Kinetics of the Reaction HOCO + O_2 in the Gas Phase

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Using the discharge flow method, the kinetics of the gas phase reaction

$$\mathrm{HOCO} + \mathrm{O_2} \rightarrow \text{products} \qquad (1)$$

was investigated at room temperature and pressures around $p \approx 2.0$ mbar with Far Infrared Laser Magnetic Resonance (FIR-LMR) detection of HOCO, HO_2, and OH. From the measured concentration-versus-time decay profiles of HOCO in the absence and presence of a large excess of O_2, the overall rate constant of the reaction was found to be

$$k_1\,(296\ \mathrm{K}) = (9.9 \pm 1.5) \cdot 10^{11}\ \mathrm{cm^3/mol \cdot s}.$$

The main reaction channel, which leads to production of $HO_2 + CO_2$, could be established.

Key words: Chemical kinetics; Gases; Radicals; Spectroscopy; Laser Magnetic Resonance.

1. Introduction

The HOCO radical is of interest for its molecular structure as well as for its elementary chemical reactions in a number of complex reaction systems. HOCO is produced in the earth's troposphere as a reactive intermediate during the oxidation of formic acid, one of the key components in photochemical smog [1]. It is also generated as a short-lived energized intermediate (HOCO†) in the reaction OH + CO → H + CO_2 (see, e.g., [2]), which is an important elementary step in hydrocarbon flames. The distinctive mechanism of this reaction is of interest for the pronounced "non-Arrhenius" temperature dependence of its thermal rate constant (for a recent literature compilation see [3]). Recent quantum scattering studies [4] show that the tunneling lifetimes of the HOCO† with respect to dissociation to H + CO_2 have a pronounced effect on this rate constant.

The existence of the HOCO radical has been established first in a matrix study by Milligan and Jacox [5], who assigned infrared absorption bands of both the trans and cis conformations. In a consecutive matrix investigation, the trans form was concluded to be the more stable one [6], in agreement with several ab initio quantum chemical calculations (see, e.g., [7–9]). The heat of formation of HOCO (−223 kJ/mol) was determined in a photoionization mass spectrometric study by Ruscic et al. [10]. Accordingly, trans-HOCO is bound with respect to H + CO_2 by only ≈ 43 kJ/mol.

First high resolution spectra of HOCO and its isotopomer DOCO have been reported only very recently by Radford et al. [11], who observed numerous a-dipole rotational transitions in the millimeter wavelength region. Addition information on the structures of HOCO and DOCO has since become available from a series of infrared vibrational spectra [12, 13] and, especially, far infrared Laser Magnetic Resonance (LMR) spectra [14, 15]. In the LMR spectra, b-dipole transitions of trans-HOCO [14] and -DOCO [15] could be measured, which allowed the determination of the A rotational constants. With the observation of the LMR spectra, quantitative studies of the kinetics of the elementary reactions of the HOCO radical have become possible.

In the present publication we report on an investigation of the kinetics of the reaction of trans-HOCO with O_2,

$$\mathrm{HOCO} + \mathrm{O_2} \rightarrow \mathrm{HO_2} + \mathrm{CO_2}. \qquad (1)$$

The study of this reaction proved useful for the measurements of the LMR spectra of HOCO and DOCO [15] and because of the importance of this reaction in the atmosphere. The investigations were carried out by monitoring the concentrations of the reactant HOCO and the products HO_2 and OH by LMR.

After completion of the experiments, we became aware of a practically simultaneous study of the same

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reaction by Moore and coworkers [16]. Their value for the rate constant of reaction (1) is in good agreement with the result reported here.

2. Experimental

The investigations were carried out at room temperature in an isothermal discharge flow system. The experimental set-up has been described in detail in [17]. The flow reactor which was used in the present work consisted of a pyrex tube with an internal diameter of 3.96 cm. The inner surface was coated with a thin film of halocarbon wax (Halocarbon Products, #15-00). For the detection of the radicals, the flow system was connected to an LMR spectrometer [17].

HOCO radicals were generated in a moveable quartz double injector via the reaction of formic acid with Cl atoms,

$$HCOOH + Cl \rightarrow HOCO + HCl. \qquad (2)$$

Based on the value of $\Delta_F H^0_{298}(HOCO) = -223$ kJ/mol given in [10], reaction (2) is exothermic by $\Delta_R H^0_{298} = -58$ kJ/mol. HOCO radicals were found as main products, although some formation of the isomeric HC(O)O radicals cannot be fully excluded a priori. However, a considerable activation energy can be presumed for this channel. Assuming a value of $\Delta_F H^0_{298}(HC(O)O) \approx -170$ kJ/mol, based on the energy difference between HOCO and HC(O)O [7–10], formation of HC(O)O from $Cl + HCOOH$ would be just thermoneutral. The HC(O)O would undergo rapid unimolecular dissociation to $H + CO_2$.

The rate constant for reaction (2) could be estimated to be of the order of 10^{10} cm^3/mol · s. Therefore, a large excess ratio of HCOOH had to be used to avoid secondary reactions ($[HCOOH]/[Cl]_0 \geqq 10^4$). The Cl atoms resulted from the reaction of HCl with F atoms [18],

$$F + HCl \rightarrow HF + Cl, \qquad (3)$$

which were generated by dissociating traces of F_2 diluted in He ($[F_2]/[He] \leqq 10^{-4}$) in a microwave discharge in an alumina tube at the upper end of the injector. Helium served as inert carrier gas. O_2 could be admixed to the gas flow in high excess compared to the HOCO at the upper end of the main flow tube.

All gases were of the highest commercially available purities (He: 99.9999%, Praxair; Ar: 99.9999%, Praxair; O_2: 99.996%, 2% premixed in He, Messer-Grießheim; HCOOH: 98–100%, Merck). The O_2/He mixture was checked mass spectrometrically. Gases passing through the microwave discharge were further purified using a series of liquid-N_2-cooled traps. The flow rates of HCl and F_2 were controlled using needle valves and determined from the pressure rises in calibrated volumes. The other flow rates were regulated with calibrated mass flow controllers (Tylan). The HCOOH was taken from a two-stage temperature controlled saturator by bubbling He gas through the liquid. Its flow rate was determined from the vapor pressure.

HOCO was monitored with the LMR employing a laser line in CH_3OD vapour at $\lambda = 515$ µm and $B_0 = 0.007$ Tesla with π-polarization of the electric field vector of the laser radiation relative to the magnetic field [14]. The detection limit at a signal-to-noise ratio of $S/N = 1$ was approximately $6 \cdot 10^9$ molecules/cm^3. The products HO_2 and OH could be observed at $\lambda = 163$ µm and $B_0 = 0.23$ and 0.38 Tesla, respectively, with σ-polarization [19, 20].

3. Results

The rate constant for the reaction

$$HOCO + O_2 \rightarrow HO_2 + CO_2 \qquad (1)$$

was determined under pseudo first-order conditions by monitoring the decay of the HOCO concentration as a function of the injector position in the flow tube in the absence and presence of a large excess of O_2 molecules.

The measurements were carried out at a temperature of $T = 296$ K and pressures around $p \approx 2.0$ mbar. The initial HOCO concentrations were kept in the range $2 \cdot 10^{-13}$ to $6 \cdot 10^{-13}$ mol/cm^3 (depending on the initial F concentrations) so that the influence of possible secondary reactions was small. The effective rate constants describing the HOCO depletion in the absence of other reactants were found to be around (20 ± 5) s^{-1}, depending somewhat on the experimental conditions. The concentrations of the O_2 reactant were varied over one order of magnitude up to $3 \cdot 10^{-10}$ mol/cm^3, corresponding to excess ratios of $[O_2]/[HOCO] > 100$. The experimental conditions are summarized in Table 1.

Figure 1 shows some typical semilogarithmic HOCO decay plots measured for three different O_2 concentrations. These plots could be represented by

Table 1. Experimental results of the overall rate constant for the reaction HOCO + O_2 → products (1)[a].

$\bar{v}$ [m/s]	$[F]_0$ $\left[10^{-13}\,\frac{mol}{cm^3}\right]$	[HCOOH] $\left[10^{-9}\,\frac{mol}{cm^3}\right]$	$[O_2]$ $\left[10^{-10}\,\frac{mol}{cm^3}\right]$	$k_1 \cdot [O_2]$ [1/s]	k_1 $\left[10^{11}\,\frac{mol}{cm^3}\right]$
21.1	2.79	9.55	0.29	29	9.90
21.3	4.44	9.45	0.45	45	9.91
20.7	4.89	9.78	0.59	60	10.15
27.9	3.69	7.22	0.76	75	9.84
20.8	4.83	9.66	1.45	143	9.87
20.6	5.17	9.79	2.35	228	9.71
20.8	5.12	9.69	2.76	275	9.96

[a] All measurements were carried out at a temperature of $T = 296$ K and pressures around $p \approx 2.0$ mbar.

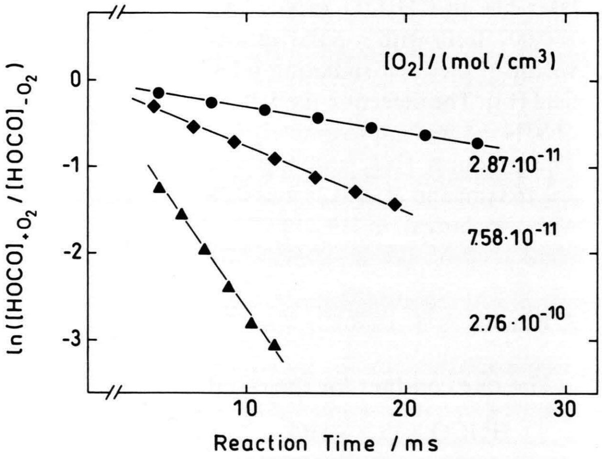

Fig. 1. Representative HOCO pseudo first-order decay plots for three different O_2 concentrations.

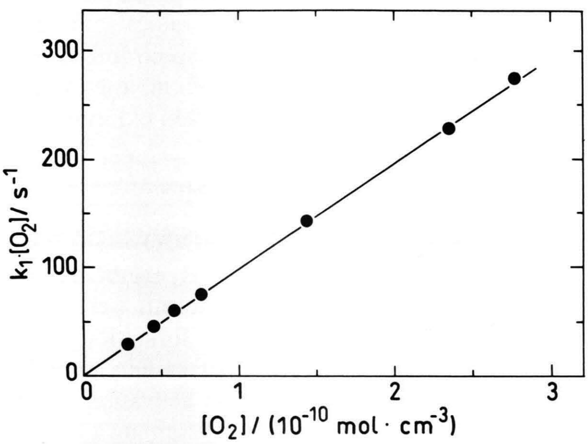

Fig. 2. Measured first-order rate constants for reaction (1) plotted versus $[O_2]$.

nice straight lines over the whole range of conditions covered without indications for deviations from pseudo first-order behaviour.

The first-order rate constants which were obtained from the slopes of these lines are plotted versus the O_2 concentrations in Figure 2. The data points in this figure are described by a straight line through the origin. The slope of this plot yields a value for the rate constant of reaction (1) of

$$k_1 = (9.9 \pm 1.5) \cdot 10^{11}\ \mathrm{cm^3/mol \cdot s}.$$

The quoted error limits include the 2σ uncertainty limit as well as estimated systematic errors.

4. Discussion

In addition to the HOCO radicals, HO_2 and OH radicals could be detected in the reaction system under the same experimental conditions. From the ratio of the detection sensitivities for HO_2 and OH with the LMR, determined using the reactions $F + H_2O_2$ and $F + H_2O$, the absolute concentration of OH was found to be at least two orders of magnitude below that of HO_2. The HO_2 is produced as a direct product of reaction (1),

$$HOCO + O_2 \rightarrow HO_2 + CO_2,\ \Delta_R H^0_{298} = -156\ \mathrm{kJ/mol}. \tag{1 a}$$

The rise of the measured HO_2 concentrations as a function of reaction time could be represented by a first-order rate law with rate constants similar to those obtained from the HOCO profiles. A comparison of the absolute concentrations of HOCO and HO_2 indicated that HO_2 must be the main product.

Formation of a collisionally stabilized peroxy addition complex according to

$$HOCO + O_2 \xrightarrow{+M} HOC(O)O_2 \tag{1 b}$$

should not play a main role at the low pressures used. However, without further information on the stability of the $HOC(O)O_2$ complex, this possibility cannot be ruled out a priori for atmospheric pressures.

Pertaining to the observed formation of very small concentrations of OH, direct channels such as

$$HOCO + O_2 \rightarrow OH + CO_3, \quad \Delta_R H^0_{298} = +90\ \mathrm{kJ/mol}, \qquad (1\,c),$$

$$HOCO + O_2 \rightarrow OH + CO_2 + O, \quad \Delta_R H^0_{298} = +118\ \mathrm{kJ/mol}, \qquad (1\,d)$$

are highly endothermic and cannot play a role here. However, formation of small amounts of OH in the reaction system could result from secondary reactions. In particular, the HO_2 formed in reaction (1 a) may react with HOCO. This reaction might be fast and could produce OH according to

$$HO_2 + HOCO \rightarrow OH + OH + CO_2, \quad \Delta_R H^0_{298} = -122\ \mathrm{kJ/mol}. \qquad (4)$$

Furthermore, minor concentrations of H atoms from HC(O)O formed in the Cl + HCOOH source reaction could generate OH via their fast reaction with HO_2 [21],

$$H + HO_2 \rightarrow OH + OH. \qquad (5)$$

Being radical-radical reactions, (4) and (5) are slow at the low initial HOCO concentrations used. Nevertheless, numerical simulations indicated that they can explain the observed OH.

The OH radicals could lead to a reformation of HOCO in the reaction system according to

$$OH + HCOOH \rightarrow HOCO + H_2O, \qquad (6\,a)$$

$$OH + HCOOH \rightarrow HC(O) + H_2O. \qquad (6\,b)$$

However, it is emphasized that, under the conditions used, reactions (4)–(6) cannot affect the result for the rate constant for reaction (1) to a significant degree. First, reaction (6 a) would just compensate for the extra loss of HOCO via reaction (4). Second, the experimental conditions were chosen such that $k_1 \cdot [HOCO] \cdot [O_2] \gg k_4 \cdot [HOCO] \cdot [HO_2]$. Assuming a reasonable upper limit for k_4 of $\approx 5 \cdot 10^{13}\ \mathrm{cm^3/mol \cdot s}$, this is fulfilled for $[O_2]/[HOCO]_0 \gg k_4/k_1 \approx 50$. With values up to $[O_2]/[HOCO]_0 > 500$ at the highest O_2 concentrations used, the experimental conditions were on the safe side. Third, contributions of reactions (5) and (6) would lead to strong deviations of the measured HOCO decay profiles from pseudo first-order behaviour, for which there were no indications. Thus, the influence of reactions (4)–(6) on the value for k_1 should remain within the quoted uncertainty limits.

Eventually, the present result for the rate constant of reaction (1) can be compared to that obtained by Moore and coworkers [16]. These authors generated HOCO radicals by 193 nm photodissociation of acrylic acid and monitored their decay in the presence of O_2 by detecting infrared absorption transitions. The rate constants of the reaction were measured to be $k_1 = 1.1 \cdot 10^{12}$ and $1.3 \cdot 10^{12}\ \mathrm{cm^3/mol \cdot s}$ with CF_4 and CO_2 as buffer gases, respectively. These values and the result of the present study are in good agreement.

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