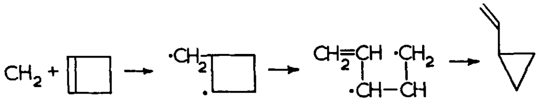
Long-lived Triplet States and Their Occurrence in Carbene Reactions

By H. M. FREY

(*The University, Southampton*)

THE reactions of methylene produced by the direct photolysis of keten, diazomethane, and diazirine are consistent with the radical being in its singlet state.[1] There appear to be two characteristic reactions of singlet methylene with hydrocarbons, (1) stereospecific addition to double bonds, and (2) insertion in carbon–hydrogen bonds. Triplet methylene may be produced, with some difficulty, by carrying out reactions in the presence of very large excesses of inert gases,[2,3] or, more readily, by the mercury-photosensitized decomposition of keten[4] or the benzophenone-sensitized decomposition of diazomethane.[5] Triplet methylene is characterised by the absence of the insertion reaction and the non-stereospecific nature of the addition reaction. It is also apparent that the triplet radicals or molecules formed by triplet addition reactions are relatively longer lived than the corresponding singlet species.[6] Thus in gas-phase experiments triplet species of this type have more chance of being collisionally stabilised at any particular pressure. We adduce evidence below for the occurrence of some triplet methylene in the direct photolysis of the various methylene precursors and also show how the postulate of the existence of triplet states in several analogous systems leads to a simplification in the interpretation of many of the experimental results.

The photolysis of diazomethane or keten in the presence of *cis*-hex-2-ene gives rise to 1,2-diethylcyclopropane by addition of the methylene to the double bond.[7] At very low pressures the initially formed *cis*-1,2-diethylcyclopropane can undergo a reversible *cis–trans*-isomerization before being collisionally stabilised. However even at pressures where all the initially formed *cis*-compound would be stabilized, some *trans*-1,2-diethylcyclopropane was detected. We suggest this compound is formed by a path involving the addition of triplet methylene to the olefin, and hence some triplet methylene is formed in the direct photolysis of keten and diazomethane. Supporting evidence for this comes from the observation that in the presence of oxygen the yield of the *trans*-cyclopropane is drastically reduced.[3] The photolysis of diazomethane or keten in the presence of excess of cyclobutene yields all the expected products formed by the addition and insertion of the singlet methylene and their rearrangement products. As well as these compounds, vinylcyclopropane is formed in quite appreciable quantities at high pressures (~20%). We envisage that this compound arises from the addition of triplet methylene as follows:—



Again photolysis in the presence of oxygen virtually suppresses the formation of this compound.[8] Addition of methylene (from keten) to ethylene yields cyclopropane which may isomerize to

---

[1] W. von E. Doering and P. LaFlamme, *J. Amer. Chem. Soc.*, 1956, **78**, 5447; P. S. Skell and R. C. Woodworth, *ibid.*, 1956, **78**, 4496; R. C. Woodworth and P. S. Skell, *ibid.*, 1959, **81**, 3383; H. M. Frey, *Proc. Roy. Soc.*, 1959, *A*, **251**, 575.

[2] F. A. L. Anet, R. F. W. Bader, and A. M. van der Auwera, *J. Amer. Chem. Soc.*, 1960, **82**, 3217.

[3] H. M. Frey, *J. Amer. Chem. Soc.*, 1960, **82**, 5947.

[4] F. J. Duncan and R. J. Cvetanović, *J. Amer. Chem. Soc.*, 1962, **84**, 3593.

[5] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1962, **84**, 1015.

[6] D. W. Placzek and B. S. Rabinovitch, *Canad. J. Chem.*, 1965, **43**, 820, and references quoted therein.

[7] H. M. Frey, unpublished experiments.

[8] C. S. Elliott and H. M. Frey, unpublished experiments.

propene unless deactivated. An early observation[9] that at low pressures the ratio of cyclopropane to propene was decreased by the presence of oxygen is readily explicable if it is assumed that some triplet methylene is present in the system. The observations of Strachan and Noyes[10] on the effect of the presence of oxygen on the quantum yield for the formation of ethylene in the photolysis of keten can be explained by postulating[11] the formation of $\cdot CH_2COCH_2\cdot$ with a relatively long lifetime. The reaction of this radical with oxygen and its long lifetime are both consistent with it being a triplet species formed by the reaction of triplet methylene with keten. It is possible that the formation of acetylene and ethane in this system also involves the intermediacy of triplet methylene. The yield of ethylene in the photolysis of mixtures of diazirine and cyclopropane, with diazirine : cyclopropane from 1 : 2 to 1 : 70, is independent of this ratio.[12] This implies that the ethylene precursor cannot react with cyclopropane, and is readily explained if the photolysis yields some triplet methylene. This presumably reacts with diazirine to give ethylene and nitrogen but is unable to insert in the carbon–hydrogen bonds of cyclopropane. The photolysis of diazirine also yields some diazomethane[12,13] and the yield appears to be pressure-independent over a wide pressure range. The diazomethane cannot be formed as a vibrationally excited ground-state molecule since its lifetime would be too short. For the same reason it cannot be produced in the same electronic state as results from the direct photolysis of diazomethane. We suggest that this photoisomerization proceeds by intersystem crossing to give triplet diazomethane.

To account for the pressure-dependence of the yields of ethylene and acetylene in the photolysis of methyldiazirine[14] it is necessary to postulate the formation of ethylene by two distinct paths. These two species of ethylene have very different lifetimes with respect to decomposition to acetylene and hydrogen. We suggest that the longer lived species is triplet ethylene probably formed from triplet ethylidene. The absence of any addition reactions of the ethylidene in this system would be consistent with this radical being in the triplet state. The occurrence of two "types" of ethylene has already been postulated to account for the results in the mercury-photosensitized reactions of ethylene.[15,16] Recently, as a result of their work on the photolysis of ethane at 1470 Å, McNesby and Hampson concluded that one of the processes (which may involve triplet ethylidene) produces ethylene as a triplet, which does not decompose into acetylene and hydrogen.[17] The absence of these triplets in the photolysis of diazoethane[18] and methylketen[19] may be rationalised in terms of the production of much less energetic species in these systems, which are not able to undergo intersystem crossing.

In essentially the same manner the results on the photolyses of pentamethylenediazirine[20] and 3-t-butyldiazirine[21] require the formation of two molecules, in each system, of the same chemical identity but with different lifetimes. The longer lived species in each case is probably in the triplet state, and may be formed by rearrangement of the appropriate triplet carbene. Finally the photolysis of 3,3-dimethyldiazirine at low pressures yields small quantities of cyclopropane. The yields are almost pressure-independent.[22] These results are readily explicable if the cyclopropane is formed from triplet propene (from triplet dimethylcarbene). The formation of cyclopropanes from triplet olefins has already been noted previously.[23]

A crude semi-quantitative treatment of the data at present available suggests that the photolysis of keten (at ~3130 Å) and diazomethane (at ~4360 Å) results in the formation of between 20 and 30% of methylene in the triple state. In the case of methyldiazirine the triplet species accounts for about 40% of the primary process.

(*Received*, *May* 21*st*, 1965.)

---

[9] H. M. Frey and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1957, **79**, 6373.
[10] A. N. Strachan and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, 1954, **76**, 3258.
[11] G. B. Kistiakowsky and K. Sauer, *J. Amer. Chem. Soc.*, 1956, **78**, 5699.
[12] J. A. Bell, personal communication.
[13] M. J. Amrich and J. A. Bell, *J. Amer. Chem. Soc.*, 1963, **86**, 292.
[14] H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 1965, 1700.
[15] A. B. Callear and R. J. Cvetanović, *J. Chem. Phys.*, 1956, **24**, 873.
[16] D. W. Setser, B. S. Rabinovitch, and D. W. Placzek, *J. Amer. Chem. Soc.*, 1963, **85**, 862.
[17] J. R. McNesby, personal communication.
[18] H. M. Frey, *J. Chem. Soc.*, 1962, 2293.
[19] G. B. Kistiakowsky and B. H. Maham, *J. Amer. Chem. Soc.*, 1957, **79**, 2412.
[20] H. M. Frey, *Pure Appl. Chem.*, 1964, **9**, 527.
[21] H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 1965, 3101.
[22] H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 1962, 3514.
[23] M. Avrahmi and P. Kebarle, *J. Phys. Chem.*, 1963, **67**, 354; R. J. Cvetanović and L. C. Doyle, *J. Chem. Phys.*, 1962, **37**, 543.