Vacuum-Ultraviolet (147.0 and 123.6 nm) Photolysis of *trans*- and *cis*-1,2-Dimethylcyclopropanes

Tanis S. Pendleton, Michael Kaplan, and Richard D. Doepker*

Department of Chemistry, University of Miami, Coral Gables, Florida 33124 (Received August 30, 1979)
Publication costs assisted by the University of Miami

The photochemical decompositions of *trans*- and *cis*-1,2-dimethylcyclopropanes were investigated at 147.0 and 123.6 nm with standard rare gas resonance lamps. The observed products in the scavenged photolysis system were hydrogen, propylene, acetylene, ethylene, 1,3-butadiene, *trans*- or *cis*-2-butenes, pentadienes, allene, methylacetylene, and 1,2-butadiene, listed in decreasing importance. Quantum yields for each of the products were determined in experiments performed in both the presence and the absence of additives. Nitric oxide and oxygen were employed as radical scavengers, whereas hydrogen sulfide and hydrogen iodide were used as radical interceptors. Four radical species were identified and quantified, including methyl, vinyl, allyl, and a mixed C_4H_7 system. In both systems, ten primary processes have been proposed and the quantum efficiencies assigned for each primary reaction channel. The quantum efficiency for the methylene elimination channel ranged between 0.07 to 0.10 for both systems at both wavelengths. *trans*-1,2-Dimethylcyclopropane led exclusively to the *trans*-2-butene, whereas the *cis*- produced only the *cis*-2-butene.

Introduction

This study continues the investigation of substituted cyclopropanes by observing the vacuum-UV photochemical decompositions of the two geometrical isomers, *trans*- and *cis*-1,2-dimethylcyclopropanes, at 147.0 and 123.6 nm. These two molecules were of special interest because of the opportunity to compare their reaction channels with that of 1,1-dimethylcyclopropane, particular attention being given to the methylene elimination channel.

1,1-Dimethylcyclopropane has been investigated in this laboratory by Binkewicz and Kaplan[1] who obtained a primary quantum yield of 0.34 (at 147.0 nm) for the methylene elimination channel. Collin et al.[2] have recently reported the vacuum-UV photolysis of the same compound above and below the ionization energy. They also observed that the expulsion of methylene from the cyclopropane ring was a major primary reaction channel having a quantum efficiency of 0.35 at 147.0 nm. Seven major fragmentation processes were seen below the ionization energy. These results of Collin et al. were in basic agreement with our own study.

The isomerization of *trans*- and *cis*-1,2-dimethylcyclopropanes (*t*-DMCP, *c*-DMCP) has been the object of a number of studies. Kopecky et al.[3] observed that in the addition of methylene to either *trans*- or *cis*-2-butene, in solution, the resulting *trans*- or *cis*-1,2-dimethylcyclopropane did not isomerize to any great extent, probably because of rapid deactivation. However, studies in the gas phase show extensive isomerization.[4-9] The products of this isomerization are *cis*- and *trans*-1,2-dimethylcyclopropanes, *trans*- and *cis*-2-pentenes, 2-methyl-1-butene, and 2-methyl-2-butene. This photochemical process is exactly analogous to the thermal isomerizations of the two 1,2-dimethylcyclopropanes,[10,11] where the geometrical isomerization is considerably faster than the structural isomerization.

Further work by Dees and Koob[12] on the *cis*-dimethylcyclopropane system was carried out at 165, 147.0, and 123.6 nm. As observed before,[13] one of the primary processes of this system is

$$c\text{-DMCP} + h\nu \rightarrow CH_2 + cis\text{-}2\text{-}C_4H_8 \qquad (1)$$
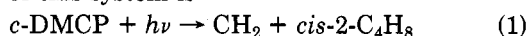
At 165 and 147.0 nm, no isomerization of the *cis*-2-butene was observed. However, a pressure-dependent isomerization to *trans*-2-butene was observed at 123.6 nm. The quantum yield of total 2-butene did not vary over the pressure range investigated. Conceivably, methylene could be eliminated from one of the methyl groups in the parent molecule, resulting in the production of methylcyclopropane, which would then isomerize to *cis*- and *trans*-2-butenes, 1-butene, and isobutene. At 147 and 165 nm, no *trans*-2-butene was produced; so at these energies this reaction is not competitive. It could occur at higher energies, although this does not appear likely because no isobutene was identified as a product at 123.6 nm. Therefore, it has been concluded that the only source of 2-butene is the primary photoelimination of methylene from the unsubstituted ring position of *cis*-1,2-dimethylcyclopropane (eq 1).

Experimental Section

Materials. *trans*- and *cis*-1,2-Dimethylcyclopropane (Chemical Samples Co.) were purified by vapor chromatography by using a 25 ft, 30% squalane on Chromosorb P column. The purity of the material after the purification process was greater than 99.9%. The purification of other materials has been described elsewhere.[14,15]

Irradiation and Analysis. The vacuum-ultraviolet photolyses were investigated at room temperature (25 °C) in a standard, static system with a 600-cm³ reaction vessel and a gettered xenon (147.0 nm) or krypton (123.6 nm) resonance lamp. Irradiation procedures, including photoionization, have been reported previously.[3,16] Analyses were performed by vapor chromatography (25 ft, 30% squalane at 60 °C and 6 ft phenyl isocyanate on Porosil C) and mass spectrometry (CEC 21-103C) as also reported earlier.[3,16]

Actinometry. The chemical actinometers used at 147.0 nm were cyclobutene, $\Phi_{C_4H_4} = 0.23$,[16] and cyclopentene, $\Phi_{C_2H_4} = 0.28$.[17] At 123.6 nm the actinometers were again cyclobutene, $\Phi_{C_4H_4} = 0.13$[16] and cyclopentene, $\Phi_{C_2H_4} = 0.20$.[17] The ionization efficiency of *trans*-1,2-dimethylcyclopropane was determined with photoionization techniques and was found to be 0.02 at 123.6 nm by using a value of 0.16 for cyclopentene.[18]

Results

The quantum yields of the major products of the photolyses of *trans*- and *cis*-1,2-dimethylcyclopropanes at 147.0 and 123.6 nm are reported in Tables I–V. These are

TABLE I: Quantum Yields in the Photolysis of *trans*-1,2-Dimethylcyclopropane 147.0 nm

t-DMCP, torr:	0.2	2.0	2.0	0.5	2.0	2.0
additive, torr:	none	none	(N$_2$) 54	(NO) 0.03	(NO) 0.1	(NO) 0.2 (N$_2$) 100
CH$_4$	0.06	0.05	0.04	0.02	0.03	0.02
C$_2$H$_2$	0.20	0.26	0.21	0.24	0.22	0.26
C$_2$H$_4$	0.26	0.29	0.29	0.22	0.22	0.21
C$_2$H$_6$	0.14	0.18	0.11			
C$_3$H$_6$	0.40	0.42	0.49	0.35	0.40	0.42
C$_3$H$_4$[a]	0.02	0.01	0.02	0.01	0.01	0.01
C$_3$H$_4$[b]	0.05	0.07	0.06	0.05	0.05	0.06
1,3-C$_4$H$_6$	0.09	0.13	0.10	0.12	0.14	0.14
trans-2-C$_4$H$_8$	0.08	0.10	0.10	0.10	0.10	0.10
1,2-C$_4$H$_6$	0.01	t[c]	t[c]	t[c]	0.01	t[c]
C$_5$H$_8$	nd[d]	0.06[e]	nd[d]	nd[d]	0.07[f]	nd[d]
H$_2$	nd[d]	0.40	nd[d]	0.49	0.54	nd[d]

[a] Methylacetylene. [b] Allene. [c] Trace. [d] Not determined. [e] 1,4-C$_5$H$_8$ (0.01); 2-methyl-1,3-butadiene (0.03); trans-1,3-C$_5$H$_8$ (0.01); cis-1,3-C$_5$H$_8$ (0.1). [f] 1,4-C$_5$H$_8$ (0.01); 2-methyl-1,3-butadiene (0.03); trans-1,3-C$_5$H$_8$ (0.02); cis-1,3-C$_5$H$_8$ (0.01).

TABLE II: Quantum Yields in the Photolysis of *trans*-1,2-Dimethylcyclopropane in the Presence of HI or H$_2$S at 147.0 nm

t-DMCP, torr:	2.0	2.0	1.0	1.0	6.0	15
additive, torr:	(H$_2$S) 0.2	H$_2$S 0.3	(HI) 0.15	(N$_2$) 82 (HI) 0.10	(HI) 0.6	(HI) 0.08
CH$_4$	0.36	0.41	0.49	0.52	0.48	0.50
C$_2$H$_2$	0.26	0.29	0.23	0.30	0.26	0.23
C$_2$H$_4$	0.30	0.32	0.35	0.33	0.33	0.31
C$_2$H$_6$	0.03	0.03	0.03	0.01	0.02	0.03
C$_3$H$_6$	0.36	0.39	0.54	0.58	0.53	0.54
C$_3$H$_4$[a]	0.02	0.01	0.02	0.02	0.01	0.02
C$_3$H$_4$[b]	0.05	0.04	0.06	0.05	0.04	0.04
1,3-C$_4$H$_6$[c]	t[d]	t[d]	0.22	0.21	0.22	0.20
trans-2-C$_4$H$_8$	0.07	0.08	0.10	0.10	0.10	0.13
1,2-C$_4$H$_6$	t[d]	t[d]	0.01	0.01	t[d]	0.01
cis-2-C$_4$H$_8$			t[d]	t[d]		t[d]
C$_5$H$_8$	nd[e]	nd[e]	nd[e]	nd[e]	nd[e]	nd[e]

[a] Methylacetylene. [b] allene. [c] 1,3-C$_4$H$_6$ and 1-butene. [d] Trace. [e] Not determined.

TABLE III: Quantum Yields in the Photolysis of *trans*-1,2-Dimethylcyclopropane at 123.6 nm

t-DMCP, torr:	1.0	5.0	24.0	0.8	5.0	25.0
additive, torr	none	none	none	(NO) 0.5	(NO) 0.3	(NO) 1.5
CH$_4$	0.02	0.02	0.02	0.02	0.01	0.01
C$_2$H$_2$	0.19	0.18	0.17	0.19	0.18	0.18
C$_2$H$_4$	0.20	0.22	0.19	0.20	0.19	0.22
C$_2$H$_6$	0.08	0.09	0.09			
C$_3$H$_6$	0.28	0.31	0.31	0.31	0.30	0.31
C$_3$H$_4$[a]	0.03	0.02	0.02	0.01	0.01	0.01
C$_3$H$_4$[b]	0.04	0.03	0.03	0.03	0.03	0.02
1,3-C$_4$H$_6$	0.07	0.08	0.08	0.07	0.09	0.09
trans-2-C$_4$H$_8$	0.07	0.08	0.08	0.08	0.07	0.09
1,2-C$_4$H$_6$	0.02	0.01	0.03	0.02	0.03	0.02
C$_5$H$_8$	nd[c]	nc[c]	nd[c]	0.07[d]	0.06[e]	nd[c]
H$_2$	0.40	0.38	nd[c]	0.54	0.48	nd[c]

[a] Methylacetylene. [b] Allene. [c] Not determined. [d] 1,4-C$_5$H$_8$, (0.01); 2-methyl-1,3-butadiene, (0.03); trans-1,3-C$_5$H$_8$ (0.02); cis-1,3-C$_5$H$_8$, (0.01). [e] 1,4-C$_5$H$_8$, (0.01), 2-methyl-1,3-butadiene, (0.03); trans-1,3-C$_5$H$_8$ (0.01); cis-1,3-C$_5$H$_8$, (0.101).

representative data collected under a variety of experimental conditions.

Although propylene appears to be pressure dependent in Table I, having an increasing quantum yield with in-

TABLE IV: Quantum Yields in the Photolysis of *trans*-1,2-Dimethylcyclopropane in the Presence of H$_2$S or HI, at 123.6 nm

t-DMCP, torr:	1.0	15.0	1.0	7.0	7.0
additive, torr:	(H$_2$O) 0.1	(H$_2$S) 1.5	(HI) 0.1	(HI) 0.35	(HI) 0.7
CH$_4$	0.43	0.41	0.47	0.43	0.48
C$_2$H$_2$	0.19	0.18	0.19	0.18	0.19
C$_2$H$_4$	0.24	0.21	0.25	0.24	0.25
C$_2$H$_6$	0.02	0.02	0.02	0.02	0.02
C$_3$H$_6$	0.32	0.35	0.43	0.39	0.42
C$_3$H$_4$[a]	0.01	0.01	0.01	0.02	0.01
C$_3$H$_4$[b]	0.02	0.02	0.03	0.03	0.02
1,3-C$_4$H$_6$[c]	0.01	0.01	0.15	0.16	0.16
trans-2-C$_4$H$_8$	0.07	0.07	0.09	0.12	0.11
1,2-C$_4$H$_6$	0.01	t[d]	0.02	0.03	0.02
cis-2-C$_4$H$_8$	0.01	0.01	0.01	0.02	0.02
C$_5$H$_8$	nd[e]	nd[e]	nd[e]	nd[e]	nd[e]

[a] Methylacetylene. [b] Allene. [c] 1,3-C$_4$H$_6$ and 1-butene. [d] Trace. [e] Not determined.

TABLE V: Quantum Yields in the Photolysis of *cis*-1,2-Dimethylcyclopropane

λ, nm:		147.0			123.6	
c-DMCP, torr:	1.0	1.0	1.0	1.0	1.0	1.0
additive, torr:	none	(NO) 0.1	(H$_2$S) 0.15	(HI) 0.10	none	(NO) 0.1
CH$_4$	0.02	0.01	0.54	0.53	0.04	0.02
C$_2$H$_2$	0.21	0.24	0.30	0.23	0.39	0.37
C$_2$H$_4$	0.21	0.20	0.23	0.25	0.31	0.25
C$_2$H$_6$	0.07		0.04	0.03	0.16	
C$_3$H$_6$	0.33	0.35	0.42	0.40	0.49	0.46
C$_3$H$_4$[a]	0.01	0.01	0.02	0.02	0.03	0.02
C$_3$H$_4$[b]	0.03	0.03	0.03	0.04	0.04	0.04
1,3-C$_4$H$_6$	0.10	0.14	0.02	0.19[d]	0.10	0.13
cis-2-C$_4$H$_8$	0.05	0.07	0.04	0.09	0.10	0.09
1,2-C$_4$H$_6$	0.01	0.02	t[c]	0.01	0.02	0.02
trans-2-C$_4$H$_8$			0.01			

[a] Methylacetylene. [b] Allene. [c] Trace. [d] 1,3-C$_4$H$_6$ = 0.13, C$_4$H$_8$ = 0.6.

creasing pressure, an examination of the complete data collected would indicate that this is an artifact of the selections of the "representative" points. No definitive pressure-dependent products, including propylene, were seen over the pressure range of 0.2–50 torr. The addition of up to 200 torr of N$_2$ also appeared to have no effect on the product quantum yields.

Irradiation times were selected to hold the conversion below 0.1% for the experiments in which quantum yields were obtained. When radical scavengers were present, all products appeared to be independent of irradiation time. The analysis procedure used in this study would not detect C$_6$ products, and no major effort was expended to locate possible C$_6$ products.

Discussion

The photolysis of *trans*- or *cis*-1,2-dimethylcyclopropane at 147.0 nm results in the formation of neutral excited molecules which fragment into molecular products and/or radicals. At 123.6 nm some ionization may accompany these reaction channels, but with an ionization efficiency of but 2%, this primary reaction channel may be neglected.

Reaction Channels. The most predominant product is propylene, which appears to be formed by several different pathways. As with other cyclic hydrocarbons,[1,2,19] 1,2-dimethylcyclopropane may dissociate directly into ethylene and propylene (eq 2). This process is exothermic by 185

$$t\text{-DMCP} + h\nu \rightarrow C_2H_4 + C_3H_6 \qquad (2)$$

kcal/mol at 147.0 nm, with an additional 36 kcal/mol if

the 123.6-nm wavelength is used. If the bulk of the "excess" energy were concentrated on either of the product fragments, that fragment would be expected to further dissociate. If "ethylene" (CH_3–CH^*) were to contain this "excess" energy, acetylene or possibly a vinyl radical would result (eq 3–5). If reaction 5 were occurring, the ethylene

$$C_2H_4^* \rightarrow C_2H_2 + H_2 \qquad (3)$$

$$\rightarrow C_2H_3 + H \qquad (4)$$

$$\xrightarrow{M} C_2H_4 \qquad (5)$$
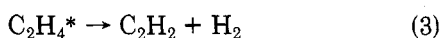
quantum yields should exhibit a pressure effect. However, no such effect is observed; thus this reaction channel may be eliminated. Reaction 3, the major reaction channel for an ethylene molecule with "excess" energy, is assumed to occur nearly simultaneously with propylene formation and is the only reaction leading to the formation of acetylene. Reaction 4 must also be considered, since the presence of vinyl radicals is demonstrated through the use of either H_2S[20] or HI[21] as radical interceptor. Vinyl radical yields may be quantified by subtracting the quantum yield of ethylene formation in the presence of NO or O_2 from its yield when either H_2S or HI is present in the photolysis system.

If the "propylene" fragment ($CH_3CHCH_2^*$) carried away the "excess" energy, reaction 6 may occur, leading to the

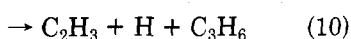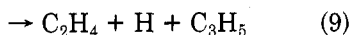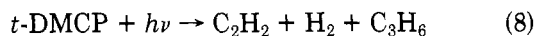$$C_3H_6^* \rightarrow C_3H_4 + H_2 \qquad (6)$$
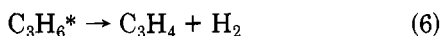
formation of methylacetylene or allene.

It can be seen in Tables I–V that the quantum yield of propylene increases in the presence of hydrogen iodide but not with added hydrogen sulfide. This would indicate the presence of allyl radicals,[22] since hydrogen iodide is known to intercept both the allyl and the vinyl form of the C_3H_5 radical whereas hydrogen sulfide intercepts only the vinyl form. The presence of allyl (C_3H_5) radicals would be accounted for through reaction 7. As in the case of ethylene,

$$C_3H_6^* \rightarrow C_3H_5 + H \qquad (7)$$
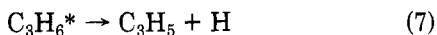
the collisional deactivation of the $C_3H_6^*$ fragment is of little importance in the pressure range used in this study. This is demonstrated through the very weak (if any) pressure effect observed for propylene. The formation of propylene, therefore, can be attributed to the reaction channels 2, 8, 9, and 10.

$$t\text{-DMCP} + h\nu \rightarrow C_2H_2 + H_2 + C_3H_6 \qquad (8)$$

$$\rightarrow C_2H_4 + H + C_3H_5 \qquad (9)$$

$$\rightarrow C_2H_3 + H + C_3H_6 \qquad (10)$$

The most probable reaction pathway for the formation of 1,3- and/or 1,2-butadiene involves the elimination of a terminal methyl radical and a hydrogen atom (eq 11).

$$t\text{-DMCP} + h\nu \rightarrow CH_3 + H + 1,3\text{-}C_4H_6/1,2\text{-}C_4H_6 \qquad (11)$$
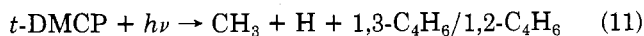
If the methyl group elimination and ring cleavage occurred before the hydrogen atom elimination, some of the resulting C_4H_7 radicals could lead to *trans*- and *cis*-2-butenes and 1-butene in the presence of hydrogen iodide. Indeed the quantum yields of these compounds increase under these conditions. It must be noted, though, that the C_4H_7 yields observed in the presence of HI are over and above the butadiene yields. Although reaction 11 is exothermic by 92 kcal/mol, further decomposition does not appear likely because of the lack of a pressure-dependence of the 1,3-butadiene quantum yield. It is further assumed that reaction 11 is the only reaction pathway leading to the

formation of 1,3- and 1,2-butadienes. It should be noted that the presence of H_2S decreases the yield of 1,3-butadiene (Tables II and IV). This effect has been noted previously in this laboratory[19] and by Collin et al.,[23] who attribute this to a rapid bimolecular process between HS and 1,3-butadiene.

Considering the formation of *cis*- and *trans*-2-butenes and 1-butene in the presence of HI, reaction 12 must also

$$t\text{-DMCP} + h\nu \rightarrow CH_3 + C_4H_7 \qquad (12)$$
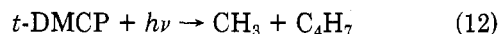
be considered as a possible primary process. This process is quantified by subtracting the sum of the quantum yields for 1,3-butadiene plus *trans*-2-butene, in the presence of NO, from the similar sum including *cis*-2-butene when HI is present.

The elimination of a second methyl (eq 13) should result

$$t\text{-DMCP} + h\nu \rightarrow 2CH_3 + C_3H_4 \qquad (13)$$

in the formation of allene, although isomerization to methylacetylene may also result. The cleavage of the C_4H_7 fragment formed through the elimination of the terminal methyl may also produce ethylene and a vinyl radical (eq 14). This reaction has been postulated as a primary re-

$$t\text{-DMCP} + h\nu \rightarrow CH_3 + C_2H_4 + C_2H_3 \qquad (14)$$
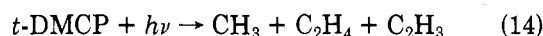
action channel in the vacuum-UV photolysis of ethyl-cyclopropane[19] and 1,1-dimethylcyclopropane.[1,2] It does not appear, though, that reaction 14 is important in the photolyses of the 1,2-dimethylcyclopropanes.

The formation of 2-methyl-1,3-butadiene, *trans*- and *cis*-1,3-pentadienes, and 1,4-pentadiene all proceed through the elimination of two hydrogen atoms from the photoexcited 1,2-dimethylcyclopropane molecule (eq 15).

$$t\text{-DMCP} + h\nu \rightarrow 2H + C_5H_8 \qquad (15)$$
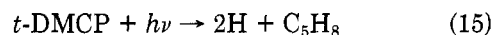
The elimination of methylene from the cyclopropane ring would produce a C_4H_8 fragment with the 2-butene structure. The fact that no *cis*-2-butene is formed in the presence of NO or O_2 indicates that the fragment formed is exclusively *trans*-2-butene (eq 16). This reaction is

$$t\text{-DMCP} + h\nu \rightarrow CH_2 + trans\text{-}2\text{-}C_4H_8 \qquad (16)$$
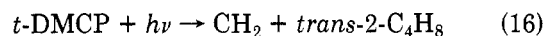
exothermic by 113.5 kcal/mol whereas the isomerization energy for 2-butene is about 62–63 kcal/mol.[12] The fact that no isomerization of the C_4H_8 fragment occurs leads to several conclusions. First, the two C–C bonds in the cyclopropane ring are broken simultaneously (within a molecular vibration or two). The methylene radical eliminated in this process is in the singlet state.[13] In addition, no more than 62–63 kcal/mol could have been carried off by the C_4H_8 fragment. This leaves at least 50 kcal/mol on the methylene. Since the first excited state is about 20 kcal/mol above the lowest singlet state,[13] the methylene probably is in this excited singlet state.

The results of the *cis*-1,2-dimethylcyclopropane system agree with the mechanism proposed for the *trans*-1,2-dimethylcyclopropane except that *cis*-2-butene is formed instead of *trans*-2-butene in the methylene elimination pathway.

The photolyses of *trans*- and *cis*-1,2-dimethylcyclopropanes at 123.6 nm introduces 36 kcal/mol more energy than the photolysis at 147.0 nm. This new energy (10.0 eV) is below the ionization energy of 10.8 eV[24] for both *trans*- and *cis*-dimethylcyclopropanes; thus ionization should be of no concern here. The photolysis at 123.5 nm can be expected to be very similar to the photolysis at 147.0 nm, although product distribution is generally dependent on excitation energy.
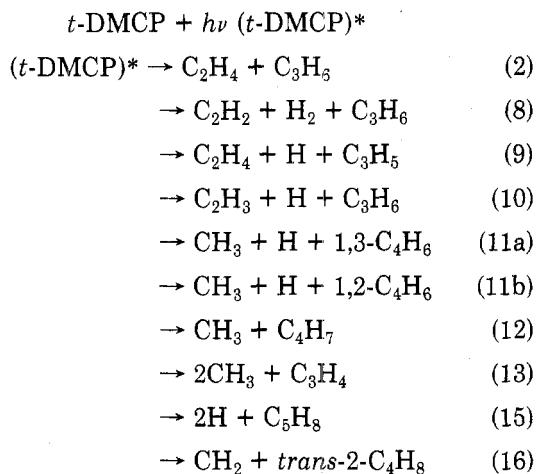
TABLE VI: Photolysis of *trans*- and *cis*-1,2-Dimethylcyclopropanes: Summary of Quantum Yields

	t-DMCP		*c*-DMCP	
	147.0 nm	123.6 nm	147.0 nm	123.6 nm
C_2H_2	0.24	0.18	0.23	0.37
C_2H_4	0.21	0.20	0.20	0.25
C_3H_6	0.39	0.30	0.34	0.46
$C_3H_4{}^a$	0.01	0.01	0.02	0.03
$C_3H_4{}^b$	0.06	0.03	0.03	0.04
1,3-C_4H_6	0.18	0.09	0.13	0.13
trans/cis-2-C_4H_8	0.10	0.08	0.07	0.10
1,2-C_4H_8	t^c	0.03	0.01	0.02
C_5H_8	0.07	0.07	nd^d	nd^d
H_2	0.52	0.48	nd^d	nd^d
CH_3	0.50	0.46	0.53	nd^d
C_2H_3	0.10	0.05	0.05	nd^d
C_3H_5	0.15	0.13	0.08	nd^d
C_4H_7	0.04	0.12	0.07	nd^d

^{a} Methylacetylene. ^{b} Allene. ^{c} Trace. ^{d} Not determine.

Quantum Yields. The quantum yields of the primary reaction products are summarized in Table VI. On the basis of these values and the above mechanistic examination the reaction channels shown in Scheme I seem to best characterize the vacuum-UV photolysis to *t*-DMCP.

Scheme I

$$t\text{-DMCP} + h\nu \ (t\text{-DMCP})^*$$

$$(t\text{-DMCP})^* \rightarrow C_2H_4 + C_3H_6 \quad (2)$$

$$\rightarrow C_2H_2 + H_2 + C_3H_6 \quad (8)$$

$$\rightarrow C_2H_4 + H + C_3H_5 \quad (9)$$

$$\rightarrow C_2H_3 + H + C_3H_6 \quad (10)$$

$$\rightarrow CH_3 + H + 1,3\text{-}C_4H_6 \quad (11a)$$

$$\rightarrow CH_3 + H + 1,2\text{-}C_4H_6 \quad (11b)$$

$$\rightarrow CH_3 + C_4H_7 \quad (12)$$

$$\rightarrow 2CH_3 + C_3H_4 \quad (13)$$

$$\rightarrow 2H + C_5H_8 \quad (15)$$

$$\rightarrow CH_2 + trans\text{-}2\text{-}C_4H_8 \quad (16)$$

The quantum yields of 1,3-butadiene (eq 11a), 1,2-butadiene (eq 11b), acetylene (eq 8), *trans*-2-butene (eq 16), methylacetylene and allene (eq 13), and the pentadienes (eq 15) directly reflect the quantum efficiencies of those primary reaction channels. This is likewise true for the vinyl radical (eq 10), the allyl radical (eq 9), and the isomers of the C_4H_7 radical (eq 12). These individual quantum yields quantify specific primary reaction channels owing to the fact that they are unique to only one reaction channel. The "excess" ethylene and propylene after the above assignments thus leads to the quantum efficiency of reaction 2. Thus the product quantum yields summarized in Table VI generate the quantum efficiencies presented in Table VII.

Summary and Conclusion

The primary quantum efficiencies for both *trans*- and *cis*-1,2-dimethylcyclopropanes are reported in Table VII. These are tentative assignments, since only through extensive labeling experiments can the nature of the intramolecular rearrangements be fully estimated. Data used to arrive at Table VII were collected with an estimated accuracy of better than 10% for the quantum yields. Larger error limits apply for radical yield determinations since the resulting quantum yields were obtained as a difference between two quantum values with their own error limits. Hydrogen yields require experimental conditions and operations that also would be expected to produce increased error limits. In these cases, the estimated error is around 15%.

The proposed reaction channels given in Table VII reflect the absence of a definitive pressure effect that might permit the grouping of certain reaction channels into a single primary process followed by secondary decomposition and/or rearrangements. The reaction channels and their quantum efficiencies presented do, however, suggest the course of the primary excited molecule with regard to its ultimate conclusion at the pressure range of this study and the energy of the radiation used.

It must be noted that insufficient data were collected at 123.6 nm for *cis*-1,2-dimethylcyclopropane to evaluate reliably all the primary reaction channels.

TABLE VII: Quantum Yields for the Primary Reaction Channels in the Vacuum-UV Photolysis of *trans*- and *cis*-1,2-Dimethylcyclopropanes

	t-DMCP		*c*-DMCP	
	147.0 nm	123.6 nm	147.0 nm	123.6 nm
$Me_2C_3H_4 + h\nu \xrightarrow{8} C_2H_2 + H_2 + C_3H_6$	0.24	0.18	0.23	0.37
$\xrightarrow{10} C_2H_3 + H + C_3H_6$	0.10	0.05	0.03	0.09
$\xrightarrow{2} C_2H_4 + C_3H_6$	0.06	0.07	0.08	0.25
$\xrightarrow{9} C_2H_4 + H + C_3H_5$	0.15	0.13	0.10	
$\xrightarrow{11a} CH_3 + H + 1,3\text{-}C_4H_6$	0.18	0.09	0.13	0.13
$\xrightarrow{11b} CH_3 + H + 1,2\text{-}C_4H_6$	0.00	0.03	0.01	0.02
$\xrightarrow{12} CH_3 + C_4H_7$	0.04	0.12	0.07	nd
$\xrightarrow{13} 2CH_3 + C_3H_4$	0.07	0.04	0.05	0.07
$\xrightarrow{15} 2H + C_5H_8$	0.07	0.07	nd	nd
$\xrightarrow{16} CH_2 + C_4H_8$	0.10	0.08	$\geqslant 0.07$	$\geqslant 0.10$
total	1.01	0.86	0.77	1.03

References and Notes

(1) Binkewicz, J. B.; Kaplan, M., Doepker, R. D., unpublished results.
(2) Collin, G. J.; Gagmon-Deshauries, H.; Suguet, M.; Bukla, K. P.; Simard, J. L. *J. Photochem.* **1978,** *9,* 449.
(3) Kopecky, K. R.; Hammon, G. S.; Leersmakers, P. A. *J. Am. Chem. Soc.* **1961,** *83,* 2397.
(4) Rabinovitch, B. S., Setser, D. W. *J. Am. Chem. Soc.* **1961,** *83,* 750.
(5) Frey, H. M. *J. Am. Chem. Soc.* **1960,** *82,* 1947.
(6) Setser, D. W.; Rabinovitch, B. S. *Can. J. Chem.* **1962,** *40,* 1425.
(7) Frey, H. M. *Proc. R. Soc. London, Ser. A* **1959,** *251,* S7S.
(8) Bell, J. A. *J. Am. Chem. Soc.* **1965,** *87,* 4966.
(9) Simons, J. W.; Rabinovitch, B. S. *J. Phys. Chem.* **1964,** *68,* 1322.
(10) Flowers, M. C.; Frey, H. M. *Proc. R. Soc. London, Ser. A* **1960,** *257,* 122.
(11) Flowers, M. C.; Frey, H. M. *Proc. R. Soc. London, Ser. A* **1961,** *260,* 424.
(12) Dees, K.; Koob, R. D. *J. Phys. Chem.* **1973,** *77,* 759.
(13) Dhingra, A. K.; Koob, R. D. *J. Phys. Chem.* **1970,** *74,* 4490.
(14) Doepker, R. D. *J. Phys. Chem.* **1969,** *73,* 3219.
(15) Hill, K. L.; Doepker, R. D. *J. Phys. Chem.* **1972,** *76,* 3153.
(16) De Leon, A.; Doepker, R. D. *J. Phys. Chem.* **1971,** *75,* 3656.
(17) Tu, C.-K.; Doepker, R. D. *J. Photochem.* **1974/75,** *3,* 13.
(18) Leschaux, R.; Searles, S.; Sieck, L. W.; Ausloos, P. *J. Chem. Phys.* **1971,** *54,* 3411.
(19) Lopez, E.; Doepker, R. D. *J. Phys. Chem.* **1978,** *82,* 753.
(20) Ausloos, P.; Lias, S. *J. Chem. Phys.* **1966,** *44,* 521.
(21) Ausloos, P.; Rebbert, R. E.; Lias, S. C. *J. Photochem.* **1973/74,** *2,* 267.
(22) Collin, G. J.; Wieckowski, A. *J. Photochem.* **1978,** *8,* 103.
(23) (a) Collin, G. J.; Perrin, P.; Gaucher, C. M. *Can. J. Chem.* **1972,** *50,* 2391. (b) Collin G. J.; Perrin, P. *Ibid.* **1972,** *50,* 2400.
(24) Dewar, J. S. *J. Am. Chem. Soc.* **1967,** *89,* 3966.

Vibrational Energy Transfer in a Diffusion-Flow Cyclopropane-d_2 System

J. F. Burkhalter,[†] E. Kamaratos,[‡] and B. S. Rabinovitch*

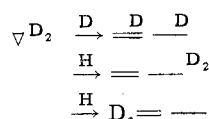*Department of Chemistry, University of Washington, Seattle, Washington 98195 (Received October 9, 1979)*

Publication costs assisted by the Office of Naval Research

In a previous paper, the diffusion cloud technique was applied to the c-C_3H_6 isomerization system. Vibrational energy transfer upon collision was measured. Relative reaction rates were measured and, by calibration from other work, were converted to absolute rate constants. In the present study, absolute rate constants for cyclopropane-d_2 were determined in a diffusion-flow system. The relative rates of the competitive isotopic isomerization channels were measured for two bath gases, N_2 and He, at two temperatures, 973 and 1073 K. Values of the average energy down-jump size $\langle \Delta E \rangle$ were computed from both the absolute rates and the isotopic relative rates by suitable modeling.

Introduction

The diffusion cloud technique[1] has been used by us to measure vibrational energy transfer for cyclopropane in an earlier study.[2] In that work, only relative rate constants could be determined and a calibration of rates derived from other work[3] was used to find absolute values. In the work reported in this study, we have modified the diffusion cloud apparatus in order to make total collection of all of the sample that issues from the reactor. In this way, some rate measurements have been made under similar reaction conditions to those used in the previous study. This has permitted a direct test of the previously used calibration.

We have simultaneously extended the study to the measurement of competitive isotopic rates by use of the substrate cyclopropane-*1,1-d_2*. Isotopic rate effects in this system and vibrational energy transfer have previously been studied in static and flow reactors.[3,4] Due to the fast transport in the diffusion cloud apparatus, higher temperature effects can be studied. The unimolecular isomerization of cyclopropane-*1,1-d_2* proceeds as follows:

$$\triangle^{D_2} \xrightarrow{\ D\ } \xmid \quad \overset{D}{\underset{}{\text{—}}} \quad D$$
$$\xrightarrow{\ H\ } \xmid \quad \overset{}{\underset{}{\text{—}}}\ D_2$$
$$\xrightarrow{\ H\ } D_2 \xmid \quad \text{—}$$

where the migrating atom is shown.

In the present note, absolute rates and comparative isotopic rates are reported for two bath gases, N_2 and He,

at two temperatures, 973 and 1073 K. Vibrational energy transfer amounts were computed from these measurements.

Experimental Section

Apparatus and Procedure. The diffusion cloud apparatus has been previously described.[2] Flow velocities in the reactor were varied between 8 and 45 cm s^{-1}. The apparatus was modified slightly by inclusion of two liquid-nitrogen-cooled traps, a large (50-mm diameter) glass trap followed by a stainless steel protective trap, between the diffusion chamber and the main Roots pump. In this way, all products and remaining reactant were trapped. The glass trap could be isolated by two 1-in. brass Veeco bellows valves, then warmed, and the product–reactant mixture transferred and collected through a separate sideline. It was analyzed by GC with a 500-ft 30% 3 M $AgNO_3$/ethylene glycol–Chromosorb P column to separate the deuteriopropene isomers and cyclopropane.

Treatment of Data. GC analysis of the reaction mixture yielded three peaks which corresponded to the three isomers of dideuteriopropylene (propylene-*1,1-d_2*, propylene-*3,3-d_2*, and propylene-*2,3-d_2*). The ratio of rate constants due to D migration and H migration was determined from the simple expression

$$\frac{k(\text{D})}{k(\text{H})} = \frac{C(\text{propylene-}2,3\text{-}d_2)}{C(\text{propylene-}1,1\text{-}d_2) + C(\text{propylene-}3,3\text{-}d_2)}$$

where C is the experimentally determined product concentration.

The absolute rate constant for total reaction was calculated by using a method described in detail by Mulcahy[5] for flow reactors. By this method, one first calculates the

[†] NSF ERG fellow. Chemical Research and Development Dept., Halliburton Services, Duncan, Okla.
[‡] Department of Chemistry, Tougaloo College, Tougaloo, Miss. 39174.