substrate temperature of 200-700 K. The average kinetic energy divided by 2k is slightly lower than the corresponding substrate temperature between 500-700 K and increases as the crystal temperature increases. However, it increases as the crystal temperature decreases from 500 to 200 K and becomes higher than the substrate temperature below 300 K. At 200 K, the distribution is considerably wider than the Maxwellian distribution and there is a significant amount of HD leaving the surface with 1900 K translational energy. The waveform measurement indicates that the residence time increases as the crystal temperature decreases from 700 to 300 K and decreases for some of the incident atoms as the crystal temperature decreases from 300 to 200 K.

The striking experimental findings are interpreted by assuming

that some of the incident atoms can react with chemisorbed atoms at high coverage before they are in thermal equilibrium with the surface. This mechanism is very different from the previous explanation of hot products¹⁴⁻¹⁹ in which the activation barrier is believed to be the origin of the excess energy.

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Kinetic Study of the NO₃-CH₂O Reaction and Its Possible Role in Nighttime **Tropospheric Chemistry**

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The kinetics of the reaction $NO_3 + CH_2O \rightarrow HONO_2 + HCO$ (14) have been studied by using in situ, long-path (170 m), infrared and visible spectroscopy to follow the reactants and products in dilute mixtures of O_3 , NO_2 , and CH_2O in N_2/O_2 at 700 torr (25 ± 2 °C). The concentrations of O₃, NO₂, CH₂O, N₂O₅, CO, HONO₂, and HCO₂H were determined as a function of time through their characteristic infrared absorption bands by using a Fourier transform infrared spectrometer system. The concentrations of NO₃ and NO₂ were followed by using the characteristic visible absorption bands monitored by a differential optical absorption spectrometer. The kinetic data were analyzed by using both rates of product formation (CO) and reactant removal (N2O5, NO3, CH2O) and computer simulations of the complex reactions which follow reaction 14 in these systems. The results show that the use alone of N_2O_5 decay rates in the presence and absence of CH_2O to derive k_{14} estimates can lead to significant error as a result of the generation of secondary radicals (HO₂, HO) following the primary reaction 14 and the subsequent reactions of HO with CH₂O and HO₂ with NO₃. The present data provide the estimate $k_{14} = (6.3 \pm 1.1) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (25 \pm 2 \text{ °C}).$

Introduction

Interest in the chemical reactions of the NO₃ free radical in the atmosphere has grown in recent years, following the direct spectroscopic observations of this species in the stratosphere¹ and the troposphere.²⁻⁷ Evidence for the chemical reactions of NO₃ with organic trace components of the troposphere can be inferred from laboratory studies carried out as early as 1961. At that time Tuesday observed that gaseous mixtures of N₂O₅, O₂, and aldehydes gave as the major reaction product peroxyacyl nitrates.⁸ In view of the detailed mechanistic considerations of a later vintage,⁹⁻¹³ it now seems highly probable that the first step in initiation of the RCOO₂NO₂ formation in the studies of Tuesday involved the NO₃ free radical.

$$N_2O_5 (+M) \rightarrow NO_3 + NO_2 (+M)$$
(1)

$$NO_3 + NO_2 (+M) \rightarrow N_2O_5 (+M)$$
 (2)

$$NO_3 + RCHO \rightarrow HONO_2 + RCO$$
 (3)

$$RCO + O_2 \rightarrow RCOO_2$$
 (4)

$$RCOO_2 + NO_2 \rightarrow RCOO_2 NO_2$$
 (5)

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The studies of Morris and Niki¹³ and Japar and Niki¹⁴ gave the first estimates of the NO₃-CH₃CHO and NO₃-alkene reaction rate constants. Recent interest in the reactions of NO3 with organic molecules relates in part to the potential for free-radical and product generation which these reactions provide during the nighttime hours when the concentration of NO3 maximizes in the

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troposphere. In previous work we have accepted the NO₃-CH₃CHO rate constant data of Morris and Niki,¹³ assigned this rate constant also to the then undetermined rate constant for the NO₃-CH₂O reaction, and computer simulated the NO₃ chemistry in the polluted troposhere using a simplified yet reasonably complete tropospheric reaction mechanism.^{15,16} The results suggested in theory that the NO₃-aldehyde reactions can generate, during the nighttime hours, significant concentrations of free radicals (HO₂, CH₃COO₂, etc.) and important reactive products such as HONO₂, CH₃COO₂NO₂, and H₂O₂.

Recently rather extensive new rate data have appeared for the NO₃ reactions with various organic molecules, including the NO_3 -CH₂O reaction.¹⁷⁻²² The reported rate constant for the NO3-CH2O reaction is much smaller than that reported previously for the NO₃-CH₃CHO reaction, and the conclusions about the importance of the aldehyde reactions in nighttime tropospheric chemistry are open to question.¹⁸ However, in all previous and recently published studies of the NO3-organic molecule reactions, the rate constants were determined by assuming a highly simplified reaction mechanism. The NO₃ radical was assumed to be at equilibrium with NO_2 and N_2O_5 . The rates of disappearance of N_2O_5 were measured in experiments in the presence and absence of added organic reactant. Without added organic reactant the decay of the N₂O₅ was controlled largely by the rate of its removal at the wall in reaction 6, and the apparent first-order rate constant

$$N_2O_5 + H_2O(wall) \rightarrow 2HONO_2$$
 (6)

 k_6 was assumed to be independent of added organic reactant gas. The acceleration of the N_2O_5 decay rate observed with the organic reactant present was attributed to the NO₃-organic molecule (RH) reaction 7. Estimates of k_7 were made by using the simple relation

$$NO_3 + RH \rightarrow products$$
 (7)

8.

$$(R_{N_2O_5})_{RH} - (R_{N_2O_5})_0 = k_7 K_{1,2} [N_2O_5] [RH] / [NO_2]$$
 (8)

There are some potential problems which may complicate this method of k_7 determination. We found that reactions which follow reaction 7, where $RH = CH_2O$, generate HO_2 free radicals.²³ Both HO₂ and various RO₂ free radicals can be expected as products from the various NO₃-RH reactions which have been studied. Furthermore, it is well established that the NO_3 - NO_2 reaction involves two reactive channels, one forming N_2O_5 and one producing NO, NO_2 , and O_2 :

$$NO_3 + NO_2 (+M) \rightarrow N_2O_5 (+M)$$
 (2)

$$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$$
 (9)

It is clear that both HO₂ radicals and NO₃ will react with the NO product of reaction 9:

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

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$$NO_3 + NO \rightarrow 2NO_2$$
 (11)

It seems probable that the NO_3 radical reaction with HO_2 will occur to remove NO_3 in these mixtures as well:

$$HO_2 + NO_3 \rightarrow HONO_2 + O_2$$
 (12)

Furthermore, the HO free radicals formed in reaction 10 will react in part with the organic reactant RH:

$$HO + RH \rightarrow R + H_2O \tag{13}$$

Obviously a large number of seemingly important reactions occur in the N_2O_5 -RH systems in addition to reactions 1-4. The magnitude of the error which may be introduced when only reactions 1-4 are assumed to occur and relation 5 is employed to estimate k_3 remains uncertain. There is a further problem in this and previous work which arises in the uncertainty of the equilibrium constant $K_{1,2}$ required for the estimate of k_7 in relation 8. Recent studies of Tuazon et al.²⁴ gave estimates of $K_{1,2}$ which are much lower than those used in all previous studies.

It was clear that a more direct experimental determination of the CH₂O-NO₃ reaction rate constant and the N₂O₅ \rightleftharpoons NO₃ + NO₂ equilibrium constant were necessary to test adequately the Stockwell and Calvert¹⁵ conclusion concerning the importance of the tropospheric, nighttime chemistry induced by the NO₃aldehyde reactions. We have redetermined $K_{1,2}$ in other studies²⁵ and report in this work a determination of the rate constant for reaction 14.

$$NO_3 + CH_2O \rightarrow HONO_2 + HCO$$
 (14)

Experimental Section

The present studies were made by following spectroscopically the time dependence of the concentrations of all of the reactants, O_3 , NO₂, and CH₂O (ppm range) in 700 torr of N_2/O_2 mixtures (near 25 °C) and the major products of the reactions, N_2O_5 , $HONO_2$, CO, HCO_2H , and NO_3 . The reactions were studied in a large glass reactor (6.3-m length, 445-L total volume) equipped with an internal multiple reflection system (5.31-m base path) which was adjusted to 32 passes and a total optical path of 170 m. This system has been described previously.^{26,27} In a first series of experiments which we performed, all analyses were based upon the infrared bands of reactants and products as monitored by using an infrared beam from a Nernst glower and a Fourier transform infrared spectrometer (Digilab FTS-20). NO₃ could not be determined directly in these experiments because of its low infrared extinction coefficient and low concentration, but its concentration was inferred from the measured $K_{1,2}$ values²⁵ and the measured concentrations of N_2O_5 and NO_2 . In a second set of experiments the alternate use was made of the infrared beam and a visible beam (tungsten-iodine lamp, Osram HLX64655) filtered to avoid photolysis of NO_3 and NO_2 . In the latter experiments a visible differential optical absorption system was employed to follow NO₃ and NO₂ directly, while all other species were determined by using the infrared beam as before. Infrared spectra were collected (1-cm⁻¹ resolution) by averaging over 10 or 100 scans of the interferometer which required 1 or 10 min, respectively. Concentrations of HONO₂, O₃, CH₂O, CO, and N_2O_5 were estimated by using several methods of absorption data reduction: (a) Absorbance band integration of characteristic absorption regions were useful for several compounds in this system. The resolution-insensitive, integrated band intensities (cm² molecule⁻¹ cm⁻¹), $\int \epsilon d(1/\lambda)$, are as follows (limits on the inte-

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TABLE I: Experimental Conditions and Rate Constant Estimates for the NO₃-CH₂O Reaction 14

| run no. | temp, K | initial concn, ^a ppm | | | molecule ⁻¹ s ⁻¹ | | $10^{16}k_{14}$, cm ³ molecule ⁻¹ s ⁻¹ | | |
|---------|---------|---------------------------------|-------------------|---------------------|--|----------------|--|----------------|---------------|
| | | [NO ₂] | [O ₃] | [CH ₂ O] | 16 | 2 ^c | 3 ^d | 4 ^e | 55 |
| 1 | 296.3 | 7.33 | 7.29 | 8.36 | 7.8 ± 1.8 | 16 ± 3 | 6.0 ± 1.3 | 9.4 ± 1.8 | 6.1 |
| 2 | 296.7 | 11.97 | 11.93 | 3.49 | 6.2 ± 0.5 | 22 ± 4 | 5.9 ± 0.6 | 9.0 ± 1.3 | 6.2 |
| 3 | 298.0 | 3.80 | 5.13 | 4.65 | 7.4 ± 1.2 | 15 ± 2 | 6.6 ± 1.1 | 7.7 ± 0.8 | 6.5 |
| 4 | 298.1 | 4.94 | 6.35 | 6.22 | 6.0 ± 1.2 | 15 ± 2 | 5.3 ± 1.0 | 7.7 ± 1.0 | 6.4 |
| 5 | 299.2 | 3.48 | 8.80 | 2.94 | 7.7 ± 2.0 | 15 ± 5 | 6.6 ± 1.6 | 6.8 ± 2.5 | 5.4 |
| 6 | 299.1 | 4.68 | 19.5 | 5.98 | 7.4 ± 1.8 | 11 ± 1 | 4.5 ± 1.1 | 6.0 ± 0.7 | 5.6 |
| 7 | 299.4 | 4.75 | 5.19 | 6.06 | 6.3 ± 0.7 | 10 ± 1 | 5.5 ± 0.5 | 5.5 ± 0.3 | 5.8 |
| 8 | 299.6 | 4.79 | 9.35 | 3.05 | 6.6 ± 1.5 | 13 ± 2 | 5.5 ± 1.1 | 6.2 ± 0.1 | 6.0 |
| 9 | 300.4 | 5.29 | 8.29 | 6.09 | 6.8 ± 1.8 | 11 ± 1 | 5.0 ± 1.3 | 6.4 ± 0.8 | 5.8 |
| av | | | | | | | 5.7 ± 0.7 | 7.2 ± 1.4 | 6.0 ± 0.4 |

Grand Average $k_{14} = (6.3 \pm 1.1) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

^a Total pressure of the reacting mixtures was 700 torr (N_2/O_2) ; 1 ppm (25 °C) = 2.462 × 10¹³ molecules cm⁻³. ^b Calculated from the rates of CO and CH₂O change using eq 17 (runs 6-9) or 18 (runs 1-5). ^c Calculated from the rate of loss of N_2O_5 and NO_3 using eq 19 (runs 6-9) or 20 (runs 1-5). ^d Calculated from eq 44. ^c Calculated from eq 45. ^f Estimated from best visual fit by computer simulation of all product rates using adjustable values for k_{12} , k_{14} , and k_6 ; all other rate constants as shown in Table II.

gration include the stated range of the band or portion of the band employed): HONO₂, 5.89 \times 10⁻¹⁸ (840–930 cm⁻¹) and 1.22 \times 10^{-17} (1270–1360 cm⁻¹); N₂O₅, 2.01 × 10^{-17} (725–760 cm⁻¹) and $1.91 \times 10^{-17} (1225 - 1270 \text{ cm}^{-1}); \text{NO}_2, 1.80 \times 10^{-17} (1580 - 1650)$ cm⁻¹); CH₂O, 3.92×10^{-18} (1720–1800 cm⁻¹) and 7.33×10^{-18} $(2725-1360 \text{ cm}^{-1})$; O₃, integrated band intensities were pressure sensitive: for 990–1070 cm⁻¹, 6.04×10^{-18} (700 torr), 5.28×10^{-18} (350 torr), and 3.48×10^{-18} (100 torr); for 2070–2135-cm⁻¹ band, 6.02×10^{-19} (350–700 torr) and 5.06×10^{-19} (100 torr); the latter O₃ band was also corrected for the absorbance due to CO when this gas was present; CO, $1.58 \times 10^{-18} (2145 - 2210 \text{ cm}^{-1})$. (b) Independent estimates of several of the compounds were made by using extinction coefficient data ($[\ln (I_0/I)/cl \text{ ppm}^{-1} \text{ m}^{-1})$ for certain characteristic absorption peaks: CH_2O , 1.10×10^{-3} (2280) cm⁻¹), 1.20×10^{-3} (2801 cm⁻¹), 1.10×10^{-3} (2814 cm⁻¹), 1.00×10^{-3} (2862 cm⁻¹), 8.41×10^{-4} (2882 cm⁻¹); CO, values of ϵ were a function of concentration; peak wave numbers employed, 2160, 2114, 2175, 2177, and 2182 cm⁻¹; NO₂, 2.03×10^{-3} (1602 cm⁻¹), $2.62 \times 10^{-3} (1627 \text{ cm}^{-1}); \text{ O}_3, 4.88 \times 10^{-3} (1025 \text{ cm}^{-1}), 7.68 \times 10^{-3} (1025 \text{ cm}^{-1}), 7.68$ 10^{-3} (1060 cm⁻¹); for the NO₂ and O₃ band peaks were taken as the average maxima drawn through the peak fine structure of the major peaks; HCO_2H , 1.96×10^{-3} (1090 cm⁻¹), 6.18×10^{-3} (1102 cm^{-1}), 2.33 × 10⁻³ (1120 cm⁻¹). (c) Whole band spectral subtraction was used as a third means of concentration estimation using spectra of calibrated standards for N₂O₅, HONO₂, NO₂, CH₂O, CO, HCO₂H, and O₃ (in 700-torr N_2/O_2 mixtures). Standard spectra of CO, CH₂O, and HCO₂H were determined by introducing accurately measured pressures (MKS Baratron manometers) of the pure vapor into calibrated volumes on the gas introduction system. Formaldehyde monomer was prepared from the pure polymer and purified by the method described by Spence and Wild.²⁸ Nitrogen dioxide standards were introduced into the reaction vessel in a similar fashion, but correction was made for the amount of NO₂ present as N_2O_4 (2NO₂ \Rightarrow N_2O_4) at the temperature and pressure of the measurement in the calibrated gas introduction bulb. N_2O_5 standard spectra were prepared by using O_3 -NO₂ mixtures with the amount of N_2O_5 at a given time calculated from the measured NO2 and HONO2 and an assumed nitrogen mass balance. The amount of ozone in standard ozone spectra was estimated by gas-phase titration with added NO and measurement of the NO₂ yield. Standard nitric acid spectra were determined by introducing HONO₂ vapor (from a 70% HONO₂ solution) simultaneously into three calibrated bulbs sealed to the introduction system.²⁶ The contents of two of the three were individually frozen at liquid-nitrogen temperature while that in the third bulb was introduced to the cell. The amount of HONO₂ in the two reference bulbs (and hence the amount introduced from the third bulb) was determined by titration using standard NaOH solution. Eight separate determinations were averaged in this case. The absorption of all of the species except CO follow the BeerLambert law well over the concentration range encountered in this study. The extinction data obtained in this work are in good accord with those reported in our previous work and by others.

The differential optical absorption spectrometer was specially designed and constructed with a 0.3-m grating and equipped with an array of 1024 photodiodes (Schmeltekopf, to be submitted for publication). NO₂ was followed in the 404–453-nm region using 0.50-nm resolution. A differential absorption cross section, 3.30 $\times 10^{-19}$ cm² molecule⁻¹ was determined for the band at 448.4 nm at this resolution. The NO₃ was monitored in the spectral region at 606–680 nm. We employed a differential absorption cross section for NO₃ at 662.1 nm of 1.73×10^{-17} cm² molecule⁻¹. This value is consistent with those reported by Ravishankara and Wine²⁹ and Graham and Johnston³⁰ when adjustment is made for resolution differences.

In each of the experiments carried out in this work, O_3 in O_2 was introduced first to the evacuated cell through five parallel input ports along the cell length. The exact amount (in the range 5-31 ppm) was determined by infrared absorption with the total gas pressure at 100 torr. A measured amount of CH₂O vapor was then swept into the cell and mixed well with the O_3 by using dry N₂ gas (evaporated from a liquid-nitrogen supply) up to 300-torr final pressure. Then the reaction mixture was scanned to determine the initial concentrations of O₃ and CH₂O from absorption data. The reaction was initiated and the reactants turbulently mixed by sweeping into the cell a measured amount of NO_2 in dry nitrogen gas. A final pressure of 700 torr was employed in all experiments. In runs 6-9 of Table I the background spectra of the empty cell were taken before the experiment was initiated, and several spectra of the reacting mixture were collected during 1-min periods using the infrared and visible beams alternately every 10 min or so throughout the 90-min period of most experiments. In runs 1-5 of Table I the infrared analysis alone was employed, and spectra were collected over 10-min cycles. The initial concentrations of the nine experiments reported here are summarized in Table I.

Discussion

General Observations on the Mechanism of the O_3 - NO_2 -CH₂O- O_2/N_2 Reaction Mixture. The present study allows an in-depth look at the products and mechanism of the NO₃-CH₂O reaction. We have chosen the O₃- NO_2 -CH₂O- O_2/N_2 mixture at 700 torr as the source of the desired reactants. For our experimental conditions there is no measurable reaction of CH₂O with either O₃ or NO₂ over the 90-min duration of an experiment. However, when all three of the reactants (O₃, CH₂O, and NO₂) are mixed, rapid chemical changes occur involving each of the reactants and several products. The time variations of the various

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Figure 1. Time dependence of the product and reactant concentrations in the reaction of $O_3-NO_2-CH_2O-O_2/N_2$ mixture (run 8 of Table I).

species are shown for a typical experiment in Figure 1 (run 8 of Table I). The major changes can be understood readily in terms of well-studied chemical reactions involving the many species present in the mixture. Note in Figure 1 that as $[O_3]$ and $[NO_2]$ decrease, $[N_2O_5]$ and $[NO_3]$ rise; then both N_2O_5 and NO_3 concentrations decrease slowly as $[HONO_2]$ rises. It is clear that the O_3 - NO_2 reaction 15 generates the NO_3 in the system, and this species equilibrates quickly with NO_2 to form N_2O_5 in reactions 1 and 2:³⁰

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \tag{15}$$

$$NO_3 + NO_2 (+M) \rightleftharpoons N_2O_5 (+M)$$
(2,1)

It is a reasonable hypothesis that the NO₃ radical initiates the observed decay of CH₂O and the formation of CO and HONO₂. In Figure 1 it can be seen that the amount of initial formaldehyde which has disappeared at any time is nearly equal to the CO formed at that time. In our initial study of the CH₂O, O₃, NO₂ system,²³ we observed that HO₂ radicals were generated as a major initial product of the NO₃-CH₂O reaction. All of these observations suggest that reaction 14 describes well the elementary reaction between NO₃ and CH₂O and that reaction 16 always follows reaction 14. Also formed from CH₂O but not shown in

$$NO_3 + CH_2O \rightarrow HONO_2 + HCO$$
(14)

$$HCO + O_2 \rightarrow CO + HO_2 \tag{16}$$

Figure 1 is a very small amount of HCO_2H , the expected product of the HO_2 -CH₂O reactions.

The product analysis in the present study is reasonably complete and accurate as evidenced by the relatively good carbon and nitrogen mass balances which exist for the various experiments; see Table II. The average C- and N-atom balances remain in reasonable accord with the initial values for all of the 6–21 different measurement periods during a given run. It appears that even the usually transient nitric acid product is not removed by wall adsorption significantly during the period of the experiments. In addition to reaction 14 as a source of HONO₂ we expect some of this compound to be formed from the reaction of N_2O_5 with adsorbed H_2O on the surface of the glass reaction cell. The slow loss of pure N_2O_5 vapors in the "dry" cell is accompanied by the appearance of HONO₂, and the following reaction must occur also in the $CH_2O-NO_2-O_3$ reaction mixture:

$$N_2O_5 + H_2O(wall) \rightarrow 2HONO_2 \tag{6}$$

It is instructive to examine quantitatively the present data in terms of the very simple reaction sequence 15, 1, 2, 14, 16, and 6 to see how well these reactions alone can explain the results.

Evaluation of the k_{14} Rate Constant Using the Simplified Reaction Scheme. We expect simple rate laws analogous to

TABLE II: Average Nitrogen and Carbon Mass Balances in the $N_2O_5\mathchar`-O_2\mathchar`-N_2O=O_2\mathchar`-N_2$ Reacting Mixtures

| | run length, | | concn, ^a ppm | | | | |
|---------|----------------|---------------|-------------------------|--------------|------------------|--|--|
| run no. | min | $[CH_2O]_0^b$ | av $\sum C^{c}$ | $[NO_2]_0^b$ | av $\sum N^d$ | | |
| 1 | 88 | 8.36 | 8.36 ± 0.50 | 7.33 | 7.41 ± 0.26 | | |
| 2 | 84 | 3.49 | 3.49 ± 0.29 | 11.70 | 11.97 ± 0.26 | | |
| 3 | 78 | 4.65 | 4.52 ± 0.14 | 3.80 | 3.77 ± 0.05 | | |
| 4 | 75 | 6.22 | 6.17 ± 0.26 | 4.94 | 4.86 ± 0.25 | | |
| 5 | 71 | 2.94 | 3.03 ± 0.15 | 3.92 | 3.48 ± 0.26 | | |
| 6 | 70 | 5.98 | 5.89 ± 0.85 | 4.70 | 4.68 ± 0.13 | | |
| 7 | 101 | 6.06 | 5.77 ± 0.45 | 4.49 | 4.75 ± 0.24 | | |
| 8 | 73 | 2.99° | 2.99 ± 0.19 | 4.56 | 4.79 ± 0.16 | | |
| 9 | 71 | 6.33 | 5.60 ± 0.37 | 4.92 | 5.29 ± 0.24 | | |
| | | | | | | | |

^a1 ppm (25 °C) = 2.462×10^{13} molecules cm⁻³. ^bRepresents $\sum_{i=1}^{n} ([CH_2O]_i + [CO]_i + [HCO_2H]_i)/n$, where n = 6-21 measurements made over the course of the run. ^c Estimated from the pressure of the gaseous mixture of N₂O₄/NO₂ or pure CH₂O in the calibrated bulb on the introduction system. ^dRepresents $\sum_{i=1}^{n} ([NO_2]_i + [HONO_2]_i + 2[N_2O_5]_i + [NO_3]_i)/n$ where n = 6-21 measurements made over the course of the run. ^c Estimated from the initial infrared spectrum; error in bulb pressure measurement.

relation 8 to describe the reaction system if only reactions 15, 1, 2, 14, 16, and 6 are important in the loss of CH_2O and N_2O_5/NO_3 and the formation of CO.

$$-R_{\rm CH_2O} = R_{\rm CO} = [\rm NO_3][\rm CH_2O]k_{14}$$
(17)

$$-R_{\rm CH_{2}O} = R_{\rm CO} = k_{14}K_{1,2}[N_2O_5][\rm CH_2O]/[\rm NO_2]$$
(18)

$$-R_{N_2O_5} - R_{NO_3} = [NO_3][CH_2O]k_{14} + [N_2O_5]k_6 - [O_3][NO_2]k_{15}$$
(19)

$$-R_{N_2O_5} - R_{NO_3} = k_{14}K_{1,2}[N_2O_5][CH_2O]/[NO_2] + [N_2O_5]k_6 - [O_3][NO_2]k_{15}$$
(20)

The functions 17 and 19 can be used to estimate k_{14} for experiments in which the [NO₃] was measured directly (runs 6–9 of Table I) or functions 18 and 20 for those runs in which [NO₃] was inferred from measured NO₂, N₂O₅ and $K_{1,2}$ estimates (runs 1–5 of Table I). Values of $K_{1,2}$ were calculated from $K_{1,2} = 8.4 \times 10^{26}e^{-11180/T}$ molecules cm⁻³ as recommended by Graham and Johnston.³¹

Rates of change of the [CO], [CH₂O], and [NO₃] + [N₂O₅] were derived from tangents drawn at several points along the appropriate concentration-time plots for each experiment. These were used together with the necessary reactant concentration data for the corresponding times to calculate the values of k_{14} shown in Table I under the columns headed by $(k_{14})_{max}$. Note that the estimates under column 1, derived from rates of change of CO and CH₂O, are only about one-half those calculated from the $d[N_2O_5]/dt + d[NO_3]/dt$ data of column 2. It is immediately evident that relations 17-20 alone cannot describe this system well. Obviously there are other N₂O₅ and/or NO₃ removal paths which occur in this system in addition to reactions 15, 1, 2, 14, 16, and 6. The previous use of only these reactions in all NO₃-RH rate constant studies must be questioned.

Complete Reaction Mechanism for the O_3 - NO_2 - CH_2O - O_2/N_2 System. A more detailed consideration of the chemistry of this system points to several other potentially important reactions. First there are several sources of NO, a potential reactant for NO₃, which must occur in this system:

$$NO_3 + NO_2 \rightarrow NO + NO_2 + O_2 \tag{9}$$

$$O_3 + NO_2 \rightarrow NO + 2O_2 \tag{21}$$

$$NO_3 + M \rightarrow O_2 + NO + M \tag{22}$$

Reaction 9 has been well studied, and its rate constant determined accurately by Graham and Johnston.³¹ Reaction 21, a minor channel accompanying the major NO_2 -O₃ reaction 15, has been

considered previously by Graham and Johnston^{31,32} and Wu et al.33 as a possible means of rationalizing the observed stoichiometry of the NO_2-O_3 reaction. If reaction 15 were always followed by N_2O_5 formation in reaction 2, then the ratio $\Delta[NO_2]/\Delta[O_3]$ would equal 2.00 in reacting NO_2-O_3 mixtures.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{15}$$

$$NO_3 + NO_2 (+M) \rightarrow N_2O_5 (+M)$$
 (2)

Wu et al. found Δ [NO₂]/ Δ [O₃] = 1.88 ± 0.15 in O₃-rich mixtures and 1.68 ± 0.15 in NO₂-rich mixtures at the "completion" of the reaction. Graham and Johnston found $\Delta[NO_2]/\Delta[O_3] = 1.89$ \pm 0.08 for reactions between 20% and 60% toward completion. These workers felt that reaction 21 may not be responsible for the observed stoichiometry variation from 2.00 since no NO₂ chemiluminescence could be detected in their reacting mixture of O_3 and NO_2 ; if NO were present they expected the following: $O_3 + NO \rightarrow NO_2^* + O_2; NO_2^* \rightarrow NO_2 + h\nu$. However, the non-light-producing, fast reaction of NO3 with NO (NO3 + NO \rightarrow 2NO₂) could compete successfully with the O₃-NO reaction and raise greatly the detection limits required to observe the minor occurrence of reaction 21. In fact, reaction 21 appears to offer a unique explanation of the $\Delta[NO_2]/\Delta[O_3]$ data; it allows an insensitivity of the stoichiometric ratio to the extent of the reaction (20-60%) as observed by Graham and Johnston. Computer simulations of the O₃-NO₂ reaction mixture for the conditions employed by Graham and Johnston and Wu et al. show that reaction 21 can account well for the observations of both groups. We find that taking $k_{21}/(k_{21} + k_{15}) = 0.030$ allows a reasonable fit of all of the $\Delta[NO_2]/\Delta[O_3]$ measurements in the NO₂-rich NO₂-O₃ mixtures. In O₃-rich mixtures the measured stoichiometry as observed in the computer simulations is very sensitive to the time chosen for the measurement at the "completion" of the reaction. At no point has NO₂ been depleted completely in the reaction mixture. The N2O5-catalyzed decomposition of O3 continues to occur in the system, and NO₂ continues to be regenerated as well as react throughout the reaction. If one picks a 95–99% conversion of NO_2 for the time of the measurement, then simulations give values of $\Delta[NO_2]/\Delta[O_3]$ similar to those reported by Wu et al. for the O3-rich mixtures. We feel that all of the stoichiometry results are in accord with the occurrence of reaction 21 with the k_{21} value picked here.

The occurrence of reaction 22 is suggested to rationalize both the high-temperature NO3 decomposition observed by Schott and Davidson³⁴ and the experiments of Graham and Johnston³¹ made near room temperature. This evidence will be reviewed in a subsequent publication.³⁵ For the conditions employed here (700 torr) the reaction should be in the second-order region $(k_{23}/k_{23(\infty)})$ $\simeq 0.066$ as judged from the observed pressure dependence of reaction 23, which is of similar molecular complexity to reaction 22).

$$O + NO_2 + M \rightarrow NO_3 + M$$
 (23)

The generation of NO in the NO₂-O₃-CH₂O system makes available a variety of other reaction pathways for NO₃ and other species present. Thus, NO₃ and O₃ will react in reactions 11 and 24, respectively, and HO₂ radicals will generate HO radicals in reaction 10:

$$NO_3 + NO \rightarrow 2NO_2$$
 (11)

$$O_3 + NO \rightarrow O_2 + NO_2$$
 (24)

$$HO_2 + NO \rightarrow HO + NO_2 \tag{10}$$

The reactive HO radicals formed in reaction 10 also arise in this system through the sequence of reactions 25 and 26 which leads to O_3 decay:

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$$HO_2 + O_3 \rightarrow HO + 2O_2 \tag{25}$$

$$HO + O_3 \rightarrow HO_2 + O_2 \tag{26}$$

HO radicals will attack CH₂O and form the minor observed product, HCO₂H, and presumably HO₂CH₂OH, a metastable intermediate species.³⁶⁻³⁹

$$HO_2 + CH_2O \rightleftharpoons HO_2CH_2O \rightleftharpoons O_2CH_2OH$$
 (27,28)

$$2O_2CH_2OH \rightarrow 2OCH_2OH + O_2$$
 (29)

$$O_2CH_2OH + NO \rightarrow OCH_2OH + NO_2$$
 (30)

$$O_2CH_2OH + HO_2 \rightarrow HO_2CH_2OH + O_2$$
(31)

$$OCH_2OH + O_2 \rightarrow HCO_2H + HO_2$$
 (32)

HO₂ radicals are expected in theory to react with NO₂ to form the metastable species, HO_2NO_2 ; for our conditions HO_2NO_2 is expected to be below the detection limit of the present analytical methods ($[HO_2NO_2]_{max} \simeq 0.04$ ppm from simulations).

$$HO_2 + NO_2 (+M) \rightarrow HO_2NO_2 (+M)$$
(33)

$$HO_2NO_2 (+M) \rightarrow HO_2 + NO_2 (+M)$$
(34)

In addition HO₂ radicals will combine to generate H₂O₂ although, again, this product is expected to be below the detection limits $([H_2O_2]_{max} \simeq 0.04 \text{ ppm}).$

$$2HO_2 (+M) \rightarrow H_2O_2 + O_2 (+M)$$
 (35)

Another potential sink for the NO3 radical in these systems is the reaction with HO₂:

$$NO_3 + HO_2 \rightarrow HONO_2 + O_2 \tag{12}$$

Although there are no experimental data related to this reaction of which we are aware, the occurrence of several analogous reactions requires its consideration in this system; see the discussion which follows.

The HO radicals formed in reactions 10 and 25 will react rapidly with several of the molecules present in this system:

$$HO + CH_2O \rightarrow H_2O + HCO$$
(36)

$$HO + NO_2 (+M) \rightarrow HONO_2 (+M)$$
(37)

$$HO + NO (+M) \rightarrow HONO (+M)$$
 (38)

$$HO + CO (+O_2) \rightarrow HO_2 + CO_2$$
(39)

$$HO + HO_2 \rightarrow H_2O + O_2 \tag{40}$$

inn

$$HO + O_3 \rightarrow HO_2 + O_2 \tag{26}$$

$$HO + H_2O_2 \rightarrow H_2O + HO_2 \tag{41}$$

$$HO + HONO_2 \rightarrow H_2O + NO_3 \tag{42}$$

$$HO + HO_2NO_2 \rightarrow H_2O + NO_2 + O_2$$
(43)

It is apparent that there is a very large number of elementary reactions, in fact 36 reactions, required to describe the chemistry which occurs in this system. Fortunately most of these reactions have been well studied, and their rate constants are known with reasonable precision. These are summarized in Table III.

These mechanistic considerations suggest to us why the very simple treatment of relations 17-20, based upon only five chemical reactions, did not give us consistent estimates of k_{14} . The several other loss mechanisms identified for CH2O, N2O5, and NO3 and the new formation step for CO indicate that the simplified relations 17-20 can only provide upper limits to the true value of k_{14} ; for this reason we have labeled these estimates as $(k_{14})_{max}$ in Table I, columns 1 and 2.

Evaluation of k_{14} Using the Complete Reaction Mechanism. A more rigorous treatment of the reaction system in terms of the

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| TABLE III: | Reaction M | fechanism and | Rate Constant | s Employed in | Computer | Simulations of | the Reactions in (| $\mathbf{O}_3 - \mathbf{NO}_2 - \mathbf{CH}_2 \mathbf{O} - \mathbf{O}_2 / \mathbf{N}_2$ |
|--------------|------------|---------------|---------------|---------------|----------|----------------|--------------------|---|
| Gaseous Mixe | tures | | | | | | | |

| reaction | k(25 °C, 700 torr), cm ³ molecule s ⁻¹ | temp-dependent k |
|--|---|--|
| $(15) O_3 + NO_2 \rightarrow NO_3 + O_2$ | 3.15×10^{-17} | $1.2 \times 10^{-13} e^{-2450/T}$ |
| $(21) O_3 + NO_2 \rightarrow NO + 2O_2$ | 9.7 × 10 ⁻¹⁹ ∮ | 1.2 × 10 € |
| (2) $NO_3 + NO_2 (+M) \rightarrow N_2O_5 (+M)$ | 8.61×10^{-13} | Troe expression, ref 30 |
| (1) $N_2O_5(+M) \rightarrow NO_3 + NO_2(+M)$ | 4.59×10^{-2} | $K_{1,2}(k_2)$ where $K_{1,2} = 8.4 \times 10^{26} e^{-11180/4}$ |
| (9) $NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$ | 4.04×10^{-16} | $2.50 \times 10^{-14} e^{-1230/T}$ |
| (6) $N_2O_5 + H_2O(wall) \rightarrow 2HONO_2$ | (see text) | |
| (11) $\dot{NO}_3 + \dot{NO} \rightarrow 2NO_2$ | 1.90×10^{-11} | temperature independent |
| $(49) 2NO_3 \rightarrow 2NO_2 + O_2$ | 2.29×10^{-16} | $8.5 \times 10^{-13} e^{-2450/T}$ |
| $(24) O_3 + NO \rightarrow NO_2 + O_2$ | 1.82×10^{-14} | $2.2 \times 10^{-12} e^{-1430/T}$ |
| (14) $NO_3 + CH_2O \rightarrow HONO_2 + HCO$ | (see text) | |
| (16) HCO + $O_2 \rightarrow HO_2 + CO$ | 5.5×10^{-12} | $3.5 \times 10^{-12} e^{140/T}$ |
| (35) $2HO_2 (+M) \rightarrow H_2O_2 + O_2 (+M)$ | 2.74×10^{-12} | $2.5 \times 10^{-13} e^{560/T} + 1.7 \times 10^{-33} [M] e^{1000/T}$ |
| $(25) \operatorname{HO}_2 + \operatorname{O}_3 \rightarrow \operatorname{HO} + 2\operatorname{O}_2$ | 2.00×10^{-15} | $1.4 \times 10^{-14} e^{-580/T}$ |
| (10) $HO_2 + NO \rightarrow HO + NO_2$ | 8.28×10^{-12} | $3.7 \times 10^{-12} e^{240/T}$ |
| $(33) \operatorname{HO}_2 + \operatorname{NO}_2 (+M) \rightarrow \operatorname{HO}_2 \operatorname{NO}_2 (+M)$ | 1.42×10^{-12} | Troe expression, ref 30 |
| (34) $HO_2NO_2 (+M) \rightarrow HO_2 + NO_2 (+M)$ | 8.95×10^{-2} | Troe expression, ref 30 |
| (48) $HO_2 + NO_2 \rightarrow HONO + O_2$ | 2.97×10^{-15} | not known |
| (12) $HO_2 + NO_3 \rightarrow HONO_2 + O_2$ | (see text) | |
| (27) $HO_2 + CH_2O \rightarrow O_2CH_2OH$ | 1.69×10^{-14} | not known |
| $(28) O_2 CH_2 OH \rightarrow HO_2 + CH_2 O$ | 1.50 | not known |
| (29) $2O_2CH_2OH \rightarrow 2OCH_2OH + O_2$ | 9.94×10^{-14} | not known |
| $(30) O_2 CH_2 OH + NO \rightarrow OCH_2 OH + NO_2$ | 2.81×10^{-13} | not known |
| $(31) O_2 CH_2 OH + HO_2 \rightarrow HO_2 CH_2 OH + O_2$ | 1.76×10^{-14} | not known |
| (32) $OCH_2OH + O_2 \rightarrow HCO_2H + HO_2$ | 1.49×10^{-14} | not known |
| $(36) \text{ HO} + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{HCO}$ | 1.00×10^{-11} | temperature independent |
| (37) HO + NO ₂ (+M) \rightarrow HONO ₂ (+M) | 1.11×10^{-11} | Troe expression, ref 30 |
| (38) HO + NO (+M) \rightarrow HONO (+M) | 4.57×10^{-12} | Troe expression, ref 30 |
| $(39) \text{ HO} + \text{CO} (+\text{O}_2) \rightarrow \text{HO}_2 + \text{CO}_2$ | 2.59×10^{-13} | $1.35 \times 10^{-13} (1 + p(atm))$ |
| $(40) \text{ HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ | 1.07×10^{-10} | none |
| $(26) HO + O_3 \rightarrow HO_2 + O_2$ | 6.84×10^{-14} | $1.6 \times 10^{-12} e^{-940/1}$ |
| $(41) \operatorname{HO} + \operatorname{H}_2\operatorname{O}_2 \to \operatorname{H}_2\operatorname{O} + \operatorname{HO}_2$ | 1.66×10^{-12} | $2.1 \times 10^{-12} e^{-18/T}$ |
| $(42) \text{ HO} + \text{HONO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_3$ | 1.28×10^{-13} | $9.4 \times 10^{-15} e^{-7/6/1}$ |
| $(43) HO + HO_2NO_2 \rightarrow H_2O + NO_2 + O_2$ | 4.65×10^{-12} | $1.3 \times 10^{-12} e^{-300/2}$ |
| (50) HONO + HONO ₂ \rightarrow 2NO ₂ + H ₂ O | 2.71×10^{-17} | not known |
| $(22) \operatorname{NO}_3 + \operatorname{M} \rightarrow \operatorname{O}_2 + \operatorname{NO} + \operatorname{M}$ | 7.05×10^{-23} | see text |

 a Rate constants are largely from ref 30. Others are discussed or referenced in the text.

more complete reaction scheme outlined leads to the rate expression 44 based upon CO formation rate and/or CH_2O loss, and relation 45 based upon N_2O_5 and NO_3 loss:

$$k_{14} = \frac{R_{\rm CO}F}{[\rm NO_3][\rm CH_2O]} = \frac{(-R_{\rm CH_2O} + R_{\rm HCO_2H})F}{[\rm NO_3][\rm CH_2O]}$$
(44)

where $F = R_{14}/(R_{14} + R_{38})$.

$$k_{14} = (-R_{N_2O_5} - R_{NO_3} - R_6 + R_{15})G/([NO_3][CH_2O])$$
 (45)

where $G = R_{14}/(R_{14} + R_9 + R_{11} + R_{12} + R_{23})$. In experiments for which [NO₃] values were not measured directly, they are calculated as before from [NO₃] = $k_{1,2}[N_2O_5]/[NO_2]$ using the $K_{1,2}$ values suggested by Graham and Johnston.³¹

It can be observed by comparing relations 44 with 17 and relations 45 with 19 that the values of k_{14} estimated by the complete functions are related by the fractions F and G; k_{14} from eq 44 = $F(k_{14})_{max}$ from eq 17, and k_{14} from eq 45 = $G(k_{14})_{max}$ from eq 19. One may observe further that the rate terms R_{CO} and $-R_{CH_{2}O} + R_{HCO_{2}H}$ in eq 44 represent the total measured rate of H-atom abstraction from CH₂O which occurs by NO₃ and HO radicals. When we multiply by F, the fraction of the total H-atom abstraction from CH₂O which occurs by NO₃ radicals, then the rate of CH₂O loss due to reaction 14 alone is obtained. Similarly, the term, $-R_{N_2O_5} - R_{NO_3} - R_6 + R_{17}$, in relation 45, is equal to the total rate of NO₃ removal by all reactions. When we multiply by G, the fraction of the total NO₃ radicals which are removed by the NO_3 -CH₂O reaction, then the rate of NO_3 removal by reaction 14 alone is obtained. For our conditions these fractions F and G are not unity and cannot be neglected. They can be estimated readily by using the complete reaction mechanism of Table III and computer simulations of the chemical changes which occur in this system for each of the experiments.

An excellent fit of the theoretical product, reactant concentration-time plots for each of the observed products and reactants

can be obtained by using only three rate constant variables and the currently accepted rate constants for the other 33 reactions given in Table III. The variables are the rate constants for the $N_2O_5-H_2O(wall)$ reaction 6, the HO_2-NO_3 reaction 12, and the desired unknown rate constant 14 for the NO₃-CH₂O reaction. Several alternative methods of treating reaction 6 were tried in this study. The first approach was to use a fixed first-order decay constant for the N_2O_5 which was consistent with that observed for N_2O_5 decay in the reaction cell in the absence of CH_2O (about 10^{-4} s⁻¹). In other runs we varied the choice of a fixed value of k_6 (in the range 0-1.5 × 10⁻⁴ s⁻¹) to achieve the best N₂O₅ decay profile in trial simulations of the given experiment. However, we found that a third and best method (best computer fits, most physically realistic) of treating reaction 6 was to consider it to be a second-order heterogeneous reaction between N_2O_5 and a very limited supply of water adsorbed on the cell surface. The results of these computer tests suggest that the N_2O_5 removes the surface water effectively in the early part of the experiments and that reaction 6 becomes an unimportant loss mechanism for N_2O_5 after the first 10 min or so of the reaction. The use of one or another method of treatment of reaction 6 caused very little change in the k_{14} value derived from the simulations of a given experiment.

Reaction 12 was required in our mechanism in order to match successfully the $[NO_3]$ and $[O_3]$ decay curves. Although we are unaware of any experimental data available today which relate to this reaction, there are 10 well-studied analogous reactions in the literature which suggest its likely importance. Note in Figure 2 the correlation between the overall enthalpy changes and the measured rate constants (298 K) for the analogous general reaction 46 involving the HO₂ radicals:

$$HO_2 + X \to HX + O_2 \tag{46}$$

Data are available for $X = O_3$, NO_2 , HO_2 , Br, CH_3O_2 , ClO, BrO, Cl, O, and HO free radicals. In view of this correlation and the



Figure 2. Plot of the enthalpy change vs. rate constant for a series of reactions of the type $HO_2 + X \rightarrow HX + O_2$; most of the rate constant data are from ref 5; data for HO_2 - NO_2 from Howard⁴³ and HO_2 -Br from Poulet et al.⁴⁴

exothermicity of reaction 12, $\Delta H^{\circ}_{12} = -51.6$ kcal/mol, a reasonable value for k_{12} would lie in the range $2 \times 10^{-12} < k_{12} <$ 2×10^{-11} cm³ molecule⁻¹ s⁻¹ at 298 K. As we varied k_{12} in computer simulations, we found that the best fits of the data were had with $k_{12} \simeq (2.5 \pm 1.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in reasonable accord with the expectations based on the enthalpy-rate constant relationship of Figure 2. An experimental determination of this rate constant through a more direct method is desirable to test our tentative conclusions about the significance of reaction 12 and to eliminate the degree of freedom which the adjustable k_{12} values allow in the simulations. It is clear that the complete mechanism chosen for the computer simulation of the product, reactant concentration-time profiles in the various experiments is relatively unique with few variables left to adjust arbitrarily. It is based largely upon known reactions for which other more direct evidence points and for which reasonably reliable rate data exist. To the very limited extent that flexibility in the reaction mechanism and rate constant choices remain, these choices do not affect strongly the calculated k_{14} . In illustration of this point consider several changes which were made in the mechanism during the course of the current study. In many initial studies we were able to achieve reasonable fits of the product concentration-time data by using a maximum rate constant for reaction 9; $k_9 = 2.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (298 \text{ K}).^{40}$

$$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2 \tag{9}$$

However, our subsequent reevaluation of the literature related to reaction 940 led us to accept the much lower estimate of Graham and Johnston³¹ for the k_9 values near room temperature. An equally good computer match of the experimental data was possible, but the addition of two other channels for NO generation from NO₃, reactions 21 and 22, then compensated for the choice of smaller k_0 The generation of some minimum amount of NO in the O₃-NO₂-CH₂O system was a key to a good simulation of the data. Yet in the final analysis, the values of F, G, and k_{14} estimated by using the two very different options for forming NO

led to essentially the same values for F, G, and k_{14} in a given experiment. Using the complete mechanism of Table III and the adjustment of k_6 , k_{12} , and k_{14} to obtain the best visual fit of the product and reactant concentration-time profiles in a given run, we derived estimates of F and G required to correct $(k_{14})_{max}$ estimates. These factors varied from experiment to experiment, and they were weakly dependent on the extent of the reaction which had occurred in the given run. Specific F and G values were derived for each of the three to six times during a given run where estimates of R_{CO} , R_{CH_2O} , or $R_{NO_3} + R_{N_2O_5}$ were made from the data.

Note in Table I, columns 1 and 2, that the highly divergent $(k_{14})_{max}$ values obtained by the two methods involving relations 17 and 18 or 19 and 20 give nearly equal estimates of k_{14} (columns 3 and 4 of Table I) when the fractions F and G are employed to correct the $(k_{14})_{max}$ values as theory suggests. This provides additional credence to the data treatment given here.

There are three different estimates of k_{14} which can be derived from each experiment: (a) $R_{\rm CO}$, $R_{\rm CH_{2O}}$ data and relation 44; (b) $R_{\rm N_{2O_5}} + R_{\rm NO_3}$ data and relation 45; and (c) the k_{14} value derived from the best visual fit of all of the product and reactant concentration-time data using the computer simulations. The average values for k_{14} derived from these three methods are as follows: $(5.7 \pm 0.8) \times 10^{-16}$, $(7.2 \pm 1.4) \times 10^{-16}$, and $(6.0 \pm 0.4) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹, respectively. The overall average of all of the data gives $k_{14} = (6.3 \pm 1.1) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (applicable over the limited temperature range employed here, 296-300 K).

In the recent studies of Atkinson et al.,¹⁹ who employed the approximate method defined by relation 20, the authors derive $k_{14} = (3.23 \pm 0.26) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (298 \text{ K}).$ This estimate is about a factor of 2 lower than ours. If the several complications which we identified were present in the experiments of Atkinson et al., then we would expect their value to be higher than ours since G values greater than unity are not possible in theory. One possible cause for an underestimation of the value of k_{14} lies in a change in the N₂O₅ wall loss rate with CH₂O addition. In theory the rate of N_2O_5 -H₂O(wall) reaction may have decreased from the clean cell conditions as the wall composition was altered in the use of CH₂O-rich reactant mixtures in the studies of Atkinson et al. Thus, CH₂O could remove the available H_2O through its hydration reaction, $CH_2O + H_2O(wall)$ ► HOCH₂OH(wall). If this were the case and none of the other complications which we considered previously were important for their conditions, than their k_{14} estimates could be low from this cause, but it is highly unlikely that the magnitude of the change in k_{14} estimate would be as high as factor of 2.

It should be observed that the initial concentrations of reactants NO_2 and CH_2O employed by Atkinson et al. were up to 100 times those employed in our work, while the $[N_2O_5]$ was very similar to that which we employed. Thus, the NO_3 concentrations would be significantly lower (as low as 1/100th of that present in our experiments), and the rate of HO₂ removal by CH₂O and NO₂ would be significantly higher. Possible interference from the HO₂-NO₃ reaction is expected to be unimportant for their conditions. Thus, it is likely that other reasons for the discrepancy in k_{14} estimates must be sought. Tuazon et al.²⁴ noted that all of the recently reported NO₃-RH rate constants from the Pitts group would be raised by a factor of 1.8 if they used their measured value of $K_{1,2}$. However, they did not recommend this procedure. If this correction is made to the reported value, then their data give $k_{14} \simeq (6.0 \pm 0.5) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in excellent agreement with our estimate, $(6.3 \pm 1.1) \times 10^{-16} \text{ cm}^3$ molecule⁻¹ s⁻¹. We do not accept the lower $K_{1,2}$ estimate of Tuazon et al.²⁴ in view of other data related to this equilibrium; our data agree within the experimental error with those of Graham and Johnston³¹ and Malko and Troe.⁴²

It is possible that some unidentified persistent error is present in the extinction data employed both by Tuazon et al. in their

⁽⁴⁰⁾ Hampson, R. R.; Garvin, D. NBS Spec. Publ. (U.S.) 1978, No. 513. The rate constant function $k_9 = 2.3 \times 10^{-13} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which is favored by Hampson and Garvin and attributed to Baulch et al.⁴¹ was miscopied from the original review of Baulch et al.; the exponential term should be $e^{-1600/T}$.

⁽⁴¹⁾ Baulch, D. L.; Drysdale, D. D.; Horne, D. G. "Evaluated Kinetic Data for High Temperature Reactions"; Butterworths: London, 1973; Vol. 2.

⁽⁴²⁾ Malko, M. W.; Troe, J. Int. J. Chem. Kinet. 1982, 14, 399.
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⁽⁴⁴⁾ Poulet, G.; Laverdet, G.; Le Bras, G. J. Chem. Phys. 1984, 80, 1922.

equilibrium studies and in the kinetic studies of Atkinson et al. An error in the $\epsilon_{N_2O_5}$ could not affect the results since a d(ln $[N_2O_5])/dt$ term result from the solution of 20 for k_{14} and such an error would cancel out. However, if the ϵ_{NO_2} which they employed was too large and hence led to low $[NO_2]$ estimates in both the kinetic and equilibrium studies, then a cancellation of this error would result when their $K_{1,2}$ was combined to calculate k_{14} . Whatever the source of the differences in the k_{14} estimates, we recommend as the current best estimate $k_{14} = (6.3 \pm 1.1) \times$ 10^{-16} cm³ molecule⁻¹ s⁻¹. Note that for the k_{14} estimates derived from runs 1-5 of Table I (for which NO₃ was not measured directly) are inversely proportional to the value of $K_{1,2}$ chosen. This is also the case for the computer simulations of all of the runs (1-9) in Table I. Thus, if the estimates of Tuazon et al. are chosen, these k_{14} estimates become larger than those reported here by a factor of 1.8. The k_{14} estimates we derived from runs 6-9 of Table I, in which direct determinations of NO3 were made, are not dependent on the choice for $K_{1,2}$. To clarify the proper choice of $K_{1,2}$ for these experiments we have carried out a direct redetermination of $K_{1,2}$ which we will report separately.²⁵

The present estimate of k_{14} , although twice that reported by

Atkinson et al., is only about one-half of that which was assumed in our recent simulations of the nighttime chemistry of the polluted troposphere. We expect that the theoretical rate of HO₂ radical generation through reaction 14 will be about one-half of that found in our previous work. However, recent rate constant estimates suggest that the NO₃-CH₃CHO reaction may have a larger influence than we suggested in the earlier theoretical study. If one applies the suggested 1.8 factor to the recently reported NO₃- \dot{CH}_3 CHO rate constant,¹⁹ then a value of $k_{47} \simeq (2.5 \pm 0.5) \times$ 10^{-15} cm³ molecule⁻¹ s⁻¹ is obtained.

$$NO_3 + CH_3CHO \rightarrow HONO_2 + CH_3CO$$
 (47)

This estimate of k_{47} is twice that used in our previous study. If correct then peroxyacetyl nitrate generation during the nighttime hours can be twice as great as we had previously estimated. A preliminary evaluation of our experimental study of reaction 47 confirms the Atkinson et al. conclusion that $k_{47} > k_{14}$; the results of our determination of k_{47} will be published later.

Registry No. NO3 radical, 12033-49-7; CH2O, 50-00-0.

A Model for the Chains in Amphiphilic Aggregates. 1. Comparison with a Molecular Dynamics Simulation of a Bilayer

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A simple model for the packing of amphiphiles into spherical and cylindrical micelles and into bilayers is described. Each aggregate is assumed to have a hydrophobic core which contains only the hydrocarbon chains of the amphiphiles. All possible internal bond sequences of a single amphiphile are generated. When an ensemble average is taken over all these conformations, the hydrophobic core of the aggregate is packed at liquid hydrocarbon density throughout. Without exception, results derived from the model show the same qualitative trends as results derived from a molecular dynamics simulation of a bilayer involving 128 chains. In most cases, the quantitative agreement between the two sets of results is very close indeed. After an extensive analysis involving both experimental and theoretical evidence, it is concluded that the combined amplitude of all the independent "splay" and "twist" distortion modes of the local director of the bilayer is very small. Cooperative tilting of the chains in a bilayer exists only over length scales comparable to a chain diameter and even then only to a limited extent.

Introduction

Both this paper and the next one are concerned with the behavior of the hydrocarbon chains in amphiphilic aggregates. A simple theoretical model is presented which attempts to give a detailed and reasonably accurate view of the conformational state of the chains in spherical micelles, in cylindrical micelles (or hexagonal phases), and in bilayers.

If either temperature or aggregate geometry precludes an array of parallel frozen chains, the small difference in energy between trans and gauche conformers ($\sim 1kT$ at room temperature)¹ leads us to expect a liquid-like aggregate interior with considerable configurational disorder in the chains. This expectation is borne out by experiments on micelles²⁻⁴ and on hexagonal and lamellar phases.⁵⁻⁸ (In the case of lamellar phases we are only concerned

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with the high-temperature liquid crystalline phase. In order to account for the phase transition to the gel phase, it is necessary to recognize that frozen all-trans chains are packed at a higher density than fluid chains and hence have stronger van der Waals attractions.9,10)

From the experience we have of liquid-state physics we expect that the combined action of short-range intermolecular repulsive forces and longer range van der Waals attractions will ensure that the density of chain packing in the liquid hydrophobic core is, within narrow limits, the same as in bulk *n*-alkane phases. In the case of curved aggregates, if the surface of the aggregate is a surface of tension, there will be a Laplace pressure acting on the aggregate interior. Nevertheless, for any reasonable value of the net surface tension acting at the aggregate surface ($\gamma < 10$ mN/m), it is clear than even for small spherical micelles (say, with a radius of 15 Å), this Laplace pressure leads to a negligible increase in density. Thus, assuming that the compressibility of

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