J. Phys. Chem. A **1997,** *101,* 55−59

Relative Rate Study of the Reactions of Acetylperoxy Radicals with NO and NO_2: Peroxyacetyl Nitrate Formation under Laboratory Conditions Related to the Troposphere

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Received: July 26, 1996; In Final Form: September 30, 1996⊗

A relative rate study has been performed on the reactions $CH_3C(O)O_2^{\bullet} + NO_2 + M \rightarrow CH_3C(O)O_2NO_2 + M$ (1) and $CH_3C(O)O_2^{\bullet} + NO \rightarrow CH_3^{\bullet} + CO_2 + NO_2$ (2) in an atmospheric flow system in which the relative yields of $CH_3C(O)O_2NO_2$ (PAN) have been measured as a function of the ratio of reactants [NO]/[NO_2]. Over the temperature range 247−298 K, at a total pressure of ∼1 atm, the ratio was independent of temperature, $k_1/k_2 = 0.41 \pm 0.03$, where the error limits are 2σ. The results are discussed with reference to other relative rate measurements of k_1/k_2 and to absolute measurements of k_1 and k_2. The atmospheric implications of the ratio k_1/k_2 in relation to PAN are briefly considered.

Introduction

Peroxyacetyl nitrate ($CH_3C(O)OONO_2$, PAN) is formed in the atmosphere in the oxidative degradation of many organic compounds of both anthropogenic and biogenic origin.[1,2] It is an important oxidant component of summer smog and can cause eye irritation and plant damage.[3] Moreover, PAN acts as a temporary reservoir for reactive intermediates involved in summer smog formation, and it plays an important role in the transport of NO_x in the troposphere. It is therefore essential to establish accurate data on the kinetics and mechanisms of its formation and removal for inclusion in models of atmospheric chemistry.

The precursor of PAN in the atmosphere is the acetyl peroxy radical ($CH_3C(O)OO^{\bullet}$), which is mainly formed from the hydroxyl radical initiated oxidation of acetaldehyde. The initial reaction produces an acetyl radical which is rapidly oxidized to the corresponding acetylperoxy radical under atmospheric conditions:

$$HO^{\bullet} + CH_3CHO \rightarrow H_2O + CH_3CO^{\bullet}$$

$$CH_3CO^{\bullet} + O_2 + M \rightarrow CH_3C(O)OO^{\bullet} + M$$

In the polluted atmosphere, there are two main competing reactions for the acetylperoxy radical:

$$CH_3C(O)OO^{\bullet} + NO_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3C(O)OONO_2 + M \tag{1,−1}$$

$$CH_3C(O)OO^{\bullet} + NO \xrightarrow{k_2} CH_3C(O)O^{\bullet} + NO_2 \tag{2}$$

where reaction 2 is followed by the fast reaction

$$CH_3C(O)O^{\bullet} \xrightarrow{\text{fast}} CH_3^{\bullet} + CO_2 \tag{3}$$

Note that since PAN is relatively unstable, its decomposition via reaction −1 has to be included.

The ratio of the rate constants, k_1/k_2, and the thermal decomposition rate constant, k_{-1}, are key values in the atmospheric chemistry of PAN. Computer-modeling studies of the troposphere have shown that the uncertainties in the rate constants of the PAN chemistry are important when calculating the ozone formation.[4] The kinetics of the thermal decomposition of PAN have been extensively studied and the rate coefficients (k_{-1}) are well established.[5] Absolute rate coefficients have been reported[6−8] for reaction 1 and there have been two recent direct measurements[9,10] of k_2 over a range of temperatures. The rate coefficient ratio, k_1/k_2, has been measured in several relative rate studies for PAN[11−15] and a few analogous peroxyacyl nitrates.[16−19]

Prior to the present study, however, only indirect determinations of the ratio k_1/k_2 for PAN have been carried out. Cox et al.[11] and Cox and Roffey[12] measured the NO to NO_2 conversion and absolute yields of PAN and derived k_1/k_2 from a kinetic analysis involving complex reaction schemes. Hendry and Kenley,[13] Kirchner et al.,[14] and Tuazon et al.[15] investigated the rate of the thermal decomposition of PAN as a function of the [NO]/[NO_2] ratio and obtained values of k_1/k_2 at temperatures above 283 K.

In the present work, the ratio, k_1/k_2, was measured by a method involving the production of acetylperoxy radicals from the photolysis of biacetyl in the presence of O_2:

$$(CH_3CO)_2 + h\nu \rightarrow 2CH_3CO^{\bullet} \tag{4}$$

$$CH_3CO^{\bullet} + O_2 + M \rightarrow CH_3C(O)OO^{\bullet} + M \tag{5}$$

By measuring the resulting relative PAN concentrations as a function of the [NO]/[NO_2] ratio, we have been able to measure k_1/k_2 at atmospheric pressure and at lower temperatures than hitherto reported.

Experimental Section

Materials. The synthetic air (PanGas) was a mixture of 20% O_2 and 80% N_2. Mixtures of nitric oxide (1004 ± 2 ppm) in N_2 and nitrogen dioxide (960 ± 2 ppm) in synthetic air were supplied by Carbagas. The following chemicals were used without further purification other than bulb-to-bulb distillation: biacetyl (2,3-butadione, Fluka, ≥99%), acetyl chloride (Fluka, ≥99%), acetaldehyde (Fluka, ≥99.5%). PAN was synthesized by the liquid-phase nitration of peracetic acid in *n*-tridecane solution.[20,21]

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⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1996.

S1089-5639(96)02266-9 CCC: $14.00

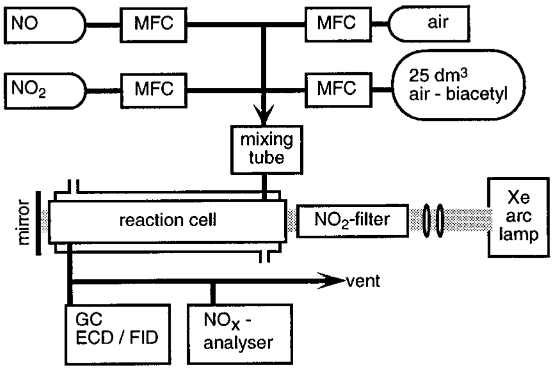

Figure 1. Schematic diagram of the atmospheric flow reactor system.

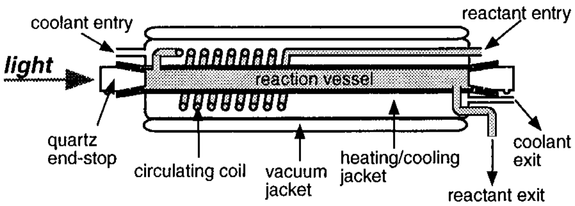

Figure 2. Detailed drawing of the flow reactor.

Flow System. A schematic diagram of the apparatus is shown in Figure 1. The experiments involved flowing an air mixture through an irradiated reactor with a residence time of about 50 s and analyzing the reactants and PAN product either by gas chromatography (GC-ECD-FID) or with an NO_x chemiluminescence analyzer. The experiments were carried out at atmospheric pressure (965 ± 5 hPa) and over the temperature range 247−343 K.

A steady flow of synthetic air containing biacetyl, NO, and NO_2 in the ppm range was established through the reaction vessel. Mass flow controllers (MFC, Brooks, Model 5850E) consisting of a flow sensor, a control valve and an electronic control system allowed the separate control of all the concentrations without affecting the total flow, which was constant over the time scale of the experiments and usually at the rate of 400 $cm^3\ min^{-1}$. The mass flow controllers were calibrated for air (80% N_2 and 20% O_2) and were unaffected by the low concentrations of reactants in the mixtures. These calibrations were regularly checked using soap-bubble flow meters.

NO in nitrogen and NO_2 in air were taken from commercial cylinders. For biacetyl, an 8000 ppm mixture in synthetic air was prepared and stored in a 25 dm^3 glass bulb at a pressure of about 1250 hPa. To prepare such a mixture, the evacuated bulb was first filled with about 10 hPa of the biacetyl using a precision pressure gauge and then synthetic air was added. Preliminary attempts to generate the air−biacetyl mixture by multiple dilution of a slow flow of air bubbled through a liquid sample of biacetyl failed, owing to the lack of long-term stability.

The combined gas streams from the MFCs were passed through a gas-mixing device consisting of a glass tube containing a series of Teflon baffles (Sulzer Chemtech) prior to entering the flow reactor. All connections were made with Teflon or PFA tubing (3 mm i.d.) which was covered with aluminum foil to prevent prephotolysis of the reactants.

The flow reactor (see Figure 2) has already been used to investigate gas-phase reactions under conditions related to the troposphere.[22,23] The Pyrex reaction vessel consisted of three concentric chambers. The inner tube was the actual reaction vessel with an internal diameter of 2.9 cm and a length of about 56 cm. The vessel was irradiated through evacuated glass stoppers with quartz end windows. A thermostated fluid consisting of a 1:1 mixture of propylene glycol and water was circulated (thermocirculator, Lauda RKS 20) through the middle chamber to maintain a uniform temperature in the reaction vessel. Before entering the reaction vessel, the gas mixture was equilibrated at the reactor temperature by passage through a Pyrex coil surrounded by the thermostated fluid in the middle chamber. A metal shield was wrapped around the outer surface of the inner glass tube to prevent the irradiating light beam from entering the middle chamber. The outermost chamber was a vacuum jacket, to reduce the heat flux between the reactor and its surroundings.

The reaction vessel was illuminated by a solar simulator (Polytec XS 1000) consisting of a 1 kW Xe arc lamp. The light passed to the flow reactor through a set of collimating lenses, a water filter, an air mass filter (AM2, cutoff at 330 nm) and an NO_2 filter. The latter was used to minimize photolysis of NO_2 in the reactor and consisted of a glass cell with quartz windows filled with air containing about 1.5% NO_2 at atmospheric pressure and had a transmission of 10% at 400 nm and 20% at 460 nm. Under these conditions biacetyl was photolyzed over the spectral region 350−450 nm but photolysis of NO_2 was negligible.

Analysis. The PAN was measured using a gas chromatograph (Carlo Erba HRGC 5300) operated at 35 °C and fitted with an electron capture detector (ECD) at 100 °C. Gas samples were drawn from the exit of the reactor through a 2 m fused silica capillary (i.d. 0.56 mm) at a flow rate of 20 $cm^3\ min^{-1}$ and transferred via an automatic gas sampling valve using a 100 μL stainless steel loop into a cryotrap (Carlo Erba). The compounds were separated on a 16 m capillary column[24] (4% PS-255) with H_2 as the carrier gas at a flow rate of 10 $cm^3\ min^{-1}$. The PAN retention time was 2.0 min under these conditions.

Linearity and calibration checks of the ECD were carried out by measuring ppb levels of PAN simultaneously with the GC-ECD, the NO_x analyzer, and an FTIR spectrometer (BIORAD FTS45). The PAN samples for the calibration were prepared by passing air through a solution of PAN in *n*-tridecane and subsequently diluting this gas stream with pure air using mass flow controllers. The ECD response for PAN was linear up to a mixing ratio of 500 ppb and the detection limit (3σ) was 0.5 ppb.

NO and NO_2 were measured with a commercial chemiluminescence $NO-NO_2-NO_x$ analyzer (Thermo Environmental Instruments Inc., Model 42) fitted with a stainless steel NO_2 to NO converter operating at a temperature of 625 °C. The instrument was calibrated with standard mixtures of NO and NO_2. Additionally, the conversion rate (99%) was checked by gas-phase titration of the NO standard with ozone.

Measurement of the Rate Data. During each experiment only the concentrations of NO and NO_2 were varied. All other parameters such as temperature, total flow, reaction time, light intensity, and the biacetyl concentration were kept constant. A typical set of experimental results under the fixed conditions described above is shown in Figure 3. Starting with no NO in the mixture, the $[NO]/[NO_2]$ ratio was increased to a value of about 4 and subsequently decreased stepwise back to 0, and at each selected value of the $[NO]/[NO_2]$ ratio the relative amount of PAN formation was measured. This procedure confirmed that the system was stable over the time scale of the experiments. Typical levels of reactants and products, in units of ppm, were [NO] 0−4, $[NO_2]$ 1−5, [biacetyl] 25, and [PAN] 0.01−0.1.

As a check on the proposed mechanism for PAN formation in this study, a range of additional experiments was carried out as follows: (i) as described above but with different flow rates,

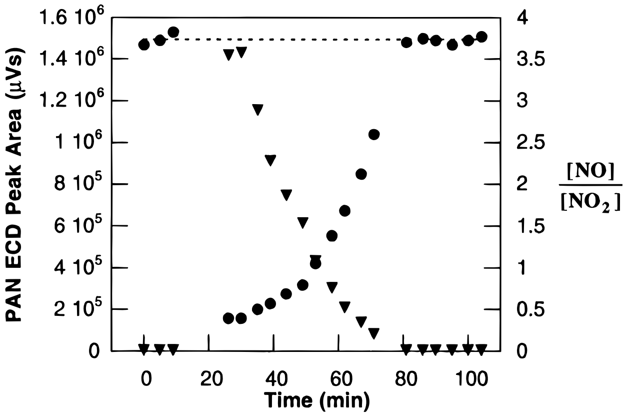

Figure 3. Plot of the measured relative mixing ratios of PAN (●) as a function of [NO]/[NO$_2$] (▼) for $T = 25$ °C. The dashed line shows the PAN$^{[NO]=0}$ value used in the calculations.

153 and 916 cm^3 min^{-1}; (ii) with the photolysis of CH$_3$COCl as the radical source; (iii) with the photolysis of Cl$_2$ in the presence of CH$_3$CHO as the radical source; (iv) with the reaction vessel lined with a thin Teflon sleeve. In all cases the kinetic data were consistent with the results of the main studies (see Results and Discussion).

Results

In the presence of relatively high concentrations of NO and NO$_2$, the formation of PAN and CO$_2$ is governed by reactions 1 and 2. Thus we can write the rate equations:

$$\mathrm{d[PAN]/d}t = k_1[\mathrm{CH_3CO_3}]_t[\mathrm{NO_2}]_t \qquad \text{(I)}$$

$$\mathrm{d[CO_2]/d}t = k_2[\mathrm{CH_3CO_3}]_t[\mathrm{NO}]_t \qquad \text{(II)}$$

on the assumption that reaction −1 is negligible, which holds at low temperatures. Taking the ratio of eqs I and II and integrating over time assuming that [NO]$_0$ and [NO$_2$]$_0$ are constant give the following equation

$$\frac{[\mathrm{PAN}]_t}{[\mathrm{CO_2}]_t} = \frac{k_1}{k_2}\frac{[\mathrm{NO_2}]_0}{[\mathrm{NO}]_0} \qquad \text{(III)}$$

where the subscripts 0 and t indicate concentrations at the beginning of the experiment and at time t, respectively.

Initially we had intended to measure the CO$_2$ formation as well as the PAN formation. This, however, was not possible as we discovered that the PAN decomposed to yield CO$_2$ in the infrared instrument which was used to measure the CO$_2$ from the reaction. There were also additional problems in dealing with the ambient levels of CO$_2$ in the atmosphere of the laboratory which interfered with the product CO$_2$ levels in the ppb range. We have therefore resorted to a kinetic analysis based solely on the measurement of the PAN formation.

If the production of the acetyl peroxy radical is independent of the [NO]/[NO$_2$] ratio and there are no reactions of the acetyl peroxy radical that are dependent on the [NO]/[NO$_2$] ratio other than (1) and (2), then the sum of ([PAN]$_t$ + [CO$_2$]$_t$) is independent of the [NO]/[NO$_2$] ratio. This sum can be determined by measuring $[\mathrm{PAN}]_t^{[\mathrm{NO}]=0}$, which is [PAN]$_t$ when [NO]/[NO$_2$] = 0 and therefore [CO$_2$]$_t$ = 0. Thus, independent of the [NO]/[NO$_2$] ratio, [CO$_2$]$_t$ can be expressed as

$$[\mathrm{CO_2}]_t = [\mathrm{PAN}]_t^{[\mathrm{NO}]=0} - [\mathrm{PAN}]_t \qquad \text{(IV)}$$

Combination of eqs III and IV yields the expression

$$\frac{[\mathrm{PAN}]_t^{[\mathrm{NO}]=0}}{[\mathrm{PAN}]_t} = \frac{[\mathrm{NO}]_0}{[\mathrm{NO_2}]_0}\frac{k_2}{k_1} + 1 \qquad \text{(V)}$$

On the basis of eq V the ratio of the rate constants k_1/k_2 was derived by a linear least-squares fit from the plots of $[\mathrm{PAN}]_t^{[\mathrm{NO}]=0}$/[PAN]$_t$ as a function of [NO]/[NO$_2$]. A typical plot of the present data is shown in Figure 4, which is derived from the raw data of Figure 3.

The rate coefficient ratios found in this study are listed in Table 1, where the errors quoted are 2σ. No significant temperature dependence is found in the temperature range 247−298 K, and the average of these measurements is 0.41 ± 0.03, where the error is 2 times the standard deviation. Above 298 K the decomposition reaction −1 cannot be neglected, and these measurements yield a ratio which is underestimated as will be discussed later.

Discussion

Checks on the Proposed Mechanism of PAN Formation. As noted in the Results and in Table 1, the measurements of k_1/k_2 at 310 and 343 K show considerably lower values of the ratio than over the temperature range 247−298 K. This effect can be explained by the onset of the decomposition of PAN, reaction −1, in relation to the time scale of the flow experiments. Thus at 343 K we calculate the half-life of PAN at high [NO]/[NO$_2$] ratios to be 3.5 s compared to the residence time in the flow system of ~50 s for the standard flow rate of 400 cm^3 min^{-1}. As further evidence of this situation we have compared the experimental results to those from a kinetic model of the reaction scheme (reactions 1−5) using the rate coefficients recommended by IUPAC.[5] Details of the modeling calculations are presented elsewhere,[25] and the results are shown in Figure 5, where the agreement is reasonably satisfactory.

Further checks on the mechanism were carried out with alternative sources of acetyl radicals, namely, the photolysis of CH$_3$COCl (with the air mass filter removed) and the photolysis of Cl$_2$ in the presence of CH$_3$CHO. In both cases the results for k_1/k_2 were consistent with the data derived from the biacetyl photolyses. It should be noted, however, that when we used relatively high ratios of [CH$_3$CHO]:[Cl$_2$], the values of k_1/k_2 increased to ~0.6. This we believe was due to the presence of substantial concentrations of OH radicals in the system, generated from the oxidative chain reaction[12] involving CH$_3$ radicals produced as result of reaction 2. These OH radicals add to the generation of PAN via OH-initiated attack on CH$_3$CHO which affects our assumption that the rate of formation of the acetyl radical is independent of the [NO]/[NO$_2$] ratio. Such additional OH-initiated PAN formation is not possible with the photolytic radical sources, CH$_3$COCOCH$_3$ and CH$_3$COCl, since OH attack on both of these molecules is unlikely to yield acetyl radicals and hence acetylperoxy radicals and PAN under the conditions of the present experiments.

Additional experiments were performed with the main radical source from the photolysis of biacetyl but with higher and lower flow rates through the reaction vessel, as recorded in Table 1. The results show no systematic trend with increasing flow rate, although in view of the higher errors involved at the lower flow rate and the relatively low mixing ratio of NO and NO$_2$ at the higher flow rate, we have not included these data in calculating the average value of k_1/k_2 over the temperature range 247−298 K.

Langer et al.[26] have reported that heterogeneous reactions of PAN are too slow to have an influence on PAN decomposition under typical atmospheric conditions but may affect laboratory

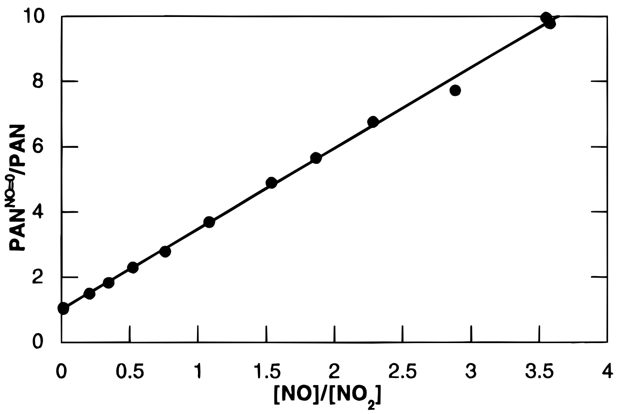

Figure 4. Kinetic plot of the ratio of PAN measured as a function of $[NO]/[NO_2]$ according to eq V for $T = 25$ °C, based on measurements shown in Figure 3.

TABLE 1: Rate Constant Ratios, k_1/k_2, as a Function of Temperature at Atmospheric Pressure (965 hPa)

temp/K	k_1/k_2[a]	temp/K	k_1/k_2[a]
247	0.417 ± 0.019	290	0.430 ± 0.025
253	0.391 ± 0.015	290	0.444 ± 0.046[e,g]
263	0.401 ± 0.015	290	0.468 ± 0.019[f,g]
273	0.436 ± 0.02[b]	298	0.405 ± 0.013
282	0.428 ± 0.018	310	0.324 ± 0.015[g]
283	0.417 ± 0.02[c]	343	0.044 ± 0.005[g]
289	0.407 ± 0.01[d]		

[a] Errors are the sum of 2σ from linear least-squares fit and 2σ of $PAN^{[NO]=0}$ determination. [b] Acetyl chloride as the radical source. [c] Acetaldehyde + Cl_2 as the radical source. [d] Teflon sleeve inserted into the reactor. [e] Total flow 153 cm^3 min^{-1}. [f] Total flow 916 cm^3 min^{-1}. [g] Not used to calculate the average (see text).

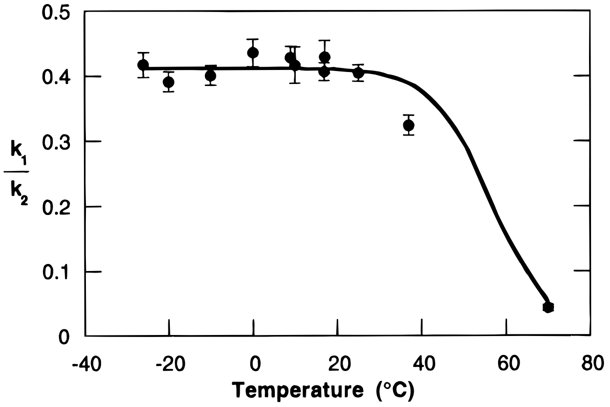

Figure 5. Comparison of present data on k_1/k_2 with a kinetic model of the reaction scheme: (●) measured ratios, (solid line) modeled ratios.

measurements of PAN, through the decomposition of the acetylperoxy radical or PAN itself at a surface. In the present system, with a surface-to-volume ratio of about 1.4 cm^{-1} and relatively high mixing ratios of NO and NO_2, the possible heterogeneous reactions[26] are negligible in relation to the short residence time (~50 s) in the flow reactor. As further evidence that heterogeneous reactions are not important in the present system, an experiment was carried out with the Pyrex reaction vessel lined with a Teflon sleeve. The kinetic data measured with the Teflon surface were consistent with the results of the main studies carried out with a Pyrex surface (see Table 1).

The above kinetic treatment assumes that [NO] and $[NO_2]$ do not change significantly during the course of the reaction. Of course, reactions 1 and 2 affect the mixing ratios of these two compounds, and every methyl radical produced leads to further NO to NO_2 conversion.[11] However, in our system the changes in the mixing ratios of NO_2 and NO brought about by these reactions are relatively small since the sum of the mixing ratios of NO and NO_2 was at least an order of magnitude higher than the mixing ratios of the products, PAN and CO_2. In addition, the photolysis of NO_2 was minimized by the presence of the NO_2 filter in the light train. Direct experimental confirmation of the essential stability of the ratio $[NO]/[NO_2]$ during the course of a reaction was obtained by switching on and off the light or the flow of biacetyl while monitoring NO and NO_2.

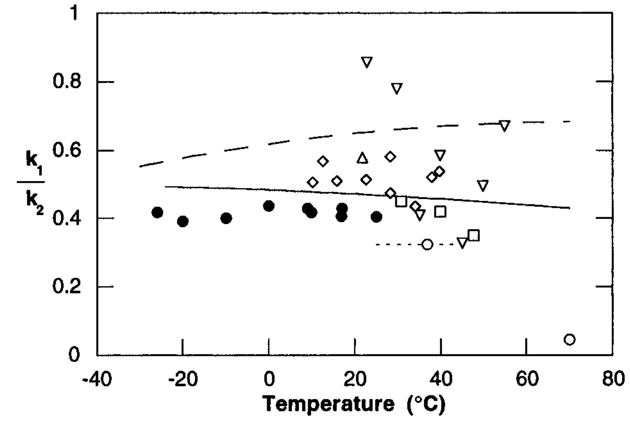

Figure 6. Comparison of present data on k_1/k_2 with literature values: (●) this study, (○) this study, at temperature where reaction −1 is significant; (△) Cox et al.;[11] (▽) Cox and Roffey;[12] (□) Kirchner et al.;[14] (◇) Tuazon et al.;[15] (- - -) Hendry and Kenley;[13] (—) ratio of the absolute rate coefficients of Bridier et al.[6] and Villalta and Howard;[9] (— — —) ratio of the absolute rate coefficients of Bridier et al.[6] and Maricq and Szente.[10]

The photolysis of the PAN product during the course of the experiments can be neglected for a number of reasons. First there is very little overlap of the absorption spectrum[27] of PAN with the photolytic light ($\lambda > 330$ nm). In addition, during the course of a run < 0.5% of the biacetyl was photolyzed, and the absorption cross sections of biacetyl are orders of magnitude higher than those of PAN under the experimental conditions. Finally, if the PAN photolysis was significant it would be expected that the values of k_1/k_2 would show a dependence on contact time i.e., flow rate through the reactor, which is not the case (see data of Table 1).

Comparison with Literature Data. Figure 6 shows a plot of the present results in relation to previous determinations of k_1/k_2 as a function of temperature and at pressures close to 1 atm. Our temperature independent value of $k_1/k_2 = 0.41 \pm 0.03$ is in agreement with the value $k_1/k_2 = 0.48 \pm 0.07$ recommended in the IUPAC evaluation[5] and by Wallington et al.[28] on the basis of the data of Cox and Roffey,[12] Kirchner et al.,[14] and Tuazon et al.[15] Note that in the present study we have been able to extend the relative rate measurements down to a temperature of 247 K and at the same time have considerably improved the precision of the measurements.

Also shown in Figure 6 are values of k_1/k_2 calculated from absolute measurements of k_1 and k_2. The values of k_1 are from Bridier et al.,[6] which form the basis of the recommendations for k_1 in the IUPAC evaluation[5] and the NASA panel evaluation.[29] These two groups differ in their representation of the pressure effect on k_1 according to the Troe formulation. Here we have calculated k_1 at 1 atm pressure as a function of temperature from the values $k_0 = 2.7 \times 10^{-28}(T/298)^{-7.1}$ [M] cm^3 molecule^{-1} s^{-1}, $k_\infty = 1.21 \times 10^{-11}(T/298)^{-0.9}$ cm^3 molecule^{-1} s^{-1}, $F_c = 0.30$, and $N_c = 1.41$ derived by Bridier et al.[6] over the temperature range 248−393 K. These k_1 values have been combined with the two recent determinations of k_2

to derive the lines plotted in Figure 6. Villalta and Howard[9] have reported $k_2 = 8.1 \times 10^{-12} \exp(270/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200−402 K, from a direct study of the acetylperoxy radicals using mass spectrometry. Maricq and Szente,[10] on the other hand, have reported $k_2 = 2.1 \times 10^{-12} \exp(570/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 228−353 K, from transient IR absorption of NO_2 and time-resolved UV spectroscopy of the acetylperoxy radicals. It is clear from the two resulting lines shown in Figure 6 that there is a significant difference, about 30% at 298 K, in the calculated values of k_1/k_2 at atmospheric pressure based on the studies of Villata and Howard[9] and of Maricq and Szente.[10] Until this discrepancy is resolved, it is difficult to compare the calculated values of k_1/k_2 with those measured in the relative rate studies, although at face value the calculated ratios k_1/k_2 derived from the study of Villata and Howard[9] are in better agreement with the present data than are those of Maricq and Szente.[10]

Atmospheric Implications. While at altitudes above 7 km photolysis is the major loss process of PAN,[30,27] the lifetime (τ) of PAN in the warmer parts of the troposphere is controlled by the rate of its thermal dissociation, reaction −1. In addition, however τ is dependent upon reactions 1 and 2 and may be expressed according to eq VI, based on a steady-state assumption for the acetylperoxy radical concentration:[12]

$$\tau = \left(1 + \frac{k_1}{k_2}\frac{[NO_2]}{[NO]}\right)(k_{-1})^{-1} \qquad \text{(VI)}$$

For example, at a temperature of 263 K in the free troposphere, taking a typical[31] [NO]/[NO_2] ratio of 3, the lifetime is 20 days, based on the value of k_1/k_2 determined here and the value of k_{-1} recommended by IUPAC.[5] This lifetime is 2.2 times lower when calculated simply on the basis of reaction −1. Thus the ratio of rate coefficients, k_1/k_2, plays a significant role in the lifetime of PAN in the troposphere and consequently affects the transport of PAN and therefore the ozone generation.

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