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(NASA-TM-80666) RATE CONSTANT FOR THE
REACTION OF HYDROXYL RADICAL WITH
FORMALDEHYDE OVER THE TEMPERATURE RANGE
228-36 K (NASA) 17 p HC A02/MF A01 CSCL 07D

N80-21463

Unclas
G3/25 18140



Technical Memorandum 80666

Rate Constant for the Reaction of Hydroxyl Radical with Formaldehyde Over the Temperature Range 228-362 K

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MARCH 1980

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Space Administration

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FORMALDEHYDE OVER THE TEMPERATURE RANGE 228-362 K

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ABSTRACT

Absolute rate constants for the reaction $\text{OH} + \text{H}_2\text{CO}$ have been measured over the temperature range 228-362K using the flash photolysis-resonance fluorescence technique. The results were independent of variations in $[\text{H}_2\text{CO}]$, total pressure $[\text{Ar}]$ and flash intensity (i.e., initial $[\text{OH}]$). The rate constant was found to be invariant with temperature in this range, the best representation being $k_1 = (1.05 \pm 0.11) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ where the error is two standard deviations. This result is compared with previous absolute and relative determinations of k_1 . The reaction is also discussed from a theoretical point of view.

INTRODUCTION

The reaction of the hydroxyl radical with formaldehyde is of interest in high temperature combustion studies,¹ in an explanation for CO formation in the atmosphere of Jupiter,² and in methane oxidation in the troposphere and stratosphere of the earth.³ In all these instances, H_2CO is a product of hydrocarbon oxidation. For the Jovian atmosphere, it is proposed that H_2CO is formed primarily in the reaction $\text{O} + \text{CH}_3$. Loss processes include photolysis² and reaction with H and OH.^{2a} In the stratosphere, H_2CO is formed as a product of the low temperature oxidation of atmospheric methane. It is removed by photolysis and by reaction with OH, O and Cl. The reactions $\text{O} + \text{H}_2\text{CO}$ and $\text{Cl} + \text{H}_2\text{CO}$ are relatively minor loss processes for formaldehyde at most altitudes in the stratosphere.⁴ Rate constant measurements for these reactions have been recently reported by us as well as other workers.^{5,6} Reaction with OH is a major sink for H_2CO at all altitudes in the upper atmosphere,⁴ but there have been no direct measurements of the absolute rate constant at the low temperatures prevailing there.

The mechanism of the reaction has been usually assumed to be H atom abstraction



although there is little or no direct evidence for this. Recently, Horowitz

et al.⁷ have proposed the additional reaction channel



Additional work is required to test the validity of this suggestion.

Room temperature measurements of the absolute rate constant for the reaction



have been made using the discharge flow-mass spectrometric technique (DF-MS) with OH in excess^{8,9} and by the flash photolysis-resonance fluorescence technique (FP-RF) with H₂CO in excess.¹⁰ Herron and Penzhorn⁸ obtained a lower limit $k_1 \geq 0.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Morris and Niki⁹ give $k_1 = (1.4 \pm 0.3_5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and Atkinson and Pitts¹⁰ report $k_1 = (0.94 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, all at $298 \pm 2 \text{ K}$. There have been three relative rate constant determinations at room temperature. Morris and Niki,¹¹ using the DF-MS technique, measured OH + H₂CO relative to OH + C₃H₆ and obtained the result $k_1 = (1.5 \pm 0.1_5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Niki et al.¹² employed Fourier Transform Infra-red Spectroscopy (FTIR) with OH + C₂H₄ as the reference reaction and obtained $k_1 = (1.5 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Smith¹³ measured OH + H₂CO relative to OH + OH using the DF-MS technique and reports $k_1 = 0.65 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

There have been only two variable temperature studies of the reaction, one absolute¹⁰ and one relative.¹³ Atkinson and Pitts¹⁰ give $k_1 = 1.25 \times 10^{-11} \exp(-88 \pm 150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the temperature interval 299 to 426 K while Smith's¹³ results from 268 to 334 K may be represented by $k_1 = 6 \times 10^{-11} \exp(-635 \pm 250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This later study is the only one below room temperature but its usefulness is considerably reduced by the fact that the rate parameters of the reference reaction OH + OH are far more uncertain than those for OH + H₂CO itself.

An inspection of the available rate data thus shows disagreement by a factor of two at room temperature, a factor of five in the Arrhenius

pre-exponential factor and a factor of seven in the activation energy. All of these are well beyond any reasonable estimates of error. Further, as noted above, there are no reliable rate data at low temperatures. Because of these discrepancies and the need for low temperature rate data for atmospheric modeling, we have undertaken the present study. We report here absolute rate constant measurements over the temperature range 228-362 K.

EXPERIMENTAL

The present experiments were performed by the flash photolysis-resonance fluorescence (FP-RF) technique. The apparatus and specific techniques are quite similar to those reported previously;^{14,15} however, we have replaced the reaction cell and vacuum housing assembly.

The new cell is a black teflon coated brass cylinder whose internal dimensions are three inches in diameter and three inches in length. Fluorescence is observed coaxially in the center of one end wall of the cylinder. Honeycomb baffling occupies the other end of the cylinder. Resonance and flash lamp radiation enter the cell at right angles both to each other and to the detection port on the cylinder surface at about one and a quarter inches from the detection end wall. Optically flat windows or lenses (0.75 inch aperture) are compression sealed to the cell through either Viton or silicone rubber "O" rings. The cell has entrance and exit tubes for premixed gas flows. Also entrance and exit tubes are attached for cooling gas. The cell has eight interconnected and equally spaced one sixteenth inch channels through the brass wall to provide a continuous path for the cooling gas. In addition it has eight equally spaced connected channels to accommodate an insulated nicrome heating element. Temperature is measured by a chromel-alumel thermocouple which is positioned inside the cell near the fluorescence volume but out of the line of sight of the photomultiplier which detects the resonantly scattered photons. The cell assembly is placed inside a brass vacuum chamber which has optical access ports for detection, resonance light, and photolysis light admission. Thus, this newly constructed equipment, while retaining all of the functions of the previous design, has as its principal advantage significantly lower scattered background light compared to the earlier cell.

For the reported experiments, the source of OH radicals is flash photolysis of water. OH resonance radiation ($\lambda = 306 \text{ nm}$) is produced from a water saturated discharge in Ar at 17 torr. This radiation is highly collimated and slightly focused by a lens and collimator system before entering the cell. The fluorescent photons are collected and focused by a lens-collimator-interference filter (Ditric Optics, Inc., 310 nm, FWHM = 11 nm) optical system onto an EMR 541 N photomultiplier tube. The fluorescent photons are recorded in repetitive flashes by a multichannel analyzer operating in the multiscaling mode. The photoflash light is also spectrally isolated by a Ditric Optics, Inc. interference filter centered at 157.5 nm with a skewed FWHM of -13 and +25 nm, the maximum transmittance being 28%. This filtering technique also has the added advantage of decreasing the scattered light due to photoflash interference. The initial yield of OH from the photodecomposition of H_2O using this filter was 19% of that obtained using a LiF window ($\lambda > 105 \text{ nm}$). This factor reflects the spectrally integrated effects of wavelength dependent transmission, H_2O absorption, and photoflash intensity. We roughly estimate from a consideration of these factors and yields of H from H_2O photolysis, that initial $[\text{OH}]$ is about $1 \times 10^{11} \text{ cm}^{-3}$ for these experiments.

The experiments, and particularly the handling of H_2CO , were carried out in a similar way as described previously.⁶ We found no unusual behavior with $\text{H}_2\text{O}-\text{H}_2\text{CO}-\text{Ar}$ mixtures as long as the flow rate of the premixed ternary mixture was sufficiently high. The present cell is larger than that in our previous investigations, and we estimate that the contents of our new cell are completely replenished every 2-3 flashes.

Experiments were carried out at four temperatures from 228-362 K with substantial variations of $[\text{H}_2\text{CO}]$ and total pressure. Due to the presence of the interference filter in the photoflash optical path and a practical upper limit on flash intensity, the variation of flash intensity is somewhat limited compared to that used in other studies from this laboratory. Over this limited range, however, no flash intensity effects were observed. Experiments were performed with and without added $[\text{H}_2\text{CO}]$ in order to assess the diffusional loss corrections for OH. The observed pseudo-first-order OH radical decay plots were strictly linear under both conditions, and the

diffusional corrections were typically less than 15% except for some experiments at 362 K where this contribution was 35%.

Argon (Matheson, 99.9995%) for mixture preparation and Argon (Goddard grade, water pumped) for the resonance lamp were both used without further purification. Deionized water was used as received in the discharge resonance lamp but was bulb to bulb distilled, the middle fraction being retained, for mixture preparation. Formaldehyde was prepared from paraformaldehyde as described previously.^{6a} Mass spectral analysis showed the sample to be 99.7% pure with water being the only measurable impurity.

RESULTS

Under the pseudo-first-order conditions employed in this study, with $[H_2CO] \gg [OH]$, the decay of OH radicals is given by

$$\ln[OH] = -k_{\text{observed}} t + \ln[OH]_0 \quad (2)$$

The observed pseudo-first-order decay constant is represented by

$$k_{\text{observed}} = k_1 [H_2CO] + k_d \quad (3)$$

where k_1 is the bimolecular rate constant for reaction (1), and k_d is the first-order rate constant for OH radical diffusion from the reaction volume viewed by the photomultiplier. k_{observed} and k_d are obtained by linear least squares methods from plots of the logarithm of accumulated counts against time, where accumulated counts are proportional to $[OH]$. Typical results for the reaction at 228 K are shown in Figure 1. Values of k_1 were calculated from k_{observed} according to equation (3). The values obtained for k_1 are reported in Table 1 for the various conditions employed in this study. At each temperature, experiments were performed with variations in total pressure, $[H_2CO]$, and flash intensity. The errors are one standard deviation values as determined from repeat determinations at the indicated experimental condition. The flash energies reported are the effective flash energies entering the cell through the 157.5 nm interference filter. The results show that k_1 is invariant with temperature over the range of $228 \leq T \leq 362$ K. The

best representation for this temperature range is $k_1 = (1.05 \pm 0.11) \times 10^{-11}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where the error is twice the standard deviation of the mean.

DISCUSSION

The earlier results for k_1 have been reviewed in the Introduction. The present result at 298 K, $k_1 = (0.99 \pm 0.11) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is in excellent agreement with that of Atkinson and Pitts¹⁰ who report $(0.94 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These workers used the same technique as the present (FP-RF).

Results reported at this temperature from absolute^{8,9} and relative^{11,13} DF-MS measurements at low pressure suggest a k_1 value ~30-50% higher^{8,9,11} and ~35% lower¹³ than those obtained by FP-RF. The relative FTIR result of Niki et al.,¹² which employs an entirely different type of experimental system, is in closer agreement with the discharge flow than with the FP-RF results. Thus, a disagreement, which may arise from unknown systematic errors, exists for this reaction at 298 K.

The present result, $k_1 = (1.05 \pm 0.11) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $228 \leq T < 362$ K, extends those of Atkinson and Pitts¹⁰ who report $(0.94 \pm 0.10) \times 10^{-11}$, $(0.94 \pm 0.10) \times 10^{-11}$ and $(1.03 \pm 0.11) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299, 356, and 426 K, respectively. Although these authors preferred to represent their data by the temperature dependent expression, $k_1 = 1.25 \times 10^{-11} \exp(-88 \pm 150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the individual values differ amongst themselves by less than the error at any of their experimental temperatures. Thus, a simple average is an adequate representation. If the present results and those of Atkinson and Pitts¹⁰ are combined, the rate constant can be best represented by $k_1 = (1.01 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $228 \leq T \leq 426$ K. This result is to be contrasted to the only other temperature dependent study, that of Smith,¹³ which leads to $k_1 = 6 \times 10^{-11} \exp(-635 \pm 250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This disagreement probably arises, at least in part, from the fact that k_1 was measured relative to the reaction



and the temperature dependence of this reaction is virtually unknown over the temperature range of interest here (i.e., 200-500 K). Although recent reviews¹⁶ suggest an Arrhenius expression for k_4 consistent with that used by Smith,¹³ it must be emphasized that these are all based on a measured value of k_4 at 300 K and an estimated activation energy. The older review by Baulch et al.¹⁷ gives the most detailed summary of the bases for the various estimates including their own.

It therefore appears that reaction (1) occurs with no energy barrier and possibly through two reactive channels,



reactions (1a) and (1b) being exothermic by 34 and 22 kcal/mole, respectively. Path (a) can be considered to be concerted whereas path (b) undoubtedly would require the formation of an adduct as in the isoelectronic case, $\text{OH} + \text{C}_2\text{H}_4$,^{16b} forming the radical species, HOCH_2O . An important question is whether this radical is formed with excess vibrational energy (i.e., chemically activated) because then the re-dissociation to $\text{OH} + \text{H}_2\text{CO}$, in competition with dissociation to other products and collisional stabilization, becomes a possibility. Pressure dependence in k_1 might then be possible. The heat of formation of the adduct can be estimated from that of $\text{CH}_2(\text{OH})_2$ ¹⁸ on the assumption that the OH bond strength is ~ 105 kcal/mole. Then the calculation for the enthalpy change from reactants to adduct yields a value of ~ -22 kcal/mole. Even though this estimate is uncertain, the adduct, if it is formed, could be vibrationally excited. If the energy barrier from adduct to $\text{HCOOH} + \text{H}$ (path(b)) is lower lying than that for re-dissociation to reactants, pressure dependence might not be observable. It is also possible that the concerted path (a) could arise from such an excited adduct although the direct $\text{HO}-\text{H}-\text{C}$ abstraction path seems more plausible. Clearly the present results give no preference as to which reaction channel dominates.

In an attempt to understand the present experimental results, we have carried out theoretical calculations with absolute reaction rate theory where

k_1 is given by:

$$k_1 = \frac{kT}{h} \frac{q^\ddagger}{q_{\text{H}_2\text{CO}} q_{\text{OH}}} e^{-E/RT} \quad (5)$$

Our approach in this case is not to use the BEBO method in order to specify configuration and energy, since the parameters would have to be adjusted (parameterized triplet repulsion) in order to gain the experimental result that $E = 0$. Rather, we ask what do the experimental results imply about the activated complex?

Eq. (5) has been evaluated with known partition functions and the result is

$$k_1 = (1.70 \times 10^{-10}/T^{3/2}) q_v^\ddagger [(ABC)^\ddagger/(ABC)_F]^{1/2} \quad (6)$$

where A, B, and C are the principal moments of inertia for the activated complex and formaldehyde, and q_v^\ddagger is the vibrational partition function for the activated complex (note that $q_{\text{vH}_2\text{CO}}$ and q_{vOH} are both unity over the present temperature range). Since there is the above noted uncertainty about reaction paths, we have considered two models for the activated complex, (1) HO--H--CHO where the forming and breaking bonds are colinear, and (2) HO--CH₂O where the forming bond results in a tetrahedral structure. Moments of inertia were calculated for these complexes as a function of the parameter, r, where r is the HO--H bond distance in model (1) and is the HO--C bond distance in model (2). The results for model (1) are that $[(ABC)^\ddagger/(ABC)_F]^{1/2}$ has values of 17, 23, 37, and 56 at $r = 1.5, 2.0, 3.0$ and 4.0 \AA , respectively. For the tighter model (2), the respective values are 8, 12, 24, and 40. Thus, for either model with the known value for k_1 , q_v^\ddagger can be evaluated for the four experimental temperatures of the present study. In most ART calculations two low lying bending vibrations in the activated complex make the largest contribution to q_v^\ddagger . On the assumption that these are degenerate, values can be calculated for each model so that agreement with experiment is obtained. The calculations are obviously parametric and therefore cannot be used to indicate a preference for paths (a) and (b). Briefly, the allowed value for

the bending vibration is very low for the close interaction ($r = 1.5 \text{ \AA}$, ν_b is 55 and 35 cm^{-1} for models (1) and (2), respectively) and increases to higher values for longer interaction ($r = 4.0 \text{ \AA}$, ν_b is 115 and 90 cm^{-1} for models (1) and (2), respectively). Since it is generally true that bending force constants are greater (and ν_b is larger) for tight complexes, either tight complex ($r = 1.5 \text{ \AA}$) would not be indicated. In fact, the exercise suggests that in order to tolerate such a large temperature independent rate constant, the complex must be quite loose so that "reasonable" values of bending frequencies are allowed.

Lastly, reaction (1) occurs in several systems of environmental importance. As mentioned in the Introduction, it plays a significant role in high temperature combustion systems and low temperature atmospheric phenomena. A recent review¹⁹ of kinetic data for methane-air combustion suggests that $k_1 = 8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1500 K. The increase over the value $k_1 = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, recommended here for $228 \leq T \leq 426 \text{ K}$, is probably not unreasonable nor unexpected considering the large temperature interval. Rate studies over the range 500-1500 K are now feasible using high temperature fast flow systems^{20,5b} and would bridge the gap between the presently available low and high temperature studies. The impact of the present results for low temperature atmospheric modeling is that the rate of H_2CO loss by reaction with OH is now shown to be greater than expected from previous studies. Thus at 228 K, which corresponds to an altitude of 25 km in stratospheric modeling calculations, extrapolation of the Atkinson and Pitts¹⁰ data leads to an underestimate of k_1 by about 20%. A far more serious discrepancy arises from Smith's¹³ study since use of the Arrhenius expression derived from his data results in a value of k_1 at 228 K which is a factor of three lower than the present observation at that temperature.

ACKNOWLEDGMENT:

J.V.M. acknowledges support by NASA under Grant NSG 5173 to Catholic University of America.

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FIGURE CAPTION

Figure 1. Examples of reaction- \ominus , and diffusion- \blacksquare , first order decay plots at $T = 228$ K. The lines are from linear least squares analysis of the data points. Both experiments were carried out at a flash energy of 52 J, a total pressure of 30 torr, and $P_{\text{H}_2\text{O}} = 60$ mtorr. $P_{\text{H}_2\text{CO}} = 0.94$ mtorr for the reaction experiment. $k_{\text{observed}} = 487 \pm 26 \text{ s}^{-1}$ and $k_d = 30 \pm 2 \text{ s}^{-1}$.

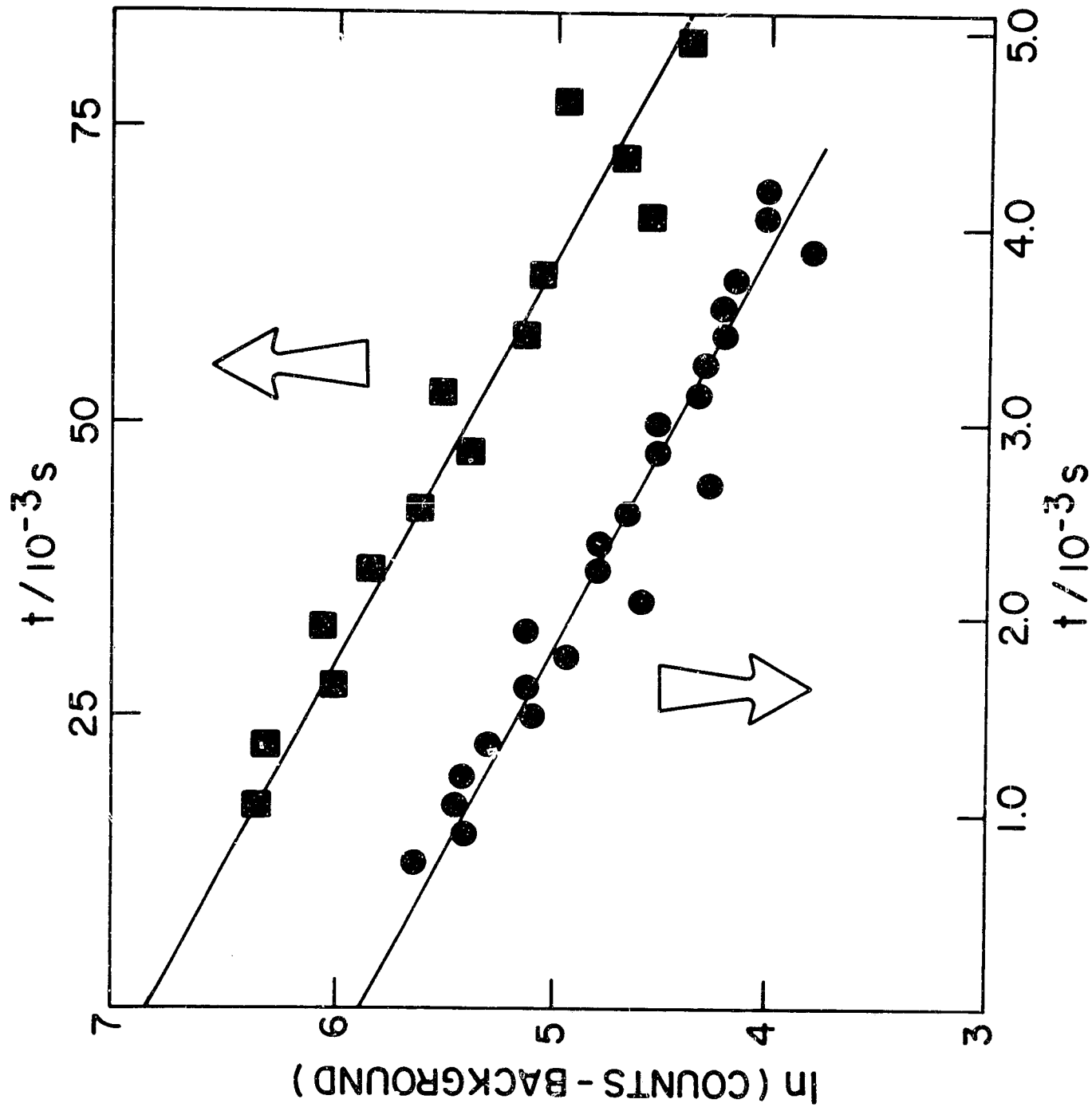


Table 1. Rate data for the flash photolysis-resonance fluorescence study of the reaction $\text{OH} + \text{H}_2\text{CO}$

| T (K) | [H ₂ CO] (mTorr) | [H ₂ O] (mTorr) | [Ar] (torr) | Flash energy ^a (J) | No. of expts. | k ₁ ^b |
|----------|--------------------------------|-------------------------------|----------------|----------------------------------|------------------|---|
| | | | | | | (10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹) |
| 228 | 0.50 | 40 | 20 | 24 - 35 | 5 | 11.23 ± 1.56 |
| | 0.63 | 40 | 20 | 47 - 52 | 3 | 11.30 ± 0.17 |
| | 0.94 | 60 | 30 | 52 | 1 | 11.60 |
| | 1.00 | 80 | 40 | 11 - 35 | 5 | 11.09 ± 0.77 |
| | | | | | 14 | 11.22 ± 0.98 ^c |
| 257 | 0.63 | 40 | 20 | 43 - 57 | 3 | 10.20 ± 1.16 |
| | 0.76 | 40 | 20 | 47, 52 | 2 | 10.13 ± 1.46 |
| | 0.94 | 60 | 30 | 39, 47 | 2 | 10.17 ± 0.22 |
| | 1.14 | 60 | 30 | 43 | 2 | 9.48 ± 0.48 |
| | 1.25 | 80 | 40 | 43 | 1 | 10.48 |
| | 1.52 | 80 | 40 | 43 | 2 | 11.38 ± 0.26 |
| | | | | | 12 | 10.28 ± 0.90 ^c |
| 298 | 1.00 | 40 | 20 | 43, 59 | 2 | 9.94 ± 0.74 |
| | 1.13 | 60 | 30 | 43, 55 | 2 | 9.42 ± 0.48 |
| | 1.50 | 60 | 30 | 36 - 55 | 3 | 10.28 ± 0.93 |
| | 1.00 | 80 | 40 | 43, 57 | 2 | 8.12 ± 0.70 |
| | 2.00 | 80 | 40 | 21 - 57 | 3 | 10.08 ± 0.94 |
| | 1.69 | 90 | 45 | 45 | 1 | 8.74 |
| | 1.50 | 120 | 60 | 21 - 58 | 4 | 9.23 ± 1.08 |
| | 2.25 | 120 | 60 | 31 - 52 | 4 | 10.28 ± 1.34 |
| | 2.00 | 160 | 80 | 21 - 57 | 4 | 10.93 ± 0.72 |
| | | | | | 25 | 9.86 ± 1.13 ^c |
| 362 | 0.62 | 20 | 20 | 24, 39 | 2 | 8.55 ± 0.56 |
| | 0.94 | 40 | 20 | 43, 52 | 2 | 11.29 ± 1.22 |
| | 1.23 | 40 | 20 | 24, 39 | 2 | 10.51 ± 3.25 |
| | 0.92 | 30 | 30 | 24, 39 | 2 | 11.58 ± 1.44 |
| | 1.41 | 60 | 30 | 43, 52 | 2 | 10.09 ± 2.28 |
| | 1.85 | 60 | 30 | 24, 39 | 2 | 10.66 ± 0.89 |
| | 1.23 | 40 | 40 | 24 - 43 | 4 | 10.50 ± 0.38 |
| | 1.88 | 80 | 40 | 43, 52 | 2 | 9.58 ± 2.03 |
| | 2.47 | 80 | 40 | 24, 39 | 2 | 11.33 ± 1.81 |
| | | | | | 20 | 10.46 ± 1.50 ^c |

^a 157.5 nm filter on flash lamp
^b Error limit in k₁ is one standard deviation
^c Mean value of k₁ at that temperature

BIBLIOGRAPHIC DATA SHEET

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|---|---|---|------------|
| 1. Report No. TM 80666 | 2. Government Accession No. | 3. Recipient's Catalog No. | |
| 4. Title and Subtitle Rate Constant for the Reaction of Hydroxyl Radical with Formaldehyde Over the Temperature Range 228-362 K | | 5. Report Date March 1980 | |
| | | 6. Performing Organization Code 691 | |
| 7. Author(s) L. J. Stief, D. F. Nava, W. A. Payne, J. Michael | | 8. Performing Organization Report No. | |
| 9. Performing Organization Name and Address Goddard Space Flight Center Greenbelt, Maryland 20771 | | 10. Work Unit No. | |
| | | 11. Contract or Grant No. | |
| 12. Sponsoring Agency Name and Address | | 13. Type of Report and Period Covered Technical Memorandum | |
| | | 14. Sponsoring Agency Code | |
| 15. Supplementary Notes | | | |
| 16. Abstract Absolute rate constants for the reaction $\text{OH} + \text{H}_2\text{CO}$ have been measured over the temperature range 228-362 K using the flash photolysis-resonance fluorescence technique. The results were independent of variations in $[\text{H}_2\text{CO}]$, total pressure $[\text{Ar}]$ and flash intensity (i.e., initial $[\text{OH}]$). The rate constant was found to be invariant with temperature in this range, the best representation being $k_1 = (1.05 \pm 0.11) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ where the error is two standard deviations. This result is compared with previous absolute and relative determinations of k_1 . The reaction is also discussed from a theoretical point of view. | | | |
| 17. Key Words (Selected by Author(s)) | | 18. Distribution Statement | |
| 19. Security Classif. (of this report) U | 20. Security Classif. (of this page) U | 21. No. of Pages 15 | 22. Price* |