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TEMPERATURE DEPENDENCE OF THE REACTIONS OF SINGLET AND TRIPLET DIPHENYLCARBENE. EVIDENCE FOR REVERSIBLE YLIDE FORMATION IN THE REACTION WITH ALCOHOLS[ǂ]

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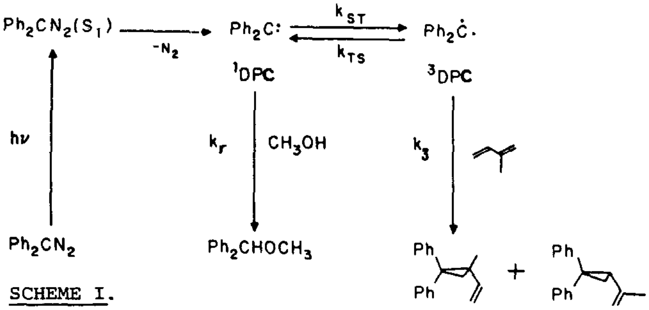
SUMMARY. The temperature dependences of the reaction of singlet diphenylcarbene are consistent with reversible intermediate formation.

The insertion reaction of diphenylcarbene (DPC) into the OH bonds of alcohols has received considerable attention.[1-4] It is generally accepted that it is the singlet state of DPC (^{1}DPC), in equilibrium with the ground triplet state (^{3}DPC), that reacts with the alcohols. However, the reaction mechanism is not yet fully understood, and recent kinetic data[5] have been viewed as inconsistent with the "conventional mechanism" shown in Scheme I. We now describe the effect of temperature on the products of the reaction of DPC with methanol, and with isoprene, in several solvents. These findings, together with measurements of product isotope effects, provide additional insight into the carbene-alcohol reaction and are consistent with an articulation of the conventional mechanism. DPC yields benzhydryl methyl ether upon reaction with methanol, and two isomeric cyclopropanes with isoprene.[6,7] At sufficiently low concentrations of the carbene quenchers, equilibrium between ^{1}DPC and ^{3}DPC is more rapid than reaction. At sufficiently high concentrations, isoprene efficiently traps ^{3}DPC but does not compete for ^{1}DPC in the presence of methanol, which is a poor quencher of ^{3}DPC, but a very efficient quencher of ^{1}DPC.[6,7] The methanol reaction monitors ^{1}DPC and the isoprene reaction monitors ^{3}DPC. In Figure 1 is shown the effect of temperature on the ratio of the quantum yields for triplet (Q^3) and singlet (Q^1) product formation in several solvents.[8] In each solvent triplet products are more favored at low and high temperatures than at intermediate temperatures. In Figure 2 are shown the results of similar experiments for CH_3OD and t-butanol.

The activation parameters for the addition of ^{3}DPC to the double bonds of isoprene were obtained by measuring the absolute rate constant for this reaction at various temperatures, in a conventional laser flash photolysis experiment.[7] A normal Arrhenius activation energy of 3.1



SCHEME I.

[ǂ] Dedicated to Harry Wasserman on the occasion of his 65th birthday.

kcal/mol and pre-exponential factor of 2.8×10^8 s^{-1} were determined.

The non-linear plots of Figures 1 and 2 are thus assigned to an unusual temperature dependence for the reaction of ^{1}DPC with methanol. Temperature dependent aggregation of alcohols in solution is well known;[9] however, methanol and t-butanol are known to have very different aggregation properties,[9] but show essentially the same behavior in these experiments.

We propose that these results can be interpreted in terms of the conventional mechanism with the additional steps shown in eqns. 1 and 2. ^{1}DPC/alcohol is a reversibly formed dissociable intermediate which is formed at a diffusion controlled rate (i.e., $k_1=k_{diff}$). In this case the observed rate constant for reaction of ^{1}DPC with an alcohol (k_r) is not a simple constant, but

$$^1\text{DPC} + \text{alcohol} \rightleftarrows {}^1\text{DPC/alcohol} \qquad k_1,\ k_{-1} \qquad (1)$$

$$^1\text{DPC/alcohol} \rightarrow \text{ether} \qquad k_2 \qquad (2)$$

is given in eqn. 3. This mechanism is identical to that previously proposed to account for the unusual temperature dependencies of the reactions of singlet phenylchlorocarbene with alkenes,[10] and also that which has been suggested for the reaction of singlet fluorenylidene with alcohols.[11]

$$k_r = \frac{k_1 k_2}{k_{-1} + k_2} \qquad (3)$$

According to Scheme I the ratio Q^3/Q^1 obeys eqn. 4.[6,7]

$$Q^3/Q^1 = \frac{k_{st}}{k_{ts} + k_3[\text{IP}]} \quad \frac{k_3[\text{IP}]}{k_r[\text{ROX}]} \qquad X = H,D \qquad (4)$$

k_{st} is known and is assumed to have zero temperature dependence.[7] It is further assumed that the temperature dependence of k_{ts} can be calculated using the known free energy difference between the triplet and singlet states of DPC.[7] Thus, the temperature dependence of k_r can be determined at each experimental temperature, and is shown in Figure 3 for three alcohols in isooctane. Above -10°C, k_r increases as the temperature decreases, a situation which is commonly observed for the kinetic situation of eqns. 1 and 2. At lower temperatures k_r decreases, presumably as it becomes determined by the rate of diffusion (k_1) in the solvent.[10]

The kinetic scheme is supported by the observed isotope effects. At low temperatures the reaction rate is determined by the competition between reversal to starting materials and reaction from the intermediate. An intermediate which is consistent with both the present results and previous proposals,[3] is an ylide species in which the vacant carbenic p orbital interacts with the lone-pair electrons of the alcohol. Reaction from the ylide involves a proton transfer and should, thus, exhibit a secondary isotope effect. At low temperatures the reaction becomes dominated by the rate of diffusion, and therefore the isotope effect is significantly reduced.

The dramatic solvent effect is due to the difference in energy between the ground state ^{3}DPC and ^{1}DPC, which is known to be solvent dependent.[7,12] The energy difference is smaller in polar solvents, such as CH_3CN, which results in an increased yield of the singlet ether product. In non-polar solvents, such as isooctane, a larger energy gap results in more of the cyclopropane triplet products.

In view of the assumptions involved in the calculations, the temperature dependences of k_r shown in Figure 3 should be considered to be qualitative rather than quantitative. Certainly no information concerning the structure of the intermediate can be drawn from the kinetic analysis. However, it is encouraging that the qualitative behavior in k_r is similar to that previously observed in the absolute rate behavior of other singlet carbene reactions.[10]

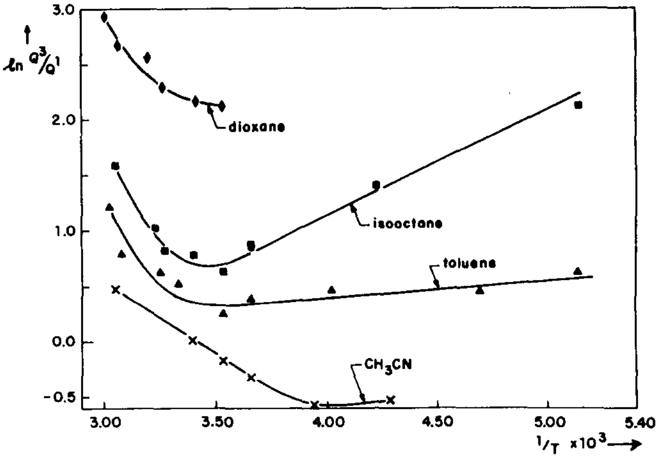


Figure 1. Plots of temperature dependence of the reaction of DPC with methanol and isoprene in several solvents. $[Ph_2CN_2]$ = 1.5 mM; $[CH_3OH]$ = 0.005 M; [IP] = 1 M.

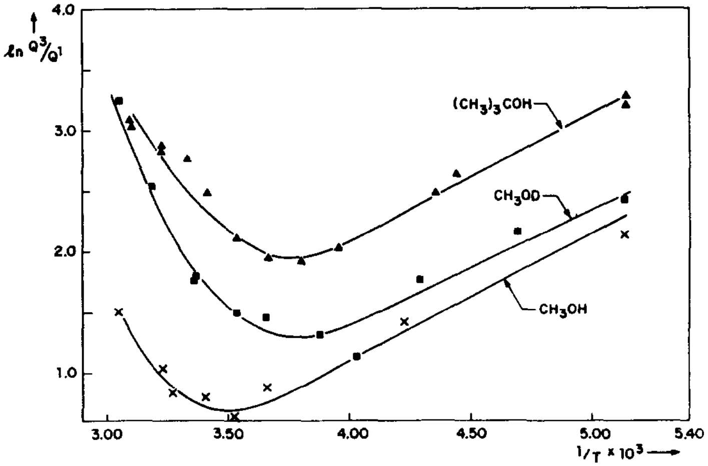


Figure 2. Plots of temperature dependence of the reaction of DPC with alcohols and isoprene in isooctane. $[Ph_2CN_2]$ = 1.5 mM; [alcohol] = 0.05 M; [IP] = 1 M.

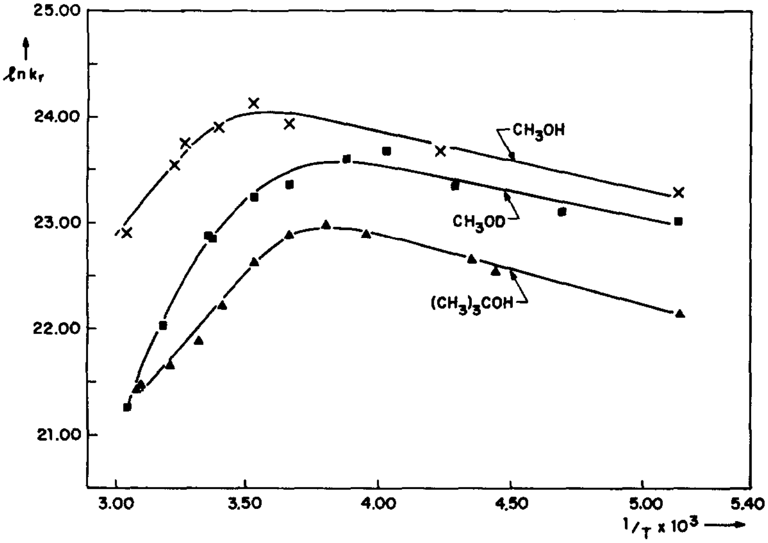


Figure 3. Arrhenius plots of the temperature dependence of the reaction of ^{1}DPC with alcohols in isooctane.

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