

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

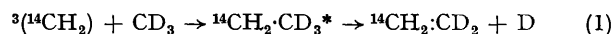
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Summary Triplet methylene is very unreactive with alkanes, surviving $>10^9$ collisions with CD_4 before reacting with methyl radicals to form ethylene plus a hydrogen atom.

THE chemical reactivity of methylene has been the subject of considerable controversy. While singlet methylene reacts rapidly¹ 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 $>10^{-3}$ 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.



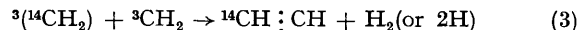
The fate of methylene has been followed through the use of $^{14}CH_2$ or CHT tracers in the 313 nm photolysis of $^{14}CH_2:CO$ or CHT:CO, in the presence of 400–600 torr of substrate. Standard techniques of radio gas chromatography have been used for analysis, including isotopic separations such as that of $^{14}CH_2:CHD$ and $^{14}CH_2:CD_2$ from $^{14}CH_2:CH_2$ (or of the monotrinitiated $C_2H_xD_{3-x}T$ 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:

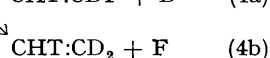
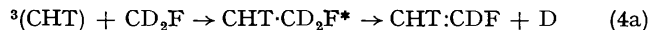
(a) suppression of all such radical-radical products by small concentrations of O_2 scavenger; (b) the presence in

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

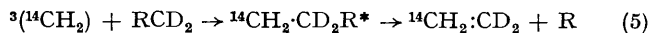
the CD₄ system of [¹⁴C]acetylene, as expected for reaction (3);¹ (c) the absence of any reaction of ¹⁴CH₂:CO when



CH₃ groups are generated by 366 nm photolysis of azo-methane in keten-alkane mixtures, indicating that alkyl radical attack on the keten is not important; (d) the increase of "CH₃ products," including [¹⁴C]ethylene during cophotolysis of ¹⁴CH₂:CO and azomethane at 313 and 334 nm, confirming that methyl radical is a precursor of [¹⁴C]ethylene; (e) the observation of tritiated vinyl fluoride in CHT:CO-CD₃F, as required for the CD₂F reaction (4a), analogous to (1)—as well as CHT:CD₂ and CHT:CHD from (4b) (perhaps) and (2), respectively; (f) an increase in [¹⁴C]acetylene



and decrease in ¹⁴CH₂:CHD and ¹⁴CH₂:CD₂ from ¹⁴CH₂:CO-CD₄ at high pressures (2000 torr)—at this pressure, more efficient collisional stabilization of CH₂D·CD₃* formed by ¹CH₂ 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-C₅D₁₂ and C₂D₆, but in reduced yield for more highly branched hydrocarbons for which the abstraction reaction (6) proceeds sufficiently rapidly to remove much of the ³CH₂ before collision with a radical.



The overall steady-state radical concentration in our system—photolysis times of several hours—is approximately 10¹¹ radicals/cm³, 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 CD₄ of <10⁻⁹, and corresponding lifetimes >10⁻² sec. Indeed, we have no evidence that ³CH₂ has reacted with CD₄ at all in our system—the methyl radicals may not come from reaction (6), but solely from decomposition of CH₂D·CD₃* formed in the ¹CH₂ 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 10⁴ of ethylene is formed during photolysis, the collision efficiencies for the reactions of ³CH₂ with keten and ethylene must be <10⁻⁷ and <10⁻⁵ respectively.

The addition of ³CH₂ to CH₃ 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 ³CH₂ 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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