The Reactions of Triplet Methylene with Alkyl Radicals in Ordinary Photolysis Systems

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Summary Triplet methylene is very unreactive with alkanes, surviving $>10^9$ collisions with CD_4 before reacting with methyl radicals to form ethylene plus a hydrogen atom.

THE chemical reactivity of methylene has been the subject of considerable controversy. While singlet methylene reacts rapidly[1] and rather indiscriminately[2,3] with various substrates, triplet methylene is more selective[2,4] and has been shown by study of reactive competition between O_2 and but-2-ene to survive without chemical reaction $>10^4$ collisions with the olefin.[5] An upper limit on the reactivity of $^3CH_2$ with CH_4 has been set as $>10^4$ collisions/reaction from spectroscopic study of methylene during flash photolysis.[1] We now report "steady-state" photolysis studies of keten–alkane mixtures in which triplet methylene is found to be so unreactive toward the stable molecules, that it usually survives for $>10^{-2}$ sec., and eventually reacts with other radicals in the system. Such a radical–radical reaction is illustrated in reactions (1) and (2) for $^{14}CH_2$ with the CH_2D and CD_3 radicals found in CD_4. No alternative mechanisms for the formation of mono- and di-deuteriated ethylenes have been suggested for such systems; undeuteriated $^{14}CH_2{:}CH_2$ can arise from the attack of $^1CH_2$ or $^3CH_2$ on $^{14}CH_2{:}CO$,† and has long been identified as a known reaction path in such systems.

$$^3(^{14}CH_2) + CD_3 \rightarrow {}^{14}CH_2{\cdot}CD_3^* \rightarrow {}^{14}CH_2{:}CD_2 + D \qquad (1)$$

$$^3(^{14}CH_2) + CH_2D \rightarrow {}^{14}CH_2{\cdot}CH_2D^* \rightarrow {}^{14}CH_2{:}CHD + H \qquad (2a)$$

$$\searrow {}^{14}CH_2{:}CH_2 + D \qquad (2b)$$

The fate of methylene has been followed through the use of $^{14}CH_2$ or CHT tracers in the 313 nm photolysis of $^{14}CH_2{:}CO$ or CHT:CO, in the presence of 400—600 torr of substrate. Standard techniques of radio gas chromatography have been used for analysis, including isotopic separations such as that of $^{14}CH_2{:}CHD$ and $^{14}CH_2{:}CD_2$ from $^{14}CH_2{:}CH_2$ (or of the monotritiated $C_2H_xD_{3-x}T$ counterparts). About 70% of the methylene so produced is found as $^1CH_2$ and reacts rapidly by the reactions characteristic of the singlet spin state. These reactions persist in the presence of O_2 scavenger.

Confirmation that radical–radical reactions involving triplet methylene are indeed occurring has involved these additional experimental verifications:

(a) suppression of all such radical–radical products by small concentrations of O_2 scavenger; (b) the presence in

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† $^1(^{14}CH_2)$ or $^3(^{14}CH_2)$ with $CH_2{:}CO$ is an alternative path.

the CD_4 system of [^{14}C]acetylene, as expected for reaction (3);[1] (c) the absence of any reaction of $^{14}CH_2{:}CO$ when

$$^3(^{14}\mathrm{CH_2}) + {}^3\mathrm{CH_2} \rightarrow {}^{14}\mathrm{CH} \vdots \mathrm{CH} + \mathrm{H_2}(\text{or } 2\mathrm{H}) \qquad (3)$$

CH_3 groups are generated by 366 nm photolysis of azomethane in keten–alkane mixtures, indicating that alkyl radical attack on the keten is not important; (d) the increase of "CH_3 products," including [^{14}C]ethylene during cophotolysis of $^{14}CH_2{:}CO$ and azomethane at 313 and 334 nm, confirming that methyl radical is a precursor of [^{14}C]ethylene; (e) the observation of tritiated vinyl fluoride in CHT:CO–CD_3F, as required for the CD_2F reaction (4a), analogous to (1)—as well as CHT:CD_2 and CHT:CHD from (4b) (perhaps) and (2), respectively; (f) an increase in [^{14}C]acetylene

$$\begin{array}{ll} ^3(\mathrm{CHT}) + \mathrm{CD_2F} \rightarrow \mathrm{CHT{\cdot}CD_2F^*} \rightarrow \mathrm{CHT{:}CDF} + \mathrm{D} & (4a) \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \searrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathrm{CHT{:}CD_2} + \mathrm{F} & (4b) \end{array}$$

and decrease in $^{14}CH_2{:}CHD$ and $^{14}CH_2{:}CD_2$ from $^{14}CH_2{:}CO$–CD_4 at high pressures (2000 torr)—at this pressure, more efficient collisional stabilization of $CH_2D{\cdot}CD_3^*$ formed by $^1CH_2$ insertion appreciably reduces the methyl radical concentration, thereby tending to suppress reactions (1) and (2), while making (3) more likely because of the lower concentration of other competing radicals; (g) reactions (2) and (5) are observed in good yield for neo-C_5D_{12} and C_2D_6, but in reduced yield for more highly branched hydrocarbons for which the abstraction reaction (6) proceeds sufficiently rapidly to remove much of the $^3CH_2$ before collision with a radical.

$$^3(^{14}\mathrm{CH_2}) + \mathrm{RCD_2} \rightarrow {}^{14}\mathrm{CH_2{\cdot}CD_2R^*} \rightarrow {}^{14}\mathrm{CH_2{:}CD_2} + \mathrm{R} \qquad (5)$$

$$\begin{array}{ll} ^3\mathrm{CH_2} + \mathrm{RH} \rightarrow \mathrm{CH_3} + \mathrm{R} & (6) \\ \quad \text{or } \mathrm{RD} \rightarrow \mathrm{CH_2D} + \mathrm{R} & \end{array}$$

The overall steady-state radical concentration in our system—photolysis times of several hours—is approximately 10^{11} radicals/cm^3, or about 10^{-9} times the molecule concentration The observation of radical–radical reactions for triplet methylene implies collision efficiencies for triplet methylene reaction with CD_4 of $< 10^{-9}$, and corresponding lifetimes $> 10^{-2}$ sec. Indeed, we have no evidence that $^3CH_2$ has reacted with CD_4 at all in our system—the methyl radicals may not come from reaction (6), but solely from decomposition of $CH_2D{\cdot}CD_3^*$ formed in the $^1CH_2$ insertion reaction. Since these triplet reactions with radicals occur in systems containing 1 part in 100 of keten, and in which about 1 part in 10^4 of ethylene is formed during photolysis, the collision efficiencies for the reactions of $^3CH_2$ with keten and ethylene must be $< 10^{-7}$ and $< 10^{-5}$ respectively.

The addition of $^3CH_2$ to CH_3 is > 90 kcal./mole exothermic, with an activation energy toward loss of a hydrogen atom from the excited ethyl radical of only 40 kcal./mole.[6] Consequently, decomposition occurs in $< 10^{-11}$ sec.,[6] with no appreciable collisional stabilization of the excited ethyl radicals. Similarly, the reactions of $^3CH_2$ with other radicals should be highly exothermic and proceed rapidly to decomposition. Some of these reactions should be readily observable in other steady-state systems.

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