Rate coefficients for $\text{H+NO}_2\rightarrow\text{OH+NO}$ from high pressure flow reactor experiments

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Abstract: Rate coefficients for the reaction \( H^+NO_2 → OH + NO \) (R1) were determined over the nominal temperature and pressure ranges of 737-882 K and 10-20 atm, respectively, from spatially resolved measurements in two different flow reactor facilities: one laminar and one turbulent. The title reaction is important in a variety of situations including \( NO ↔ NO_2 \) interconversion in the power extraction stage of gas turbines, exhaust gas recirculation (EGR)-affected ignition in reciprocating engines, and for \( H \) atom titration in elementary gas phase kinetics experiments. This work determines absolute values of \( k_1 \) with reference to the relatively well known rate coefficients for \( H^+O_2+M → HO_2+M \) (R2.M) for \( M = Ar \) and \( N_2 \) and a quasi-steady state \( NOx \) plateau (QSSP) method that measures the ratio of \( k_1 \) to \( k_{2,M} \). At QSSP conditions established during \( NOx \)-perturbed \( H_2 \) oxidation, this rate coefficient ratio is algebraically determined (i.e., without complex kinetic model fitting) from measurements of the temperature, pressure, and \( NO_2 \) and \( O_2 \) mole fractions taken from the quasi-steady plateau reaction. Values of \( k_1 \) determined here are in very good agreement with a present fit \((k_1(T) = 2.5 \times 10^{13} T^{0.218} \text{ [cm}^3/\text{mol/s]}\)) to the theoretical variable reaction coordinate – flexible transition state theory (VRC-FTST) \( k_1 \) expression of Su et al. (2002), as well as extrapolation of the experiment-advised expression of Ko & Fontijn (1991) to higher temperatures. Present uncertainties in \( k_1 \) determinations also overlap the uncertainty band for the experiment-based, temperature-invariant \( k_1 \) value from Su et al. for \( 195 \leq T (K) \leq 2000 \). Finally, it is to be noted that while measurements from the laminar reactor are new to the literature, the \( k_1 \) determinations from the turbulent flow reactor are based on reinterpretation of experiments performed by Mueller et al. (1998) intended to determine \( k_{2,M} \) relative to \( k_1 \).

Keywords: \( NOx \) chemistry, Flow reactor, Rate Constant, Hydrogen Reactions

1. Introduction

The reaction

\[
H + NO_2 → OH + NO
\]  

(R1)

is relevant to a wide range of disparate processes, including \( H \)-atom titration and \( OH \) radical generation for fundamental gas phase chemistry studies [1-6], chemical processing [7], \( NOx \) cycling in the exhaust of air-breathing combustors [8, 9], ignition conditioning in exhaust gas recirculation (EGR) in engine applications [10], and nitramine monopropellant combustion [11]. The most recent comprehensive study of the rate coefficient for R1 appears to be that of Su et al. [12], which compiled post-1978 temperature-dependent experimental determinations [13, 14] of \( k_1 \) (all for \( T \leq 760 \text{ K} \)), added additional high temperature determinations of \( k_1 \) (~1100-2000 K), and developed a theoretical treatment for the \( H+NO_2 \) reaction system. Over the temperature
range of ~200-2000 K, there appears to be approximately ±35% consensus among the nominal experimental values as well as the theoretical expression for \( k_1 \).

Notably, all of the experimental \( k_1 \) determinations compiled by Su et al. were made at sub-atmospheric pressures, which are conditions that do not favor collisional stabilization of the \( \text{H} \rightarrow \text{NO}_2 \) reaction intermediate into isomeric \( \text{HNO}_2 \) species. Therefore, present efforts consider the reaction of \( \text{H} + \text{NO}_2 \) at substantially higher pressures in order to assess whether at these conditions, this reaction may be considered to proceed simply according to R1 and \( k_1(T) \) or whether a net impact (e.g., excluding fast HONO dissociation to \( \text{OH} + \text{NO} \)) of chemistry subsequent to \( \text{H} \rightarrow \text{NO}_2 \) reaction complex stabilization is evident. A potential consequence of the latter case is that treatment of \( \text{H} + \text{NO}_2 \) kinetics at pressures and temperatures relevant to many energy conversion applications might require more thorough description than by R1 and \( k_1(T) \). Preliminary arguments of Ko and Fontijn [14] suggest that achieving stabilization rates competitive to \( k_1 \) may require pressures in excess of 100 atm. However, neither of the more detailed theoretical studies of Nguyen et al. [15] or Su et al. provides an unambiguous suggestion as to the conditions of temperatures, pressures, and bath gases for which stabilization may be important, though Nguyen and coworkers highlight a qualitative shift in the detailed mechanism for the apparent R1 reaction at a characteristic pressure of 10 atm.

This study determines rate coefficients for R1 from stable species profiles measured in one of two flow reactor facilities. Results of NOx-perturbed \( \text{H}_2 \) oxidation experiments conducted in the Princeton high pressure laminar flow reactor facility (HPLFR) for \( \text{Ar} \) and \( \text{N}_2 \) bath gases are presented for the first time. Conditions for these experiments span nominal temperatures and pressures of 737-825 K and 10-20 atm. Results from the turbulent Princeton variable pressure flow reactor (VPFR) for 819-882 K and 10-14 atm have been reinterpreted from the study of Mueller et al. [16], which used similar NOx-perturbed \( \text{H}_2 \) oxidation experiments to determine rate coefficients for the reaction

\[
\text{H} + \text{O}_2 (+M) \rightarrow \text{HO}_2 (+M) \quad \text{(R2.M)}
\]

for \( M = \text{Ar} \) and \( \text{N}_2 \). Species measurements from both facilities are interpreted using a quasi-steady state NOx plateau (QSSP) method that determines the ratio of \( k_1 \) and \( k_{2,M} \). Absolute, uncertainty-bounded values of \( k_1 \) are then derived with reference to \( k_{2,M} \) (\( M = \text{Ar}, \text{N}_2 \)). The extracted values of \( k_1 \) are then compared to the existing experimental values and a theory-based expression for \( k_1 \) appearing in the study of Su et al.

2. Experimental

The HPLFR facility used to generate experimental measurements for this study has been discussed elsewhere [17, 18] and will only be briefly described here. The original work of Mueller et al. [16, 19] presents the turbulent flow reactor (VPFR) experiments and procedures used to generate the corresponding data, which are reinterpreted here. The quasi-steady state NOx plateau (QSSP) technique employed in this paper for rate coefficient extraction has also been described elsewhere [16, 18, 20, 21]. Accordingly, this section provides only a brief discussion of the present QSSP interpretation of the experiments conducted in the flow reactor facilities considered.

2.a HPLFR Facility. Experiments in the HPLFR generate stable species mole fraction profiles for reactants/intermediates/products as a function of axial position in the reactor test section. The facility can access temperatures up to 1000 K, pressures from ~1-30 atm, and residence times spanning tens of milliseconds to several seconds. Under appropriate operating
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conditions such as those accessed in present HPLFR experiments, steady one-dimensional species-position profiles can be interpreted as zero-dimensional species-time profiles, which can be used to extract fundamental rate coefficient information (as here) or provide overall reaction progress validation data for combustion chemistry modeling [17].

The facility is comprised of three principal subsystems. Reactants are prepared in the Feed/Calibration Subsystem, which generates a steady flow of premixed, preheated gaseous reactants supplied by calibrated thermal mass flow controllers. This flow is sent to the quartz reactor duct of the Reactor Subsystem through a heated, insulated transfer line. The Reactor Subsystem is composed of a wall-mounted PID-thermostatted three-zone tube furnace enclosing a 38 mm outer diameter (OD) stainless steel pressure shell, which in turn encloses the duct. Under conditions favoring reaction, the premixed gas feed converts into products as it flows along the reactor duct and subsequently exhausts from the reactor. A heat-shielded, hot water-cooled, convection quench probe with integrated thermocouple continuously extracts a small, quenched sample flow from a given axial coordinate in the duct test section. This flow passes through heated transfer lines into the Sample Analysis Subsystem. For the experiments described here, this consists of an online FTIR spectrometer in series with a micro gas chromatograph. A screw drive translates the probe axially through the duct, enabling sample collection along the duct axis.

Temperature in the test section is monitored by a 0.025 cm OD Inconel-sheathed type-K thermocouple that passes through the orifice in the end of the sample probe and extends 5 cm beyond the probe tip. Radiative heating of the thermocouple bead is estimated to contribute ~6 K uncertainty to measured temperatures at the most extreme (~1000 K) conditions in the HPLFR, assuming a radiative environment (pressure vessel wall) differing from the local gas temperature by ~20 K and a conservative thermocouple emissivity of unity.

2.b Interpretive Approach. The validity of idealizing assumptions often used to interpret flow reactor experiments generally depends on the coupling among species, energy, and momentum fields inside of the reactor [22, 23]. However, as discussed in this section and implied elsewhere [16, 18, 20, 21, 24, 25], exceptional features of the QSSP conditions considered in this work significantly reduce the potential complexities of flow reactor measurement interpretation from the experimental facilities considered herein. Ashmore and Tyler [20] appear to have first identified QSSP behavior in their static reactor study of the slow reaction of H₂ and O₂ in the presence of small, sensitizing concentrations of NO₂ at 633 K and relatively low pressures. Under certain conditions, they noted that a stationary (quasi-steady state) partial pressure of NO₂ was attained during the reaction, even as the overall H₂ oxidation reaction progressed. Based on additional details of their experiments, Ashmore and Tyler rationalized that at quasi-steady state NO₂ plateau (QSSP) conditions, the reaction system obeys the relationship

\[
\frac{[O_2]}{[NO_2]}_{QSSP} = \frac{k_1}{k_{2,M}}_{T,P,M}
\]  

In Eq. 1, the partial pressure scaling originally discussed by Ashmore and Tyler have been transformed to units of molar concentration, and parameters for pressure P and total gas composition M have been specified in reference to well established pressure-dependencies in \(k_{2,M}\). For sake of clarity, \(k_{2,M}\) refers to the effective bimolecular rate coefficient for R2.M. Under QSSP conditions, one of \(k_1\) or \(k_{2,M}\) may be determined from a given value of the other rate coefficient and experimentally measured QSSP concentrations of NO₂ and O₂, and the total gas concentration M implicit in \(k_{2,M}\). This simple relationship forms the basis for present \(k_1\)
determinations from experimental flow reactor measurements, subject to several caveats discussed below.

Using both HPLFR experimental measurements and complex kinetic modeling results, Fig. 1 demonstrates essentially the same QSSP behaviors (i.e., NO\textsubscript{2} plateau during slow oxidation of H\textsubscript{2}) as observed by Ashmore and Tyler in their work. The NO\textsubscript{x}-perturbed H\textsubscript{2} oxidation kinetic model used here is a hybrid based on the models of Li et al. [26] and Mueller et al. [27], and no kinetic or transport parameters have been adjusted to achieve better agreement with the overlaid HPLFR experimental data. Figure 1 shows that reaction progress may be divided into an induction chemistry transient followed by a region in which QSSP conditions are achieved. Equation 1 holds only in the QSSP region, where reaction Scheme 1 prevails and overall reaction is sensitive only to the rates of R1 and R2.M.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Overlay of measured and simulated species and temperature profiles for HPLFR Experiment 2 (initial conditions in Table 1). Reaction progress is treated as isothermal at a nominal temperature of 752 K. At these conditions, the plug flow velocity is 18.2 cm/s. The unshaded plot area indicates the induction transient, while the shaded area indicates the region in which QSSP conditions prevail. Measurements: ● – O\textsubscript{2}, ○ – H\textsubscript{2}×0.75, ● – NO\textsubscript{2}×100, Δ – T×15 (K). Modeling results for radially-resolved reacting shear layer flow: (solid lines) – cross section-averaged (equivalent to plug flow), (dashed lines) – reactor wall, (dotted lines) – centerline. All three model-generated profiles have been uniformly coordinate-shifted by 7.0 cm to account for non-ideal initialization [22] that does not bear on present interpretations.}
\end{figure}

Whether for laminar HPLFR or similar turbulent VPFR results, quantitative interpretation of the induction chemistry transient is not advisable due to 1) the generally problematic definition of true initial conditions for flow reactors, discussed extensively in [22], and 2) confounding contributions of several additional reactions beyond those contained in Scheme 1. In addition to these reasons, CHEMKIN-based [28] 2-D reacting shear layer flow modeling presented in Fig. 1 suggests that the induction chemistry transient in the HPLFR is significantly affected by laminar flow field development after the HPLFR duct expansion, as well as differential advection rates across streamlines in fully-developed laminar flow. Influence of these processes applies only to the HPLFR induction transient, after which the local rates of reaction, radial diffusion, and advection adjust to satisfy essentially equal (within typical measurement uncertainty) species mole fractions across the radial reactor coordinate. Accordingly, the QSSP region of these experiments may be modeled using traditional area-averaged (plug flow), steady one-dimensional or transient zero-dimensional flow reactor assumptions with provisions for non-ideal initialization [22]. Moreover, the negligible radial variation in species mole fractions permits k\textsubscript{1} extraction according to Eq. 1 since the QSSP region is governed by the essentially zero-dimensional QSSP chemistry described in Scheme 1. It should be noted that this treatment
and the behavior indicated in Fig. 1 hold specifically for the HPLFR QSSP experiments presently considered and do not necessarily generalize beyond these conditions.

**Scheme 1.** Reactions active at quasi-steady state NOx plateau (QSSP) conditions.

\[
\begin{align*}
H + NO_2 & \rightarrow OH + NO \\
HO_2 + NO & \rightarrow OH + NO_2 \\
H_2 + OH & \rightarrow H_2O + H \\
H + O_2 (+ M) & \rightarrow HO_2 (+ M)
\end{align*}
\]

Additional insight into QSSP conditions may be obtained from considering the set of elementary reactions active at these conditions. In accordance with experimental observations by Ashmore and Tyler, conversion of H\textsubscript{2} to H\textsubscript{2}O under QSSP conditions is a relatively slow process, which indicates that a subset of non-explosive H\textsubscript{2}/O\textsubscript{2} chemistry dominates the QSSP system. The NO\textsubscript{2} present must react with species in the H\textsubscript{2}/O\textsubscript{2} chemical system to establish a quasi-steady concentration even as slow oxidation of H\textsubscript{2} occurs. Assuming a relatively slow initiation reaction like H\textsubscript{2} + O\textsubscript{2} $\leftrightarrow$ HO\textsubscript{2} + H has occurred to produce an initial radical pool, then Scheme 1 represents a minimal elementary reaction set to describe the observed QSSP behavior. In this scheme, the total NOx is conserved in a catalytic cycle as NO\textsubscript{2} consumes H atoms to form NO in R1, and NO consumes HO\textsubscript{2} to form NO\textsubscript{2} in R3. Both of these reactions produce OH, which quickly reacts with H\textsubscript{2} in R4 to form H\textsubscript{2}O and H atom. The H atoms produced from R4 associate with O\textsubscript{2} through termolecular reaction R2.M to form HO\textsubscript{2} or re-enter the reaction cycle in R1. Any HO\textsubscript{2} produced by R2.M re-enters the reaction cycle in R3. A consequence of the catalytic NOx cycle is that QSSP chemistry may begin with trace NO\textsubscript{2} dopant, trace NO dopant, or a mixture of NO and NO\textsubscript{2}. In all cases, the system relaxes to the same quasi-steady NO\textsubscript{2} plateau concentration through a transient response. Both the HPLFR and VPFR experiments considered here take advantage of this result and use NO as the sensitizing NOx species.

Finally, it is worth mentioning that both Bromly et al. [24] and Ashman and Haynes [29, 30] have measured NOx-perturbed H\textsubscript{2} oxidation in atmospheric pressure laminar flow reactors. As in the higher pressure flow reactor experiments of Mueller et al. [16] reinterpreted here, these experiments were initially motivated by determination of k\textsubscript{2,M}. It is likely that many of these atmospheric pressure experiments can similarly be reinterpreted as k\textsubscript{1} QSSP determinations, provided that issues of laminar flow field, induction chemistry, and secondary reactions are considered. Such reinterpretation has not been pursued in this work since the conditions considered would appear to add little to the database of experimental k\textsubscript{1} determinations.

3. **Results and Discussion**

3.a **Laminar Flow Reactor Experiment.** Eight HPLFR experiments to determine k\textsubscript{1} have been conducted at temperatures of 727-825 K and pressures of 10-20 atm. Nominal initial experimental conditions are given in columns (b)-(g) of Table 1. Experiments 3 and 4 for B = Ar and Experiments 6 and 7 for B = N\textsubscript{2} are repetitions conducted consecutively at essentially the same nominal reaction conditions. The significance of indicating nominal bath gases with “B” instead of “M” will become apparent below.

Except for the slightly high k\textsubscript{1} determination from Experiment 8, which was conducted at the lowest pressure (10 atm) and highest temperature (825 K) found in this data set, each of the other k\textsubscript{1} determinations is within 10% of the $1.10 \times 10^{14}$ cm\textsuperscript{3}/mol/s data set mean. Based on both
empirically demonstrated QSSP behavior and kinetic modeling results, there appears to be no reason to discard the outlying experiment.

Table 1. Summary of HPLFR (laminar reactor) experimental conditions and $k_1$ determinations.

<table>
<thead>
<tr>
<th>Experiment Reference</th>
<th>Bath Gas</th>
<th>$P$ (atm)</th>
<th>$T$ (K)</th>
<th>$H_2$ (ppm)</th>
<th>$O_2$ (ppm)</th>
<th>NO (ppm)</th>
<th>$[O_2]/[NO_2]$*</th>
<th>$k_1/k_{2,B}^{\text{a}}$</th>
<th>$k_{2,B}^{\text{b}}$ $\left(10^{11} \text{cm}^3/\text{mol}/\text{s}\right)$</th>
<th>$k_1^{\text{c}}$ $\left(10^{14} \text{cm}^3/\text{mol}/\text{s}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ar</td>
<td>18.0</td>
<td>747</td>
<td>12622</td>
<td>13100</td>
<td>97.3</td>
<td>167.0</td>
<td>185.5</td>
<td>6.88 ± 27%</td>
<td>1.10 ± 32%</td>
</tr>
<tr>
<td>2</td>
<td>Ar</td>
<td>15.0</td>
<td>752</td>
<td>19223</td>
<td>16851</td>
<td>96.3</td>
<td>150.0</td>
<td>159.9</td>
<td>5.71 ± 27%</td>
<td>1.06 ± 32%</td>
</tr>
<tr>
<td>3</td>
<td>Ar</td>
<td>12.0</td>
<td>755</td>
<td>19215</td>
<td>18847</td>
<td>96.2</td>
<td>194.5</td>
<td>219.1</td>
<td>4.57 ± 27%</td>
<td>1.00 ± 32%</td>
</tr>
<tr>
<td>4</td>
<td>Ar</td>
<td>12.0</td>
<td>751</td>
<td>19215</td>
<td>18847</td>
<td>96.2</td>
<td>194.6</td>
<td>220.2</td>
<td>4.62 ± 27%</td>
<td>1.02 ± 32%</td>
</tr>
<tr>
<td>5</td>
<td>N$_2$</td>
<td>20.0</td>
<td>737</td>
<td>23961</td>
<td>11677</td>
<td>184.4</td>
<td>75.1</td>
<td>79.2</td>
<td>13.9 ± 21%</td>
<td>1.10 ± 27%</td>
</tr>
<tr>
<td>6</td>
<td>N$_2$</td>
<td>17.3</td>
<td>738</td>
<td>21374</td>
<td>13957</td>
<td>184.5</td>
<td>87.9</td>
<td>92.8</td>
<td>12.1 ± 20%</td>
<td>1.12 ± 27%</td>
</tr>
<tr>
<td>7</td>
<td>N$_2$</td>
<td>17.3</td>
<td>742</td>
<td>21374</td>
<td>13957</td>
<td>184.5</td>
<td>91.3</td>
<td>95.3</td>
<td>12.0 ± 20%</td>
<td>1.14 ± 26%</td>
</tr>
<tr>
<td>8</td>
<td>N$_2$</td>
<td>10.0</td>
<td>825</td>
<td>10717</td>
<td>19920</td>
<td>93.9</td>
<td>219.5</td>
<td>225.2</td>
<td>5.66 ± 16%</td>
<td>1.28 ± 23%</td>
</tr>
</tbody>
</table>

*Values of $[O_2]/[NO_2]$ averaged over QSSP region of reaction; *Profile-averaged values of $([O_2]/[NO_2])^*$, which have been corrected for contributions to $k_{2,M}$ of species other than bath gas B, see Eq. 2 and discussion in text.

Column (h) of Table 1 presents $[O_2]/[NO_2]$ ratios determined by profile averaging over the extent of each experimentally measured QSSP region. This ratio is the fundamental QSSP experimental observable from the HPLFR experiments. For the present experiments, this ratio has an estimated 2σ uncertainty of ~16% based on the following forward propagation of 2σ experimental uncertainties by the usual assumptions: 5% due to profile-averaging variance; 10% due to overall NO$_2$ mole fraction determination; 5% due to O$_2$ mole fraction based on repeatability of micro gas chromatograph measurements; 2% (~15 K in absolute temperature measurement) due to combined systematic thermocouple uncertainties and assumptions of isothermality at the nominal reaction temperature; and 8% due to two-dimensional flow field departures from plug flow (cf. Fig. 1). Though not properly a factor in the $[O_2]/[NO_2]$ ratio, the ~16% measurement uncertainty cited above includes an additional 4% contribution due to both systematic uncertainties in absolute pressure and slight fluctuations about the nominal pressure during each experiment. This experimental pressure uncertainty affects $[M]$ implicit in the reference value of $k_{2,M}$ used for $k_1$ extraction; however, it seems fitting to discuss it here along with the other experimental contributions to $k_1$ uncertainty estimation.

The accuracy of $[O_2]/[NO_2]$ in determining $k_1/k_{2,M}$ is additionally subject to satisfying the QSSP assumptions made by the present interpretive framework. Here, this interpretive uncertainty is considered with reference to the study of Mueller et al. [16], which found ~3% deviation of QSSP extractions of $k_{2,B}$ from the average value of $k_{2,B}$ extracted by complex kinetic model fitting of experimental H$_2$, NO, and NO$_2$ profiles measured at QSSP conditions. Though this interpretive uncertainty has been derived for $k_{2,B}$, such uncertainty generally indicates the consistency of the QSSP interpretation with the more frequently employed method [16, 24, 25, 29, 30] of complex kinetic model fitting.

For extremely dilute QSSP systems in which contributions to $k_{2,M}$ of gases other than the bath gas can be neglected, the $[O_2]/[NO_2]$ ratio and $k_{2,M}$ for M corresponding to the bath gas B can be used directly in Eq. 1 to determine $k_1$. However, at present conditions, the abundance and relative collisional efficiencies of H$_2$, O$_2$, and H$_2$O (determined by H atom balance) modestly influence the net value of $k_{2,M}$. In other words, $M \neq B$ and hence the QSSP-relevant value $k_{2,M} \neq k_{2,B}$. In order to extract $k_1$ from Eq. 1 with reference to values of $k_{2,B}$ available from the literature, the characteristic value of $[O_2]/[NO_2] = k_1/k_{2,M}$ must be corrected to a new value (*) such that
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\[
([\text{O}_2]/[\text{NO}_2])^* = \frac{k_1}{k_2,\text{B}}
\]  (2)

and

\[
k_{2,\text{M}} = k_{2,\text{B}} \times ([1-X_{\text{O}_2}-X_{\text{H}_2}-X_{\text{H}_2\text{O}}] + \varepsilon_{\text{O}_2,\text{B}}X_{\text{O}_2} + \varepsilon_{\text{H}_2,\text{B}}X_{\text{H}_2} + \varepsilon_{\text{H}_2\text{O},\text{B}}X_{\text{H}_2\text{O}}).
\]  (3)

For a species \(i\), the terms \(\varepsilon_{i,\text{B}}\) and \(X_i\) represent the relative (to \(B\)) collisional efficiency for \(k_{2,\text{LPL}}\) and the measured mole fraction, respectively. Prior to profile-averaging, HPLFR measurements of \([\text{O}_2]/[\text{NO}_2]\) were corrected according to Eq. 2 using the relative collisional efficiencies of Burke et al. [31], the linear blending rule of Eq. 3, and “Consensus” \(k_{2,\text{B}}\) values for \(B = \text{Ar}\) and \(\text{N}_2\) as described below.

![Fig. 2.](image_url)

Fig. 2. Comparison of pressure-dependent \(k_{2,\text{Ar}}\) expressions at 752 K: (solid line) – Consensus, (dashed line) – [32], (dash-dot line) – [25], (dotted line) – [33]. The shaded region is ±10% of the Consensus expression and used for purposes of illustration; uncertainties in \(k_{2,\text{Ar}}\) are somewhat higher (e.g., column (j) of Table 1). Data points are reciprocal \(k_{2,\text{Ar}}\) QSSP determinations from HPLFR Experiments 1-4 near 752 K.

The corrected \(([\text{O}_2]/[\text{NO}_2])^* = \frac{k_1}{k_2,\text{B}}\) ratios in column (i) of Table 1 may be used to determine \(k_1\) given \(k_{2,\text{B}}\), or vice versa. In order to determine \(k_1\), “Consensus” values of \(k_{2,\text{B}}\) were developed by taking the arithmetic mean of the ten unique (each for \(\text{Ar}\) and \(\text{N}_2\)) pressure-dependent \(k_{2,\text{B}}\) expressions used by the twelve “best performing” \(\text{H}_2\) combustion models as determined by Zsély et al. [34]. The range in \(k_{2,\text{B}}\) at a particular temperature is indicative of the present literature uncertainty in the \(R2,\text{B}\) rate coefficient at these conditions. For the conditions considered here, the values of \(k_{2,\text{B}}\) determined by the Consensus treatment are in generally excellent agreement with literature pressure-dependent elementary reaction kinetics recommendations [25, 32, 33].

Using the Consensus \(k_{2,\text{B}}\) expressions described above, specific values of \(k_{2,\text{B}}(T, P)\) for each nominal experimental condition have been computed and are given in column (j) of Table 1. Characteristic 2\(\sigma\) uncertainties in \(k_{2,\text{B}}\) have been assigned according to the twice the standard error of the expressions used to form the Consensus ensemble. Column (k) of Table 1 also presents the corresponding nominal determinations of \(k_1\) for each experiment along with net 2\(\sigma\) uncertainty including the quadrature-summed ~16% in overall measurement uncertainty, ~6% in interpretive method uncertainty, and (\(T, P, B\))-specific \(k_{2,\text{B}}\) uncertainty appearing in column (j).

As additional validation of the present rate coefficient extraction approach, the corrected \(k_1/k_{2,\text{B}}\) ratios in column (i) of Table 1 may be used to determine \(k_{2,\text{B}}\) given \(k_1\). Though the intent of Fig. 2 is primarily to compare Consensus and literature \(k_{2,\text{B}}\) expressions used for \(k_1\) determination, the figure also shows the reciprocal \(k_{2,\text{Ar}}\) determinations for Experiments 1-4. In this case, experiment-derived \(k_1/k_{2,\text{B}}\) ratios have been interpreted with a present fit to the variable reaction coordinate – flexible transition state (VRC-FTST) expression evident in the study of Su et al.:
Clearly, there is very good agreement among the nominal QSSP-derived experimental values, the Consensus, and the expressions recommended by elementary \( k_2.B \) studies.

3.b Turbulent Flow Reactor Experiment. Mueller and coworkers [16] conducted ten experiments in the Princeton VPFR facility at pressures of 10-14 atm and average temperatures of 819-882 K. The original intent of these experiments was to determine \( k_2.B \) relative to \( k_1 \); however, the present study reinterprets the “Steady-state” \( k_{2,M} \) experimental QSSP results of Mueller et al. to instead determine absolute values of \( k_1 \) based on Consensus \( k_2.B \) values. Column (e) of Table 2 presents \( k_{2,M} \) = \( k_{2,\text{eff}[M]} \) values derived from the “Steady-state” \( k_{2,\text{eff}} \) results tabulated in that study. From these, bath gas uncorrected profile-averaged \([O_2]/[NO_2]\) ratios (column (f)) have been inferred with reference to the \( k_1 \) expression [14] originally used by Mueller et al. in their determination of \( k_{2,\text{eff}} \). This inference is in lieu of determining explicit values of \([O_2]/[NO_2]\) by examining the results of each VPFR experiment, which do not appear to be readily available [16, 19]. The present estimate for the uncertainty of the \([O_2]/[NO_2]\) ratios in these experiments is the 10% “profile fitting” uncertainty reported in the uncertainty analysis provided in [16], which presumably accounts for contributions to overall measurement uncertainty due to profile averaging, \( NO_2 \) and \( O_2 \) mole fraction determination, etc.

Despite the fact that the full set of VPFR experimental species profiles does not appear to be available, the inferred \([O_2]/[NO_2]\) has still been corrected for bath gas effects. Whether for \( B = \text{Ar} \) or \( \text{N}_2 \), the expected species mole fractions at the 50% extent of measured reaction and their respective collisional efficiencies [31] yields an essentially constant \( \sim 7\% \) increase from \([O_2]/[NO_2]\) to \(([O_2]/[NO_2])^*\). A corresponding absolute \( \pm 7\% \) (i.e., not assumed to sum in quadrature) has been included with other contributions to \( k_1 \) uncertainty to account for the present inability to interrogate each experimental profile. Finally, the corrected \(([O_2]/[NO_2])^*\) ratios are used with uncertainty-quantified Consensus \( k_{2,B} \) values (Table 2 column (h)) to determine the value of \( k_1 \) from each VPFR experiment. Column (i) of Table 2 presents these nominal rate coefficient determinations along with their net \( 2\sigma \) uncertainty including the quadrature-summed \( \sim 10\% \) in overall measurement uncertainty, \( \sim 6\% \) in interpretive method uncertainty, and (\( T, P, B \))-specific \( k_{2,B} \) uncertainty appearing in column (j). This net uncertainty also includes the additional \( \pm 7\% \) contribution due to consideration of bath gas effects. Save for the somewhat outlying result of Experiment A, the other VPFR \( k_1 \) determinations are within 10%
of the $1.05 \times 10^{14}$ cm$^3$/mol/s data set mean. Assuming, as is apparent in Eq. 4 and prior studies of $k_1$, either small or negligible temperature dependence for $k_1(T)$, the turbulent-flow VPFR results are in very good agreement with the laminar-flow HPLFR results.

3.c Discussion. Figure 3 compares the present $k_1$ flow reactor-QSSP determinations to experimental and theoretical results presented in [12] for $T \leq 1000$ K. The high pressure HPLFR rate coefficient determinations agree well with the low pressure flash photolysis measurements of Ko and Fontijn [14] over the narrow range of overlapping temperatures. Further, all of the present $k_1$ determinations are in good agreement with the recommended $k_1$ expression of [14] extrapolated to $T > 760$ K, the present fit (Eq. 4) to the theory-based VRC-FTST expression of Su et al. [12], and the recommended temperature-independent value of [12] developed from experimental $k_1$ determinations over the range 195-2000 K.

The present agreement between the high pressure flow reactor determinations and literature benchmarks developed from low pressure experiments suggests that reaction of H+NO$_2$ may be considered to proceed according to R1 at pressures of up to 20 atm, at least for the temperature range studied here. The rate of stabilization is apparently not competitive with $k_1$ at such conditions. If stabilization of the H—NO$_2$ reaction intermediate does occur at these temperature and pressures, the net impact of any subsequent non-dissociative chemistry (i.e., reactions of stabilized intermediates yielding products other than H+NO$_2$ or OH+NO) is not evident to within the measurement and interpretation uncertainties of the present experiments. When considering only the experimental results (including the higher temperature measurements of [12] not shown in Fig. 3) the trend in nominal $k_1$ values would appear to qualitatively assert the modest temperature dependence suggested by Ko and Fontijn. However, the experimental uncertainties remain large enough that a temperature-independent recommendation for $k_1$ is also satisfactory. Together, these observations suggest a persisting “indeterminacy” [12] with regard to both temperature and pressure dependencies for the H+NO$_2$ reaction.
4. Conclusions

Species evolution results from laminar flow (HPLFR) and turbulent flow (VPFR) reactor facilities have both been used to determine rate coefficients for the reaction $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$ (R1) from NOx-perturbed $\text{H}_2$ oxidation experiments conducted in the temperature/pressure range of 737-882 K/10-20 atm. At the conditions considered in this study, a quasi-steady state NOx plateau (QSSP) is established, during which slow $\text{H}_2$ oxidation is controlled almost exclusively by R1 and $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ (R2.M). Experimental measurements of QSSP concentrations of O$_2$ and NO$_2$ provide $k_1/k_{2,M}$, from which the value of $k_1$ can be determined given $k_{2,M}$ (or vice versa). Here, literature-based “Consensus” expressions for $k_{2,\text{Ar}}$ and $k_{2,\text{N}_2}$ were developed and utilized to extract absolute, uncertainty-bounded $k_1$ values from the experimental measurements. This study appears to be the first to combine the QSSP technique with flow experiments in order to extract values of $k_1$, and it also appears to be the first experimental study of $k_1$ to access pressures well in excess of 1 atm.

Though the two flow reactor facilities considered in this study differ in many aspects of reactor design – markedly so with regard to flow regime – the values of $k_1$ determined from the two reactors are consistent about a representative value of $k_1 \sim 1.05 \times 10^{14}$ cm$^3$/mol/s. These measured values are in good agreement both with the low pressure experimental results of Ko and Fontijn [14] near 760 K, as well as a present fit (Eq. 4) to the theoretical expression of Su et al. [12]. Combined with other values of $k_1(T)$ from the literature, the $k_1$ extractions of this study may suggest a mild temperature dependence for this rate coefficient; however, experimental uncertainties at all temperatures remain large enough that the temperature-independent, experiment-based recommendation of [12] also remains a valid interpretation.

Within the ~25-35% representative 2σ uncertainties estimated for each $k_1$ extraction in this study, no net influence of pressure on $k_1$ was observed. This suggests that for the relatively high pressure conditions studied, the net reaction of H+NO$_2$ is not significantly influenced by stabilization of the H—NO$_2$ reaction intermediate to form isomers of HNO$_2$. For these conditions, the reaction may be considered to proceed by R1 at a rate governed by $k_1$.

Finally, it is worthwhile to note that the VPFR (turbulent reactor) experimental measurements originate from the study of Mueller et al. [16], which used QSSP and profile-fitting techniques to determine $k_{2,M}$ from a given $k_1$ expression. With regard to these experiments, the present study has reciprocally reinterpreted the fundamental QSSP [O$_2$]/[NO$_2$] measurements in order to instead extract $k_1$. Though not attempted here, there remains potential for similar QSSP reinterpretations of several other existing $k_{2,M}$-motivated studies [20, 24, 29, 30].

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6. Notes

Portions of this work appear in Chapters 2 and 3 of the thesis of Haas [18]. Any coincidental material has been used with permission. A substantially similar, although more detailed version of this work has also been submitted for publication elsewhere. Upon publication, this alternative version should be considered to supersede the present manuscript.
Sub Topic: Reaction Kinetics

7. References