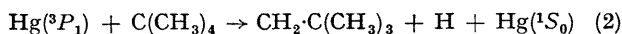
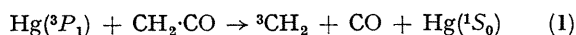


Singlet Methylene formed in the Mercury-photosensitized Decomposition of Keten

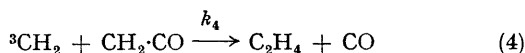
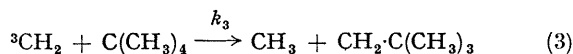
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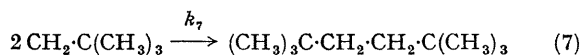
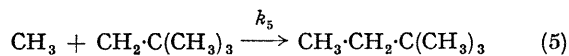
THE appearance of a recent note on the reactions of methylene produced by the mercury-photosensitized decomposition of keten¹ prompts us to report some of our results which are germane to the reactivity of triplet methylene. There is still some uncertainty about the reactions of this species, and, in particular, whether it can undergo an insertion reaction in the carbon-hydrogen bonds of paraffins. Evidence has been adduced that, though a minor pathway, insertion does take place with propane and butane.² The systems investigated were very complex and even the presence of a small amount of singlet methylene would invalidate this conclusion. On the basis of the spin-conservation rule and some chemical observations,³ the mercury-photosensitized decomposition of keten was previously believed to be a source only of triplet methylene. In an attempt to determine quantitatively the extent of any triplet insertion reaction we have investigated the sensitized photolysis of keten in the presence of neopentane. The expected primary processes are;



followed in the absence of an insertion reaction by,

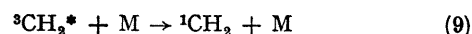
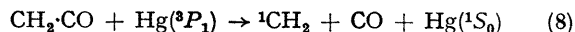


Other reactions of importance include the formation of ethane and acetylene by reactions of ${}^3\text{CH}_2$ with keten by abstraction followed by radical recombination. Hydrogen atoms from (2) may abstract from their precursor to give more neopentyl radicals or add to keten to give CH_3CO and possibly ultimately methyl radicals. As ethylene builds up in the system hydrogen atoms will also be consumed by it, giving ethyl radicals. Recombination of the radicals formed by (3) will yield 2,2-dimethylbutane, the same product as would be formed by direct insertion. However these radicals will also yield ethane and 2,2,5,5-tetramethylhexane.



From collision theory we expect $k_5/k_6^{1/2}k_7^{1/2} = 2$. By using this relationship and the measured yields of ethane, dimethylbutane, and tetramethylhexane we may calculate

the yield of dimethylbutane formed by direct insertion. Our analytical data show that only about one half of the dimethylbutane arises by reaction (5). Even when correction is made for the formation of dimethylbutane by other radical paths, and by the insertion reaction of singlet methylene formed by the small amount of keten decomposed by the direct absorption of light, we find that a large fraction of the dimethylbutane must arise by an insertion reaction. Thus, either the insertion reaction of triplet methylene is a major reaction pathway or there must be an appreciable concentration of singlet methylene in our system. We reject the first alternative on the basis of studies in other systems, and conclude that in the sensitized decomposition of keten in the presence of paraffins considerable quantities of singlet methylene are formed. The genesis of the singlet methylene presents a problem and we suggest two alternatives;



Reaction (8) involving the direct formation of singlet methylene is spin-forbidden, but this should not be a serious objection in this case, since there must be a very appreciable mixing of states in the mercury atom (*N.B.* the intense absorption of the 2537 Å line). Alternatively, the initially formed triplet methylene may undergo a collisionally induced spin-inversion. The reverse is believed to occur in many systems, and since the energy separation between the states is thought to be small and the initially formed triplet methylene must have a considerable excess of energy, this process (9) must be seriously considered.

The extent to which reaction (9) may occur in various systems will depend on the rates of reaction of triplet methylene with whatever reactants are present. Thus, even though with paraffins the evidence for singlet methylene is strong, it is possible that in the presence of olefin reactants little singlet methylene will be formed due to the relatively high reactivity of triplet methylene with unsaturated compounds. Even if singlet methylene is formed by reaction (8), the alternative we favour, the apparent ratio of singlet to triplet products can be a misleading measure of the relative yields of the two spin states of methylene unless *all* the singlet and triplet products are measured. In most systems the relatively high yields of ethylene, formed from both singlet and triplet methylene reactions and the formation of some polymer make such calculations impractical.

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