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Generation and Absolute Reactivity of an Aryl Enol Radical Cation in Solution

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Laser flash photolysis of 1-bromo-1-(4-methoxyphenyl)acetone in acetonitrile leads to the formation of the α-acyl 4-methoxybenzyl radical that under acidic conditions rapidly protonates to give detectable amounts of the radical cation of the enol of 4-methoxyphenylacetone. This enol radical cation is relatively long-lived in acidic acetonitrile ($\tau \approx 200$ μs), which is on the same order of magnitude as the radical cations of other 4-methoxystyrene derivatives. Rate constants for deprotonation of the radical cation and the acid dissociation constant for the enol radical cation were also determined using time-resolved absorption spectroscopy. Deprotonation is rapid, taking place with a rate constant of 3.9×10^6 s^{-1}, but the enol radical cation is found to be only moderately acidic in acetonitrile having a p$K_a = 3.2$. The lifetime of the enol radical cation was also found to be sensitive to the presence of oxygen and chloride. The sensitivity toward oxygen is explained by oxygen trapping the vinyloxy radical component of the enol radical cation/vinyloxy equilibrium, while chloride acts as a nucleophile to trap the enol radical cation.

Introduction

While a considerable body of data is available on enol radical cations in the gas phase,[1] much less is known about the chemistry of these reactive species in solution. This scarcity of information is largely due to the thermodynamic and kinetic instability of most simple enols, which would otherwise be ideal precursors with which to generate enol radical cations. Data that are available come largely from studies by Schmittel[2−6] who showed that enol radical cations are produced by chemical or electrochemical oxidation of stable, sterically hindered enols, as well as by selective oxidation of enols available in solution at very low concentrations as the unstable tautomer of ketones. These methods have led to information about the electrochemical and thermodynamic properties of some enol radical cations, as well as some data on their reactivity in solution.[3]

While fast scanning cyclic voltammetry has been used successfully to detect radical cations of stable triaryl enols,[4] chemical or electrochemical techniques are not particularly well-suited for the direct detection of short-lived enol radical cations.[7] A fast reaction technique such as laser flash photolysis should be more suitable provided that the radical cations of interest can be produced photochemically. Photochemical methods such as photoionization or photoinduced electron transfer commonly used in laser studies to generate alkene radical cations in solution[8,9] require a sufficiently concentrated solution of the neutral alkene. For enol radical cations, the relative instability of most enols means this requirement is not generally satisfied, and an alternative method is needed. One possibility is to generate photochemically the conjugate base of an enol radical cation, such as a vinyloxy radical, in a solution that is sufficiently acidic to generate the radical cation by protonation. Vinyloxy radicals could in principle be produced by hydrogen-atom transfer from the enolic OH of the enol to a photogenerated hydrogen-atom acceptor such as the *tert*-butoxyl radical,[10] Scheme 1 (path a). This again, however, requires a significant concentration of the unstable enol, and thus has no advantage over a direct irradiation or photosensitized method. On the other hand, vinyloxy radicals can also be described in terms of their α-acyl radical resonance form which can be produced from appropriate, stable precursors such as α-haloketones by photohomolysis,[11,12] Scheme 1 (path b). Protonation at oxygen would then give the enol radical cation.

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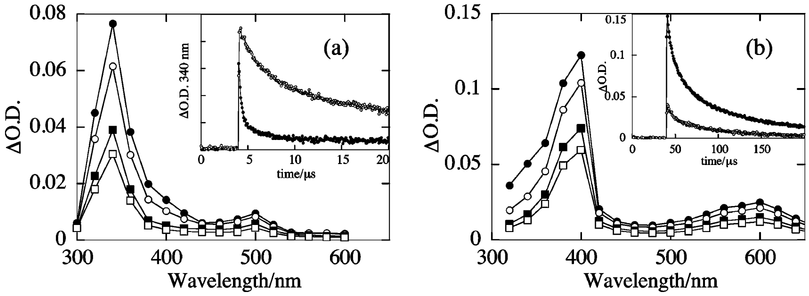
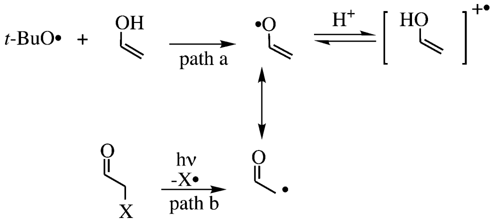
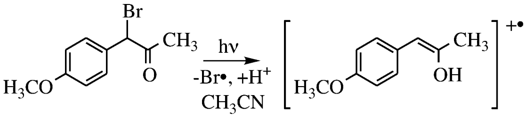


FIGURE 1. (a) Transient absorption spectrum (●) 0.16 *μ*s, (○) 1.6 *μ*s, (■) 7.2 *μ*s, and (□) 12 *μ*s after 266-nm laser irradiation of 1-bromo-1-(4-methoxyphenyl)acetone in N_2-saturated acetonitrile (22 ± 1 °C). Inset shows the decay trace at 340 nm under (●) N_2- and (○) O_2-saturated conditions. (b) Transient absorption spectrum (●) 0.16 *μ*s, (○) 1.6 *μ*s, (■) 7.2 *μ*s, and (□) 12 *μ*s after 266-nm laser irradiation of 1-bromo-1-(4-methoxyphenyl)acetone in N_2-saturated acetonitrile with 0.10 M $HClO_4$ (22 ± 1 °C). Inset shows decay traces at (●) 400 and (○) 600 nm under the same conditions.

SCHEME 1



The results described in the present work show that the latter strategy can be used to photochemically convert 1-bromo-1-(4-methoxyphenyl)acetone to the radical cation of the enol of 4-methoxyphenylacetone, eq 1.



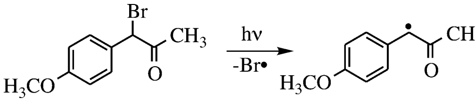
(1)

Generation of the enol radical cation using this method allows for the measurement of several fundamental properties of this reactive intermediate, including its absolute lifetime in solution, and acid dissociation constant. The present work also represents the first direct spectroscopic detection of the radical cation of an unstable enol in solution.

Results

Figure 1a shows the transient absorption spectra generated upon 266-nm irradiation of 1-bromo-1-(4-methoxyphenyl)acetone in nitrogen-saturated acetonitrile. The spectra are characterized by a single transient with a strong absorption maximum at 340 nm and a much weaker band at 500 nm. This transient is quite long-lived under nitrogen-saturated conditions and decays in a second-order manner over several tens of microseconds. In oxygen-saturated acetonitrile, the transient decays much more quickly with a first-order rate constant of 3.3×10^6 s^{-1}. Such oxygen quenching is consistent with the transient being a radical species, but the magnitude of the quenching is somewhat smaller than observed for benzylic radicals that typically decay in oxygen-saturated acetonitrile ($[O_2] \approx 9.0$ mM)[13] with observed rate constants near 10^8 s^{-1}. The decay is unaffected by the presence of nucleophiles such as azide or chloride, indicating that the transient is not the α-keto carbocation that might be generated by photoheterolysis of the carbon−bromine bond.

These results are all consistent with identification of the transient as the α-acyl 4-methoxybenzyl radical generated by photohomolysis of the C−Br bond, eq 2.



(2)

In particular, the observations that the transient is not quenched by nucleophiles, but is sensitive to oxygen are expected for a radical species. Furthermore, the reduced reactivity of the transient toward oxygen is similar to that observed for other α-keto benzyl radicals.[11] The possibility that the transient is the α-bromo-4-methoxybenzyl radical that would be formed by α-cleavage of the precursor must also be considered; however, previous literature reports provide strong evidence that homolytic cleavage of the C−Br bond is the main reaction upon irradiation α-haloketones in solution.[11,12] For example, a study of the photochemistry of 1,3-dibromo-1,3-diphenylacetone, a precursor that is quite similar to that used in the present work, demonstrates convincingly that the cleavage of the C−Br bond dominates over the possible α-cleavage process.[12]

In acidic (0.10 M $HClO_4$), nitrogen-saturated acetonitrile, the 340 nm band is no longer observed and in its place are two new absorption bands, one strong band at 400 nm and a second weaker band at 600 nm, Figure 1b. These two bands show identical kinetic behavior, decaying slowly in a second-order manner over a time period of approximately 200 *μ*s. The identical kinetic behavior indicates that the absorption spectrum represents the presence of a single transient species possessing two absorption bands. The absorption spectrum is very similar to that previously observed for 4-methoxy substituted styrene radical cations, which are characterized by one strong absorption band near 380 nm and a second weaker one near 600 nm.[8,9] The spectrum is especially similar to the radical cation of 1-(4-methoxyphenyl)-2-methyl-1-propene which has two methyl groups attached to the *β*-position of the oxidized carbon−carbon double

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[13] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

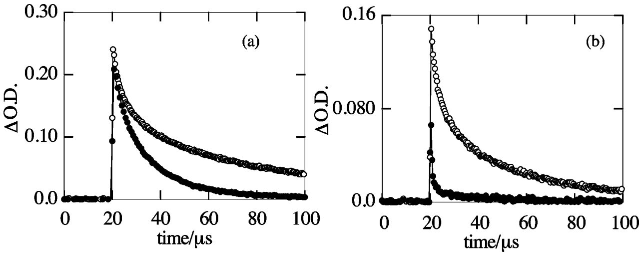
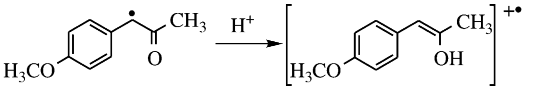


FIGURE 2. Time-resolved changes at 400 nm upon 266-nm laser irradiation of 1-bromo-1-(4-methoxyphenyl)acetone in acetonitrile with (a) 0.10 M $HClO_4$ and (b) 0.001 M $HClO_4$ under (○) N_2-saturated and (●) O_2-saturated conditions.

bond.[14] Thus, on the basis of the similarity of the absorption spectrum obtained under acidic conditions with the absorption spectra of 4-methoxystyrene radical cations, together with the requirement that acidic conditions are needed to observe the spectrum, the transient generated upon laser irradiation of 1-bromo-1-(4-methoxyphenyl)acetone is assigned to the radical cation of the enol of 4-methoxyphenylacetone, eq 3.



(3)

In oxygen-saturated 0.10 M $HClO_4$ in acetonitrile, the bands at 400 and 600 nm assigned to the enol radical cation are still observed with no significant decrease in intensity. Oxygen does have an effect on the rate constants, with the enol radical cation now decaying in a first-order manner with an observed rate constant of 7.8×10^4 s^{-1}, Figure 2a. The effect of oxygen was also determined in a less acidic solution using 0.001 M $HClO_4$ in acetonitrile. Under these conditions, the 400 and 600 nm bands are still observed, but oxygen now has a much more dramatic effect on the decay of these bands with the rate constant for decay increasing to 2.5×10^6 s^{-1}, Figure 2b.

As shown in Figure 3a, only a small decrease in the yield of the radical cation as measured by the maximum optical density at 400 and 600 nm after the laser pulse is observed as the concentration of the $HClO_4$ is lowered from 0.10 to 0.01 M. Further decreases in acid concentration to 10^{-4} M $HClO_4$ result in a substantial decrease in radical cation yield, and at still lower concentrations almost no radical cation is observed. Over the same acid concentration range, the maximum optical density at 340 nm moves in the opposite direction and increases upon going from the higher to the lower acid concentrations. The shape of this increase is similar to the decrease observed at 400 and 600 nm.

At $HClO_4$ concentrations of 0.10 and 0.01 M, the radical cation is fully formed promptly within the laser pulse, indicating that formation of the radical cation takes place with a rate constant greater than ca. 5×10^7 s^{-1}. At lower acid concentrations between 0.1 and 0.5 mM $HClO_4$, a distinct time-resolved formation of the radical cation can be observed, Figure 3b. Over this range, the rate constants for growth of the enol radical cation increase in a linear manner with respect to increasing acid concentration, Figure 3c. Linear least-squares analysis gives a slope of $(1.3 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1} and an intercept of $(3.9 \pm 0.3) \times 10^6$ s^{-1}.

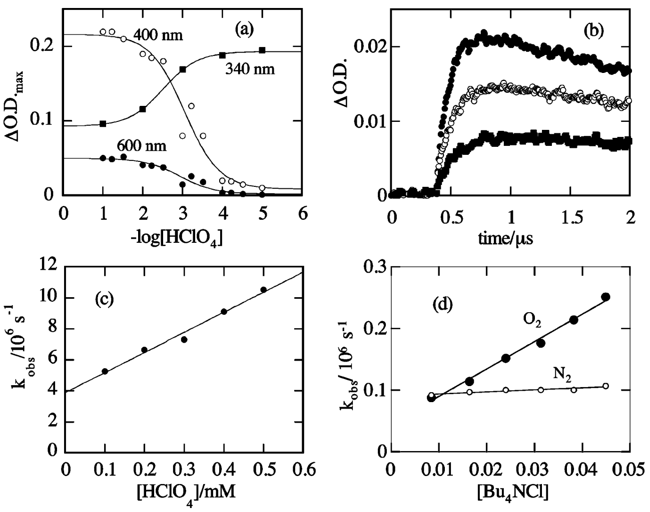


FIGURE 3. (a) Maximum optical density at (○) 400, (●) 600, and (■) 340 nm upon 266-nm irradiation of 1-bromo-1-(4-methoxyphenyl)acetone in N_2-saturated acetonitrile. The solid lines are lines-of-best-fit obtained using eq 5 (see text). (b) Time-resolved absorption changes at 600 nm upon 266-nm laser irradiation of 1-bromo-1-(4-methoxyphenyl)acetone in (■) 0.1 mM, (○) 0.2 mM, and (●) 0.4 mM $HClO_4$ in N_2-saturated acetonitrile. (c) Relationship between observed rate constants for growth of the radical cation at 600 nm and concentration of $HClO_4$ in N_2-saturated acetonitrile. (d) Relationship between observed rate constant for the decay of the enol radical cation at 600 nm and the concentration of $(C_4H_9)_4NCl$ in (○) N_2- and (●) O_2-saturated acetonitrile. All results obtained at 22 ± 1 °C.

Figure 3d shows the relationship between the decay of the enol radical cation in 0.10 M $HClO_4$ in acetonitrile in the presence of chloride ion under N_2- and O_2-saturated conditions. The radical cation decay is unaffected by chloride ion concentration in N_2-saturated solution, but does increase in the O_2-saturated solution. Linear least-squares analysis of data obtained in the presence of air gives a second-order rate constant for reaction with chloride of 4.5×10^6 M^{-1} s^{-1}.

Discussion

Several substituted styrene radical cations have been studied in acetonitrile using time-resolved laser techniques, and in each case, the radical cations showed distinctive UV-vis absorption spectra characterized by a strong absorption band near 360−400 nm and a second weaker band near 600 nm.[8,9,14] Slight variations in the absorption maxima and the relative intensity of the two bands as a function of substituent have been observed, with groups attached to the β-carbon typically pushing the maximum at lower wavelengths closer to 400 nm. Overall, the absorption spectrum of the transient obtained upon laser irradiation of 1-bromo-1-(4-methoxyphenyl)acetone in acidic acetonitrile possesses all of these features, which leads us to identify the transient as the radical cation of the enol of 4-methoxyphenylacetone.

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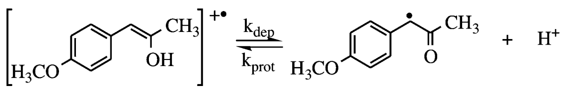
The sensitivity of the maximum absorption of the transient at 400 and 600 nm as a function of acid content is also consistent with its identification as the enol radical cation, and can be attributed to changes in the equilibrium concentration of the radical cation and its conjugate base, the vinyloxy radical, eq 4. Thus, at high concentration of acid, the equilibrium is shifted to the side of the radical cation, and the intensity of the absorption at 400 and 600 nm is maximized. At lower acid concentrations, the radical becomes the dominant species and absorption due to the enol radical cation is diminished.



(4)

If the assumption is made that the intensity of the absorption in 0.10 M $HClO_4$ represents a situation where the equilibrium is shifted completely to the side of the radical cation ($Abs_{100\%RC}$), absorption measurements made at 400 or 600 nm as a function of acid content, $Abs_{x\%RC}$, can be treated using eq 5 to determine the acidity constant, K_a, for the enol radical cation.

$$\mathrm{Abs}_{x\%\mathrm{RC}} = \mathrm{Abs}_{100\%\mathrm{RC}}\frac{[\mathrm{H}^+]}{[\mathrm{H}^+] + K_a} \tag{5}$$

As shown in Figure 3a, the decrease in absorption at 400 and 600 nm as a function of decreasing acid concentration fit well to this expression. Nonlinear least-squares fitting of data to eq 5 gave an acid dissociation constant, $K_a = (8.8 \pm 2.0) \times 10^{-4}$ M, or $pK_a = 3.1 \pm 0.2$, for the enol radical cation/vinyloxy radical equilibrium.

A second method for determining the acidity of the enol radical cation is from the relationship between the observed rate constant for enol radical cation formation and acid concentration. Since the formation of the radical cation represents the formation of the enol radical cation/vinyloxy radical equilibrium state, the observed rate constant for formation of the radical cation is the sum of the rate constants for protonation, k_{prot}, and deprotonation, k_{dep}, $k_{obs} = k_{dep} + k_{prot}[H^+]$. According to this expression, the relationship between the observed rate constants and the concentration of acid should be linear, with the slope corresponding to the rate constant for protonation of the radical, and the intercept giving the deprotonation rate constant. Thus, a value of the rate constant for deprotonation of $k_{dep} = (3.9 \pm 0.3) \times 10^6$ s^{-1} is obtained from the intercept of the plot shown in Figure 3c, and a protonation rate constant of $k_{prot} = (1.3 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1} can be obtained from the slope. The ratio of these values then leads to the acid dissociation constant for the enol radical cation in acetonitrile, $K_a = (3.0 \pm 0.3) \times 10^{-4}$ M, or $pK_a = 3.5 \pm 0.1$. This value is somewhat smaller than the K_a value measured above using the absorption data, presumably due to systematic errors in the two different methods used to determine K_a. An average of the two independent determinations gives an acidity constant $pK_a = 3.2 \pm 0.2$ for the radical cation of the 4-methoxyphenylacetone enol in acetonitrile.

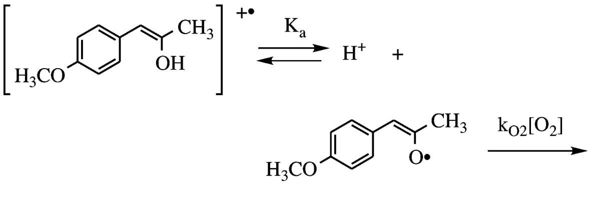
Acidity constants using a thermodynamic cycle based on enol oxidation potentials and enol OH bond dissociation energies have been estimated for 2,2-diaryl and 1,2-diarylethenol radical cations in acetonitrile.[15] Acidity constants for the radical cations of these stable enols range from $pK_a = 5.7$ for the 2,2-dimesitylethenol radical cation to $pK_a = 1.3$ for the 1,2-dimesityl-2-methylethenol radical cation. The pK_a of 3.2 for the radical cation of the enol of 4-methoxyphenylacetone measured in the present work lies well within this range of acidity constants, which provides added confidence that the processes responsible for the effects of acid concentration on the transient yields are related to the radical cation-vinyloxy radical equilibrium.

The rate constant for deprotonation, $k_{dep} = 3.9 \times 10^6$ s^{-1}, is also consistent with the previous estimates that the radical cation of the 2,2-dimesitylethenol deprotonates with a rate constant greater than 10^5 s^{-1} at room temperature.[15] Deprotonation rate constants for 1-aryl-2,2-dimesitylethenol radical cations in acetonitrile are considerably slower ranging from 2.5×10^3 to 1.3×10^4 s^{-1} depending on the nature of the aryl group.[15] The extra aryl substituent in these enol radical cations is thought to provide considerable stabilization to the radical cation, thus decreasing their deprotonation rate constants.

The lifetime of the radical cation of the enol of 4-methoxyphenylacetone is quite long in nitrogen-saturated acetonitrile, decaying in an approximately second-order manner over 200 μs. This long lifetime was not entirely unexpected. Under the acidic conditions used in this work, deprotonation, which otherwise would be the primary mode of decay, is not a reaction pathway that leads to rapid consumption of the radical cation. The enol radical cation would then be expected to behave in a manner similar to other 4-methoxystyrene radical cations. Indeed, the decay of the enol radical cation under nitrogen-saturated conditions is much like that previously observed for the anethole radical cation, which also decays in a second-order manner over a time period of 100 μs in acetonitrile.[9]

On the other hand, previous studies with other 4-methoxystyrene radical cations have shown that these intermediates tend to be largely unreactive toward oxygen, but highly reactive toward anionic nucleophiles such as chloride ion.[8,9] The opposite situation is observed in the present work, with the decay of the radical cation of the 4-methoxyphenylactone enol appearing to be sensitive to oxygen concentration, but insensitive to the presence of chloride except under oxygenated conditions.

These unusual observations can be attributed to the unique properties of the enol radical cation as compared to other styrene radical cations. In the case of oxygen quenching, the increased rate constant for the decay of the radical cation is caused by the rapid equilibrium between the enol radical cation and its conjugate base, the vinyloxy radical. Thus, once the enol radical cation/vinyloxy radical equilibrium is established, the addition of oxygen will consume the vinyloxy radical, eq 6. In an attempt to maintain the equilibrium, the enol radical cation will also be consumed by rapid deprotonation to the vinyloxy radical.



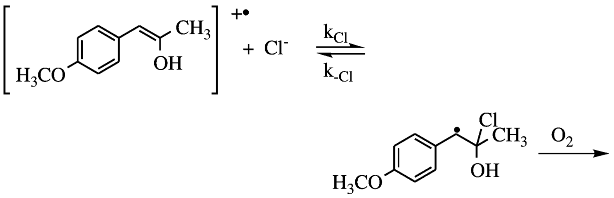
(6)

The rate law that describes this situation, eq 7, predicts that the observed quenching by oxygen should be weak at high concentrations of acid, but more significant at low acid concentrations.

$$k_{\mathrm{obs}}{}^{\mathrm{O_2}} = \frac{k_{\mathrm{o_2}}[O_2]K_{\mathrm{a}}}{[\mathrm{H^+}] + K_{\mathrm{a}}} \tag{7}$$

The behavior shown in Figure 2 matches closely that predicted by eq 7: in 0.10 M $HClO_4$ in acetonitrile, the observed rate constant of 7.8×10^4 s^{-1} for the decay of the radical cation in the presence of oxygen is considerably slower than the observed rate constant of 2.5×10^6 s^{-1} obtained in O_2-saturated acetonitrile at lower, 0.001 M $HClO_4$, acid concentration.

A somewhat similar explanation can be offered for the observation that the radical cation reacts with chloride under oxygenated conditions, but not under nitrogen-saturated conditions. It has previously been shown[16] that 1-arylethyl radicals bearing a chloride leaving group on the carbon adjacent to the radical center, such as radicals produced by addition of a nucleophile to an alkene radical cation, are prone to rapid dissociation of the leaving group to regenerate the radical cation. Dissociation of the leaving group is greatly accelerated by the presence of electron-donating groups, particularly by groups attached to the carbon adjacent to the radical center.[16] The benzylic radical produced by addition of chloride to the enol radical cation bears both a methyl group and a strongly electron-donating hydroxy group that should greatly accelerate the dissociation of chloride, eq 8.



(8)

If these substituents enhance the rate constant for loss of chloride from the radical, $k_{-\mathrm{Cl}}$, to the point where dissociation is more rapid than addition of chloride, $k_{\mathrm{Cl}}[\mathrm{Cl}^-]$, no acceleration in the rate of decay of the radical cation would be observed. However, the situation changes in the presence of oxygen. Under these conditions, oxygen can competitively trap the radicals produced by addition of chloride to the radical cation, thus reducing the fraction of radicals that return to the radical cation. Thus, the addition of oxygen provides a new reaction pathway for the consumption of the radical as well as the radical cation.

If dissociation is more rapid than trapping of the radical by oxygen, the rate constant of 4.5×10^6 M^{-1} s^{-1} determined from the slope of the quenching plot, Figure 3d, represents the combination of rate constants shown in eq 9.

$$k = \frac{k_{\mathrm{Cl}}}{k_{-\mathrm{Cl}}} k_{\mathrm{O_2}}[\mathrm{O_2}] = 4.5 \times 10^6\ \mathrm{M^{-1}\ s^{-1}} \tag{9}$$

A value for $k_{\mathrm{O_2}}[\mathrm{O_2}] \approx 9 \times 10^7$ s^{-1} can be estimated using the assumption that the benzylic radical is quenched at the diffusion limit by oxygen ($k_{\mathrm{O_2}} \approx 1 \times 10^{10}$ M^{-1} s^{-1}) together with the concentration of oxygen in oxygen-saturated acetonitrile ($[\mathrm{O_2}] \approx 9$ mM).[13] Thus, the ratio of the rate constants for addition and loss of chloride, $k_{\mathrm{Cl}}/k_{-\mathrm{Cl}} \approx 0.05$ M, can be determined, with the ratio representing the association constant for the equilibrium shown in eq 8. This equilibrium constant is about 4000-fold smaller than the association constant, $k_{\mathrm{Cl}}/k_{-\mathrm{Cl}} = 200$ M for addition of chloride to the radical cation of 4-methoxystyrene in a solvent, 2,2,2-trifluoroethanol, that has a much greater ability to promote dissociation than acetonitrile.[16] The small value of the association constant for the addition of chloride to the enol radical cation would thus illustrate the powerful ability of the hydroxy group to stabilize the radical cation side of the equilibrium.

Conclusions

The results in the present work clearly show that protonation of a photogenerated α-acyl radical can lead to the formation of an enol radical cation. This strategy has allowed the detection of the radical cation of an unstable enol for the first time in solution using a photochemical technique and to determine several parameters, including the lifetime, the rate constant for deprotonation and the acidity constant of the radical cation in acetonitrile. Studies on generating a range of structurally diverse enol radical cations by protonation of appropriate photogenerated α-acyl radicals are currently in progress.

Experimental Section

Acetonitrile used for the kinetics experiments was spectroscopic grade (Omnisolve, BDH). Perchloric acid solutions were prepared by adding a weighed amount of concentrated (60%) perchloric acid to a known volume of acetonitrile to generate 1.0 M $HClO_4$ in acetonitrile. This solution was then diluted with appropriate amounts of acetonitrile to obtain desired concentrations of perchloric acid. The precursor, 1-bromo-1-(4-methoxyphenyl)acetone was prepared by addition of bromine to 4-methoxyphenylacetone (Aldrich) according to a literature procedure[17] and purified by recrystallization from petroleum ether.

The nanosecond laser flash photolysis system at Dalhousie University is of standard design and has been previously described.[16] For kinetic measurements, the samples, typically 2 mL, were contained in 7 × 7 mm^2 laser cells made out of Suprasil quartz tubing and bubbled with a slow stream of dry nitrogen or oxygen for 15 min prior to laser irradiation. All kinetics experiments were carried out at room temperature, 22 ±1 °C. For spectra, larger amounts of the sample solutions were placed in a reservoir, and the solution continuously flowed through a 7 × 7 mm^2 sample cell to ensure that only fresh solution was irradiated. For both kinds of experiments, the excitation source was the fourth harmonic from a Spectra Physics Nd:YAG GRC-100 laser (266 nm; ≤ 8 ns/pulse; ≤ 20 mJ/pulse).

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