

THE HIGH PRESSURE PHOTOLYSIS OF ALKENES AND ALKYNES I: CALCULATION OF THE USEFUL PRESSURE RANGE

JANUSZ GAWŁOWSKI

Department of Chemistry, Warsaw University, Zwirki i Wigury 101, 01-089 Warsaw (Poland)

GUY J. COLLIN

Département des Sciences Fondamentales, Université du Québec à Chicoutimi, Chicoutimi, Quebec G7H 2B1 (Canada)

(Received December 8, 1982; in revised form April 28, 1983)

Summary

The main aim of this work is to determine the appropriate pressure range for the study of the isomerization processes involved in the vacuum UV photolysis of alkenes. We used the Rice-Ramsperger-Kassel-Marcus theory and weak collision models with an average transferred energy of 10, 5 or 1 kcal mol⁻¹. The results indicate that C₅ and C₆ alkenes are suitable molecules for this investigation at pressures above 1 atm, and that smaller alkenes have too short a lifetime to be stabilized in collisions. The same trends are observed in calculations involving alkyne molecules.

1. Introduction

The isomerization of alkenes by photosensitization using the 254 nm mercury line has been known since the late 1950s [1]. The hydrogen shift results in double-bond migration and cyclization leading to the formation of cyclopropane and cyclobutane rings [1 - 5]. *Cis-trans* isomerization and formation of 1-olefins has been observed in the direct photolysis of 2-olefins at 202.6 - 206.2 nm [6]. We have recently observed isomerization in the direct photolysis of tetramethylethylene and trimethylethylene [7, 8]. It is tempting to assume that hydrogen atom migration in the electronic excited state could be one of the main channels leading to the hot excited ground state. Few isomers have been observed at irradiation wavelengths below 254 nm and this may be due to the high energy content or to the dissociation of isomers at the low pressures normally used in these experiments.

Very few studies of gaseous alkynes have been performed, except of course in the case of acetylene [9]. The photolyses of gaseous 1-butyne and 1-hexyne have been explained on the basis of rupture of the primary β (C-C) bond [10 - 12]. Intermolecular and intramolecular hydrogen abstraction by

an excited triple bond take place as a result of the liquid phase photolysis of 1- or 5-decyne and cyclononyne respectively [13].

A possible method of investigating these reactions in gaseous olefinic systems is to freeze hot molecules in collisions by applying a sufficiently high pressure. Reactions in electronically excited states are believed to be much faster than the dissociation from the ground state [5, 6]. The main aim of the present work is to calculate the pressure range required to stabilize energized molecules at various photon energies and with various quenchers.

2. Calculations

The enthalpies of formation of alkenes and radicals at zero temperature were taken from the literature [14 - 18]. The threshold energies for the relevant processes were also taken from the literature. The excitation energies of the molecules were calculated from the sum of the energy of the incident photon and the average internal thermal energies of the molecules.

In the calculation we used the step-ladder model for weak collisions and assumed that the energy transferred in the collision of the energized molecules with the parent alkene was 10 kcal mol^{-1} . The energy transfer was reduced to 5 kcal mol^{-1} and 1 kcal mol^{-1} for other polyatomic gases and permanent gases respectively [19 - 21]. The step-ladder model is not as effective as other models, such as exponential models, but it is easy to use in calculations and the errors are not significant, particularly in the high pressure region [19]. We chose 1-alkenes as good representatives of the olefins with the same molecular weight. The rate constant for $\beta(\text{C}-\text{C})$ bond rupture is higher than or similar to those of other olefins with the same number of carbon atoms, regardless of the location of the double bond [22]. For example, if 2-alkenes are produced from 1-alkenes by photolysis, or vice versa, the above argument implies that the stabilization effect would be similar for both molecules. When there is no $\beta(\text{C}-\text{C})$ bond, *e.g.* in methyl-substituted ethylenes, the rate constants for the rupture of the $\beta(\text{C}-\text{H})$ and $\alpha(\text{C}-\text{C})$ bonds is much smaller, as will be shown later. Rice-Ramsperger-Kassel-Marcus (RRKM) methods [20, 21] were used to calculate the rate constants of unimolecular dissociation. In the calculations it was assumed that the photoexcited molecule had transferred into the hot ground state with all the energy randomized over all the internal degrees of freedom. The main dissociative channel for C_4 , C_5 and C_6 alkenes is the rupture of the $\beta(\text{C}-\text{C})$ bond since it is the weakest. In propylene we have calculated that the allylic $\text{C}-\text{H}$ bond rupture and the vinylic $\text{C}-\text{C}$ bond rupture have similar rate constants [23].

The assignments of vibrational motion in the parent molecule were taken from the literature [22]. The torsional motion around the single $\text{C}-\text{C}$ bond was changed to hindered rotation with energy barriers of 700 cm^{-1} and 1000 cm^{-1} for the vinylic $\text{C}-\text{C}$ bond and for other $\text{C}-\text{C}$ bonds respectively

[24]. Loose transition states were synthesized from the allyl and the required alkyl radicals with free rotation around the breaking C—C bond. The remaining four frequencies were chosen to fit the experimental values [22]. The Arrhenius parameters calculated from the assignments were in the range $10^{16.3}$ – $10^{16.4}$. The vibration frequencies of the allyl and methyl radicals were taken from the literature [14, 15], and those of the ethyl and propyl radicals were calculated using the Rabinovitch method [25]. The frequencies of the transition states for propylene dissociation are given elsewhere [23]. The collision frequencies were calculated from the viscosity data [26] by assuming that 10 kcal mol^{-1} , 5 kcal mol^{-1} and 1 kcal mol^{-1} are transferred to the parent molecule, the SF_6 molecule and the argon atom respectively. The Beyer–Swineheart–Stein–Rabinovitch algorithm with grain size 4 cm^{-1} was used to calculate the density and sum of states [27, 28]. The Pitzer rotor approximation and the Stein–Rabinovitch corrections were used for the hindered rotations [29].

In alkyne molecules the vibrational models and pertinent Arrhenius parameters were taken from ref. 30. The Arrhenius parameters were in the range $10^{15.5}$ – 10^{16} and the energy thresholds for the $\beta(\text{C—C})$ bond ruptures were similar to or slightly higher than those for the alkenes.

3. Results and discussion

Figure 1 shows the relative dissociation yields of the 1-pentene molecule photoilluminated at 254, 185 and 147 nm *versus* the pressure for various collision partners. The pressures required for 50% stabilization of the energized molecules are reported in Table 1. The pressure range in which stabilization occurs is between 0.1 and 10 times the values shown in this table. As expected molecules with a large number of degrees of freedom are

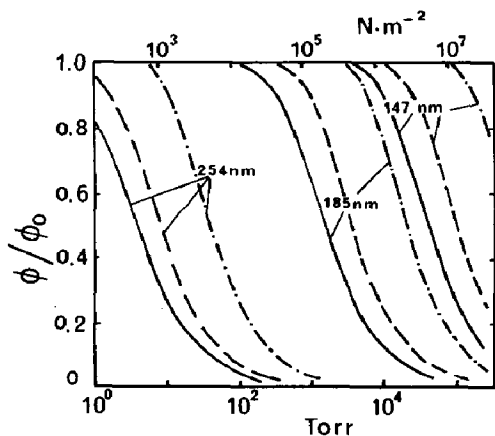


Fig. 1. The pressure dependence of the dissociation yield of the 1-pentene molecule at various wavelengths and energy steps in collision: —, 10 kcal mol^{-1} ; ---, 5 kcal mol^{-1} ; - · - ·, 1 kcal mol^{-1} .

TABLE 1

Pressure required for the 50% stabilization of energized molecules in the photolysis of 1-alkenes

λ (nm)	$\langle \Delta E \rangle$ (kcal mol ⁻¹)	Pressure (atm) of the following alkenes				
		C_3H_6	$1-C_4H_8$	$1-C_5H_{10}$	$1-C_6H_{12}$	$1-C_6D_{12}$
254	10	0.005	0.26	0.007	10^{-4}	
	5	0.1	0.5	0.009	10^{-4}	
	1	0.5	2.6	0.06	10^{-3}	
184.9	10	66	66	2	0.08	0.01
	5	132	132	4.5	0.2	0.02
	1	200	200	26	1.1	0.13
174	10	— ^a	— ^a	6.5	0.2	
	5			13	0.4	
	1			65	2.5	
163.3	10	— ^a	— ^a	13	0.65	0.09
	5			26	1.3	0.2
	1			150	7.6	1.0
147	10	— ^a	— ^a	65	2.6	0.5
	5			130	6.6	1.2
	1			200	40	7.4

^aThe calculated pressure is too high for experiments to be feasible.

stabilized at a lower pressure than those with a small number of degrees of freedom. Propylene is an exception as in this case a higher threshold energy results in a lower rate constant. Thus it is clear that an investigation of the isomerization reaction for photolysis at wavelengths below 200 nm in an experimentally feasible pressure range is only possible for C_5 and C_6 alkenes. The appropriate experimental conditions for C_3 and C_4 alkenes will probably lie in the condensed phase. Cycloisomers should be observed in the same pressure ranges. *Ad hoc* calculations performed for the ring opening reactions of methylcyclopropane and ethylcyclopropane using models reported in the literature [31] and appropriate energy values showed that the stabilization pressure is lower than that for corresponding 1-alkenes. Finally, fully deuterated alkene molecules require a lower pressure for stabilization (Table 1).

Figure 2 shows the same trend for the alkyne molecule. It appears that the stabilization of the vibrationally excited ground states of 1-hexene and 1-hexyne occurs at rather similar pressures. However, the 1-butyne excited molecule can be stabilized much more easily than the 1-butene molecule because the Arrhenius parameter for 1-butyne is smaller and the energy threshold is higher. Moreover it has been observed in very low pressure pyrolysis [30] and shock tube experiments [32] with alkyne molecules that the retroene process is much more important than the $\beta(C-C)$ bond rupture. The calculations indicate that at a high energy content similar to that

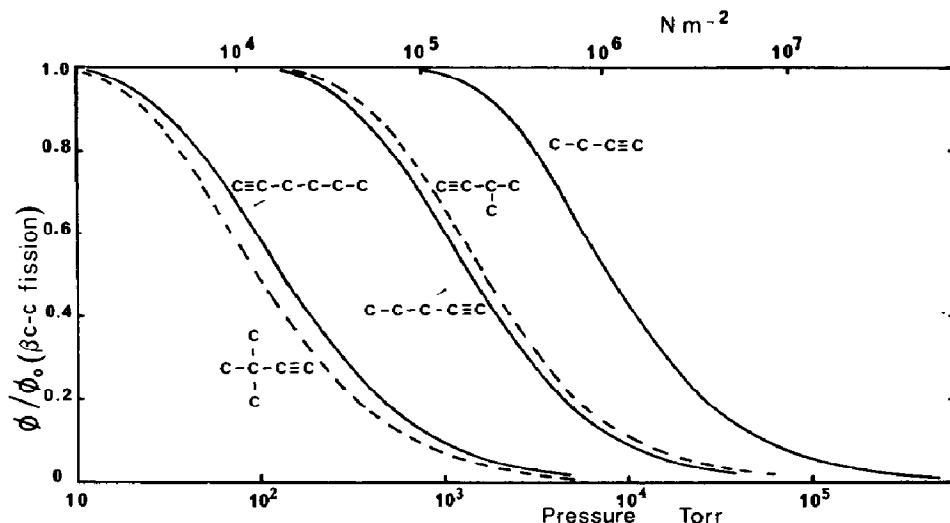


Fig. 2. The pressure dependence of the $\beta(\text{C}-\text{C})$ dissociation yield for various alkyne molecules at 184.9 nm and an energy step of 5 kcal mol⁻¹.

available in the vacuum UV region the fission process is much more likely (Fig. 3), in agreement with experiments [11, 12].

Of course, the present results are only approximate. It must be recalled that the randomization of energy which is the keystone of the RRKM theory may not be complete in these systems. If it is not complete, it results in a higher dissociation rate constant because smaller degrees of freedom are involved in randomization. For example, in 1-hexene it can be assumed that in the photoabsorption process the energy is accumulated in the vicinity of the double bond, *i.e.* in the chromophoric group. Then the transformation of the electronically excited state into the hot vibrational ground state results in the liberation of energy in part of the molecule. Thus the photon energy is distributed among all the degrees of freedom of the molecule and dissociation may occur before randomization is complete. Some experimental results show that this is probably the case for higher photon energies [33]. However, the lifetime of the electronically excited states could be long enough for part of the energy, mainly vibrational, to be dissipated in collisions before the transition to the ground state occurs. This will lead to a lower dissociation rate constant for this ground state.

Some experimental results reported in the literature agree with the data shown in Table 1. In the indirect photolysis of 1-pentene at 254 nm higher isomer yields were observed at pressures below 100 Torr [4]. In the direct photolysis of tetramethylethylene at 184.9 nm high isomer yields are observed at pressures between 1 and 400 Torr [7]. The absence of cyclocompounds in the photolysis of 1-hexene at 185 nm [12], even though the experiments were performed in the correct pressure range (5 - 100 Torr), is very interesting. Chesick [6] did not observe cyclocompounds in the direct photolysis of *cis*-2-hexene at 202.6 - 206.2 nm, but cyclization was found to be

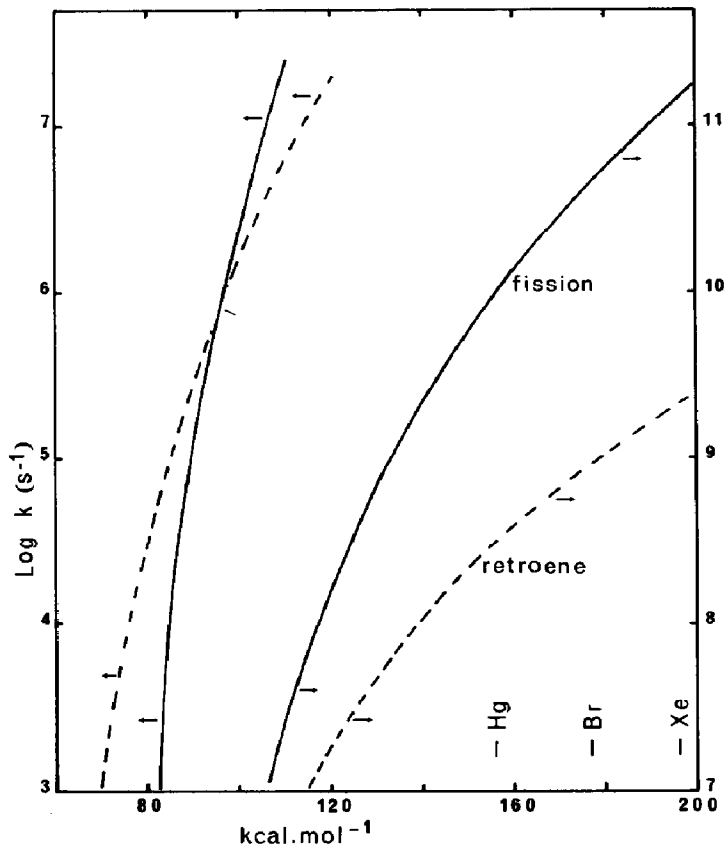


Fig. 3. The dependence of the rate constants for $\beta(\text{C}-\text{C})$ bond fission and the retroene process of 1-pentyne *us.* the energy content of the excited molecule. The corresponding energies of the 184.9 nm (mercury), 163 nm (bromine) and 147 nm (xenon) lines are shown in the lower right-hand corner of the figure.

one of the main reaction channels in the mercury-photosensitized experiments with straight chain olefins performed at 254 nm [1 - 4]. These results indicate different behaviour for the straight and branched photoexcited olefins. The latter olefins produced cyclocompounds in either direct photolysis at 184.9 nm or indirect photolysis at 254 nm. It is too early for final conclusions to be drawn, but, as has been mentioned previously, it can be assumed that cyclization is produced by Rydberg excited states [7]. Further experiments are needed to clarify this important point.

Isomerization of trimethylethylene has also been observed at low pressures but with lower yields [8]. We are planning experiments to determine whether the observed low quantum yields are the result of the low pressure used or of differences in either the molecular structure or the photophysical properties of electronically excited states.

Acknowledgments

We acknowledge the Professor exchange supported by the National Science and Engineering Research Council of Canada and the Université du Québec for free access to the computer centre. We also appreciate the kindness of Guy Simard for his assistance with the computing.

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