Tetrahedron Vol. 45, No. 16, pp. 5065 to 5072, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00

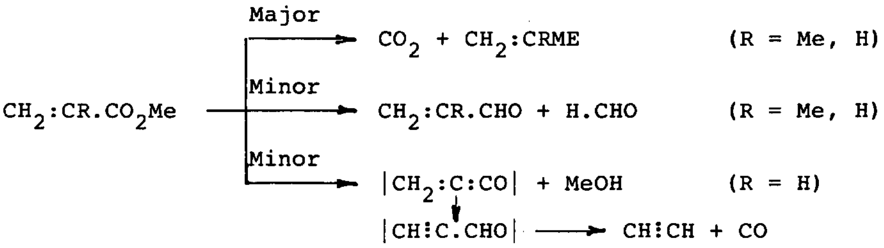
LASER POWERED HOMOGENEOUS DECOMPOSITION OF METHYL ACRYLATE AND METHACRYLATE

Josef Pola
Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences,
165 02 Prague - Suchdol (Czechoslovakia)

(*Received in UK* 9 *May* 1989)

ABSTRACT - The continuous wave CO_2 laser-powered decomposition of methyl acrylate and methacrylate sensitized by sulfur hexafluoride was examined in order to determine the course of reaction in the absence of wall effects. The reactions are dominated by acyl-oxygen cleavage and have radical-chain mechanism.

The gas-phase thermolysis of alkyl esters with β-hydrogen[1], as well as β,γ-unsaturated aliphatic acids[2] have been intensively investigated. Similar reaction of esters having unsaturation immediately adjacent to the $-CO_2-$ grouping has attracted less attention[3] and it is known to proceed via competing decarboxylation, acyl-oxygen and alkyl-oxygen scissions. With methyl acrylate (MA) and methyl methacrylate (MMA) the decarboxylation pathway predominates (Scheme 1), but this is so in packed reactors were both decompositions can be surface-assisted and can thus proceed heterogeneously.



Scheme 1

It was of our interest to study truly homogeneous course of MA and MMA decomposition by using the technique of continuous-wave (cw) CO_2 laser powered homogeneous pyrolysis[4] which we previously applied[5] to other surface-assisted organic reactions. The technique uses absorption of the laser radiation in an inert and energy-conveying sulfur hexafluoride and ensures reactions to occur in a small volume of the gas-phase far from reactor walls that remain at ambient temperature.

The irradiation of MA-SF_6 mixtures with cw CO_2 laser yields carbon monoxide, ethene and acrolein as the major products along with substantially lower quantities of ethine and methane and traces of propene and 2-propynal. The product distribution as the reaction progresses is illustrated in the Figure 1, where final amounts of ethine and methane were below 0.04 and 0.07 kPa, respectively, and those of propene and 2-propynal were below 3 percent of ethene.

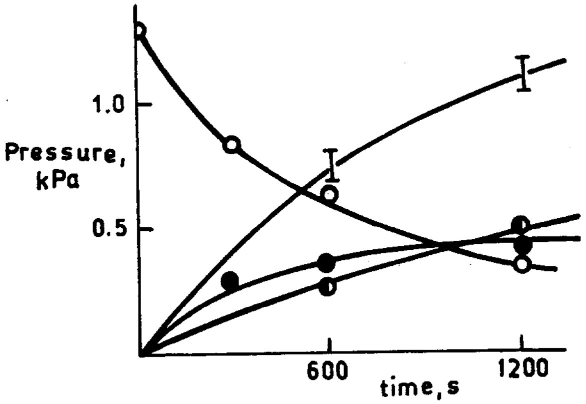


Figure 1. Reaction progress of the laser powered (10 W) decomposition of MA in MA-SF_6 (both 1.3 kPa) mixture
MA (○), CH_2:CH.CHO (●), C_2H_4 (◐), CO (I).

The irradiation of MMA-SF_6 mixtures with cw CO_2 laser affords propene, carbon monoxide and methacrolein together with some ethene, methane and very small quantities of MA and a C_4H_8 compound (Table I). We note that methane and ethene are formed in comparable amounts and that the ethene/propene ratio is higher as content of SF_6 in parent mixture is increased.

Table I Laser powered decomposition of methyl methacrylate[a]

SF_6 (mol %)	Total pressure (kPa)	Conversion %	Products (kPa)							
			acrolein	C_3H_6	CO	C_2H_4	CH_4	C_2H_2	C_4H_8	MA
35	3.1	61	0.20	0.80	0.8--0.9	0.10	0.10	0.02	$\sim$0.01	0.01
55	2.7	68	0.09	0.50	0.5--0.7	0.10	0.10	0.04	$\sim$0.01	0.01

[a] Laser output 10 W

After repeating many runs with both MA and MMA, a white material was deposited on the entrance window and the walls of the reactor and its i.r. spectrum /940 (s), 980 (w), 1060 (m), 1200 (m), 1270 (m), 1400 (w), 1450 (w), 1750 (vs), 2960 (m) and 3450 (m) cm^{-1}/ resembles, except for bands at 1750 and 3450 cm^{-1}, the i.r. spectrum of polyoxymethylene[6].

The laser-driven reactions differ remarkably from conventional thermolyses in that they do not yield carbon dioxide, which implies that the decarboxylation occurring as a major channel under surface conditions is precluded, if decompositions of MA and MMA occur solely in the gas-phase. The results show that homogeneous decompositions of MA and MMA are dominated by acyl-oxygen scission and lead to aldehyde (acrolein or methacrolein) and formaldehyde, the latter undergoing polymerization. Partial fragmentation of formaldehyde into carbon monoxide and hydrogen cannot be excluded. The occurrence of MA, methane and ethene during MMA decomposition suggests that C-Me cleavage in parent MMA can compete with acyl-oxygen scission. Higher content of methane and ethene at higher SF_6 content indicates that the importance of the former process increases with higher mean effective temperature. Assuming the known decompositions of acrolein and methacrolein into CO and appropriate alkene[3] and similar laser induced CO elimination from propynal[7], we presume that Scheme 2 can explain processes occurring in the "wall-less" reactor and that the other reactions important during conventional fragmentation[3] must have occurred as heterogeneously catalysed steps.

The alkene products might be also considered as being derived by decarbonylation of the $CH_2{:}CR.\dot{C}{:}O$ radical, followed by H-abstraction by the vinyl radical, as is illustrated below.

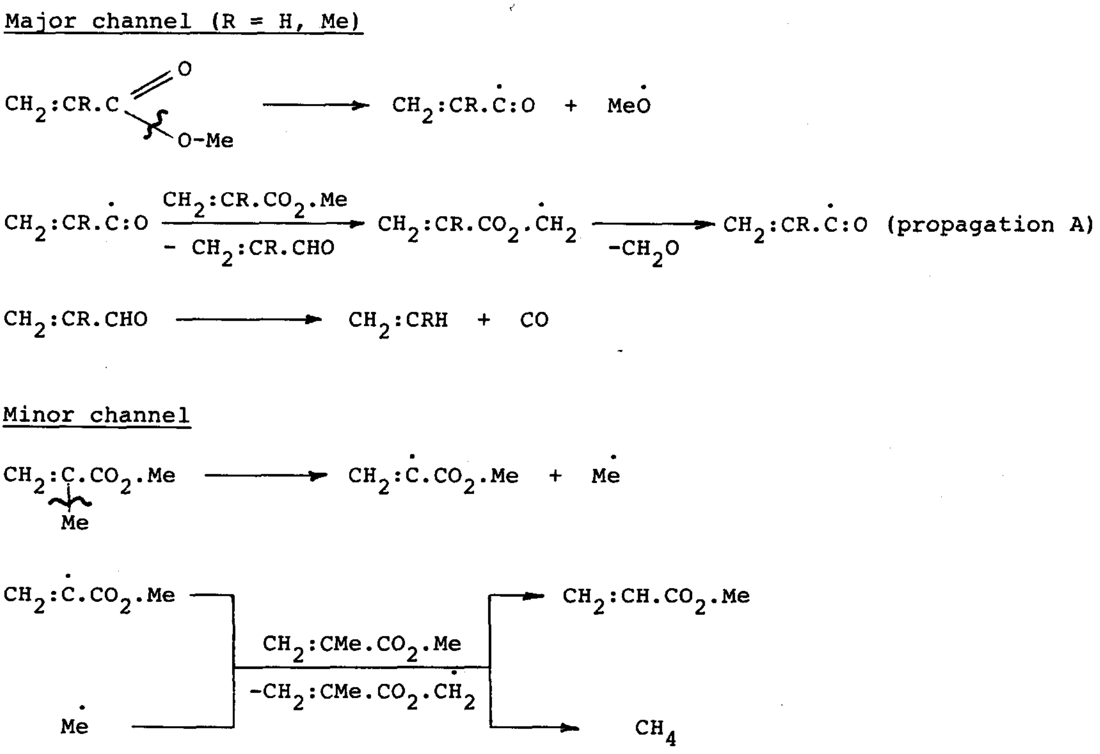
$$CH_2{:}CR.\dot{C}{:}O \xrightarrow[-CO]{} CH_2{:}\dot{C}R$$

$$\begin{tikzcd} CH_2{:}\dot{C}R \arrow[r, "CH_2{:}CR.CO_2Me", "-\ CH_2{:}CRH"'] & CH_2{:}CR.CO_2.\dot{C}H_2 \arrow[r, "-\ CH_2O"'] & CH_2{:}CR.\dot{C}{:}O \arrow[d, "-\ CO"] \\ & & CH_2{:}\dot{C}R \end{tikzcd}$$

(propagation B)

In fact, the rate of decarbonylation of similar acetyl radical is known to increase relative to that of the H-abstraction by this radical with increasing pressure and temperature and both reactions are measurable above certain temperature limit[8]. The presence of substantial amounts of the $CH_2{:}CR.CHO$ aldehydes among the products of the laser induced decompositions of MA and MMA can, however, be only consistent with Scheme 2, since these aldehydes can not arise via the alternative propagation B.

Scheme 2 gets support from mass spectra of both methyl esters and from the inhibition of the decomposition rates by radical scavengers. The initial



Major channel (R = H, Me)

$$CH_2{:}CR.C(=O)\text{-}O\text{-}Me \longrightarrow CH_2{:}CR.\dot{C}{:}O + Me\dot{O}$$

$$CH_2{:}CR.\dot{C}{:}O \xrightarrow[-\,CH_2:CR.CHO]{CH_2:CR.CO_2.Me} CH_2{:}CR.CO_2.\dot{C}H_2 \xrightarrow[-CH_2O]{} CH_2{:}CR.\dot{C}{:}O \text{ (propagation A)}$$

$$CH_2{:}CR.CHO \longrightarrow CH_2{:}CRH + CO$$

Minor channel

$$CH_2{:}C(Me).CO_2.Me \longrightarrow CH_2{:}\dot{C}.CO_2.Me + \dot{M}e$$

$$CH_2{:}\dot{C}.CO_2.Me,\ \dot{M}e \xrightarrow[-CH_2:CMe.CO_2.\dot{C}H_2]{CH_2:CMe.CO_2.Me} CH_2{:}CH.CO_2.Me,\ CH_4$$

Scheme 2

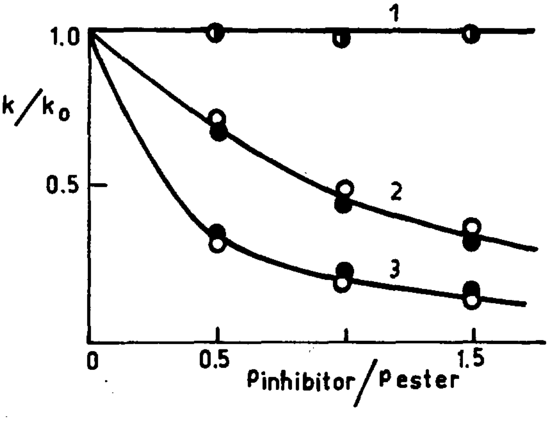


Figure 2. The effect of radical chain inhibitor on the rate of laser powered (12 W) decomposition of MA (○), MMA (●) and cyclohexene (◑) with reactant (2.7 kPa) - SF_6 (4 kPa) - inhibitor (0-4 kPa) - Ar mixtures at total pressure 13.3 kPa

Curves 1 and 3 relate to propene inhibitor, curve 2 relates to cyclohexene inhibitor; k_o is uninhibited rate constant.

cleavage of the acyl-oxygen bond is observed when MA and MMA fragment under electron impact; the dominating peaks in mass spectra at 20 eV (m/z, relative intensity) are those relating to M-OCH_3 ions:

MA : 86 (1), 85 (14), 68 (3), 59 (3), 58 (11), 57 (3), 55 (100), 44 (2), 43 (6), 42 (17), 32 (2), 28 (4), 27 (25).

MMA: 100 (23), 99 (14), 85 (8), 82 (4), 69 (67), 59 (6), 48 (2), 57 (1), 56 (6), 55 (8), 54 (2), 45 (1), 43 (5), 41 (100), 40 (12), 39 (12), 30 (3), 29 (4), 28 (4).

Similar pattern of MA fragmentation is observed also at 70 eV [9]. A marked inhibition caused by propene and cyclohexene (Fig. 2) unambiguously reveals the occurrence of chains. This effect of radical-chain scavengers was studied in excess of argon not to alter temperature distribution in reactant - SF_6 mixtures upon additions of these probing agents - it is seen that reaction rate of molecular retro-Diels-Alder decomposition of cyclohexene into ethene and 1,3-butadiene keeps constant regardless propene admixtures.

Strong convention currents move the gas through the local hot zone, where decomposition occurs, into lower temperature regions[4,10] where reaction can be quenched and radical-chains made short compared to normal conditions of temperature homogeneity. The use of chemical thermometer[4,11] to establish the Arrhenius parameters for MA and MMA decomposition in the presence of radical scavengers can thus lead to values reflecting significant suppression of radical chains. Cyclohexene retro-Diels-Alder reaction whose Arrhenius parameters are known[12] served as both radical-chain retarder and chemical thermometer and allowed to estimate that data of the log k_{total} vs. T_{eff}^{-1} plot for MA and MMA decompositions can be fitted with the only line (Fig. 3). The values E_a = 316 kJ/mole and log(A,s^{-1}) = 16.8 are very close to those accepted[13] for simple fission of molecules into two radicals and appear to be associated with the initial acyl-oxygen cleavage.

Data on fragmentation of simple alkyl esters without β-hydrogen in alkyl moiety come mainly from photolytic studies[14] and the mechanism of thermal fragmentation still remains the subject of continuing interest[15]. Here presented results reveal that mechanism of thermolysis of methyl esters of α,β-unsaturated acids is dramatically changed by surface effect and stress that care should be taken to eliminate these effects in understanding reaction data properly. The results also help to understand reaction course of the laser-induced reaction between MMA and silane[16].

EXPERIMENTAL

Experiments were carried out in a stainless steel tube (10 cm long, inner diameter 3.6 cm) equipped with two NaCl windows, a valve and a sleeve

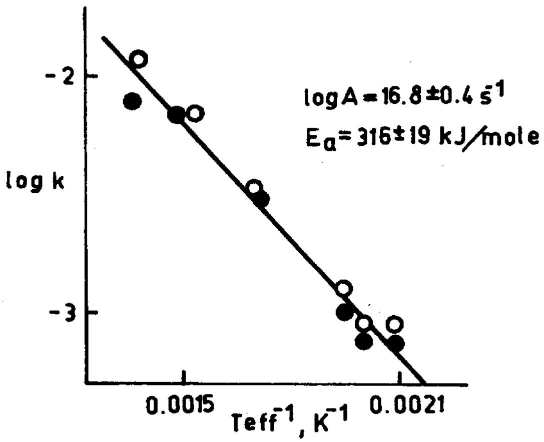


Figure 3. The Arrhenius log k vs T_{eff}^{-1} plot for decomposition of MMA (●) and MA (○). The experiments carried out with 10-17 W laser output, and MA or MMA (2.7 kPa) - SF_6 (4-8 kPa) - cyclohexene (6.7 kPa) mixtures.

with rubber septum. A tunable continuous-wave CO_2 laser operated at the P(20) line of the $00^01 \rightarrow 10^00$ transition and its beam, focused with a Ge lens (focal length 10 cm) was checked for constant output (power meter, Physical Institute, Prague) and wavelength (spectrum analyzer, 16-A model, Optical Eng. Co.).

In a typical experiment, the tube was filled with pre-mixed MA (or MMA)-SF_6, MA (or MMA)-SF_6-cyclohexene (or propene)-Ar, or MA (or MMA)-cyclohexene-SF_6 mixtures, and an initial i.r. spectrum was taken. The sample was then irradiated in a vertically positioned cell, the beam entering from below and the extent of reaction was followed on a Perkin-Elmer model 621 i.r. spectrometer by periodically taking the i.r. spectrum of the sample. The products of the decompositions were also analyzed by gas chromatography-mass spectrometry (GC-MS Shimadzu, model QP 1000) by using columns packed with Porapak P, silicon oil-deactivated alumina and silicon elastomer OV-1. Pressures of reactants and products were calculated from known optical densities of authentic samples at suitable wavelengths (820 cm^{-1} - MA and MMA, 1140 and 2660 cm^{-1} - cyclohexene, 1300 and 3000 cm^{-1} - methane, 730 cm^{-1} - ethine, 910 cm^{-1} - propene, 2815 cm^{-1} - acrolein, 2780 cm^{-1} - methacrolein, 2160 cm^{-1} - carbon monoxide) and by carrying out mass fragmentography of mixtures using SF_6 as internal standard.

Effective mean temperatures and Arrhenius parameters of the MA and MMA decompositions were estimated by means of the technique for noninteracting system[4] and using cyclohexene decomposition as a chemical thermometer[4]. Mean effective temperature was calculated as $E_a/2.303$ (log A-log k), where E_a and log A are taken from ref.[12] and k relates to total reaction rate constant observed.

The reaction rates of retro-Diels-Alder decomposition of cyclohexene an those of the decomposition of MA and MMA in excess of cyclohexene were obtained as first-order rate constants.

Methyl acrylate, methyl methacrylate, cyclohexene and sulfur hexafluoride (all Fluka) were commercial products.

ACKNOWLEDGEMENT

The author thanks Mr. J. Vítek for technical assistance.

REFERENCES

1 R. Taylor in "The Chemistry of Functional Groups, Supplementary Vol. B, Acid Derivatives", S. Patai, ed., Wiley, New York 1979.

2 a) D.B. Bigley, J.C. Thurman, J. Chem. Soc. (B) 1968, 436. b) D.B. Bigley, R.W. May, J. Chem. Soc. (B) 1967, 557. c) D.B. Bigley, R.H. Weatherhead, R.W. May, J. Chem. Soc., Perkin 2 1977, 592, 745.

3 a) H.M. Mackinnon, P.D. Ritchie, J. Chem. Soc. 1957, 2564, 2556, 2107. b) R.L. Forman, H.M. Mackinnon, P.D. Ritchie, J. Chem. Soc. (C) 1968, 2016. c) R.L. Forman, H.M. Mackinnon, P.D. Ritchie, J. Chem. Soc. (C) 1968, 2013, 2016.

4 W.M. Shaub, S.H. Bauer, Int. J. Chem. Kinet. 7, 509 (1975).

5 a) J. Pola, J. Chem. Soc. Perkin Trans. 2, 1983, 231. b) J. Pola, Int. J. Chem. Kinet. 15, 1119 (1983). c) J. Pola, M. Farkačová, P. Kubát, A. Trka J. Chem. Soc. Faraday Trans. 1, 80, 1499 (1984). d) J. Pola, J. Ludvík, J. Chem. Soc. Perkin 2, 1987, 1727. e) E.A. Volnina, P. Kubát, J. Pola, J. Org. Chem. 53, 2612 (1988). f) M. Sedláčková, J. Pola, J. Anal. Appl. Pyrol. 14, 179 (1988). g) J. Pola, J. Včelák, J. Anal. Appl. Pyrol. 10, 257 (1987). h) J. Pola, Z. Chvátal, J. Fluor. Chem. 37, 197 (1987).

6 M. Kraft, Struktur und Absorptionsspektroskopie der Kunstoffe, Verlag Chemie, Weinheim 1973, p. 135.

7 H. Stofast, R. Pfister, J.R. Huber, J. Phys. Chem. 89, 5074 (1985).

8 a) E. O'Neal, S.W. Benson, J. Chem. Phys. 36, 2196 (1962). b) K.W. Watkins, W.N. Word, Int. J. Chem. Kinet. 6, 855 (1974). c) P.M. Kroger, S.J. Riley, J. Chem. Phys. 67, 4483 (1977).

9 a) K. Ohya, Y. Yotsui, K. Yamazaki, M. Sano, Org. Mass. Spectry. 18, 27 (1983). b) A.J. Bowles, E.F. Brittain, W.O. George, Org. Mass. Spectry 2, 809 (1969).

10 a) P. Kubát, J. Pola, Coll. Czech. Chem. Commun. 50, 1537 (1985). b) J. Zhu, E.S. Yeung, J. Phys. Chem. 92, 2184 (1988).

11 W.C. Danen, J.C. Jang in "Laser Induced Chemical Processes", J.I. Steinfeld ed., Plenum Press, New York, 1981.

12 S.W. Benson, H.E. O'Neal, Kinetic Data on Gas Phase Unimolecular Reactions, NSRDS, National Bureau of Standards, Washington, D.C., 1970.

13 S.W. Benson, Thermochemical Kinetics, Wiley, New York 1976, p. 96.

14 a) J.D. Coyle, Chem. Rev. 78, 97 (1978). b) E. Hassinen, J. Koskikallio, Acta Chem. Scand. A 33, 625 (1979) and refs. therein.

15 a) W.H. Richardson, H.E. O'Neal in "Comprehensive Chemical Kinetics", C.H. Bamford, C.F.H. Tipper eds., Elsevier, New York, Vol. 5, 1972. b) M.M. Aly, M.Z.A. Badr, A.M. Fahmy, S.A. Mahgoub, Can. J. Chem. 61, 1532 (1983). c) E. Ghibaudi, A.J. Colussi, J. Chem. Soc., Chem. Commun. 1984, 433. d) M.M. Gil'burd, F.B. Moin, Kinet. Katal. 13, 836 (1972). e) K.G.P. Sulzmann, D.E. Baxter, M. Khazra, J. Phys. Chem. 89, 3561 (1985). f) L. Carlsen, H. Egsgaard, P. Pagsberg, J. Chem. Soc. Perkin 2, 1981, 1256.

16 R. Alexandrescu, J. Morjan, C. Grigoriu, I.N. Michailescu, Z. Bastl, J. Tláskal, R. Mayer, J. Pola, Appl. Phys. A 46, 275 (1988).