
CO₂ LASER INDUCED DECOMPOSITION OF PROPYLENE OXIDE

Marie JAKOUBKOVÁ and Josef POLA

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchbát*

Received January 18, 1990

Accepted March 19, 1990

The continuous-wave (cw) CO₂ laser induced decomposition of propylene oxide yields propanal, propanone and methyl vinyl ether as primary isomerization products. The absence of allylol and great amounts of ethene among products of ensuing fragmentation of primary products make the reaction different from conventional thermal decomposition of propylene oxide. CW CO₂ laser induced decomposition of methyl vinyl ether affords propanal as isomerization product and shows thermal interconvertibility of propylene oxide and methyl vinyl ether.

Thermal gas-phase organic chemistry shows many examples of reactions wherein heterogeneous contributions from hot reactor surface determine reaction mechanism. These steps are often very difficult to obviate and true homogeneous mechanism remains hidden from the observer. The technique of cw CO₂ laser induced reactions in the presence of energy conveying SF₆ enables¹ to run chemical reactions homogeneously and was used by us to reveal truly homogeneous mechanisms and reaction products even at high conversions (see e.g. refs^{2,3}).

The conventional thermolysis of propylene oxide^{4,5} (PEO) yields a mixture of primary products which are propanal (PAL), propanone (PNE), methyl vinyl ether (MVE) and allylol (ALL). These compounds undergo decomposition into hydrocarbons and CO. The thermolysis was assumed to take place as a homogeneous unimolecular isomerization accompanied with radical involving fragmentations of the primary products, but several findings cast doubt on truly homogeneous and solely unimolecular nature of the formation of the primary products. These are a higher total rate constant in the packed reaction vessel compared to unpacked one, an ambiguous decline of the total rate constant with decreasing pressure, different shapes of plots of percentage of the particular product against percentage of the overall reaction in the absence or presence of nitric oxide (all ref.⁵) and the sensitivity of the initial rates formation of PAL and ALL to reactor coatings⁴.

Regarding the fact that surfaces may play an active role even in gas-phase thermal reactions conducted in seasoned vessels, we undertook a study of the cw CO₂ laser photosensitized (SF₆) decomposition of PEO to reveal whether the distribution of products in this homogeneous decomposition differs from that earlier reported^{4,5} for

conventional pyrolysis. We wished to show whether surface assistance is important in promotion of the formation of some of the earlier observed primary products.

The irradiation of PEO-SF₆ mixtures affords PAL as main product together with lesser amounts of MVE and PNE. Interestingly, no ALL was observed. Possible intermediacy of this compound can be excluded on the basis of the reaction conducted to low conversion (Table I, run 1). As for the products of the secondary decompositions, ethene prevails over methane, ethane and propane, and propene along with C-4 hydrocarbons are produced in little quantities (Table I.). The ratio PAL/PNE (or MVE) in our experiments is comparable to those observed during conventional pyrolysis between 650 and 720 K (ref.⁵), but amounts of ethene in our experiments are much higher. Propene admixtures decrease both the total rate of the PEO decomposition (Fig. 1) and the amounts of fragmentation products (Runs 2 and 3 in Table I). This is similar to conventional pyrolysis and serves as an indication of radical chains during the laser induced reaction. The results indicate that the formation of ALL, which might occur via a C—O bond cleavage and the 1,4-hydrogen shift from CH₃ group to oxygen, is under conventional pyrolysis a surface assisted process.

The great amount of ethene among the products of the laser induced decomposition of PEO cannot be explained on the grounds of the known⁶ thermal, radical-chain decompositions of the primary products. PAL yields mostly ethane and carbon monoxide, while PNE affords methane, carbon monoxide and ketene, neglecting other minor products.

Thermal decomposition of MVE yields⁷ PAL that was assumed⁷ to be formed through an ionic intermediate in the rearrangement process. Such processes are known to be facilitated by surface. The laser induced decomposition of MVE,

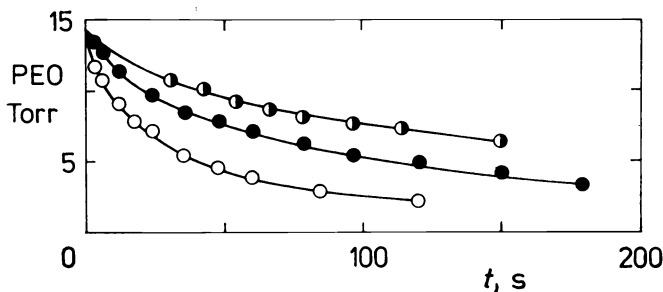


FIG. 1

The effect of propene on the rate of CO₂ laser powered decomposition of propylene oxide with PEO (2.1 kPa)-SF₆ (0.5 kPa)-propene (0-6.7 kPa)-argon mixtures at total pressure 26.6 kPa. ○ 0 kPa propene; ● 2.7 kPa propene; ● 6.7 kPa propene; *t* irradiation time

TABLE I
Representative runs with CO₂ laser induced pyrolysis of propylene oxide^a

Run	Initial mixture, kPa				Conversion %	Products ^b , wt. %									
	PEO	SF ₆	C ₃ H ₆	Ar		CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	C ₄ H ₈	MVE	PAL	PNE	
1	3.2	0.8	--	22.6	8 ^c	8.2	3.1	28.0	0.6	1.9	0.1	8.5	49.0	---	
2	2.2	0.5	--	23.9	66	8.5	6.1	26.9	4.1	3.1	0.8	2.5	36.2	11.7	
3	2.2	0.5	4.0	20.0	60	3.2	1.4	9.1	3.0	--	1.1	12.8	52.6	14.9	

^a Analysis by gas chromatography; ^b CO and ketene observed in IR spectra are not included; ^c focused beam.

TABLE II
Representative runs with laser induced pyrolysis of methyl vinyl ether^a

MVE	Initial mixture, kPa				Conversion %	Products ^b , wt. %									
	SF ₆	C ₃ H ₆	Ar	CH ₄		C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	CH ₃ CHO	PAL				
2.1	0.5	--	--	22.6	28	22.6	15.2	23.9	6.2	3.9	15.0	13.2	---		
2.1	0.5	--	--	25.3	55	25.3	10.2	16.0	3.3	2.2	20.8	22.0	---		
2.1	0.5	--	--	21.0	75	21.0	19.5	23.2	8.4	4.3	15.7	6.0	---		
2.1	0.5	4.0	--	19.9	23	19.9	5.5	28.3	2.0	3.5	22.9	17.9	---		
2.1	0.5	1.3	22.6	18.8	41	18.8	5.8	41.1	1.1	--	21.5	5.5	---		

^a Analysis by gas chromatography; ^b CO and ketene observed in IR spectra are not included.

carried out in this work under conditions comparable to those of the laser induced decomposition of PEO, gives significant quantities of ethanal and PAL together with comparable amounts of methane, ethane and ethene (Table II). It thus appears that the major reaction channel is an isomerization of MVE into PAL and fragmentation of MVE into CH_3^{\bullet} and $\text{CH}_2=\text{CH}-\text{O}^{\bullet}$ radicals. Furthermore, our data show that $\text{MVE} \rightarrow \text{PAL}$ isomerization is clearly a homogeneous process occurring without surface assistance. The fragmentation products gathered in Table II can be explained by the recombination of CH_3^{\bullet} radicals and by the abstraction of hydrogen by CH_3^{\bullet} and $\text{CH}_2=\text{CH}-\text{O}^{\bullet}$ from parent MVE or PAL to form methane and ethanal. Ethene can arise from the abstraction of hydrogen by $\text{CH}_2=\text{CH}^{\bullet}$ radical produced upon the $\text{O}-\text{CH}$ cleavage of parent MVE, or by abstraction reactions shown below.



The products of thermal decompositions of MVE, PAL and PNE show that ethene is not a dominant product of either of these reactions. It appears that ethene can be produced by decomposition of PAL. Not only Eq. (A), but also decomposition of the ethyl radicals $\text{C}_2\text{H}_5^{\bullet} \rightarrow \text{C}_2\text{H}_4 + \text{H}^{\bullet}$ can be responsible for high yields of ethene. The latter was assumed⁸ as a reason for the increasing amount of ethene with increasing temperature during the thermal decomposition of PAL.

Channels for the thermal isomerization of PEO should involve biradical stage, since the obtained⁵ Arrhenius parameters for the PEO decomposition are in line with those for unimolecular reactions taking place via biradical intermediate⁹. It may be that direct formation of PAL from PEO (involving the fission of the $\text{C}-\text{O}$ bond and 1,2-shift of the CH_3 group) demands less energy than direct formation of PNE, ALL and MVE that involve the cleavage of the $\text{C}-\text{O}$ bond and migration of hydrogen or shift of the CH_3 group from carbon to oxygen. The homogeneous nature of thermal interconvertibility of MVE and PAL proved in this work makes, however, reaction scheme more complicated, and it is clear that deeper insight into the reaction mechanism of PEO isomerization cannot be advanced without further data.

EXPERIMENTAL

Experiments were carried out in a glass tube (10 cm long, inner diameter 3.6 cm) equipped with two NaCl windows, a valve and a sleeve with rubber septum. A tunable cw CO_2 laser operated at the $P(20)$ line of the $00^{\circ}1 \rightarrow 10^{\circ}0$ transition. The constant laser output (8 W) was monitored by power meter (Physical Institute, Prague). In some experiments, laser beam was focused by a germanium lens. In a typical run, the tube was filled with pre-mixed PEO-SF₆-propene-argon mixtures and infrared spectrum was taken before and after the irradiation. The products of the decomposition were also analysed on a gas chromatograph (Chrom 3 coupled with integrator CI 100, columns packed with 5% β, β' -oxydipropionitril on Chromosorb G-NAW and with alumina deactivated by silicone oil, programmed temperature 60–120°C). Their structure was

verified on a GC-MS quadrupole spectrometer (Shimadzu model QP 1000) and their quantities assessed on the basis of the known detector sensitivity coefficients of authentic samples. MVE was prepared after the procedure¹⁰, other compounds used in this work were commercially available chemicals.

REFERENCES

1. Shaub W. M., Bauer S. H.: *Int. J. Chem. Kinet.* 7, 509 (1975).
2. Pola J.: *Tetrahedron* 45, 5065 (1989) and references therein.
3. Pola J.: *Spectrochim. Acta*, 46A, 607 (1990) and references therein.
4. Blades A. T.: *Can. J. Chem.* 46, 3283 (1968).
5. Flowers M. C.: *J. Chem. Soc., Faraday Trans.* 1, 73, 1927 (1977).
6. Berces T. in: *Comprehensive Chemical Kinetics* (C. H. Bamford and C. F. H. Tipper, Eds), Vol. 5. Elsevier, Amsterdam 1975.
7. Bailey W. J., diPetro J.: *J. Org. Chem.* 42, 3899 (1977).
8. Ref.⁶, p. 254.
9. Benson S. V.: *Thermochemical Kinetics*, p. 117. Wiley, New York 1976.
10. Shostakovski M. F., Tupaev P. V.: *Z. Obshch. Khim.* 21, 1830 (1951).

Translated by the author (J.P.).