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First Measurements of Absolute Rate Constants for Oxacarbene Intermediates Produced in the Photochemistry of Benzocyclobutenedione[1]

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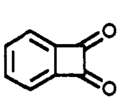
Abstract: The photochemistry of benzocyclobutenedione in solution has been examined by use of laser flash photolysis techniques. Two rapid processes appear to compete. One leads to the formation of the long-lived bisketene IV, which can be readily observed (λ_{max} 380 nm). The other process leads to oxacarbene III. This carbene could not be monitored directly, but probing techniques, with pyridine and adamantanethione as probes, lead to readily detectable ylides that can be employed to characterize the kinetic behavior of III. Thus, III lives about 20 μs in toluene and can be trapped by typical carbene scavengers such as alcohols. Carbene trapping by alcohols is in fact a complex reaction, since it also leads to equilibration with a short-lived intermediate (studied in detail in methanol/acetonitrile) that in turn can be trapped by alcohols, azides, and halides. This intermediate is tentatively assigned to carbocation VIII formed by solvent protonation of III.

The photochemistry of benzocyclobutanedione (I) has been the subject of several studies in solution and in matrices at cryogenic temperatures.[4-9] A variety of intermediates have been proposed, depending on the experimental conditions; in addition to the excited states of I, these include biradical II, oxacarbene III, bisketene IV, and benzyne V.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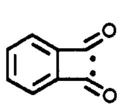
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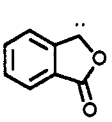
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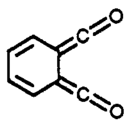
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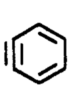
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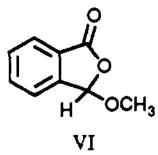
Benzyne has been proposed as an intermediate in the photolysis of I under matrix isolation conditions, on the basis of both spectral data and the observation of dimeric products.[7-9] In one case, the bisketene and its methanol trapping products have been observed.[8]

Solution photoproducts from I are primarily derived from trapping of oxacarbene III. For example, in methanol the major product is VI, while in the absence of trapping agents oxacarbene dimers are formed.[4-6] Olefin trapping products have also been observed.[5] Products resulting from trapping of the bisketene by electron-deficient olefins such as maleic anhydride to give (2 + 4) addition products such as VII have also been reported.[5] More recently, it has been suggested that in some cases oxacarbene-like trapping products can arise from rearrangement of (2 + 2) cycloadducts of the bisketene with olefins.[10] Theoretical calculations of the cycloaddition of ketenes and olefins have also been reported.[11]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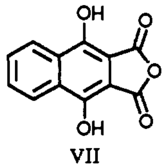
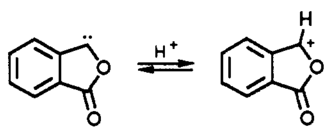

VII

Not only have the intermediates II-V never been characterized in solution, but in fact, the pathways that permit their interconversion have not been established. Although it is generally accepted that oxacarbene formation usually occurs in a stepwise process through the biradical rather than in a concerted fashion,[12] the mechanism for bisketene formation has not been clearly established. Other factors that may require consideration are the possibilities of an equilibrium between the oxacarbene and bisketene and reversible oxacarbene formation. Furthermore, protonation of a number of carbenes has been observed,[13-16] and protonation of the oxacarbene to give carbocation VIII (reaction 1) may also occur under favorable conditions.



III VIII (1)

The present study was undertaken in an attempt to address some of these problems, in particular the direct detection of some of the postulated intermediates. Our work involves the use of laser flash photolysis techniques and has led to the first absolute measurements of rate constants and lifetimes for III and to the direct detection of IV; we also raise specific questions as to the possible involvement of VIII in the chemistry of the oxacarbene. Further, our results on pyridine and thione trapping of the oxacarbene provide unequivocal evidence for its intermediacy in the photochemistry of I.

Results

Excimer laser excitation of solutions of I in nonhydroxylic solvents leads to the rapid (<20-ns) formation of a long-lived intermediate showing an absorption maximum at 380 nm. Figure 1 (top) shows the spectrum of this intermediate in toluene; spectra in other solvents were essentially identical. We assign this intermediate ($\tau > 100$ μs) to bisketene IV (vide infra).

When similar experiments are carried out in some hydroxylic solvents, such as methanol, we observe the formation of a short-lived intermediate, in addition to the same bisketene absorption mentioned above. Figure 2 shows typical decay traces illustrating the short- and long-lived components at two different methanol concentrations. The total absorption spectrum at short times is similar to that for IV, although it appears to be somewhat

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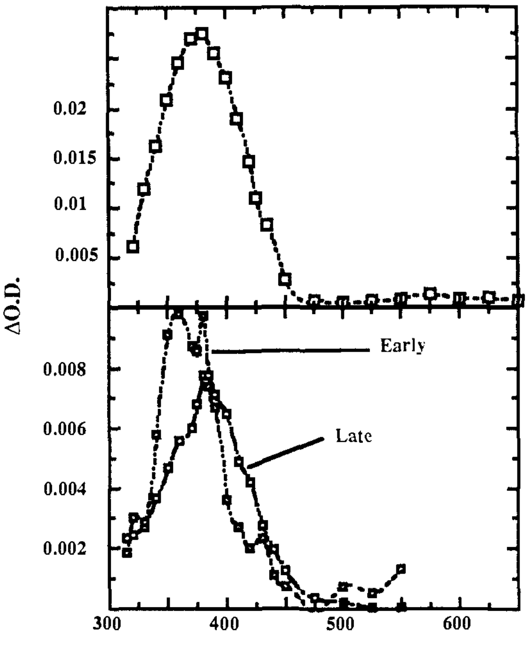

Figure 1. Transient absorption spectra produced by 308-nm excitation of benzocyclobutenedione in toluene (top, 1.1-μs delay) and in 6 M methanol/acetonitrile (bottom). The late spectrum in the latter solvent was measured 2.9 μs after the laser; the early spectrum was measured during the first 100 ns after the laser pulse and corrected for the late absorption and has been expanded ×3.

Table I. Lifetimes of the Short-Lived Intermediate Detected in Acetonitrile/Methanol Mixtures

[CH_3OH] (M)	τ (μs)	[CH_3OH] (M)	τ (μs)
3	1.05	12	0.20
6	0.40	24	0.16

blue-shifted. A difference spectrum based on the absorption over the first 100 ns after the laser pulse minus the absorption of IV after 2.9 μs has also been included in Figure 1 (bottom); it should be noted that this spectrum probably contains a significant contribution from signals due to IV. It should also be noted that neither the amount of bisketene nor its decay is affected by the presence of the short-lived intermediate.

Attempts To Characterize the Short-Lived Species. Establishing the identity of the species responsible for the short-lived transient described above has proved difficult. One of the possible candidates is carbocation VIII, and many of the experiments carried out on this intermediate were designed to test this hypothesis. The lifetime of the short-lived intermediate is an inverse function of the methanol concentration. The lifetimes obtained in various acetonitrile/methanol mixtures are summarized in Table I; from these data it is possible to estimate that methanol quenching occurs with a rate constant of approximately (3.4 ± 0.3) × 10^5 M^{-1} s^{-1}. Many experiments were carried out in 6 M methanol in acetonitrile, under which conditions the short-lived intermediate has a lifetime of 400 ns. For comparison, in 6 M methanol-*O-d* the lifetime is ~600 ns.

The short-lived intermediate is readily quenched by bromide ions (added as tetra-*n*-butylammonium bromide) with a rate constant of (4.0 ± 0.4) × 10^7 M^{-1} s^{-1}. The bisketene that is also formed in this system did not appear to be quenched by bromide at the highest concentration employed. Similar experiments with chloride (added as the tetramethylammonium salt) led to a rate constant for quenching of k_q ~ 1.6 × 10^7 M^{-1} s^{-1}.

Experiments with azide showed clear evidence for rapid and efficient quenching, although both the short- and long-lived components were quenched and kinetic separation of the two processes proved difficult. In fact, quenching of the bisketene by azide is not unexpected since azide also scavenges transient enols by promoting their reketonization.[17] While we could not determine an accurate rate constant, it was clear that quenching of the short-lived intermediate was rapid, with a rate constant in the vicinity of 10^9 M^{-1} s^{-1}.

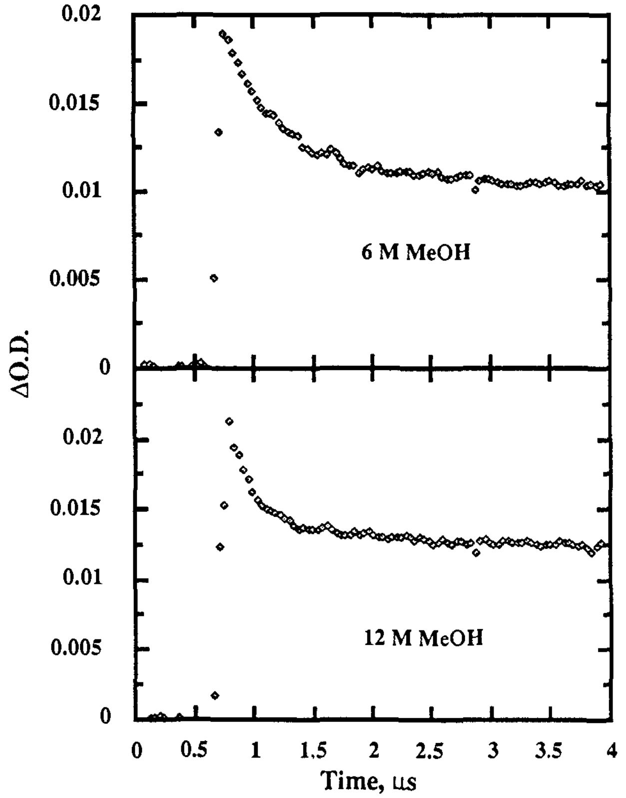

Figure 2. Decay of the transient absorption at 390 nm following 308-nm excitation of benzocyclobutenedione in methanol/acetonitrile mixtures.

Attempts to promote cation formation by using 2,2,2-trifluoroethanol (TFE) as solvent were unsuccessful. However, the explanation for this observation is probably related to the results of studies on the carbene intermediate (vide infra) that have demonstrated that TFE is an excellent scavenger for this species.

It should be noted that while alcohols such as methanol were required to produce the short-lived intermediate, its yield (as measured from the transient optical density before decay) was largely independent of the methanol concentration in the molar concentration range examined (see Table I).[18] This, combined with the fact that the short-lived species does not show a resolved growth on our time scale, suggests that if the carbene is its precursor, then both species must reach a rapid equilibrium within 20 ns. Furthermore, this equilibrium must be considerably shifted in favor of the observable short-lived species even at the lower (3–6 M) alcohol concentrations employed.

Pyridine, which proved to be very useful in characterizing the carbene (vide infra), was also found to quench the short-lived intermediate with a rate constant of ~1.7 × 10^8 M^{-1} s^{-1} in 6 M methanol in acetonitrile.

Kinetics of Carbene Decay and Intermolecular Reactions. It appears reasonable to assume that carbene III will have a singlet ground state.[19–22] A number of carbenes of the Ph$\ddot{C}$X type (e.g., Ph$\ddot{C}$Cl and Ph$\ddot{C}OCH_3$) have been detected by laser flash photolysis and typically have absorption maxima around 290 nm.[19,22]

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Table II. Rate Constants for Reactions of Carbene III at Room Temperature

substrate	solvent	τ_c (μs)	k_{py} or k_c (M^{-1} s^{-1})	probe
pyridine	toluene	20	$(7.7 \pm 0.4) \times 10^8$	direct
pyridine	6 M CH_3OH/ACN	0.35	$(1.4 \pm 0.3) \times 10^8$	direct
pyridine	acetonitrile	2	$(7.6 \pm 0.6) \times 10^8$	direct
2-propanol	toluene		$(1.7 \pm 0.3) \times 10^5$	pyridine
methanol	toluene		$(3.4 \pm 0.5) \times 10^5$	pyridine
ethanol	toluene		$(3.5 \pm 0.4) \times 10^5$	pyridine
adamantanethione (X)	toluene		$(1.1 \pm 0.2) \times 10^9$	direct
TFE	toluene		$(1.2 \pm 0.1) \times 10^8$	thione

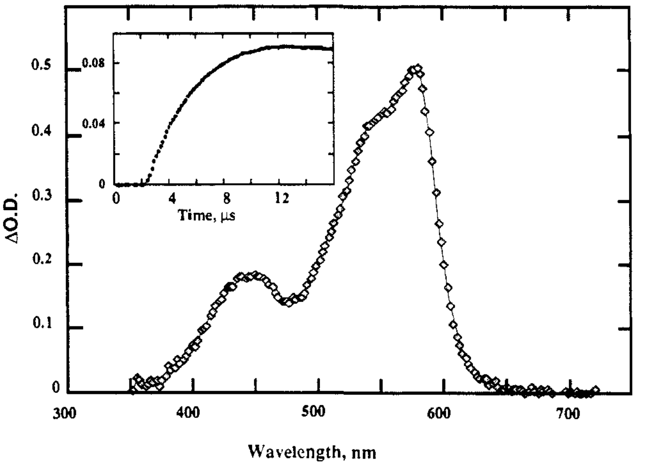

Figure 3. Transient absorption spectrum measured 1 μs after 308-nm excitation of benzocyclobutenedione in toluene containing 0.05 M pyridine. Inset: Growth of the transient absorption at 550 nm for a similar sample containing 0.133 mM pyridine.

In these systems, detection of the carbene is made possible by the spectral characteristics of the diazirine precursors normally used. These have a window in the spectral region where the carbene can be monitored. Unfortunately, I does not have such a window in its absorption spectrum, and samples that have a suitable absorption at the laser wavelength (308 nm) are strongly absorbing at shorter wavelengths. In practice, this means that it is not possible to monitor transient signals at $\lambda < 315$ nm. In spite of this problem, we made several attempts to detect the carbene directly using 308-nm excitation; not surprisingly, these were not successful. We also attempted to monitor at shorter wavelengths using 266-nm laser excitation and a slightly lower concentration of I. However, no additional transients attributable to carbene III could be detected at $\lambda > 310$ nm in acetonitrile, and at 300–310 nm only net bleaching was observed, suggesting that the extinction coefficient of the ketone (which of course is destroyed) exceeds that of the carbene. The sample was not sufficiently transparent to work at shorter wavelengths.

An alternate approach that is frequently employed in laser flash photolysis is to use a "probe" molecule that will react with the "invisible" species of interest to yield an easily detectable and characterizable signal. The probe can then be used to monitor the kinetic behavior of the intermediate toward added substrates. Recent work from Platz's laboratory has shown that pyridine ylides can be readily employed as probes in carbene reactions.[23] A number of pyridine ylides have already been reported in the literature.[23-28]

In the case of carbene III derived from I, we find that addition of pyridine leads to a strong, readily detectable absorption with λ_{max} at 575 nm in toluene and a shoulder at 550 nm. The corresponding transient absorption spectrum and a trace showing its formation (inset) are illustrated in Figure 3. The signal is very long-lived ($\tau > 40$ μs) in toluene, although it is quenched by polar hydroxylic substrates such as methanol. We attribute the signal to a pyridine ylide formed by reaction of III with pyridine on the basis of the clear correlation of its spectral characteristics and kinetic behavior with those of other pyridine–carbene ylides. The formation of the ylide (see inset in Figure 3) follows pseudo-first-order kinetics. The corresponding rate constant, k_{growth}, is related to the rate constants of interest according to eq 2, where

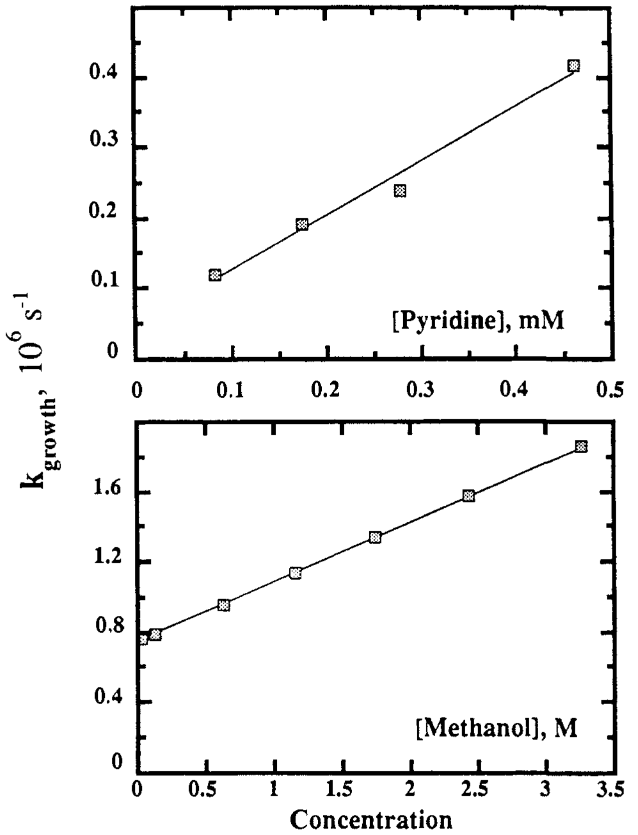

Figure 4. Rate constant for growth of the pyridine ylide at 550 nm in toluene: (top) as a function of the pyridine concentration; (bottom) as a function of the methanol concentration.

$$k_{growth} = \tau_c^{-1} + k_{py}[\text{pyridine}] \qquad (2)$$

τ_c is the carbene lifetime in the absence of pyridine and k_{py} is the observable rate constant for carbene scavenging by pyridine. Figure 4 shows a plot according to eq 2 for toluene as solvent. The values of k_{py} are strongly solvent dependent, although this dependence is largely with the hydrogen-bonding ability of the solvent rather than its polarity. This point is illustrated by the fact that acetonitrile and toluene have essentially the same rate constant. The corresponding rate constants, as well as the carbene lifetimes determined from the intercepts of plots such as those in Figure 4, are listed in Table II. The carbene lifetime in toluene should be regarded as a lower limit since the values obtained varied somewhat from one measurement to the next, probably due to minor amounts of impurities in the solvent.

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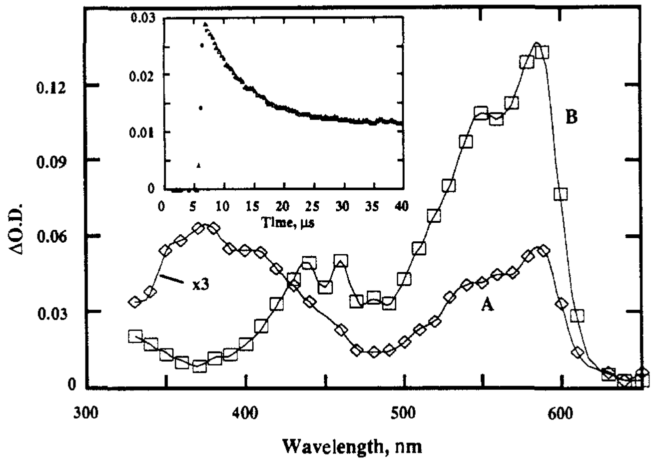


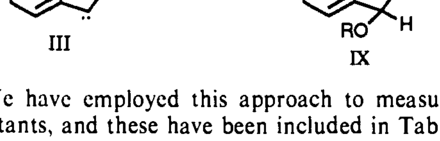
Figure 5. Transient absorption spectra measured 0.6 (A) and 30 (B) μs after 308-nm excitation of benzocyclobutenedione in toluene containing 0.277 mM pyridine. Inset: Transient decay trace for the same sample monitored at 370 nm.

The bisketene can still be detected in the presence of the pyridine ylide at relatively low concentrations of pyridine. Figure 5 shows two spectra recorded at 0.6 and 30 μs after laser excitation of the diketone in toluene containing 0.28 mM pyridine. The early spectrum shows both the bisketene and ylide, while at a longer delay only the ylide remains. A decay trace monitored at 370 nm for the same sample (inset in Figure 5) clearly shows the decay of the bisketene as well as some residual absorption due to a small amount of ylide absorption at this wavelength. Both the decay rate of the bisketene and the amount of residual absorption due to ylide at 370 nm increase as the pyridine concentration is increased; as a result, the bisketene can only be monitored at low pyridine concentrations. Under these conditions, its yield is not reduced by scavenging of the carbene with pyridine. The enhanced rate of decay of the bisketene in these experiments is presumably due to its trapping by pyridine. However, the shortening of the bisketene lifetime was not accompanied by the formation of more ylide; further, in methanol where the carbene and bisketene lifetimes are dramatically different, the kinetics extrapolated to [pyridine] = 0 are only consistent with the carbene lifetime, not the bisketene. Thus, in this time scale the carbene is the only precursor to the ylide.

In addition to the studies mentioned above, it is possible to employ the signals due to the pyridine ylide to examine carbene reactions with other substrates. Thus, if a substrate X is added to a sample containing pyridine, the growth kinetics for the ylide will still follow pseudo-first-order kinetics, but the corresponding rate constant will be given by

$$k_{\mathrm{growth}} = \tau_c^{-1} + k_{\mathrm{py}}[\mathrm{pyridine}] + k_c[\mathrm{X}] \qquad (3)$$

where k_c is the observable rate constant (vide infra) for reaction of the carbene with X. For example, in the case of alcohols:



(4)

III IX

We have employed this approach to measure several rate constants, and these have been included in Table II. A representative plot for methanol according to eq 3 is given in Figure 4.

We were particularly interested in testing TFE as a possible carbene quencher; this is in connection with our failed attempts (vide supra) to stabilize the cation in this solvent. Unfortunately, attempts to use pyridine as a probe were not successful. While it was clear that TFE was scavenging the carbene, it also reduced dramatically the ylide signals to the point that monitoring the kinetics was quite difficult. We were able to establish by UV spectroscopy that TFE interacts strongly with pyridine, in effect reducing the concentration of free pyridine available for carbene scavenging. It is thus clear that nitrogen bases are not good probes in the presence of acidic solvents.

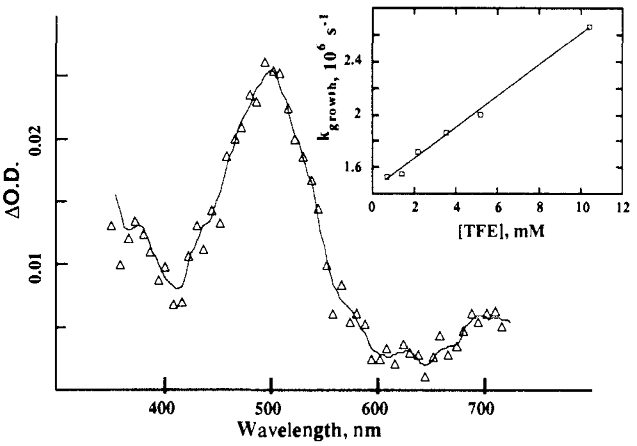
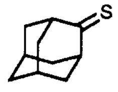


Figure 6. Transient absorption spectrum measured 5 μs after 308-nm excitation of benzocyclobutenedione in toluene containing 0.016 M adamantanethione. Inset: Rate constant for the growth of the thiocarbonyl ylide as a function of TFE concentration.

In view of the problems mentioned above, we attempted the use of adamantanethione (X) as a probe. Adamantanethione



X

and bis(*tert*-butyl)thioketone have been shown to be excellent carbene scavengers, yielding long-lived ylides with strong absorptions in the visible region.[29] For example, the ylide from diphenylcarbene and X shows $\lambda_{\max}$ at 500 nm. We find that III reacts readily with X to yield an intermediate with $\lambda_{\max}$ at 505 nm (Figure 6), which we attribute to the corresponding thiocarbonyl ylide; its absorptions are substantially weaker than those of the pyridine ylide discussed earlier. With this technique it was possible to determine the rate constant for TFE quenching of the carbene (see inset in Figure 6), which has also been included in Table II. Clearly, TFE is an excellent carbene scavenger. In comparison, dimethoxycarbene reacts with TFE with a rate constant of 6.9×10^7 $\mathrm{M^{-1}\,s^{-1}}$.[21]

Sensitization and Quenching Experiments for Bisketene IV. Neither the yield of the bisketene nor its lifetime was affected by the addition of 0.048 M 1,3-cyclohexadiene. This indicates that the bisketene is formed from either the singlet diketone or a short-lived triplet ($\tau \leq 5$ ns), in agreement with the fact that under no conditions were we able to observe a growth of the 370-nm signal. However, the bisketene could be readily produced by use of xanthone as a sensitizer with 337-nm laser excitation under conditions where there was no direct excitation of the diketone. Thus, addition of diketone to xanthone in acetonitrile led to quenching of the xanthone triplet at 600 nm with a rate constant of 7.6×10^9 $\mathrm{M^{-1}\,s^{-1}}$ and with the concomitant formation of the bisketene at 370 nm. Although these results demonstrate that the triplet diketone does generate the bisketene, they do not require that its production via direct excitation of the diketone also proceed through the triplet.

Independent Generation of Cation VIII. Attempted generation of cation VIII by mixing hydroxyphthalide with 96% sulfuric acid or chlorosulfonic acid failed to give ionization. However, this cation could be generated by mixing dichloromethane solutions of hydroxyphthalide with trifluoromethanesulfonic acid. A red solution was obtained and found to be stable over periods of hours at ambient temperature. Quenching of this solution with methanol at 0 °C gave methoxyphthalide VI as the major product in 80%

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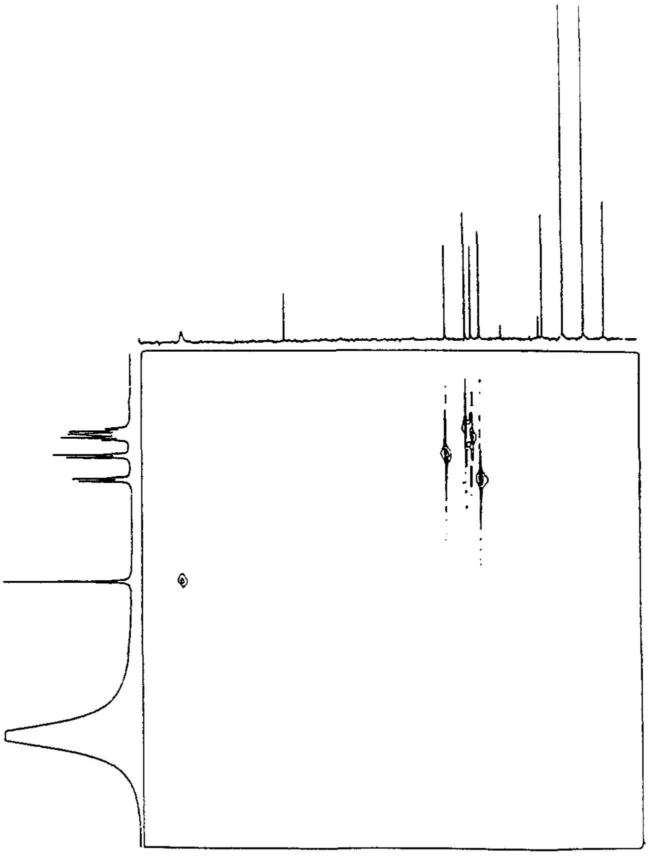
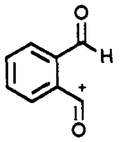


Figure 7. HX correlation spectrum of carbocation VIII in dichloromethane-d_2.

yield. The ^{13}C NMR spectrum of this solution was obtained (Figure 7) showing low-field signals at 179.4 and 199.8 ppm assigned to the carbonyl and benzylic cation carbons, respectively. These values compare with chemical shifts of 175–185 ppm for the carbonyl carbon of benzoates and 201 ppm for the benzylic cation carbon in benzyl methoxymethyl cations but are not consistent with the open-form acylium ion XI, which would be expected to show peaks at 156 and 190 ppm for the acylium cationic carbon and carbonyl carbon, respectively, as compared with model systems.[30-32]



XI

The 2D spectra including ^{13}C–^1H correlation and *J*-correlated spin-echo were obtained and corroborated the spectral assignments (see Figure 7). The UV spectrum of VIII showed a maximum at 330 nm. The stable red solution probably indicates that VIII also has a very weak transition in the visible. These results differ somewhat from the absorption spectrum of the short-lived transient obtained from the laser flash experiment (Figure 1).

Discussion

Recent work by Platz, Liu, et al.[23,25,27,28] has established that pyridine is an excellent probe for the study of otherwise "undetectable" carbenes. Our work takes advantages of this development to characterize for the first time the kinetic behavior of an oxacarbene produced in the rearrangement of a benzocyclobutenedione. Spectrally, the transient of Figure 3 is in line with pyridine ylides observed from other carbenes, such as phenylchlorocarbene. For example, for the ylide from III we have obtained λ_{max} of 575 nm in toluene; for comparison, λ_{max} is 480 nm for phenylchlorocarbene[23] and 535 nm for 1-naphthylcarbene.[24] III appears to be slightly more reactive toward pyridine than phenylchlorocarbene; for example, the rate constants in toluene are 7.7×10^8 and 3.35×10^8 M^{-1} s^{-1} for III and phenylchlorocarbene, respectively. The remarkable solvent dependence of the observable rate constant for pyridine quenching (see Table II) is rather unusual. Platz et al.[33] have examined the rate constants in detail in the case of phenylchlorocarbene and have found little solvent effect. For example, the rate constants in toluene, acetonitrile, propionitrile, and ethyl acetate are between 2.9 and 4.0 $\times$ 10^8 M^{-1} s^{-1}, and only in the case of hexane were they found to be significantly different (7.5×10^8 M^{-1} s^{-1}); unfortunately, the study does not include any hydroxylic solvents due to their high reactivity toward phenylchlorocarbene. On the other hand, our study of III reveals that while the rate constants in acetonitrile and toluene have the same value, addition of 6 M methanol to acetonitrile decreases the value by a factor of 4.5. It is tempting to suggest that this is the result of the displacement of the carbene $\leftrightarrow$ carbocation equilibrium in favor of the latter; see reaction 1.

Thus, if methanol promotes carbene protonation (see reaction 5), as has been suggested in related systems,[13-16] it would also cause a decrease in the effective carbene concentration. Thus, the

$$\text{(ylide)} \xleftarrow[\text{pyridine}]{k_{\text{trapping}}} \text{III} + CH_3OH \overset{K_{eq}}{\rightleftharpoons} \text{VIII} + CH_3O^- \quad (5)$$

observable rate constant k_{py} is given by

$$k_{py} = \frac{k_{\text{trapping}}}{K_1}$$

where k_{trapping} is the "true" rate constant for free carbene, K_1 the equilibrium constant (which could contain the methanol concentration),[34] and k_{py} the experimental value. Clearly, the changes in rate constant are not conclusive evidence for the occurrence of reaction 1; however, they do reinforce other pieces of evidence presented herein that also support carbene protonation. For example, the apparent reaction of III with alcohols is rather slow in comparison with the rate constants for other singlet[22,35,36] and even triplet carbenes.[37] However, it should be noted that some of these comparisons are complicated by the role of the monomer–oligomer equilibrium in methanol, especially in nonpolar solvents. These slow rate constants for reaction with alcohols, while not compelling, are consistent with a preference for protonation of the carbene (vide infra) and may reflect the combined reactivity of the species in the equilibrium of reaction 1. The experimental rate constant will simply be the sum of the rate constants for each species times its observed equilibrium abundance in the system.

The substitution pattern on III suggests that its ground state should be a singlet. All other carbenes with at least one halogen or oxygen atom at the carbene center are known to have singlet ground states.[19,20,22,36,38]

The formation of a thiocarbonyl ylide by addition to the C=S bond of adamantanethione is not unprecedented.[29] The rate constant of 1.1×10^9 M^{-1} s^{-1} obtained for III is in line with the values of 6.4×10^9 and 1.3×10^9 M^{-1} s^{-1} reported for fluorenylidene and diphenylcarbene, respectively.[29] Interestingly, in this

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case the nature of the carbene (singlet or triplet) does not appear to have much effect on the rate constant for addition. In addition to providing supporting evidence for the carbene assignment, this particular probe has allowed us to establish the high reactivity of the carbene toward trifluoroethanol (presumably via insertion) and thus understand why this carbocation-stabilizing solvent fails to assist the formation of VIII. Clearly, if the carbene is a *precursor* for the carbocation, any molecule that provides an efficient chemical pathway for carbene removal will be unable to yield cation, even if it could stabilize this species once it was formed. It should also be noted that high reactivities of other carbenes toward TFE have also been observed.[21]

The formation of the bisketene is not surprising, since benzocyclobutenone is known to yield the corresponding monoketene efficiently.[39] This intermediate is also very long lived, and its spectroscopic properties compare well with those of IV. Our data suggest that IV is not produced via carbene III but rather is formed by a parallel competitive process (e.g., involving biradical II). Several experiments in the presence of moderate amounts of pyridine ylide indicate that the yield of bisketene is not affected by scavenging of the carbene with pyridine. However, these experiments are somewhat complicated by the fact that the ylide absorptions are very intense and interfere even in the spectral region where the bisketene absorbs. Experiments in the presence of conjugated dienes did not indicate any change in the yield or lifetime of the bisketene; such an observation is consistent with either a very short-lived triplet or a singlet precursor. While the direct photolysis of I does not provide conclusive evidence as to the multiplicity of the precursor for IV, xanthone sensitization experiments provide conclusive proof that IV *can* be formed from the triplet state of I.

The presence of the fast component in the transient decay traces that we monitored at wavelengths around 370 nm is intriguing. Clearly, methanol promotes the formation of this species and also acts as a quencher for it. The rate constant for quenching derived from the effect of methanol on the fast component of the decay at 370 nm is 3.4×10^5 M^{-1} s^{-1} and is within experimental error identical with the value derived from ylide growth studies (compare Tables I and II). The lifetime for this decay (400 ns) measured at 370 nm in 6 M methanol/acetonitrile is also in satisfactory agreement with the extrapolated carbene lifetime on the basis of the pyridine quenching of the carbene in the same solvent (Table II). We could therefore ask whether the species monitored at 370 nm is in fact carbene III. We believe this is not the case, *since this signal is only observed in alcohol-containing solvents, methanol in particular*. It is absent in other solvents examined, from acetonitrile to toluene. Further, comparison with other singlet carbenes (such as phenylchlorocarbene and methoxyphenylcarbene) suggests that the carbene absorptions should be expected at shorter wavelengths.[19,22] As with other data in this work, the results are consistent with the involvement of carbocation VIII although the spectroscopic evidence is less compelling (vide infra).

It should be noted that the signals that we monitor at 370 nm are produced instantaneously in the time scale (<10 ns) of our experiments. This implies that if carbocation VIII is produced via protonation of III, then the equilibrium between the two must be established very rapidly; thus, the observed signal at 370 nm would be the decay of the carbocation in equilibrium with the carbene. Consistent with this interpretation, the lifetimes are the same whether the carbocation (370 nm) or the carbene (via a pyridine probe) is monitored. Thus, at least in methanol, all the rate constants that we have measured involve an equilibrium mixture of the two species and lead to the same kinetic data regardless of which equilibrium component is monitored.

The spectrum obtained upon direct laser excitation of I in methanol/acetonitrile is shown in Figure 1. At long times, the spectrum is that expected for the bisketene IV, whereas at short times it is shifted toward the blue. The spectrum for cation VIII in dichloromethane/trifluoromethanesulfonic acid shows λ_{max} at ~330 nm. The difference between this position and the long λ_{max} obtained in the laser experiments may have two origins. First, it is possible that the shift may be partially due to the different solvents used. Second, even the short time spectrum of Figure 1 may be significantly contaminated by bisketene absorptions that would cause an apparent red shift of λ_{max}. The related cation (2-phenyl-1,3-dioxolan-2-ylium ion) has a similar absorption spectrum with a maximum at 260 nm and a shoulder between 300 and 350 nm.[40]

In summary, our experiments have provided direct evidence for two of the proposed intermediates in the solution photochemistry of benzocyclobutenedione. Although the bisketene could be readily observed in a variety of solvents, the oxacarbene could not be directly monitored, presumably since it absorbs at wavelengths shorter than 300 nm. However, probe techniques with use of either pyridine or adamantanethione lead to readily detectable ylide signals and allow the measurement of lifetimes for the oxacarbene and rate constants for its reaction with typical carbene scavengers. In alcohol solvents the oxacarbene is in equilibrium with a short-lived intermediate that we have tentatively assigned to the carbocation formed by protonation of the carbene. Under these conditions the rate constants measured reflect the combined behavior of both intermediates.

Experimental Section

Materials. Benzocyclobutenedione and adamantanethione were prepared according to literature procedures.[41,42] 1,3-Cyclohexadiene (Aldrich) was distilled and xanthone (Fluka) was recrystallized before use. Other reagents and solvents were used as received.

Laser Flash Photolysis. The laser flash photolysis facility has been described.[43,44] For these experiments, a Lumonics TE-860-2 excimer laser with a Xe/HCl gas mixture (308 nm; ~5-ns pulses; ≤20 mJ/pulse) or a Molectron UV-24 nitrogen laser (337.1 nm; ~8-ns pulses; ≤10 mJ/pulse) was used. For most of the experiments the sample was flowed through a cell constructed from 7×7 mm^2 quartz tubing. All samples were deaerated by nitrogen purging unless otherwise indicated. Lifetime measurements are straightforward between 10 ns and 100 μs. Lifetimes outside this range (e.g., bisketene IV) may not be accurate.

NMR Experiments. NMR acquisitions were carried out on a Bruker AM-300 spectrometer. Both the C–H-correlated as well as ^1H–^1H COSY 2-D acquisitions were performed with pulse sequences accessed from the Bruker software library.

Preparation of Carbocation VIII. A 30-mg portion of 2-carboxybenzaldehyde (mostly in cyclized hydroxyphthalide form) was dissolved in 0.5 mL of CD_2Cl_2. Then, a few drops of triflic acid were added to the solution at room temperature. A pale brown color was observed. The NMR spectra of carbocation VIII were obtained: ^1H NMR δ 8.34 (m, 1 H), 8.41 (m, 1 H), 8.58 (d, 1 H, $J = 7.7$ Hz), 8.82 (d, 1 H, $J = 7.7$ Hz), 9.78 (HC^+); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 199.8 (HC^+), 179.4 (C=O), 143.2, 139.5, 138.2, 136.8 (aromatic carbons), 128.3, 1226.8 (aromatic quaternary carbons).

Quenching of Carbocation VIII with Methanol. A 300-mg portion of 2-carboxybenzaldehyde was dissolved in 5.0 mL of dichloromethane and 2.0 mL of methanol. Then, 1.0 mL of triflic acid was added and the solution was stirred for 10 min. No color change was observed. The solvent was removed under reduced pressure. The mixture was separated by TLC (silica gel/dichloromethane) to give methoxyphthalide VI (80%): ^1H NMR δ 3.62 (s, 3 H, OCH_3), 6.34 (CH), 7.62 (m, 2 H, aromatic protons), 7.75 (d, 1 H, aromatic proton, $J = 7.6$ Hz), 7.91 (d, 1 H, aromatic proton, $J = 7.6$ Hz); MS, m/e 164 (M^+).

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