vents retard the β-scission of this alkoxyl.

Finally, in the case of 2-phenylethyl hyponitrite, we may assume that the excess of alcohol over aldehyde (0.024 M) in the product mixture represents the amount of alkoxyls which abstracted a hydrogen atom from the medium rather than from another caged alkoxyl. The sum of β-scission products (toluene plus 2(bibenzyl)) is also 0.024 M and suggests that the rate constants for β-scission and H abstraction from solvent are comparable. A recent determination[2a] led to $k_{\text{scission}} = 3.7 \times 10^7$ sec^{-1} in benzene at 45 °C for this alkoxyl. We estimated the pseudo-first-order decay of *tert*-butoxyl in isooctane as 2.5×10^7 s^{-1} (vide infra). The 2-phenylethoxyl radical is about 3 times more reactive in H abstraction toward benzhydrol than *tert*-butoxyl,[2a] which brings the agreement between calculated rates for scission and abstraction to within a factor of 2 if the reactivities of the two alkoxyls toward isooctane are similarly related.

Conclusion

trans-Alkyl hyponitrites represent a well-behaved class of compounds whose decomposition rates are less subject to induced decomposition and solvent effects than some other sources of radicals. The shock sensitivity of the compounds disappears on dilution. The major sources of sample loss appear to be volatilization, which affects hyponitrites with alkyl groups as large as *tert*-butyl,[29,30] and adventitious photosensitized decomposition in aromatic solvents or of hyponitrites with aromatic rings.

Acknowledgment. This work was supported in part under Grant No. DAAG29-78-C-0001 with the U.S. Army Research organization. We wish to thank Dr. Peter Klemchuk for samples of Irganox inhibitors, Susan A. Brotherton and Thomas Dannison for performing some of the mass spectral analyses, David Rataj for construction of electronic interfaces and development of software, Marshall D. Muller for synthetic assistance, Dr. James D. Spain for computer software, and Dr. Philip S. Gill for assistance with the thermal analysis.

Registry No. Methyl hyponitrite, 86886-15-9; isopropyl hyponitrite, 86886-16-0; *n*-butyl hyponitrite, 86886-17-1; cyclohexyl hyponitrite, 86886-18-2; *tert*-butyl hyponitrite, 82554-97-0; *tert*-amyl hyponitrite, 85972-35-6; 2-phenylethyl hyponitrite, 86886-19-3; benzyl hyponitrite, 86886-20-6; 1-phenylethyl hyponitrite, 82522-46-1; silver hyponitrite, 7784-04-5; methyl iodide, 74-88-4; 2-propyl bromide, 75-26-3; *n*-butyl iodide, 542-69-8; 1-phenylethyl bromide, 585-71-7; 2-phenylethyl iodide, 17376-04-4; 2-phenylethyl bromide, 103-63-9; cyclohexyl bromide, 108-85-0.

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[29] Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 6478-85.

[30] Early workers were unable to distill the lower hyponitrites at reduced pressure, although this was presumably due to their thermal decomposition.[28]

Reactivity of Superoxide Ion with Ethyl Pyruvate, α-Diketones, and Benzil in Dimethylformamide

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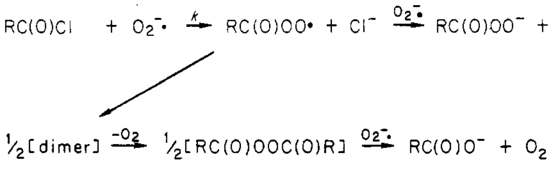
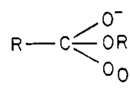
The dominant net reaction of $O_2^{-}\cdot$ with α-dicarbonyls such as ethyl pyruvate, 2,3-butanedione, and 2,3-pentanedione is proton abstraction from their enol tautomer. The rate-limiting step is first order for each reactant, the net products are enolate plus O_2 and H_2O_2, and the second-order rate constants (k) are the same, within experimental error, for the three substrates ($k = (4 \pm 1) \times 10^3$ M^{-1} s^{-1}). For the reaction of benzil (an α-dicarbonyl that cannot enolize) with $O_2^{-}\cdot$ the rate-limiting step is first order for each reactant, and the second-order rate constant (k) is $(2 \pm 1) \times 10^3$ M^{-1} s^{-1}. The process appears to involve an initial nucleophilic addition by $O_2^{-}\cdot$ to carbonyl carbon, followed by a dioxetane closure on the other carbonyl carbon and reductive cleavage by a second $O_2^{-}\cdot$ to give two benzoate ions and O_2.

Previous work has demonstrated that in aprotic media superoxide ion ($O_2^{-}\cdot$) adds nucleophilically to carbonyl carbons.[1-3] For those with adequate leaving groups (acid chlorides and carboxylate esters), the net reaction yields the carboxylate or peracid anions (eq 1). With acid chlorides the diacyl peroxide is a stable intermediate with limiting amounts of $O_2^{-}\cdot$ but is reduced by excess $O_2^{-}\cdot$ (eq 1 and 2).[1] In the case of esters the net rate depends on the leaving group ($R'O^-$) of the activated complex I.[4]



(1)

$$RC(O)Cl + RC(O)OO^- \xrightarrow{-Cl^-} RC(O)OOC(O)R \xrightarrow{2O_2^{-}\cdot} 2RC(O)O^- + 2O_2 \quad (2)$$



I

Thus, in pyridine the bimolecular rate constant, k_2, for the reaction of $O_2^{-}\cdot$ with ethyl acetate is 1.1×10^{-2} M^{-1} s^{-1}, and with phenyl acetate it is 160 M^{-1} s^{-1}. Because of the absence of a viable leaving group there is not a net reaction between $O_2^{-}\cdot$ and benzaldehyde. The same is true for

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[1] Johnson, R. A. *Tetrahedron Lett.* **1976**, 331.

[2] San Filippo, J., Jr.; Romano, L. J.; Chern, C.-I.; Valentine, J. S. *J. Org. Chem.* **1976**, *41*, 586.

[3] San Filippo, J., Jr.; Chern, C.-I.; Valentine, J. S. *J. Org. Chem.* **1976**, *41*, 1077.

[4] Gibian, M. J.; Sawyer, D. T.; Ungermann, T.; Tangpoonpholvivat, R.; Morrison, M. M. *J. Am. Chem. Soc.* **1979**, *101*, 640.

0022-3263/83/1948-3733$01.50/0

benzophenone and simple aliphatic ketones.[4]

Because nucleophilic addition of $O_2^{-}\cdot$ to carbonyl carbon appears to be a general tendency in aprotic media, we became interested in the net reaction chemistry of superoxide ion with the α-dicarbonyl group in several molecules. Ethyl pyruvate, which has such a group in association with an ester function that should at least react in a fashion akin to ethyl acetate,[4] is an important metabolic intermediate. It, along with 2,3-pentanedione and 2,3-butanedione, represents α-dicarbonyls that can enolize to some extent in aprotic media.

An earlier study[5] of the reactivity of $O_2^{-}\cdot$ with benzil (an α-dicarbonyl that cannot enolize) concluded that the primary step is an electron-transfer to produce an anion radical intermediate. With an α,β-tricarbonyl lactone, dehydroascorbic acid, $O_2^{-}\cdot$ appears to add to the α-keto carbon and then to undergo a dioxetane closure to the β-keto carbon with cleavage and reduction by a second $O_2^{-}\cdot$ to give threonate and oxalate.[6] Two previous studies[2,3] discuss the oxidative cleavage of α-diketones and α-keto esters by KO_2/18-crown-6 ether after reaction times of 24 h. The prolonged combination of reactants and intermediates with residual water may have allowed secondary reactions to produce OH^- and peroxides. Their involvement would obscure the primary chemistry and the mechanistic interpretations.

The present study has made use of electrochemically generated $O_2^{-}\cdot$ as a titrant for the determination of reaction stoichiometries and as a homogenous reagent for the measurement of reaction kinetics.

Experimental Section

Materials. Reagent grade *N,N*-dimethylformamide (DMF) from Burdick and Jackson (H_2O, 0.010%) was used as received. The supporting electrolyte, tetraethylammonium perchlorate (TEAP), was obtained from G. F. Smith Chemical Co. and was dried on a vacuum line before use. Ethyl pyruvate (Sigma), 2,3-pentanedione (Eastman), and 2,3-butanedione (Eastman) were used without further purification. Benzil (Matheson Coleman and Bell) was recrystallized from methanol. All other materials and gases were reagent grade and were used as received.

Instrumentation. Cyclic voltammetric measurements were made by use of a three-electrode potentiostat–galvanostat constructed with operational amplifiers[7] or a Princeton Applied Research Model 173/175/179 potentiostat–galvanostat. The voltammograms were recorded with a Houston Instruments Omnigraphic X–Y recorder. The working electrode was a Beckman platinum inlay electrode (area 0.23 cm^2). The auxiliary electrode was a platinum flag electrode, which was placed in a solvent-filled compartment that was isolated from the bulk solution by a fine or medium-porosity glass frit. The reference electrode was a Ag/AgCl (aqueous tetramethylammonium chloride) cracked-glass-bead electrode which was adjusted to 0.000 V vs. SCE.[6] The reference electrode was located inside a solvent-filled Luggin capillary in the cell assembly.

Controlled-potential electrolysis experiments made use of a cylindrical platinum-mesh working electrode and a Princeton Applied Research Model 175/179 potentiostat–digital coulometer.

Kinetic data for substrate–$O_2^{-}\cdot$ reactions were obtained by use of either a Beckman Model 1855 platinum rotated disk assembly (electrode area 0.34 cm^2) with one of the potentiostats or by a Pine Instruments Co. platinum–platinum rotated ring–disk electrode that was controlled by a Model RPE 3 dual potentiostat.

Methods. All experiments were carried out in DMF (0.1 M TEAP) at 25 °C. Superoxide was electrochemically generated by controlled-potential electrolysis at −1.2 V vs. SCE with O_2 flowing through the cell at 1 atm. After electrolysis the solution was bubbled with argon to remove any residual O_2. The $O_2^{-}\cdot$ concentration was determined by measurement of the anodic voltammetric peak current at −0.7 V vs. SCE. The current at the platinum inlay electrode was standardized by controlled-potential coulometric assay of the $O_2^{-}\cdot$ concentration. Concentrations of O_2 were determined by cyclic voltammetry in a calibrated, gas-tight, low-headspace electrochemical cell. The products from the $O_2^{-}\cdot$ reactions were identified and assayed by use of thin-layer chromatography, gas chromatography, high performance liquid chromatography, and acid–base titrations. Reaction stoichiometries were determined by titration of a known concentration of $O_2^{-}\cdot$ in DMF with aliquots of substrate. The residual $O_2^{-}\cdot$ was determined by anodic voltammetry.

The kinetics for the substrate–$O_2^{-}\cdot$ reactions were measured under pseudo-first-order conditions. With a tenfold excess of substrate the decay in concentration of an added aliquot of $O_2^{-}\cdot$ was monitored with a platinum rotated-disk electrode that was set at 0.0 V vs. SCE. An alternative approach for the kinetic measurements made use of a rotated Pt–Pt ring–disk electrode that was controlled by a dual potentiostat. Dissolved O_2 (either 1 or 0.21 atm) was reduced at the disk to $O_2^{-}\cdot$, which traveled to the ring where it was oxidized to O_2. The ratio of currents, i_{ring}/i_{disk}, decreased when a reactive substrate (with $O_2^{-}\cdot$) was present in excess. Pseudo-first-order rate constants were determined for the $O_2^{-}\cdot$–α-dicarbonyl reactions with a tenfold (or greater) excess of substrate by use of analytical functions.[8] The measured constants exhibited a first-order dependence on substrate concentration.

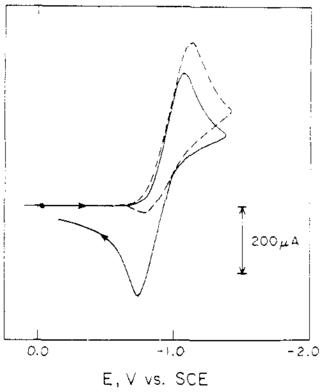

Figure 1. Cyclic voltammograms for the reduction of 4.8 mM O_2 (1 atm) in dimethylformamide (0.1 M tetraethylammonium perchlorate) at a platinum electrode (area, 0.23 cm^2) in the absence (—) and in the presence (- - -) of 10 mM 2,3-butanedione. The cathodic (upper) peak height from an initial negative scan at a rate of 0.1 V s^{-1} is proportioned to the O_2 concentration at the electrode surface. The anodic peak (lower) height that results from reversal of the scan direction is proportional to the $O_2^{-}\cdot$ concentration (produced by the reduction of O_2) that diffuses to the electrode surface during the life of the experiment: saturated calomel electrode (SCE) vs. NHE, +0.244 V.

Results

Figure 1 illustrates a cyclic voltammogram for O_2 in the absence (solid line) and in the presence of 2,3-butanedione (dashed line). For an initial negative voltage scan O_2 is reduced to $O_2^{-}\cdot$. Reversal of the scan causes the $O_2^{-}\cdot$ to be oxidized back to O_2; the peak height for the oxidation is proportional to the amount of $O_2^{-}\cdot$ in the solution at the electrode surface. In the presence of 2,3-butanedione the amount of $O_2^{-}\cdot$ at the electrode surface is diminished (shown by a smaller anodic peak current) because there is a net reaction between it and $O_2^{-}\cdot$. The enhanced cathodic current with the presence of butanedione is due to the production of O_2 from the primary reaction products. When 2,3-pentanedione or ethyl pyruvate is present

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[5] Boujlel, K.; Simonet, J. *Tetrahedron Lett.* **1979**, 1063.

[6] Sawyer, D. T.; Chiericato, G., Jr.; Tsuchiya, T. *J. Am. Chem. Soc.* **1982**, *104*, 6273.

[7] Goolsby, A. D.; Sawyer, D. T. *Anal. Chem.* **1967**, *39*, 411.

[8] Albery, W. J.; Hitchman, M. L. "Ring-Disc Electrodes"; Clarendon Press: Oxford, 1971.

Table I. Stoichiometries and Kinetics for the Reaction of $O_2^{-}\cdot$ with α-Dicarbonyls in Dimethylformamide (0.1 M Tetraethylammonium Perchlorate) at 25 °C[a]

substrate (S, 1-20 mM)	$O_2^{-}\cdot$/S	O_2 released/S	products (per S)	pK'_a[b]	k_{bi},[c] $M^{-1}\ s^{-1}$
2,3-butanedione	1 ± 0.2	0.5 ± 0.2	H_2O_2, enolate (1)	18	(4 ± 1) × 10^3
2,3-pentanedione	1 ± 0.2	0.5 ± 0.2	H_2O_2, enolate (1)	18	(3 ± 1) × 10^3
ethyl pyruvate	1 ± 0.2	0.5 ± 0.2	H_2O_2, enolate (1)	21	(4 ± 2) × 10^3
phenol[b]	1 ± 0.2	0.5 ± 0.2	H_2O_2, phenolate (1)	20	1 × 10^4
benzil	2 ± 0.3	1.0 ± 0.3	benzoate (2)		(2 ± 1) × 10^3

[a] Decay of $O_2^{-}\cdot$ in the presence of at least a tenfold excess of substrate monitored by rotating-disk voltammetry at 0.0 V vs. SCE. The kinetic experiments with the ring-disk electrode involved in situ generation of $O_2^{-}\cdot$ from O_2 at the disk (−1.0 V vs. SCE), with the $O_2^{-}\cdot$ decay monitored by the ring (0.0 V vs. SCE) in the presence of at least a tenfold excess of substrate. [b] Reference 9. [c] Pseudo-first-order rate constant divided by substrate concentration, $k_{obsd}/[S]$.

in an O_2 solution, effects on the oxygen electrochemistry almost identical with those of Figure 1 are observed.

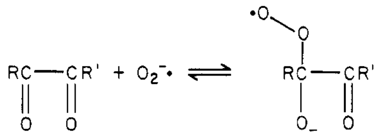
The reaction stoichiometries between $O_2^{-}\cdot$ and these three α-dicarbonyls are 1:1 on the basis of titrations. In each case 0.5 equiv of $O_2/O_2^{-}\cdot$ is produced in the product solution. Acidification of the product solution from a 1:1 combination of $O_2^{-}\cdot$ and α-dicarbonyl consumes 1 equiv of acid/substrate and yields all of the original substrate as well as some H_2O_2. These results as well as those for the $O_2^{-}\cdot$–benzil reaction are summarized in Table I. The effective acidities (pK'_a) for the enols of these α-dicarbonyls as well as for phenol in DMF also are listed in Table I.

The reaction stoichiometry for the combination of $O_2^{-}\cdot$ and benzil is 2:1 with the quantitative production of two benzoate ions and one O_2 molecule (Table I). Significant quantities of other products are not detected. As with the other α-dicarbonyls, addition of benzil to a DMF solution of O_2 has the effect on the cyclic voltammetry that is illustrated by Figure 1. Direct electron-transfer reduction of benzil in DMF occurs at a peak potential of −1.16 V vs. SCE, which is sufficiently negative of the $O_2/O_2^{-}\cdot$ redox couple ($E°' = -0.84$ V vs. SCE in DMF) to not interfere with the O_2 reduction peak. A large excess of benzil causes the $O_2/O_2^{-}\cdot$ peak to become a preceding shoulder on its reduction peak.

The decay of the $O_2^{-}\cdot$ concentration when it is in the presence of ethyl pyruvate is illustrated by the rotated-disk data of Figure 2. Such traces for each of the α-dicarbonyl substrates have been used to determine pseudo first-order rate constants. Variation of substrate concentration has confirmed that each process is first-order in substrate and in $O_2^{-}\cdot$ and that the rate-limiting step is a second-order process. The rate laws and constants also have been determined by the rotating ring–disk method.[8] The average values for the second-order rate constants are summarized in Table I.

Discussion and Conclusions

Protic α-Dicarbonyls. The absence of any substrate redox products from the combination of superoxide ion with 2,3-butanedione, 2,3-pentanedione, and ethyl pyruvate is consistent with the earlier observation that the nucleophilic addition of $O_2^{-}\cdot$ to carbonyl carbon must be accompanied by a viable leaving group to have a net reaction.[4] In this respect these three α-dicarbonyls are equivalent to benzaldehyde, and the $O_2^{-}\cdot$ adduct dissociates to the initial reactants (eq 3).



$$\mathrm{RC(=O)C(=O)R'} + O_2^{-}\cdot \rightleftharpoons \mathrm{RC(O^-)(O\!-\!O\cdot)C(=O)R'} \qquad (3)$$

The keto carbonyl of ethyl pyruvate has the same limitation, but the ester carbonyl should be hydrolyzed by $O_2^{-}\cdot$ at a rate that is roughly the same as that for ethyl acetate (k_2, 1.1 × 10^{-2} $M^{-1}\ s^{-1}$).[4]

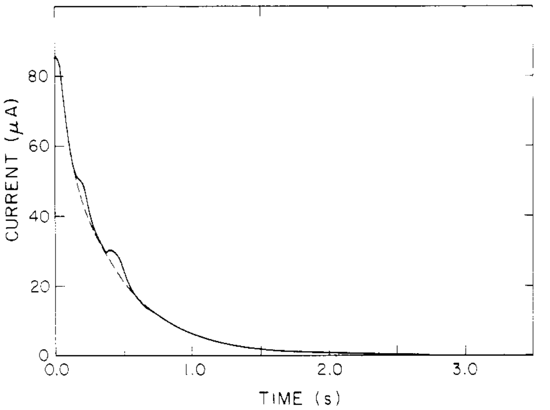


Figure 2. Decay of the anodic current for the oxidation of $O_2^{-}\cdot$ at a rotated Pt-disk electrode (1000 rpm, 0.34 cm^2) after the addition of ethyl pyruvate (to give an initial concentration of 4 mM) to a 0.4 mM $O_2^{-}\cdot$ solution in DMF. The oscillations at short times were due to mixing, which required about 0.4 s. The smoothed curve conforms to a pseudo-first-order decay process (it gives a straight-line curve when replotted as an exponential function; the slope is equal to $-k_1$).

A recent study[9] has illustrated the effective Brønsted basicity of $O_2^{-}\cdot$ via its propensity to disproportionate to H_2O_2 and O_2. For example, in dimethylformamide the net reaction between O_2^{-} and phenol ($K_a = 10^{-20}$) is rapid ($k_{bi} = 10^4\ M^{-1}\ s^{-1}$) and complete (eq 4). In general, the relative

$$O_2^{-}\cdot + PhOH \rightarrow {}^{1}/_{2}H_2O_2 + {}^{1}/_{2}O_2 + PhO^- \qquad (4)$$

$$K = 10^{49}/K_a = 10^{29}$$

rates for the proton-induced disproportionation of $O_2^{-}\cdot$ are inversely proportional to the K_a values for substrates with oxo protons.

Reference to Table I indicates that the three α-dicarbonyls with α-hydrogen atoms exhibit rapid net reactions with $O_2^{-}\cdot$ and that their reaction stoichiometries, kinetics, and products are consistent with a proton-induced disproportionation of $O_2^{-}\cdot$. Via enolization these α-bicarbonyls have acidities in DMF that are roughly equal to that of phenol (see Table I). The latter reacts with $O_2^{-}\cdot$ via a disproportionation process[9] that has the stoichiometry and kinetics that are summarized in Table I; these are essentially the same as are observed for the three enolized α-dicarbonyls.

Because the product of the rapid $O_2^{-}\cdot$ enol reaction is the enolate (which hydrolyzes with trace H_2O in the workup of the product solution to give the original α-dicarbonyl), the net primary reaction is proton abstraction

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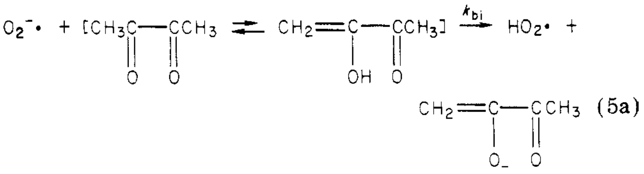
(9) Chin, D.-H.; Chiericato, G., Jr.; Nanni, E. J., Jr.; Sawyer, D. T. *J. Am. Chem. Soc.* **1982**, *104*, 1296.

by $O_2^-\cdot$ from the enol tautomer with disproportionation of $HO_2\cdot$ (eq 5 for 2,3-butanedione).

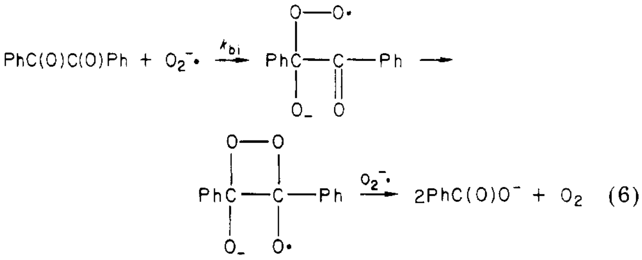


$$O_2^-\cdot + [CH_3C(=O)C(=O)CH_3 \rightleftharpoons CH_2{=}C(OH)C(=O)CH_3] \xrightarrow{k_{bi}} HO_2\cdot + CH_2{=}C(O^-)C(=O)CH_3 \quad (5a)$$

$$HO_2\cdot + HO_2\cdot \xrightarrow{fast} H_2O_2 + O_2 \quad (5b)$$

An analogous interpretation has been given for the deprotonation of 1,3-diketones by KO_2/18-crown-6 ether in benzene.[10] The resulting enolates are reported to be resistent to oxidation by O_2 and $O_2^-\cdot$.

Benzil. The absence of α-hydrogens precludes enolization of benzil (PhC(O)C(O)Ph). Hence, it does not have significant protic character and cannot induce disproportionation of $O_2^-\cdot$ via transfer of a proton. The reaction stoichiometry, kinetics, and products for the facile $O_2^-\cdot$-benzil process (Table I) are consistent with nucleophilic addition to a carbonyl carbon as the primary step, followed by cyclization on the second carbonyl carbon to give a dioxetane radical (eq 6). In the presence of excess $O_2^-\cdot$ the latter is reduced and dissociates to give two benzoate ions and O_2 (Table I). Such a dioxetane closing has precedent for the unsaturated carbons of vinyl peroxy radicals.[11] However, the present system involves a radical addition to a carbon–oxygen double bond, which is believed to be a novel process.



(6)

The chemistry for the $O_2^-\cdot$-benzil reaction appears to be analogous to that for the oxygenation by $O_2^-\cdot$ of dehydroascorbic acid (an α,β-tricarbonyl) to give threonate ion and oxalate.[6] For the latter system a mechanistic path similar to eq 6 has been proposed on the basis of the reaction stoichiometries, kinetics, and products (the rate constant (k_{bi}) in DMF is 3.3×10^4 M^{-1} s^{-1}).

The earlier suggestion[5] that $O_2^-\cdot$ reacts by electron transfer to benzil is not consistent with the respective reduction potentials in DMF (benzil, $E^{\circ\prime} \approx -1.2$ V vs. SCE; $O_2/O_2^-\cdot$, $E^{\circ\prime} \approx -0.8$ V) and the rapid reaction rate. Also, initial formation of benzil anion radical via electron transfer would lead to a diversity of products via subsequent reactions with O_2, $O_2^-\cdot$, and the media. The observed 2:1 $O_2^-\cdot$-benzil reaction stoichiometry with the exclusive quantitative production of two benzoate ions and one O_2 molecule and facile second-order kinetics are consistent with the initial nucleophilic addition to carbonyl carbon that is outlined by eq 6.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-8212299. We are grateful to Professor Julian L. Roberts, Jr. (University of Redlands) for assistance with the kinetic measurements by means of the rotated ring–disk electrode technique.

Registry No. O_2^-, 11062-77-4; 2,3-butanedione, 431-03-8; 2,3-pentanedione, 600-14-6; ethyl pyruvate, 617-35-6; benzil, 134-81-6.

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(10) Frimer, A. F.; Gilinsky-Sharon, P.; Aljadeff, G. *Tetrahedron Lett.* 1982, *23*, 1301.

(11) Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 698.

Photochemical Behavior of 2-Phenylbenzoxazole. Synthesis of 1,3-Diazetidine via the Intermolecular $[2_\pi + 2_\pi]$ Cycloaddition of Two Carbon–Nitrogen Double Bonds

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The photochemical behavior of 2-phenylbenzoxazole (1) in cyclohexane solutions is investigated. In concentrated solutions, photodimerization of 2-phenylbenzoxazole is observed ($\phi \simeq 0.08$). In dilute solutions, this reaction is no longer efficient, and only a very slow reaction with cyclohexane takes place, leading to photoaddition and photosubstitution products with a low quantum yield ($\phi < 1.5 \times 10^{-3}$). Photosensitization and quenching experiments as well as heavy-atom effects indicated that the two reactions derive from different excited states. The photodimerization occurs from the singlet excited state and the reaction with the solvent from the triplet state. Photodimer 2 is stable in the solid state at room temperature but reverts to 1 quantitatively in solution. The rate of the cycloreversion reaction can be enhanced either by catalysis or by irradiation. The activation barrier determined by UV measurements was found to be 90 kJ mol^{-1}. By use of microcalorimetric experiments, the molar enthalpy of reversion was found to be −116 kJ mol^{-1}. For application of this new system to light energy conversion, the recycling capacity of the interconvertion process as well as the heterogeneous catalysis of the thermal reversion was studied.

Although the photochemical behavior of compounds containing C=N double bonds is now being extensively investigated, it has not developed as rapidly as the photochemistry of carbonyl compounds.[1-3] The reason gen-

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