

Photolysis of Methoxyethene-Neopentane-Ketene Mixtures in the Presence of Oxygen (A Chemical Activation Study)

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Summary: The reactions of methylene with methoxyethene in the presence of oxygen was investigated with Ketene as methylene precursor. The observed products were methoxycyclopropane, (E)- and (Z)-1-methoxyprop-1-ene, ethoxyethene, 3-methoxyprop-1-ene and 2-methoxypropene. The rate of methylene addition to double bands and insertion into C-H bonds of methoxyethene relative to the rate of insertion into C-H bond of neopentane are reported. RRKM calculations were carried out to estimate the extent of chemically activated decomposition in the system.

Introduction

Although the first study of the reactions of methylene with olefins to produce vibrationally excited cyclopropanes was carried out more than a quarter of a century ago [1], these reactions have been of particular interest recently [2-5] due to their importance in the understanding of the theories of unimolecular reactions and energy transfer processes. The present work on the reaction of singlet methylene with methoxyethene was undertaken primarily in an attempt to obtain the efficiencies of intermolecular energy transfer from highly excited molecules, utilizing competitive reactions. The study also extend the range of substrate molecules whose reaction with methylene have been investigated.

Experimental

a. Materials

Ketene was prepared by pyrolytic decomposition of acetic anhydride in a quartz tube at $\sim 520^\circ\text{C}$ by the method of Jenkins [6] and purified by repeated trap to trap distillation between -80 to -196°C . The purified sample was stored as a gas in a blackend glass bulb at a pressure of less than 80 torr [7].

Methoxyethene was purchased from Fluke AG (Switzerland) and was used without further purification. Oxygen (99.98%), (British Oxygen Company). All the other chemicals used were commercially available.

b. Apparatus

All experiments were performed in a static vacuum system equipped with greaseless stopcocks. The photolyses were performed in cylindrical Pyrex cells, wrapped in aluminium foil and fitted with a quartz window at one end. Two cell sizes were used; one 380 mm long and 26 mm diameter (used for low pressure photolyses) and the other of 95 mm long and 26 mm diameter. A Mazda 250 W medium pressure mercury lamp was used for photolyses. The output of the lamp was partially focussed into a Bausch and Lomb monochromator (model number 33-86-07) with an entrance slit of 5.36 mm and an exit slit of 3.00 mm. The reactants were transferred from the storage bulb in to the reaction cell at measured pressures. After photolyses the photolysis cell was connected to the vacuum line. The Toeplor pump was then used to transfer the reaction mixture to the gas chromatographic sampling loop.

c. Experiment

The photolysis mixtures, made up of methoxyethene, ketene, oxygen and neopentane in the ratios of 6:1:1.5:1 respectively, were irradiated at 313 and 334 nm at a total pressure between 1-276 torr.

d. Analysis

Analyses were performed on a Perkin Elmer 452 gas chromatograph equipped with a flame

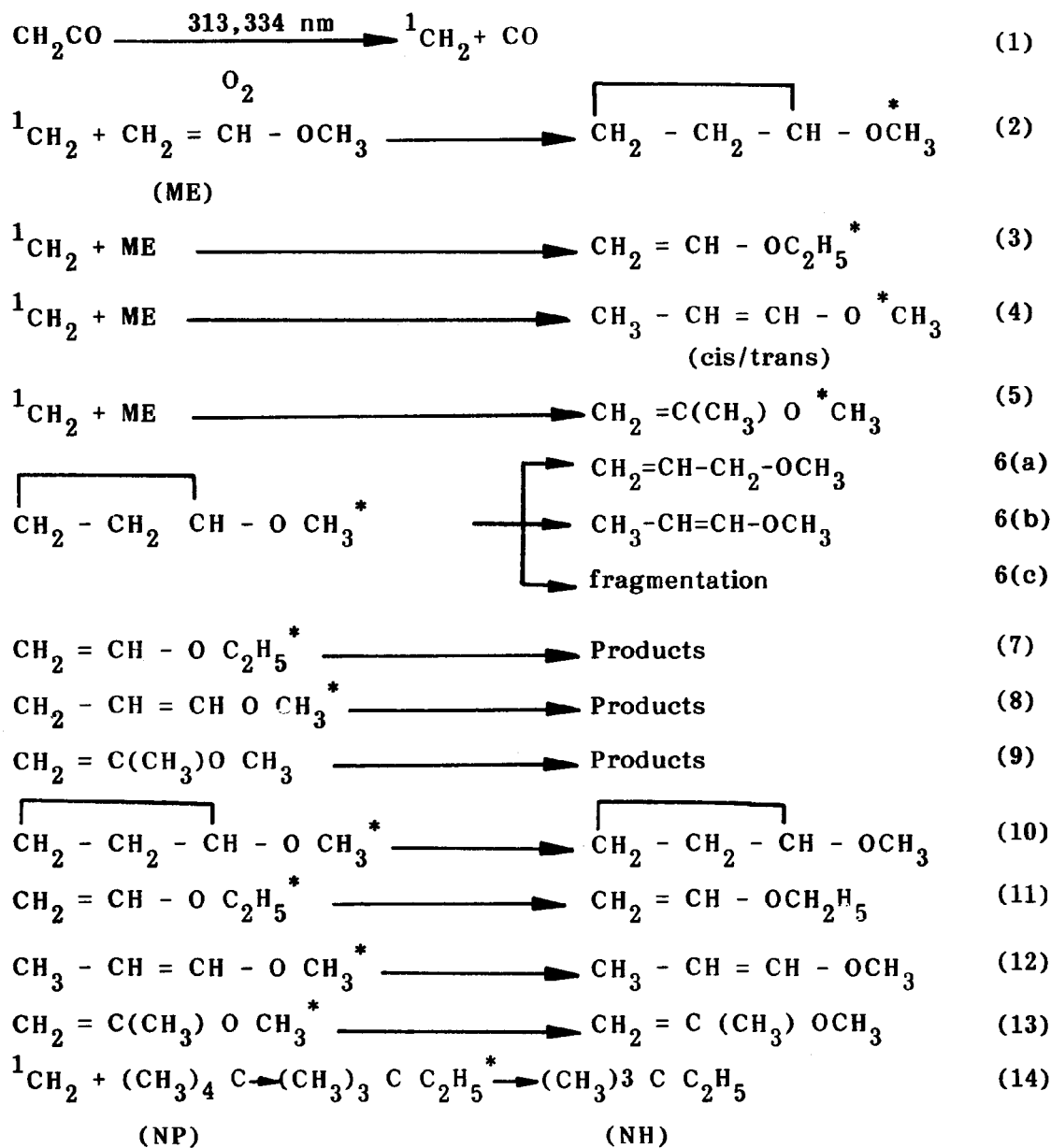
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ionization detector. A 50 m Squalane SCOT column was used at 0°C with 3 cm³/min helium carrier flow. The sample was split after the sampling loop and only 1/10 was passed through the column. All product peaks were well separated under these conditions, and all compounds were identified by comparison of retention times with known samples and by g.l.c./mass spectrometry (Kratos MS 30 mass spectrometer).

Results and Discussion

The reaction of singlet methylene in the gas phase with methoxyethene, gave 'hot' methoxycyclopropane, ethoxyethene, *cis/trans*-1-methoxyprop-1-ene and 2-methoxyprop-1-ene as addition and insertion products.

The following reaction scheme summarises reactions pertinent to this study:



Scheme 1

where ω is the collision frequency and asterisk represents the chemically activated molecules.

Application of the steady state approximation in the above reaction scheme gives the relative yields of neohexane and methoxycyclopropane as a function of pressure as:

$$\frac{Y_{NH}}{Y_{MC}} = \frac{k_{14}}{k_2} \frac{[NP]}{[ME]} \left(1 + \frac{k_s}{\omega}\right) \quad (15)$$

where k_s is the rate constant for the decomposition of 'hot' methoxycyclopropane i.e. $k_s = k_{6a} + k_{6b} + k_{6c}$, k_{14} is the rate constant for the reaction (14) and k_2 is for reaction (2) in above scheme. A plot of l.h.s. of the equation (15) versus $1/\omega$ sec⁻¹ for 313 nm photolyses is shown in figure (1). The slope of the line yields the average decomposition rate of the 'hot' molecule. From the value of the intercept the rate of insertion of singlet methylene into C-H bonds of neopentane relative to addition to carbon-carbon double bond may be found using the following expression:

$$\frac{k_{NH}}{k_{MC}} = \frac{Y_{NH} \times P_{ME} \times \text{Calibration factor of ME} \times D_{MC}}{Y_{MC} \times P_{NP} \times \text{Calibration factor of NH} \times D_{NH}}$$

Where P's are the initial reactants pressures and D's are the assumed path degeneracies.

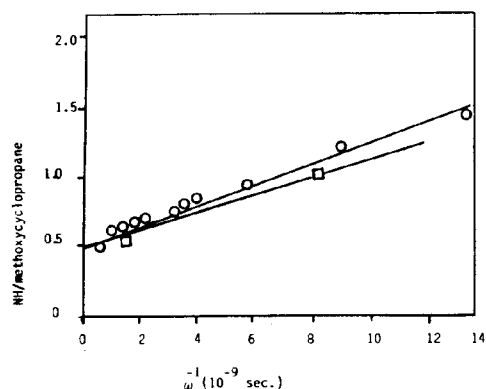


Fig. 1: Plot of neohexane/methoxycyclopropane against $1/\omega$ for methoxyethene/neopentane/ketene/ O_2 photolyses: (O) Experimental results at 3130 A; (□) theoretically calculated results by RRKM theory.

Similar plots have been made for other chemically activated products from methylene reactions (see figure 2,3 and 4) and data is given in table 1 and 2. A comparison of these results with the corresponding insobutene and propene system indicate that the replacement of an alkyl substituent by methoxy on ethene has no effect, within experiment errors, on the initial rate of attack of methylene to various bonds in methoxyethene system.

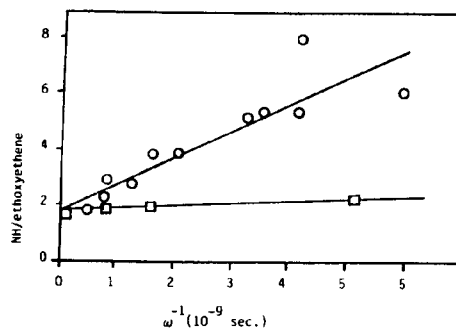


Fig. 2: Plot of neohexane/ethoxyethene against $1/\omega$ for methoxyethene/neopentane/ketene/ O_2 photolyses: (O) Experimental results at 3130 A; (□) theoretically calculated results by RRKM theory.

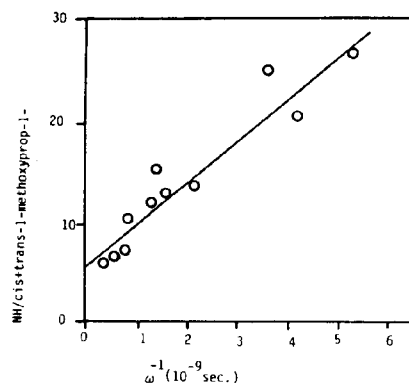


Fig. 3: Plot of neohexane/cis+trans-1-methoxyprop-1-ene against $1/\omega$ for methoxyethene/neopentane/ketene/ O_2 photolyses at 3130 A.

The time dependence of the reaction was investigated at 313 nm with the mixture of methoxyethene, ketene, oxygen and neopentane in ratios described previously, with a total pressure of

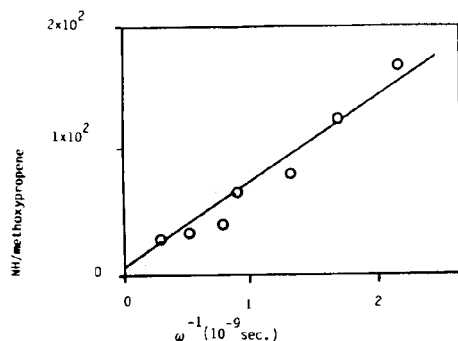


Fig. 4: Plot of neohexane/2-methoxypropene against $1/\omega$ for methoxyethene/neopentane/ketene/ O_2 photolyses at 3130 A.

65 torr. As the amount of neohexane increased linearly with time the rate of production of methylene must be constant, this in turn means that a small amount of ketene has been photolysed. All chemical activated products in this system showed similar time dependence.

To investigate the effect of the energy content of methylene on the reaction the photolysis wavelength was increased to 334 nm. The relative rates for the formation of methoxycyclopropane, *cis/trans*-1-methoxyprop-1-ene, ethoxyethene and 2-methoxyprop-1-ene were identical at the two wavelengths. However the rate of decomposition of the chemically activated products was considerably reduced on increasing the wavelength as a consequence of the methylene having a lower internal energy content.

Decomposition of chemically activated methoxycyclopropane

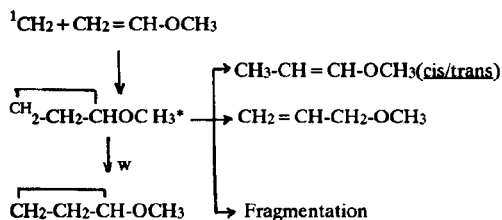
Methoxycyclopropane is formed by the addition of singlet methylene to the double bond of methoxyethene. Chemically activated methoxycyclopropane is expected to undergo decomposition by three parallel pathways to give isomeric products or to be collisionally stabilised to methoxycyclopropane (reaction 2,6 and 10, scheme 1). The minimum energy content in excess of thermal energies of initially formed methoxycyclopropane E_{min} was estimated from the heats of formation of all the species under the conditions of the study to be $448.3 \text{ kJ mole}^{-1}$ (see appendix 1) at 313 nm. The activation energies for isomerization pathways were determined in a

Table 1: Experimental rate constants for decomposition of chemically activated products from photolysis of methoxyethene/neopentane/ O_2 /ketene mixture at 313 n.m.

	k experimental rate constant (sec^{-1}) 313 n.m.
k5	$1.44 \times 10^8 \pm (6\%)$
k6a	$0.22 \times 10^8 \pm (6\%)$
k7	$2.0 \times 10^9 \pm (15\%)$
k8	$9.0 \times 10^8 \pm (10\%)$

separate study [8] and are quoted in Appendix 2.

RRKM calculations were carried out to estimate the extent of chemically activated decomposition in the system based on the following reaction scheme:



Scheme 2

The detailed description of the parameters used in the RRKM calculations are given in Appendix 2. With a value of E_{min} , the minimum energy content of the 'hot' methoxycyclopropane 415 kJ mole^{-1} and a step size of 30 kJ mole^{-1} for intermolecular energy transfer (step-ladder model), a reasonable fit to the experimental data was obtained for the overall decomposition of 'hot' methoxycyclopropane (see figure 1). The thermochemical calculations, based on the heat of formation of methoxycyclopropane and methoxyethene from group additivity and heat of formation of methylene [8] $\Delta H_{fo}(\text{CH}_2) = 426.8 \text{ kJ mole}^{-1}$ gave $E_{min} = 448.3 \text{ kJ mole}^{-1}$. If the difference in thermochemically estimated and fitted value of E_{min} is equated entirely to the uncertainties involved in heat of formation of methoxycyclopropane this leads to a value of $\Delta H_{f298}(\Delta\text{OCH}_3) = -63.6 \text{ kJ mole}^{-1}$ (cf. group additivity value = $-96.6 \text{ kJ mole}^{-1}$).

Table 2: Rate constants for addition of methylene to double bonds and insertion into C-H bonds of olefins relative to insertion into C-H bonds of neopentane at 3130 Å on per bond basis

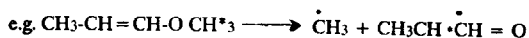
Olefins	¹ CH ₂	=	C ₍₁₎ -H	C ₍₂₎ -H	-OCH ₃	-CH ₃	Ref.
² ¹ CH ₂ = CH-CH ₃	CH ₂ CO	7.23	0.50	0.70	-	0.70	a
² ¹ CH ₂ = C(CH ₃) ₂	CH ₂ CO	7.2*	-	0.78	-	0.70	b
² ¹ CH ₂ = CH-OCH ₃	CH ₂ CO	8.1	0.4 (±20%)	0.72	0.8(±30%)	-	This work

*This value was assumed to obtain the subsequent values of C-H insertion as no direct data exists for this system with added neopentane.

a. F.H. Dorer and B.S. Rabinovitch, *J. Phys. Chem.*, **69**, 1964 (1965).

b. G.W. Taylor and J.W. Simons, *Int. J. Chem. Kinet.*, **3**, 25, 9(1971).

The behaviour of *cis/trans*-1-methoxyprop-1-ene and 2-methoxyprop-1-ene in the pressure region of the experimental study causes some doubts about whether or not they are formed in part from 'hot' methoxycyclopropane: they seem to be undergoing rapid secondary decomposition.



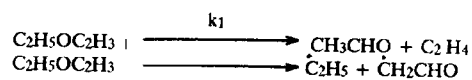
On the basis of experimental results one can suggest that the major source of these is the direct insertion of methylene into C-H bonds as shown in equation (4,5,8 and 9, scheme 1).

The overall rate of decomposition of 'hot' methoxycyclopropane is much higher than its isomerization to 3-methoxyprop-1-ene. This difference suggests that the major pathway for the decomposition of methoxycyclopropane is fragmentation to other products as observed in thermal study [8]. There is no evidence for the chemically activated formation of 3-methoxyprop-1-ene. Due to the large amount of fragmentation, with little isomerization of 'hot' methoxycyclopropane, determination of the efficiencies of energy transfer using this system was not possible.

Decomposition of chemically activated ethoxyethene

This compound is formed by the direct insertion of singlet methylene to the C-H bond of the

methyl group of methoxyethene as shown by (equation 3 and 7 of scheme 1): The behaviour of this product relative to the insertion of the methylene to the C-H bond of neopentane with total pressure is shown in figure (2). RRKM calculations were carried out, based on the Arrhenius parameters reported by M. Rossi and D.M. Golden [9] for the thermal decomposition to ethanal and ethene. The experimental and calculated results are shown in figure (2). The large discrepancy between experimental and theoretical values for the decomposition of chemically activated ethoxyethene suggests that this product must be lost by some alternative pathway in addition to the one leading to ethanal and ethene. Recently R.N. Rosenfeld and co-workers [10] observed that ethoxyethene yielded not only ethanal and ethene, the products of retro-ene molecular elimination, but also significant amount of ketene, ethene and butane upon multiphoton dissociation by an intense CO₂ laser, i.e.



A high activation energy reaction path, the bond scission, is held responsible for the occurrence of the latter products which are believed to be due to secondary reaction of radicals produced in the reaction.

APPENDIX I : THERMOCHEMICAL CALCULATIONS FOR THE METHYLENE PLUS METHOXYETHENE SYSTEM AT 298K

Thermochemical calculations for the methoxyethene plus methoxycyclopropane system at 298K.

The heats of formation of methoxyethene and methoxycyclopropane were calculated from group additivity values tabulated by S.W. Benson.

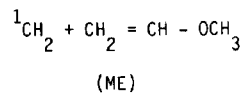
Compound $\Delta H_f^0(298)/\text{kJ mole}^{-1}$

methoxyethene -111

methoxycyclopropane -96.6

ethoxyethene -145.4

The value for the heat of formation of methylene $\Delta H_f^0(\text{CH}_2, {}^1A_1)$ has been the subject of much controversy in the past and currently accepted value is $426.8 \text{ kJ mole}^{-1}$. This value is used for the calculations.



The minimum excess energy of MC (E_{min}) in the above reaction is given by the equation:

$$\Delta H_f^*(298)({}^1\text{CH}_2) + E_{\text{excess}}({}^1\text{CH}_2) + \Delta H_f^0(298) \text{ (ME)} + E_{\text{act}} = \Delta H_f^0(298) \text{ (MC)} + E_{\text{min}}$$

where

$$\Delta H_f^0(298)({}^1\text{CH}_2) = H_f^0({}^1\text{CH}_2) + E_{\text{thermal}}({}^1\text{CH}_2)$$

and

$E_{\text{excess}}({}^1\text{CH}_2)$, at 3130 Å from has been estimated by Simons to be $24.3 \text{ kJ mole}^{-1}$.

Substituting the values for the various terms involved in the above equation gives

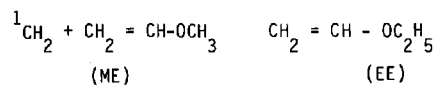
$$434.2 + 24.3 - 111 + 4.2 = -96.6 + E_{\text{min}}$$

$$E_{\text{min}} = 434.2 + 24.3 - 111 + 4.2 + 96.6$$

$$= 448.3 \text{ kJ mole}^{-1}$$

Therefore based on the above equation, the minimum energy content of chemical activation formed MC is $448.3 \text{ kJ mole}^{-1}$, however, a value of 415 kJ mole^{-1} has been used to obtain the reasonable fit to the experimental data.

Similarly, the minimum energy content of ethoxyethene was calculated at 3130 Å from the energetics based on the following reaction scheme:



$$\Delta H_f^0(298)({}^1\text{CH}_2) + E_{\text{excess}}({}^1\text{CH}_2) + \Delta H_f^0(298) \text{ (ME)} + E_{\text{act}} = \Delta H_f^0(298) \text{ (EE)} + E_{\text{min}}$$

$$434.2 + 24.3 - 111 + 4.2 = -145.4 + E_{\text{min}}$$

$$E_{\text{min}} = 497.1 \text{ kJ mole}^{-1}$$

Vibrational Frequencies

3100(1)	3000(2)	3050(2)	2900(1)
2850(1)	1460(2)	1450(3)	1300(1)
1250(1)	1220(1)	1200(2)	1150(3)
1100(4)	1050(3)	800(2)	400(3)
250(1)	180(1)		

Activated complex for the formation of 3-methoxyprop-1-en

E_0 for reaction $21203 \text{ cm}^{-1} \text{ molecule}^{-1}$
($253.7 \text{ kJ mole}^{-1}$) path degeneracy 4.

Vibrational frequencies

3100(1)	3000(2)	3050(2)	2900(1)	2850(1)
1450(3)	1440(2)	1250(2)	1200(2)	1150(1)
1100(2)	1050(2)	800(1)	420(1)	400(3)
675(1)	250(1)	180(1)	850(1)	750(2)

Activated complex for the formation of fragmentation products.

E_0 for reaction $21385 \text{ cm}^{-1} \text{ molecule}^{-1}$
($255.8 \text{ kJ mole}^{-1}$) path degeneracy 2.

Vibrational frequencies

3100(1)	3000(2)	3050(2)	2900(1)	2850(1)
1100(2)	680(1)	1250(2)	420(1)	1450(3)
1200(2)	1050(2)	850(1)	750(2)	1440(2)
1150(1)	400(3)	25(1)	800(1)	180(1)

APPENDIX 2

(a) Input parameters used for RRKM calculations on chemically activated decomposition of methoxycyclopropane produced by the reaction of methylene with methoxyethene. All vibrational frequencies are in cm^{-1} .

Molecular Parameters (methoxycyclopropane)

Collision diameter = 5.5 Å

Collision number = $1.20 \times 10^7 \text{ s}^{-1} \text{ Torr}^{-1}$

Initial energy content = $34687 \text{ cm}^{-1} = 415 \text{ kJ mole}^{-1}$

Temperature = 298 K

A stepladder collisional model was assumed with a step size of 2500 cm^{-1} .

Vibrational frequencies (degeneracies in brackets)

3100(1)	3050(2)	3000(3)	2850(1)	2900(1)
1460(2)	1450(3)	1250(1)	1200(1)	1150(3)
1100(2)	1050(3)	850(2)	800(1)	750(2)
400(3)	250(1)	180(1)		

Activated complex for cis/Trans-1-methoxyprop-1-ene formation:

E_0 for reaction $19340 \text{ cm}^{-1} \text{ molecule}^{-1}$
($231.4 \text{ kJ mole}^{-1}$) path degeneracy 4.

(b) Input parameters used for RRKM calculations on chemically activated decomposition of ethoxyethene.

Molecular parameters (ethoxyethene):

Minimum energy content = 41552 cm^{-1} ($497.1 \text{ kJ mole}^{-1}$)

Vibrational frequencies and degeneracies

3080(4)	2910(5)	1640(1)	1430(3)	1320(3)
1170(1)	1070(4)	960(1)	800(3)	580(1)
350(4)	200(2)	100(1)		

Activated complex parameters

Path degeneracy 1 $E_0 = 15208 \text{ cm}^{-1} \text{ molecule}^{-1}$
($181.9 \text{ kJ mole}^{-1}$)

Vibrational frequencies

3080(2)	2910(6)	1640(1)	1430(3)	1320(3)
1170(1)	1070(3)	1050(1)	960(1)	850(2)
700(1)	600(2)	400(2)	350(4)	

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