified, but this is very likely. With this reservation, we can tentatively conclude that the photoreduction process for γ-butyrolactone is very efficient,[11] suggesting that the reactive state is n–π*. The proposal that photoreduction occurs *via* a ^{3}(n–π*) state rather than ^{1}(n–π*) is made plausible by the reactions of Wagner[12] for the photoreduction of acetone and by the results of Schaffner, *et al.*, for the photoreduction of steroid ketones[13] which show that the singlet state is very much less reactive toward photoreduction than the triplet state (about three orders of magnitude for acetone). If these results can be generalized to other aliphatic carbonyl compounds, including esters, the very large rate constant we have observed for photoreduction of γ-butyrolactone is inconsistent with the reactive state being a singlet.

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(9) R. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(10) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **6**, 99 (1968).

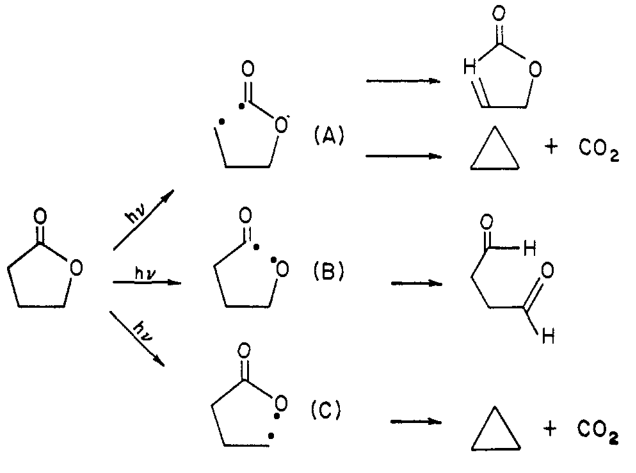
(11) R. Simonaitis, G. W. Cowell, and J. N. Pitts, Jr., *Tetrahedron Letters*, **38**, 3751 (1967).

(12) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2503 (1967).

(13) P. Keller, H. Wehrli, K. Schaffner, and O. Jeger, to be published.

Intermediates and Products. The formation of allyl formate and succinaldehyde is analogous to the formation of unsaturated aldehydes in the photolysis of cyclic ketones. In the case of ketones, it has been shown that formation of the aldehyde proceeds through α fission giving a diradical intermediate which is followed by an intramolecular disproportionation.[14] We propose that in the case of γ-butyrolactone the same mechanism is involved, except that α fission can lead to two types of diradicals, A and B (Chart I).

Chart I



Strong evidence for the formation of diradical A is that in the photolysis of α-methyl-γ-butyrolactone both *cis*- and the *trans*-crotyl formates are formed. The formation of B has not been proven but this intermediate seems reasonable. The formation of cyclopropane and carbon dioxide and the small amount of propylene could arise either from A or from the diradical C produced by β fission, or both. It is not possible from our data to decide between these two alternatives. Chart I summarizes the reactions involved. The yields of ethylene and CO are minor and the mechanism of their formation is not readily apparent.

The Nature of the Excited States Responsible for Product Formation. The Effect of Olefins and Biacetyl on Product Formation Yields. The photosensitized isomerization of monoolefins has been utilized as a means of identification of high-energy (75 kcal) triplet species in solution and in the vapor phase.[15] Cundall and coworkers have used the sensitized *cis–trans* isomerization of butene-2 to study energy-transfer processes from acetone,[16] acetaldehyde,[17] benzene, and pyridine[18] as donors and to elucidate the states involved in the photodecomposition of acetone and acetaldehyde in the vapor phase. A detailed investigation of the energy-transfer process from acetone to pentene-2 in solution was made by Borkman and Kearns.[8] In the present study, the effect of olefins on product formation yields was investigated in order to clarify the nature of the state or states from which product originates.

In the presence of *cis*-butene, product quenching was observed and *cis*-butene isomerized to *trans*-butene with a quantum yield of 0.37 ± 0.07 when $(\Phi^0 - \Phi)/\Phi^0$ was 0.66. No additional products could be detected when *cis*- or *trans*-butene was used as quencher. The predicted quantum yield for isomerization, based on the assumption that the quenching process is triplet energy transfer to the butene-2, is given by $\alpha[(\Phi^0 - \Phi)/\Phi^0]\Phi_{\mathrm{isc}}$, where α is the probability that excited butene decays to the *trans* configuration and Φ_{isc} is the intersystem crossing quantum yield for γ-butyrolactone. A value of 0.58 for α was calculated from the benzene-sensitized photostationary *trans* to *cis* ratio determined by Cundall, Fletcher, and Milne.[18] The maximum predicted quantum yield is 0.39. This is in good agreement with the actual value of 0.37. This fact, coupled with the result that no additional products are formed in the presence of butene-2, shows that product quenching is predominantly due to energy transfer from γ-butyrolactone to *cis*-butene. Since the quenching constants are the same for all quenchers, it is also likely that product quenching with cyclohexene and biacetyl is also predominantly due to energy transfer. Both cyclohexene and biacetyl are well-known acceptors of triplet-state energy. With cyclohexene as quencher, several additional products in small amounts were detected but were not characterized. These could arise from competing (<10%) hydrogen abstraction from the cyclohexene.

The data for allyl formate and cyclopropane quenching with cyclohexene were found to obey the Stern–Volmer equation (eq 1) up to $\Phi^0/\Phi = 5.5$ for allyl formate

$$\Phi^0/\Phi = 1 + k_q\tau[\mathrm{Q}] \qquad (1)$$

and cyclopropane, where [Q] is the quencher concentration. This allows us to conclude that at least 90% allyl formate and cyclopropane originate from the triplet state since calculation shows that even 10% of unquenchable singlet reaction would have caused appreciable curvature in the Stern–Volmer plot.

The quenching of succinaldehyde is considerably less than that of the other products, and one concludes that it comes from a different state. Whether this state is a singlet or an unquenchable triplet it is not possible to say.[19] This result is consistent with the findings of Ausloos on aliphatic esters, which showed that products obtained from the α carbon–oxygen fission originate from a different state than the products obtained from α carbon–carbon fission.[3a]

In the use of the Cundall technique for unequivocal identification of triplets, it is necessary to show that singlet-singlet or singlet–triplet energy transfer is not involved. The most reliable way of doing this is to show that quenching of donor fluorescence does not occur. Unfortunately, no emission from γ-butyrolactone could be observed, and such a direct approach is not possible. However, our quenching results (*vide infra*) and the absence of singlet–singlet or singlet–triplet transfer for the systems acetone–butene-2[16] and benzene–butene-2,[18] studied by Cundall and coworkers, for the acetone–pentene-2 system examined by Borkman and Kearns,[8] and the acetone–piperylene

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[14] R. L Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

[15] W. A. Noyes and T. Unger, *Advan. Photochem.*, **4**, 49 (1966).

[16] R. B. Cundall and A. S. Davies, *Proc. Roy. Soc.* (London), **A290**, 563 (1966).

[17] R. B. Cundall and A. S. Davies, *Trans. Faraday Soc.*, **62**, 2793 (1966).

[18] R. B. Cundall, F. J. Fletcher and D. G. Milne, *ibid.*, **60**, 1146 (1964).

[19] If the state responsible for succinaldehyde formation precedes the state responsible for allyl formate formation and if the dialdehyde is quenched slightly, eq 1 is not strictly true. However, since the quenching is very small, we make the approximation that eq 1 holds.

system investigated by Rebbert and Ausloos[20] suggest that singlet–singlet and singlet–triplet transfer are probably also unimportant in the present case.

It is likely that all products have the first excited singlet state as a precursor. The small quenching of succinaldehyde by olefins and biacetyl argues that at most the singlet state is quenched only slightly as well and that the major quenching is due to triplet–triplet transfer from the lactone to all quenchers.

In addition, the quenching constants for allyl formate with biacetyl as quencher are identical with those for olefins as quenchers (Table I), showing that the quenching efficiencies of biacetyl and the olefins are the same. This result is taken as evidence against singlet–singlet or singlet–triplet transfer to olefins and singlet–singlet transfer to biacetyl from γ-butyrolactone.[21] The efficiency of singlet energy transfer to the olefins is expected to be lower than to biacetyl for the following reasons. Singlet–singlet transfer from γ-butyrolactone (singlet state at about 110 kcal) to olefin (singlet state at about 138 kcal)[22] would be greatly endothermic, consequently unimportant. Singlet–triplet energy transfer from lactone to olefin is spin forbidden; hence it is expected to be of low efficiency. Thus, the failure to observe any difference in quenching efficiency between the olefins and biacetyl also suggests that singlet–singlet or singlet–triplet energy transfer from γ-butyrolactone to the olefins is probably not important.

Since the quenching constants are equal for all quenchers, this also strongly suggests that energy transfer occurs at diffusion-controlled rates to all quenchers. We believe this to be the first example of diffusion-controlled triplet–triplet energy transfer to monoolefins in solution. This is not unreasonable because if the n–π^* state singlet–triplet splitting for esters is similar to that for other unconjugated carbonyl compounds, it would place the lactone triplet at 100–105 kcal as compared to about 80 kcal for monoolefins.[23]

The conclusion that the allyl formate and cyclopropane originate from the triplet state is also consistent with the quenching of these products by isopropyl alcohol. As has already been pointed out (*vide supra*), photoreduction probably occurs from the triplet state of the lactone, and, if the photodecomposition products were to originate from the singlet state, no quenching by isopropyl alcohol would be observed.

From the quenching constants (Table I) and the bimolecular diffusion-controlled rate constant (k_D = 4 × 10^9 mole $l.^{-1}$ sec^{-1} in neat γ-butyrolactone),[24] the lifetime of the triplet state of γ-butyrolactone can be calculated as 1.2 × 10^{-9} sec^{-1}. This lifetime is the inverse sum of all rate constants for deactivation of the excited state, and, if we assume that the sole process for deactivation is decomposition to the biradical intermediates, the inverse of the lifetimes is the sum of rate constants for decomposition of the triplet state to the diradicals A and C. It is interesting to compare the lifetime for γ-butyrolactone with that for cyclopentanone which is 4 × 10^{-9} sec.[11]

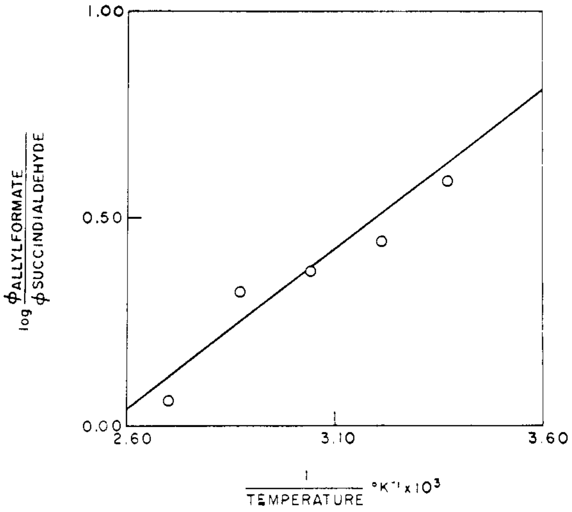

Figure 6. Arrhenius plot for $\Phi_{\text{allyl formate}}/\Phi_{\text{succinaldehyde}}$.

Concentration Dependence of Quantum Yields. The constancy of the quantum yields of allyl formate and cyclopropane with concentration (Table III; succinaldehyde dependence was not determined) shows the following: (a) there is no solvent effect in going from neat lactone as the solvent to acetonitrile, and (b) all bimolecular processes are unimportant. It is conceivable, for example, that triplet lactone could be photoreduced by γ-butyrolactone itself. The lack of a concentration dependence of the quantum yields rules out this possibility.

Effect of Oxygen. The absence of any quenching of allyl formate, succinaldehyde, and cyclopropane yields in air-saturated γ-butyrolactone is consistent with the very short triplet lifetime of 1.2 × 10^{-9} sec. The 5–10% quenching of the above products in lactone saturated with pure oxygen is about what would be expected from the diffusion-controlled quenching data with the olefins and biacetyl.[25]

Effect of Temperature. The intramolecular abstraction of a hydrogen atom by the diradical intermediates in the photolysis of γ-butyrolactone and cyclic ketones is competitive with the intramolecular radical recombination to give the starting material. If the hydrogen atom abstraction step has a greater temperature dependence than the recombination step, an increase in allyl formate and succinaldehyde yields is expected. Similarly, the elimination of CO_2 from biradical A or C could also be temperature dependent.

The results (Table III) show that the effect of temperature is not large, but it is clear that with increasing temperature there is a decrease of allyl formate and an increase of succinaldehyde and cyclopropane. Moreover, the sum of these quantum yields is relatively constant and an Arrhenius plot of $\Phi_{\text{allyl formate}}/\Phi_{\text{succinaldehyde}}$ is linear (Figure 6). These results suggest that the observed temperature dependence is in the decomposition of a common intermediate rather than in the decomposition of the two intermediates (di-

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(20) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **86**, 4803 (1964).

(21) Identical quenching constants would also be obtained for diffusion-controlled triplet–triplet transfer in the lactone–olefin system and diffusion-controlled singlet–singlet transfer in the lactone–biacetyl system only if the lifetimes of the singlet and triplet state are identical.

(22) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947).

(23) D. F. Evans, *J. Chem. Soc.*, 2753 (1959).

(24) Calculated from the Debye equation and the measured viscosity of γ-butyrolactone.

(25) The oxygen concentration in γ-butyrolactone saturated with pure oxygen is not known, but a value of 10^{-2} *M* is reasonable if the oxygen solubility in the lactone is similar to that in other esters.

radicals A and B). From the slope of the plot in Figure 4, a difference in the Arrhenius activation energies of 1.8 kcal for these two products can be determined.

Experimental Section

Apparatus and Methods of Analysis. γ-Butyrolactone was irradiated in a cyclindrical Cary quartz cell of 1-cm path length. The Teflon stopper of the cell was provided with a small hole through which a syringe needle could be inserted for withdrawing samples for gas chromatographic analysis. With this arrangement, a single injection into a chromatograph equipped with a flame detector and a cyanosilicone XF 1500 column (60°, 10 ft × $^1/_8$ in.) permitted the analysis of allyl formate, cyclopropane, and ethylene. A Carbowax 20M (155°, 10 ft × $^1/_8$ in.) column was used for the analysis of succinaldehyde. The solutions were all flushed with nitrogen prior to irradiation. This procedure was found to be more than sufficient since the same results were obtained when the solutions were degassed by repeated freeze–thaw cycles or when air saturated.

For the analysis of carbon monoxide and carbon dioxide, a different procedure was used. The volatile fraction at $-196°$ was removed with a Toepler pump and its volume determined with a calibrated gas buret. Mass spectrometric analysis showed this fraction to consist entirely of carbon monoxide. A second fraction was taken at $-78°$. This fraction consisted of cyclopropane, carbon dioxide, and ethylene. Mass spectrometric analysis yielded the mole ratio of cyclopropane to carbon dioxide. The cell employed for irradiations in which carbon monoxide and carbon dioxide analyses were performed was larger (3-cm diameter and 0.5-cm path length) and equipped with an approprirate arrangement for degassing.

The experiments were performed with a Hanovia low-pressure mercury lamp (type) emitting mainly the 2537-Å resonance line and with the 2380-Å line of a medium-pressure mercury lamp (Hanovia Type A, 500 w). The beam of the resonance lamp was concentrated with a lens and passed through a 3-cm chlorine filter to remove radiation at higher wavelengths, and the light from the medium pressure lamp was rendered monochromatic with a Bausch and Lomb monochromator. For runs above room temperature, the cell was enclosed in an aluminum block furnace.

The identification of products was accomplished by the usual instrumental method, and in each case the spectral properties were compared to those of authentic samples. The actinometry employed was ferrioxalate.

Materials. The γ-butyrolactone was obtained from the Matheson Co. and was fractionated with a spinning-band column, retaining the middle fraction. Examination of the absorption spectrum of the neat lactone (1-cm path length) showed a shoulder beginning at 3100 Å. Since this absorption was suspected as being due to impurities, the lactone was subjected to charcoal treatment until all absorption above 2700 Å was virtually eliminated. The lactone thus purified shows a sharp rise in absorption beginning at 2600 Å. After the charcoal treatments, the lactone was again subjected to a fractionation, the middle fraction being retained. Glpc analysis showed the remaining impurities to be 0.1%.

The cyclohexene was purified by fractionation and chromatography over alumina; *cis*- and *trans*-butene (Phillips) were used without further purification. Biacetyl and isopropyl alcohol were purified by fractionation. The acetonitrile used was Matheson "chromato" quality. All solutions were made up immediately after purification and used without delay.

Acknowledgment. This research was supported by Grant AP 00109, National Center for Air Pollution Control. R. S. also wishes to acknowledge support from an Air Pollution Special Fellowship, 1964–1967.

Electron Spin Resonance in *t*-Butyl-Substituted Semiquinones. The Hyperfine Structure of *t*-Butyl Protons

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Abstract: The electron spin resonance spectra of three *p*-benzosemiquinones and four *o*-benzosemiquinones with *t*-butyl substituents have been obtained. Resolution of *t*-butyl proton hyperfine splittings has been accomplished in all but one of the radicals. The most reasonable interpretation of the splittings is in terms of carbon–carbon hyperconjugation which produces unpaired spin density in the β-carbon atom tetrahedral orbitals. Spin density is then transferred to the protons by a spin-polarization mechanism. The Q value for the latter mechanism is approximately 44 gauss, which indicates that tetrahedral orbitals are more effective than p_z orbitals in polarizing hydrogen 1s orbitals. Hückel molecular orbital calculations are performed to fit the data; the results indicate that the *t*-butyl group is probably more inductive than the methyl group and that an interaction between the carbonyl group and a *t*-butyl group *ortho* to it may occur.

The effect of ring substitution on the electron spin resonance (esr) spectra of semiquinone radical anions has been the subject of a number of papers.[3-10] The effect of chloro and methyl substitution in *p*-benzosemiquinone on the ring proton hyperfine splitting (hfs) can be accounted for by the additivity rules of Venkataraman and Fraenkel.[6] The hfs of the methyl protons has been explained in terms of hyperconjugation by Bersohn.[5] Vincow and Fraenkel[7] did a Hückel molecular orbital (HMO) calculation on *p*-benzosemiquinones in which the parameters were varied to obtain the best fit for the ring proton hfs. This calculation

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