Gas-Phase Reactions of the Vinoxy Radical with O_2 and NO

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We have used the technique of laser-induced fluorescence to study the addition reactions of the 2-oxoethyl (vinoxy) radical with O_2 and NO as a function of temperature and pressure. The bimolecular rate constants for the reaction with NO are observed over the major portion of the transition region from the low- to high-pressure limits and are well fit at room temperature and M = N_2 by the expression of Troe[14] with coefficients k_0 = 6.53 (±0.85) × 10^{-29} cm^6 $molecule^{-2}$ s^{-1}, k_∞ = 2.51 (±0.30) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, and F_c = 0.54 (±0.08). A much smaller pressure dependence is observed for the reaction of vinoxy with O_2. Similarities between the reactions of vinoxy radicals and alkyl radicals are discussed.

Introduction

The 2-oxoethyl (vinoxy) radical has recently been identified as a major product of the gas-phase reactions of oxygen atoms with primary olefins, both under homogeneous[3] and molecular beam conditions.[4,5] Since these elementary oxygen-atom reactions are involved in photochemical smog cycles[6,7] and in the high-temperature combustion of unsaturated hydrocarbons,[8] C_2H_3O is an important intermediate in these systems. Because there is essentially no information available on the reactivity of this radical, its role in these complex oxidation processes cannot be assessed quantitatively.

The laser-induced fluorescence (LIF) spectrum of C_2H_3O has now been identified and its characteristics reported.[9] These studies provide the information needed to both identify and monitor this free radical in time-resolved experiments. Using LIF detection of this intermediate, we have now studied two of its important reactions, those with O_2 and NO. The results of these investigations are reported here.

The reactions of the vinoxy radical should have similarities with those of alkyl radicals. Ab initio theoretical calculations indicate that the ground electronic state (X,1^2A) of C_2H_3O is essentially a carbon-centered radical resembling the valence-bond structure (I) while the second

$$\underset{\text{I}}{\cdot CH_2\text{-}CH{=}O}$$

excited state (B,2^2A), from which the LIF is observed and which lies 3.57 eV above the ground state, involves a small lengthening of the CC bond and a large increase in the CO bond distance to yield a species with much more oxygen radical character.[10]

The first excited state (A,1^2A′) which involves an out-of-plane orientation of the oxygen lone-pair electrons, has been detected by infrared absorption, and lies ~1.0 eV above the ground state.[3] Because the reactions of the carbon-centered alkyl radicals with O_2 and NO proceed by addition, we have performed experiments as a function of pressure to search for evidence of similar pathways in the reactions studied.

Experimental Section

The apparatus used for the determination of vinoxy radical kinetic parameters has been described in detail recently,[11] only the details particular to the current work will be discussed. Vinoxy radicals were produced by 193-nm photolysis of methyl vinyl ether using an ArF excimer laser (Lumonics 860) with typical pulse energy of 75 mJ and operating at a repetition rate of 10 Hz. The excimer output was collimated before the reaction cell yielding photolysis pulse energies of 10–30 mJ. Fluorescence was excited by a flash-lamp pumped dye laser (Chromatix CMX-4) operating at 337 nm and was collected at right angles to the counterpropagating lasers beams by means of a telescope, isolated by an interference filter (λ_{max} = 400 nm, fwhm = 50 nm) and detected by an RCA 31000A PMT.

In order to confirm the identity of the vinoxy radical and choose the excitation wavelength for the kinetic studies, we recorded the vinoxy radical excitation spectrum in the same apparatus. The result agrees well with the spectrum reported by Inoue and Akimoto.[9]

The reaction cell consists of a 5-cm stainless steel cross with 30-cm glass sidearms through which the lasers propagate and a saphire window for monitoring the fluorescence. The cell was contained in a forced-air oven equipped with ports for the sidearms and light collecting optics. Oven temperatures were constant to ±1 K.

Metered flows of methyl vinyl ether, reactant (O_2 or NO), and buffer gas (N_2 or SF_6) were mixed and flowed through the cell at total flow rates of 0.2 to 2.0 1/min. Reactant partial pressures were calculated from the measured flow rates and total pressure. The methyl vinyl ether and NO were prepared as dilute mixtures in the buffer gas used and flowed from the mixing tank. N_2, O_2, and SF_6 flowed from commercial cylinders. Typical pressures used were 1–5 mtorr of methyl vinyl ether, 0–200 mtorr of NO or 0–3 torr of O_2, and 2–300 torr total pressure. Air Products Industrial Grade N_2 (99.998%) and O_2 (99.5%) and Matheson methyl vinyl ether (99.5%), NO (99%), and SF_6 (99.9%) were used without further purification.

The gas purity specifications quoted by the supplier for the reactant gases O_2 and NO are such that use without purification is possible. The principal impurities in O_2 are Ar and N_2 both of which are inert in this application. The only other impurity above the 10-ppm level is total hydrocarbons and we have observed in separate experiments

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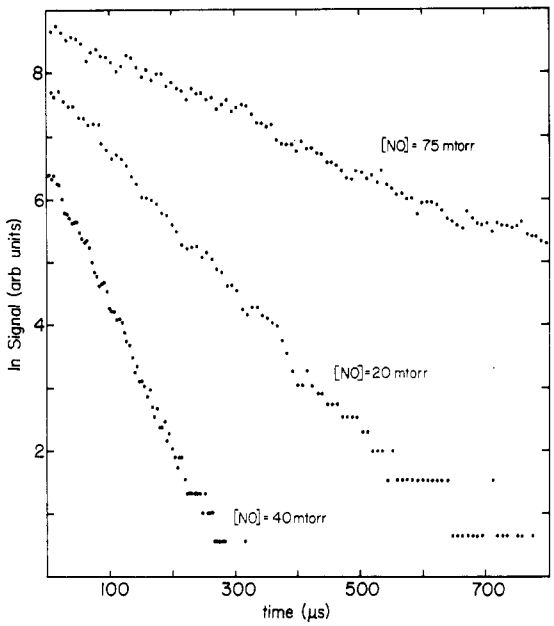

Figure 1. Plot of the observed vinoxy radical concentration decay as a function of time for three NO pressures. All three decays were measured at room temperature and 100 torr of N_2 total pressure. For clarity of presentation, every second point is plotted for the fastest decay and every fourth for the other two decays.

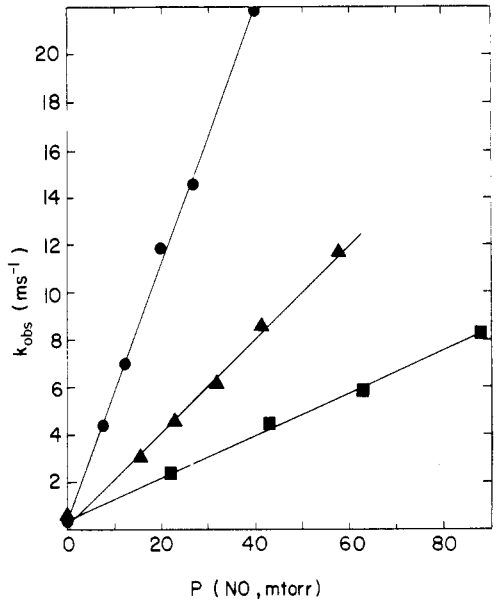

Figure 2. Plot of the observed vinoxy radical decay constant (k_{obsd}) for the reaction of vinoxy + NO at 295 K vs. the NO pressure using N_2 as the buffer gas. Three different total pressures are shown: (■) 2.5, (▲) 10, and (●) 100 torr.

that vinoxy is unreactive toward butane and propene at torr concentrations. The NO impurities include CO_2, N_2, and N_2O which are unreactive and NO_2 which is present at a sufficiently low concentration (~500 ppm) that it provides no competition for the relatively fast vinoxy + NO reaction.

The experiments were performed under pseudo-first-order conditions. The vinoxy decay rate was measured by varying the time delay between the two lasers over the range 100 μs to 5 ms. The experiments were started after 100 μs to avoid interference from vibrational relaxation in the nascent radical and prompt emission from excimer-excited products. The fluorescence signal was averaged by a boxcar integrator and digitized and stored by a Nicolet 1180 computer for later analysis. When no added reactant was present, we observed a slow disappearance of vinoxy radicals, which was approximately first order, which we attribute to reaction with the photolysis precursor. When reactants were present the vinoxy disappearance was first order and was well fit by a single exponential over the 4–6 reaction lifetimes observed.

The LIF product studies were conducted in a similar manner. The dye laser was tuned to the OH resonance at 306.5 nm and the OH concentration profile was recorded. In a separate investigation, we used a flow reactor coupled to a photoionization mass spectrometer[12] to observe other products of the vinoxy + O_2 reaction. The vinoxy radicals were produced by H atom abstraction from ethylene oxide by Cl atoms formed in the IR multiphoton dissociation of C_6F_5Cl.

Results

We have measured second-order rate constants for the reactions of vinoxy radicals with O_2 and NO for a range of total pressures with both N_2 and SF_6 as the buffer gas. For each of the total pressure/buffer gas combinations, vinoxy radical decay profiles were measured for a range of O_2 or NO partial pressures. Representative data for the reaction of vinoxy + NO at room temperature and a total pressure of 100 torr of N_2 are shown in in Figure 1. The first-order decay constants obtained were plotted vs. reactant pressure, and the second-order rate constant was obtained from the slope of the line fit to each data set. This is illustrated for three total pressures of N_2 in Figure 2. The intercept of the fitted line, which in all cases was less than 5% of the maximum measured vinoxy decay rate, was essentially independent of total pressure. This supports our contention that this zero reactant decay reflects vinoxy radical reaction with the photolytic precursor rather than reaction with buffer gas impurities (intercept proportional to total pressure) or diffusion from the sampling zone (intercept inversely proportional to total pressure). The complete set of measured rate constants for this reaction (12 pressures between 2.5 and 300 torr) at room temperature (295 K) and N_2 buffer gas is listed in Table I and shown in the lower panel of Figure 3. The uncertainties listed ($\pm 1\sigma$) refer to the precision of the data as evidenced by the scatter in the second-order plots. Consideration of possible systematic errors in the components of the rate constant calculations, the largest of which is the uncertainty in the determination of the reactant pressure, leads to an estimate of ±20% for the accuracy of these rate constants. We appear to have covered the major portion of the transition region between the high- and low-pressure limits.

TABLE I: Bimolecular Rate Constants for the Reaction of Vinoxy + NO at 295 K

P_{N_2}, torr	$10^{12}k_{bi}$ ($\pm 1\sigma$), cm^3 $molecule^{-1}$ s^{-1}	P_{N_2}, torr	$10^{12}k_{bi}$ ($\pm 1\sigma$), cm^3 $molecule^{-1}$ s^{-1}
2.5	2.70 ± 0.08	40	11.6 ± 0.5
4	4.06 ± 0.24	60	13.5 ± 0.6
6	4.98 ± 0.18	80	16.2 ± 0.6
10	6.03 ± 0.21	100	16.8 ± 0.4
20	8.60 ± 0.49	150	17.7 ± 0.6
30	10.7 ± 0.7	300	18.8 ± 0.6

We also measured bimolecular rate constants at two pressures (10 and 40 torr) using SF_6 as the buffer gas. The measured rate constants were 15% higher than the N_2 values at both of the pressures used.

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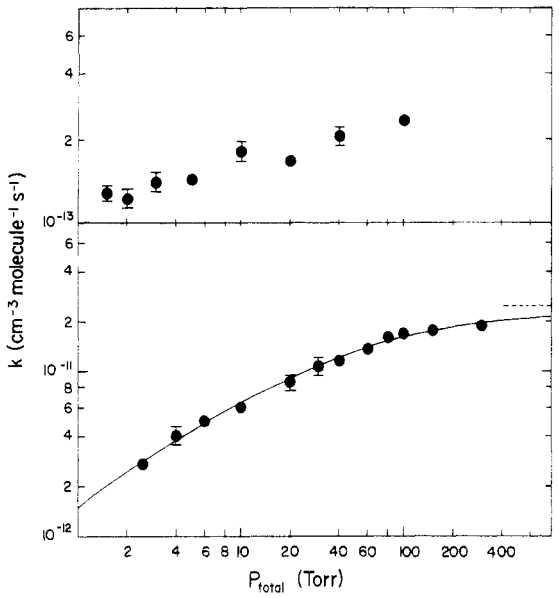

Figure 3. Bimolecular rate constants for vinoxy reactions vs. total pressure with N_2 as the buffer gas at 295 K: upper panel, reaction of vinoxy + O_2; lower panel, data for the reaction of vinoxy + NO. The line shown is the result of a semiempirical fit described in the text.

TABLE II: Bimolecular Rate Constants for the Reaction of Vinoxy + O_2 as a Function of Pressure and and Temperature

P_{Total}, torr	$10^{13}k_{bi}$ ($\pm 1\sigma$), cm³ molecule⁻¹ s⁻¹	M	T, K
1.5	1.14 ± 0.04	N_2	295
2	1.09 ± 0.05		
3	1.29 ± 0.06		
5	1.33 ± 0.04		
10	1.79 ± 0.09		
20	1.60 ± 0.03		
40	2.08 ± 0.09		
100	2.46 ± 0.06		
5	0.79 ± 0.06	N_2	476
15	0.97 ± 0.04		
40	1.23 ± 0.09		
100	1.65 ± 0.14		
10	1.88 ± 0.06	SF_6	292
40	2.50 ± 0.11		
90	2.50 ± 0.14		
40	2.21 ± 0.07	SF_6	385
95	2.92 ± 0.24		
40	1.78 ± 0.06	SF_6	473
90	2.21 ± 0.08		

Analogous measurements were performed for the vinoxy + O_2 reaction. All the bimolecular rate constants obtained are listed in Table II and the room temperature (295 K), N_2 buffer gas measurements are plotted in the upper panel of Figure 3. We were prevented from performing experiments at lower total pressures in the O_2 series due to the larger O_2 reactant pressures needed and at higher pressures by fluorescence quenching. The pressure dependence observed over the range available to us (1.5–100 torr) is much smaller than for the vinoxy + NO reaction. We also observe a small negative temperature dependence of the reaction rate constant.

The search for products of the C_2H_3O + O_2 reaction yielded equivocal results. Although OH was observed to appear as vinoxy radicals were reacting, the growth rate of the OH radical concentration did not mirror the decay rate of the C_2H_3O reactant. The OH signal half-growth time was three times longer than the half-life of C_2H_3O at 10 torr of N_2 total pressure. Nearly the same OH appearance rate constant was obtained at 25 torr as at 10 torr. The uncertainty in these measurements is very large however as the OH produced reacts rapidly with the methyl vinyl ether used as the vinoxy precursor (and present at a pressure of 10 mtorr in these experiments) and the OH fluorescence signal is therefore small. The detection of mass 30 (H_2CO?) as a product of the reaction using mass spectrometry was not adequately time resolved to conclude that the observed signal corresponded to an initial product.

Discussion

C_2H_3O + NO Reaction. The rate constants measured for the C_2H_3O + NO reaction display the characteristic pressure dependence of a simple addition reaction.[13] There is no evidence of any leveling off of the rate constant at low pressures which indicates that this reaction does not proceed to any significant extent by any alternate pressure-independent routes under the conditions of our study (e.g., H-atom transfer or adduct decomposition by alternate pathways). The reaction probably produces 2-nitrosoethanal

$$CH_2CHO + NO \underset{k_r}{\overset{k_f}{\rightleftharpoons}} NOCH_2CHO^*$$

$$NOCH_2CHO^* + M \xrightarrow{k_s} NOCH_2CHO + M$$

The pressure dependence of the bimolecular rate constant k_{bi} for the overall reaction (defined by $-d[C_2H_3O]/dt = k_{bi}[C_2H_3O][NO]$ was fit to a semiempirical expression developed by Troe:[14]

$$\log k_{bi} = \log\left[\frac{k_0[M]}{1 + k_0[M]/k_\infty}\right] + \frac{\log F_c}{1 + [\log (k_0[M]/k_\infty)]^2} \quad (1)$$

where $k_0[M]$ and k_∞ are the low- and high-pressure limiting values of k_{bi}, respectively. The second term in eq 1, which contains the adjustable broadening factor F_c, provides a useful approximate correction to the Lindemann–Hinshelwood expression for k_{bi} to take into account the changing energy dependence of k_r with pressure. A nonlinear least-squares procedure was used to obtain values of k_0, k_∞, and F_c which provided the best fit of the data points to eq 1. The values obtained are k_0 = 6.53 (±0.85) × 10^{-29} cm⁶ molecule⁻² s⁻¹, k_∞ = 2.51 (±0.30) × 10^{-11} cm³ molecule⁻¹ s⁻¹, F_c = 0.54 (±0.08).

The values of k_{bi} obtained from eq 1 with these parameters are shown in Figure 3 with the measured data points.

The two sets of experiments which were performed with SF_6 as a diluent gas (at total pressures of 10 and 40 torr) yielded values of k_{bi} which were essentially the same as those obtained when N_2 was used at these same pressures. The two values of k_{bi} obtained in the SF_6 experiments were each about 15% higher than the corresponding values from the N_2 experiments. This qualitative difference is in the expected direction, since SF_6 is a more efficient collision partner than in N_2.[15] Since the uncertainty in the measured rate constants is greater than this 15% difference, these results cannot be used to gain more quantitative knowledge of the relative collision efficiencies for energy removal by these two bath gases.

C_2H_3O + O_2 Reaction. The pressure and temperature dependencies of the C_2H_3O + O_2 bimolecular rate constants which we have measured are all consistent with an

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addition reaction which is near the high-pressure limit. The $C_2H_3O + O_2$ bimolecular rate constant displays a significantly smaller pressure dependence over the range of conditions covered (1.5–100 torr at 295 K) than does the rate constant of the reaction of this radical with NO. The rate constant decreased by only a factor of 2 through this 70-fold lowering of the pressure.

The experiments performed at elevated temperatures with two different diluent gases (N_2 and SF_6) show a small decrease in the rate constant at each pressure when the temperature is raised. At higher temperatures, the pressure dependence is almost the same as that at ambient temperature. There are, however, indications in the data that the pressure dependence becomes somewhat greater as the temperature increases.

The addition reaction which is most likely involves the formation of a peroxy radical

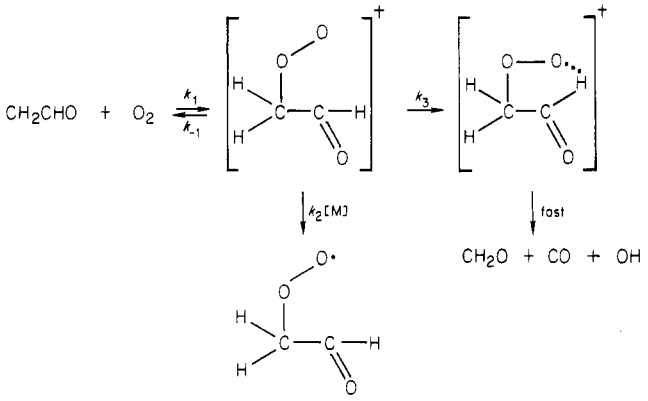
$$CH_2CHO + O_2 \underset{k_{r'}}{\overset{k_r}{\rightleftharpoons}} O_2CH_2CHO^* \xrightarrow{k_{s'}} O_2CH_2CHO + M$$

There is information in the literature which indicates indirectly that the vinoxy + O_2 reaction should be close to the high-pressure limit near 1 torr total pressure. The isoelectronic allyl + O_2 addition reaction has recently been studied both at high pressures by Pilling and co-workers,[16-18] at Oxford and at low pressures by Bayes and Ruiz[18,19] at UCLA. Extrapolation of the low-pressure results to the high-pressure ones indicates that the falloff region of this reaction at ambient temperature is centered near 15 torr, $P_{1/2}$ = 10–20 torr. A simple RRK calculation predicts that $P_{1/2}$ for the vinoxy + O_2 rate constant should be lower than this pressure by about a factor of 10, somewhere near 1 torr. This difference is due to the fact that the vinoxy·O_2 adduct has a stronger R–O_2 bond (25–28 kcal/mol) than does the allyl·O_2 complex (~19 kcal/mol).[17] The weaker allyl–O_2 bond results from the loss of resonance energy of the allyl radical when it forms the allylperoxy radical.[20,21] The vinoxy radical has essentially no resonance energy.[10,22]

A falloff region for the $C_2H_3O + O_2$ reaction centered at $P_{1/2}$ = 0.5–1.5 torr would also be indicated if one presumed that the pressure dependence of this reaction would be similar to that of an alkyl radical + O_2 reaction involving an alkyl radical of comparable size and complexity to the vinoxy radical. Such a conjecture seems reasonable since the R–O_2 bonding should be comparable for two carbon-centered radicals without any resonance stabilization. The $C_2H_5 + O_2$ reaction pressure dependence has recently been reported by Plumb and Ryan who report a $P_{1/2}$ value of ~2 torr.[23] The vinoxy + O_2 falloff region should lie at somewhat lower pressures. The $C_4H_7 + O_2$ reaction is pressure independent at 1 torr indicating a falloff region centered at a significantly lower pressure.[24]

The preceding discussion implies a rather low k_∞ for the vinoxy + O_2 reaction. The isoelectronic allyl + O_2 reaction exhibits analogous behavior. Kinetic measurements on the allyl + NO reaction result in a $k_\infty > 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at room temperture in Ar[25] while O_2 reaction seems to have a $k_\infty < 1 \times 10^{-12}$.

Since the vinoxy + O_2 reaction could not be studied at pressures which were low enough to observe a significant portion of the falloff region, one cannot exclude the possibility that this reaction may also proceed by additional pressure-independent routes. One distinct possibility is an alternate decomposition pathway for the excited $C_2H_3O{\cdot}O_2$ adduct, one which involves internal 1,4 migration of an H atom:



Such rearrangements are known in alkylperoxy and in alkoxy radicals.[26-28] The internal energy of the $C_2H_3O{\cdot}O_2$ adduct (25–28 kcal/mol) could be great enough to overcome the barrier to this internal migration. If this were true, we would expect to see a vinoxy disappearance rate that was the sum of a pressure-independent path that leads to fragmentation and a pressure-dependent addition reaction. Unfortunately both experiments which were performed to search for the products of this alternate pathway were inconclusive.

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Registry No. Vinoxy radical, 4400-01-5; O_2, 7782-44-7; NO, 10102-43-9.

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