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

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Diphenylcarbene in its excited triplet state (^{3*}DPC) 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 ^{3*}DPC with a series of alcohols was monitored by the decrease in the fluorescence lifetime of ^{3*}DPC. Based on the relative reactivities of the alcohols, along with the observed kinetic isotope effect, it is concluded that ^{3*}DPC, in a similar way to ^{1}DPC, 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.[1,2] 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,[3,4] to form ethers as the principal products.[5-8]
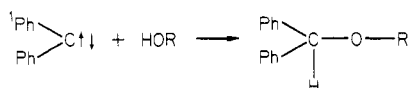
The rate of the ether formation depends on the choice of alcohol. For example, the above alcohols exhibit an ordering of reactivity with ^{1}DPC given by methanol > 2-propanol > 2-methyl-2-propanol.[8-10] It has been noted that the relative reactivity of the three alcohols follows the relative lability of the O–H bond and/or the relative Lewis basicity of the alcohols.[11] 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.[12]

It was recently shown by us that the reactivity of the electronically excited triplet diphenylcarbene (^{3*}DPC) differs substantially from the ground triplet.[13] For example, unlike the ground triplet carbene, ^{3*}DPC is readily attacked by methanol and the reaction proceeds at the surprising rate of $(3.1 \pm 0.4) \times 10^{8}$ M^{-1} s^{-1}. Whether the significant reactivity of ^{3*}DPC 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

TABLE I: Reaction Rate Constants and Relative Reactivities of Alcohols with ^{3*}DPC and ^{1}DPC in CH$_3$CN at 20 °C

alcohol	^{3*}DPC[a]		^{1}DPC[b]	
	$10^{-8}(^{3*}k_q)$, M^{-1} s^{-1}	rel reactivity	$10^{-10}(^{1}k)$, M^{-1} s^{-1}	rel reactivity
CH$_3$OH	3.1 ± 0.4	1.0	2.1 ± 0.5	1.0
CH$_3$OD	2.02 ± 0.08	0.7		
i-C$_3$H$_7$OH	1.46 ± 0.04	0.5	1.3 ± 0.3	0.6
i-C$_3$H$_7$OD	0.92 ± 0.05	0.3		
t-C$_4$H$_9$OH	0.83 ± 0.08	0.3	0.62 ± 0.15	0.3

[a] This work. [b] The reaction rate constants of alcohols with ^{1}DPC were obtained from competitive chemical quenching experiments.[4,5]

of ^{3*}DPC that characterize the mode of reaction followed by ^{3*}DPC with alcohols.

The ^{3}DPC was generated by photodissociation of diphenyldiazomethane (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 ^{3}DPC to ^{3*}DPC.[13,14] The fluorescence lifetime of ^{3*}DPC was shortened as a function of added alcohol and was monitored directly by using a picosecond streak camera–OMA apparatus as described earlier.[15] Table I gives the reaction rate constants as determined from a Stern–Volmer analysis of the fluorescence lifetime changes of ^{3*}DPC induced by the alcohols at several different concentrations (Figure 1).[16]

A comparison of the observed rate constants for methanol, 2-propanol, and 2-methyl-2-propanol in their reaction with ^{3*}DPC 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 ^{3*}DPC closely parallels the

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(15) Wang, Y.; McAuliffe, M.; Novak, F.; Eisenthal, K. B. *J. Phys. Chem.* **1981**, *85*, 3736.
(16) Figure 1 demonstrates that the pseudo-first-order fluorescence decay rate of ^{3*}DPC follows a linear dependence on the alcohol concentration (0–4 M) for all alcohols studied. However, at high methanol concentration (>4 M), a concave 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 Scaiano[17] for further discussion of this effect, which is clearly manifested in the phenyl-chlorocarbene system.
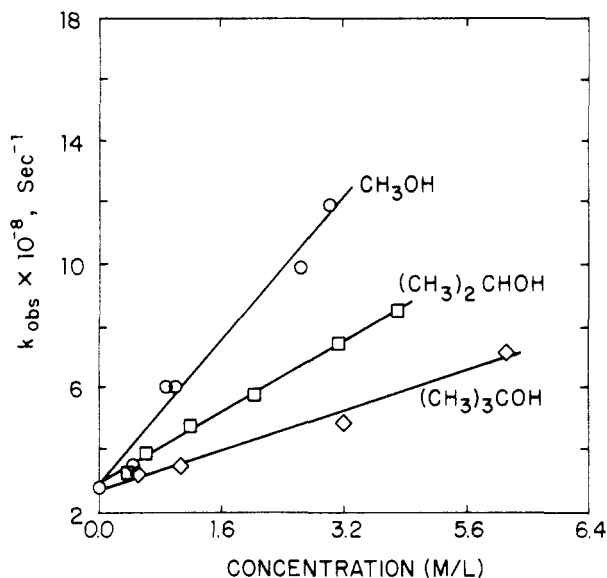(17) Griller, D.; Liu, M.; Scaiano, J. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

Figure 1. ^{3*} DPC decay rate as a function of alcohol concentration in degassed acetonitrile: methanol (O); 2-propanol (□); 2-methyl-2-propanol (◊).

relative lability/acidity of the alcohols.[11] This observation supports the mechanism that ^{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 ^{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 ^{3*}DPC; however, such is not the case.

The interpretation that ^{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 ^{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 ^{3*}DPC.[18,19] It was found that neither diethyl ether nor THF influences the normal fluorescence lifetime (3.8 ± 0.3 ns) of ^{3*}DPC. The lack of any discernable quenching of ^{3*}DPC by the two ethers, in contradistinction to the alcohols, indicates that simple C–H abstraction α 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 $k_H/k_D = 1.54 \pm 0.26$ for methanol and $k_H/k_D = 1.59 \pm 0.13$ 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.[20-22] We thus note that although the isotope effect indicates an attack on the OH bond, it is unlikely that the reaction is an O–H abstraction leading to an alkoxy-diphenylmethyl radical pair.

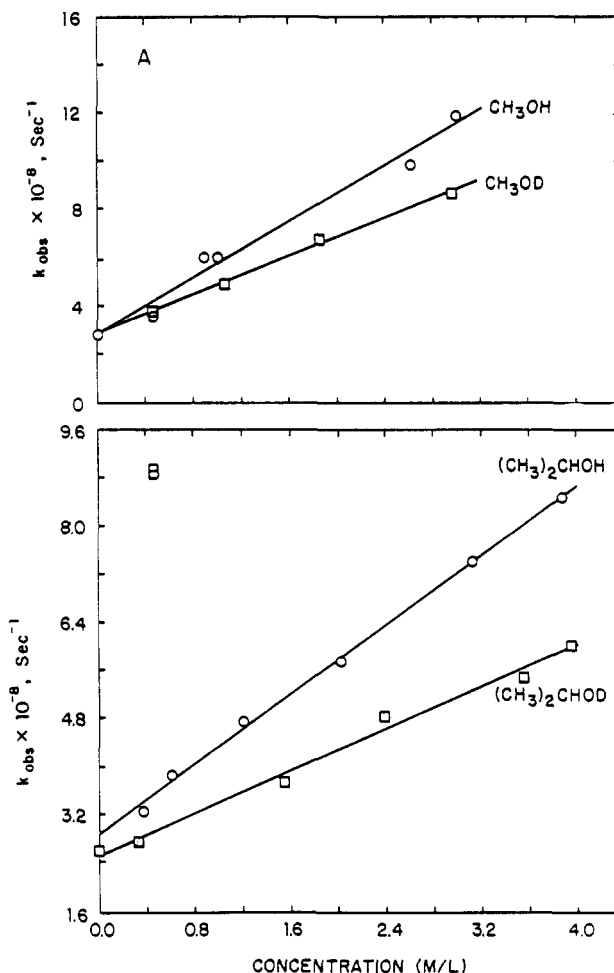Further support for ^{3*}DPC attacking the OH bond rather than a CH bond is obtained by the comparison of

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

Scheme I
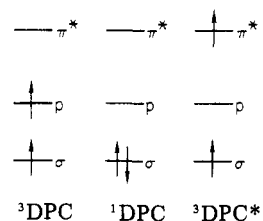
the relative rates of reaction of ^{3*}DPC vs. ^{1}DPC with methanol, 2-propanol, and 2-methyl-2-propanol (see Table I). Although ^{1}DPC is more reactive than ^{3*}DPC by nearly two orders of magnitude, the relative reactivities of the alcohols are strikingly similar. The conclusion one may draw from this correlation is that ^{3*}DPC probably reacts with alcohols in a manner analogous to the ^{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 ^{3*}DPC follows a concerted mechanism in its reaction with alcohols, as it has been proposed for ^{1}DPC, then it is expected that the resulting ether will be formed in an excited triplet state.

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:[23-26]

$$\Delta H°_{rx} = \Delta H°_f(Ph_2CHOCH_3) + E_T(^3*Ph_2CHOCH_3) - \Delta H°_f(DPC) - E_T(^3*DPC) - \Delta H°_f(CH_3OH) \simeq [(-6) + (80) - (108) - (59) - (-48)] \text{ kcal/mol} = -45 \pm 15 \text{ kcal/mol}$$

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.

Registry No. CH_3OH, 67-56-1; CH_3OD, 1455-13-6; i-C_3H_7OH, 67-63-0; i-C_3H_7OD, 3979-51-9; t-C_4H_9OH, 75-65-0; diphenylcarbene, 3129-17-7.

(23) The measured heat of formation for CH_3OH 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).

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