Reaction between NO₃ and CH₂O in Air: A Determination of the Rate Constant at $295 \pm 2 K$

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The reaction between NO₃ and CH₂O was studied in a 450-L glass/Teflon chamber by using FT-IR spectroscopy as the analytical technique. NO3 was obtained in equilibrium with N2O5 introduced from evaporation of the solid phase into the cell or generated in the cell itself by reacting NO₂ with O₃. Experiments were performed in both cases at 295 ± 2 K and 740 Torr in purified air. ¹³CH₂O was used to avoid spurious effects on the measured CO; ¹³C¹⁸O was introduced to estimate the OH radical concentration in the system from the buildup of the oxidation product ¹⁶O¹³C¹⁸O. ¹³CH₂O, ¹³C¹⁶O, N₂O₅, O3, NO2, and H13COOH time-dependent concentrations were measured and the data fitted on the basis of a model involving 31 reactions, with the aid of the FACSIMILE computer program. A rate constant for the reaction $NO_3 + CH_2O$ equal to (5.4) \pm 1.1) × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹, at 295 \pm 2 K and 740 Torr, has been obtained assuming for the reactions N₂O₅ $\pm M$ NO₃ + NO₂ an equilibrium constant equal to 5.3 × 10¹⁰ molecules cm⁻³. Significant differences have been found between the measured concentrations of OH and HCOOH with respect to those predicted by the model. In the framework of this study, the absolute strength of the ν_6 band of H¹²COOH (1045-1150 cm⁻¹) has been measured equal to (3.48 ± 0.5) × 10⁻¹⁷ cm molecule⁻¹.

Introduction

The nitrate radical NO_3 , generated in the atmosphere by several photochemical and chemical processes, is rapidly destroyed by photolysis during the day. At nighttime, however, produced by the reaction of NO_2 with O_3 , it builds up to concentrations which have been measured to range from less than 1 pptv in clean air¹ up to hundreds of pptv in polluted tropospheric air.² NO_3 is recognized to react with several chemical species which are present as trace components in the atmosphere; in recent years, efforts have been made to study kinetics and mechanisms of these reactions in order to evaluate their role in atmospheric chemistry.

The reaction between NO₃ and CH₂O has recently been studied in laboratory experiments by two groups;^{3,4} in both cases the mechanism of the reaction is assumed to proceed via hydrogen abstraction

$$CH_2O + NO_3 \rightarrow CHO + HNO_3$$
 (1)

followed in air by

$$CHO + O_2 \rightarrow HO_2 + CO$$
 (2)

In ref 3 N_2O_5 was introduced in the reaction chamber and NO_3 generated from the thermal equilibrium

$$N_2O_5 \xrightarrow{+M} NO_3 + NO_2$$
 (3)

reacted with excess CH₂O in air. The enhanced decay of N₂O₅ in the presence of CH₂O was attributed to reaction 1, and a rate constant k_1 equal to $(3.23 \pm 0.26) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 760 Torr and 298 K was derived accordingly. NO3 radical concentrations were not directly measured but calculated from reaction 3 with an equilibrium constant equal to 5.4×10^{10} molecules cm^{-3,5} More recently, an increase of the rate constant for reaction 1 to $(5.8 \pm 0.47) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ has been suggested by the same authors⁶ as resulting from the use of a revised value for the equilibrium constant equal to 2.99×10^{10} molecules cm^{-3} (average of data measured in ref 7 and 8).

 O_3 - NO_2 - CH_2O in N_2/O_2 at 700 Torr and 298 K was used in the experiments of ref 4; NO₃ was generated from the reaction $NO_2 + O_3 \rightarrow NO_3 + O_2$ being rapidly in equilibrium with N_2O_5 . The kinetic data were analyzed by using both rates of product formation and reactant removal and computer simulations of a complex chemical scheme involving a total of 35 reactions to account for the chemistry due to generation of secondary radicals (OH, O_2H) following the primary reaction (1). Some of the experiments were performed with a direct determination of the NO3 radical concentration; otherwise this parameter was calculated from reaction 3 by using for the equilibrium constant a value equal to 5.33×10^{10} molecules cm⁻³. The overall average of all the data derived by three different estimates of k_1 obtained from each one of the nine experiments gave a value equal to (6.3 ± 1.1) $\times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ with a substantial agreement between the rate constants derived by using direct or indirect determinations of the NO₃ radical concentration.

In this study, either N_2O_5 or $NO_2 + O_3$ was employed in different experiments as a source of NO3 radicals; long-path infrared absorption FT spectroscopy was used to measure the concentrations of N2O5, NO2, HNO3, O3, CH2O, CO, and HCOOH in the system. NO3 concentrations were calculated from reactions 3 assuming a value for the equilibrium constant equal to 5.3×10^{10} molecules cm^{-3.9}

Isotopically labeled CH₂O (¹³CH₂O) was reacted with NO₃ to improve the specificity in the determination of the reaction product ¹³C¹⁶O. In addition, taking advantage of the nonreactivity of CO with NO₃,^{10 13}C¹⁸O was added to the system to derive an estimate of the OH radical concentration from the measurement of its oxidation product ${}^{16}O{}^{13}C{}^{18}O$. The measured time-dependent concentrations were computer-modeled, using the FACSIMILE program developed at Harwell,¹¹ on the basis of a scheme of 31 reactions taken from ref 4. From this analysis the rate constant for reaction 1 was obtained to be equal to $(5.4 \pm 1.1) \times 10^{-16} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 295 \pm 2 K and 740 Torr.

The use of either N_2O_5 or $NO_2 + O_3$ allowed us to compare the effects of these two different sources of NO3 radicals; the estimate of the OH radical concentration offered another pa-

Noxon, J. F. J. Geophys. Res., C: Oceans Atmos. 1983, 88, 11017.
 Platt, U.; Perner, D.; Winer, A. M.; Harris, G. W.; Pitts, J. N., Jr. Geophys. Res. Lett. 1980, 7, 89.
 Atkinson, R.; Plum, C. N.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. J. Phys. Chem. 1984, 88, 1210.
 Cantrell, C.; Stockwell, W. R.; Anderson, L. G.; Busarow, K. L.; Perner, D.; Schmeltekopf, A.; Calvert, J. G.; Johnson, H. S. J. Phys. Chem.

^{1985, 89, 139.}

⁽⁵⁾ Malko, M. W.; Troe, J. Int. J. Chem. Kinet. 1982, 14, 399.

⁽⁶⁾ Finlayson-Pitts, B. J.; Pitts, J. N., Jr. Atmospheric Chemistry: Wiley: New York, 1986; p 504.

⁽⁷⁾ Tuazon, E. C.; Sanhueza, E.; Atkinson, R.; Carter, W. P. L.; Winer,
A. M.; Pitts, J. N., Jr. J. Phys. Chem. 1984, 88, 3095.
(8) Kircher, C. C.; Margitan, J. J.; Sander, S. P. J. Phys. Chem. 1984, 88, 1022 4370.

⁽⁹⁾ Graham, R. A.; Johnston, H. S. J. Phys. Chem. 1978, 82, 254. (10) Hjorth, J.; Ottobrini, G.; Restelli, G. Int. J. Chem. Kinet. 1986, 18,

^{819.}

⁽¹¹⁾ Chance, E. M.; Curtis, A. R.; Jones, I. P.; Kirby, C. R. U.K. At. Energy Res. Establ., Harwell, [Rep.] 1977, AERE-R 8775.

rameter to further assess the capacity of the model to account for secondary reactions occurring in the chemical system used. In spite of the fairly good agreement observed for the values of the rate constant k_1 derived in this study and in ref 4, significative differences were found for the measured concentrations of HCOOH and OH radicals with respect to those predicted by the model.

In the context of this study the absolute intensity of the ν_6 band of H¹²COOH centered at about 1105 cm⁻¹ was determined equal to $(3.48 \pm 0.5) \times 10^{-17}$ cm molecule⁻¹, about a factor of 2 larger than the value presently reported in the literature. The same strength within the experimental uncertainty $(3.64 \pm 0.5) \times 10^{-17}$ cm molecule⁻¹ was measured for the intensity of the H¹³COOH band centered at about 1096 cm⁻¹.

Experimental Section

The experiments were performed in a 450-L total volume gas reactor made of a 1.5-m-long, 60-cm-diameter glass tube with Teflon-coated flanges. A multiple reflection White type mirror system was included in the reactor, adjusted to give a total optical path of 84 m and coupled to a Bruker IFS 113 V FT spectrometer. Spectra at time intervals of about 17 min were recorded by co-adding in about 12 min 50 scans of the interferometer at 0.06-cm⁻¹ instrumental resolution, subsequently transformed with Happ-Genzel apodization.

Reactants were mixed in purified air obtained from commercial bottles at 740-Torr total pressure. N_2O_5 , prepared in solid form according to the procedure in ref 12, was introduced into the cell by a stream of purified air while removing the glass bulb with N_2O_5 from the dry ice-methanol bath. As an alternative method, N_2O_5 was generated by mixing NO_2 (from a 1% commercial gas mixture of NO_2 in synthetic air) and O_3 formed in purified air by means of a silent discharge ozone generator. The $^{13}CH_2O$ polymer to 373 K under vacuum, purifying the gas stream by passing it through a dry ice-methanol trap, and finally condensing the formaldehyde in a liquid nitrogen cooled trap. $^{13}C^{18}O$ (99% enriched) was added at concentrations on the order of 2 ppmv. Isotopic abundances were taken from the manufacturer's specifications.

Time-dependent concentrations of N₂O₅, HNO₃, NO₂, ¹³C¹⁶O, ¹³C¹⁸O, ¹⁶O¹³C¹⁸O, ¹³CH₂O, and H¹³COOH were followed from their infrared spectral absorptions. Reduction of these data to concentrations was performed by using the integrated band intensity $(1/cl \int_{\text{band}} \ln (I_0/I) d\nu)$ or the peak absorption coefficient $(1/cl \ln (I_0/I)$, where I_0 and I are the incident and transmitted intensity at the wavenumber ν , c is the concentration, and l is the total beam path in the gas cell.

Integrated band intensities and peak absorption coefficients were determined by using various calibration techniques from spectra recorded with the same conditions (gas pressure and temperature, instrumental resolution, concentration range) as for the experiments. N_2O_5 was measured from the 1225-1270-cm⁻¹ band and HNO₃ from the 1270-1350-cm⁻¹ band; integrated band intensities equal to respectively $(3.8 \pm 0.3) \times 10^{-17}$ and $(4.3 \pm 0.6) \times 10^{-17}$ cm molecule^{-1 13} were used. NO₂ was measured from the absorption lines at 1600 and 1598.4 cm⁻¹; peak absorption coefficients at 0.06-cm⁻¹ instrumental resolution, derived from calibrated gas mixtures of NO₂ in air, equal to $(1.4 \pm 0.1) \times 10^{-18}$ and $(5.6 \pm$ $(0.6) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ were used. The ν_3 band centered at about 1042 \mbox{cm}^{-1} was used to measure the O_3 concentration, with an integrated band intensity (990-1070 cm⁻¹) equal to (1.7 ± 0.3) \times 10⁻¹⁷ cm molecule⁻¹ calibrated by comparison with the response of a Dasibi UV absorption monitor.

Interference-free absorption lines were used to measure the concentrations of ${}^{13}C^{18}O$ from the intensities of the analogous transitions of other CO isotopic species.¹⁰ The compiled line intensity¹⁴ of the P(17) ${}^{16}O^{13}C^{18}O$ transition at 2252.697 cm⁻¹



Figure 1. FT-IR spectrum (run 4, Table II) showing the absorption due to H¹³COOH.

was used $(1.5 \times 10^{-18} \text{ cm molecule}^{-1})$ to evaluate the buildup of this species. In the air spectrum (340 ppmv CO_2 ; 300 ppbv N_2O ; 17 ppbv ¹⁶O¹³C¹⁸O) this transition accounts for 27.5% of the total absorption of the spectral line at 2253 cm^{-1} (2252.6–2253.8 cm^{-1}); the remaining is due to ${}^{14}N_2{}^{16}O$ (49.1%) and ${}^{13}C{}^{16}O_2$ (23.4%) transitions. However, this spectral line is sensitive to variations in the concentration of ${}^{16}O^{13}C^{18}O$ by more than 10 times with respect to ${}^{14}N_2O$ and 200 times with respect to ${}^{13}C{}^{16}O_2$. ${}^{13}CH_2O$ was measured from the absorptions at about 2771, 2777, and 2786 cm⁻¹. Peak absorption coefficients at 0.06-cm⁻¹ instrumental resolution, equal to $(6.0 \pm 0.3) \times 10^{-19}$, $(6.4 \pm 0.5) \times 10^{-19}$, and $(5.1 \pm 0.6) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$, respectively, were determined by sampling air containing ${}^{13}CH_2O$ from the 450-L gas cell. A known volume equivalent to a few percent of the total cell volume was passed at 1-2 L min⁻¹ flow rate through water in two impingers in series. The solution was stabilized with a small amount of methanol to prevent oxidation to formic acid and with HgI₂ to prevent microbiological degradation. Determinations of formaldehyde content were then performed by measurement of the fluorescence of 3,5-acetyl-1,4-dihydrolutidine, formed by the Hantzsch reaction.15

H¹³COOH was measured from the sharp Q-branch of its absorption band centered at 1097 cm⁻¹. H¹³COOH was generated in the gas cell by oxidation of ${}^{13}CH_2O$ in the gas phase; samples were taken from the cell as previously described before and after recording spectra and bubbled in 0.1% NaOH solution. Formate ion contents determined by ion chromatography were used to derive from the linear part of the curve of growth absolute integrated intensities for the total band (1040-1140 cm⁻¹) and for the Q-branch (1093.5–1099.0 cm^{-1}) equal to respectively (3.64 \pm 0.5) × 10⁻¹⁷ and (4.7 \pm 0.5) × 10⁻¹⁹ cm molecule⁻¹. The integrated intensity of the ν_6 band (1045–1150 cm⁻¹) of H¹²COOH was also measured by using the described calibration procedure. A value equal to $(3.48 \pm 0.5) \times 10^{-17}$ cm molecule⁻¹ (860 cm⁻² atm⁻¹ at 296 K) was measured. This value is nearly a factor of 2 larger than the only value reported in ref 16 equal to 435.5 cm^{-2} atm⁻¹ at 296 K, which however is quoted in the compilation as "preliminary". The comparison for the Q-branch intensity shows similar or larger discrepancies. The value of 110 cm⁻² atm⁻¹ measured in this work $(1102-1108 \text{ cm}^{-1})$ is much larger than the value of 36 cm⁻² atm⁻¹ of ref 17, 20 cm⁻² atm⁻¹ of ref 18, and 54 cm^{-2} atm⁻¹ that can be calculated from the compilation of ref 16.

⁽¹²⁾ Schott, G.; Davidson, N. J. J. Am. Chem. Soc. 1958, 80, 1841.

⁽¹³⁾ Hjorth, J.; Ottobrini, G.; Cappellani, F.; Restelli, G. J. Phys. Chem. 1987, 91, 1565.

⁽¹⁴⁾ Rothman, L. S.; Gamache, R. R.; Barbe, A.; Goldman, A.; Gillis, J. R.; Brown, L. R.; Toth, R. S.; Flaud, J. M.; Camy-Payret, C. Appl. Opt. 1983, 22, 2247.

⁽¹⁵⁾ Bisgaard, P.; Moelhave, C.; Rietz, P.; Wilhardt, P. Anal. Lett. 1983, 16, 1457.

⁽¹⁶⁾ Chedin, A.; Husson, N.; Scott, N. A.; Cohen-Hallaleh, I.; Berroir, A. The GEISA Data Bank, 1984 version, revised October 1986. Laboratoire de Meteorologie Dynamique du C.N.R.S.: Palaiseau, France, 1986; Report LMD-127.

⁽¹⁷⁾ Maker, P.; Niki, H., unpublished, quoted in ref 18.

⁽¹⁸⁾ Goldman, A.; Murcray, F. H.; Murcray, D. G.; Rinsland, C. P. Geophys. Res. Lett. 1984, 11, 307.

TABLE I: Reaction Mechanisms and Rate Constants Used in Computer Simulations of the Reactions in the N_2O_5 -CH₂O- N_2/O_2 and NO_2 - O_3 -CH₂O- N_2/O_2 Gaseous Mixtures

	rate			
	constant ^a			
reaction	(295 K)			
(1) $CH_{2}O + NO_{1} \rightarrow CHO + HNO_{2}$				
(2) HCO + O ₂ \rightarrow CO + HO ₂	5.5×10^{-12}			
(3a) $N_2O_5 \xrightarrow{M} NO_2 + NO_3$	4.59×10^{-2}			
(3b) $NO_2 + NO_3 \xrightarrow{M} N_2O_5$	8.61×10^{-13}			
(4) $CH_2O + OH \rightarrow CHO + H_2O$	1.00×10^{-11}			
(5a) $CH_2O + HO_2 \rightarrow O_2CH_2OH$	1.69×10^{-14}			
(5b) $O_2CH_2OH \rightarrow CH_2O + HO_2$	1.50 ^b			
(6) $2O_2CH_2OH \rightarrow 2OCH_2OH + O_2$	9.94×10^{-14}			
(7) $O_2CH_2OH + NO \rightarrow OCH_2OH + NO_2$	2.81×10^{-13}			
(8) $OCH_2OH + O_2 \rightarrow HO_2 + HCOOH$	1.49×10^{-14}			
$(9) \text{ HO}_2 + \text{O}_3 \rightarrow \text{HO} + 2\text{O}_2$	2.00×10^{-15}			
(10) $HO_2 + NO \rightarrow HO + NO_2$	8.28×10^{-12}			
(11) $N_2O_5 + H_2O(wall) \rightarrow 2HNO_3$	variable			
(12) $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	4.04×10^{-16}			
(13) NO + NO ₃ \rightarrow 2NO ₂	1.90×10^{-11}			
(14) $2NO_3 \rightarrow 2NO_2 + O_2$	2.29×10^{-16}			
(15) $2HO_2 \xrightarrow{M} H_2O_2 + O_2$	2.74×10^{-12}			
(16a) $HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	1.42×10^{-12}			
(16b) $HO_2NO_2 \xrightarrow{M} HO_2 + NO_2$	8.95×10^{-2b}			
(17) $HO_2 + NO_3 \rightarrow HNO_3 + O_2$	2.5×10^{-12}			
(18) $O_2CH_2OH + HO_2 \rightarrow HO_2CH_2OH + O_2$	1.76×10^{-14}			
(19) HO + NO ₂ \xrightarrow{M} HNO ₃	1.11×10^{-11}			
(20) HO + CO $\xrightarrow{O_2}$ HO ₂ + CO ₂	2.59×10^{-13}			
(21) HO + HO ₂ \rightarrow H ₂ O + O ₂	1.07×10^{-10}			
$(22) O_3 + NO_2 \rightarrow NO_3 + O_2$	3.15×10^{-17}			
$(23) O_3 + NO_2 \rightarrow NO + 2O_2$	9.7×10^{-19}			
$(24) O_3 + NO \rightarrow NO_2 + O_2$	1.82×10^{-14}			
(25) HO + NO $\stackrel{M}{\rightarrow}$ HONO	4.57×10^{-12}			
(26) HO + O ₃ \rightarrow HO ₂ + O ₂	6.84×10^{-14}			
(27) HO + $H_2O_2 \rightarrow H_2O + HO_2$	1.66×10^{-12}			
(28) NO ₃ + M \rightarrow O ₂ + NO + M	7.05×10^{-23}			

^{*a*}All rate constants except for reaction 11 are taken from ref 4; in cm^3 molecule⁻¹ s⁻¹. ^{*b*}In s⁻¹.



Figure 2. Time-dependent concentrations of reactants and reaction products during run 5 (Table II).

Peak absorption coefficients for the H¹²COOH Q-branch measured in spectra recorded at 1-cm⁻¹ instrumental resolution in this study and in that of ref 4 appear to be in good agreement: $(6.1 \pm 2.5) \times 10^{-3}$ ppm⁻¹ m⁻¹ against 6.18×10^{-3} ppm⁻¹ m⁻¹. However, the instrumental resolution used (1 cm^{-1}) is close to the width of the Q-branch at 700 Torr, and a dependence of the peak absorption coefficient on the product concentration times beam path length used is to be expected. Since this parameter is not specified in ref 4, the comparison is only indicative.

During each experiment, spectra were recorded at time intervals of about 17 min and continued until the N₂O₅ absorption was too weak to be reliably measured. The duration of the experiments was typically 1.5 h, and none lasted more than 2.5 h. The N₂O₅ half-life in zero air in the cell at 295 ± 2 K was found to vary from 2.8 to 5.6 h. CH₂O when mixed in the cell with zero air and ozone, at the concentration used in the experiments, did not exhibit any appreciable decay for periods equal to 2.5 h. Figure 2 shows the time dependence of product and reactant concen-

TABLE II: Initial Concentrations	of CH ₂ O and N	N ₂ O ₅ and Rate
Constant, k_1 , Derived (I) from the	Model Fit or (II) from Eq a for
the Different Experiments ^a		•

run	initial concn, ppm				
no.	CH ₂ O	O ₃	N ₂ O ₅	$k_1(\mathbf{I})^b$	$k_1(II)^b$
1	15.6	0	2.3	3.2	
2	8.0	0	2.6	5.6	3.9
3	7.9	15.9	3.0	4.5	4.2
4	12.8	11.0	4.6	6.6	4.0
5	5.8	7.3	7.6	5.5	3.6
6	6.4	4.4	4.7	7.3	6.5
7	13.6	0	1.5	4.8	7.0
8	6.7	0	8.32	3.5	3.9
9	13.8	7.2	3.4	7.9	
				av 5.4 ± 1.1	av 4.6 ± 1.0

 a The O_3 concentration indicates when CH_2O was reacted with the NO_2 + O_3 mixture. b In $10^{-16}~cm^3$ molecule^-1 $s^{-1}.$

trations measured for run 5 of Table II.

Results and Discussion

The rate constant for reaction 1 was evaluated for both of the different initial experimental conditions, $N_2O_5 + CH_2O$ and NO_2 $+ O_3 + CH_2O$, by using two different procedures. In the first one, k_1 was obtained from a best fit to the time-dependent concentrations of N₂O₅, ¹³CH₂O, NO₂, O₃, ¹³C¹³O, performed by applying the FACSIMILE computer program to a scheme of 31 reactions, shown in Table I, taken from the scheme of 35 reactions of ref 4, leaving out only four reactions considered to be of negligible importance. The rate constants given in ref 4 were used, replacing only the decay rate of N_2O_5 in the cell with the value measured for the experimental setup of this study. From the spread of N_2O_5 decay time values observed, it follows that this parameter is rather uncertain; however, it was found to have a negligible influence on the determination of k_1 . From this procedure a value equal to $(5.4 \pm 1.1) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ was obtained. The rate constant k_1 was also determined from the equation

$$k_1 = \Delta [{}^{13}\text{C}{}^{16}\text{O}] / \{ (K[\text{NO}_2]_{\text{m}} / [N_2\text{O}_5]_{\text{m}}) [{}^{13}\text{CH}_2\text{O}]_{\text{m}} \Delta t \}$$
(a)

where $[NO_2]_m$, $[N_2O_5]_m$, and $[{}^{13}CH_2O]_m$ are the mean concentrations and $\Delta[{}^{13}C{}^{16}O]$ is the buildup observed for the time interval Δt .

In those runs where OH radicals could be detected from the increase of the 2253-cm⁻¹ absorption, a correction to $\Delta^{13}C^{16}O$] was applied to account for the reaction

$$CH_2O + OH \rightarrow CHO + H_2O$$
 (4)

which followed by reaction 2 also leads to CO formation.

A value for k_1 equal to $(4.7 \pm 1.0) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹, not significantly different from that determined as previously described, was calculated by this second procedure. The first value of k_1 equal to $(5.4 \pm 1.1) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ is, however, preferred due to the approximation involved in eq a, where the average concentrations were used. The results of the experiments are given in Table III.

The indirect evaluation of the NO₃ radical concentration introduces a dependence of the calculated k_1 values on the equilibrium constant K of reactions 3, which has been recently matter of some debate.^{5,7–9,19,20} In this study the datum of ref 9 has been preferred because most of the determinations of K agree with this value. The dependence, k_1 vs 1/K, is clearly linear in eq a and nearly linear in the computer fit; substituting for K the lowest reported datum⁷ equal to 2.91 × 10¹⁰ molecules cm⁻³ would in-

⁽¹⁹⁾ Burrows, J. P.; Tyndall, G. S.; Moortgat, G. K. Chem. Phys. Lett. 1985, 119, 193.

⁽²⁰⁾ Perner, D. A.; Schmeltekopf, A.; Winkler, R. H.; Johnston, H. S.; Calvert, J. G.; Cantrell, C. A.; Stockwell, W. R. J. Geophys. Res., D: Atmos. 1985, 90, 3807.

TABLE III: Comparison of Model Predictions and Experiments: Ratio of the Final Modeled over Measured Concentrations for HCOOH and for ¹⁶O¹³C¹⁸O in Different Runs^a

run no.	[HCOOH], ppm	[¹⁶ O ¹³ C ¹⁸ O], ppm
3	0.52	1.01
4	0.91	0.72
5	0.27	0.29
6	0.31	
7	4.4	
8	1.7	
9	0.65	0.46

^{a 16}O¹³C¹⁸O is directly related to OH via reaction 20 of Table I.

crease the k_1 values derived by a factor of approximately 1.8. The mass balance calculated for carbon resulted to be equal to $98.2 \pm 2\%$; no similar calculation could be made for nitrogen due to wall loss of HNO₃.

When the fit to the model was used, the measured concentrations of CO, O₃, CH₂O, and N₂O₅ were found in generally good agreement with the predicted values. The agreement was better for the experiments using $NO_2 + O_3$ as a source of NO_3 ; that might be simply due to the achievement of larger concentrations for the reaction products which then could be more accurately measured.

On the other hand, deviations were found for HCOOH and for OH as derived from the ¹⁶O¹³C¹⁸O buildup and reaction.²⁰ Only in the case of the presence of O_3 in the system were measurable changes in the ¹⁶O¹³C¹⁸O concentration seen. The deviations given in Table III appear well beyond the uncertainties associated with the reduction of the spectral data. Also in the case of NO₂ the measured concentrations differ from the model predictions, but these deviations appear to be of random nature and escape any speculation.

HCOOH is the expected product of the reaction $HO_2 + CH_2O$ according to the reaction sequence involving also NO as discussed in ref 4:

$$HO_2 + CH_2O \rightleftharpoons O_2CH_2OH$$
 (5)

$$2O_2CH_2OH \rightarrow 2OCH_2OH + O_2 \tag{6}$$

$$2O_2CH_2OH \rightarrow 2OCH_2OH + O_2$$
(6)

$$O_2CH_2OH + NO \rightarrow OCH_2OH + NO_2$$
(7)

$$OCH_2OH + O_2 \rightarrow HO_2 + HCOOH$$
(8)

$$OCH_2OH + O_2 \rightarrow HO_2 + HCOOH$$
 (8)

The results of Table III show that, in the experiments where O_2 was used, the measured concentrations of HCOOH largely exceeded the model predictions; the contrary occurred in the two runs where only N_2O_5 was introduced into the cell.

OH radical formation in the system occurs through the reactions

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{9}$$

$$HO_2 + NO \rightarrow OH + NO_2$$
 (10)

with the second reaction giving a negligible contribution. The uncertainty in the evaluation of the OH radical concentration was rather large $(\pm 15\%)$, but the deviations from the model still appear to be significant.

The route to formation of HCOOH goes almost exclusively through reaction 6 while that to the formation of OH, in O₃containing gas mixtures, goes through reaction 9. The constants for equilibrium 5 and reactions 6 and 9 were then varied in an attempt to rationalize the observed discrepancies between model and experiments; no satisfactory fit could be obtained by varying only one of these parameters at a time. One might think to introduce other reactions which would have the common characteristic of representing reduction of peroxy radicals to oxy radicals: reactions of this kind involving the NO₃ radicals might be a possibility.

If in modeling the experiments where O₃ was present the OH radical concentration is underestimated, this error would lead to an overestimate of the rate constant k_1 . In fact, if the k_1 values derived from the experiments using N2O5 are separated from those obtained from the experiments using $NO_2 + O_3$, this tendency is actually evidenced, though not statistically quite significant: $(6.4 \pm 1.4) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{NO}_2 + \text{O}_3) \text{ against } (4.3)$ \pm 1.1) × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ (N₂O₅).

Varying the value of the equilibrium constant K in the computer simulation did not lead to significantly better fits to the experimentally measured concentrations of OH and HCOOH.

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