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LOW-PRESSURE AND HIGH-PRESSURE PYROLYSIS [1]

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ABSTRACT

Low-pressure and high-pressure pyrolyses of ethylene oxide and 1,2,3-thiadiazole are discussed. Pyrolyses at low pressures have been carried out applying the gas-phase Curie-point pyrolysis technique and compared to available high-pressure data.The important interplay between quenching of reactive species and "hot" molecules, either by molecule-wall (low-pressure) or molecule-molecule (high-pressure) collisions, and collision free decompositions is discussed.

INTRODUCTION

The major important difference between low-pressure and high-pressure pyrolyses appears to be the mean life-time and the subsequent collisionally induced quenching, i.e. activation/deactivation, of reactive species and/or "hot" molecules. As a consequence of the very low molecule-molecule collision frequency in low-pressure reactors, the mean life time of reactive species, i.e. highly labile compounds, however, being present in a thermodynamically stable state, typically will be controlled by the reactor dimensions, the subsequent quenching being introduced by molecule-wall interactions. On the other hand, "hot" molecules, which are not in a thermodynamically stable state may decompose collision-free before interacting with the reactor walls. In contrast to this, the pyrolyses at high pressures typically will involve very short, however, pressure-dependent, mean life-times of the reactive species, the quenching of the latter taking place as results of molecule-molecule interactions.

The present paper discusses molecule-molecule and molecule-wall collisions as important reaction parameters in gas phase pyrolyses, as well as the important interplay between collisionally induced quenching of reactive species and "hot" molecules and the possible collision-free relaxation of the latter.

EXPERIMENTAL

Low-pressure pyrolyses were carried out applying the gas-phase Curie-point principle as described in detail previously [2,3]. A selection of reactors was applied. All reactors were 120 mm in length, the central 50 mm constituting the hot zone. The reactors differed in diameter, the radii being equal to 1.9, 4.0, 6.0, and 10.0 mm, respectively. In all reactors the orifice was of circular shape, the radius being 0.6 mm. The filament was constructed, as described previously [4], of an iron tube (o.d. 1.0 mm) coated with a 10-20 μm layer of gold [5]. The pyrolysis products were passed directly into the ion source of a Varian MAT CH 5D mass spectrometer.

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The pyrolyses were carried out at a filament temperature of 1043K. Assuming an energy transfer coefficient for molecule-filament collisions of ca. 0.8 [4,6], the "temperature" of the primary generated products can be estimated to be ca. 800K.

Modelling of the behaviour of single molecules in the applied low-pressure reactors was carried out applying the previously developed Monte-Carlo procedure [6]. In Table 1 mean-flight distances and mean flight-times of molecules in the applied low-pressure reactors are given. In the present context the figures refer to distances and times between the primary collision at the hot filament surface and the subsequent collision with the reactor walls. Hence, in the case of "hot" molecules, mean flight-time equals mean life-time, as it is assumed that these species will not survive the collision with the reactor walls.

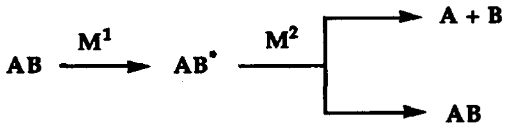
Table 1. Mean flight distances and lifetimes as a function of reactor radius [a]

reactor radius mm	*mean flight-distance* mm	*mean flight-time* μs
1.9	1.90	3.1
4.0	4.63	7.4
6.0	7.16	11.5
8.0	9.56	15.4
10.0	12.15	19.5

[a] molecular weight: 44, molecular "temperature": 800K

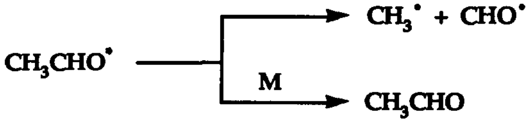
RESULTS AND DISCUSSION

Molecule-wall and molecule-molecule collisions are important reaction parameters in pyrolysis studies at low-pressure and high-pressure conditions, respectively. Typically a pyrolysis mechanism can be expressed as subsequent excitation and quenching by interaction with collision partners (M), the latter may be molecules or surfaces. The relative distribution between the products corresponding to the deactivation and the fragmentation (or any other type of reaction prevailing) pathways, respectively, is the collision efficiency, which typically will be less than 1.0. In addition to the collisionally induced quenching of AB^*, collision free fragmentation should be considered.



To elucidate the effect of the quenching of reactive species and "hot" molecules by molecule-wall collisions, we carried out a series of pyrolyses in low pressure reactors exhibiting identical geometric features exept from an increasing diameter. This fact enabled us to study the product composition as a function of the mean-life time of the primary generated reactive species, expressed as the average period of time between generation at the hot filament surface to the first collision with the reactor wall, the latter being at ambient temperature. It is emphasized that in the applied low-pressure pyrolysis set-up the generation of the primary pyrolysis products is a result of single collisions between the reactant and the hot filament surface [6]. Two systems have been studied. These are ethylene oxide and 1,2,3-thiadiazole.

In the course of time, the pyrolysis of ethylene oxide has been investigated by several groups [7-9], however, typically at high pressures. It is generally accepted that the mechanism involves an excited ("hot") acetaldehyde molecule, which may decompose collision free into methyl- and formyl radicals or be quenched to "cold" acetaldehyde upon collison. Thus, it has been reported [10] that pyrolysis of ethylene oxide at 1 atm afforded 95% acetaldehyde, whereas only half of the "hot" acetaldehyde will be quenched to acetaldehyde at 10 torr.



If a similar quenching of "hot" acetaldehyde molecules prevail for collisions with reactor walls at ambient temperature, an increasing amount of acetaldehyde among the pyrolysis products upon pyrolysis of ethylene oxide would be expected with decreasing reactor diameter and, hence, decreasing mean life-time of the "hot" acetaldehyde (cf. Table 1). Based on direct analysis of daughter ion (DADI) mass spectrometry the amount of acetaldehyde relative to unpyrolysed ethylene oxide could be calculated (cf. Fig. 1), whereas the total degree of ethylene oxide decomposition, corresponding to the primary formation of "hot" acetaldehyde was calculated based on electron impact MS in combination with DADI-MS. In Fig. 2 the amount of acetaldehyde, formed upon pyrolyses of ethylene oxide, relative to the amount of primary generated "hot" acetaldehyde is visualized as a function of mean life-time of the latter (cf. Table 1).

It is convincingly demonstrated that a decrease in mean life-time gives rise to an increased amount of acetaldehyde due to collisionally induced quenching of the "hot" species upon interaction with the reactor walls. The curved shape should be noted. At low mean life-times the CH_3CHO/CH_3CHO^* ratio approaches assymptotically the value 0.16, which can be described as the surface collision efficiency. Thus, 16% of the "hot" acetaldehyde molecules are collisionally deactivated to acetaldehyde, whereas the remaining 84% apparently decompose by fragmentation upon collision with the reactor walls. The deviation from the 0.16 value for increased mean life-times visualizes the effect of the collision-free fragmentation of CH_3CHO^*. Since the collision-free decomposition of CH_3CHO^* is a simple unimolecular reaction, the rate constant for this reaction, k^*, can be obtained from a conventional first-order lnDev vs. time plot, Dev being the deviation from the assymptotic value. Hence, the unimolecular rate constant k^*, at 800K, for decomposition of CH_3CHO^* is determined to be $2x10^5$ s^{-1}, which appears to be significantly lower than the roughly estimated value of $10^{7.5}$ s^{-1}, which has been reported by Benson[10].

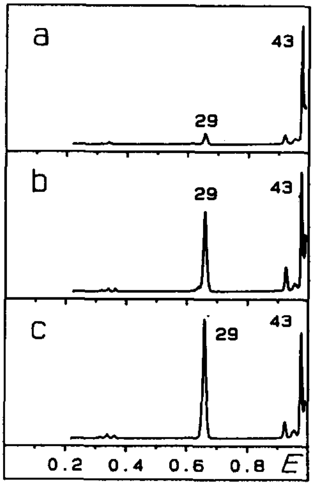


Fig. 1. DADI spectra of the electron impact induced molecular ions (m/z 44) of a: acetaldehyde, b: ethylene oxide following pyrolysis (1043K, reactor radius 1.9 mm), and c: ethylene oxide.

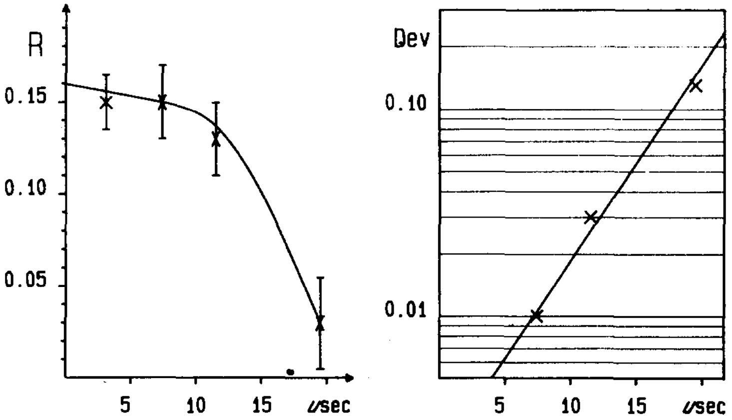
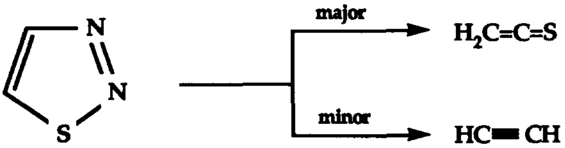


Fig. 2. The ratio CH_3CHO/CH_3CHO^* as function of calculated mean flight time of the "hot" acetaldehyde, and Arrhenius plot corresponding to the fragmentation of CH_3CHO^*.

A second example, where collision processes may play a dominant role, is the pyrolysis of 1,2,3-thiadiazole. It is well know that pyrolysis of the latter predominantly leads to the formation of thioketene [11,12], however, we reported recently additionally formation of minor amounts of acetylene [5].



The formation of acetylene was discussed in terms of possible collision-free sulfur extrusion from a primary generated •CH-CH-S• biradical, which alternatively collisionally induced would lead to thioketene, a mechanism which a priori would be in accordance with pyrolysis studies at higher pressures, where acetylene apparently is absent [13].

In Table 2 the yield of thioketene relative to unpyrolyzed thiadiazole and the ratio between the yields of acetylene and thioketene, given as the intensity ratios I_{58}/I_{86} and I_{26}/I_{58}, respectively, found in the field-ionization (FI) mass spectra, are summarized for three low-pressure reactors. It should be noted that large differences in the FI sensitivities may prevail. Thus, these ratios can not be taken as a direct measure for concentrations.

Table 2. Pyrolysis- Mass Spectrometry of 1,2,3-thiadiazole

mean flight distance mm	I_{58}/I_{86}	I_{26}/I_{58}
1.90	41	5
7.16	27	3
12.15	14	6

It is unambigously demonstrated that the I_{26}/I_{58} ratio, i.e. the ratio between the formation of acetylene and thioketene apparently is unsensitive towards mean flight-distance, and, hence, mean life-time of the primary generated biradical. It must on this basis be concluded that the primary reactive species in the case of thiadiazole pyrolysis, apparently is generated in a thermodynamically stable state, which upon collision with the reactor walls give rise to the formation of both acetylene and thioketene. However, it cannot be excluded that e.g. acetylene is formed directly upon collision with the hot filament surface, whereas thioketene apparently is a results of collisionally quenching of the above mentioned biradical. The latter assumption may gain some support from the fact that using a reactor with the wall coated with XE-60 silicone polymer lead to a I_{26}/I_{58} ratio identical to that obtained using an uncoated reactor of similar geometry.

An additional feature which should be noted is the apparent increase in yield of thioketene upon decrease in reactor diameter. This is, however, based on previous calculations, expected, as it has been shown that for tube-like reactors the collision frequency apparently is higher than the theoretically predicted [6].

CONCLUSION

Based on the above presented results it can be concluded that collisional quenching of reactive species and "hot" molecules is an important reaction parameter, which, as well as the possible interplay with collision-free reactions, should be taken into account both in low-pressure and in high-pressure pyrolysis studies in order eventually to explain the route of formation for the observed products. It can furthermore be concluded that low-pressure pyrolysis studies of the here described design to some extent can mimic high-pressure studies, when narrow reactors, i.e. system leading to low mean life-times of the primary generated products, are applied. It should, however, be remembered that major differences in molecule-wall and molecule-molecule collisions may prevail.

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