chloride was added until the blue color was discharged. The ammonia was allowed to evaporate and the residue partitioned between water (100 mL) and ether (150 mL). Standard workup of the organic phase afforded 184 mg of 3-acetyl-1,4,4-trimethylcyclopentene (**16**) ($\nu_{>=0}$ 1709 cm^{-1} and vinyl proton resonance at δ 5.22) and 1-acetyl-3,5,5-trimethylcyclopentene ($\nu_{>=0}$ 1671 cm^{-1} and vinyl proton resonance at δ 6.42), alone with contaminating diphenyl disulfide (δ 7.25, complex).

B. A mixture of **13** (292 mg, 1 mmol), zinc powder (654 mg, 10 mmol), and acetic acid (10 mL) was stirred for 20 h at room temperature. After zinc was removed by filtration, the solution was diluted with water and extracted with ether. The latter was washed and dried and solvent removed to provide 142 mg of pure **16:** ^1H NMR δ 0.97 (3 H, s), 1.24 (3 H, s), 1.75 (3 H, d, J = 1 Hz), 2.07 (3 H, s), 3.19 (1 H, m), 5.22 (1 H, m); IR (film) ν_{max} 1709 cm^{-1}; MS *m/e* 152 (M^+), 109 (base peak) 43.

C. A solution of **6** (282 mg, 1 mmol) in 5 mL of ether was slowly added to lithium dimethylcuprate (5 mmol) freshly prepared from cuprous iodide (962 mg, 5 mmol) and methyllithium (6.82 mL of 1.48 M, 10 mmol) in 20 mL of ether. After the mixture had stood overnight, it was quenched into dilute ammonium hydroxide and worked up to provide 286 mg of crude product. Kugelrohr distillation (100 °C, 7 Torr) gave 92 mg of pure **17:** ^1H NMR δ 1.7 (3 H, m), 2.15 (3 H, s), 1.87 (6 H, m), 3.05 (1 H, m), 5.47 (1 H, m); IR (film) ν_{max} 1712 cm^{-1}. Compound **17** was kept for several hours in 10 mL of 95% ethanol containing 3 drops of concentrated HCl. Dilution and workup in the usual fashion gave 82 mg of ketone **18:** ^1H NMR δ 1.38 (3 H, d, J = 7 Hz), 1.7-2.2 (7 H, complex), 2.33 (3 H, s), 6.72 (1 H, br s); IR (film) ν_{max} 1688 cm^{-1}.

Acknowledgments. We are grateful to the National Science Foundation for support of this research. Dr. Joseph F. Bieron carried out the initial synthesis and methylation of **5**.

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Effect of pH on the Behavior of Duroquinone Triplets[1]

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Abstract: The triplet state of duroquinone has a pK_a of -0.1. The protonated form interacts with benzyl alcohol and chloride ions with rate constants which are about two orders of magnitude faster than those of the neutral form. Duroquinone triplets are quenched by a variety of inorganic anions, including OH^-, for which the rate constant is 1.5×10^9 M^{-1} s^{-1}. Quenching by amines and its pH dependence have also been examined.

Introduction

The photochemistry of carbonyl compounds in the presence of potential electron donors has been the subject of numerous studies.[2,3] Several of these studies have utilized aqueous solvents,[4-8] and some have investigated the effect of acid-base equilibria of the substrates on their reactivity,[9] but the examination of the effect of pH on the behavior of excited carbonyls has been rather uncommon.[10-13] In particular, duroquinone (DQ) has been the subject of a few studies which illustrate the strong oxidizing character of its triplet state,[4,7,14-18] a property which is shared by other quinone triplets. However, the acid-base properties of the duroquinone triplet have received no attention.

In this paper we report results on the behavior of duroquinone triplets in the range of pH 12 to $H_0 - 2$. The wide variations observed in these processes reflect the reactivity of the triplet toward hydroxide ions, the acid-base properties of some substrates (e.g., amines), and the acid-base equilibrium in the triplet manifold of duroquinone.

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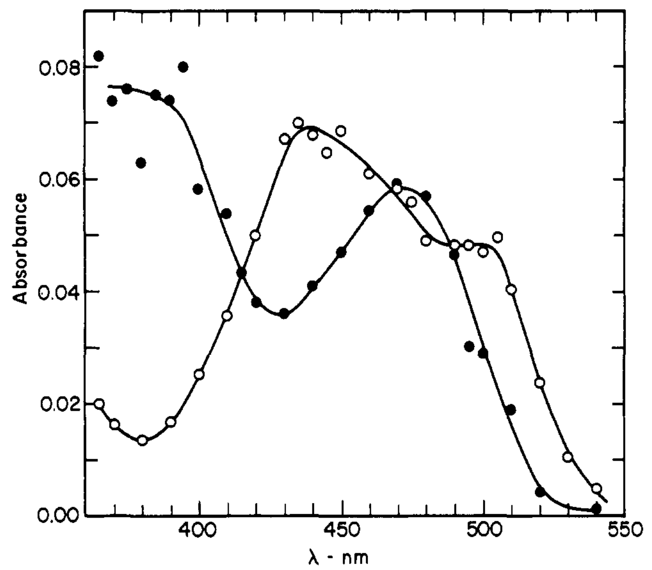


Figure 1. Absorption spectra of the duroquinone triplet: (○) neutral form; (●) protonated form.

Experimental Section

Materials. Duroquinone (Aldrich) was recrystallized twice from ethanol. Methanol (Aldrich, Gold Label) was used as received. Water was triple distilled. All other organic chemicals were either distilled or recrystallized. Inorganic anions were used as either the sodium or potassium salt (Baker Analyzed reagents). The pH was adjusted with phosphate buffers or, in the very acid limit, perchloric acid.

Sample Preparation. Unless otherwise indicated, experiments were carried out at room temperature in deaerated solutions; the solvent was a 1:4 (v/v) mixture of methanol and water and the concentration of duroquinone was typically 0.002 M. The samples were contained in Suprasil quartz cells of 3-mm optical path. In the case of the spectroscopic studies the cell was part of a flow system.

Flash Photolysis. The samples were excited with the pulses (337.1 nm, ~3 mJ, 8 ns) from a Molectron UV-400 nitrogen laser. The monitoring system consisted of a pulsed Eimac VIX-150 lamp, a high-intensity monochromator, and an RCA-4840 photomultiplier tube. The rise time of the detection system was <2 ns. Further details have been given elsewhere.[19]

Results and Discussion

The triplet state of DQ (^{T}DQ) was monitored through its characteristic intense absorption spectrum, which at pH >1 agrees well with that reported in the literature[7,14,16,17] (Figure 1). At pH <0[20] the triplet state shows a different spectrum, also illustrated in Figure 1. The decay of the triplet is faster in strong acid than at pH >0 (e.g., $\tau_T \sim 0.3$ μs at pH -0.8 and 1.9 μs at pH 0.7). The difference cannot be attributed to interactions with methanol since the same effect can be observed in pure water and in 2-propanol-water (1:4). Some effect from potential impurities in the perchloric acid is possible in the very acid limit. Figure 2 shows a plot of the absorption at 390 nm (where the two species absorb quite differently) vs. pH, from which we obtain a pK_a value of -0.1 for the duroquinone triplet.

The same pK_a value can be obtained from a study of the rate of interaction of duroquinone triplets with a substrate as a function of pH. Chloride ions were found to be suitable for this purpose. In these experiments the lifetime of the duroquinone triplets was monitored at 490 nm as a function of chloride ion concentration at several pH values. Figure 3 illustrates the plots of τ_T^{-1} vs. [Cl$^-$], while the inserts show typical time profiles. The slopes of these plots correspond to the rate constants of interaction of ^{T}DQ and ^{T}DQH$^+$ with Cl$^-$.[21] These rate constants have been plotted against pH in Figure 2 (left scale) and the pK_a value derived from this plot is in good agreement with that calculated from the spectral changes. Chloride ions are found to quench ^{T}DQ and ^{T}DQH$^+$ with rate constants of 1×10^7 and 1×10^9 M^{-1} s^{-1}, respectively.

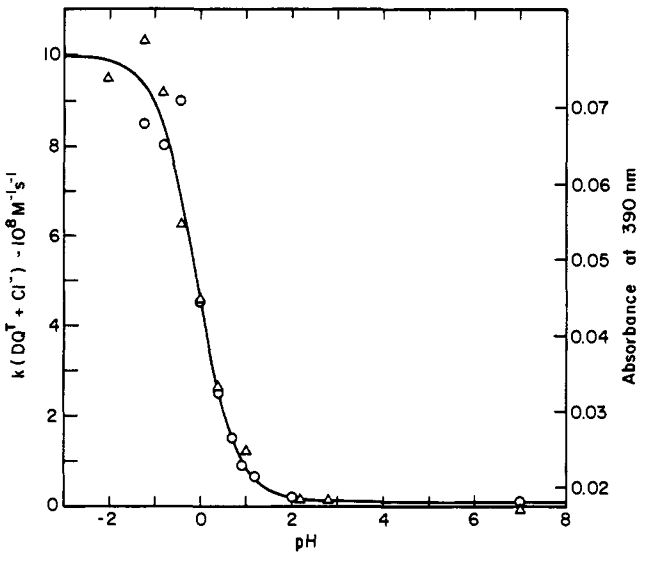


Figure 2. Effect of pH on the absorption (△) (right) and the rate constant of quenching (○) (left) of duroquinone triplet leading to the evaluation of pK_a = -0.1. The pH scale below zero represents values of H_0 adjusted with perchloric acid.

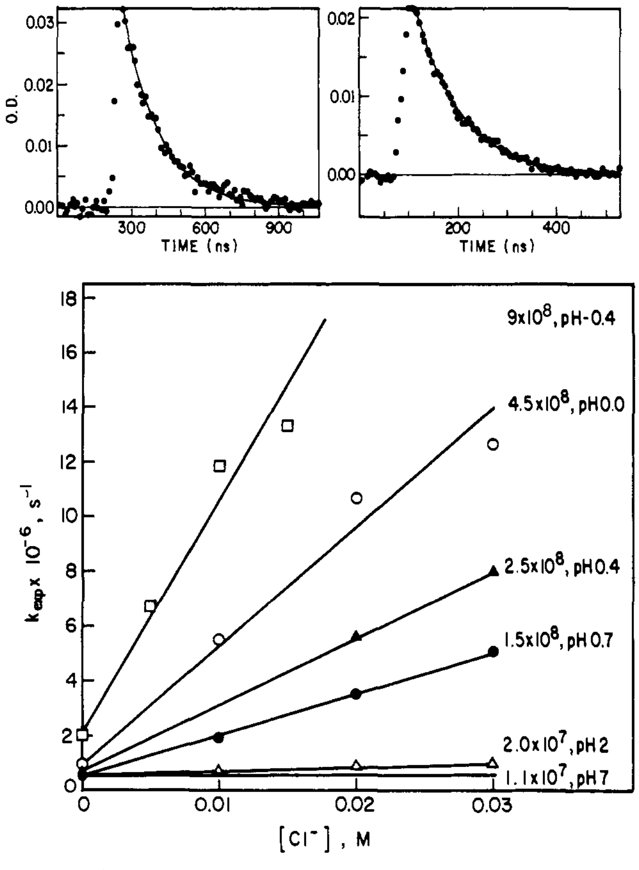


Figure 3. Plots of the pseudo-first-order rate of quenching vs. [Cl$^-$] at different pH values. The two traces at the top show typical time profiles of absorption (left, 445 nm, solution containing 0.5 M Cl$^-$ at pH 7; right, 490 nm, solution containing 0.01 M Cl$^-$ at pH 0.8).

The efficient interaction of inorganic anions with ^{T}DQ is a rather common process and also takes place with bromide, iodide, and hydroxide ions. The latter is responsible for the short triplet lifetime of ^{T}DQ in basic media (e.g., $\tau_T \sim 60$ ns at pH 12). Table I shows a summary of quenching rate constants; they follow the order of the oxidation potentials,

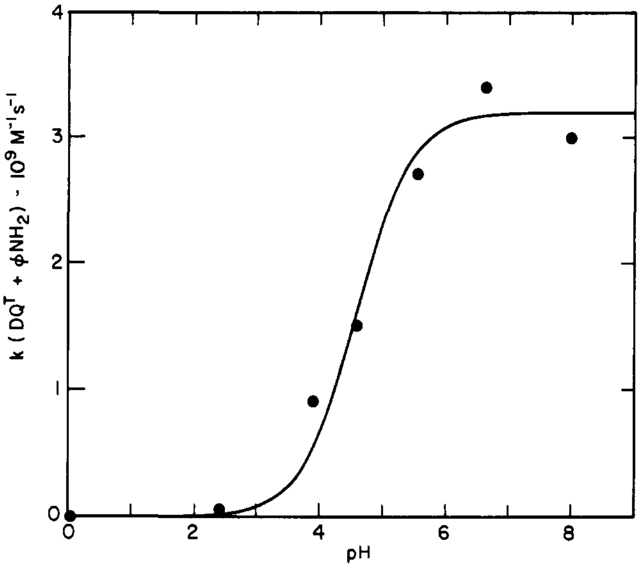


Figure 4. Effect of pH on the rate of quenching by aniline.

suggesting the involvement of charge transfer. We have observed that triplet quenching by inorganic anions did not lead to detectable formation of semiquinone radicals; only in the case of OH^- do we observe the formation of $DQ^{-}\cdot$ with about 10% efficiency. This yield of $DQ^{-}\cdot$ does not require the presence of methanol (used as a cosolvent). Experiments with water at pH 11.6 gave similar results, and the identity of $DQ^{-}\cdot$ was further verified by ESR. The quenching of ^{T}DQ by halide ions is not the result of a heavy-atom effect as shown experimentally by the inefficiency of Cs^+ as a quencher. We conclude that the formation of a charge-transfer complex is followed predominantly by a back reaction rather than complete electron transfer.

The increase in reactivity of the triplet state upon protonation was also observed in its quenching by benzyl alcohol, where the rate constants are 8×10^5 M^{-1} s^{-1} at pH 7 and 2.7×10^7 M^{-1} s^{-1} at pH -2. This pattern of reactivity is likely to be quite general, though the measurements in strong acid tend to be rather difficult as a result of the short triplet lifetime, making the generality of the process somewhat difficult to confirm.

Another question related to the effect of pH upon triplet reactivity is that of the interaction with protonated amines as compared with that of the basic form.[2,3,9] We find that the reactivity of simple monoamines (see Table I) drops to insignificant values upon protonation. For example, aniline quenches ^{T}DQ with a rate constant of 3×10^9 M^{-1} s^{-1}, similar to that determined previously for diphenylamine.[14] As the pH is decreased the quenching by aniline becomes slower and reaches $\sim 10^7$ M^{-1} s^{-1} at pH 0. The dependence of k_q on pH (Figure 4) leads to a pK_a value of 4.6, in agreement with the pK_a of aniline in the literature,[22] and clearly points to protonation of the amino group as responsible for the drop in reactivity. Further increase in the acidity to H_0 -2 does not show any increase in the reactivity of the anilinium ion, indicating that it is not efficiently oxidized even by the protonated duroquinone triplet.

A similar trend was observed with aliphatic amines. Judging from the rate of quenching by trimethylamine and α-alanine in basic solutions, aliphatic amines are about an order of magnitude less reactive than the aromatic ones. A strong substituent effect on their reactivity can also be seen from the results in Table I.[23] Substituting methylamine with a sulfonate or a cyano group decreases the rate constant by approximately one and two orders of magnitude, respectively. All the above aliphatic amines show a large decrease in reactivity when the pH is dropped below their respective pK_a values. The protonated amines react about two orders of magntiude more slowly than their basic forms, in agreement with previous data.[9] Ammonia has a similar behavior, i.e., $k_q = 3 \times 10^6$ M^{-1} s^{-1} for NH_3, but $<10^5$ M^{-1} s^{-1} for NH_4^+ (Table I). Of all the amines examined only Dabco (diazabicyclooctane) shows some reactivity even when it is diprotonated, and yields durosemiquinone quite efficiently.

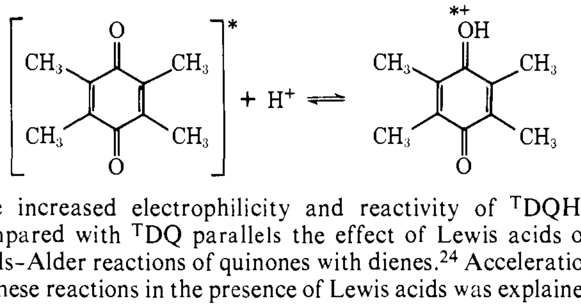
Table I. Rate Constants for Quenching of Duroquinone Triplets

triplet species	quencher	pH	k_q/M^{-1} s^{-1}
^{T}DQ	Cl^-	7	1×10^7
$^{T}DQH^+$	Cl^-	-2	1×10^9
^{T}DQ	OH^-	10–12	1.5×10^9
^{T}DQ	Br^-	7	4×10^9
^{T}DQ	I^-	7	9×10^9
^{T}DQ	$C_6H_5CH_2OH$	7	8×10^5
$^{T}DQH^+$	$C_6H_5CH_2OH$	-2	2.7×10^7
$^{T}DQH^+$	$(CH_3)_2CHOH$	-2	$<10^5$
^{T}DQ	$C_6H_5NH_2$	8	3×10^9
^{T}DQ	$C_6H_5NH_3^+$	2.4	5×10^7
$^{T}DQH^+$	$C_6H_5NH_3^+$	-2	$\leqslant 10^7$
^{T}DQ	$(CH_3)_3N$	11	3×10^8
^{T}DQ	$(CH_3)_3NH^+$	7	$\leqslant 10^7$
^{T}DQ	$(C_2H_5)_3NH^+$	2	$\leqslant 10^6$
$^{T}DQH^+$	$(C_2H_5)_3NH^+$	-2	$\leqslant 10^6$
^{T}DQ	Dabco[a]	2.1	1.3×10^7
^{T}DQ + $^{T}DQH^+$	Dabco[a]	0	3×10^6
^{T}DQ	$CH_3CH(CO_2^-)NH_2$	10.2	1×10^8
^{T}DQ	$CH_3CH(CO_2^-)NH_3^+$	5.4	$\sim 5 \times 10^5$
^{T}DQ	$^-O_3S\,CH_2NH_2$[b]	7.2	2.7×10^7
^{T}DQ	$NCCH_2NH_2$ + $NCCH_2NH_3^+$[c]	5.3	$\sim 1 \times 10^6$
^{T}DQ	$CNCH_2NH_3^+$	3.3	$<10^5$
^{T}DQ	NH_3	10–11	3×10^6
^{T}DQ	NH_4^+	4–5	$<10^5$

[a] Diazabicyclooctane. This compound is doubly protonated at this pH. [b] pK_a = 5.8. [c] pK_a = 5.3.

Experiments in strong acid show that even $^{T}DQH^+$ does not react significantly with protonated amines.

Finally, we come to the question of the site of reaction in $^{T}DQH^+$. Since this ion reacts about two orders of magnitude more rapidly than the neutral ^{T}DQ it is reasonable to assume that reaction takes place at the protonated site, i.e., that this site is the stronger electrophile, or that the acid-base equilibrium can be formally represented by



The increased electrophilicity and reactivity of $^{T}DQH^+$ compared with ^{T}DQ parallels the effect of Lewis acids on Diels-Alder reactions of quinones with dienes.[24] Acceleration of these reactions in the presence of Lewis acids was explained by complexation with the quinone, i.e., formation of the acidic species, which then reacts more rapidly.[24] Quenching of ^{T}DQ by a charge-transfer mechanism is expected to accelerate with increasing electrophilicity as it actually does in the case of Cl^- and benzyl alcohol upon going from ^{T}DQ to $^{T}DQH^+$. Quenching by a hydrogen-abstraction mechanism may not necessarily take place more rapidly with the protonated form.

The pK_a of ^{T}DQ is 7 units higher than that of the ground-state molecule.[25] This pK_a is somewhat similar to that of the protonation of *p*-hydroxyphenoxyl radical.[26] This comparison indicates some similarity between the quinone triplet and the phenoxyl radical which parallels that between alkoxyl radicals and ketone triplets.[3]

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Regioselectivity in the Addition of Singlet and Triplet Carbenes to 1,1-Dimethylallene. A Probe for Carbene Multiplicity

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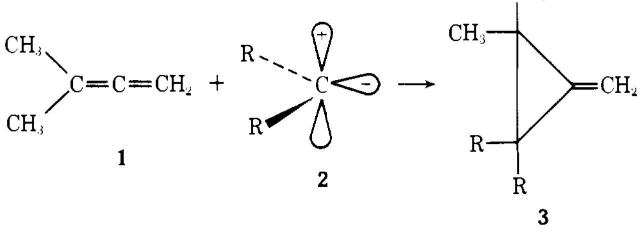
Abstract: Singlet carbenes add preferentially to the more substituted bond of 1,1-dimethylallene (**1**), to give methylenecyclopropanes **3** as the major product. In contrast, many triplet carbenes add with differing regioselectivity, giving the thermodynamically preferred isopropylidenecyclopropanes, **10**. A mechanism involving an intermediate trimethylenemethane, **8**, has been suggested for this product. This regioselectivity probe has been applied to diphenylcarbene and the nitrophenylcarbenes and suggests a reaction occurring through the triplet state in direct photolysis of the diazoprecursors. Benzophenone-sensitized photolysis of ethyl phenyldiazoacetate (**32**) in **1** gave the methylenecyclopropane **33** as the major product. This fact, along with the observed largely stereospecific addition to *cis*-2-butene, suggests a singlet reacting carbene despite the initially generated triplet state. Singlet monoarylcarbenes add to **1** with increasing selectivity as a function of electron-donating ability of the substituent. This feature implies that electron-donor groups stabilize the singlet state. Benzophenone-sensitized decomposition of aryldiazomethanes, **40**, also gave large amounts of methylenecyclopropanes **41**. This was interpreted in terms of predominant singlet reaction despite the initially generated triplet state. Even in the case of electronegative substitution in **40**, singlet pathways remained important. These results suggest that the solution chemistry of triplet phenylcarbene is quite different from that of the matrix-generated triplet.

The chemical literature over the past 25 years contains vast amounts of information on divalent carbon intermediates (carbenes).[2] The possibility of dual multiplicities was recognized quite early in the history of carbene chemistry.[3] To date, the primary method for distinguishing carbene multiplicities has been based on the Skell hypothesis, that is, singlets will add to olefins in a stereospecific fashion while triplet additions will be stepwise and give loss of stereospecificity.[3]

Scheme I



We have been interested in the mechanistic and synthetic aspects of the addition of carbenes to 1,1-dimethylallene (**1**), as a preparative entry into substituted methylenecyclopropanes.[4] From a mechanistic standpoint, it is felt that a singlet electrophilic carbene, **2**, should add in a concerted manner preferentially to the more substituted bond of **1** to give the methylenecyclopropane **3** as in Scheme I. This prediction is supported by the addition of dihalocarbenes to **1** in which methylenecyclopropanes **3** (R = halogen) are the sole products.[5] Our studies[4] have shown that monoarylcarbenoids also add predominantly to the more substituted bond of **1**. These carbenoids are not as selective as the dihalocarbenes and small, but significant, amounts of the isopropylidenecyclopropanes resulting from the addition to the less substituted bond of **1** are formed.

In contrast, we have observed that triplet methylcarboethoxycarbene, generated by the benzophenone-sensitized decomposition of ethyl diazopropionate (**4**), affords only the

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