Picosecond Laser Studies on the Reaction of Excited Triplet Diphenylcarbene with Alcohols

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Diphenylcarbene in its excited triplet state (3DPC) is quite reactive with alcohol, unlike the ground triplet state. The excited triplet diphenylcarbene was generated in a two-pulse experiment with UV picosecond pulses. The reaction of 3DPC with a series of alcohols was monitored by the decrease in the fluorescence lifetime of 3DPC. Based on the relative reactivities of the alcohols, along with the observed kinetic isotope effect, it is concluded that 3DPC, in a similar way to 1DPC, preferentially attacks the O-H bond, rather than the C-H bond of the alcohols.

One of the fundamental properties of diphenylcarbene (DPC) is its ability to react with alcohols. Although the exact details of the mechanism are still questioned, it is known that DPC reacts with most alcohols predominately from its lowest singlet state, which is at an energy of 3.5-4.1 kcal/mol above the ground triplet state.4,5 It has been noted that the relative reactivity of the three alcohols follows the relative lability of the O-H bond and/or the relative Lewis basicity of the alcohols.6 It is noteworthy that the triplet state of DPC is also involved in reactions with alcohols, though to a far lesser extent than is the singlet state of DPC, producing hydrogen abstraction derived products.7

It was recently shown by us that the reactivity of the electronically excited triplet diphenylcarbene (3DPC) differs substantially from the ground triplet.8 For example, unlike the ground triplet carbene, 3DPC is readily attacked by methanol and the reaction proceeds at the surprising rate of (3.1 ± 0.4) × 10^8 M^-1 s^-1. Whether the significant reactivity of 3DPC with alcohols reflects a difference in reaction mechanism for the ground and excited triplet states was not established. In this Letter, we report the kinetic results obtained from a quenching study.

The reaction rate constants of alcohols with 3DPC in CH-CN at 20 °C are presented in Table I. The reaction rate constants for 1DPC were obtained from competitive chemical quenching experiments.9,10

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>3DPC Reaction Rate Constant (10^-11 M^-1 s^-1)</th>
<th>1DPC Reaction Rate Constant (10^-11 M^-1 s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂OH</td>
<td>3.1 ± 0.4</td>
<td>2.1 ± 0.5</td>
</tr>
<tr>
<td>CH₂OD</td>
<td>3.02 ± 0.08</td>
<td>0.7</td>
</tr>
<tr>
<td>i-C₃H₇OH</td>
<td>1.46 ± 0.04</td>
<td>1.3 ± 0.3</td>
</tr>
<tr>
<td>i-C₃H₇OD</td>
<td>0.09 ± 0.05</td>
<td>0.3</td>
</tr>
<tr>
<td>t-C₃H₇OH</td>
<td>0.03 ± 0.08</td>
<td>0.62 ± 0.15</td>
</tr>
</tbody>
</table>

* This work.  b The reaction rate constants of alcohols with 1DPC were obtained from competitive chemical quenching experiments.9,10

Table I shows that the reactivity of 3DPC that characterizes the mode of reaction followed by 3DPC with alcohols.

The DPC was generated by photodissociation of diphenyl-diazomethane (2 × 10^-3 M) in degassed acetonitrile following excitation with a single picosecond laser pulse at 264 nm. A second time delayed pulse, also at 264 nm, was used to excite 1DPC to 3DPC.11 The fluorescence lifetime of 3DPC was shortened as a function of added alcohol and was monitored by using a picosecond streak camera-OMA apparatus as described earlier.12 Table I gives the reaction rate constants as determined from a Stern–Volmer analysis of the fluorescence lifetime changes of 3DPC induced by the alcohols at several different concentrations (Figure 1).13

A comparison of the observed rate constants for methanol, 2-propanol, and 2-methyl-2-propanol in their reaction with 3DPC shows that there is an ordering of reactivity. It is seen that methanol is the most reactive, while 2-methyl-2-propanol is the least. The observed ordering of the alcohol reactivities with 3DPC closely parallels the

(4) Turk, N.; Eisenhal, K. B.; Hefferon, G.; Dupuy, C.; Sitzmann, E., to be published.
(16) Figure 1 demonstrates that the pseudo-first-order fluorescence decay rate of 3DPC follows a linear dependence on the alcohol concentration (0-4 M) for all alcohols studied. However, at high methanol concentration (≥4 M), a concord downward curvature in the plot was observed. This was the only alcohol which exhibited nonlinear behavior, and can be interpreted as arising from the aggregation of methanol at high concentration. See the work of Griller, Liu, and Scaino14 for further discussion of this effect, which is clearly manifested in the phenylchlorocarbene system.

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relative lability/acidity of the alcohols. This observation supports the mechanism that \textsuperscript{3}DPC reacts with the OH bond of the alcohol. It is noted that if the C–H bond of the alcohol were attacked by \textsuperscript{3}DPC, as in the ground triplet state reaction, then one would not expect to see the observed trend in the rates. For example, since 2-propanol has a more labile C–H bond than does methanol, it would be anticipated, if hydrogen abstraction were taking place, that 2-propanol would react faster than methanol with \textsuperscript{3}DPC; however, such is not the case.

The interpretation that \textsuperscript{3}DPC attacks the O–H bond rather than the C–H bond of the alcohols is supported by two additional experimental results. First, diethyl ether or tetrahydrofuran was substituted for the alcohols to see if they could affect the fluorescence of \textsuperscript{3}DPC. It is noted that the ethers should be similar to the alcohols in so far as its C–H bond reactivity and its ability to serve as an electron donor for \textsuperscript{3}DPC. It was found that neither diethyl ether nor THF influences the normal fluorescence lifetime (3.8 ± 0.3 ns) of \textsuperscript{3}DPC. The lack of any discernable quenching of \textsuperscript{3}DPC by the two ethers, in contradistinction to the alcohols, indicates that simple C–H abstraction to the oxygen is not important. Second, kinetic isotope effects are observed for methanol and 2-propanol. Substitution of the hydroxyl proton with deuterium on the alcohol leads to a reduction in the rate of reaction pointing to involvement of the O–H bond in the excited triplet state reaction (see Figure 2). The relative rates are $k_{3H}/k_{2D} = 1.54 ± 0.26$ for methanol and $k_{3H}/k_{2D} = 1.59 ± 0.13$ for 2-propanol. The magnitude of the change indicates that we are not observing a primary isotope effect, since primary deuterium isotope effects involving linear transition states generally fall in the range of 3 or greater.

Further support for \textsuperscript{3}DPC attacking the OH bond rather than a CH bond is obtained by the comparison of

![Figure 1. \textsuperscript{3}DPC decay rate as a function of alcohol concentration in degassed acetonitrile: methanol (O); 2-propanol (O); 2-methyl-2-propanol (O).](image1)

![Figure 2. Deuterium isotope effect on the decay rate of \textsuperscript{3}DPC as a function of alcohol concentration: (A) methanol and methanol-O-d; (B) 2-propanol and 2-propanol-O-d.](image2)

Scheme 1

\[ \begin{align*}
\text{\textsuperscript{3}DPC} & \rightarrow \text{\textsuperscript{1}DPC} \rightarrow \text{\textsuperscript{3}DPC}^* \\
\end{align*} \]

the relative rates of reaction of \textsuperscript{3}DPC vs. \textsuperscript{1}DPC with methanol, 2-propanol, and 2-methyl-2-propanol (see Table I). Although \textsuperscript{3}DPC is more reactive than \textsuperscript{3}DPC by nearly two orders of magnitude, the relative reactivities of the alcohols are strikingly similar. The conclusion one may draw from this correlation is that \textsuperscript{3}DPC probably reacts with alcohols in a manner analogous to the \textsuperscript{1}DPC reaction with alcohols.

A simple model which accounts for the similar reactivity of both the lowest singlet and the excited triplet with alcohol is given in Scheme I. The key point is the presence of an empty low-lying orbital for both states. It should be noted that the ground triplet diphenylcarbene does not have an empty low-lying orbital, whereas the excited triplet does, due to promotion of an electron to an upper orbital.

At this point, it is interesting to consider that if \textsuperscript{3}DPC follows a concerted mechanism in its reaction with alcohols, as it has been proposed for \textsuperscript{1}DPC, then it is expected that the resulting ether will be formed in an excited triplet state.

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From an estimate of the energetics, one would predict that the concerted reaction of $^3$DPC with methanol leading to the triplet benzhydryl methyl ether will be exothermic by approximately 45 kcal/mol:\(^\text{23-26}\)

$$
\Delta H^\circ_{rx} = \Delta H^\circ_f(\text{Ph}_2\text{CHOCH}_3) + E_T(^3\text{Ph}_2\text{CHOCH}_3) - \Delta H^\circ_f(\text{DPC}) - E_T(^3\text{DPC}) - \Delta H^\circ_f(\text{CH}_3\text{OH}) \approx [(-6) + (80) - (108) - (59) - (-48)] \text{ kcal/mol} = -45 \pm 15 \text{ kcal/mol}
$$

(23) The measured heat of formation for CH$_3$OH is given by ref 24. The heat of formation for DPC is taken from ref 26 (calculated by Benson's group additivity method, ref 24). The triplet energy ($E_T$) of $^3$DPC is calculated from its fluorescence at 480 nm. The heat of formation of benzhydryl methyl ether is calculated from ref 24 and 25, and its triplet energy is estimated from that of related compounds (ref 27 and 28).


From these estimates, it is also seen that the ground triplet would not be as energetically favored as the excited triplet, whereas the singlet would be more so, for a concerted reaction leading to the ether.

In conclusion, our results show that $^3$DPC is readily quenched by alcohols and that, unlike the ground triplet, the preferred route of reaction involves attack on the O-H bond, rather than the C-H bond of the alcohols.

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**Registry No.** CH$_3$OH, 67-56-1; CH$_3$OD, 1455-13-6; i-C$_3$H$_7$OH, 67-63-0; i-C$_3$H$_7$OD, 3979-51-9; t-C$_4$H$_9$OH, 75-65-0; diphenylcarbene, 3129-17-7.