by a water molecule. This is significant, inasmuch as the uncatalyzed reaction could, at least in principle, have been a process in which water acts as a proton donor (cf. eq 5) and not as a nucleophile.

It is interesting that, whereas the methylthio group in the present system slows ketene hydration, the hydroxyl group in the analogous phenylhydroxyketene, **10**, accelerates it—by a factor of 140 in the case of the uncatalyzed reaction, the only process for which a rate constant for **10** is available.[10] It can be argued that this acceleration is the expected result, for the electron-withdrawing inductive effect of oxygen should stabilize the negative charge of the enolate ion being formed by nucleophilic attack of water on the ketene. It may seem strange, therefore, that a methylthio group is rate-retarding, for the electronic effect of sulfur should be similar to that of oxygen, at least in direction if not in magnitude. Recent calculations of the effects of substituents on ketene stability, however, show the hydroxyl group to be appreciably destabilizing but the thiol group to be slightly stabilizing;[11] this difference leads to a differential initial state effect that makes the oxygen-substituted ketene the more reactive. It is known, also, that steric effects in the transition state play an important role in ketene reactions and the larger size of the methylthio group would be expected to have an adverse effect on reactivity.

Acknowledgment. We are grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico of Brazil for a fellowship to J.J. Jr. and the Natural Sciences and Engineering Research Council of Canada, the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the United States National Institutes of Health for further financial support of this work.

---

[10] Chiang, Y.; Kresge, A. J.; Pruszynski, P.; Schepp, N. P.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 792–794.

[11] Gong, L.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1991**, *113*, 6021–6028.

Laser Flash Photolysis Studies on 4-Oxocyclohexa-2,5-dienylidenes[1]

B. R. Arnold and J. C. Scaiano*,[2]

Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

G. F. Bucher and W. W. Sander*

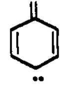
Institut für Organische Chemie der Technischen Universität, Braunschweig, Federal Republic of Germany

Received July 14, 1992

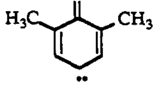
Reactions of 4-oxocyclohexa-2,5-dienylidene (**1**) and two derivatives have been investigated using laser flash photolysis techniques. Photolysis of 4-diazocyclohexa-2,5-dien-1-one (**4**) in 1,1,2-trichlorotrifluoroethane allows the indirect detection of the corresponding carbene **1**. This carbene reacts with triplet oxygen at close to the diffusion-controlled rate, forming the carbonyl *O*-oxide (λ_{max} = 470 nm). Reaction of triplet **1** with moderate concentrations of cyclohexane leads to formation of phenoxyl radical (λ_{max} = 395 nm). At high concentrations or in neat cyclohexane the predominant path appears to be carbene insertion into the C–H bond. Other reactions examined include O–H insertion in methanol and the indirect formation of ylides from acetone, acetonitrile, and pyridine. The reactivity pattern that emerges indicates that carbene **1** and its derivatives, **2** and **3**, have triplet ground states and that the singlet–triplet energy gap is moderately large. Ylide formation is only observed when the reactants are present in low concentrations and involve a two-step reaction from the triplet carbene; no ylides are observed in neat acetone or acetonitrile suggesting that for the singlet carbene insertion into C–H bonds is favored over direct ylide formation.

Introduction

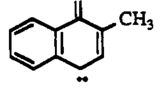
Quinone diazides are among the most stable diazo compounds known. Their remarkable stability is due to the fact that they may be partially described as internal diazonium phenoxides, thus lowering their energy by resonance. This raises the question whether the carbenes formed by photolysis of quinone diazides display unexpected stability as well. To date, anthronylidene has been the only carbene derived from a 1,4-quinone diazide that has been studied by means of laser flash photolysis,[3] although the solution chemistry of several derivatives of 4-oxocyclohexadienylidene has been fairly well developed.[4] We undertook a study of the solution chemistry of the 4-oxocyclohexa-2,5-dienylidene (**1**), 3,5-dimethyl-4-oxocyclohexa-2,5-dienylidene (**2**), and 3-methyl-4-oxobenzocyclohexadienylidene (**3**) in order to establish how **1** and its derivatives would fit into the pattern of carbene reactivity.



1



2



3

Carbene **1** and its derivatives have been studied in solution by product studies. In most cases **1** adds to olefins

---

[1] Issued as NRCC-33323.

[2] Present address: Department of Chemistry, University of Ottawa, Ottawa, Canada K1N 6N5.

[3] Field, K. W.; Schuster, G. B. *J. Org. Chem.* **1988**, *53*, 4000.

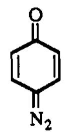
[4] Ershov, V. V.; Nikiforov, G. A.; Jonge, C. R. d. *Quinonediazides*; Elsevier: Amsterdam, 1981.

stereospecifically while in reactions with alcohols O–H insertion is preferred over C–H abstraction.[4,5] It has also been observed that 1 initiates polymerizations or undergoes C–H abstraction reactions from hydrocarbons.[6] The spin state from which chemical reactions predominantly occur appears to be very dependent on the experimental conditions.

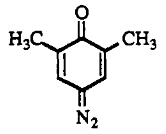
The initial experimental evidence on the spin multiplicity of ground state 1 was based on the ESR studies of Wasserman and Murray,[7] who irradiated powdered 4-diazo-cyclohexa-2,5-dienone at 4 K with a high-pressure mercury arc lamp and showed that 1 has a triplet ground state. Recent ESR measurements in Ar-matrix have confirmed these results.[8] The UV- and IR-spectroscopic characteristics of 1 have been examined in detail.[9] The UV-spectrum (in Ar-matrix) shows a maximum at 290 nm with further medium and weak bands at 338, 351, 367, and 379 nm and a very broad and weak absorption around 530 nm. The IR-spectrum of 1, matrix-isolated in Ar, displays a C=O stretching vibration at 1497 cm^{-1}, indicating a C–O bond order of significantly less than 2. Carbenes 2 and 3 exhibit similar spectral properties; the most notable difference is a shift of ν(C=O) to 1558 cm^{-1} for 3, which is indicative of a higher C–O bond order in this case.[10] The ground-state electronic structure of these carbenes may then be described as the combination of a phenoxy radical (π-system) and a phenyl radical (σ-system).

Experimental Section

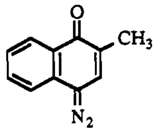
The laser system used in these experiments has been described in detail elsewhere.[11,12] Solutions of 4-diazocyclohexa-2,5-dienone in 1,1,2-trichlorotrifluoroethane (Freon-113) of about 2 × 10^{-5} M in concentration were either photolyzed in a flow system using 337-nm excitation from a Molectron UV-24 nitrogen laser or in static cells (7 × 7 mm Suprasil) using 308-nm excitation from a Lumonics TE-860-2 excimer laser operated with Xe/HCl/He mixtures. Freon-113 was obtained from Fluka, BDH, or Aldrich and was distilled and rinsed over an alumina column until no improvements in the UV base line or cut-off were observed. Likewise, carbon tetrachloride (Fisher) was purified twice over alumina. The carbene precursors, 4-diazocyclohexa-2,5-dienone (4), 4-diazo-2,5-dimelthylcyclohexa-2,5-dienone (5), and 4-diazo-2-methylbenzocyclohexadienone (6) were prepared according to literature procedures.[13,14] Further purification of 4 was achieved by sublimation under high vacuum prior to use. Cyclohexane, methanol, acetone, acetonitrile, and pyridine were purchased from Fisher chemicals and used as received. Oxygen was used both pure and in standard mixtures with nitrogen (1.03% and 3.87%, obtained from Matheson). Further variation in the O_2/N_2 mixtures was obtained by using a flow gas-mixing unit.



4



5



6

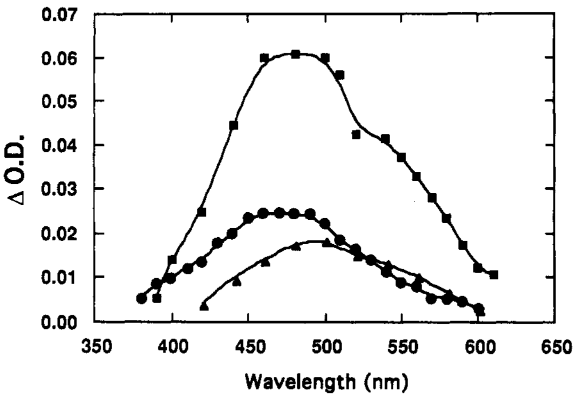


Figure 1. Absorption spectra of the carbonyl *O*-oxides 7 (●), 8 (▲), and 9 (■) in Freon-113, recorded 1 μs after laser excitation of the diazo precursor.

All reactions were performed in Freon-113 as solvent. Attempts to generate the carbenes in neat carbon tetrachloride, cyclohexane, or acetonitrile did not lead to identifiable species; therefore all quenchers were added to Freon-113 solutions of the diazo compound. All reactions were carried out at ambient temperature.

Results and Discussion

Monitoring 1 directly in Freon-113 solution proved to be difficult. In an Ar-matrix 1 shows an absorption maximum at 290 nm,[9] with additional absorptions at 379 nm (m, very sharp) and around 530 nm (vw, broad). Given that carbene-precursor 4 also absorbs at 290 nm (a difference spectrum is observed in laser flash photolysis experiments, rather than an absolute spectrum) the observation of 1 at this wavelength would be anticipated to be difficult. We were unable to positively identify any transient signals belonging to any of the carbenes. Mass spectrometric analysis of the products formed from the photolysis of 1 with Freon-113 showed that the main product is derived from an insertion of the carbene into a carbon–chlorine bond (vide infra). Since we were unable to observe the carbenes directly we have used competitive kinetic techniques to probe their reactivity. The probe reaction we have used is the formation of the carbonyl oxides as described below. The lifetimes of carbenes 1, 2, and 3 in Freon-113 in the absence of additional quencher can be obtained from an extrapolation of quenching plots to zero quencher concentration. For 1, this approach gives τ = 1.65 μs while 2 and 3 were somewhat longer lived, with lifetimes of τ = 2.0 and 2.5 μs, respectively. By comparison carbene 1 is known to react with CCl_4 forming cyclohexadienone 10, which can be isolated.[15] Addition of carbon tetrachloride to the Freon-113 solutions containing oxygen as a probe yields a rate constant of reaction of 3.2 × 10^6 M^{-1} s^{-1} for the formation of 10 from triplet 1. Thus, the reactivity of this carbene is about 50 times greater toward carbon tetrachloride than toward Freon-113.

Reaction with Triplet Oxygen. Triplet oxygen is known to react with triplet carbenes forming carbonyl *O*-oxides at close to the diffusion-controlled rate.[16-18] This also proved to apply for carbenes 1, 2, and 3. The corresponding *p*-benzoquinone *O*-oxides were readily detected, with absorption maxima at 470 (7), 500 (8) and 480 nm (9), as shown in Figure 1. The carbonyl *O*-oxides have been

---

(5) Kirmse, W.; Lelgemann, R.; Friedrich, K. *Chem. Ber.* **1991**, *124*, 1853.

(6) Vorotnikov, A. P.; Davydov, E. Y.; Topygin, D. Y. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1985**, 1275.

(7) Wasserman, E.; Murray, R. W. *J. Am. Chem. Soc.* **1964**, *86*, 4203.

(8) Sander, W.; Müller, W.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 572.

(9) Sander, W.; Bucher, G.; Reichel, F.; Cremer, D. *J. Am. Chem. Soc.* **1991**, *113*, 5311.

(10) Bucher, G.; Sander, W. *J. Org. Chem.* **1992**, *57*, 1346.

(11) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(12) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(13) Puza, M.; Doetschman, D. *Synthesis* **1971**, 481.

(14) Reid, W.; Dietrich, R. *Chem. Ber.* **1961**, *94*, 387.

(15) Plekhanova, L. G.; Nikiforov, G. A.; Ershov, V. V. *J. Org. Chem. USSR* **1972**, *8*, 819 (original publication *Zh. Org. Khim.* **1972**, *8*, 809).

(16) Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391.

(17) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616.

(18) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem.* **1989**, *54*, 1612.

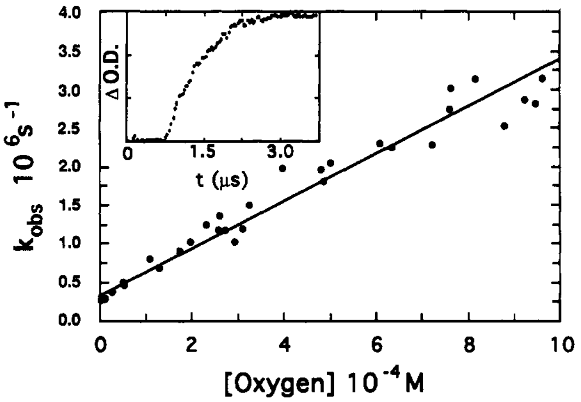
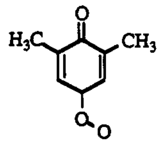


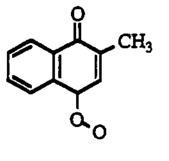
Figure 2. Plot of the pseudo-first-order rate constant for the formation of 7 against oxygen concentration. Inset: growth trace for 7 monitored at 480 nm in a Freon-113 solution saturated with 1% oxygen-in-nitrogen.

observed matrix-isolated in Ar where 7 exhibits a very broad λ_{max} at 460 nm[19] while 8 and 9 have λ_{max} of 486 nm and 472 nm, respectively,[10] all slightly blue shifted from the solution maxima. For comparison, the carbonyl *O*-oxides of diphenylmethylene[16] and fluorenylidene[17] show maxima at 410 and 450 nm, respectively, while 1-naphthaldehyde *O*-oxide[20] has a maximum at 435 nm. The carbonyl *O*-oxide derived from anthronylidene shows λ_{max} of 465 nm.[3]


7



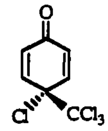
8



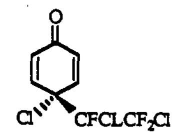
9

A plot of the observed pseudo-first-order rate of carbonyl *O*-oxide formation versus oxygen concentration yields $k_1 = 2.9 \times 10^9$ M^{-1} s^{-1} for carbene 1 (Figure 2), while carbenes 2 and 3 both react with a rate constant of 2.7×10^9 M^{-1} s^{-1}. These rate constants fall into the range expected on the basis of those reported in the literature for the formation of other carbonyl oxides.[21] The lifetimes of the *p*-benzoquinone *O*-oxides examined are all longer than 20 μs, making them excellent probes for competitive kinetic analysis.

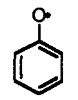
Reaction with Cyclohexane. Photolysis of 4 in Freon-113 solutions containing moderate concentrations of cyclohexane produces a transient with a very sharp absorption maximum at 395 nm. This absorption is assigned to the phenoxyl radical 12. This phenoxyl radical



10



11


12

has been characterized previously[22] and has its λ_{max} ~400 nm.[22,23] When produced from phenol by abstraction with *tert*-butoxyl radicals in Feon-113 we also obtained λ_{max} at 395 nm.

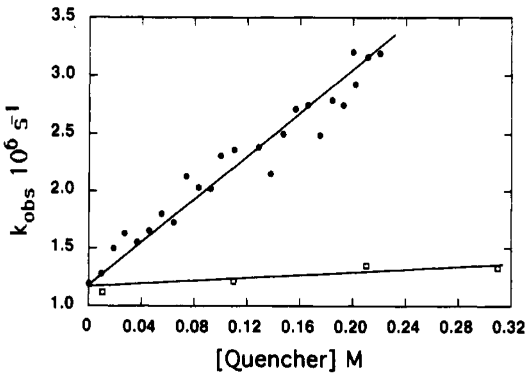


Figure 3. Quenching of 1 by cyclohexane (●) (see eq 1) and by methanol (□) in Freon-113, monitored using 7 as a probe.

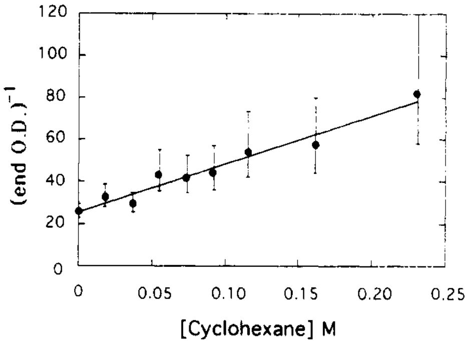


Figure 4. Plot for the quenching of 1 by cyclohexane according to eq 2.

Given the modest extinction coefficient of 12,[22] it was not possible to obtain an accurate rate constant for reaction with cyclohexane from the growth kinetics of the phenoxyl radical. However, this kinetic information is accessible by monitoring the rate of formation of 7 as a function of the concentration of cyclohexane at constant partial pressure of oxygen (Figure 3). The data are analyzed according to eq 1 where k_{extl} is the pseudo-first-order rate constant

$$k_{extl} = k_0 + k_p[O_2] + k_1[c\text{-}C_6H_{12}] \qquad (1)$$

associated with the buildup of the carbonyl oxide, k_1 is the rate constant for the reaction of interest, k_p is the rate constant for reaction with the probe (oxygen in this case), and k_0 is the rate constant for carbene decay in the absence of oxygen or substrate ($k_0 = \tau_0^{-1}$).

The slope of the plot of the rate constant for carbonyl oxide buildup (k_{extl}) against cyclohexane concentration yields a rate constant $k_1 = 8.4 \times 10^6$ M^{-1} s^{-1} for reaction of 1 with cyclohexane.

Similar kinetic data can be derived from a Stern–Volmer approach. Here the reciprocal of carbonyl *O*-oxide yield is related to the product $k_1\tau$ according to eq 2, where "end OD" is the transient absorbance due to the carbonyl oxide once its formation is complete and is derived from the plateau region of the experimental traces. The superscript "o" indicates data acquired in the absence of cyclohexane.

$$(\text{end OD})^{-1} = (\text{end OD}^{o})^{-1} + \frac{k_1\tau}{(\text{end OD}^{o})}[c\text{-}C_6H_{12}] \qquad (2)$$

The value of τ in eq 2 refers to the carbene lifetime in the presence of the concentration of oxygen employed as a probe. Thus, taking $\tau = 0.63$ μs the result is $k_1 = 8.3 \times 10^6$ M^{-1} s^{-1} (Figure 4), in excellent agreement with the method of eq 1. This agreement can be taken as an indication that at these low cyclohexane concentrations most

---

(19) Sander, W. *J. Org. Chem.* **1988**, *53*, 2091.

(20) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928.

(21) Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; pp 239.

(22) Schuler, R. H.; Buzzard, G. K. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 563.

(23) Das, P. K.; Encinas, M. V.; Steenken, S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4162.

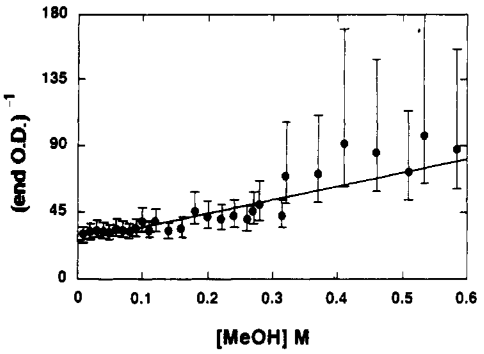


Figure 5. Effect of methanol on the yield of carbonyl oxide 7 plotted according to eq 3 (see text).

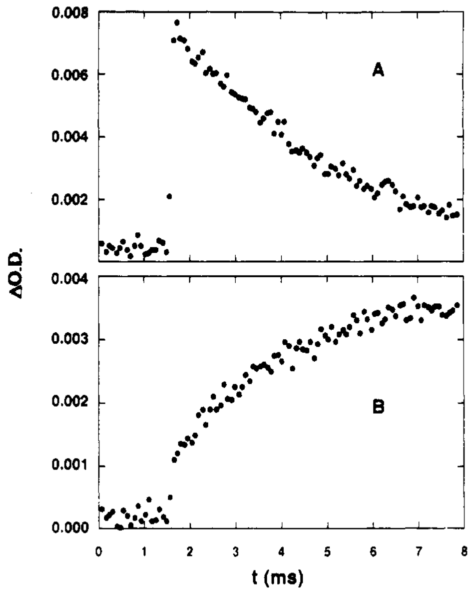


Figure 6. Decay of the 620-nm transient and growth of the ylide for the reaction of 1 with acetone in Freon-113.

Table I. Absorption Maxima for Various Ylides in Freon-113

compd	carbene	scavenger	λ_{max} (nm)
13a	1	acetone	500
13b	2	acetone	510
16	3	acetone	470
14	1	acetonitrile	540
17	3	acetonitrile	465
15	1	pyridine	560
18	3	pyridine	465

of the carbene reaction occurs after initial singlet–triplet equilibration and that other processes (e.g., reaction from the initially formed singlet state with cyclohexane) do not contribute to the yield of phenoxyl radical.

Laser excitation of 4 in oxygen-saturated cyclohexane solvent yields only trace amounts of carbonyl *O*-oxide 7, while in deaerated solutions no phenoxyl radicals were detected. It is known from CIDNP experiments that carbene 1 and its derivatives react with alkanes preferentially via an insertion route from the singlet.[4,24] Hence, in pure cyclohexane most of the carbene is scavenged in the singlet state prior to spin equilibration; only a very small fraction is able to undergo intersystem crossing to the ground-state triplet. As a result, in neat cyclohexane there are negligible yields of triplet-derived products such as the carbonyl *O*-oxide and phenoxyl radicals.

Reaction with Methanol. Methanol quenching experiments were carried out with diazo compounds 4 and 6. No transient could be observed upon photolysis of these diazos in Freon- 113 solutions containing methanol or in neat methanol. As in the case of cyclohexane as quencher, the rate constants of the reaction of 1 and 3 with methanol were obtained using carbonyl *O*-oxide formation at fixed oxygen partial pressure as a probe reaction. A representative plot has been included in Figure 3 and illustrates the dramatic difference in reactivity with the example of cyclohexane discussed above. The rate constants derived from plots of this type are not very accurate as a result of the small effect of methanol on the decay rates; our best values are 2×10^5 and 5×10^5 M^{-1} s^{-1}, for carbene 1 and 3, respectively. The error in these values is probably a factor of 2. The low rate constants observed in this work are consistent with a moderately large separation between the singlet and triplet levels of these carbenes.[21,25]

An alternate approach to the study of the effect of methanol on the carbene involves a Stern–Volmer-type study similar to that described for cyclohexane (see Figure 4 and eq 2), where τ_{ox} refers to the carbene lifetime in the

$$(\text{end OD})^{-1} = (\text{end OD}^{\circ})^{-1} + \frac{k_1\tau_{ox}}{(\text{end OD}^{\circ})}[\text{methanol}] \quad (3)$$

presence of a fixed concentration of oxygen and the "end OD" terms refer to the carbonyl oxide signals under these conditions. While it is not clear if the plot is truly linear, kinetic analysis (see Figure 5 for a representative plot) leads to Stern–Volmer slopes of 95 and 37 M^{-1} for 1 and 3, respectively, for a solution saturated with 1.05% oxygen-in-nitrogen. If one assumes that the triplet carbene is the species quenched, these data lead to apparent rate constants of 4×10^6 and 2×10^6 M^{-1} s^{-1}, respectively. There is a clear discrepancy between this result and the slower quenching observed in the time-resolved experiments (see Figure 3). In fact, the time-resolved data would predict that quenching should be barely detectable. The most common cause for discrepancies between time-resolved and Stern–Volmer kinetic data is the involvement of a different reaction intermediate. In our system this is an indication of extensive singlet carbene quenching prior to spin equilibration, and therefore the Stern–Volmer analysis reflects predominantly singlet rather than triplet reactivity.

An estimate of the singlet lifetime may be obtained if it is assumed that the singlet is quenched at the diffusion-controlled rate and that triplet quenching by methanol is negligible. This puts the singlet lifetimes for 1 and 3 in the 100–500 ps range.

Ylide Formation. The photolysis of diazo compound 4 in pure acetonitrile does not yield a transient spectrum that may be assigned to the ylide. However, laser excitation of quinone diazides 4–6 in Freon-113 in the presence of small concentrations of acetone, acetonitrile, or pyridine all lead to the observation of transient species with a λ_{max} of ~620 nm which then thermally rearrange to give species that are tentatively assigned to the corresponding ylides 13–18. The identity of the first formed transient is unknown, although it is possible that triplet biradical addition products are formed that then undergo intersystem crossing followed by intramolecular charge separation to produce the ylides. The 620-nm growth is consistent with the decay of the carbene, and the ylide growth occurs concurrently with the decay of the 620-nm transient; the two traces in Figure 6 illustrate this effect. This trans-

---

[24] Nikoforov, G. A. Doctor of Science Thesis, Academy of Science: Moscow, 1979.

[25] Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* 1984, *106*, 198.

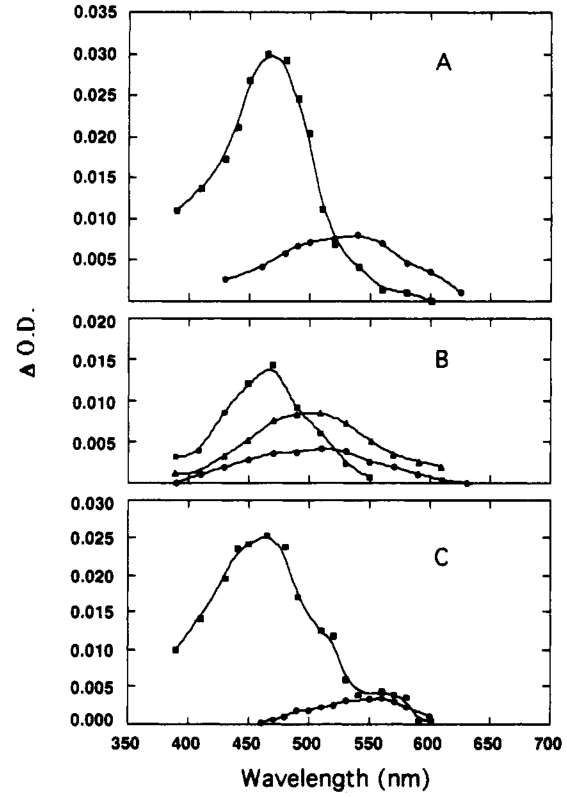
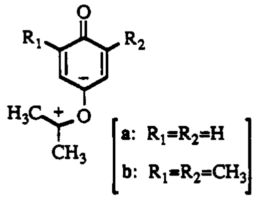
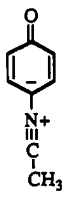


Figure 7. Spectra of the ylides formed by reaction of 1 (●), 2 (▲), and 3 (■) with (A) acetonitrile, (B) acetone, and (C) pyridine.

formation occurs with a lifetime of 3.2 μs and 2.7 μs for **13a** and **15**, respectively. The sample of **1** in the presence of acetonitrile was not sufficiently stable to accurately measure the interconversion leading to **14**. Surprisingly, the 620-nm transient is virtually independent of which reactant (acetone, acetonitrile, or pyridine) is used, suggesting that the chromophore must be almost exclusively centered on the carbene-derived moiety. Preliminary experiments indicate that ylide **13a** is quenched by maleic anhydride. The corresponding absorption maxima of the ylides can be found in Table I.



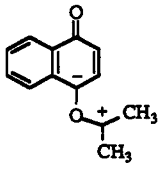
13



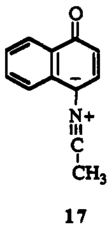
14

15

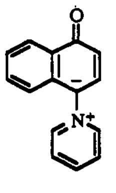
The data in Table I as well as the spectra in Figure 7 show that the absorption maxima of ylides derived from carbenes **1** and **2** are significantly red-shifted in relation to ylides formed by reaction of the benzo-annealated derivative **3**; this is particularly obvious in the case of the acetonitrile and pyridine ylides. Comparison with λ_{max} for similar species reported in the literature reveals that **14**, **15**, and **18** absorb at the red edge of the known ylide spectra. For example, the acetonitrile ylides derived from fluorenylidene[26] and 1-naphthylcarbene[27] exhibit λ_{max} of 400 nm. The long-wavelength absorption is presumably due to the extended O-system, with participation of resonance structures of internal phenoxide character. Another difference between the ylides of **1** and **3** lies in the intensity of the observed signals. Particularly in the case of the acetonitrile and pyridine ylides **14** and **15** the absorptions were often very weak; **3** however, gives ylides which are readily monitored.



16



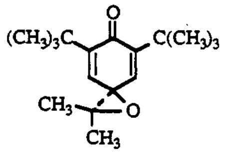
17



18

Chemical evidence for the formation of 3,5-di-*tert*-butyl-4-oxocyclohexadienylidene nitrile ylides had already been gained by Kende et al.,[28] who upon thermolysis of the diazo precursor in acrylonitrile found a 2:1 acrylonitrile–carbene adduct that could only have been formed by 1,3-dipolar cycloaddition of the ylide to the C=C double bond of another acrylonitrile molecule. The fact that 308-nm excitation of **4** in neat acetonitrile leads to no detectable transient absorption requires that the exclusive reaction path under these conditions be C–H insertion, eventually forming 4-hydroxybenzylcyanide.

Ershov et al.[4,15] have reported the formation of spirooxirane **19**, which indicates the intermediacy of the acetone ylide. However, in acetophenone as solvent the same authors found products of an insertion into methyl C–H bonds. This behavior can be explained in terms of a singlet carbene, which is both nucleophilic and electrophilic. The actual course of the reaction then depends on factors such as solvent polarity and acidity. As in the acetonitrile case the singlet must prefer insertion over ylide formation while the triplet, through an intermediate, leads eventually to the ylide.



19

Given our observation that ylides are derived from the *triplet* carbene, it is reassuring that its formation is a stepwise process involving at least one other intermediate on the pathway to ylide formation, even if the nature of this intermediate has not been fully elucidated.

Conclusion

These results of our laser flash photolysis studies show that triplet 4-oxocyclohexadienylidene and the two derivatives examined in this work exhibit a reactivity which is similar to related carbenes such as anthronylidene or 1-naphthylcarbene. The overall reactivity observed is comparable to that reported for diarylcarbenes with a moderately large T–S separation. The singlet species that is generated directly by 308-nm excitation of the diazo precursor exhibits remarkable reactivity in that it rapidly undergoes C–H insertion reactions with solvents such as cyclohexane and acetonitrile. As a result of this reactivity the singlet does not lead to ylides, although these can be formed via the triplet. This unusual reaction involves an intermediate with an absorption in the 620-nm region.

---

(26) Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227.

(27) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *Chem. Phys. Lett.* **1983**, *97*, 446.

(28) Kende, A. S.; Hebeisen, P.; Sanfilippo, P. J.; Toder, B. H. *J. Am. Chem. Soc.* **1982**, *104*, 4244.

Acknowledgment. Thanks are due to S. E. Sugamori and G. Charette for technical assistance. G.F.B. would like to express his special gratitude to the Fonds der Chemischen Industrie for a grant. We also thank the Natural Sciences and Engineering Research Council of Canada and the SFB 247 der Chemischen Institute, Heidelberg, for financial support.

Registry No. **1**, 3225-37-4; **2**, 53905-02-5; **3**, 138435-10-6; **4**, 932-97-8; **5**, 937-37-1; **6**, 99230-11-2; **7**, 118949-77-2; **8**, 144084-88-8; **9**, 99967-24-5; **10**, 144084-89-9; **12**, 2122-46-5; **13a**, 144084-90-2; **14**, 144084-91-3; **15**, 19329-94-3; Freon-113, 76-13-1; O_2, 7782-44-7; MeOH, 67-56-1; cyclohexane, 110-82-7.

Stereoselectivity and Reversibility of Electrophilic Bromine Addition to Stilbenes in Chloroform: Influence of the Bromide–Tribromide–Pentabromide Equilibrium in the Counteranion of the Ionic Intermediates

Roberto Bianchini* and Cinzia Chiappe

Dipartimento Chimica Bioorganica, via Bonanno 33, Pisa 56126, Italy

Received July 20, 1992

Two equilibria were found in chloroform solutions of $Bu_4N^+Br^-$ and Br_2, leading to tribromide and pentabromide salts. The electronic spectra and formation constants of both ($K_3 = 2.77\ (0.13) \times 10^4\ M^{-1}$ and $K_5 = 3.51\ (0.35) \times 10^5\ M^{-2}$ at 25 °C) were computed from spectrophotometric data. The stability of the Br_3^- species in chloroform resulted to be at least 3 orders of magnitude lower than in 1,2-dichloroethane. A change from prevalent formation of *d,l*-1,2-dibromo-1,2-diphenylethane to prevalent formation of meso dibromide, accompanied by a cis–trans isomerization of the unreacted olefin, has been observed in the bromination of *cis*-stilbene with decreasing reagent concentrations, when the bromide–tribromide–pentabromide equilibrium in the counteranions of the ion pairs intermediates is shifted in favor of the Br^- form. The results show that these intermediates are reversibly formed even when the anion is Br^-.

The electrophilic addition of bromine to alkenes is one of the most investigated reactions. It is well known[1] that its apparently simple mechanism is stepwise in nature and proceeds through the formation of bromonium or bromocarbonium bromide,[2] or tribromide,[3] intermediates, subsequently collapsing to addition products. A new important feature recently reported for this reaction pertains to the reversibility of the formation of the ionic intermediates.[4] In methanol and ethanol this reversibility has been admitted only for highly congested bromonium ions.[5] In contrast, in 1,2-dichloroethane a relevant internal return has been shown with uncongested olefins, too, and this requires that nucleophilic attack in the product forming step is slow.[4e] One explanation for the difference between the two types of solvents assumes[6] that in halogenated hydrocarbons the product-forming step is slow since the counter tribromide ion is not a highly nucleophilic species, so that the effective nucleophile must be provided by dissociation of the very stable Br_3^-, a process which is not necessarily fast.[7] In order to check this rationalization, an investigation of the olefin bromination in a solvent in which the stability of the Br_3^- ion is reduced appeared promising.

Here we are reporting on a study of the equilibria involving Br^-, Br_3^-, and Br_5^- anions in a low polarity aprotic solvent, chloroform, and on their influence on the product distribution of the electrophilic addition of Br_2 to *cis*- and *trans*-stilbene. We demonstrate that reversibility of theionic intermediate formation can occur even when a significant amount of Br^- is present as counteranion, at sufficiently low bromine concentration.

Results

The Br^-–Br_3^-–Br_5^- Equilibrium. The UV-vis spectra of solutions of tetrabutylammonium bromide (TBAB) and Br_2 in ethanol-free chloroform[8] were taken, at the concentrations reported in the Experimental Section, in the 250–500-nm range. An absorption band with $\lambda_{max} = 272$ nm was apparent in solutions containing a slight Br_2 over Br^- excess (curve a of Figure 1). When a large Br_2 excess was used, a new absorption band appeared, besides the 272-nm one, in the 290–330-nm interval (curves b, c, and d of Figure 1). These phenomena were considered as evidence for the formation of Br_3^- and Br_5^- anions from Br^- and Br_2, as already observed in 1,2-dichloroethane,[9] according to eqs 1 and 2.

$$Br^- + Br_2 \overset{K_3}{\rightleftharpoons} Br_3^- \qquad (1)$$

$$Br^- + 2Br_2 \overset{K_5}{\rightleftharpoons} Br_5^- \qquad (2)$$

---

[1] See, for instance: (a) Schmid, G. H. *The Chemistry of Double-Bonded Functional groups*, Suppl. A.; Patai, S., Ed. Wiley: New York, 1989; Vol. 2, Part 1, p 699. (b) V'yunov, K. A.; Ginak, A. I. *Russ. Chem. Rev.* (*Engl. transl.*) **1981**, *50*, 151. (c) De la Mare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: New York, 1982; pp 136–137.

[2] (a) Garnier, F.; Donnay, R. H.; Dubois, J.-E. *J. Chem. Soc., Chem. Commun.* **1971**, 829. (b) Modro, A.; Schimd, G. H.; Yates, K. *J. Org. Chem.* **1979**, *44*, 4221.

[3] (a) Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1985**, *107*, 2464. (b) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504.

[4] (a) Brown, R. S.; Gedye, R.; Slebocka-Tilk, H.; Buschek, J. M.; Kopecky, K. R. *J. Am. Chem. Soc.* **1984**, *106*, 4515. (b) Bellucci, G.; Chiappe, C.; Marioni, F. *J. Am. Chem. Soc.* **1987**, *109*, 515. (c) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Spagna, R. *J. Am. Chem. Soc.* **1988**, *110*, 546. (d) Bennet, A. J.; Brown, R. S.; Slebocka-Tilk, H.; Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1990**, *112*, 6310. (e) Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1991**, *113*, 8012.

[5] (a) Ruasse, M.-F.; Motallebi, S.; Galland, B.; Lomas, J. S. *J. Org. Chem.* **1990**, *55*, 2298. (b) Ruasse, M.-F.; Motallebi, S.; Galland, B. *J. Am. Chem. Soc.* **1991**, *113*, 3440.

[6] Ruasse, M.-F.; Motallebi, S. *J. Phys. Org. Chem.* **1991**, *4*, 527.

[7] Ruasse, M.-F. *Acc. Chem. Res.* **1990**, *23*, 87, footnote 23.

[8] See Experimental Section.

[9] Bellucci, G.; Bianchini, R.; Chiappe, C.; Ambrosetti, R. *J. Am. Chem. Soc.* **1989**, *111*, 199.

0022-3263/92/1957-6474$03.00/0 © 1992 American Chemical Society