# Evidence for the Formation of Vibrationally Excited Triplet 1,3-Biradicals in the Hg $^3P_1$ Photosensitized Decomposition of *cis*- and *trans*-3,4-Dimethyl-$\Delta^1$-pyrazoline

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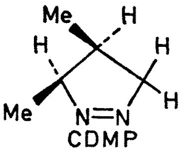
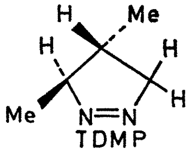
*Summary* Mercury photosensitized decomposition of *cis*- and *trans*-3,4-dimethyl-$\Delta^1$-pyrazoline vapour yields vibrationally excited triplet biradical intermediates which undergo pressure-dependent isomerizations to form olefins or cyclization to dimethylcyclopropanes.

WE report preliminary results on the Hg $^3P_1$ photosensitized decomposition of both *cis*- and *trans*-3,4-dimethyl-$\Delta^1$-pyrazoline vapour[1] (CDMP and TDMP, respectively). The findings provide evidence that highly vibrationally excited triplet 1,3-biradical species are intermediates in the decomposition, and that several concurrent isomerizations of the biradical occur. Although photosensitized decomposition of cyclic azo-compounds is believed to yield biradicals,[2] to our knowledge this is the first evidence for vibrational excitation of biradicals from the sensitized decomposition of cyclic azo-compounds.


CDMP


TDMP

Each reactant was decomposed (1—1·5%) while being circulated through the 329 cm$^3$ photolysis cell by a solenoid-driven piston pump. The relative hydrocarbon product yields were determined by g.l.c. (see Table). In addition, $N_2$ was a major product, and traces of *cis*- and *trans*-but-2-ene were also identified as resulting from the primary decomposition.

*Decomposition of* 3,4-*dimethyl*-$\Delta^1$-*pyrazoline*

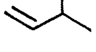
| | | | Products,[a] mole % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reactant | Conditions | Pressure/Torr | (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) |
| TDMP | Hg | 4·8 | 27 | 16 | 12 | 14 | 10 | 1·5 | 1·3 | 18 | Tr | Tr |
| TDMP | Hg, Ar | 700 | 56 | 25 | 3·4 | 3·6 | 2·6 | 1·1 | | | | |
| TDMP[b] | $Ph_2CO$ | Soln. | 72·0 | 26·2 | 0·7 | | | 0·8 | 0·3 | | | |
| TDMP[b] | 3200 Å | 5·6 | 37·2 | 24·4 | | 0·5[c] | | 16·4 | 14·5 | | 5·7 | |
| CDMP | Hg | 1·7 | 25 | 15 | 11 | 14 | 9·9 | 1·7 | 1·7 | 21 | Tr | Tr |
| CDMP | Hg, Ar | 700 | 66 | 30 | 0·4 | | | 1·1 | 1·1 | 1·4 | Tr | Tr |
| CDMP[b] | $Ph_2CO$ | Soln. | 70·6 | 26·8 | 0·8 | | | 1·5 | 0·1 | | | |
| CDMP | 3200 Å | 5·6 | 37·6 | 43·0 | | 1·6[c] | | 4·7 | 4·8 | | | 7·2 |

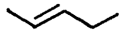
[a] Total yield deviates slightly from 100% owing to rounding off. [b] Ref. 3. [c] Total pent-2-ene. Tr = Trace.

There is significantly more olefin formation in the TDMP (4·8 Torr) and CDMP (1·7 Torr) Hg photosensitized decomposition than in the benzophenone photosensitized decomposition in benzene solution.[3] Also, the olefin product distribution is quite different from that in the direct photolysis at *ca.* 3200 Å and 5·6 Torr.[3] 3-Methylbut-1-ene and *cis*- and *trans*-pent-2-ene predominate in the photosensitized decomposition whereas large amounts of 2-methylbut-2-ene and 2-methylbut-1-ene are formed by direct photolysis.[3] Typical data from ref. 3 are included in the Table for comparison. When Ar (700 Torr) was added, the yields of 3-methylbut-1-ene and *cis*- and *trans*-pent-2-ene decreased by a factor of 3—4 for TDMP and to a much greater extent for CDMP. Also, the yields of *trans*-1,2-dimethylcyclopropane and *cis*-1,2-dimethylcyclopropane increased, that of *trans*-dimethylcyclopropane to a greater extent than that of *cis*-dimethycyclopropane for both pyrazolines. The distribution of pentene and dimethylcyclopropane products approaches that characteristic of liquid phase systems with increasing system pressure.

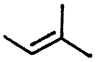

(1)

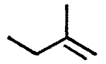

(2)


(3)


(4)


(5)


(6)


(7)

$C_2H_6$

(8)


(9)


(10)

The main mechanism of the sensitized decomposition of both CDMP and TDMP appears to involve triplet 1,3-biradicals, as shown by the formation of 3-methylbut-1-ene. 3-Methylbut-1-ene is not a product of direct photolysis of CDMP or TDMP,[3] nor of the thermal isomerization of *cis*- or *trans*-1,2-dimethylcyclopropane.[4] It is formed when triplet methylene reacts with either *cis*- or *trans*-but-2-ene,[5,6] and has been interpreted to arise in those systems through addition of triplet methylene to an olefinic carbon atom to form a 1,2-dimethyl-1,3-trimethylene triplet biradical.[6] This is the same biradical that would be formed if both CDMP and TDMP were to decompose by elimination of $N_2$ (assuming spin conservation). The biradical may then rearrange through a 1,4-hydrogen shift[6] or a 1,2-methyl shift[7] to form 3-methylbut-1-ene. The other major olefin products found in the present work are also formed in the triplet methylene systems, and may arise through methyl group migrations in the biradical.[6]

A concerted mechanism is unlikely since such a decomposition mode would be expected to give a product distribution that reflects the stereochemical nature of the reactant and since our distribution is basically independent of starting isomer.

Ring and Rabinovitch[8] have reported that increasing pressure (by dilution with $N_2$) in the reaction of triplet methylene with *cis*-but-2-ene results in inhibition of olefin formation, and enhancement of dimethylcyclopropane yields. They have suggested that the pressure effect is due to the collisional deactivation of a vibrationally excited 1,2-dimethyl-1,3-trimethylene triplet biradical (or triplet 1,2-dimethylcyclopropane) intermediate. The qualitative similarities between the pressure effect observed in this work and Ring and Rabinovitch's triplet methylene experiments lead us to believe that we are forming a vibrationally excited triplet intermediate, which is most probably a triplet biradical.

The mercury photosensitized decomposition of pyrazoline vapour appears to provide a relatively 'clean' source of triplet biradicals, free from the possible complications encountered in methylene–olefin systems.[8] It also affords the opportunity of studying the chemistry of triplet biradicals in more detail than appears possible in solution photolysis where olefin formation is largely quenched. Specifically, gas phase work allows the investigation of reaction channels having larger activation energies than the cyclization to form cyclopropanes.

The small yields of 2-methylbut-2-ene and 2-methylbut-1-ene are relatively less affected by added Ar, and may be formed, at least in part, by direct photolysis. They were observed as products of direct photolysis at 3130 Å, and were only weakly pressure-dependent.[3] Approximately 2% of the decomposition products in the Table may be due to direct photolysis as estimated from the u.v. absorption spectrum of both 3,4-dimethylpyrazolines at 2537 Å. The traces of *cis*- and *trans*-but-2-ene may also result from direct photolysis.

The ethane yields were eliminated by the addition of small amounts of molecular oxygen ($O_2$: DMP *ca.* 0·05—0·1). Also, the yields of 3-methylbut-1-ene, *cis*-pent-2-ene, and *trans*-pent-2-ene were reduced in the presence of oxygen. In oxygen-free experiments, some higher hydrocarbons which are currently unidentified, but are estimated to be approximately $C_8$ from g.l.c. retention times, were found. These results suggest that methyl radicals, perhaps formed by decomposition of the intermediate biradicals, are present in this system.

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