CHEMICAL EFFECTS OF LOW ENERGY ELECTRON IMPACT ON HYDROCARBONS IN THE GAS PHASE

III. Cyclopropane *

R. DERAI and J. DANON

Laboratoire de Physico-Chimie des Rayonnements (associé au CNRS), Université Paris-Sud, Centre d'Orsay, 91405 Orsay, France

Received 23 December 1975

The simulated radiolysis of cyclopropane with low energy electrons (3.5 to 15.0 eV) was investigated. The setup used for the irradiations has been described previously. Appearance curves of the various products formed under electron impact were determined. The features observed on these curves yield various indications.

(1) Some products arise from the dissociation of excited molecules. Contributing states are the following ones: a triplet state at 7.4 eV, singlet states at 6.7 and/or 7.7 eV, at 8.55 eV, at 9.4 and/or 9.95 eV and superexcited states lying/around 10.2 eV. As in other hydrocarbons studied, the electron impact excitation cross section shows a steep increase at the ionization potential. (2) Other products result from ion fragmentation and ion-molecule reactions.

A reaction scheme was proposed to account for the chemical effects associated with excited states and the yields of excited molecules in dissociating states were derived from experimental data. The observations relative to excited molecule fragmentation are in conformity with photolysis data. Additional information on the decomposition processes of molecules excited in the triplet state at 7.4 eV, in the singlet states at 6.7 and/or 7.7 eV and in the superexcited states were obtained.

Owing to the complexity of ionic mechanisms it was not possible to distinguish between the contributions of ionization and excitation. Only the radiation chemical yield of products, G (products), was evaluated. The values found for G (products) just above the ionization potential are close to the data obtained in conventional radiolysis which could indicate that secondary electrons having such energies play an important role in radiation chemistry.

1. Introduction

The present paper belongs to a series concerned with the study of simulated radiolysis of gaseous hydrocarbons with low energy electrons. Results obtained with neopentane and propene are published elsewhere [1,2]. As mentioned in ref. [1], such studies are particularly interesting for investigations on the role played by low energy secondary electrons in radiation chemistry. They bridge the gap between conventional radiolysis studies and those based on the direct determination of transient species formed under electron impact. The case of cyclopropane, a cyclic hydrocarbon, isomeric of propene, is considered here.

This compound presents the following characteris-

* This work is a part of the Thèse de Doctorat d'Etat of R. Derai.

tics. As indicated by fig. 1 which compares optical absorption [3] and electron impact threshold excitation [4] spectra cyclopropane has three triplet states at 7.4, 9.0 and 9.8 eV (see ref. [3]) and four singlet states, a valence state at 8.55 eV [6] and three Rydberg states at 7.7, 9.4 and 9.95 eV [7]. A weak absorption band relative to a symmetry forbidden transition evidenced at 6.7 eV by Wagner and Duncan [8] does not appear on the optical absorption spectrum presented in fig. 1. This spectrum includes however a strong absorption band with a maximum at 10.2 eV which corresponds to superexcited states [6]. The ionization potential of cyclopropane lies at this energy [9]. Fragmentation is known to lead to various ions: allyl, allene, vinyl, allenyl and acetylene ions appear at 12.0, 12.4, 13.6, 14.4 and 14.6 eV respectively [9]. All these fragment ions undergo rapid reactions with cyclopropane molecules [10-17]. Data on photolysis with





Fig. 1. Comparison between excitation spectra: (a) photon impact [3], (b) electron impact [4].

8.4, 10.0 and 11.6-11.8 eV photons [18, 19] and on radiolysis [20, 21] of this compound are also available.

2. Experimental

337

The setup described in ref. [33a] was used with however slight modifications (see ref. [1] for details). Its principle is recalled here. A flow system was adopted in order to limit secondary effects on the products formed. This system involves three chambers, I, II and III, separated by two holes of small conductance with a differential pumping between two of them, I and II. The electrons are produced by a tungsten filament located in the source chamber I which is maintained at a low pressure by a high speed pumping. The electron optics are such that the electrons are directed through the central compartment II, reach the derived energy at the entrance of the reaction chamber III and undergo collisions with the gas within an equipotential volume, at a constant pressure $P_{\rm HI}$, in this last chamber. The gas sample is introduced at a constant flow rate in the reaction chamber and is removed through the central compartment by a second pump. This compartment allows one to obtain a high pressure gradient between the electron source and the reaction zone and permits a satisfactory electron flow. The electron beam is confined by a 300 G magnetic field. The electron optics include the possibility of determining before each irradiation the energy definition of the incident electron beam by the retarding potential method.

The irradiations of flowing cyclopropane (35 cm³ s⁻¹) were performed at 1×10^{-2} torr with electrons having energies, E_0 , between 3.5 and 15.0 eV. Electron energy definition was ± 0.6 eV. Products up to C_5 compounds were analyzed by gas chromatography. The detection limit was 10^{-4} molecules of product formed per incident electron. The analytical conditions were those indicated in ref. [1].

Cyclopropane from Matheson Co., Inc., which contained propene as the most important impurity (0.29%) was used.

3. Results

3.1. Nature of the products

The products observed include compounds up to C_5 . Some products (allene, ethylene, hydrogen, methane, acetylene and 1-butene) are formed from 6.0 eV. Others (cyclopropene, propyne and ethane) appear at 8.0 eV. Propane and small quantities of various C_4 and C_5 compounds [22] are observed only above 10.0 eV. Low energy electron impact on cyclopropane leads also to propene. Analysis of this compound was possible above 10.8 eV only. It cannot be excluded that it is formed below this energy. Small yields ($< 10^{-2}$ molecules per incident electron) of this compound cannot be detected easily since, as indicated above, it is an important impurity of cyclopropene.

3.2. Carbon-hydrogen balance

The H/C ratio is always slightly higher than 2, the expected value. This indicates a lack in products characterized by an H/C ratio smaller than 2. Among nonidentified products, diallyl (C_6H_{10}) could be an important one. The yields of this compound, which satisfy the carbon-hydrogen balance represent less than R. Derai, J. Danon/Low energy electron impact on hydrocarbons. III

Table 1

Yields of d	lially and 1	-butene :	at various	electron e	nergics.
Yields are	expressed a	is 10 ⁻² e	vents per	incident el	ectron

Product	Yield	Yields							
	7.0 eV	8.0 eV	8.5 eV	9.0 eV	9.5. eV	10.0 eV	10.5 eV		
C ₆ H ₁₀ 1-C ₄ H ₈	0.08 0.18	0 0	0.04 0.06	0.12 0.14	0.71 0.20	1.16 0.30	2.08 0.48		

10% of the yields of all the observed products. They are compared to the yields of 1-butene in table 1.

3.3. Appearance curves

Product appearance curves or product yields ([X]) versus electron energy (E_0) curves are presented in figs. 2 to 8. (Product yields are expressed in number of molecules formed per incident electron.) Omitted curves relative to C₄ and C₅ compounds are similar to



Fig. 2. Appearance curve for allene.





333





Fig. 4. Appearance curve for (a) methane and (b) acetylene.

that of propane. Distinct energy domains can be noted from the breaks observed on these curves:

D _i :	$6.0 \text{ eV} < E_0 < 8.0 \text{ eV}$
D ₂ :	$8.0 \mathrm{eV} < E_0 < 9.0 \mathrm{eV}$
D3:	9.0 eV $< E_0 < 10.0$ eV
D ₄ :	$10.0 \text{ eV} < E_0 < 12.5 \text{ eV}$
D5:	12.5 eV $< E_0 <$ 15.0 eV.

Below 10.0 eV, i.e., in the excitation range, allene, ethylene, hydrogen, methane, acetylene and 1-butene (figs. 2 to 5) appear at 6.0, 8.0 and 9.0 eV; ethane, propyne, and cyclopropene (figs. 6 and 7) at 8.0 and 9.0 eV only. Appearance curves are linear in domains D_2 and D_3 . In domain D_1 , three different kinds of appearance curves are noted: one curve is linear (allene in fig. 2) others are resonant in shape with a maximum around 7.0 eV and zero yields at 8.0 eV (methane, acetylene and 1-butene in figs. 4 and 5).











Others again correspond to the superposition of the two previous kinds (ethylene and hydrogen in fig. 3). Dotted lines on these latter curves allow distinction between the linear and resonant components of the yields (see table 2).

Above 10.0 eV, i.e., in the *ionization range*, all the products formed in the excitation range, *except*





1-butene, exhibit at the ionization threshold (10.0-11.0 eV) a steep increase in yields. These products can be classified in two groups A and B according to the behaviour of their yields above this energy. Yields either decrease (group A: allene and cyclopropene) or increase (group B: ethylene, hydrogen, methane, acetylene, ethane and propyne). Products such as propane, propene, and C₄ and C₅ compounds (fig. 8) which appear at 10.0 eV and 1-butene behave differently. Their yields increase gradually with electron energy. They belong to group C. A break is noted at 12.5 eV in the appearance curves of two products of this group: propene and 1-butene. As in the simulated radiolysis study of neopentane [1] where similar features were observed and analyzed thoroughly, the appearance curves in group B can be visualized as the superposition of those characteristic of groups A and C.



Fig. 8. Appearance curve for (a) propane and (b) propene (dotted line allows the evaluation of $[C_3H_6]_8$ in domain D_2 and D_3).

Table 2

Distinction between linear and resonant components of the yields in domain D_1 at 7.0 eV. Yields are expressed as 10^{-2} events per incident electron

Product	Yields at 7.0 eV					
	Linear component (L)	Resonant component (R)				
Allene	0.079	0				
Ethylene	0.128	0.089				
Hydrogen	0.079	0.178				
Methane	0	0.059				
Acetylene	0.	0.158				
1-Butene	0	0.178				

4. Discussion

336

4.1. Filiations of the observed products with respect to the excited and ionized states of cyclopropane

Table 3 compares the appearance potentials of the various observed products with the energies of the ex-

cited and ionized states of cyclopropane. Correlations between the products which characterize each domain and these states are deduced from this comparison.

4.1.1. Excitation range

A tentative assignment of the states involved in product formation is the following. In domain D_1 ,

Table 3

Comparison between product appearance potentials (AP) and literature data

· ·	Spectroscopic spectrometric	: [3,8] and mass data [9]	Present results	
·· .	Excited state Ion	E (eV) AP (eV)	Characteristic products	AP (eV) domain
· ·	C ₃ H ⁺ ₃	14.4		
• _	$C_2H_3^+$	13.6	propene, 1-butene	D5
	C ₃ H ⁺	12.4	(-12.5
	C3H ⁺ 5	12.0	C ₄ and C ₅ compounds, propane propene, 1-butene,	
			ethylene *, hydrogen * methane *, acetylene *, ethane * propyne *	D4
	SE C3H6 (IP)	10.2	allene *, cyclopropene *	
•	S ₅	9.95	(-10.0
	T3	9.8	∫ allene, propyne	
	S ₄	9.4	ethylene, hydrogen methane, acetylenc, ethane	D ₃
•	T ₂	9.0	· <u>- · · · · · · · · · · · · · · · · · ·</u>	- 9.0
	S3	8.55	allene, propyne, cyclopropene ethylene, hydrogen methane, acetylene, 1-butene, ethane	D ₂
				- 8.0
	S ₂ T ₁	7.7 7.4	(methane [‡] , acetylene [‡] 1-butene [‡]	•
	S ₁	6.7	{ ethylene [†] [‡] , hydrogen [†] [‡]	Dį
8 . 4 . <u>1</u>	(ET)	6.0	(unono	- 6.0

S: singlet state; T: triplet state; SE: superexcited state; IP: ionization potential; ET: excitation threshold; \ddagger : yields exhibit a maximum; \ddagger : yields increase linearly with electron energy; \ddagger : yields increase steeply at the ionization potential.

products whose yields increase linearly with electron energy (allene) are ascribed to the singlet states at 6.7and/or 7.7 eV reached by allowed transitions^{*} whereas products whose yields exhibit a maximum around 7.0 eV and become zero at 8.0 eV (methane, acetylene, and 1-butene) are due to the triplet state at 7.4 eV resulting from a spin-forbidden transition. These singlet and triplet states are responsible for the formation of ethylene and hydrogen, as shown by the composite character of their appearance curves (see Results and table 2).

The products characteristic of domains D_2 and D_3 (methane, acetylene, 1-butene, ethylene, hydrogen, allene, propyne, cyclopropene and ethane) are ascribed to singlet states. Allowed transitions to such states would account for the linear shape of appearance curves. The singlet state at 8.55 eV is involved in domain D_2 , the singlet states at 9.4 and/or 9.95 eV in domain D_3 .

The triplet states at 9.0 and 9.8 eV seem to have a negligible contribution.

4.1.2. Ionization range

As in other hydrocarbons studied, neopentane [1], propene [2], methane [33b], a striking feature is observed at the ionization threshold: the yields of the products observed in the excitation range increase steeply as soon as the ionization potential is reached. However, in the present case, not all products present this sharp increase. 1-Butene exhibits a particular behaviour: its yield increases gradually above 10.0 eV. This exception rules out the possibility of an experimental artifact namely a steep variation of deposited electron energy. This argues also against the possibility of a steep variation of the fragmentation probability of excited molecules when their excitation energy reaches the ionization potential. As demonstrated in the paper relative to neopentane [1], the feature observed at the ionization threshold where ionization is negligible is correlated with superexcitation. The conclusion that electron impact produces superexcited molecules with a much higher cross section than excited molecules applies to cyclopropane too.

Above the ionization threshold, contribution from ionization must be considered. It has appeared impos-

sible to establish the detailed filiations of the observed products with respect to neutral and ionic precursors in domains D_4 and D_5 . The reaction scheme is too complex for such an analysis to be made. As mentioned above, various ions are formed between 10.0 and 15.0 eV and their reactions are numerous [9–17]. Only one correlation appears clearly: the break observed around 12.5 eV on the appearance curves of propene and 1-butene corresponds well to the appearance potentials of allyl and/or allene ions.

However, gross filiations can be established from the appearance curves as suggested by observations made in neopentane study [1].

(1) Products of group C (1-butene, propane, C_4 and C_5 compounds) are due uniquely to ions. Their yields increase gradually with electron energy as the ionization cross section does.

(2) Superexcited molecules, formed at least partly by a resonant process, are main precursors of products in group A (allene and cyclopropene). These products have the same typical appearance curve as 2,2-dimethylbutane formed in the simulated radiolysis of neopentane which has been demonstrated to be representative of the production of such precursors (see ref. [1]).

(3) Products of group B (methane, acetylene, ethylene, hydrogen, propyne and ethane) result from both neutral and ionic precursors in agreement with the analysis proposed to explain the shape of their appearance curves (see Results).

4.2. Chemical effects associated with excitation

4.2.1. Reaction scheme

The reaction scheme proposed to explain the observations in the excitation range and just above the ionization potential when ionic contribution is negligible is presented in fig. 9.

Primary processes – As proposed in photolysis studies [18,19], the first step involves ring rupture with formation of trimethylene radicals which either dissociate directly according to processes (III), (IV) and (V) (mechanism Δ) or isomerize to propene prior to dissociation according to processes (I) to (VI) (mechanism D). Processes (III), (IV) and (V) are common to both mechanisms.

Secondary reactions – The free radicals formed in primary processes undergo reactions (1) to (5) which occur either on the walls or in the gas phase. Only reaction (5) needs walls for the recombination product

^{*} The transition at 6.7 eV which is symmetry forbidden is likely to be allowed in the case of low-energy electron impact.

Primary pro	Cesses	
cC3H6, cC3	$H_6^{**} \rightarrow CH_2 - CH_2 - CH_2^* \rightarrow C$	$_{3}H_{6}^{*} \rightarrow dissociation$
	4	(mechanism D
	dissociation (mechanism A)	
•••	(
oC - 11≢ C	Mechanism D	
C.316 01 CC	$3\pi_6 \rightarrow C_3H_5 + H$	(D)
	$\rightarrow CH_3 + C_2H_3$	(11)
	\rightarrow CH ₂ + C ₂ H ₄	(III)
	$\rightarrow C_3H_4 + H_2$	(IV)
	$\rightarrow C_3H_4 + 2H$	(V)
	\rightarrow C ₂ H ₂ + CH ₃ + H	(VI)
	Mechanism Δ	
cC ₃ H [*] ₆ or cC	$_{3}H_{6}^{**} \rightarrow CH_{2} + C_{2}H_{4}$	(111)
	\rightarrow C ₃ H ₄ + H ₂	(IV)
	$-C_3H_4 + 2H$	(V)
Secondary re	eactions	
$CH_3 + C_2H_3$	$H_3 \rightarrow CH_4 + C_2H_2$	(1)
$C_2H_3 + C_2H_3$	$H_3 \rightarrow C_2 H_2 + C_2 H_4$	(2)
$CH_3 + C_3H_3$	5 → C ₄ H ₈	(3)
C3H5 + C3H	$H_5 \rightarrow C_6 H_{10}$	(4)
CH3 + CH3	[₩] C ₂ H ₆	(5)
CH ₃ + H	' ₩ _{CH4}	(6)
$C_2H_3 + H$	[₩] _→ C ₂ H ₄	(7)
C3H5 + H	W C3H6	(8)
H+H	$\frac{W}{H_2}$	(9)

Fig. 9. Reaction scheme. $cC_3H_6^*$: excited molecules; $cC_3H_6^{**}$: superexcited molecules.

to be stabilized. Disproportionation is the most probable fate of vinyl radicals [23,24]. Combination is favored in the case of allyl radicals [25,26].

Reactions involving hydrogen atoms were considered to occur only on the walls [reactions (6) to (9)]. Gas-phase reactions (6') to (9') where the recombination product is not stabilized and dissociates into fragments similar or not to those involved in their formation

CH₃ + H → (CH₄) → CH₃ + H , (6') C₂H₃ + H → (C₂H₄) → C₂H₂ + H₂ , (7') C₃H₅ + H → (C₃H₆) → C₃H₅ + H or C₂H₃+CH₃,(8')

$$H+H \rightarrow (H_2) \rightarrow H+H$$

(9')

were assumed to have a negligible probability since hydrogen atoms diffuse 30 times more rapidly than large radicals [4] and hence their steady concentration in the gas phase is low. This assumption is well supported experimentally. It will be seen in the appendix that omission of reaction (7') receives a good experimental justification.

Reactions of methylene radicals on cyclopropane were also omitted. Products expected from these reactions (methylcyclopropane, cis- and trans-2-butene [27-32]) are not observed. The same argumentation applies to other reactions omitted: reactions of methylene radicals with hydrogen atoms and other free radicals; reactions between allyl and vinyl radicals (see appendix). Gas-phase or wall-catalyzed reactions of hydrogen atoms with cyclopropane molecules were neglected too. Such reactions would lead to cyclopropyl radicals which are not observed.

Absence of methylene radicals reactions is noteworthy. A similar situation is found in simulated radiolysis of propene [2]. The suggestion made in this case is retained here: methylene radicals are probably formed in ground triplet state and undergo a wallcatalyzed chain reaction with cyclopropane leading to a non-analyzed high molecular weight compound $(CH_2)_n$.

4.2.2. Yields of excited molecules involved in product formation

The yields of excited molecules in dissociating states (total yield N_E and individual yields N_I , N_{II} , N_{III} , N_{IV+V} and N_{VI}) were evaluated from experimental data, using the relations presented in the appendix. The corresponding results are summarized in table 4. Some of these yields (N_E , N_I , N_{III} and N_{IV+V}) are plotted versus electron energy in fig. 10. Table 5 shows the relative importance of the various decomposition processes considered.

The yields of excited molecules which dissociate according to processes (IV) and (V) cannot be evaluated separately.

Only limits were obtained for process (I). It was not indeed possible to determine experimentally the yield of propene resulting from reaction (8) below 10.8 eV. A similar situation is found in domains D_2 and D_2 for processes (II) and (VI) which lead to the

.338

R. Derai, J. Danon/Low energy electron impact on hydrocarbons. III

Table 4

Yields of excited molecules at different electron energies (6.0 eV $< E_0 < 10.5$ eV). Yields are expressed as 10^{-2} events per incident electron. Subscripts specify the decomposition process involved

Process	Yields				·			*
	7.0 eV	·	8.0 eV	8.5 eV	9.0 eV	9.5 eV	10.0 eV	10.5 eV
	D	4						•
NI	0.36-0.54	0	0	0.14-0.34	0.38-0.78	1.62-2.22	2.26-3.06	5.34
NII	0.26	0	0	0.16-0.07	0.34-0.16	0.65-0.28	1.04-0.35	1.98-0
NIII	0	0.13	0.26	0.81	1.24	2.63	4.55	18.60
N _{IV+V}	0	0.08	0.12	0.48	0.78	2.03	3.32	14.98
NVI	0	0	0	0-0.09	0-0.18	0-0.37	0-0.69	1.98-3.96
NE	0.62-0.80	0.21	0.38	1.59-1.79	2.74-3.14	6.93-7.53	11.17-11.97	42.88
		+	+	ţ	<u> </u>	ţ	ł	¥
		E	\mathbf{D}_1		$\widetilde{D_2}$		D ₃	D4
	50 - 40 - 30 - 20 -	4.10 ²	a	ļ	C C		-16	

Fig. 10. Yields of excited molecules formed in dissociating states (mean values) and involved in decomposition processes (1), (11), (IV) plus (V) (curves a, b, c and d respectively). Abscissa of curves b, c and d are shifted lettwards by 5, 10 and 15 eV respectively.

same products.

Mechanisms D and Δ occur in the whole energy range but they are distinguished in domain D₁ only. It appears in tables 4 and 5 that cyclopropane molecules excited in the singlet states at 6.7 eV and/or 7.7 eV dissociate according to processes (III) and (IV) (mechanism Δ) whereas cyclopropane molecules excited in the triplet state at 7.4 eV dissociate according to processes (I) and (II) via isomerization to propene (mechanism D). A good agreement was found between

Process	Relative importance								
	7.0 eV		8.0 eV	8.5 eV	9.0 eV	9.5 eV	10.0 eV	10.5 eV	
-	Mechanism D	Mechanism Δ	•						
I	59-68	0	0	9-19	14-25	23-29	20-25	12	
II	41–32	0.	0	10-4	12-5	9-4	10-3	5-0	
III	0	62	68	51-45	4539	38-35	4038	43	
IV + V	0	38	32	30-27	29-25	30-27	30-28	35	
VI	0	0	0	0-5	06	0-5	06	5-10	
		4	ţ	Ļ	ţ	ţ	ł	¥	
			~	<u> </u>	~	<u> </u>	~	P	

Relative importance of the decomposition processes of excited molecules between 8.0 eV and 10.5 eV. Yields are expressed as percent total decomposition

Table 6

Yields of primary free radicals at 7.0 eV. Yields are expressed as 10^{-2} events per incident electron

Relation (primary free radical)	Yield at 7.0 eV			
(d') (vinyl)	0.26			
(e') (methyl)	0.24			

the yields of vinyl and methyl radicals, resulting from process (II) (see table 6). The N_{II}/N_I ratio associated with this triplet state is between 41/59 and 32/68. This observation is discussed in a separate paper [34] on the chemical effects associated with propene triplet states. Cyclopropane molecules excited in the triplet state at 7.4 eV are expected indeed to isomerize in propene molecules excited in the triplet states at 4.4, ~6.1 and 7.7 eV.

Observations in domain D_2 (columns 5 and 6 of tables 4 and 5) show that cyclopropane molecules excited in the singlet valence state at 8.55 eV dissociate mainly according to processes (III) and (IV)+(V). This agrees well with photolysis studies using 8.4 eV photons [18,19] where ethylene and C_3H_4 compounds are the most abundant products. A contrast with observations relative to the corresponding triplet state at 7.4 eV is noted which could indicate that intersystem crossing to this state is of small importance.

In domain D_3 (columns 7 and 8 of tables 4 and 5) processes (1), (111) and (1V) + (V) are the most important decomposition channels. These processes consequently are characteristic of dissociation of cyclopropane molecules excited in the higher singlet Rydberg states at 9.4 and 9.95 eV. Process (I) and hence mechanism D are relatively more important for these states than for the singlet valence state at 8.55 eV.

It appears on column 9 of table 4 and on fig. 10 that the yields of excited molecules which dissociate according to processes (III), (IV) + (V) and (VI) increase steeply at the ionization threshold in domain D_4 whereas this sharp increase is absent for process (I) and a similar situation seems to apply to process (II). Superexcited molecules which have been shown to be responsible for the sharp discontinuity in product yields occurring at the ionization threshold dissociate consequently according to processes (III), (IV) + (V)and (VI). Processes (I) and (II) are negligible decomposition channels of such molecules. This observation parallels that relative to the negligible contribution of superexcited molecules to 1-butene formation. Moreover, the fact that process (VI) is relatively more important at the ionization threshold than in domain D_3 (see table 5) indicates that the fragmentation degree is higher in superexcited molecules than in excited molecules.

4.3. Chemical effects above the ionization potential

As mentioned already it is not possible to perform a detailed analysis of chemical effects occurring above the ionization potential owing to the large complexity of ionic mechanism. The only tractable data concern the total yield of (nonpolymeric) products from which

340

Table 5.

the radiation chemical yield of products, G(products), can be calculated assuming that all the electron energy is deposited in the medium [36]. The values found for G(products) between 11 and 13 eV increase from 9.7 to 12.5; they compare well with that obtained in conventional radiolysis studies, i.e., 9.2 [21]. Secondary electrons having energies just above the ionization potential thus appear to play an important role in radiation chemistry. A similar conclusion arose from other simulated radiolysis studies (see ref. [1] for instance).

5. Conclusions

The simulated radiolysis of cyclopropane with low energy electrons (3.5 eV to 15.0 eV) brought a large bulk of experimental data on the electron impact dissociation of this compound.

As in other similar studies (see ref. [1] for instance) some data were deduced directly from striking features observed on appearance curves. Others required a detailed analysis of the chemical reactions of the reactive species formed under electron impact. This analysis was sometimes complex and not unambiguous but appeared also selfconsistent as shown by some a posteriori checks.

The most important statements from the present work are the following ones.

(1) Some products result from the dissociation of excited molecules. All the excited states of cyclo-propane are dissociative: (i) the triplet state at 7.4 eV;
(ii) the singlet states at 6.7 and/or 7.7 eV, at 8.5 eV and at 9.4 and/or 9.95 eV; (iii) the superexcited states around 10.2 eV.

(2) Other products are associated with ionization. However, owing to the complexity of ionic mechanisms, it was not possible to derive detailed correlations between ionized states and products.

(3) Observations relative to the fragmentation processes of excited molecules agree with photolysis data: trimethylene radicals resulting from ring rupture either dissociate directly (mechanism Δ) or isomerize to propene prior to dissociation (mechanism D). Additional information was obtained concerning the triplet state at 7.4 eV, the singlet states at 6.7 and/or 7.7 eV and the superexcited states. Mechanism D prevails in the first case, mechanism Δ applies to the second case. Both mechanisms are involved in the dissociation of superexcited molecules. It is found moreover that the fragmentation degree is higher in superexcited molecules than in excited molecules.

(4) Information concerning primary processes also was obtained. Some of them are peculiar to cyclopropane: intersystem crossing from the singlet state at 8.55 eV to its parent triplet at 7.4 eV is of negligible importance.

Others corroborate data obtained in simulated radiolysis of neopentane [1] and hence support the same conclusions: (i) the electron impact excitation cross section shows a steep increase at the ionization potential; (ii) superexcitation could be at least partly a resonant process; (iii) secondary electrons having energies just above the ionization potential appear to play an important role in radiation chemistry.

Appendix: Evaluation of the yields of excited molecules in dissociating states (6.0 eV $\leq E_0 \leq 10.5$ eV) [35]

The following general relations can be derived from the reaction scheme presented in fig. 9.

$$N_{\rm E} = N_{\rm I \to VI}, \qquad (a)$$

$$N_{I} = [C_{3}H_{5}] = [1 - C_{4}H_{8}] + 2[C_{6}H_{10}] + [C_{3}H_{6}]_{8}(b)$$

$$N_{r} = [H_{1}] = 2([H_{2}] - [C_{2}H_{4}]) + [CH_{4}] - [C_{2}H_{2}]$$

+(
$$[C_2H_2]_2$$
 + $[C_2H_4]_7$) + $[C_3H_6]_8$, (c)

$$N_{\rm H} = [C_2H_3] = ([C_2H_2]_1 + [C_2H_2]_2) + ([C_2H_2]_2 + [C_2H_4]_7), \qquad (d)$$

$$N_{11} = [CH_3]_{11} = [CH_4] + [1 - C_4H_8] + 2[C_2H_6]$$

$$- [C_2H_2] + ([C_2H_2]_1 + [C_2H_2]_2), \qquad (e)$$

$$N_{\rm III} = [C_2H_4] - ([C_2H_2]_2 + [C_2H_4]_7), \qquad (f)$$

$$N_{\rm IV+V} = [C_3 H_4]$$
, (g)

$$N_{V1} = [C_2H_2] - ([C_2H_2]_1 + [C_2H_2]_2),$$
 (h)

$$N_{\rm E} = 2[{\rm H}_2] - [{\rm C}_3{\rm H}_4] + [{\rm C}{\rm H}_4] + [{\rm C}_2{\rm H}_4] + ([{\rm C}_2{\rm H}_2]_2 + [{\rm C}_2{\rm H}_4]_7) + [{\rm C}_3{\rm H}_6]_8.$$
(i)

These relations involve unknown terms such as $([C_2H_2]_1 + [C_2H_2]_2)$ and $([C_2H_2]_2 + [C_2H_4]_7)$ and terms such as $[C_3H_6]_8$ and $[C_6H_{10}]$ whose determination was not performed as already mentioned

(analysis of propene was possible only above 10.8 eV). As will be seen later ($[C_2H_2]_2 + [C_2H_4]_7$) can be calculated and reasonable limits can be proposed for ($[C_2H_2]_1 + [C_2H_2]_2$) and $[C_3H_6]_8$. The values for $[C_6H_{10}]$ which satisfy the carbon-hydrogen balance (see table 1) lead always to a very good agreement between relations (b) and (c).

A.1. Evaluation of $([C_2H_2]_2 + [C_2H_4]_7)$ and $([C_2H_2]_1 + [C_2H_2]_2)$

Domain D_1 – Products due to the singlet states at 6.7 and/or 7.7 eV (linear component in table 2) are assumed to result from primary processes (III) and (IV) only, therefore via direct dissociation of trimethylene radicals (mechanism Δ). Products due to the triplet state at 7.4 eV (resonant component in table 2 which vanishes at 8.0 eV are assumed to be formed by processes I and II followed by secondary reactions (1) to (4), (8) and (9) therefore via isomerization of trimethylene radicals into propene and subsequent dissociation (mechanism D).

In such conditions, the linear and resonant components of ethylene and hydrogen yields can be written as follows:

 $[H_2]_9 = [H_2]_R, \qquad [H_2]_{IV} = [H_2]_L, \\ [C_2H_4]_2 = [C_2H_4]_R, \qquad [C_2H_4]_{III} = [C_2H_4]_L.$

Relations (c) to (i) become then

Results obtained with relations (d'), (e') are presented in table 6. This table shows that a good agreement is reached between these two relations. According to table 2, relations (f')_R, (h')_R and (g')_L are well satisfied. These observations together with the fact that the only products observed at 8.0 eV are ethylene and hydrogen give some support not only to the method used to distinguish between the two linear and resonant components in the appearance curve of this product but also to the proposed reaction scheme. In particular, omission of reaction (7') and of interaction between vinyl and allyl radicals is entirely justified.

Domains D_2 and D_3 – The whole reaction scheme involving indistinguishable mechanisms D and Δ is considered here.

The unknown term $([C_2H_2]_2 + [C_2H_4]_7)$ is deduced from the comparison between relations (d) and (e) which leads to relation (k):

$$[CH_4] + [1-C_4H_8] + 2[C_2H_6] - [C_2H_2]$$

= ([C_2H_2]_2 + [C_2H_4]_7). (k)

Relations (b) to (l) become then

÷

$$N_{I} = 2([H_{2}] - [C_{3}H_{4}]) + 2[CH_{4}] - 2[C_{2}H_{2}] + [1-C_{4}H_{8}] + 2[C_{2}H_{6}] + [C_{3}H_{6}]_{8}, \quad (c')$$

$$N_{\rm H} \approx [\rm CH_4] + [1-\rm C_4H_8] + 2[\rm C_2H_6] - [\rm C_2H_2] + ([\rm C_2H_2]_1 + [\rm C_2H_2]_2), \qquad (e'')$$

$$N_{\rm III} \approx [C_2H_4] - ([CH_4] + [1 - C_4H_8] + 2[C_2H_6])$$

$$[C_2H_2],$$
 (f")

$$N_{\rm IV+V} = [C_3H_4]$$
, (g")

$$N_{\rm VI} = [C_2H_2] - ([C_2H_2]_1 + [C_2H_2]_2), \qquad (h'')$$

$$\mathcal{N}_{E} = 2[H_{2}] - [C_{3}H_{4}] + 2[CH_{4}] - [C_{2}H_{2}]$$
(i")
+ [1-C_{4}H_{8}] + 2[C_{2}H_{6}] + [C_{2}H_{4}] + [C_{3}H_{6}]_{8}.

Limits can be found to $N_{\rm H}$ and $N_{\rm VI}$ since

$$0 \leq ([C_2H_2]_1 + [C_2H_2]_2) \leq [C_2H_2], \qquad (1'')$$

$$[CH_4] + [1-C_4H_8] + 2[C_2H_6] \ge N_{II} \ge [CH_4]$$

+
$$[1-C_4H_8] + 2[C_2H_6] - [C_2H_2],$$
 (m")

$$0 \le N_{V1} \le [C_2 H_2]$$
. (n")

Domain D_4 at the ionization threshold (10.5 eV) - As in domains D_2 and D_3 , both mechanisms D and Δ are involved in the primary stage and cannot be distinguished. Secondary reactions such as (2) and (7) are negligible. The term ($[C_2H_2]_2 + [C_2H_4]_7$) given by relation (k) appears indeed to be zero.

342

Relations (b) to (i) are considerably simplified:

$$N_{I} = 2([H_{2}] - [C_{3}H_{4}]) + [CH_{4}]$$

$$- [C_{2}H_{2}] + [C_{3}H_{6}]_{8}, \qquad (c''')$$

$$N_{II} = [C_{2}H_{2}]_{1}, \qquad (d''')$$

$$N_{IV+V} = [C_{3}H_{4}], \qquad (f''')$$

$$N_{V1} = [C_{2}H_{2}] - [C_{2}H_{2}]_{1}, \qquad (h''')$$

$$N_{E} = 2[H_{2}] - [C_{3}H_{4}] + [CH_{4}]$$

$$+ [C_{2}H_{4}] + [C_{3}H_{6}]_{8}. \qquad (i''')$$

Limits to N_{11} and N_{V1} are deduced from relation

Limits to N_{II} and N_{VI} are deduced from relation (I''')

$$0 \le [C_2 H_2]_1 \le [CH_4]$$
, (1")

 $[CH_4] \ge N_{II} \ge 0, \qquad (m''')$

$$[C_2H_2] - [CH_4] \le N_{VI} \le [C_2H_2] . \qquad (n''')$$

A.2. Evaluation of $[C_3H_6]_8$

The evaluation of the term $[C_3H_6]_8$ which appears in relations (b'), (b") and (b"") for N_I and in relations (i'), (i") and (i"") for N_E is based on the following approximation.

Domain D_1 – All hydrogen atoms formed in process (I) react on the walls which is not the case for corresponding allyl radicals. Relation (o') holds between the yields of propene and hydrogen formed in reactions (8) and (9)

$$0 \le [C_3 H_6]_8 \le [H_2]_R$$
, (o')

which allows evaluation of limits to $N_{\rm I}$ and $N_{\rm E}$:

$$2[H_2]_R \leq N_I \leq 3[H_2]_R$$
, (p')

$$2[H_2] - [C_3H_4] + [C_2H_2] + [C_2H_4] \le N_E \le 2[H_2] - [C_3H_4] + [C_2H_2] + [C_2H_4] + [H_2]_R.$$
(q')

Domain D_2 , D_3 , and D_4 at the ionization threshold – Reactions (8) and (9) are not the only wallreactions of hydrogen atoms. The approximation used in domain D_1 does not apply here. Another approximation is proposed. A hypothetical appearance curve is considered for propene resulting from reaction (8) (see dotted line in fig. 8). $[C_3H_6]_8$ is lower than the hypothetical yield read on this dotted line.

References

- [1] R. Derai, P. Nectoux and J. Danon, J. Phys. Chem., in press.
- [2] R. Derai and J. Danon, J. Phys. Chem., submitted for publication.
- [3] J.W. Raymonda and W.T. Simpson, J. Chem. Phys. 47 (1967) 430.
- [4] R. Derai, Thesis, Univ. Paris-Sud, Orsay (1975). This spectrum shows an improved resolution over Brongersma's [5].
- [5] H.H. Brongersma and L.J. Oosterhoff, Chem. Phys. Lett. 3 (1969) 437.
- [6] A.Y. Meyer, Theor. Chem. Acta 22 (1971) 271.
- [7] H. Basch, M.B. Robin, N.A. Kuebler, C. Bayer and D.W. Turner, J. Chem. Phys. 51 (1969) 52.
- [8] P. Wagner and A.B.F. Duncan, J. Chem. Phys. 21 (1953) 516.
- [9] R.F. Pottie, A.J. Lorquet and W.H. Hamill, J. Am. Chem. Soc. 84 (1962) 529.
- [10] A.G. Harrison and J.M.S. Tait, Can. J. Chem. 40 (1962) 1986.
- [11] F.H. Field, J. Chem. Phys. 20 (1952) 1734.
- [12] L.W. Sieck and J.H. Futrell, J. Chem. Phys. 45 (1966) 560.
- [13] V. Aquilanti, A. Galli, A. Giardini-Guidoni and G.G. Volpi, Trans. Faraday Soc. 64 (1968) 124.
- [14] A.A. Herod and A.G. Harrison, J. Phys. Chem. 73 (1969) 3189.
- [15] A.A. Herod, A.G. Harrison, R.M. O'Malley, A.J. Ferrer-Correia and K.R. Jennings, J. Phys. Chem. 74 (1970) 2720.
- [16] A.G. Harrison, G.P. Nagy, M.S. Chin and A.A. Herod, Int. J. Mass Spect. Ion. Phys. 9 (1972) 287.
- [17] L.W. Sieck and P. Ausloos, J. Res. Nat. Bur. St. 76A (1972) 253.
- [18] C.L. Currie, S.J.H. Okabe and J.R. McNesby, J. Phys. Chem. 67 (1963) 1494.
- [19] A.A. Scala and P. Ausloos, J. Chem. Phys. 49 (1968) 2282.
- [20] K. Yang, J. Phys. Chem. 65 (1961) 42.
- [21] G.V. Bünau and P. Kühnert, Ber. Bunsenges. Phys. Chem. 76 (1972) 913.
- [22] These compounds include: C₄H₆ (2-butyne and 1,2-butadiene), C₄H₈ (cis- and trans-2-butene), C₄H₁₀ (n-butane), C₅H₆ (cyclopentadiene), C₅H₈ (isoprene), C₅H₁₀ (2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene) C₅H₁₂ (n-pentane).
- [23] D.R.A. Cuff, G.R. Johnston and D. Price, J. Photochemistry 3 (1974) 107.
- [24] K.O. McFadden and C.L. Currie, J. Chem. Phys. 58 (1973) 1213.
- [25] M.J. Gibian and R.C. Corley, Chem. Rev. 73 (1973)441.
- [26] D.G.L. James and S.M. Kambanis, Trans. Faraday Soc. 65 (1969) 1350.
- [27] J.N. Butler and G.B. Kistiakowsky, J. Am. Chem. Soc. 82 (1960) 759.

- [28] J.N. Butler and G.B. Kistiakowsky, J. Am. Chem. Soc. 83 (1960) 1324.
- [29] H.M. Frey, Prog. React. Kin. 2 (1964) 131.
- [30] D.E. Thornton and A.N. Strachan, J. Phys. Chem. 71 (1967) 4583.
- [31] A.K. Dhingra and R.D. Koob, J. Phys. Chem. 74 (1970) 4490.
- [32] G.B. Kistiakowsky and B.B. Saunders, J. Phys. Chem. 77 (1973) 427.
- [33] (a) J. Danon, R. Derai and J. Milhaud, Adv. Rad. Res. Phys. Chem. I (1973) 159.
- (b) P. Nectoux, R. Derai and J. Danon, in preparation. [34] R. Derai and J. Danon, Chem. Phys. Lett., submitted
- for publication.
- [35] Subscripts refer to the reaction leading to the product considered.
- [36] The radiochemical yield or G-value is defined as the number of species produced or destroyed per 100 eV of energy absorbed by the system.