

## Mechanisms of Formation of Vinyoxy Radicals in the Reaction of O(<sup>3</sup>P) with Terminal Alkenes

Hongmei Su and Richard Bersohn\*

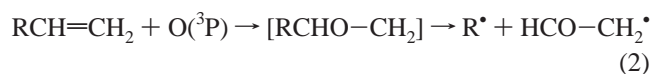
Department of Chemistry, Columbia University, New York, New York 10027

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When an O(<sup>3</sup>P) atom reacts with a terminal alkene, RCH=CH<sub>2</sub>, a vinyoxy radical can be produced by one of two mechanisms: (a) attachment of the oxygen atom to C1 followed by migration of a hydrogen atom from C1 to C2 and then release of the radical R, or (b) attachment of the oxygen atom to C2 followed or accompanied by release of the radical R. The hot band B ← X spectra of partially deuterated vinoxys allow one to distinguish between these two possibilities. The general result is that vinyoxy is produced in comparable amounts by the two mechanisms. In the reaction of O(<sup>3</sup>P) atoms with ethylene, one of the product channels is a vinyoxy and a hydrogen atom. A hydrogen atom can be directly released from the carbon atom to which the oxygen is attached or it can migrate to the other carbon forming a hot acetaldehyde. The latter then dissociates to form methyl and formyl radicals (mainly) or a hydrogen atom and a vinyoxy radical. The hot band spectra of vinoxys from the reaction of O(<sup>3</sup>P) with CHD=CHD and CH<sub>2</sub>=CD<sub>2</sub> show that while both processes occur, the majority of the hydrogen atoms are released directly rather than indirectly. Fast hydrogen atoms produced by photodissociation of H<sub>2</sub>S were shown to abstract a hydrogen atom from the methyl group of acetaldehyde yielding a hydrogen molecule and vinyoxy. The vinyoxy is vibrationally very cold despite the large available energy.

### Introduction

When an O(<sup>3</sup>P) atom reacts with the double bond of a 1,2-disubstituted alkene, R<sub>1</sub>CH=CHR<sub>2</sub>, the carbon atom to which the oxygen atom becomes attached loses a radical. If the O(<sup>3</sup>P) atom reacts with a terminal alkene, attack can be either at C1 or C2:



The ketocarbene intermediate produced in the first reaction can undergo a variety of reactions including (a) direct release of a hydrogen atom from C1 leaving behind an alkylvinyoxy, (b) breaking of the C1–C2 bond to form RCH and CH<sub>2</sub>O, (c) migration of a hydrogen atom from C1 to C2 with the formation of the vinyoxy radical and the radical R<sup>•</sup>, and (d) migration of the hydrogen atom from C1 to C2 with the subsequent breaking of the C1–C2 bond to form HCO<sup>•</sup> and RCH<sub>2</sub><sup>•</sup>. In contrast, when the O atom attaches itself to C2 the weakest bond in the molecule is the R–C2 carbon–carbon bond which then breaks. There appears to be only one likely reaction, the direct release of the R<sup>•</sup> radical, leaving behind HCO–CH<sub>2</sub><sup>•</sup>.

Identical vinyoxy radicals can be produced by either mechanism. The present study was carried out to determine which carbon atom of the alkene, C1 or C2, eventually becomes C1 of the vinyoxy radical. This question can be answered if partially deuterated alkenes are used as precursors. For example, RCH=CD<sub>2</sub> would give rise to CHD–CDO and CD<sub>2</sub>–CHO as a result of O atom attack on carbon atoms 1 and 2, respectively.

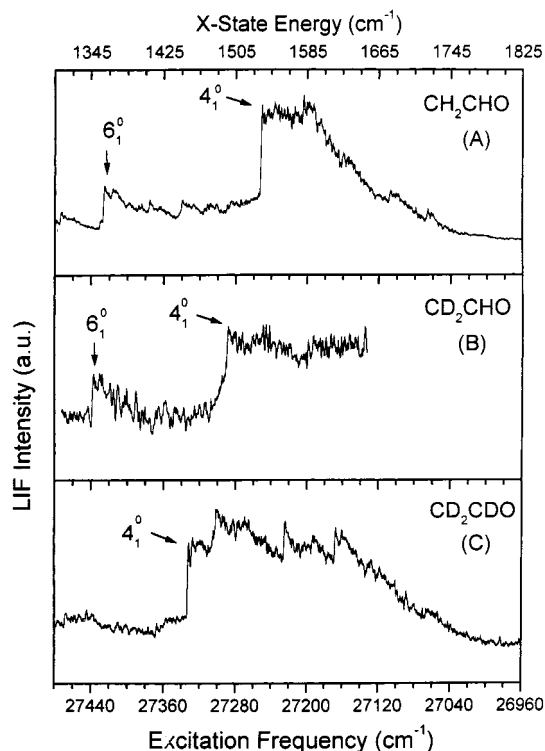
Because the spectra of these two species are sufficiently different, the ratio of vinyoxy yields from the two mechanisms can be determined.

Cvetanovic carried out an extensive study of the products of the O(<sup>3</sup>P) reactions with alkenes.<sup>1,2</sup> His general conclusion was that addition of the oxygen atom to the double bond was primarily to the less substituted carbon atom. This conclusion was based on observations that when the reaction is carried out under high pressures of a buffer gas the ultimate product is an aldehyde, RCH<sub>2</sub>CHO or an epoxide, RCHOCH<sub>2</sub> but not a ketone RCOCH<sub>3</sub>. This is in spite of the fact that the ketone is the most stable of the three isomers. The question raised in the present paper relates only to the vinyoxy product. How much of it is produced by addition to C1 and how much by addition to C2?

### Experimental Section

A 2/1 mixture of alkene/SO<sub>2</sub> was flowed through an 8 cm cubic stainless steel cell at a total pressure of 300 milli Torr. Irradiation through a quartz window by a 193 nm laser (30 mJ/pulse) produced O(<sup>3</sup>P) atoms which then react with the alkene. An excess of alkene was used to slow the formation of a sulfur deposit on the window facing the ArF laser. An XeCl excimer laser (Lambda Physik, LPX300) pumped the dye DMQ in a dye laser (2 mJ/pulse) which probed the vinyoxy product by laser-induced fluorescence (LIF) in the hot band region from 346.5 to 371 nm. Two long pass filters at 350 and 365 nm were used to absorb the scattered exciting light. Probing was typically 3 μs after the firing of the 193 nm laser. The signal from the photomultiplier was fed into a box car integrator and then into a computer. All deuterium-labeled compounds were obtained from C/D/N Isotopes, Pointe-Claire, Quebec, with the exception of 1,2-dideuterioethylene and 1,2-dideuteriopropene which were synthesized by catalytic hydrogenation of acetylene and propyne, respectively, using the Lindlar catalyst.<sup>3</sup>

\* Author to whom correspondence should be addressed. E-mail: rb18@columbia.edu.



**Figure 1.** Partial hot band spectra of  $\text{CH}_2\text{CHO}$ ,  $\text{CD}_2\text{CHO}$ , and  $\text{CD}_2\text{CDO}$ . The relatively large isotope shifts of the  $4_1^0$  band head allow identification of vinyoxy isotopomers. The X-state energy on the upper axis is relative to the lowest ground-state level.

## Results and Discussion

**A. Reactions of O(<sup>3</sup>P) with Propene Isotopomers.** The spectra reported here are all hot band spectra of isotopomers of the vinyoxy radical. Their interpretation is made possible by the detailed high-resolution spectra of Brock and Rohlfing.<sup>4</sup> The connection between these low resolution spectra and the high resolution spectra has been recently discussed.<sup>5</sup> For the present purposes the only part of the hot band spectrum which was measured is the small region encompassing the  $6_1^0$  and the  $4_1^0$  bands. These are transitions to the vibrationless B state.  $\nu_6$  is the HCO bend and  $\nu_4$  is, roughly speaking, the C–O stretch. Figure 1 shows the hot band spectrum in this region of  $\text{CH}_2\text{CHO}$ ,  $\text{CD}_2\text{CHO}$ , and  $\text{CD}_2\text{CDO}$ . Each of these radicals was a reaction product,  $\text{CH}_2\text{CHO}$  from  $\text{O} + \text{C}_2\text{H}_4$ ,  $\text{CD}_2\text{CDO}$  from  $\text{O} + \text{C}_2\text{D}_4$ , and  $\text{CD}_2\text{CHO}$  from  $\text{H} + \text{CD}_3\text{CHO}$ . The latter reaction is discussed in a later section. The hot bands probed in these experiments are observable because the rate of formation by reaction is greater than their rate of destruction by relaxation. The time delay (3  $\mu\text{s}$ ) between pump and probe results in an adequate signal due to radicals which are rotationally but not vibrationally relaxed. For this reason we make the assumption that the intensity of the  $4_1^0$  band head of a vinyoxy isotopomer is proportional to its yield.

Two points emerge from Figure 1. First of all, the  $\text{CD}_2\text{CDO}$  spectrum does not contain the  $6_1^0$  band which has evidently been shifted to higher frequency by deuteration. Second, the  $4_1^0$  band head of  $\text{CD}_2\text{CHO}$  is intermediate between that of  $\text{CH}_2\text{CHO}$  and  $\text{CD}_2\text{CDO}$ . Suppose we now assume that the isotope shifts of this band head are independent and additive. These assumptions are based on the idea that vibrations approximately localized in different parts of a molecule are nearly independent of each other. This means that the shift resulting from the replacement of  $\text{CH}_2$  by  $\text{CD}_2$  is independent

**TABLE 1: Energies of Transitions in Aldehyde Isotopomers<sup>d</sup>**

stable aldehydes	$0_0^0 n \rightarrow \Pi^*$ (cm <sup>-1</sup> )	vinyoxy isotopomers	$4_1^0$ band head of B–X (cm <sup>-1</sup> )
$\text{CD}_2\text{O}$	28302.4	$\text{CD}_2\text{CDO}^a$	27331
$\text{CHDO}$	28243.6	$\text{CHDCDO}^b$	27300*
$\text{CH}_2\text{O}$	28188.0	$\text{CH}_2\text{CDO}^b$	27290
$\text{CH}_3\text{CDO}$	29820	$\text{CD}_2\text{CHO}^a$	27287
$\text{CD}_3\text{CDO}$	29808	$\text{CHDCHO}^b$	(27264) <sup>c</sup>
$\text{CH}_3\text{CHO}$	29771	$\text{CH}_2\text{CHO}^a$	27250
$\text{CD}_3\text{CHO}$	29756		

<sup>a</sup> From Figure 1. <sup>b</sup> From Figure 2. <sup>c</sup>  $\text{CHDCHO}$  and  $\text{CHDCDO}$  are an unknown mixture of cis and trans isomers. <sup>d</sup> The data on formaldehyde and acetaldehyde are from refs 6 and 7.

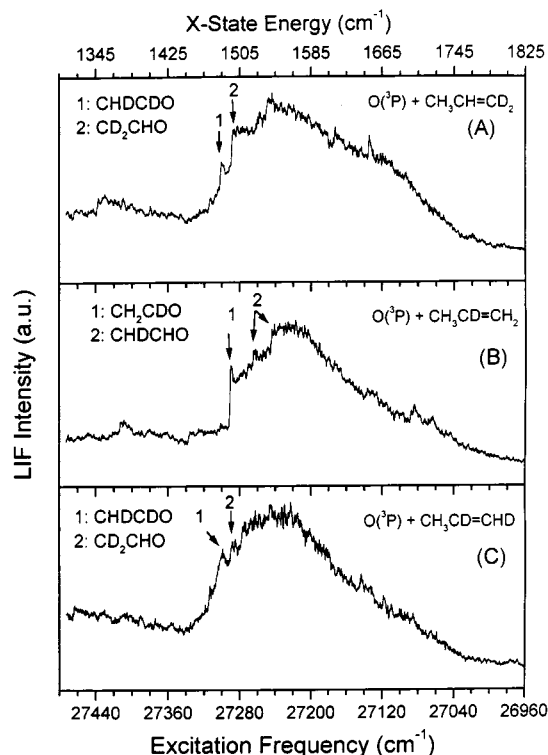
**TABLE 2: Deuterium Shifts of Electronic Transitions in Aldehydes (computed from data of Table 1)<sup>a</sup>**

	$\text{CHO} \rightarrow \text{CDO}$	$\text{CH}_3 \rightarrow \text{CD}_3$	$\text{CH}_2 \rightarrow \text{CD}_2$
$\text{CH}_2\text{O}$	55.6 cm <sup>-1</sup>		
$\text{CHDO}$	58.9		
$\text{CH}_3\text{CHO}$	49	-14	
$\text{CD}_3\text{CHO}$	55	-15	
$\text{CH}_2\text{CHO}$	44		37
$\text{CD}_2\text{CHO}$	40		
$\text{CH}_2\text{CDO}$			41

<sup>a</sup> Note that in the vinyoxy radical the isotope shift on deuteration of the aldehyde group is approximately twice as large as the shift on deuteration of a *single* methylene hydrogen atom. The differences between 40 and 44 and between 37 and 41 are explained by about 10% deviations from the additivity principle. The shift on substitution of a deuterium at one end of the molecule is slightly dependent on isotopic substitution at the other end.

of whether the aldehyde group is HCO or DCO. Similarly, the shift on replacement of HCO by DCO is independent of whether the methylene group is  $\text{CH}_2$  or  $\text{CD}_2$ . The data in Table 1 on the similar aldehydes, formaldehyde and acetaldehyde, provide an empirical justification of these two assumptions of independence and additivity. Table 2 is obtained by subtracting the energies of pairs of transitions in the isotopomers. The shifts on replacing the aldehydic hydrogen by a deuterium are all positive and similar in magnitude. The vibrations involving this hydrogen atom have lower frequencies in the excited state than in the ground state. In acetaldehyde the shifts on deuteration of the methyl group are small and negative whereas the shifts on deuteration of the methylene hydrogen atoms of vinyoxy are larger and positive. The difference may lie in the fact that in the  $n \rightarrow \pi^*$  transition of acetaldehyde the methyl group is largely a spectator. The  $\pi \rightarrow \pi^*$  transition of vinyoxy involves initial and final wave functions delocalized among all three heavy atoms. The C–H bonds of the acetaldehyde methyl group become slightly stronger in the excited state whereas the C–H bonds of the vinyoxy methylene group become weaker on excitation to the B state. Incidentally, according to an ab initio calculation the three C–H stretches of vinyoxy have all been predicted to be stronger in the B state than in the ground X state.<sup>8</sup> If this were really true, all the isotope shifts on deuteration would be negative, the opposite of what is observed.

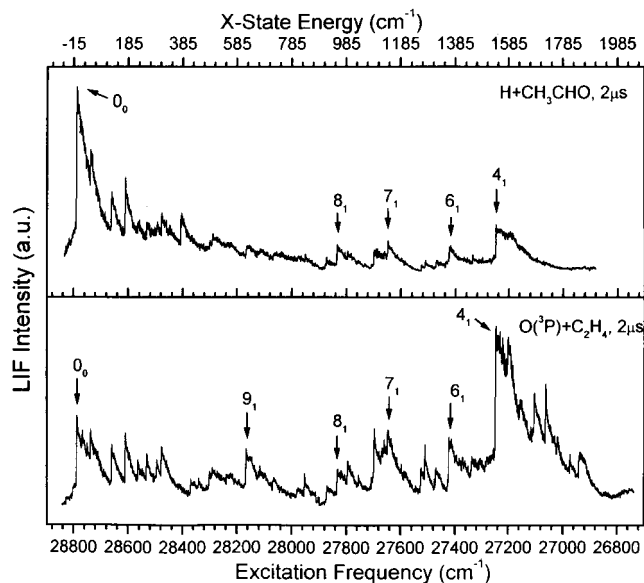
The  $4_1^0$  band positions of  $\text{CH}_2\text{CHO}$ ,  $\text{CD}_2\text{CHO}$ , and  $\text{CD}_2\text{CDO}$  extracted from Figure 1 and tabulated in Table 1 establish that the replacement of an aldehydic H by D shifts the  $4_1^0$  band head upward by 44 cm<sup>-1</sup>. The replacement of *both* methylene hydrogen atoms by deuteriums causes an upward shift of 37 cm<sup>-1</sup>. These shifts were reproducible to 1 cm<sup>-1</sup>. Assuming additivity the replacement of a single methylene H by D produces an upward shift of about half as much as replacement of both methylene H atoms.



**Figure 2.** Partial hot band spectra of the mixture of vinyoxy isotopomers produced by the reaction of  $O(^3P)$  with  $CH_3CHCD_2$ ,  $CH_3CDCH_2$ , and  $CH_3CDCHD$ .

These data can now be used to identify the source of  $4_1^0$  band heads in reactions with other propene isotopomers. For example, when oxygen atoms react with 2-deuteriopropene, the hot band spectrum shown in Figure 2B has a sharp band head at  $27290\text{ cm}^{-1}$ ,  $40\text{ cm}^{-1}$  higher energy than that of vinyoxy. It must therefore be due to  $CH_2CDO$ . The shape of the  $4_1^0$  band is quite different from the broad and flat-topped bands shown in Figure 1. It rises with increasing wavelength, suggesting that it is a superposition of broad flat bands of two vinyoxy isotopomers in roughly equal amounts. The only other possible isotopomer with a single deuterium atom is  $CHDCHO$ . To higher energy is a weak band assigned to the  $6_1^0$  transition of this same radical. The corresponding transition in  $CH_2CDO$  is shifted to higher energies because it is an HCO bend. The two peaks labeled 2 in Figure 2B are conjectured to be  $4_1^0$  band heads belonging to the same vinyoxy as the weak  $6_1^0$  band. The two peaks may correspond to cis and trans isomers. The  $4_1^0$  band head of  $CHDCHO$  should have an energy intermediate between those of  $CH_2CHO$  and  $CD_2CHO$ . The superposition of the spectra of two vinyoxys seems to explain the observations but it is difficult to determine a highly quantitative branching ratio from Figure 2B. Judging from the height of the  $6_1^0$  peak relative to the broad band around  $4_1^0$  and comparing the shape of the  $4_1^0$  bands of Figures 1A and 2B, comparable amounts of the two radicals are present. In other words, vinyoxy is produced in comparable amounts from O atom attachment to C1 and C2.

The reaction of  $O(^3P)$  with 1,1-dideuteriopropene could produce either  $CHDCDO$  or  $CD_2CHO$  depending on whether the O atom attaches itself to C1 or C2. In fact, two sharp bands of comparable heights are found at  $27287$  and  $27300\text{ cm}^{-1}$  (Figure 2A). The higher energy transition must be due to  $CHDCDO$  even though a frequency closer to  $27310\text{ cm}^{-1}$  would have been predicted. There may be a small ambiguity because of the presence of cis and trans isomers. The lower frequency is clearly that of  $CD_2CHO$ . The  $6_1^0$  band is weaker relative to



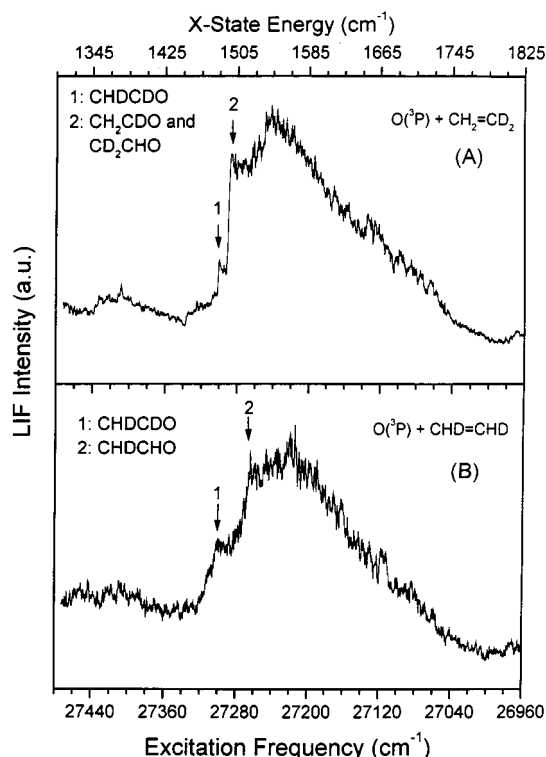
**Figure 3.** Hot band spectra of vinyoxy product of the reactions of  $O(^3P)$  with  $C_2H_4$  and  $H + CH_3CHO$ . As judged by the intensities of the hot bands relative to that of the electronic origin the vinyoxy product of the first reaction is vibrationally hot whereas that from the second is vibrationally cold.

the total  $4_1^0$  band but it is derived only from the  $CD_2CHO$  radical. It again follows that comparable amounts of vinyoxy are produced by O atom attachment to C1 and C2. Exactly the same spectrum (not shown to save space) as that shown in Figure 2A was obtained in the reaction of O atoms with 1,1-dideuteriobutene-1.

The reaction of  $O(^3P)$  with 1,2-dideuteriopropene could also produce a mixture of  $CHDCDO$  and  $CD_2CHO$ . As shown in Figure 2C the height of the  $CHDCDO$   $4_1^0$  band is much greater than that of  $CD_2CHO$ . The former could come from attachment of the O atom to C2 or attachment of the O atom to C1 followed by migration of the H atom from C1 to C2 with release of the methyl radical. As these two processes form the same radical, the experiment cannot tell us about their relative importance.  $CD_2CHO$  can only be produced by attack at C1 followed by migration of the deuterium atom from C1 to C2. Inasmuch as the  $6_1^0$  band is barely discernible, the last process has low probability. Our overall conclusion is that comparable quantities of vinyoxy are made by attachment of O atoms to C1 and C2 of a terminal alkene.

Figure 2, parts A and C, display spectra of radical mixtures all of which have two deuterium atoms and one hydrogen atom. If the hydrogen isotopes were completely scrambled, the two spectra would be identical. They are obviously different which rules out random scrambling. Figure 4, parts A and B, clearly different prove the same point. While there is no plausible mechanism for scrambling, it is nevertheless satisfying to have it disproved.

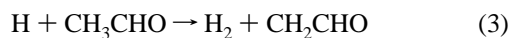
**B. The Reaction  $H + CH_3CHO \rightarrow H_2 + CH_2CHO$ .** The purpose in studying the title reaction was to find a method for synthesizing  $CD_2CHO$ . Two groups have measured the rate of this reaction.<sup>8,9</sup> Both groups assumed that the product was the acetyl radical,  $CH_3CO$ , because a species of mass 42 was a product. Also the aldehydic C–H bond is  $8 \pm 2\text{ kcal/mol}$  weaker than the methyl C–H bond. Vinyoxy has the same mass as acetyl and is not ruled out. Moreover the abstraction by hydrogen atoms is exothermic for both the acetyl and vinyoxy channels,  $-18$  and  $-10 \pm 2\text{ kcal/mol}$ , respectively. Ebers and Wagner found that  $k = (6.0 \pm 0.5) \times 10^{12} \exp(-2600 \pm 150\text{ cal mol}^{-1}/$



**Figure 4.** Partial hot band spectra of the vinoxy radicals from the reaction of O(<sup>3</sup>P) with CH<sub>2</sub>CD<sub>2</sub> and CHDCHD. The very different spectra lead to the same conclusion. Hydrogen atoms are mostly released directly rather than indirectly, following migration.

(RT) cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>). Thermal hydrogen atoms may only be able to abstract hydrogen atoms from the weaker C–H bond forming acetyl. Fast hydrogen atoms whose energy exceeds the energy barriers for abstracting both types of hydrogens may generate both vinoxy and acetyl.

The hydrogen atoms used in this reaction were generated by the photodissociation of H<sub>2</sub>S at 193.3 nm. The initial relative kinetic energy of the H atom in this case can be as high as 2.4 eV if the SH is produced in the  $\nu = 0$  state. This kinetic energy will diminish as a result of nonreactive inelastic collisions but at the time of reaction may well be far over the activation energy of 2.5 kcal/mol. The exothermicities of the two reactions



are  $10 \pm 2$  and  $17 \pm 2$  kcal/mol, respectively. The comparison in Figure 4 shows how efficient the hydrogen molecule is in removing the available energy from the vinoxy. (The reaction of H atoms with oxirane (ethylene oxide), the energy rich isomer of acetaldehyde gave only poor yields of vinoxy suggesting that the main process is ring opening to form acetaldehyde.)

**C. The Reaction of O(<sup>3</sup>P) Atoms with Ethylene.** In the reaction of O(<sup>3</sup>P) with ethylene, two pairs of products have been identified: H + CH<sub>2</sub>CHO ( $62 \pm 5\%$ ) and HCO + CH<sub>3</sub> ( $38 \pm 5\%$ ).<sup>10</sup> In other words a hydrogen atom is directly released or it migrates to the other carbon and the carbon–carbon bond breaks. Does the hydrogen atom migrate and form a hot acetaldehyde which subsequently decomposes uniquely into HCO + CH<sub>3</sub>? Are there two unimolecular decomposition channels for the hot acetaldehyde? In other words can H atoms and therefore vinoxy radicals be formed by two different mechanisms? Figure 4 shows part of the hot band spectra of the vinoxy products of the reactions of oxygen atoms with 1,1-dideuterioethylene and 1,2-dideuterioethylene. Both reactions could, in principle, produce four vinoxy isotopomers. Table 3 is an attempt to summarize the principal deductions from the spectra of Figure 4. The spectrum of the vinoxy radicals from CH<sub>2</sub>=CD<sub>2</sub> (Figure 4A) clearly shows a weak band head due to CHDCDO and a stronger one due to CH<sub>2</sub>CDO and CD<sub>2</sub>CHO. The interpretation is that most of the vinoxy radicals are formed by direct release of a hydrogen atom and a smaller fraction result from release following a migration.

The spectrum of the vinoxy product from O + CHD = CHD shown in Figure 4B is rather more complex. What does emerge is that there are no obvious band heads belonging to CH<sub>2</sub>CDO or CD<sub>2</sub>CHO. These radicals could only have been produced by hydrogen atom release after migration. They are described as weak and buried in Table 3. Had they been more intense, it should have been possible to detect their band heads. The spectrum of Figure 4B is therefore mainly that of a mixture of CHDCHO and CHDCDO. Note the peak at 27300 cm<sup>-1</sup>. In an earlier experiment on a 1/1 mixture of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub> an atomic H/D ratio of  $1.3 \pm 0.1$  was found. Both spectra of Figure 4 lead to the conclusion that the most important mechanism producing vinoxy is a direct release of a hydrogen atom following O atom attachment rather than a release following migration. As mentioned above these experiments cannot distinguish between the direct release of a particular isotopic hydrogen atom and its release by migration and subsequent release. Nevertheless, the spectra of different isotopomers as interpreted in Table 3 argue for the greater importance of direct

**TABLE 3: Mechanistic Origins of Vinoxy Isotopomers<sup>a</sup>**

peak number and intensity	vinoxy isotopomer	origin	statistical weight
O( <sup>3</sup> P) + CH <sub>2</sub> = CD <sub>2</sub>			
1 weak	CHDCDO	Migration of D followed by release of H	4
2 strong	CH <sub>2</sub> CDO	Direct release of D or migration of D followed by release of D	2
	CD <sub>2</sub> CHO	Direct release of H or migration of H followed by release of H	2
3 weak, buried	CHDCHO	Migration of H followed by release of D	4
O( <sup>3</sup> P) + CHD = CHD			
1 strong	CHDCDO	Direct release of H or migration of H followed by release of H	2
			4
2 strong	CHDCHO	Direct release of D or migration of D followed by release of D	2
			4
3 weak, buried	(CH <sub>2</sub> CDO)	Migration of H followed by release of D	2
	(CD <sub>2</sub> CHO)	Migration of D followed by release of H	2

<sup>a</sup> Band heads of radicals enclosed in parentheses are presumed to be weak and red-shifted so that they are buried in the overall 4<sub>1</sub><sup>0</sup> absorption.



release compared to indirect release, involving a preliminary migration.

While this static experiment provides no information about the time scale of the process, there is an implication that the vinoxys are formed on two different time scales. In an interesting initial experiment Abou-Zied and McDonald found that when a van der Waals complex of  $\text{NO}_2$  and  $\text{C}_2\text{H}_4$  was photodissociated at 355 nm, the rise time of the fluorescence of the vinoxy was  $217(+75 - 25)$  ps.<sup>11</sup> In this paper we have distinguished between direct release of a hydrogen atom from the same carbon atom to which the O atom is attached and indirect release which is migration followed by release. In the language of chemical dynamics release of hydrogen atoms by either mechanism is "indirect" because extensive vibrational redistribution must precede release. The pioneering picosecond experiment indicates a single relatively long time constant for release of a hydrogen atom. It is therefore consistent with, but does not prove our finding that direct release dominates.

### Conclusion

When O atoms add to isotopomers of propene, methyl radicals and isotopomers of vinoxy are one of the possible pairs of reaction products. The hot band spectra of these vinoxy radicals show that the vinoxys originate with about equal probability from addition to either carbon atom of the double bond. Cvetanovic, however, has shown that addition to the less substituted carbon atom is more likely. The apparent contradiction is explained by the fact that when an O atom joins with

C2, formation of vinoxy is the only reasonable channel. In contrast, when the O atom joins with C1, there are many open channels.

For ethylene the question which was answered was—do the hydrogen atom products result from direct dissociation from the carbon atom which is being attacked or is it a result of migration followed by dissociation? Use of isotopomers of ethylene showed that direct dissociation is the more probable but not the exclusive process. It follows that the vinoxy—hydrogen atom pair are formed on two different time scales.

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