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Carbocation Formation via Carbene Protonation Studied by the Technique of Stopped-Flow Laser-Flash Photolysis

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Abstract: Photolysis of diaryl diazo compounds in the presence of hydroxylic protonating substrates in acetonitrile leads to the formation of the corresponding carbocations. Quantum yields for these processes have been determined for the first time; for example, photolysis of diphenyldiazomethane in 1:1 acetonitrile/trifluoroethanol produces Ph_2CH^+ with a quantum yield of 0.007. The products, formed either by direct insertion or through the carbocation route, are the corresponding ethers. Kinetics analysis leads to the conclusion that carbocations are formed by protonation of the singlet carbene. Electron-rich substituents enhance carbocation yields; for example, $(4\text{-}MeOC_6H_4)_2CH^+$ is produced with a quantum yield of 0.12 in 1:1 acetonitrile/methanol or acetonitrile/trifluoroethanol. Most of the diazo precursors employed decompose rapidly in the presence of acids or strongly protonating solvents. In order to overcome this problem, we have developed the technique of stopped-flow laser-flash photolysis, which permits the study of photoreactions in thermally unstable mixtures. Strong acids (e.g., perchloric) in concentrations up to 10 mM fail to yield any carbocations. This is probably due to the short lifetime of the carbene singlet that cannot be trapped at low acid concentrations, as well as to a low-energy singlet carbene in equilibrium with the triplet following intersystem crossing; higher concentrations of acid induce diazo decomposition within the stopped-flow mixing time.

Introduction

Several recent reports have indicated that photolysis of diazo compounds in protonating solvents can lead to the formation of carbocations.[4,5] Further, it has been suggested that these carbocations may result from protonation of singlet carbenes. The scope of such experiments has generally been limited by the fact that diazo compounds, the most frequently used carbene precursors, are unstable in acids or strongly protonating solvents. Thus, literature experiments have been limited to diazo-solvent combinations which are stable for at least a few minutes and may occasionally have been carried out when the thermal reaction had proceeded to significant conversion. Experiments involving strong acids and using diazo precursors have never been reported, and only rarely have such experiments employed diazirines as sources of ground-state singlet carbenes.[6]

The electronic state of the carbene is another important consideration. Given that carbocations are expected to have singlet ground states, it is anticipated that protonation will be more facile for the singlet carbene. Simple diarylcarbenes generally have triplet ground states, although direct photolysis of the diazo precursor leads to the singlet state, which undergoes intersystem crossing to the triplet in the subnanosecond time scale. It should be noted that carbene protonation for some ground-state singlet carbenes has been inferred in the past on the basis of product studies[7-9] as well as laser photolysis work.[10,11]

In this article we report on the development of the new technique of stopped-flow laser-flash photolysis that has enabled us to overcome the difficulties related to thermal instability of the diazo compounds mentioned above. The technique should be of general applicability to systems where the poor stability of the samples may otherwise prevent photochemical studies. The carbenes studied here are diphenylcarbene and some of its substituted derivatives. We have determined quantum yields for carbocation formation and addressed the question as to which species is the true reactive intermediate. In principle, these may include the ground-state triplet carbene, the lowest singlet state, an excited singlet state, or an excited state of the diazo precursor. We conclude that our results are consistent with singlet carbene protonation.

Recent studies of carbocations using laser-flash photolysis techniques make the characterization of these intermediates straightforward.[12-17]

Results

The protonation reaction between organic carbenes and alcohols has been studied for a range of mono- and disubstituted diarylcarbenes generated photochemically from their corresponding diazo precursors. In many cases, the diazo compounds themselves are highly reactive toward the alcohols employed, generating O-H insertion products. Therefore, in order to study the reaction of these carbenes with alcohols, we have developed a stopped-flow apparatus for use with our laser-flash photolysis system.

In the presence of CF_3CH_2OH, solutions of Ph_2CN_2 in acetonitrile undergo rapid solvolyses to yield the ether product $Ph_2CH(OCH_2CF_3)$. When solutions of Ph_2CN_2 in acetonitrile are mixed rapidly with CF_3CH_2OH in the stopped-flow apparatus followed by 308-nm laser photolysis, a transient species is formed, whose kinetic and spectroscopic characteristics are consistent with those of the diphenylmethyl cation, $Ph_2C\text{-}H^+$ (τ = 150 ns, λ_{max} = 435 nm); see Figure 1. When ethanol, methanol, or water is employed as the proton donor, the lifetime of the cation is too short to be detected with nanosecond resolution, although these inter-

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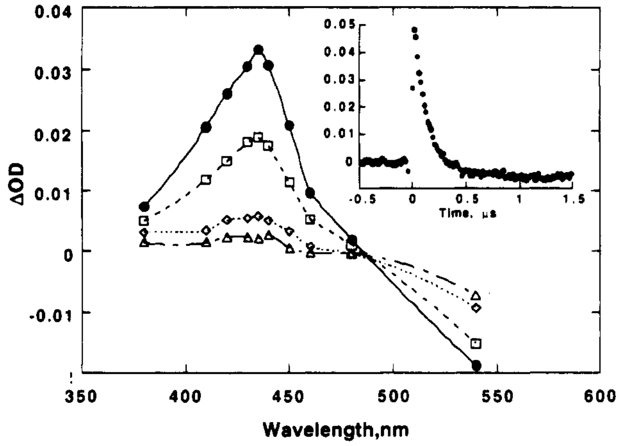

Figure 1. Spectra of Ph_2CH^+ generated by laser irradiation of diphenyldiazomethane in 1:1 trifluoroethanol/acetonitrile, monitored at 290 (●), 350 (□), 440 (◇), and 560 ns (△) following the laser pulse. Inset: Decay of $Ph_2C–H^+$ monitored at 435 nm.

Table I. Lifetime of the Cation $(4\text{-}MeOC_6H_4)_2CH^+$ in 1:1 Acetonitrile/ROH Mixtures (by Volume)

ROH	lifetime
$(CF_3)_2CHOH$	>200 μs
CF_3CH_2OH	200 μs
H_2O	10.4 μs
CH_3CH_2OH	735 ns
CH_3OH	430 ns
C_6H_5OH (1 M)	13.0 μs

mediates have been detected using picosecond techniques.[5]

Upon changing the alcohol cosolvents to dilute solutions, (up to 10 mM) of strong acids such as trifluoroacetic or perchloric acid in acetonitrile, no formation of $Ph_2C–H^+$ is observed. At acid concentrations greater than 10 mM, decomposition of the parent diazo compound occurs within the stopped-flow mixing time (about 4 ms). Further, by monitoring the disappearance of Ph_2CN_2 in the presence of dilute trifluoroacetic acid by conventional UV/vis absorption spectroscopy, we measured the second-order rate constant for this reaction in acetonitrile to be ca. 10^4 M^{-1} s^{-1}. The fact that no cation formation was observed up to an acid concentration of 10 mM indicates that under these conditions the concentration of the intermediate responsible for reaction is low and/or that the reaction rate constant is small. Triplet carbene half-lives under our experimental conditions are typically ~10 μs and occasionally longer and result from a mixture of first- and second-order processes. Typical lifetimes in the presence of 10 and 20 mM methanol are ~2.7 and 1.7 μs; i.e., the changes in lifetime are readily detectable. In contrast, 10 mM perchloric acid had no detectable effect (<10%) on the triplet carbene lifetime.[18] This places an upper limit for the observable rate constant for reaction between mineral acids and triplet carbene of $<10^6$ M^{-1} s^{-1}, or at least 20 times slower than with methanol.

The carbene protonation reaction was then investigated for the bis methoxy substituted diazo compound $(4\text{-}MeOC_6H_4)_2CN_2$. In a comparison of the ground-state reactivities of the parent diazo compound and $(4\text{-}MeOC_6H_4)_2CN_2$, solvolysis of the latter is much faster in CF_3CH_2OH; this observation highlights the requirement for the stopped-flow instrument in studying these protonation reactions. Stopped-flow laser-flash photolysis of $(4\text{-}MeOC_6H_4)_2CN_2$ in 1:1 (by volume) acetonitrile/CF_3CH_2OH yields the carbocation $(4\text{-}MeOC_6H_4)C–H^+$ as monitored at 500 nm. Under these conditions, the lifetime of the carbocation (τ = 200 μs) is 3 orders of magnitude longer than that of $Ph_2C–H^+$, reflecting the stabilizing effect of the two *p*-methoxy substituents. The long lifetime of the $(4\text{-}MeOC_6H_4)_2C–H^+$ carbocation observed in 1:1 acetonitrile/CF_3CH_2OH proved to be suitable for the study of the reactivity of this transient with other alcohols. The lifetimes of $(4\text{-}MeOC_6H_4)_2C–H^+$ in 1:1 acetonitrile/alcohol solvent mixtures are given in Table I and illustrate the strong dependence of the carbocation lifetime on the solvent nucleophile.

Table II. Decay Kinetics and Yields for Various Carbocations Produced by Protonation of $(4\text{-}XC_6H_4)_2C$: in 1:1 Trifluoroethanol/Acetonitrile

X, X	τ	λ_{max} (nm)	ΔOD exptl	Φ_{cation}
Cl, Cl	170 ns	470	0.034	0.003
H, H	130 ns	435	0.030	0.007
Me, Me	4.5 μs	465	0.11	0.016
MeO, H	30 μs	460	0.24	0.056
MeO, MeO	200 μs	500	1.36[a]	0.12

[a] ΔOD measured was 0.34 following attenuation of the laser power to 25%.

In addition to the kinetics and spectroscopic characterization of diaryl carbocations described already, we have investigated the effects of solvent and carbene substituents on the absolute and relative yields of the carbocations formed. It was noted at an early stage that not only was the lifetime of $(4\text{-}MeOC_6H_4)_2C–H^+$ much longer than for the parent $Ph_2C–H^+$ but transient absorptions measured for $(4\text{-}MeOC_6H_4)_2C–H^+$ were consistently and significantly larger than those determined for $Ph_2C–H^+$. In order to examine these phenomena more closely, a more expansive and quantitative set of transient absorption measurements were made. Lifetimes and transient absorptions (at appropriate absorption maxima) were measured for a series of five substituted carbocations following irradiation of their corresponding diazo precursors in 1:1 acetonitrile/trifluoroethanol. In considering the relative yields of the carbocations formed, care was taken to standardize the absorptions of the diazo precursors, laser power, cell orientation, etc. and account for changes in extinction coefficients for the individual carbocations. A summary of these observations is given in Table II and illustrates a clear and consistent trend between the lifetimes of the carbocations (in a given solvent composition), their relative yields, and the stabilizing properties of the aryl substituents. In addition to these pronounced substituent effects, we have investigated (i) the effect of proton source on the relative yields for a given carbocation and (ii) the absolute quantum yields for carbocation formation. In contrast to the strong substituent effect described earlier, the yield of $(4\text{-}MeOC_6H_4)_2C–H^+$ was found to be insensitive to the choice of protonating solvent ($(CF_3)_2CHOH$, CF_3CH_2OH, CH_3CH_2OH, CH_3OH, PhOH) with the exception of water, where ca. 2.3 times more carbocation was produced under otherwise identical conditions. It should also be noted that, despite the formation of cationic species in these protonation reactions, the carbocation yields were unaffected by the presence of $Me_4N^+BF_4^-$ or $Me_4N^+BPh_4^-$ (up to 10 mM). For comparison, similar salt concentrations have extensive effects when the same carbocations are generated by electron transfer from excited diarylmethyl radicals to appropriate acceptors.[19] In a comparison of a range of alcohols, the $(4\text{-}MeOC_6H_4)_2C–H^+$ intermediate was found to be the only carbocation having a sufficiently long lifetime to allow its study in all solvents of interest.

A relative scale for the formation of substituted diaryl carbocations) having been established, it seemed appropriate to determine an absolute quantum yield for this protonation reaction. In order to do this, transient absorption actinometry was carried out using the triplet state of benzophenone in benzene as an actinometer. The methodology behind this transient absorption technique has been described previously in detail.[20,21] Briefly, transient absorption changes due to $(4\text{-}MeOC_6H_4)_2C–H^+$ in acetonitrile/alcohol at 500 nm and the triplet state of benzophenone in benzene at 525 nm were measured as a function of

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(18) This also includes one case where the experimental carbene lifetime (in the absence of alcohol) approached 18 μs.

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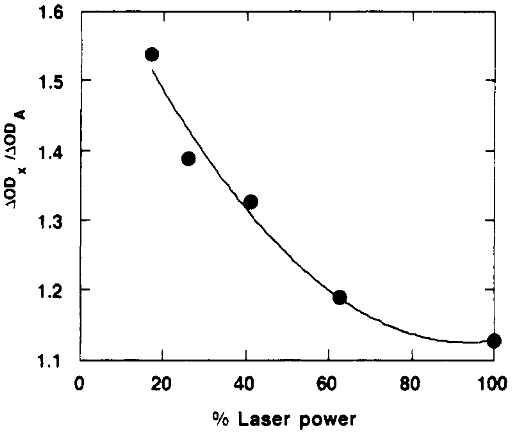

Figure 2. Determination of $\epsilon_x\Phi_x$ for $(4\text{-}MeOC_6H_4)_2C\text{-}H^+$ in 1:1 acetonitrile/methanol according to eq 1 (see text).

laser dose. The relationship between these data is then given by eq 1, where ΔOD_x and ΔOD_A represent the absorption changes

$$\epsilon_x\Phi_x = (\Delta OD_x/\Delta OD_A)\epsilon_A\Phi_A \qquad (1)$$

due to carbocation and triplet benzophenone, while ϵ_x and ϵ_A are the corresponding extinction coefficients. Finally, since the quantum yield for the formation of triplet benzophenone is 1.0, the corresponding value for the carbocation can be determined.

In two separate experiments, this analysis has been used to calculate the quantum yield for $(4\text{-}MeOC_6H_4)_2C\text{-}H^+$ formation in acetonitrile containing methanol or water (equal parts by volume in each case). A representative plot of $\Delta OD_x/\Delta OD_A$ vs laser dose is shown in Figure 2, where the slope is largely due to the partial depletion of the diazo compound at high laser power. By extrapolation of these data to 0 laser dose and use of the reported values for the extinction coefficients for sample and actinometer (110000 and 7800 M^{-1} cm^{-1}, respectively),[14,20] the apparent quantum yield for the formation of $(4\text{-}MeOC_6H_4)_2C\text{-}H^+$ in 1:1 acetonitrile/methanol is ca. 0.12. Further, if a value of 0.73 is assumed for the quantum yield for the loss of N_2 from the diazo precursor,[22] the efficiency for the carbocation formation from (presumably) the singlet carbene becomes 0.16. When this analysis was repeated with water as the proton source, this efficiency was dramatically higher (0.36). Using the value of 0.12 for the quantum yield mentioned above together with the observation that cation yields are the same for methanol and trifluoroethanol made it possible to put all the values in Table II on an absolute scale. These values (which also take into account the different extinction coefficients) are given in the last column of Table II.

Identification of the Reactive Species. Our investigations have also been extended to the identification of the reactive intermediate that precedes the carbocation formation. At the outset of these experiments this species was assumed to be the singlet carbene with a rate constant for reaction with alcohols of 10^9–10^{10} M^{-1} s^{-1}. We have performed a series of experiments that support this assignment. Firstly, when Ph_2CN_2 is laser irradiated in acetonitrile/alcohol solutions, the yield of $Ph_2C\text{-}H^+$ is independent of the concentration of alcohol for high concentrations (typically >1 M). For lower concentrations, the yield of the carbocation decreases with decreasing alcohol concentration. This can be explained in terms of the reaction of the singlet carbene with alcohol being competitive with intersystem crossing to the relatively unreactive triplet state. In 1 M alcohol the product k_q[ROH] for the singlet carbene will approach or exceed 10^{10} s^{-1}. By comparison, singlet–triplet intersystem crossing occurs with a rate constant of about 3×10^9 s^{-1}.[23,24] Thus, for alcohol concentrations <1 M the two processes can be competitive, while at sufficiently high concentrations, reaction with the alcohol becomes the only significant form of decay for the singlet carbene. Notably, despite the efficient quenching of Ph_2C: in its singlet state with alcohol concentrations >1 M, we notice that significantly higher concentrations of alcohol are required to completely quench other carbene singlet states (e.g., >7 M for $(4\text{-}MeOC_6H_4)_2C$:).

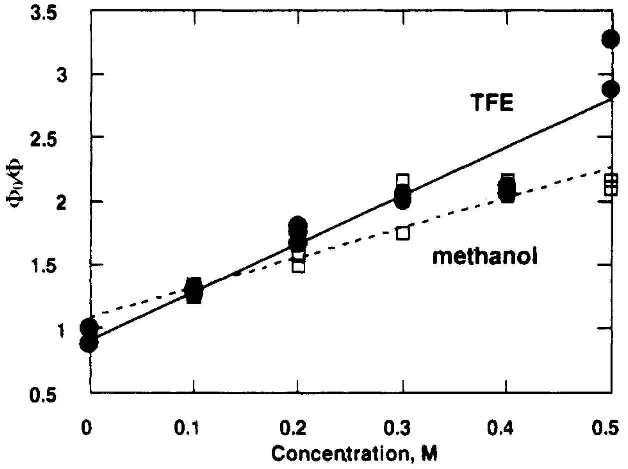

Figure 3. Stern–Volmer plots based on carbonyl oxide formation (see eq 2) for the photolysis of diphenyldiazomethane in acetonitrile using trifluoroethanol (TFE, ●) and methanol (□) as scavengers.

Table III. Comparison of Data from Various Sources for Diphenylcarbene Lifetime in Acetonitrile

source	Stern–Volmer slope (M^{-1})	τ (ps)
effect of CF_3CH_2OH on cation yield (eq 3)	2.1	210
quenching by CF_3CH_2OH of the yield of triplet carbene (eq 2)	3.8	380
quenching by CH_3OH of the yield of triplet carbene (eq 2)	2.4	240
picosecond ISC studies from the literature[23,24]		320

Two sets of quantitative competitive kinetics studies were carried out in attempts to establish the nature of the intermediate leading to carbocation formation. The dynamics of singlet carbene decay and of carbocation formation cannot be studied directly with nanosecond techniques, since these processes appear to be complete within 1 ns. However, the effect of alcohol concentration on the yields of carbocation and of triplet carbene can be studied using a Stern–Volmer type of approach. While the triplet carbene is not straightforward to monitor directly under our experimental conditions, we find that addition of oxygen transforms the triplet carbene into the readily detectable carbonyl oxide (λ_{max} 410 nm for benzophenone oxide).[25,26] The yield of carbonyl oxide (Φ_{CO}), as measured by the transient absorbtion (ΔOD) at 410 nm, is related to the rate constants of interest according to eq 2,

$$\frac{\Phi^0_{CO}}{\Phi_{CO}} = \frac{\Delta OD^0_{410}}{\Delta OD_{410}} = 1 + k_q\tau[\mathrm{ROH}] \qquad (2)$$

where the superscript "0" indicates data acquired in the absence of alcohol, k_q is the rate constant for the reaction of the precursor being scavenged with alcohol, and τ is the lifetime of this intermediate in the presence of the fixed oxygen concentration employed in these experiments. The oxygen concentration was maintained by bubbling the solution with oxygen. The corresponding plots are shown in Figure 3 and lead to Stern–Volmer slopes of 3.8 ± 1.0 and 2.4 ± 0.9 M^{-1} for trifluoroethanol and

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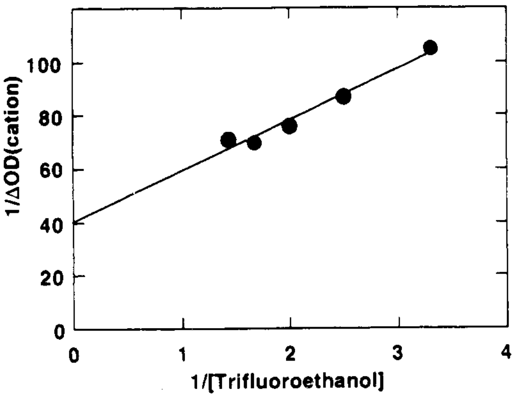
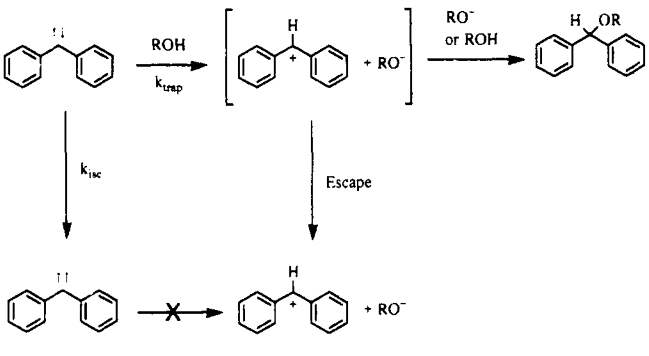


Figure 4. Plot of the cation yield as a function of (molar) trifluoroethanol concentration (see eq 3) for diphenyldiazomethane in acetonitrile, monitored at 435 nm.

Scheme I



methanol in acetonitrile. If it is assumed that the reactive species is the singlet state of the carbene and that $k_q \sim 10^{10}$ M^{-1} s^{-1},[27] then the estimated singlet carbene lifetime would be 380 and 240 ps in the same pair of solvents. Table III summarizes our results.

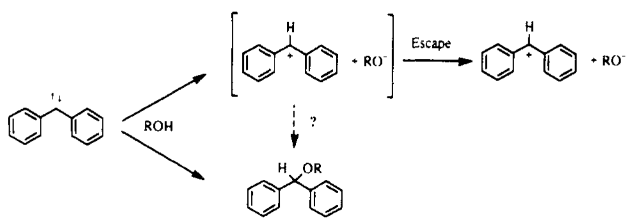
It should be noted that if we assume that the reactive species was the triplet carbene after singlet–triplet equilibration, then, based on the reported kinetics for methanol,[28] the lifetime of the triplet carbene would have to be around 100 ns, which is much longer than the experimental value under an oxygen atmosphere.

One may question whether methanol quenching of the triplet state may in fact contribute to the overall process. In other words, to what extent can 0.5 M alcohol (our highest concentration in this experiment) compete with approximately 10^{-2} M oxygen? Since all the relevant rate constants are known,[25,28] it is straightforward to estimate that in the worst-case situation less than 20% of the triplet quenching would involve the alcohol. Such an error would lead to a slightly higher Stern–Volmer slope.

The other approach employed in our competitive quenching studies consists of the determination of the effect of trifluoroethanol addition on the yield of carbocation. The competition between intersystem crossing and reaction with the proton source is illustrated in Scheme I. Kinetics analysis of this competition leads to eq 3,[29]

$$\frac{1}{\Delta \mathrm{OD}_{\mathrm{cation}}} = a + \frac{a k_{\mathrm{isc}}}{k_{\mathrm{trap}}[\mathrm{ROH}]} \qquad (3)$$

Scheme II



where "*a*" is an experimental parameter that relates the quantum yield and the transient absorptions for the carbocation. The corresponding plot is shown in Figure 4 and leads to $k_{\mathrm{trap}}/k_{\mathrm{isc}} = 2.1$ M^{-1}. If it is assumed that the singlet state is the species responsible for carbocation formation, the singlet lifetime would be 210 ps, on the basis of the known reactivity of the singlet state toward alcohols.[27]

Discussion

The results presented here confirm that carbocation formation by protonation of carbenes is a general carbene reaction in hydroxylic solvents.

Strong acids fail to induce any carbocation formation. The highest concentrations that can be employed are only ca. 10 mM, even with stopped-flow techniques; this is due to the instability of diazo compounds in acid media. These concentrations proved to be too low to capture the short-lived singlet state, even if one could anticipate that the rate constant may approach diffusion control. Interestingly, not only does the triplet state not react with strong acids but also any singlet concentration in equilibrium with the triplet must be remarkably low, since it fails to react with the acid. While we hesitate to speculate on the basis of negative results (no quenching by mineral acid), the results are compatible with an explanation in which triplet-quenching by methanol does not require the intermediacy of singlet carbenes in equilibrium,[28] while protonation would appear to require singlet participation. Thus, the surface crossing mechanism proposed for the methanol insertion reaction[28] does not appear to be operative with mineral acid. Indeed, we find it easier to rationalize the observation that different reactivities are observed for the triplet with alcohols and acids in this way than the alternate explanation (for the singlet in equilibrium) that would require drastically different reactivities by the (usually) unselective singlet state.

Carbene protonation occurs readily in protonating solvents, but the yields, at least for the parent diphenylmethylene, are quite modest. Clearly, the dominant pathway in the photolysis of diphenyldiazomethane in the presence of alcohols leads to carbene insertion into the O–H bond. We will later try to address whether the two reactions are parallel processes or represent a partition from an initial common pathway.

One may ask whether the singlet carbene is necessarily the intermediate involved in the protonation reaction. Clearly, the triplet state can be excluded from the list of possible precursors given in the Introduction, since carbocation formation is not concurrent (it is too fast) with triplet decay. The data in Table III is consistent with the cation precursor being the same intermediate that leads to the triplet carbene and inserts into alcohols. Thus, we conclude that our data do not require invoking any other precursor than the lowest energy singlet carbene. If other intermediates participate (e.g., excited diazos), their contribution must be sufficiently small that it has no impact on the overall yield of carbocation. We note that our conclusion relies heavily on Eisenthal's work using picosecond techniques,[24] where the rate constants for triplet carbene formation have been equated to those for singlet carbene decay. This assumption is consistent with our present knowledge of carbene reaction mechanisms.

Solvent effects on cation lifetimes (see Table I) are in line with those reported by other laboratories employing different precursors.[30]

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(29) Equation 3 can be readily derived by rearranging the expression for the quantum yield of cation, i.e.,

$$\Phi_{\mathrm{cation}} = \frac{\Delta \mathrm{OD}_{\mathrm{cation}}}{I_a \epsilon l} = \Phi_{\mathrm{carbene}} \frac{k_{\mathrm{trap}}[\mathrm{ROH}]}{k_{\mathrm{isc}} + k_{\mathrm{trap}[\mathrm{ROH}]}}$$

where I_a is the absorbed light dose, ϵ is the cation extinction coefficient, and l is the optical path.

(30) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913.

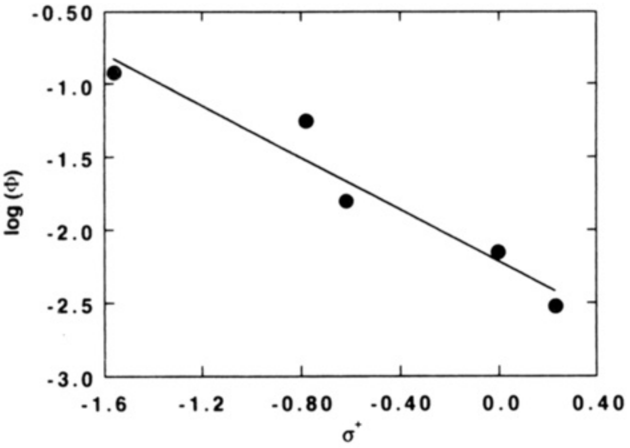


Figure 5. Plot of log Φ for cation formation vs σ^+ in 1:1 acetonitrile/methanol.

It is interesting that the yield of cations is larger when water rather than methanol is used as cosolvent. We suspect that this reflects an enhanced carbene ability to insert into an O–H bond in the case of methanol, the better nucleophile, while in protonation reactions both solvents may be comparable.

Other parameters being constant, the quantum yield of cation formation increases with electron-donor substituents, a fact that correlates well with cation lifetimes (see Table II). A Hammett plot of log Φ against σ^+ shows a reasonable correlation (see Figure 5).

We can now return to the question of the detailed reaction pathway for protonation and insertion. These are illustrated in Schemes I and II. The difference between the two possibilities is determined by the mechanism for insertion, which in one case (Scheme I) occurs via a carbocation intermediate, while in Scheme II insertion is pictured as a concerted process (although some geminate ion recombination cannot be ruled out). If we assume that escape of the ions from the solvent cage in the case of Scheme I (see intermediates in brackets) is unlikely to depend much upon the substituent, then one would have to conclude that the rates of geminate reaction of the positive and negative species to give the insertion products would depend strongly on ring substitution. While some dependence would not be unreasonable, the factor of ~40 required by our data (see Table II) would be rather surprising. Thus, we believe that our results are best interpreted by Scheme II, where insertion occurs parallel to protonation rather than as part of a common reaction pathway.

It should be noted that in hydroxylic solvents the carbocations eventually react with the solvent to yield the same ethers that are produced in the insertion reactions. In the presence of high alcohol concentrations (or in neat alcohols) the known reactivities of these carbocations,[30] as well as recent picosecond studies,[5] will lead to cation lifetimes in the subnanosecond range. Thus, from the point of view of final products, insertion can be viewed as a mixture of a concerted pathway and a stepwise carbocation (or protonation) pathway, with the latter gaining in importance for systems with electron-rich ring substituents, and is essentially the process proposed by Kirmse.[8,9] We note that in the context of our discussion the term "concerted" refers to processes that do not involve the intermediacy of distinct carbocations. Our results do not provide any information on the question of possible ylide intermediacy.[31,32]

The results reported herein, combined with a recent report from our laboratory[19] on the electron-transfer reactions of excited diphenylmethyl radicals, provide quantitative kinetics connections between the free radical, carbene, and carbocation manifolds. The results show that by judicious choice of experimental conditions these processes (see Scheme III) can take place efficiently and with high rate constants.

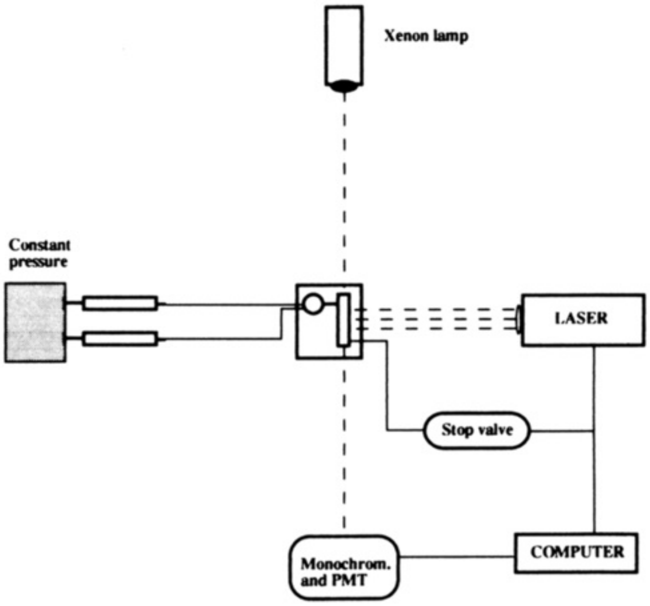
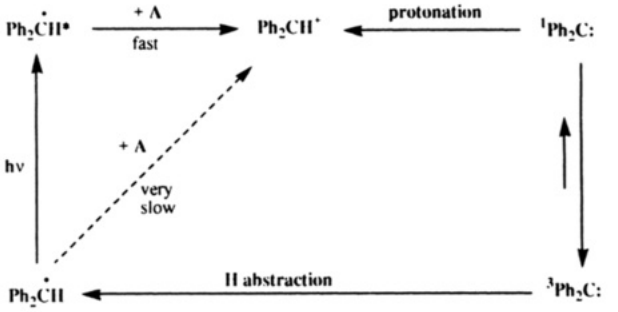


Figure 6. Schematic representation of the stopped-flow laser photolysis setup developed for this work.

Scheme III



Experimental Section

Materials. Diphenyldiazomethane and its derivatives were synthesized according to published procedures and purified by vacuum sublimation or column chromatography (neutral alumina) before use.[33] Acetonitrile (BDH, Omnisolv) used in laser experiments was dried over CaH_2 and passed through neutral alumina. 1,1,1,3,3,3-Hexafluoropropan-2-ol, 2,2,2-trifluoroethanol, phenol, tetramethylammonium tetrafluoroborate, tetramethylammonium tetraphenylborate, perchloric acid, and trifluoroacetic acid were obtained from Aldrich. Ethanol and methanol (BDH) were used as received. Oxygen from Air Products was used for the quenching of triplet diphenylmethylene.

Stopped-Flow Laser-Flash Photolysis. The stopped-flow laser-flash photolysis instrument represents an adaptation of our existing laser photolysis system which will be described in detail elsewhere. The laser system is similar to that described in earlier reports,[34,35] although our present system is controlled by a Macintosh IIci computer operating with LabVIEW-2 software. The samples were excited with pulses (308 nm, ~6 ns, ≤30 mJ/pulse) from a Lumonics EX-510 excimer laser operating with Xe/HCl/He mixtures. When the stopped-flow system described below was not required, a flow cell constructed of 7 × 7 mm² Suprasil tubing was employed.

The stopped-flow section of the instrument (see Figure 6) was based on a modified Model 2 instrument from Cantek Scientific (Winnipeg, Canada). The following stepwise procedure is employed. Solutions containing the two reactive substrates (in this case, diazo compound in acetonitrile (A) and alcohol (B)) are purged with N_2 or O_2 in 50–100-mL glass reservoirs. Aliquots of these solutions are then drawn into two 2-mL syringes which are housed in a gastight box. The box is purged with a positive pressure of N_2 where appropriate. In order to mix the solutions

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J. Am. Chem. Soc. 1993, 115, 2205-2216

for laser irradiation, a nitrogen-driven piston operating at 20–30 psi is employed. The sequential filling and emptying of the two syringes is controlled via two manually operated 3-way valves. The first of these, located between the reservoirs, syringes, and irradiation cell, controls the direction of the flowing solutions, i.e., from reservoir to syringes to cell. The second valve controls the direction of the pressure-driven piston: retraction to enable filling of the syringes from the reservoir followed by depression to facilitate the solution mixing and subsequent filling of the irradiation cell. The photolysis cell (originally designed for fluorescence work) consists of a quartz block containing a $20 \times 2 \times 2$ mm^3 rectangular cavity, with one input and one output. Optical detection of transients is carried out along the 20-mm axes with laser irradiation at right angles to the monitoring beam. The quartz block is encased in a brass holder that contains a Teflon insert aligned with the input of the quartz block. Mixing of both solutions is initiated prior to the entrance into the quartz block at the bottom of the Teflon insert. The design of the mixing chamber in the Teflon insert is the same as that originally supplied with the Cantek instrument. The output of the cell is connected to an electronic valve that controls the discharge of irradiated solution from the cell. The application of the constant-pressure piston on the front side of the cell in conjunction with an electronic valve on the back side allows the controlled mixing, static irradiation, and evacuation/refilling of the two solutions within the cell in sequence. The timing procedure for the opening and closing of the electronic valve is coupled to that of the laser system via a Stanford Model DG535 delay unit. Accordingly, solutions are flushed through the cell for 30 ms to ensure a fresh sample for each irradiation. Following the closing of the valve, a delay of 4 ms is applied to allow for complete mixing and for any turbulence to subside. Subsequent laser-flash photolysis is carried out in the usual manner followed by a repeat of the cycle. Under these conditions of applied pressure and time delays, up to 10 irradiations from a single syringe loading can be carried out without risk of secondary photolysis or any ground-state thermal reaction. All solutions flow through Teflon tubing with stainless steel or Teflon connections between glassware. For systems that are highly sensitive to oxygen, an additional sleeve of Teflon tubing, which envelops the thinner diameter flow tubing, carries a blanket of nitrogen. In this way, the deaerated solutions are not exposed to air until they have exited the photolysis cell.

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The Regioselectivity of the Birch Reduction[1,2]

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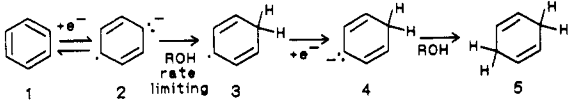
Abstract: The reaction mechanism of the Birch reduction was investigated with a view of determining how the regioselectivity is controlled. Regioselectivity is determined in the first step of radical anion protonation and in the second step of cyclohexadienyl carbanion protonation. It was ascertained that the rate-determining step of the Birch reduction of anisole was radical anion protonation, consistent with the observation of Krapcho and Bothner-By in the case of benzene reduction. A new approach to determining the regioselectivity of the two steps of the Birch reduction was devised. This was predicated on an enhanced primary deuterium isotope effect anticipated for radical anion protonation relative to that expected for cyclohexadienyl carbanion protonation. The approach utilized a partially deuterated medium. The method was applied to the reductions of anisole, 1,3-dimethoxybenzene, 3-methoxytoluene, and 2-methoxynaphthalene. The basic assumption of greater selectivity of the radical anion of the first step relative to the carbanion of the second step was explored in the cases of benzene and anisole and confirmed. In the examples studied, ortho protonation of the radical anion was found to predominate. With a view of understanding the regioselectivity of the two steps, quantum mechanical computations were carried out on several facets of the reaction. Electron density distributions of the radical anions were determined as well as the energies of radical products of some radical anion protonations. Similarly, the energies were obtained for the partially protonated radical anion species at several points along the reaction coordinate. In addition, electron densities were obtained for cyclohexadienyl anion. Theory was then correlated with experiment.

Introduction

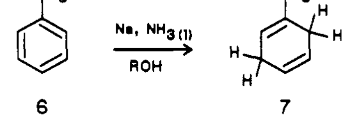
The Birch reduction[3] is one of those reactions which constitute the core of organic chemistry. It is of both synthetic utility and mechanistic interest. Though nearly 50 years old,[4] it is very widely used in present-day efforts. Nevertheless, there are major mechanistic aspects of the reduction which have not been resolved. In view of the importance of the Birch reduction, it seemed of particular value to explore these facets.

Background

The Birch reduction[5] involves protonation of the radical anion formed by addition of one electron to the reacting aromatic. This is followed by rapid addition of a second electron and protonation of the resulting carbanion to afford an unconjugated cyclohexadiene. In this mechanism, protonation of the radical anion by added alcohol is known to be rate limiting in the case of benzene[6a] (see eq 1). The Birch rule,[3b] which predicts a kinetic preference for that regioisomer with the maximum number of alkyl and/or alkoxy groups on the residual double bonds, is quite successful. Note, for example, the case of the toluene reduction in eq 2.[6a]



1 2 3 4 5 (1)



6 7 (2)

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(1) (a) This is part 228 of our general series. (b) Part 227: Zimmerman, H. E.; Baker, M. R.; Bottner, R. C.; Morrissey, M. M.; Murphy, S. *J. Am. Chem. Soc.* **1993**, *115*, 459–466.

(2) For a preliminary communication describing our initial efforts, see: Zimmerman, H. E.; Wang, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 1280–1281.

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(4) (a) Indeed, there were earlier reductions of aromatics with sodium in ammonia; however, some of these efforts[4b] argued for an erroneous mechanism. Other work[4c] provided only one example and without suggestion of the product structure: (b) Hückel, W.; Bretschneider, H. *Liebigs Ann. Chem.* **1939**, *540*, 157–189. (c) Wooster, C. B.; Godfrey, K. L. *J. Am. Chem. Soc.* **1937**, *59*, 596–597.

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