About the Radical Formation in the Pyrolysis of Formic Acid at High Temperatures

M. Klatt, M. Röhrig, and H. Gg. Wagner
Institut für Physikalische Chemie, Universität Göttingen, Göttingen

Z. Naturforsch. **47a,** 1138–1140 (1992); received September 12, 1992

The formation of radicals in the HCOOH pyrolysis was investigated in the temperature and density range between 1450 and 2450 K and $2 \cdot 10^{-6}$ and $1.2 \cdot 10^{-5}$ mol/cm^3, respectively. The small amount of radicals found indicates that a radical forming reaction path in the formic acid pyrolysis is smaller than 0.2% of the total decomposition rate.

Introduction

Formic acid (HCOOH) is an important intermediate in the oxidation of unsaturated hydrocarbons in combustion processes as well as in atmospheric reactions. For example, HCOOH is the main product in the O_3–C_2H_4 reaction [1]. It has been proposed that HCOOH is formed highly excited in the reaction of O_2 with CH_2 [2] where its subsequent decomposition into CO and H_2O and radical products has been investigated previously [3, 4].

The decomposition of formic acid is possible via several channels (thermodynamic data from [5]):

			$\Delta_r H$ (kJ/mol)
HCOOH	→	$CO_2 + H_2$	−7
	→	$CO + H_2O$	24
	→	H + COOH	411
	→	$CO_2 + 2\,H$	429
	→	HCO + OH	466
	→	H + HCOO	480

Decomposition rate of HCOOH and the product distribution have been investigated by several authors [6, 7]. The apparent activation energies of the HCOOH decomposition have been found to be 209 kJ/mol [6] or 168 kJ/mol [7] for the CO channel and 238 kJ/mol [6] or 254 kJ/mol [7] for the CO_2 channel. It has been assumed that only the stable products $CO_2 + H_2$ and $CO + H_2O$ are formed, but only the formation of CO and CO_2 has been measured directly, and the ratio of CO and CO_2 is reported [7] to be

$$\alpha = [CO]/[CO_2] = 0.16 \exp(-10\,200\ \mathrm{K}/T)\,.$$

In [6] the CO/CO_2 ratio is reported to be one at 2000 K and to be about 20 at 800 K.

Yet, there has been no investigation of the contribution of a direct radical formation path such as H + COOH or HCO + OH. These reaction paths are highly endothermic but with increasing temperature their contribution to the decomposition rate may be increasing too.

In this work we have checked the amount of H and OH formed in the HCOOH pyrolysis in the temperature range between 1600 and 2500 K with the intention to obtain an upper limit for the contribution of radical forming steps in the HCOOH decomposition.

Experimental

The experiments were carried out in two shock tubes; the one for the OH detection was made of aluminium with an inner diameter of 20 cm, and the other for the H measurements was made of stainless steel and 8 cm diameter. The detection system for OH radicals by UV absorption consists of a frequency doubled ring dye laser pumped with an Ar^+ laser. The absorption was followed with photodiodes and measured by difference amplifying.

H atoms were monitored by H-ARAS with a microwave discharge lamp as light source. Both the shock tubes and the optical setups have been described in detail previously [8–10]. The detection limit of both systems was better than $2 \cdot 10^{-12}$ mol/cm^3.

The testgases used were prepared in a flow system. A small argon flow passed a thermostated saturator

---

Reprint requests to Prof. Dr. H. Gg. Wagner, Institut für Physikalische Chemie, Universität Göttingen, Tammannstraße 6, W-3400 Göttingen, Germany.

0932-0784 / 92 / 1100-1138 $ 01.30/0. – Please order a reprint rather than making your own copy.

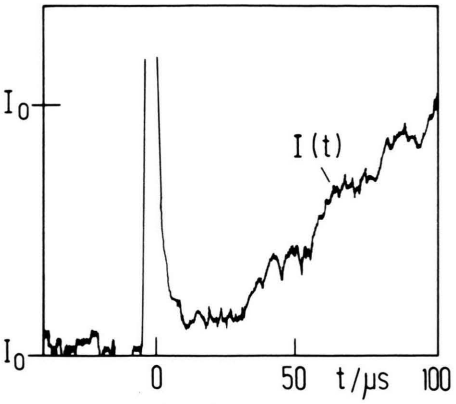

Fig. 1. Absorption profile of OH radicals at $\lambda = 308.417$ nm (Q_14-line), presented in real time; $T_2 = 2447$ K, $\varrho_2 = 2.1 \cdot 10^{-6}$ mol/cm³, 2200 ppm HCOOH.

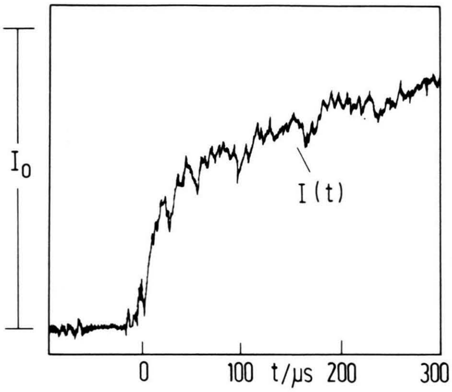

Fig. 2. Absorption signal of H atoms behind the reflected wave: $T_2 = 2243$ K, $\varrho_2 = 1.1 \cdot 10^{-5}$ mol/cm³, 820 ppm HCOOH.

filled with HCOOH and was mixed together with a flow of pure argon. Both flows were controlled by mass flow meters (Tylan Mass Flow Controller) with an accuracy of ±2%.

The substances used were HCOOH (p. a., 99.9%, Merck), Argon (6.0) and H_2 (3.0) as driver gas.

Results and Discussion

1. OH Measurements

The formation of OH radicals was investigated behind incident shock waves in the temperature range between 1400 and 2450 K and total densities around $(3 \pm 1) \cdot 10^{-6}$ mol/cm³. The HCOOH concentration was varied between $4 \cdot 10^{-9}$ and $6 \cdot 10^{-9}$ mol/cm³.

Figure 1 shows an absorption profile at 2446 K and an HCOOH concentration of $4.7 \cdot 10^{-9}$ mol/cm³. After passage of the shock front indicated by the sharp schlieren signal the absorption rises slowly to a maximum value of about 1% within 100 µs, which corresponds to a concentration of less than 10^{-11} mol/cm³ OH radicals, that is only 0.18% of the initial HCOOH concentration.

At that high temperature and that density decomposition rate constant of HCOOH is about 10^5 s^{-1} [6, 7]. That means that the OH signal observed cannot be due to a direct decomposition channel because its rise is too slowly. It is mainly due to the subsequent decomposition of H_2O which is formed in the HCOOH pyrolysis, so that a direct OH channel in the HCOOH pyrolysis should be far below 0.2%.

2. H Measurements

Lyman-α-absorption experiments were performed in the temperature range between 1860 and 2250 K behind reflected shock waves. The total densities and the HCOOH concentration were around $(1.1 \pm 0.1) \cdot 10^{-5}$ mol/cm³ and $(6 \pm 3) \cdot 10^{-9}$ mol/cm³, respectively.

The absorption profile shown in Fig. 2 was recorded at a temperature of 2250 K with an initial HCOOH concentration of $8.8 \cdot 10^{-9}$ mol/cm³. After the reflected shock front the absorption rises within 400 µs to an end value of about 84%. That corresponds to a concentration of H atoms of $2.1 \cdot 10^{-11}$ mol/cm³, which is only 0.2% of the initial HCOOH concentration.

Assuming that HCOOH decomposes completely into CO and H_2O, as proposed by Saito et al. [7], with a rate constant of $2.5 \cdot 10^5$ s^{-1} at the conditions applied in that experiment, the subsequent water decomposition produces about $2 \cdot 10^{-11}$ mol/cm³ H atoms. That means that a prevailing part of the observed signal is also not due to a direct HCOOH pyrolysis channel but due to secondary reactions as seen in the OH measurements, and the direct H channel in the HCOOH pyrolysis should be also far below 0.2%.

Conclusion

Both the OH and the H measurements, performed in the temperature and density range between 1400 and 2450 K and $2 \cdot 10^{-6}$ and $1.2 \cdot 10^{-5}$ mol/cm^3, respectively, indicate that a radical forming step in the formic acid pyrolysis system is smaller than 0.2% of the total decomposition rate.

These radicals are formed to a good deal by water decomposition, and the water gas equilibrium ($CO + H_2O = CO_2 + H_2$) will be established so that the direct radical channel in the HCOOH pyrolysis in fact may be estimated to be $\leq 10^{-4}$ of the total decomposition rate.

These results are in good agreement with previous assumptions of Shaub et al. [6] and Saito et al. [7]. The authors proposed that radical forming steps in the HCOOH pyrolysis are of minor importance because of their strong endothermicity. This is well confirmed by our measurements. Even at the highest temperature investigated the contribution of a radical channel should in fact be far below 0.2%.

That result is also in agreement with the small amount of radicals found in the reaction of CH_2 with O_2 [3, 4]. In this reaction HCOOH may be formed highly excited with an internal energy of about 740 kJ/mol. That energy is sufficiently high for a direct decomposition into $CO + H + OH$ or $CO_2 + 2\,H$, but the contribution of the radical steps has been found to be low.

The support of this work by the DFG is gratefully acknowledged.

[1] J. T. Herron and R. E. Huie, J. Amer. Chem. Soc. **99,** 5430 (1977).

[2] D. S. Y. Hsu and M. C. Lin, Int. J. Chem. Kinet. **9,** 507 (1977). – W. M. Shaub, D. S. Y. Hsu, T. L. Burks, and M. C. Lin, 18th Symp. (Int.) on Combust. (1981), p. 811.

[3] Ch. Dombrowsky, S. M. Hwang, M. Röhrig, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **96,** 195 (1992).

[4] Ch. Dombrowsky and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem., in print.

[5] C. F. Melius, private Communication, Sandia National Laboratories, Livermoore, California.

[6] D. S. Y. Hsu, W. M. Shaub, M. Blackburn, and M. C. Lin, 19th Symp. (Int.) on Combust. (1982), p. 89.

[7] K. Saito, T. Kakumoto, H. Kuroda, S. Tonii, and A. Imamura, J. Phys. Chem. **80,** 4989 (1984).

[8] K. Holzrichter and H. Gg. Wagner, 18th Symp. (Int.) on Combust. (1981), p. 769.

[9] M. Klatt, M. Röhrig, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **95,** 1163 (1991).

[10] A. Hoffmann, M. Klatt, and H. Gg. Wagner, Z. Phys. Chem. N. F. **168,** 1 (1990).