# Kinetic Study of Reactions of C<sub>2</sub>H<sub>5</sub>O and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> with NO at 298 K and 0.55 - 2 torr

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#### Abstract

The kinetics of  $C_2H_5O$  and  $C_2H_5O_2$  radicals with NO have been studied at 298 K using the discharge flow technique coupled to laser induced fluorescence (LIF) and mass spectrometry analysis. The temporal profiles of  $C_2H_5O$  were monitored by LIF. The rate constant for  $C_2H_5O + NO \rightarrow$  Products (2), measured in the presence of helium, has been found to be pressure dependent:  $k_2 = (1.25 \pm 0.04) \times 10^{-11}$ ,  $(1.66 \pm 0.06) \times 10^{-11}$ ,  $(1.81 \pm 0.06) \times 10^{-11}$  at P (He) = 0.55, 1 and 2 torr, respectively (units are cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). The Lindemann-Hinshelwood analysis of these rate constant data and previous high pressure measurements indicates competition between association and disproportionation channels:  $C_2H_5O + NO + M \rightarrow C_2H_5ONO + M$  (2a),  $C_2H_5O + NO \rightarrow CH_3CHO + HNO$  (2b). The following calculated average values were obtained for the low and high pressure limits of  $k_{2a}$  and for  $k_{2b}$ :  $k_{2a}^0 = (2.6 \pm 1.0) \times 10^{-28}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>,  $k_{2a}^{\infty} = (3.1 \pm 0.8) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_{2b}$  ca. 8 × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The present value of  $k_{2a}^0$ , obtained with He as the third body, is significantly lower than the value (2.0 ± 1.0) × 10<sup>-27</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> recommended in air. The rate constant for the reaction  $C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$  (3) has been measured at 1 torr of He from the simulation of experimental  $C_2H_5O_2$  profiles. The value obtained for  $k_3 = (8.2 \pm 1.6) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is in good agreement with previous studies using complementary methods. @ 1995 John Wiley & Sons, Inc.

## Introduction

Alkoxy and alkyl peroxy radicals are intermediates in both combustion and atmospheric oxidation of hydrocarbons. In these processes, the simplest alkoxy radicals, i.e., CH<sub>3</sub>O and C<sub>2</sub>H<sub>5</sub>O, react predominantly with oxygen and these reactions have been the most studied [1,2]. However, these alkoxy radicals react also quite rapidly with NO and NO<sub>2</sub> [1,2] and with the NO<sub>3</sub> radical, as recently shown for CH<sub>3</sub>O [3,4] and C<sub>2</sub>H<sub>5</sub>O [5,6]. Alkyl peroxy radicals also react rapidly with NO, NO<sub>2</sub> [1,2,7], as well as with NO<sub>3</sub>, as recently observed for CH<sub>3</sub>O<sub>2</sub> [3,4] and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> [5,6].

The reaction  $CH_3O + NO$  has been investigated over a range of pressure and temperature [8–10] leading to the determination of the low and high pressure limits for the association channel:

(1a) 
$$CH_3O + NO + M \longrightarrow CH_3ONO + M$$

Besides, the disproportionation channel:

(1b) 
$$CH_3O + NO \longrightarrow CH_2O + HNO$$

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was found to occur and to dominate at low pressure [9,10]. In contrast, more limited data are available for the reaction of  $C_2H_5O$  with NO. In the only direct study performed so far [9], at the pressure of 15 and 100 torr of Ar and 298 K, the rate constant was found pressure independent. The value obtained may be the sum of the high pressure limit of the association channel (2a) and the disproportionation channel (2b), similarly to the  $CH_3O + NO$  reaction:

(2a) 
$$C_2H_5O + NO + M \longrightarrow C_2H_5ONO + M$$

(2b) 
$$C_2H_5O + NO \longrightarrow CH_3CHO + HNO$$

The products of reaction (2b) have not been identified clearly, except in indirect products analysis of pyrolysis of ethyl nitrate by gas chromatography [11], and are very likely CH<sub>3</sub>CHO and HNO. The present study reports rate constant measurements for this reaction at low pressures (0.5-2 torr of He), which provide additional information on the low and high pressure limits  $k_{2a}^{\circ}$ ,  $k_{2a}^{\infty}$ , for channel (2a) and  $k_{2b}$  for channel (2b). The experiments have been performed in a discharge flow reactor with kinetic analysis of C<sub>2</sub>H<sub>5</sub>O radicals by laser induced fluorescence (LIF). Rate constant measurements have been also obtained with the same technique for the reaction:

$$(3) \qquad \qquad C_2H_5O_2 + NO \longrightarrow C_2H_5O + NO_2$$

The value of  $k_3$  recommended so far, at 298 K, is based on two absolute determinations obtained by the discharge flow mass spectrometric and pulsed radiolysis – absorption techniques, respectively [12,13]. In both studies,  $k_3$  was derived from the NO<sub>2</sub> formation kinetics. In the present study,  $k_3$  was determined from the C<sub>2</sub>H<sub>5</sub>O kinetics monitored by LIF.

## Experimental

The discharge flow reactor coupled to laser induced fluorescence (LIF) and quadrupole mass spectrometry has been previously described in detail [4] and is shown in Figure 1. The main reactor made of Pyrex was 2.5 cm i.d. and 80 cm length and the central injector was 1.0 cm i.d.  $C_2H_5O$  and  $C_2H_5O_2$  radicals were produced in the moveable central injector.



Figure 1. Schematic experimental set-up for kinetic studies of  $C_2H_5O$  radicals by discharge flow-laser induced fluorescence technique.

In our earlier study on CH<sub>3</sub>O radicals [4], the fast reaction of CH<sub>3</sub> with NO<sub>2</sub> was used to produce CH<sub>3</sub>O. In some experiments, the reaction of C<sub>2</sub>H<sub>5</sub> with NO<sub>2</sub> was similarly used to produce C<sub>2</sub>H<sub>5</sub>O radicals, C<sub>2</sub>H<sub>5</sub> being formed by the reaction of C<sub>2</sub>H<sub>6</sub> with F atoms generated by microwave discharge of F<sub>2</sub> diluted in helium. However, the C<sub>2</sub>H<sub>5</sub>O yield was too low, due to the fast reactions of C<sub>2</sub>H<sub>5</sub>O with NO<sub>2</sub> and NO, the later being a product of the C<sub>2</sub>H<sub>5</sub> + NO<sub>2</sub> reaction. Therefore, the reaction of F atoms with C<sub>2</sub>H<sub>5</sub>OH was preferred as the C<sub>2</sub>H<sub>5</sub>O source. F atoms were produced by microwave discharge in ca. 1% F<sub>2</sub>/He mixture. The reaction of F atoms with C<sub>2</sub>H<sub>5</sub>OH is known to proceed through three channels [14,15]:

$$(4a) F + CH_3CH_2OH \longrightarrow CH_3CH_2O + HF$$

$$(4b) F + CH_3CH_2OH \longrightarrow CH_3CHOH + HF$$

$$(4c) F + CH_3CH_2OH \longrightarrow CH_2CH_2OH + HF$$

The total rate constant is  $1.28 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [14]. The branching ratio of channel (4a) producing C<sub>2</sub>H<sub>5</sub>O is ca. 55% [15]. The concentration of C<sub>2</sub>H<sub>5</sub>OH was maintained in large excess (ca. 40 times) over F atoms to avoid subsequent fast reaction of ethoxy radicals with F, which can produce ethenoxy radicals CH<sub>2</sub>CHO, having an excitation spectrum which partly overlaps with that of C<sub>2</sub>H<sub>5</sub>O [16].

As the reaction of F with  $C_2H_5OH$  is fast, the reaction time in the injector was fixed at ca. 3.5 ms, which was sufficient to have a complete consumption of F atoms in the injector. Absolute measurement of F atoms concentration was made by chemical titration with  $Cl_2$ , which was introduced through the external tube of the injector. The yield of F atoms ([F] /2[F<sub>2</sub>]<sub>0</sub>) was around 0.3, due to loss of F atoms in the central injector, though a total dissociation of  $F_2$  in the discharge was observed by mass spectrometry at m/e = 38.

Considering model calculations of the chemical system in the injector (as in ref. [4]) and experimental observations, the optimized production of  $C_2H_5O$  radicals was obtained for the following initial concentrations in the injector:  $[F]_0$  ca.  $3.5 \times 10^{12}$  molecule cm<sup>-3</sup> and  $[C_2H_5OH]$  ca.  $1.5 \times 10^{14}$  molecule cm<sup>-3</sup>. Under these conditions, the concentration of  $C_2H_5O$  radicals entering the main reactor was typically ca.  $3.5 \times 10^{11}$  molecule cm<sup>-3</sup>. Due to difference in flow velocities, the ratio of concentrations of reactants in injector and reactor was around 3.

 $C_2H_5O_2$  radicals were generated in the injector by reaction of F atoms with  $C_2H_6$  in the presence of  $O_2$  as indicated in Figure 1 (F +  $C_2H_6 \rightarrow C_2H_5$  + HF,  $k = 1.6 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M$ ,  $k = 2.1 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [1] at 1 torr of helium). The reaction time in the injector, ca. 12 ms, was found appropriate. This source was found to also produce  $C_2H_5O$  along with  $C_2H_5O_2$ , which can be attributed to the following reactions:

$$(5) C_2H_5O_2 + C_2H_5 \longrightarrow 2 C_2H_5O_2$$

(6) 
$$C_2H_5O_2 + C_2H_5O_2 \longrightarrow 2 C_2H_5O + O_2$$

(7) 
$$C_2H_5O_2 + F \longrightarrow C_2H_5O + FO$$

The rate constant  $k_5$  is likely similar to that of the reaction  $CH_3O_2 + CH_3$  $(k = 4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K [17]})$ , and the value of  $k_6$  is:  $4.2 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K [7] and  $k_7$  may be assumed as  $1 \times 10^{-10} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> at 298 K referring reaction  $C_2H_5O_2 + Cl$  [18]. However, the importance of each reaction cannot be put on a quantitative basis due to uncertainties in these rate constants. Typical initial concentrations of reactants in the injector were:  $[F]_0$  ca.  $7 \times 10^{11}$ ,  $[C_2H_6]$  ca.  $5 \times 10^{13}$ ,  $[O_2]$  ca.  $3 \times 10^{15}$  (in molecule cm<sup>-3</sup>).

The completion of reaction of  $C_2H_5$  with  $O_2$  in the injector was experimentally verified by adding Br<sub>2</sub> through a side arm into the reactor.  $C_2H_5$  radicals react rapidly with Br<sub>2</sub> to produce  $C_2H_5$ Br ( $k_7 = 1.0 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K [19]):

(8) 
$$C_2H_5 + Br_2 \longrightarrow C_2H_5Br + Br$$

 $C_2H_5Br$  was observed by mass spectrometry at m/e = 108, in the absence of  $O_2$ , and was not detected in the presence of  $O_2$ . Therefore,  $C_2H_5O_2$  and  $C_2H_5O$  radicals were considered to be the only reactive species which entered the main reactor. Their initial concentrations in the main reactor were experimentally determined (see below).

Either  $C_2H_5O$  or  $C_2H_5O_2$  produced in the central injector reacted with excess NO, which entered the main reactor through a side arm tube (Fig. 1). In both chemical systems, the  $C_2H_5O$  kinetics were monitored by LIF detection in a fluorescence cell, located at the end of the main reactor. The cell was equipped with a series of baffles to minimize scattering.  $C_2H_5O$  was excited in the  $(v_{co} = 3, v_{co}'' = 0)$  band of the  $\tilde{A} \leftarrow \tilde{X}$  electronic transition at  $\lambda = 323$  nm. This band has the largest excitation cross-section and has no interference with the spectrum of ethenoxy radical CH<sub>2</sub>CHO [16]. It was also experimentally verified that there was no interference at  $\lambda = 323$  nm with the fluorescence spectrum of CH<sub>2</sub>CHO (F + CH<sub>3</sub>CHO) and CH<sub>3</sub>CHO, produced separately. CH<sub>3</sub>CHO was a possible product of either the  $C_2H_5O$  + NO reaction in the main reactor, or of the  $C_2H_5O$  self recombination in the central injector. Most of the fluorescence was emitted to appreciably longer wavelength than that of the laser radiation so that the latter could be efficiently discriminated against by suitable optical filtering.

The exciting laser beam at 323 nm was obtained from a frequency doubled dye laser (Rhodamine 101) pumped by the XeCl excimer laser. The bandwidth and pulse energy of the mildly focussed laser radiation in the cell was estimated to be ca.  $0.3 \text{ cm}^{-1}$  and  $\leq$  1 mJ, respectively. The laser was operated at 10 Hz. The undispersed fluorescence was collected at right angle to the laser beam and flow reactor, and imaged onto the P.M.T. (Hamamatsu R2560) using two plano-convex quartz lenses. A single bandpass filter was used with maximum transmittance at 400 nm and a full width half maximum bandpass of 70 nm (Corion P70-400F). The P.M.T. was operated in pulse counting mode and pulses were preamplified before discrimination and counting. The P.M.T. was operated at ca. 1400 V with the discriminator of the multichannel analyser set at ca. 125 mV, so that the mean signal pulse height was well above the pulse height of other noise sources such as preamplifier noise and electro-magnetic interference pick-up from laser discharge. The laser firing provided an optical trigger to the multichannel analyser and the fluorescence signal was integrated over 300 laser pulses for each scan. The background signal due to scattered laser radiation was measured while the discharge was switched off and subtracted from the total signal to obtain the fluorescence signal. The observed fluorescence signal was found to correspond to a single exponential decay. The measured fluorescence lifetime of  $C_2H_5O$ was 1.5  $\mu$ s, in good agreement with previous determinations [16,20]. The period of integration was monitored over 2-3 half-lives. The detection sensitivity of C2H5O was  $\leq 1 \times 10^9$  molecule cm<sup>-3</sup> (S/N = 1).

Gas mixtures were prepared using a conventional Pyrex vacuum equipped with greaseless stopcocks. Helium flow was controlled and measured by mass flow controllers. Other gas flows were measured by the decrease of the pressure in a known volume containing the gas. The total pressure in the reactor was measured with a calibrated capacitance manometer (M.K.S. Baratron). The total flow rate was sufficient to ensure that fresh flow interacts with each laser pulse. The inside of the flow tube was coated with halocarbon wax to inhibit heterogeneous reaction of radicals.

Helium was used as the flowing medium. He (Alphagaz, 99.9995%) and O<sub>2</sub> (Alphagaz, 99.995%) were passed through a liquid nitrogen trap before entering the reactor. F<sub>2</sub> (Ucar, laser quality, 5% mixture in helium) and C<sub>2</sub>H<sub>6</sub> (Ucar, 99.3%) were used without purification. Ethanol (Fluka, >99.8% with [H<sub>2</sub>O] < 0.01%) was further purified by a trap to trap distillation, and NO (Alphagaz, 99.9%) in a silica trap held at ca.  $-80^{\circ}$ C to remove traces of NO<sub>2</sub> and O<sub>2</sub>. NO<sub>2</sub> (Alphagaz, 99.9%) was purified by trap to trap distillation at ca.  $-80^{\circ}$ C and then collected at room temperature.

# Results

Reaction  $C_2H_5O + NO$ 

The rate constant for the reaction:

(2) 
$$C_2H_5O + NO \longrightarrow Products$$

has been measured at 298 K under pseudo-first-order conditions (excess of NO) at three different total pressures of helium: 0.55, 1, and 2 torr. The typical initial concentrations of the reactants were:  $[C_2H_5O] = 3.5 \times 10^{11}$  molecule cm<sup>-3</sup> and  $[NO] = (0.6 - 5.5) \times 10^{13}$  molecule cm<sup>-3</sup>. The concentration of  $C_2H_5O$  was calculated by simulation of the chemical system induced by the F +  $C_2H_5OH$  reaction in the central injector (see experimental section).

Typical decays of LIF signal intensity of  $C_2H_5O$  in the presence and absence of NO are shown in Figure 2 ( $P_{He} = 1$  torr). For kinetic analysis, only decays with rates higher than 4 times the decay in the absence of NO were considered. The  $C_2H_5O$  decays in the absence of NO were measured before and after each series of kinetics. The measured rate in the absence of NO, ( $35 \pm 10$ ) s<sup>-1</sup>, was attributed to heterogeneous loss. This rate was found to be independent of the initial  $C_2H_5O$  concentration, indicating that the gas phase self-combination of  $C_2H_5O$  was negligible in the range of the  $C_2H_5O$  concentrations used.

The pseudo-first-order plots  $(-d \ln [C_2H_5O]/dt)$  as a function of [NO] at P = 0.55, 1.0, and 2.0 torr of helium are displayed in Figure 3. The plots have been corrected for the axial diffusion of  $C_2H_5O$  in He using  $D(C_2H_5O) = 331 \text{ cm}^2 \text{ s}^{-1}$  at T = 298 K and P = 1 torr (calculated value). This correction was in the range 3-10%. The intercepts of the plots of Figure 3 were  $(62 \pm 10) \text{ s}^{-1}$ ,  $(58 \pm 20) \text{ s}^{-1}$ ,  $(42 \pm 12) \text{ s}^{-1}$  at P = 0.55, 1.0, and 2.0 torr, respectively. These values are in acceptable agreement with the wall loss rate measured in the absence of NO. The rate constant values of  $k_2$  derived from the slopes of the straight lines  $-d \ln [C_2H_5O]/dt = k_2 [NO] + k_w$  are summarized in Table I.

Reaction  $C_2H_5O_2 + NO$ 

The reaction:

(3) 
$$C_2H_5O_2 + NO \longrightarrow C_2H_5O + NO_2 \qquad \Delta H_{298 \text{ K}}^\circ = -49.3 \text{ kJ mol}^{-1}$$



Figure 2. Reaction  $C_2H_5O + NO \rightarrow$  Products (2): typical pseudo-first-order decays of  $C_2H_5O$  radicals: [NO] = 0 ( $\blacklozenge$ ),  $1.14 \times 10^{13}$  ( $\clubsuit$ ),  $1.72 \times 10^{13}$  ( $\clubsuit$ );  $2.41 \times 10^{13}$  ( $\bigstar$ ); and  $4.46 \times 10^{13}$  ( $\blacksquare$ ) (units are molecule cm<sup>-3</sup>).

has been studied at 1 torr total pressure. The range of NO concentration used in excess over  $C_2H_5O_2$  was  $(1.0-5.7) \times 10^{13}$  molecule cm<sup>-3</sup>. The range of initial  $C_2H_5O_2$  and  $C_2H_5O$  concentrations in the main reactor were:  $[C_2H_5O_2]_0 = (3.4 - 14) \times 10^{11}$  molecule cm<sup>-3</sup> and  $[C_2H_5O]_0 = (0.8 - 2.1) \times 10^{11}$  molecule cm<sup>-3</sup>. The initial concentrations of  $C_2H_5O_2$  and  $C_2H_5O$  were measured by chemical titration and calibration of the LIF signal, respectively.  $C_2H_5O_2$  radicals were titrated using a large



Figure 3. Pseudo-first-order plots for the reaction  $C_2H_5O + NO \rightarrow Products$  (2) at total pressure 0.55 torr ( $\blacklozenge$ ), 1 torr (+) and 2 torr ( $\blacklozenge$ ), T = 298 K.

Total Pressure of He (torr)	$k_2 \ (10^{-11} \ \mathrm{cm}^3 \ \mathrm{molecule}^{-1} \ \mathrm{s}^{-1})^{\mathrm{a}}$
0.55 1.0 2.0	$\begin{array}{c} 1.25 \pm 0.04 \\ 1.66 \pm 0.06 \\ 1.81 \pm 0.06 \end{array}$

TABLE I. Reaction  $C_2H_5O + NO \rightarrow$  Products (2): rate constant at 0.55, 1.0, and 2.0 torr of helium and 298 K.

<sup>a</sup> The quoted uncertainty is  $2\sigma$  and indicates precision only.

excess of NO ([NO] ca.  $50 \times [C_2H_5O_2]_0$ ) and the production of NO<sub>2</sub> was monitored by mass spectrometry at m/e = 46. The mass spectrometer was calibrated by NO<sub>2</sub> while considering  $NO_2 \iff N_2O_4$  equilibrium. The titration was made before and after each series of experiments. Excluding a minor contribution of the association channel (<1.5%), C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> was converted stoichiometrically to NO<sub>2</sub> by reaction (3). The consumption of NO<sub>2</sub> by reaction with  $C_2H_5O_2$  and  $C_2H_5O$  was negligible since these radicals reacted predominantly with excess NO via reactions (2) and (3). The absence of  $C_2H_5O$  during titration was verified by LIF signal. This titration indicated that the production yield  $[C_2H_5O_2]_0/[F]_0$  in the source was ca. 0.5. The  $C_2H_5O$ concentration produced in the  $C_2H_5O_2$  source was determined by LIF analysis. The LIF signal intensity was calibrated using the  $F + C_2H_5OH$  reaction as the source of  $C_2H_5O$  (see experimental section), while verifying that laser energy remained stable. This calibration was made by flowing  $C_2H_5OH$  into the injector, instead of the  $C_2H_6/O_2$  mixture, keeping the same flow rate of  $F_2/He$  mixture through the discharge. The calibration was repeated before and after each series of experiments to verify consistency.

The measured ratio,  $[C_2H_5O_2]_0/[C_2H_5O]_0$ , in the  $C_2H_5O_2$  source was in the range 3–7. This ratio was lower than that calculated by simulation of the reaction mechanism in the source. A missing reaction of an impurity, X, which converts  $C_2H_5O_2$  into  $C_2H_5O$  would reconcile measured and calculated ratios, if X is present at a level of 10 ppm in the helium flow and  $k = 5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Nevertheless, it is unlikely that other reactive species than  $C_2H_5O_2$  and  $C_2H_5O$  could play some role in the main reactor. In a recent kinetic study of the reactions of  $C_2H_5O_2$  and  $C_2H_5O_2$  and  $C_2H_5O_3$  molecule<sup>-1</sup> s<sup>-1</sup>. Nevertheless, it has a measured to be inferred (the ratio was not measured) to explain the  $C_2H_5O$  decay profiles observed [5].

The kinetic study of reaction (3) consisted in monitoring  $C_2H_5O$  concentration profiles as a function of time in the presence of excess NO. The rate constant  $k_3$ was derived from a fitting procedure of experimental and calculated  $C_2H_5O$  profiles. The calculated profiles were obtained by simulation of the involved chemical reactions using FACSIMILE programme [21]. In this mechanism the major steps were reactions (2) and (3):

(2) 
$$C_2H_5O + NO \longrightarrow Products$$

$$(3) \qquad \qquad C_2H_5O_2 + NO \longrightarrow C_2H_5O + NO_2$$

(9) 
$$C_2H_5O + O_2 \longrightarrow CH_3CHO + HO_2$$

 $(k_9 = 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K [1]})$ . The first order loss of  $C_2H_5O$  in the  $C_2H_5O_2$  ( $C_2H_6 + F + O_2$ ) source was measured in the absence of NO for each series of experiments. The value found,  $(14 \pm 2) \text{ s}^{-1}$ , roughly corresponded to the rate of

reaction (9). That would mean that either the wall loss of  $C_2H_5O$  was negligible or, more likely, this loss was compensated by a production process of  $C_2H_5O$ . However, the modeling of  $C_2H_5O$  profile did not significantly differ considering these two cases. The wall loss of  $C_2H_5O_2$  was found negligible by observing no change of NO<sub>2</sub> concentration with reaction time in the titration experiments of  $C_2H_5O_2$  by NO. Besides, the HO<sub>2</sub> induced chemistry was calculated to have no significant influence on the  $C_2H_5O$ profiles (HO<sub>2</sub> was mainly produced by reaction (9) in both the central injector and main reactor). The rate constant  $k_3$  was derived from the simulation in two ways, by considering either both  $k_2$  and  $k_3$ , or  $k_3$  alone, as variable parameters. In the latter case, our value of  $k_2$  was taken as a fixed parameter ( $k_2 = 1.6 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 1 torr of helium).

Typical experimental and fitted calculated profiles of  $C_2H_5O$  for two different concentrations of NO are given in Figure 4 (with both  $k_2$  and  $k_3$  as variable parameters) and in Figure 5 (with  $k_3$  as variable parameter and  $k_2$  fixed). The rate constants obtained for each kinetic runs are reported in Table II, where the error on each rate constant value corresponds to 95% confidence limits in the best fit procedure. In the case with  $k_2$  and  $k_3$  as variable parameters, the mean rate constant values obtained are:

$$k_2 = (1.4 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$
  
 $k_3 = (7.4 \pm 1.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$ 

The quoted errors are two standard deviations.

It can be noticed that the  $k_2$  value is very close to the direct determination in this work,  $k_2 = (1.66 \pm 0.06) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 1 \text{ torr of helium.}$ 



Figure 4. Typical concentration – time profiles of  $C_2H_5O$  in the kinetic study of the reaction  $C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$  (3): ( $\blacklozenge$ )  $[NO]_0 = 1.1 \times 10^{13}$ ,  $[C_2H_5O_2]_0 = 4.3 \times 10^{11}$ ,  $[C_2H_5O]_0 = 1.0 \times 10^{11}$  and ( $\clubsuit$ )  $[NO]_0 = 3.6 \times 10^{13}$ ,  $[C_2H_5O_2]_0 = 4.1 \times 10^{11}$ ,  $[C_2H_5O]_0 = 1.1 \times 10^{11}$  (units are molecule cm<sup>-3</sup>). Experimental values are shown by symbols. Solid lines are obtained by simulation with  $k_2$  and  $k_3$  as variable parameters [see text].



Figure 5. Typical concentration – time profiles of  $C_2H_5O$  in the kinetic study of the reaction  $C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$  (3): (**D**)  $[NO]_0 = 9.5 \times 10^{12}$ ,  $[C_2H_5O_2]_0 = 3.4 \times 10^{11}$ ,  $[C_2H_5O]_0 = 9.0 \times 10^{10}$  and (**O**)  $[NO]_0 = 1.5 \times 10^{13}$ ,  $[C_2H_5O_2]_0 = 3.2 \times 10^{11}$ ,  $[C_2H_5O]_0 = 8.4 \times 10^{10}$  (units are molecule cm<sup>-3</sup>). Experimental values are shown by symbols. Solid lines are obtained by simulation with  $k_3$  as variable parameters and  $k_2$  fixed at  $1.6 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [see text].

In the second case, with fixed  $k_2$ , the value obtained for  $k_3$  is:

 $k_3 = (8.2 \pm 1.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{with } 2\sigma \text{ error}).$ 

TABLE II. Determination of rate constant for the reaction  $C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$  (3), at 1 torr of He and 298 K.

$[NO]_0\;(10^{13})^{a}$	$[C_2H_5O_2]_0\;(10^{11})^a$	$[C_2H_5O]_0\;(10^{11})^{a}$	$k_2^{\ c} \ (10^{-11})^{\ b}$	$k_3^{\ c} \ (10^{-12})^{b}$	$k_3^{\ d} \ (10^{-12})^{\ b}$
0.95	3.44	0.90	$1.68 \pm 0.02$	$9.51 \pm 0.22$	$9.03 \pm 0.30$
1.08	4.28	1.00	$1.60\pm0.02$	$8.20\pm0.16$	$8.20 \pm 0.12$
1.27	4.18	1.06	$1.52 \pm 0.02$	$8.12\pm0.17$	$8.75 \pm 0.42$
1.47	3.18	0.84	$1.51\pm0.03$	$8.38\pm0.27$	$8.90 \pm 0.49$
1.89	13.70	2.13	$1.50\pm0.08$	$6.40\pm0.52$	$6.79\pm0.52$
2.30	4.18	1.10	$1.40\pm0.02$	$7.43\pm0.18$	$8.69 \pm 1.47$
2.43	4.28	1.00	$1.39\pm0.02$	$6.73\pm0.17$	$7.70\pm1.08$
2.79	3.18	0.82	$1.27~\pm~0.02$	$7.07\pm0.21$	$8.82 \pm 3.20$
2.80	14.00	2.13	$1.37~\pm~0.07$	$5.91\pm0.50$	$6.69~\pm~1.09$
3.55	4.10	1.10	$1.36\pm0.03$	$6.83 \pm 0.27$	$7.70 \pm 1.93$
3.64	4.37	1.11	$1.27\pm0.02$	$7.00\pm0.23$	$8.70 \pm 3.46$
3.76	4.37	1.13	$1.25~\pm~0.02$	$7.04\pm0.21$	$8.82 \pm 3.65$
5.66	4.55	1.11	$1.24~\pm~0.01$	$6.82\pm0.20$	$7.15~\pm~5.01$
	Mean values <sup>e</sup>		$1.41\pm0.28$	$7.35\pm1.86$	$8.15~\pm~1.62$

 $[C_2H_6]$  ca.  $3 \times 10^{14}$  molecule cm<sup>-3</sup>;  $[O_2]$  ca.  $1 \times 10^{15}$  molecule cm<sup>-3</sup>.

<sup>a</sup> Units are molecule cm<sup>-3</sup>.

<sup>b</sup> Units are  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>.

<sup>&</sup>lt;sup>c</sup> Rate constants obtained from simulation by varying both  $k_2$  and  $k_3$ .

<sup>&</sup>lt;sup>d</sup> Rate constants obtained from simulation with  $k_2$  fixed at  $1.6 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

<sup>&</sup>lt;sup>e</sup> The quoted errors are  $2\sigma$ .

The values derived for  $k_3$  in the two cases are very close. Considering the reliability of the direct measurement of  $k_2$  in this work, the determination of  $k_3$  in the second case is preferred.

#### Discussion

Reaction  $C_2H_5O + NO$ 

In the only previous direct study of the  $C_2H_5O + NO$  [9], using a pulsed photolysis – LIF technique, the rate constant was measured at 298 K and at pressures of 15 and 100 torr of argon. The rate constant was found to be the same at these two pressures:  $k_2 = (4.4 \pm 0.8) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The lower values of  $k_2$  obtained in our study at lower pressures and the observation of a pressure dependence of  $k_2$  in the low pressure range studied (0.55–2 torr) indicate that at least one channel of reaction (2) is pressure dependent. Referring to the similar reaction of CH<sub>3</sub>O with NO [9,10], the most likely channels are:

(2a)  $C_2H_5O + NO + M \longrightarrow C_2H_5ONO + M$ (2b)  $C_2H_5O + NO \longrightarrow CH_3CHO + HNO$  $\Delta H_{298 K}^{\circ} = -42.3 \text{ kJ mol}^{-1}$ 

Also referring to the reaction of  $CH_3O$  with NO [9,10], channel (2b) may occur via a direct pressure independent mechanism. It may also occur via an association-rearrangement mechanism, proceeding through the same ( $C_2H_5O$ —NO) complex as in channel (2a):

$$C_{2}H_{5}O + NO \iff C_{2}H_{5}O - NO]^{\#} \implies C_{2}H_{5}ONO$$
$$\downarrow k_{d}$$
$$CH_{3}CHO + HNO$$

Considering first a direct pressure independent mechanism for channel (2b), our experimental data together with the  $k_2$  value of ref. [9] can be analysed by means of the Lindemann-Hinshelwood (LH) expression:

$$k_{
m obs} = rac{k_{
m 2a}^0 \, [{
m M}]}{1 \, + \, k_{
m 2a}^0 \, [{
m M}]/k_{
m 2a}^\infty} \, + \, k_{
m 2b}$$

Rearrangement of this expression gives:

(I) 
$$1/(k_{\rm obs} - k_{\rm 2b}) = (1/k_{\rm 2a}^{\infty}) + (1/k_{\rm 2a}^{0})(1/[M])$$

 $1/(k_{obs} - k_{2b})$  has been plotted against 1/[M] for different  $k_{2b}$  values. For each  $k_{2b}$  value, 4 points were considered at P = 0.55, 1.0, and 2.0 torr and at the high pressure limit for which the intercept was  $1/k_{2a}^{\infty} = 1/(4.4 \times 10^{-11} - k_{2b})$ . The value  $4.4 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> was the value of  $k_{obs}$  in the high pressure limit range from ref. [9]. The best straight line from expression (I) was obtained for  $k_{2b} = 8 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Fig. 6). The low pressure limit for the rate constant of channel (2a) was derived from the slope of the straight line,  $k_{2a}^{0} = (3.0 \pm 0.3) \times 10^{-28}$ 



Figure 6. Plot of observed rate constants  $(k_{obs})$  for reaction  $C_2H_5O + NO \rightarrow$  Products (2) at different total pressures, using eq. (I):  $1/(k_{obs} - k_{2b}) = (1/k_{2a}^{\infty}) + (1/k_{2a}^{0})(1/[M])$ , based on Lindemann-Hinshelwood analysis [see text].

cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>. The reciprocal of the intercept gives the value of the high pressure limit of channel (2a):  $k_{2a}^{\infty} = (3.1 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The second approach to analyze the data is to assume that channel (2b) proceeds through the same transition complex as channel (2a). In this case, the LH expression of the observed rate constant,  $k_{obs}$ , is:

$$k_{
m obs} = rac{k_{
m 2a}^0\,[{
m M}] + k_{
m 2b}^0}{1 + ig(k_{
m 2a}^0[{
m M}] + k_{
m 2b}^0ig)/k_2^pprox}$$

with  $k_2^{\infty} = k_f$ ,  $k_{2a}^0 = (k_f/k_r) k_s$ ,  $(k_{2a}^0$ : low pressure limit of channel (2a) in the absence of channel (2b)), and  $k_{2b}^0 = (k_f/k_r)k_d$ ,  $(k_{2b}^0$ : low pressure limit of channel (2b)).

The above expression can be rearranged as:

(II) 
$$k_{\rm obs}/(1 - k_{\rm obs}/k_2^{\infty}) = k_{\rm 2b}^0 + k_{\rm 2a}^0[M]$$

The left part of this expression has been plotted as a function of [M], taking  $k_2^{\infty} = 4.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [9]. The  $k_{2b}^0$  and  $k_{2a}^0$  values derived from the intercept and slope of the least square fitted straight line respectively are:  $k_{2b}^0 = (1.5 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } k_{2a}^0 = (2.6 \pm 1.2) \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ . These values have to be divided by the factor  $(1 + k_d/k_r) = (1 + k_{2b}^0/k_2^{\infty})$  to obtain the true values of the low pressure limit of channels (2a) and (2b). These values are:  $k_{2b}^0 = (1.1 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } k_{2a}^0 = (2.2 \pm 1.2) \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ .

The comparison of these values with those obtained assuming a direct disproportionation mechanism for channel (2b) first shows that for channel (2b) the calculated rate constant of the direct reaction is similar to that of the association-rearrangement reaction in the low pressure regime. Also, in the indirect study of Batt and Milne [11], the rate constant for channel (2b) was derived as ca.  $1 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 435 K. For the association channel (2a) the calculated low pressure limits,  $k_{2a}^0$ , derived

Technique/Monitored species <sup>a</sup>	$k_3 (10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	Pressure (torr)	Reference
FP-UV/C <sub>2</sub> H <sub>5</sub> O <sub>2</sub>	$2.7\pm0.2$	44 - 676	[22]
$DF-MS/NO_2$	$8.9\pm3.0$	5 - 3	[12]
$PR-UV/NO_2$	$8.5\pm1.2$	760	[13]
$DF-LIF/C_2H_5O$	$8.2 \pm 1.6$	1	This work

TABLE III. Reaction  $C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$  (3): literature data at 298 K.

<sup>a</sup> FP-UV: Flash Photolysis – UV absorption; DF-MS: Discharge Flow – Mass Spectrometry; PR-UV: Pulsed Radiolysis – UV absorption; and DF-LIF: Discharge Flow – Laser Induced Fluorescence.

from the expressions (I) and (II), are  $(3.0 \pm 0.3) \times 10^{-28}$  and  $(2.2 \pm 1.2) \times 10^{-28}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, respectively. The average value  $(2.6 \pm 1.0) \times 10^{-28}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>, is significantly lower than the value  $(2.0 \pm 1.0) \times 10^{-27}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> in air recommended in ref. [1], even if an air to helium efficiency of c.a. 2 is considered. The above analysis clearly indicates a competition between the association and disproportionation channels in the range of pressure used, whereas for the CH<sub>3</sub>O + NO reaction, the disproportionation channel was predominant.

## Reaction $C_2H_5O_2 + NO$

The rate constant obtained for this reaction,  $k_3$ , can be compared with the literature data reported in Table III. Our value is in good agreement with the published results of Plumb et al. [12] and Sehested et al. [13]. The reason for the lower value by Adachi et al. [22] has already been discussed [12,13]. In both of these studies [12,13],  $k_3$  was obtained from pseudo-first-order kinetics of NO<sub>2</sub> formation. The secondary chemistry which could affect the NO<sub>2</sub> kinetics has been estimated to be insignificant. The secondary chemistry included reactions of C<sub>2</sub>H<sub>5</sub>O and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> with NO<sub>2</sub> and the sequence

$$C_2H_5O + O_2 \longrightarrow HO_2(+CH_3CHO) \xrightarrow{+NO} NO_2(+OH)$$

However, the secondary reactions involving  $C_2H_5O$  might have been underestimated in ref. [12], where the  $C_2H_5O_2$  source, which was the same as ours, was not considered to contain  $C_2H_5O$  as we have observed. In the present work,  $k_3$  was derived from the kinetic analysis of the other reaction product,  $C_2H_5O$ , taking into account the secondary reactions, essentially reactions (2) and (9), which were well identified. The agreement between the  $k_3$  values of the three studies ([12,13] and this work) validates the complementary methods used. These values are also in good agreement with two other determinations reported at 298 K:  $k_3 = (7.2 \pm 1.3) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [23] and  $k_3 = (8.9 \pm 3.5) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [24]. The methods used were the laser photolysis-UV absorption with kinetic analysis of  $C_2H_5O_2$  consumed [23] and the discharge flow-mass spectrometry with kinetic analysis of NO<sub>2</sub> formed [24].

# Conclusion

The present study provides additional data on the reaction of  $C_2H_5O$  with NO at low pressure, indicating that, similarly to the reaction of  $CH_3O$  with NO, two channels (association and disproportionation) are likely to occur. However, this has to be confirmed by direct analysis of the reaction products. For the reaction of  $C_2H_5O_2$ 

with NO, which is important in converting NO into NO<sub>2</sub> in the troposphere, and thus, in producing ozone, the rate constant measured in this work confirms the limited literature values obtained using complementary methods. The observed agreement also validates our experimental methodology, based on LIF kinetic analysis of  $C_2H_5O$ and computer simulation, for kinetic studies of  $C_2H_5O$  radicals.

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