The Unimolecular Decomposition of Excited Biradicals Formed by the Addition of Triplet ^{14}C-Methylene to *cis*- or *trans*-But-2-ene

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Summary Unimolecular decomposition by CH_3 loss has been observed with a half-pressure for stabilization of about 75 Torr for the excited biradicals formed by the addition of triplet $^3(^{14}CH_2)$ to both *cis*- and *trans*-but-2-ene; as much as 9% of the ^{14}C activity is found in C_8 compounds formed by radical combination reactions of ^{14}C-labelled butenyl radicals.

We have reinvestigated the reactions of the 1,2-dimethyl-1,3-trimethylene triplet biradical formed by addition of $^3CH_2$ to *cis*- and *trans*-but-2-ene[1–3] and now report results pertinent to the subsequent reactions of this intermediate radical. In our experiments, triplet $^{14}CH_2$ was formed by Hg 6 ($^3P_1$) photosensitization of $^{14}CH_2CO$, and was reacted with a 10-fold excess of the but-2-ene substrate, thus enabling the molecular fate of the methylene carbon atom to be determined by radio-gas-chromatographic analysis, uncomplicated by those non-radioactive products derived from the concurrent photosensitization of the but-2-ene itself.[4–6] The most significant new observation was that as much as 9% of the ^{14}C was eventually found in C_8 compounds, indicating an earlier decomposition of the biradical to form a ^{14}C-labelled C_4 monoradical. These observations furnish mechanistic information of interest in connection with the renewed experimentation on the chemical behaviour of the trimethylene biradical and its alkyl substituents.[7–13]

Triplet $^{14}CH_2$ reacts principally in these systems either by addition to the olefin, as in (1), or by abstraction of H to form $^{14}CH_3$, as in (3). The ^{14}C-labelled products found in these systems include ethane formed by the combination of $^{14}CH_3$ with CH_3 radicals, *tracer-labelled* 3,4-dimethylhex-1-ene (DMH), and other ^{14}C-containing C_8 compounds not individually identified, as shown in the Table. The remainder of the ^{14}C activity has been found among various other compounds, including several C_5 olefins, with essentially 100% recovery of ^{14}C.

We propose that the labelled DMH and other C_8 compounds are formed by the combination with other C_4 radicals of ^{14}C-labelled butenyl radicals resulting from the unimolecular decomposition of the vibrationally excited biradical formed in (1), as shown in (2). This reaction is analogous to the ground state singlet biradical decomposition in the pyrolysis of 1,1,2,2-tetramethylcyclopropane.[14]

Yields of some ^{14}C-labelled products[a] *from the reactions of* $^3(^{14}CH_2)$ *with but-2-ene*

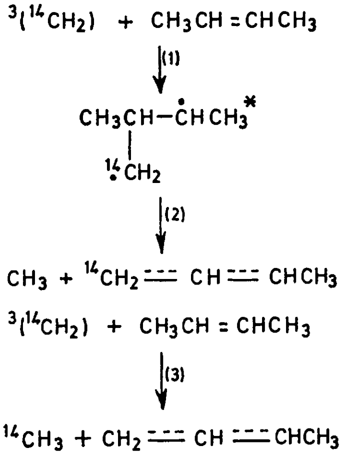
trans-But-2-ene

Total pressure (Torr)	51	200	399	597	833	1100
C_2H_6	15·9	14·2	12·2	11·0	10·0	9·1
DMH[b]	4·1	2·1	1·1	0·8	0·7	0·6
ΣC_8[b]	5·8	4·2	2·9	2·1	2·3	2·4
ΣDMC[b,c]	21·9	37·1	45·1	48·3	49·1	48·0

cis-But-2-ene

Total pressure (Torr)	49	151	486	833	1101
C_2H_6	18·7	19·0	15·7	11·9	9·3
DMH[b]	3·6	3·6	1·0	0·5	0·5
ΣC_8[b]	5·8	5·8	3·5	2·5	2·3
ΣDMC[b,c]	15·3	22·4	32·5	36·5	38·5

[a] Expressed as percent $^{14}CH_2$ appearing as each product. Typical other yields, not discussed here, included (given for *trans*-but-2-ene at 399 Torr as an example): Σpent-2-enes, 19·5%; Σ other pentenes, 7·7%; CH_4, 2·8%; isopentane, 4·5%; Σ unsaturated C_2–C_4, 3·5%; CO, 0·6%; CO_2, 0·1%. Butene: ketene = 10 in all experiments; [b] Abbreviations as defined in text; [c] The ΣDMC includes a small contribution from reactions initiated by $^1(^{14}CH_2)$.



The observation of ^{14}C-labelled 3-methylbut-1-ene, *trans*- and *cis*-pent-2-ene could signify methyl–butenyl combination following either reaction (3) or reactions (1) plus (2), and these mechanistically different paths would only be distinguishable in the product through intramolecular position of the ^{14}C. Differing intramolecular locations of radioactive tritium atoms have previously been observed with these olefinic products following the long wavelength photolysis (*ca.* 366 nm) of CHTCO–but-2-ene mixtures.[15] However, the explanation of McKnight and Rowland[15] that olefinically-tritiated 3-methylbut-1-ene is formed by an *intra*-molecular 1,2-methyl shift in a vibrationally excited biradical such as that formed in (1) should now be replaced by a mechanism involving the two-step biradical decomposition (1) plus (2), followed by methyl-butenyl combination. When carried out with ^{3}CHT from the photolysis of CHTCO, this reaction sequence leads to the tritium-labelled combination product $(CH_3)_2CHCH=CHT$. As anticipated for this two-step mechanism, the formation of $(CH_3)_2CHCH=CHT$ is collisionally suppressed at higher pressures.[15,16]

At high pressures, fragmentation of the biradical will be effectively quenched, resulting in an increased yield of dimethylcyclopropanes (ΣDMC in the table), cyclization being the only other major reaction channel available to the biradical. A similar trend in product yields has been noted in the Hg 6 ($^3P_1$) photosensitized decomposition of *cis*- and *trans*-3,4-dimethyl-Δ^1-pyrazoline.[13] Analysis of our data shows that approximately one-half of the excited biradicals decompose at about 75 Torr.

Thus the loss of methyl from the vibrationally excited triplet 1,2-dimethyl-1,3-trimethylene biradical is an example of a general molecular fragmentation process occurring in biradicals of this type to form allylically resonance stabilized radicals. Other examples of this reaction have already been reported and include the formation of allyl radicals both in the reaction of $^3CH_2$ with ethylene[17] and in the short wavelength photolysis of cyclobutanone,[18] and the production of vinyl cyclopropane *via* a resonance stabilized biradical formed by decomposition of the adduct of $^3CH_2$ with cyclobutene.[19]

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