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Rate and Equilibrium Constant of the Reaction of 1-Methylvinoxy Radicals with O_2: $CH_3COCH_2 + O_2 \leftrightarrow CH_3COCH_2O_2$[†]

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The reaction of 1-methylvinoxy radicals, CH_3COCH_2, with molecular oxygen has been investigated by experimental and theoretical methods as a function of temperature (291−520 K) and pressure (0.042−10 bar He). Experiments have been performed by laser photolysis coupled to a detection of 1-methylvinoxy radicals by laser-induced fluorescence LIF. The potential energy surface calculations were performed using ab inito molecular orbital theory at the G3MP2B3 and CBSQB3 level of theory based on the density function theory optimized geometries. Derived molecular properties of the characteristic points of the potential energy surface were used to describe the mechanism and kinetics of the reaction under investigation. At 295 K, no pressure dependence of the rate constant for the association reaction has been observed: $k_{1,298K} = (1.18 \pm 0.04) \times 10^{-12}$ cm^3 s^{-1}. Biexponential decays have been observed in the temperature range 459−520 K and have been interpreted as an equilibrium reaction. The temperature-dependent equilibrium constants have been extracted from these decays and a standard reaction enthalpy of $\Delta H_{r,298K} = -105.0 \pm 2.0$ kJ mol^{-1} and entropy of $\Delta S_{r,298K} = -143.0 \pm 4.0$ J mol^{-1} K^{-1} were derived, in excellent agreement with the theoretical results. Consistent heats of formation for the vinoxy and the 1-methylvinoxy radical as well as their O_2 adducts are recommended based on our complementary experimental and theoretical study $\Delta H_{f,298K} = 13.0 \pm 2.0$, −32.9± 2.0, −85.9 ± 4.0, and −142.1 ± 4.0 kJ mol^{-1} for CH_2CHO, CH_3COCH_2 radicals, and their adducts, respectively.

Introduction

The 1-methylvinoxy (acetonyl) radical $CH_3COC^{\bullet}H_2$ has been postulated as an intermediate in the atmospheric oxidation of acetone initiated by the OH radical.[1,2] The laser-induced fluorescence spectrum of this radical has been detected by Washida et al.[3] and Williams et al.[4] and very recently also by Imrik et al.[5] Its ultraviolet absorption spectrum has been recorded by Cox et al.[6] and also in ref 5. Despite the importance of the acetonyl radical, only very few studies have been performed on the kinetics of its reactions. The rate constant for its reaction with O_2

$$CH_3COCH_2 + O_2 \rightarrow \text{products} \qquad (1a)$$

has been measured so far by three different group: Cox et al.[6] have generated acetonyl radicals by pulse radiolysis of acetone in 1 atm of SF_6 and followed the radical concentration by time-resolved UV absorption spectroscopy, they obtained a rate constant of $k_1 = (1.5 \pm 0.3) \times 10^{-12}$ cm^3 s^{-1}. Oguchi et al.[7] have investigated this reaction using the laser photolysis/laser-induced fluorescence technique in the pressure range of 20−440 mbar of He. From the Rice−Ramsperger−Kassel−Marcus fit to the pressure dependent experimental data, the limiting high-pressure rate constants was derived by these authors to be $k_1 = 9.8 \times 10^{-13}$ cm^3 s^{-1}. The very recent study by Imrik et al.[5] measured this rate constant at 2.85 mbar by the discharge flow/laser-induced fluorescence technique to be $k_1 = (3.49 \pm 0.51) \times 10^{-13}$ cm^3 s^{-1}. All three studies have been conducted at 298 K, no temperature-dependent work on this reaction has been found in the literature.

Knowledge of accurate thermochemical properties of free radicals in of great importance in many branches of chemistry, in particular atmospheric and combustion modeling.[8] Only one experimental determination of the heat of formation of vinoxy and 1-mehtylvinoxy radicals has been found in the literature (9.9 ± 3.9 and −34.6 ± 8 kJ mol^{-1} for vinoxy and 1 methylvinoxy, respectively).[9] The technique of "thermokinetics" based on gas-phase basicity and proton affinity determined by mass spectrometry was used. After reexamination of previously published data,[10−12] they found an acceptable agreement with their results.[9] Recently, the temperature and pressure dependence of the reaction of vinoxy radicals with O_2[13] has been studied by our group. The obtained Arrhenius activation energy and heat of reaction was not in satisfactory agreement with values obtained for different theoretical studies.[7,13−15] The kinetic behavior of the vinoxy + O_2 reaction system is complicated because there is a low lying fast consecutive reaction step, namely the 1,4-H atom shift. As a result, the modeling of the weak temperature and pressure dependence was rather difficult.[13] The reaction studied in this work is of the same type of reaction system, but without the difficulties related to the fast 1,4-H atom transfer. We have thus investigated the title reaction for the first

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time in an extended temperature and pressure range using laser photolysis/laser-induced fluorescence setup in order to obtain a consistent picture of the thermochemistry of the oxidation of vinoxy and acetonyl radicals.

Experimental Section

Experiments have been performed by laser flash photolysis coupled to a detection of the 1-methylvinoxy radical by laser-induced fluorescence, LIF. Details of the experimental setup have been described elsewhere,[16] so only a brief description is given here.

Two different reaction cells have been used: a "low pressure" cell for experiments at up to 1 bar and a "high pressure" cell for pressures of up to 10 bar. Both cells are made of stainless steel and can be heated electrically to up to 600 K. Excimer laser photolysis at 193 nm (Lambda Physik LPX 202i) of 2,4-pentanedione has been used to prepare the radicals:

$$CH_3COCH_2COCH_3 + h\nu_{193\ nm} \rightarrow CH_3COCH_2 + CH_3CO \tag{I1}$$

The precursor concentration was typically between $(0.5-2) \times 10^{13}$ and $(10-40) \times 10^{13}$ molecules cm^{-3} in the low- and high-pressure experiments, respectively. With an average photolysis fluence of 20 and 50 mJ cm^{-2} in the low- and high-pressure experiments respectively, we estimate the 1-methylvinoxy radical concentration to be $(2-4) \times 10^{10}$ to $(3-20) \times 10^{11}$ molecules cm^{-3}. As a consequence, at these very low initial concentrations, radical–radical bimolecular reactions should be negligible. The same is true for the influence of other possible photolysis products from reaction I1 (CH_3CO, CH_3, and CH_3COCH_2CO): absolute concentrations will be too low to influence the observed kinetics.

Fluorescence has been excited at 341.6 nm. The probe beam (0.6×0.4 cm^2, 5 mJ/pulse) from a frequency doubled dye laser (Quantel TDL 50, DCM/LDS 698), pumped by a frequency doubled YAG laser (Quantel YG 781C) propagates antiparallel to the photolysis beam through the cell. Fluorescence has been collected perpendicular to the laser beams through a cutoff filter at $\lambda > 375$ nm by a photomultiplier and has been integrated by a boxcar integrator (EG&G 4121B).

A typical decay curve consists of 30 fluorescence intensities monitored at 30 different delay times between the two laser pulses. At each delay the signal is averaged over 50 to 100 laser shots. The delay time has been altered by a PC-controlled digital delay generator (EG&G 9650). Most experiments have been performed at a repetition rate of 10 Hz for both lasers; only a few experiments have been carried out at 1 Hz and variable total flow to check for a possible influence of photolysis products, but no effect on the decay rate has ever been observed.

The carrier gas He (99.995%, Air Liquide) has been used without further purification. The precursor 2,4-pentanedione (Acros Organics, 99%) and the reactant O_2 have been prepared as gaseous mixtures, highly diluted in helium. For low-pressure experiments, small flows (1–50 cm^3 STP min^{-1}) of these mixtures were passed through calibrated flowcontroller (Tylan FC-260) and mixed with the main flow (helium at 100–1000 cm^3 STP/min) before entering the reaction cell. For high-pressure experiments, the precursor and reactant have been premixed with 100 bar of He in a high-pressure container and have been introduced directly into the cell after sufficient mixing (one night in general).

Experiments have been performed in the pressure range 0.042–10 bar and in the temperature range 291–520 K.

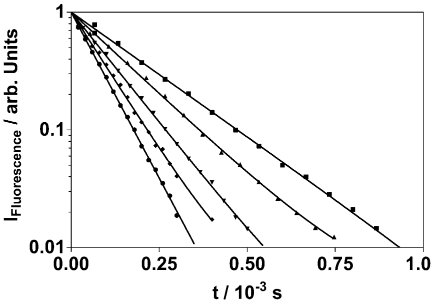


Figure 1. Typical decay of the 1-methylvinoxy radical at 355 K and 130 mbar for different O_2 concentrations: (■) 2.80×10^{15} cm^{-3} ($k^{first} = 3871 \pm 49$ s^{-1}); (▲) 4.30 (4733 ± 87); (▼) 5.87 (7297 ± 5); (◆) 8.43 (8809 ± 150); (●) 10.2 (11270 ± 87).

Details of the Calculation

For all stationary points and the transition states the geometry optimizations and frequency calculations were carried out at two levels of density function theory, B3LYP/6-31G(d), and B3LYP/6-311+G(3df,2p). In our earlier paper we have discussed in detail the accuracy of different level of ab initio calculations.[13] On the basis of that experience the thermochemistry of the title reaction was characterized by additional single point calculations using G3MP2B3[17] and CBSQB3[18] composite methods.

The standard heat of formations were calculated using the general atomization energy procedure.[18] We have used the atomization energy data of C, H, and O atoms from the standard reference tables.[19]

Results and Discussion

1-Methylvinoxy decays have been measured under pseudo-first-order conditions with respect to O_2. The obtained concentration time profiles can be described as either mono- or biexponential decays, depending on the temperature and O_2-concentration: at temperatures up to around 400 K decays were monoexponential, they became clearly biexponential above 450 K, typical behavior for a reaction in equilibrium.

Monoexponential Decays. At "low" temperatures ($T < 400$ K), 1-methylvinoxy concentration shows monoexponential decays, i.e. the reverse reaction (R-1) is too slow to be measurable under our experimental conditions. Under these conditions, the decay is governed by the association reaction (R1):

$$^{\bullet}CH_2COCH_3 + O_2 \leftrightarrow (^{\bullet})O_2CH_2COCH_3 \tag{R1}$$

A large excess of O_2 over the radical concentration has been used, allowing pseudo first-order conditions. As a consequence, radical decay kinetics obey to the simple equation:

$$-\frac{d[CH_3COCH_2]}{dt} = (k_1[O_2] + k_d)[CH_3COCH_2] \tag{1b}$$

with k_1 being the second-order rate constant, leading with $[O_2]$ = constant to $k_1^{1st} = k_1[O_2]$, the pseudo-first-order decay rate (s^{-1}). The constant k_d accounts for diffusion out of the observation volume together with possible contributions of the reaction of 1-methylvinoxy with the precursor or impurities.

A typical signal of a 1-methylvinoxy decay ($[CH_3COCH_2]$ vs reaction time) is displayed in Figure 1. The pseudo first-order decay rate k_1^{1st} is derived from the slope of plotting ln-$[CH_3COCH_2]$ vs reaction time, which then is plotted vs $[O_2]$

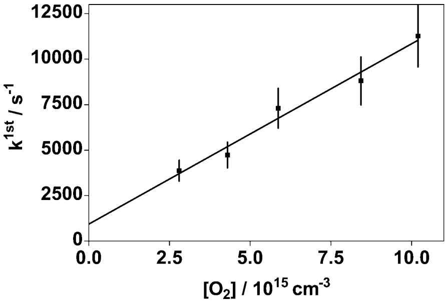


Figure 2. Pseudo-first-order rate constants from Figure 1as a function of O_2 concentration: bimolecular rate constant $k_1 = (9.9 \pm 0.8) \times 10^{-13}$ cm^3 s^{-1}; intercept $k_{loss} = 934 \pm 596$ s^{-1}. The error bars represent an estimated total error of ±15%; statistical errors are much smaller.

TABLE 1: Comparison of Thermochemical Data for the Reaction of 1-Methylvinoxy + O_2

method	ΔE_r ($T = 0$ K)	ΔH_r ($T = 298.15$ K)	ΔS_r ($T = 298.15$ K)
B3LYP/6-31G(d)	−87.7	−91.7	−157.2
B3LYP/6-311+G(3df,2p)	−82.5	−86.6	−157.0
G3MP2B3	−100.9	−104.8	−157.2
CBSQB3	−104.5	−108.5	−155.2
experiment (this work)		−105 ± 2	−143 ± 4
experiment vinoxy + O_2[13]		−101 ± 4	−144

(Figure 2). The bimolecular rate constant k_1 is obtained as the slope of such a plot, while k_d corresponds to the intercept.

The rate constant at 295 K has been found to be independent of pressure; detailed data are listed in Table 1S (Supporting Information). This reaction being an association reaction, we thus conclude that at 298 K the high-pressure limit of the rate constant is attained at 42 mbar with

$$k_{1,\infty} = (1.18 \pm 0.04) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

In Figure 3, these values are plotted together with the data from previous work: while our high-pressure limit is in good agreement with the values of Cox[6] and the extrapolated high-pressure limit of Oguchi et al.,[20] it is in contradiction with the pressure dependence found in this latter reference as well as with the value at low pressure.[5] Even though the disagreement between the experimental results is difficult to understand, it is reasonable to assume that this reaction is close to the high-pressure limit at pressures employed in this work: recent work[13] on the similar reaction of vinoxy radicals (C_2H_3O) with O_2 has shown that this reaction is very close to the high pressure limit at 650 mbar, and the rate constant decreases only by 25% at 40 mbar. The 1-methylvinoxy radical being larger than the vinoxy radical, it is difficult to understand that for this radical the rate constant decreases in the same pressure range by about 40%, as found in ref 20.

In Figure 4 are plotted the temperature dependences of the rate constant at 130 and 650 mbar. All experimental results are shown in the Supporting Information (Tables 2S and 3S). A small negative temperature dependence has been observed, slightly enhanced at 130 mbar:

$$130 \text{ mbar:} \quad k_1 = 10^{-12.50\pm0.08} \exp((374 \pm 62)/T) \text{ cm}^3 \text{ s}^{-1}$$

$$650 \text{ mbar:} \quad k_1 = 10^{-12.14\pm0.03} \exp((131 \pm 27)/T) \text{ cm}^3 \text{ s}^{-1}$$

This difference is in line with a small falloff effect at 130 mbar, enhanced with increasing temperature. Also shown in Figure 4 are the values for k_1, extracted from biexponential decays at higher temperatures (see next paragraph) and 10 bar, in excellent agreement with the measurements at 650 mbar.

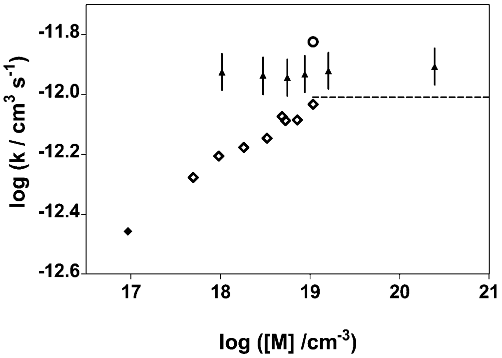


Figure 3. Fall off plot of the rate constant k_1 at $T = 298$ K: (▲) this work, error bars represent an estimated total error of ±15% on the rate constants; (◇) pressure-dependent and extrapolated high-pressure limit (- - -) by Oguchi et al.;[7] (◆) 2.85 mbar He, Imrik et al.;[5] (○) 1 bar SF_6, Cox et al.[6]

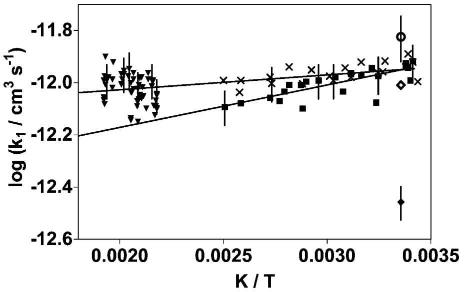


Figure 4. Arrhenius plot for the rate constant of the direct reaction R1: $\log k_1 = f(1/T)$. This work: (▼) 10 bar extracted from biexponential decays; (×) 650 mbar and (■) 130 mbar obtained from monoexponential decays, where error bars represent an estimated total error of ±15% on the rate constants; (◇) high-pressure limit extrapolated by Oguchi et al.;[7] (◆) 2.85 mbar He, Imrik et al.;[5] (○) 1 bar SF_6, Cox et al.[6]

TABLE 2: Standard Heat of Formations[a] ($T = 298.15$ K) of Vinoxy and Methylvinoxy Radicals as Well as Their O_2 Adduct Radicals, Obtained by Using the Standard Atomization Energies of C, O, and H Atoms[19]

	G3MP2B3	CBS-Q	experiment[9]	recommended[b]
$^\bullet CH_2{-}CHO$	13.4	12.6	9.9 ± 3.9	13.0 ± 2
$^\bullet CH_2{-}C(CH_3)O$	−33.3	−32.6	−34.6 ± 8.4	−32.9 ± 2
$^\bullet OOCH_2{-}CHO$	−81.8	−90.1		−85.9 ± 4
$^\bullet OOCH_2{-}C(CH_3)O$	−139.4	−144.7		−142.1 ± 4

[a] Enthalpy values in kJ mol^{-1} [b] Average of the theoretical methods.

Biexponential Decays. With increasing temperature ($T > 450$ K), the 1-methylvinoxy concentration does not decay to zero, a residual signal can be measured even at long reaction times: biexponential decays, typical for equilibrium reactions, are observed. Figure 5 shows examples of 1-methylvinoxy decays at 486 K with varying O_2-concentrations, Figure 6 shows an example of 1-methylvinoxy decays with $[O_2] = (1.6 \pm 0.5) \times 10^{16}$ cm^{-3} at three different temperatures. The behavior is typical for a reaction in equilibrium: with increasing O_2-concentration the equilibrium is shifted to the adduct side, the residual 1-methylvinoxy concentration decreases. With increasing temperature the reverse reaction (R-1) becomes more important, while the direct reaction (R1) is more or less temperature independent: the residual 1-methylvinoxy concentration increases. The second decay in this type of experiments can have different reasons: besides radical−radical reactions (or radical impurities/precursor) it can be due to a diffusion of both

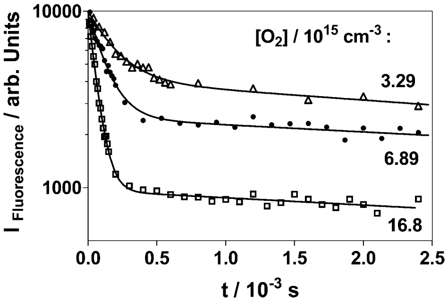


Figure 5. Typical signals for the 1-methylvinoxy decay at 10 bar and 486 ± 2 K at different O_2 concentrations.

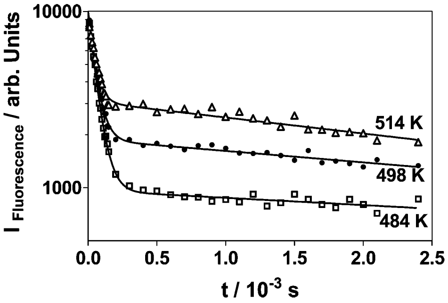


Figure 6. Typical signals for the 1-methylvinoxy decay at 10 bar with $[O_2] = (16.3 \pm 0.5) \times 10^{15}$ cm^{-3} at different temperatures.

1-methylvinoxy radical and adduct $CH_3COCH_2O_2$ out of the observation volume, but other irreversible reaction pathways like unimolecular isomerization would also deplete the equilibrium. The equilibrium constant for reaction R1 as well as the rate constant for the loss reaction have been deduced from a nonlinear fitting procedure of the biexponential decays. Reactions taken into account include the equilibrium reaction (R1) as well as an irreversible loss reactions for both the 1-methylvinoxy radical and the adduct

$$^{\bullet}CH_2COCH_3 \rightarrow \text{loss} \qquad (R_{loss1})$$

$$^{\bullet}O_2CH_2COCH_3 \rightarrow \text{loss} \qquad (R_{loss2})$$

with $k_{loss1} = k_{loss2}$. This assumption has been made on the basis that the main loss processes for both radicals are bimolecular reactions (radical−radical or radical precursor), which are supposed to have the same order of magnitude for both radicals. A possible diffusion out of the observation volume would also be on the same order of magnitude for both radicals, but it can in general be neglected for experiments at high pressure. In our earlier work on the reaction between the vinoxy radical CH_2CHO and O_2,[13] the assumption $k_{loss1} = k_{loss2}$ has not been made; here the rate for the second decay increased strongly with temperature and a mechanism has been proposed including a unimolecular isomerization of the adduct O_2CH_2CHO (see next paragraph). However in this study, the second decay did not depend on the temperature, a unimolecular loss reaction for either one of the radicals can thus be neglected in the temperature range covered in this study. As can be seen from Table 3S, the average loss for both radicals was $k_{loss} = 121 \pm 57$ s^{-1}.

The obtained equilibrium constant

$$K_{p,1} = \frac{p_{O_2CH_2OCH_3}}{p_{CH_2COCH_3}p_{O_2}} \qquad (2)$$

is shown in Figure 7 as a function of temperature, and all values can be found in Table 3S. The best fit to these data results in

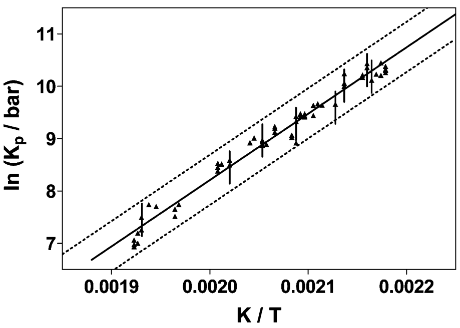


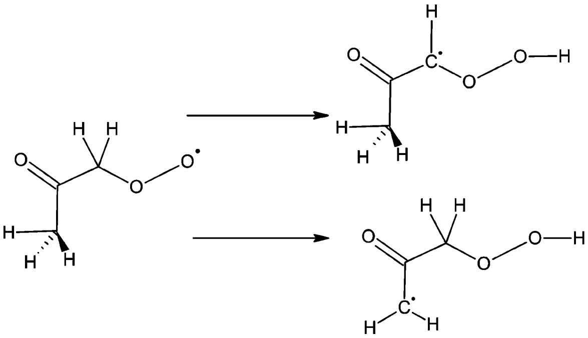
Figure 7. Van't Hoff plot of the equilibrium constant at 10 bar. The straight line shows the best fit to the experiments with $\Delta S_r = 143 \pm 4$ J mol^{-1}K^{-1} and $\Delta H_r = 105 \pm 2$ kJ mol^{-1}; the dashed line represents ±4 J mol^{-1}K^{-1} in the reaction entropy. Error bars represent an estimated total error of ±30% on the equilibrium constants.

$$\Delta S_r = -143.0 \pm 4.0 \text{ J mol}^{-1}\text{K}^{-1}$$

$$\Delta H_r = -105.0 \pm 2.0 \text{ kJ mol}^{-1}$$

The Reaction Mechanism. Reaction R1 is assumed to proceed via reversible complex formation with subsequent isomerization−dissociation steps and a possible direct H atom abstraction channel:

$$CH_3COCH_2^{\bullet} + O_2 \rightarrow CH_2COCH_2 + HO_2^{\bullet} \qquad (R2)$$



(R3)

(R4)

Figure 8 shows the B3LYP/6-311G+G(3df,2p) enthalpy diagram of the main reaction channels and the energetically less favored direct H atom abstraction (R2). The most important feature of the potential enthalpy diagram is that the entrance channel of R1 has a rather small barrier of about 7 kJ mol^{-1}. In our earlier paper on the analogous vinoxy and O_2 reaction,[13] an extended overview and comparison of different levels of theory is given, and we concluded that DFT methods with a moderately large size basis set can predict the most acceptable kinetic pictures, but detailed kinetic modeling resulted in a barrier of 1 kJ mol^{-1} for this reaction. Thus, the B3LYP/6-311+G(3df,2p) level of theory apparently slightly overestimates the barrier heights of this reaction type, but correlation ab initio methods (QCSD(T)/6-311+G(3df,2p) or CCSD(T)/6-311+G(3df,2p)) as well as composite methods (CBSQB3/G3MP2B3) predict even higher barriers. The kinetic mechanism of the title reaction will thus be discussed on the B3LYP/6-311+G(3df,2p) level of theory: the most characteristic difference between the vinoxy and 1-methylvinoxy reaction system is, that the latter one does not have the extremely weak carbonyl−hydrogen bond. The adducts formed in reaction R1 can undergo only 1,3- and 1,5-H atom transfer reactions, R3 and R4, respectively. Both reactions have a significant barriers of 83.2 and 30.6 kJ mol^{-1} above the entrance level, respectively. This feature of the reaction system

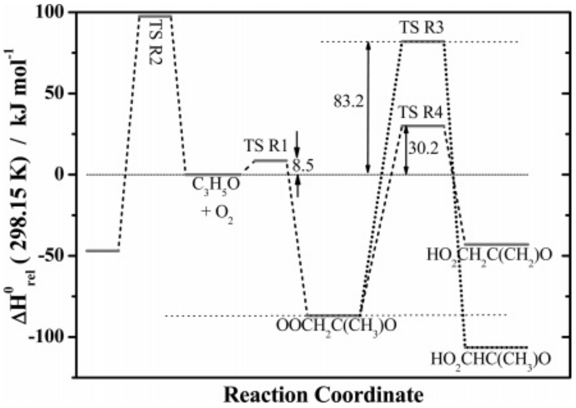


Figure 8. Enthalpy diagram for the complex reaction of 1-methylvinoxy and O_2 obtained by B3LYP/6-311+G(3df,2p) level of theory.

allows one to measure the equilibrium constants as well as its temperature dependence experimentally, as explained above.

Thermochemistry. Comparison Experiment and Theory. In Table 1, the thermochemical data obtained from the analysis of experimental data are compared with the theoretical ones. We have earlier discussed in detail that the B3LYP type of density function calculations underestimate the exothermicity of R1 type reactions[13,21] while the experimental heat of reaction is in excellent agreement with both composite methods. The geometries, frequencies and rotational constants for all four radicals are given in Table S4, and their structures are shown in Figure S1.

The reaction entropy was negative as expected in the case of bimolecular reactions, caused by the loss of external degrees of freedoms like translations and rotations. The theoretically calculated reaction entropy is somewhat lower than the experimental value.

The standard heat of formation of the 1-methylvinoxy radical and its O_2-adduct were calculated by CBSQ and the G3MP2B3 level of theory. The calculated and recommended $\Delta_f H°$ of the radicals are given in Table 2. The heat of formation of the vinoxy radical and its O_2-adduct were also calculated by the same level of theory in order to obtain a consistent picture of these radicals. The predicted $\Delta_f H°$ for the vinoxy and 1-methylvinoxy radical agree within 2 kJ mol^{-1} for both levels of theory. The agreement with the only available experimental values of Bouchoux et al.[9] is for both radicals within the experimental error. These authors discussed in detail the heat of formation of these two radicals and recommended heat of formations based on experimental and theoretical values. Their recommended values are in excellent agreement (within 1 kJ mol^{-1}) with our theoretical results.

The heats of reaction (106.1 and 112.1 kJ mol^{-1} for G3MP2B3 and CBS-Q, respectively) calculated using the theoretical heats of formation of the radicals (from Table 2) are in excellent agreement with the experimental heat of reaction (105.0 kJ mol^{-1}). On this basis we suggest the standard heats of formation of $\Delta H_{f,298K} = 13.0 \pm 2.0$, -32.9 ± 2.0, -85.9 ± 4.0, and -142.1 ± 4.0 kJ mol^{-1} for CH_2CHO, CH_3COCH_2 radicals, and their adducts, respectively.

The Benson's group additivity [22] rules are an excellent tool to check the heat of formations of homologous.[23] Group values (GV) can be extracted from the differences of the heat of formations of the corresponding homologues:

$$\Delta H_{n+1} - \Delta H_n = \mathrm{GV[C{-}(H)_3(C)]} \qquad (3)$$

Thus, the differences between the heats of formation of vinoxy and 1-methylvinoxy radicals as well as the differences between their adducts should correspond to the GV of the methyl group $C{-}(H)_3(C)$. The GV[$C{-}(H)_3(C)$] values obtained from our recommended data for the "oxy" radicals and adduct radicals were -10.9 and -13.4 kcal mol^{-1}, respectively. The GV obtained from the "oxy" radical data are in good agreement with the widely accepted GV of -10.1 kcal mol^{-1},[24] while the GV obtained from the adduct is somewhat lower. This discrepancy might be caused by the far-interaction of the H atoms of the CH_3 group in the 1-methylvinoxy adduct with the nonbonding electron pairs of the oxygen atoms.

We have also calculated the C−H bond strength of acetaldehyde and acetone using our recommended heat of formations of the vinoxy and 1-methylvinoxy radical and standard literature data:[25,26]

$$D°(\mathrm{R{-}H}) = \Delta_f H°(\mathrm{R}) + \Delta_f H°(\mathrm{H}) - \Delta_f H°(\mathrm{RH}) \qquad (4)$$

The C−H bond strengths are 399.4 and 404.4 kJ mol^{-1} for acetaldehyde and acetone, respectively, in acceptable agreement with the most recent literature data (394.6 and 411.3 kJ mol^{-1}, respectively[25,26]).

The vinoxy radicals are less stable than their atmospheric relevant isomer of carbonyl radical (CH_3CO). As a cross check we have compared the different C−H bond strengths of radicals in the reaction

$$^{\bullet}CH_2CHO \leftrightarrow CH_3C^{\bullet}O \qquad (R6)$$

Using our recommended heat of formations for the vinoxy radical and the heat of formation of the acetyl radical from ref 27, a heat of reaction for (R6) of -23.3 kJ mol^{-1} is calculated. This value is also in good agreement with the experimental bond strength difference of methyl[25] and formyl[28] C−H bonds (-20.8 kJ mol^{-1}).

Conclusion

The weak temperature and pressure dependence of the reaction of 1-methylvinoxy radicals and O_2 was studied experimentally and theoretically. An excellent agreement between measured and calculated reaction enthalpy of the title reaction has been found. The accurate heats of formation of the $^{\bullet}CH_2COCH_3$ and $^{\bullet}OOCH_2COCH_3$ radicals have been evaluated. Using our earlier experimental data on the reaction of vinoxy radicals with O_2 the accurate heat of formation of the $^{\bullet}CH_2CHO$ and $^{\bullet}OOCH_2CHO$ radicals have also been recommended. The calculated heats of formation of all four radicals ($\Delta_f H°$) are self-consistent for different levels of theory and in excellent agreement with experimental results.

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Supporting Information Available: Tables with detailed experimental conditions and rate coefficients for the pressure dependence of k_1 at 295 K (Table 1S), for the temperature dependence of k_1 at 130 and 650 mbar (Table 2S), and for the temperature dependence of k_1, k_{-1} and K_p at 10 bar (Table 3S) and Cartesian coordinates, rotational constants and harmonic vibrational frequencies of vinoxy, 1-methylvinoxy, and their O_2 adducts, obtained by the G3MP2B3 level of theory (Table S4) and a figure showing the structures of vinoxy, 1-methylvinoxy, and their O_2 adducts obtained by the G3MP2B3 level of theory (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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