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Microwave kinetic spectroscopy of reaction intermediates: O + ethylene reaction at low pressure

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A microwave spectroscopic method has been developed to study elementary reactions in real time through *in situ* observation of rotational spectra of reaction intermediates such as free radicals with lifetime as short as 1 ms. This method was applied to the $O({}^{3}P)$ + ethylene reaction in order to assess the roles of (a) vinoxy + H and (b) CH₃ + CHO channels in the initial process. The reaction was initiated by irradiating an N₂O/C₂H₄ mixture containing a trace amount of mercury with the 253.7 nm mercury resonance line, and the time evolution of vinoxy, HCO, and H₂CO was followed by measuring their microwave absorption intensities as functions of time. The branching ratio was thus determined to be 0.4 ± 0.1 and 0.5 ± 0.1 for (a) and (b), respectively, at the sample pressure of 30 mTorr. The present result agrees with those obtained by Hunziker *et al.* [J. Photochem. 17, 377 (1981)] using much higher pressures of samples, but is not compatible with the observation of Buss *et al.* [J. Photochem. 17, 389 (1981)] that (a) is dominant in collision-free conditions.

INTRODUCTION

It has been thought that microwave spectroscopy is rather difficult to apply to kinetic studies of chemical reactions; the inherent low sensitivity due to the small energy of microwave photons has limited the scope of the method. However, remarkable progress has recently been brought about for microwave spectroscopic techniques, and quite a large number of chemically reactive molecules such as free radicals and molecular ions have been detected and investigated in detail by microwave spectroscopy.^{1,2} It is to be pointed out that some of these transient species are difficult to detect by spectroscopic methods in other wavelength regions. In contrast, microwave spectroscopy permits us to observe a wide range of molecules, reactants, intermediates, and products present in a reaction system simultaneously. Furthermore, the intensities of rotational transitions are governed by the permanent dipole moment and are easily converted to abundances of molecules, whereas other spectroscopic methods rely on the transition dipole moment which is difficult to estimate in most cases. Microwave spectroscopy is suitable for samples with pressures lower than about 0.1 Torr. This may be considered as a serious limitation of the method, but its high sensitivity and high selectivity will enable us to obtain information on reaction mechanisms which is difficult, or even impossible to obtain with other methods. The present paper describes the development of microwave kinetic spectroscopy and its application to the O + ethylene reaction.

The reaction of $O({}^{3}P)$ with ethylene has been extensive-

ly investigated.^{3,4} The channel yielding $CH_3 + HCO$, which is referred to as (b), had been thought to be the most dominant initial process, until Buss et al.⁵ found by a molecular beam experiment that only vinoxy + H referred to as channel (a) occurs in collision-free conditions. Recent studies⁶⁻¹⁰ using the sample pressures of a fraction of Torr or higher have shown that channel (a) also plays an important role. The branching ratio of (a) and (b) may be pressure dependent, but has not been confirmed to be so. A low-pressure (lower than 0.1 Torr) experiment may clarify whether channel (b) is really induced by intermolecular collisions, as suggested by Hunziker et al.,7 who assumed this mechanism in order to reconcile their result of (b) dominating over (a) at high pressures with that of Buss et al.⁵ Microwave kinetic spectroscopy may throw light on this problem; the initial process of the reaction can be pursued at a low pressure $(\leq 0.1 \text{ Torr})$ by observing the microwave spectra of both transient species, vinoxy and HCO, as well as a product H₂CO in real time.

The $O({}^{3}P)$ + ethylene reaction may be initiated by a mercury sensitized reaction:

$$Hg + h\nu(253.7 \text{ nm}) \rightarrow Hg^*(^{3}P_1)$$
, (1)

$$Hg^{*}({}^{3}P_{1}) + N_{2}O \rightarrow N_{2} + O({}^{3}P) + Hg,$$
 (2)

$$O(^{3}P) + C_{2}H_{4} \rightarrow vinoxy + H$$
(3a)

 $\rightarrow CH_3 + HCO$ (3b)

$$\rightarrow CH_2 + H_2CO$$
 (3c)

$$\rightarrow$$
CH₂CO + H₂, (3d)

with low-pressure mercury lamps lit repetitively. Additional,

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information on channel (b) may be obtained from infrared laser kinetic spectroscopy¹¹ of the methyl radical.

EXPERIMENTAL

Apparatus and procedures

Figure 1 shows a block diagram of the microwave kinetic spectrometer developed in the present study. A quartz tube of 1 m in length and 9 cm in inner diameter was used as a reaction/absorption cell, which was surrounded by 15 germicidal lamps of 30 W each. A power supply could switch lamps on and off repetitively at a rate up to 1 kHz. In the present experiment, the light pulse was chosen to be typically of 4 ms duration with the rise and fall times of less than 0.2 ms, as shown in the bottom trace of Fig. 2 recorded by a pin photodiode, and with the repetition rate of 2 Hz. The flow rate of each sample gas was regulated by mass flow controllers, and component gases, after being mixed, were passed over a mercury reservoir to be saturated with mercury vapor and were then pumped through the cell by a turbomolecular pump of 250 ℓ /s. The linear flow rate was adjusted by changing the size of an aperture placed between the cell and the pump such that a reaction induced by a light pulse does not interfere with subsequent ones. The total sample pressure was about 30 mTorr, as measured by a capacitance manometer placed at the inlet of the cell; the pressure remained constant through the entire cell within 2 mTorr.

The microwave radiation in the 300 GHz region was generated by a frequency quadrupler (Millitech MU4-2T) driven by a 90 GHz klystron (OKI 90V11), fed to the reaction cell by a lens made of polytetrafluoroethylene (Teflon), and then focused onto an InSb detector (QMC) operated at liquid helium temperature. The signal was amplified by a dc video amplifier with 100 kHz bandwidth, and, after digitized by a 50 ns 8-bit transient digitizer (Kawasaki Electronica TMR-80), was transferred to a desk-top personal computer (NEC PC-9801E). An absorption signal generated by one pulse of the mercury light was digitized to 4096 data points. Then eight successive data were summed up in order to average out high-frequency random noises, and were stored as 512 data points. As a result, the effective minimum sampling time was increased to $0.4 \,\mu$ s, which was short enough for the present experiment. The rest of the microwave spectroscopic system employed was essentially identical to that previously reported.¹²

The source klystron was phase locked by a stabilizer (Microwave Systems MOS-5/PLS-60) to an RF frequency synthesizer (HP 3335 A), which was controlled by the personal computer through an IEEE-488 interface. The klystron frequency was locked to the center of an absorption line of which the time evolution was being pursued, but it was shifted by + or -1.5 MHz for the subsequent light pulse, and the difference between the two signals was recorded. This process, repeated many times, more than 100 times in most cases, eliminated reproducible noises caused by switching on and off the mercury lamps and also random noises to a great extent. Because the sample was continuously pumped out, the observed spectral intensity I_{obs} needed to be corrected to calculate the true intensity I_{corr} . In the present study, a simple, "linear" approximation was adopted, i. e.,

$$I_{\rm corr} = I_{\rm obs} \left[T/(T-t) \right], \tag{4}$$

where t is the time elapsed after the mercury lamps were switched on and T stands for an average residence time of the species under consideration in the cell. The residence time T was estimated to be typically 230 ms using the effective pumping speed which corresponded to a linear velocity of about 4 m/s in the cell as indicated by the rotational line intensity of a chemically stable species like H_2CO .

The whole experiments were performed at room temperature. Mercury lamp exposure did not raise the cell temperature more than 5 K, as the intensity of the N₂O $J = 14 \leftarrow 13$ transition at 351 667.8 MHz indicated, and the original temperature was restored within a few ms after the light pulse was turned off. Any cumulative temperature rise was ruled out, because the light pulse was of 4 ms duration in every 500 ms.

Species	v/MHz	Transition	μ/D	<i>α</i> /N	Width/MHz ^a
Vinoxy	342 311.5	17 _{0,17} -16 _{0,16}	2.843	1.83×10 ⁻¹⁷	1.43
НСО	346 708.5	$4_{0,4} - 3_{0,3}$ ($J = 4.5 - 3.5, F = 5 - 4$)	1.363	6.76×10 ⁻¹⁸	1.01
H ₂ CO	351 768.6	5 _{1,5} -4 _{1,4}	2.332	3.93×10 ⁻¹⁷	1.00

TABLE I. Transitions and absorption coefficients of vinoxy, HCO, and H₂CO.

^a FWHM.

(Showa Denko, purity of better than 99.99%), and methyl vinyl ether (Tokyo Kasei Kogyo, extra-pure grade).

Light intensity and oxygen atom production rate

The mercury light intensity absorbed was estimated from the decrease in N₂O concentration reflected on the line intensity of the J = 14-13 transition at 351 667.8 MHz, where the quantum yield for N₂O decomposition was taken to be unity.¹³ (The decrease due to temperature rise was recovered after the light pulse was turned off and thus was easily discriminated against the decrease due to decomposition.) The number of oxygen atoms generated, which was assumed to be equal to that of decomposed N₂O, was 3.5×10^{14} cm⁻³ s⁻¹ for a mixture of 20 mTorr N₂O and 10 mTorr ethylene, while the intensity of mercury light remained at its maximum value. The production rate was found to be roughly proportional to the N₂O pressure.

In addition to the N_2O /ethylene mixture, methyl vinyl ether was decomposed by mercury photosensitization. Because this reaction has been known to yield CH₃ and vinoxy radicals with the quantum yield close to unity,¹⁴ it was expected to provide us with a chance of checking the present method. The number of photons absorbed was calculated in reference to the N₂O/ethylene case using the quenching cross sections of 18 and 31.5 Å² for N₂O and methyl vinyl ether, respectively.¹⁴

Absorption coefficients of vinoxy, HCO, and H₂CO

The rotational spectra of HCO¹⁵ and H₂CO¹⁶ have been analyzed extensively, and the vinoxy radical has also recently been investigated in detail by microwave spectroscopy.¹⁷ The rotational transitions used in the present study are listed in Table I. When the thermal equilibrium is attained, the absorption coefficient α of a rotational transition is given by¹⁸

$$\alpha = [8\pi^2 N F_m v^2 / (3ckT)] [1 - hv/(2kT)] < n|\mu|m>^2 \times \Delta v / [(v_0 - v)^2 + (\Delta v)^2], \qquad (5)$$

where F_m denotes the fraction of molecules in the lower state of the transition, N the number of molecules per unit volume, $< n|\mu|m>$ the transition moment, ν and ν_0 designate the microwave and transition frequencies, respectively, and $\Delta\nu$ stands for the half-width of a line at the half-maximum of the intensity. The observed dipole moments were employed for HCO¹⁹ and H₂CO,²⁰ whereas for vinoxy an *ab initio* calculated dipole moment²¹ was assumed, because no measurements have been performed. The line width was measured in the present study for a 20/10 mTorr mixture of N_2O /ethylene. These parameters are also included in Table I.

The absorption coefficient of vinoxy may also be obtained by decomposing methyl vinyl ether, as described above. The value thus obtained was 0.8 times the value in Table I. The discrepancy is, at least in part, due to the *ab initio* calculation which tends to yield a larger dipole moment. However, because the difference is not large, the value in Table I was employed throughout the present study.

Infrared absorption measurement of CH₃

The CH₃ radical was detected by infrared diode laser kinetic spectroscopy.¹¹ The same reaction cell was used, but the Teflon lenses were replaced by NaCl windows, and mirrors were inserted in the cell for multiple reflection of the infrared beam; the path length was 40 m. Other parts of the diode laser system was the same as that reported previously.²² The frequency of the source diode was manually set at the peak frequency of an absorption line in measuring its time evolution. The F_1 component of the R(7,3) transition of the CH₃ ν_2 fundamental band at 739.760 cm⁻¹ was employed.

RESULTS

Figure 2 shows the time evolutions of vinoxy, HCO, and H_2CO derived from the observed spectral intensities; the ordinate has been converted to the abundances of the three molecules. The lowest trace represents the light pulse which initiated the reaction. For the sake of clarity, the initial parts of the evolutions are enlarged in Fig. 3, which shows that both vinoxy and HCO start to be formed right after the onset of the light pulse. In other words, both radicals are produced as primary products, indicating that both (a) vinoxy + Hand (b) $CH_3 + HCO$ channels play important roles, in agreement with the previous reports.^{7,8} A close inspection of Fig. 3 reveals that, while HCO still increases its concentration even after the light pulse is off, vinoxy reaches a maximum soon after the end of the light pulse. This observation means some HCO to be produced through secondary reactions. In contrast with the cases of vinoxy and HCO, the curve for H₂CO shows an induction period of 1 to 2 ms and steadily increases after the light pulse is switched off. Therefore, H₂CO is formed primarily by secondary reactions. However, a possibility of a small amount of H₂CO being formed initially with CH₂, i. e., channel (c), can not be ruled out completely. Ketene has not been detected so that chan-

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FIG. 2. Examples of the time evolutions of vinoxy, HCO, and H₂CO generated from a mixture of N₂O (19.9 mTorr) and ethylene (9.1 mTorr). The oxygen atom production rate was 3.5×10^{14} atoms cm⁻³ s⁻¹.

nel (d) may be disregarded.

Figures 4 show the time evolutions for three different ratios of the N_2O/C_2H_4 pressures, while keeping the total pressure at 30 mTorr. The observed evolution curves were obtained by smoothly connecting average concentrations derived from more than five runs; scatters among the observed data are indicated by vertical bars. The light pulses employed are similar to that shown in Fig. 2. As is seen from Figs. 4, the relative abundances of the three species are insensitive to the pressure ratio in the initial stage of the reaction (a few ms), but H₂CO and also HCO to some extent increase with the increase of the N₂O pressure, suggesting that secondary processes must be taken into account even in discussing the primary reaction mechanism.

Figure 5 shows the time evolution of CH_3 measured by infrared kinetic spectroscopy. It also shows a sharp rise with the onset of the light pulse, although the observed intensity has not been converted to the abundance. **DISCUSSION**

Branching ratio in the primary process

The present observation of the vinoxy, HCO, CH₃, and



FIG. 3. Initial portion of the time profiles. Conditions are the same as those of Fig. 2. The duration of the Hg light pulse is indicated by an arrow.

 H_2CO spectra has established that the following three channels are taking place in the primary process of the $O + C_2H_4$ reaction:

$$CH_2 = CH_2 + O \rightarrow CH_2CHO + H (a)$$

$$\rightarrow CH_3 + HCO (b)$$

$$\rightarrow CH_2 + H_2CO (c) . \qquad [1]$$

The third channel (c) has not been paid attention previously, but its participation has been suggested by Temps and Wagner.⁸ Another channel of ketene + H₂ may be possible and was estimated by Pruss *et al.*²³ to contribute about 5%, but the present experiment did not show any positive indication for this channel. (An attempt was made to observe the $17_{0,17} \leftarrow 16_{0,16}$ transition of ketene, but no signal was detected. This result indicates the abundance of ketene to be less than 8×10^9 molecules cm⁻³, which is about 4% of the HCO concentration.)

All the sample gases employed were obtained from the following sources and were used without further purification: ethylene (Takachiho Shoji, research grade), N_2O



FIG 4. Average time profiles of vinoxy, HCO, and H₂CO in three different mixtures: (a) N₂O 19.9 mTorr, ethylene 9.1 mTorr, and oxygen atom production rate 3.5×10^{14} atoms cm⁻³ s⁻¹. (b) N₂O 10.1 mTorr, ethylene 18.4 mTorr, and oxygen atom 1.5×10^{14} atoms cm⁻³ s⁻¹, respectively. (c) N₂O 5.6 mTorr, ethylene 23.9 mTorr, and oxygen atom 0.7×10^{14} atoms cm⁻³ s⁻¹.



FIG. 5. Time evolution of CH₃, $v_2 = 1-0$, R(7,3), F_1 ; N₂O 34 mTorr, ethylene 16 mTorr. The duration of the Hg light pulse is indicated by an arrow.

The primary products may readily react with atomic oxygen which will be present to much larger concentration in the system than any other atoms and free radicals, i. e.,

$$CH_2CHO + O \rightarrow H_2CO + HCO$$
, [2]

$$HCO + O \rightarrow CO + OH$$

$$\rightarrow CO_2 + H$$
, [3]

$$CH_3 + O \rightarrow H_2CO + H$$
, [4]

$$CH_2 + O \rightarrow CO + H_2$$

$$\rightarrow CO + 2H.$$
[5]

The rate constants of these reactions are expected to be very large, larger than 1×10^{-10} cm³ molecule $^{-1}$ s⁻¹ for some of the reactions. Therefore, these reactions must be taken into account even in analyzing primary processes of the $O + C_2H_4$ reaction.

Reactions [1]-[5] lead to the following kinetic equations:

$$\frac{d [\operatorname{vinoxy}]}{dt} = k_a [C_2 H_4] [O] - k_2 [\operatorname{vinoxy}] [O], \qquad (6)$$

$$\frac{d [\text{HCO}]}{dt} = k_b [C_2 H_4] [O] - k_3 [\text{HCO}] [O] + k_2 [\text{vinoxy}] [O], \qquad (7)$$

$$\frac{d [CH_3]}{dt} = k_b [C_2 H_4] [O] - k_4 [CH_3] [O], \qquad (8)$$

$$\frac{d [H_2CO]}{dt} = k_c [C_2H_4][O] + k_2 [vinoxy][O] + k_4 [CH_3][O].$$
(9)

Because the four species are much less abundant than C_2H_4 in the initial stage, an iterative procedure may be applied to integrate Eqs. (6)–(9). For example, [vinoxy] is approximately given by

$$[vinoxy] \sim k_a [C_2 H_4] S \tag{10}$$

with

$$S=\int_0^t [\mathbf{O}]dt\,,$$

which is inserted in the second term of the right-hand side of



FIG. 6. Abundance ratio plotted against $[vinoxy]/[C_2H_4]$: closed circle (data at t = 2 ms) and triangle (data at t = 4 ms) for [HCO]/[vinoxy] and open circle (t = 2 ms) and triangle (t = 4 ms) for $[H_2CO]/[vinoxy]$, and a, b, and c are referred to the data shown in Figs. 4(a), 4(b), and 4(c), respectively.

Eq. (6). Integration of Eq. (6) gives

$$[\text{vinoxy}] = k_a [C_2 H_4] S - (1/2) k_2 k_a [C_2 H_4] S^2 + \cdots .$$
(11)

(The second term is derived by partial integration.) Equations (7)-(9) may be integrated in a similar way to give

$$[\text{HCO}] = k_b [C_2 H_4] S - (1/2) (k_3 k_b - k_2 k_a) [C_2 H_4] S^2 + \cdots,$$
(12)

$$[CH_3] = k_b [C_2H_4]S - (1/2)k_4k_b [C_2H_4]S^2 + \cdots, \quad (13)$$

$$[H_2CO] = k_c [C_2H_4]S$$

+
$$(1/2)(k_2k_a + k_4k_b)[C_2H_4]S^2 + \cdots$$
, (14)

from which we derive

$$[HCO]/[vinoxy] = (k_b/k_a) - (k_b/2k_a)[k_3/k_a - k_2/k_b - k_2/k_a] \times [vinoxy]/[C_2H_4],$$
(15)

 $[H_2CO]/[vinoxy] = (k_c/k_a)$

+
$$(k_c/2k_a)[k_2/k_c + k_2/k_a + k_4k_b/k_ak_c][vinoxy]/[C_2H_4].$$
(16)

The observed ratios of [HCO]/[vinoxy] and $[H_2CO]/[vinoxy]$ are plotted in Fig. 6 as functions of $[vinoxy]/[C_2H_4]$, where the data at t = 2 and 4 ms are employed. As expected from Eqs. (15) and (16), both ratios show linear dependences on $[vinoxy]/[C_2H_4]$. The intercepts give (k_b/k_a) and (k_c/k_a) , or the branching ratio to be (a):(b):(c) = 1:1.21 \pm 0.23:0.31 \pm 0.03, where the uncertainties represent the confidence intervals of the fit. After taking into consideration other sources of uncertainties, the relative contributions of the three channels are determined to be $0.4_0 \pm 0.1, 0.4_8 \pm 0.1$, and $0.1_2 \pm 0.05$, respectively.

The increases of H_2CO and HCO with N_2O as shown in Figs. 4 are qualitatively explained by the present analysis. The slopes of the two straight lines in Fig. 6 should provide

some information on secondary reactions, but we have not attempted to analyze them, because other processes such as reactions with the cell wall probably need to be taken into account, but have not been well understood.

Ethylene can react directly with Hg^{*}, yielding C₂H₄, C₂H₂, and H₂ as the final products.²⁴ The intermediates of this reaction have been reported to react unimolecularly so fast that they will hardly encounter N₂O molecules not much abundant in the present system, to yield additional oxygen-containing compounds. Furthermore, only C₂H₃ and H of such intermediates may live long enough to generate oxygen-containing products, but both of them are known as minor intermediate components of the ethylene + Hg^{*} reaction. In fact, previous studies^{7,25} reported no such products generated by Hg-sensitized decomposition of N₂O/ethylene mixtures.

Branching ratio and reaction dynamics

Table II lists the branching ratio obtained by the present study to be compared with previous results. The present values agree well with those of Hunziker *et al.*⁷ derived for sample pressures of 80 to 760 Torr. Temps and Wagner⁸ reported a branching ratio for channel (b) in good agreement with the present result, although they suggested the ratio to be pressure dependent. Sridharan and Kaufman⁹ found no pressure dependence of the ratio for the sample pressure ranges similar to those of Ref. 8, but their value for channel (a) did not agree with those of Ref. 7 and the present study.

The results summarized in Table II indicate that the branching ratio is insensitive to the sample pressure from 30 mTorr to 760 Torr. This observation does not seem to reconcile with Hunziker *et al.*'s view that channel (b) is collisionally induced. The present sample pressure of 30 mTorr corresponds to the collision frequency of about 3×10^5 s⁻¹, and a collision complex of O and C₂H₄, if exists, is unlikely to survive as long as 3×10^{-6} s. Therefore, channel (b) must take place through an intramolecular path. In fact, Yamaguchi and Fueno²⁶ have shown by an *ab initio* calculation that the potential surfaces leading to channels (a) and (b) come close to each other at some reaction coordinates. According to this result, an intramolecular conversion may easily be induced between these two surfaces.

Microwave kinetic spectroscopy

The present method involves a few points which might influence the final result and thus need to be examined in some detail. The first point is how homogeneously one can produce oxygen atoms in the cell. Fortunately homogeneous distribution of oxygen is well guaranteed, because the quenching rate of mercury is an order of magnitude smaller than the fluorescence rate in an N₂O/C₂H₄ mixture of such low pressure as that employed in the present study. The second problem is reactions on the cell wall. An estimate of the diffusion coefficient²⁷ and also the diffusion rate²⁸ gives the collision rate of a reactive species with the wall to be about 70 s⁻¹. In fact, the observed decays of vinoxy and HCO could have been explained satisfactorily by adding a first-order decay of 50 s⁻¹ to the homogeneous reactions mentioned above, but such an additional path plays minor roles in de-

FABLE II. Branching	ratio of primary	channels.
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			Branching ratio of channel			
Researcher	Method ^a	Pressure/Torr	(a)	(b)	(c)	- Ref.
Hunziker et al. (1981)	a	40760	0.36 ± 0.04	0.52 ~ 0.58		7
Smalley et al.	b	50100	0.27 ± 0.05	•••		10
Temps and Wagner (1982)	c	0.75–3.0		0.35 - 0.6	< 0.05	8
Sridharan and Kaufman (1983)	d	0.4–6	0.79 ± 0.11			9
Present study	e	0.03	0.4 ± 0.1	0.5 ± 0.1	0.1 ± 0.05	
Buss et al. (1981)	f	~0	~1.0			5

^a Method: a: Mercury photosensitized decomposition in a static system, phase shift measurement, absorption of vinoxy and HCO. b: Flash photolysis of O_2 and NO in a flow system, resonance fluorescence monitoring for O and H atoms. c: Discharge flow method, LMR of HCO. d: Discharge flow method, resonance fluorescence measurement of hydrogen atoms. e: Mercury photosensitized decomposition in a flow system, pulse measurement, microwave absorption of vinoxy, HCO, and H₂CO. f: Crossed molecular beam experiments, mass spectrometric measurements of vinoxy.

riving the branching ratio.

The third problem is that reaction intermediates may be prepared in vibrationally and/or rotationally excited states, because channels (a) and (b) are both exothermic by 17 and 28 kcal mol⁻¹, respectively. Kleinermanns and Luntz²⁹ suggested that the vinoxy radical might be prepared initially in excited states of some vibrational modes. However, the relaxations among the vibrational, rotational, and translational degrees of freedom are rapid for polyatomic molecules like vinoxy, HCO, and H₂CO. These molecules possess vibrational modes which are close in frequency to those of ethylene, accelerating vibrational relaxation in the three molecules. A vibrational transition will thus be induced by collisions of 100 or less,³⁰ which corresponds to the relaxation rate larger than 3×10^{-12} cm³ molecule⁻¹s⁻¹, or to a lifetime shorter than 0.3 ms at 30 mTorr. The rotational relaxation is much faster than the vibrational relaxation. Since the present study focused attention mainly to the time interval of a few ms, all intermediate species must have been relaxed both vibrationally and rotationally.

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- ²E. Hirota, *High-Resolution Spectroscopy of Transient Molecules* (Springer, Heidelberg, 1985).
- ³R. E. Huie and J. T. Herron, in *Progress in Reaction Kinetics*, edited by R. K. Jennings and R. B. Cundall (Pergamon, Oxford, 1978), Vol. 8, pp. 1-
- K. Jennings and K. B. Cundan (Pergamon, Oxford, 1978), Vol. 6, pp. 1– 80.

- ⁴M. C. Lin, Adv. Chem. Phys. 42, 113 (1980).
- ⁵R. J. Buss, R. J. Baseman, G. He, and Y. T. Lee, J. Photochem. 17, 389 (1981).
- ⁶G. Inoue and H. Akimoto, J. Chem. Phys. 74, 425 (1981).
- ⁷H. E. Hunziker, H. Kneppe, and H. R. Wendt, J. Photochem. **17**, 377 (1981).
- ⁸F. Temps and H. G. Wagner, Max Planck Inst. Strömungsforsch. Ber. 18 (1982).
- ⁹U. C. Sridharan and F. Kaufman, Chem. Phys. Lett. 102, 45 (1983).
- ¹⁰J. F. Smalley, F. L. Nesbitt, and R. B. Klemm, J. Phys. Chem. **90**, 491 (1986).
- ¹¹H. Kanamori, J. E. Butler, K. Kawaguchi, C. Yamada, and E. Hirota, J. Chem. Phys. 83, 611 (1985).
- ¹²Y. Endo, S. Saito, and E. Hirota, J. Chem. Phys. 75, 4379 (1981).
- ¹³M. G. Bellas, Y. Rousseau, O. P. Strausz, and H. E. Gunning, J. Chem. Phys. 41, 768 (1964).
- ¹⁴R. V. Morris and S. V. Filseth, Can. J. Chem. 48, 924 (1970).
- ¹⁵G. A. Blake, K. V. L. N. Sastry, and F. C. De Lucia, J. Chem. Phys. 80, 95 (1984).
- ¹⁶R. Cornet and G. Winnewisser, J. Mol. Spectrosc. 80, 438 (1980).
- ¹⁷Y. Endo, S. Saito, and E. Hirota, J. Chem. Phys. 83, 2026 (1985).
- ¹⁸C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955); W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (Wiley, New York, 1984).
- ¹⁹B. M. Landsberg, A. J. Merer, and T. Oka, J. Mol. Spectrosc. 67, 459 (1977).
- ²⁰B. Fabricant, D. Krieger, and J. S. Muenter, J. Chem. Phys. 67, 1576 (1977).
- ²¹E. S. Huyser, D. Feller, W. T. Borden, and E. R. Davidson, J. Am. Chem. Soc. **104**, 2956 (1982).
- ²²C. Yamada and E. Hirota, J. Chem. Phys. 78, 669 (1983).
- ²³F. J. Pruss, Jr., I. R. Slagle, and D. Gutman, J. Phys. Chem. 78, 663 (1974).
- ²⁴A. B. Callear and R. J. Cvetanović, J. Chem. Phys. 24, 873 (1956).
- ²⁵R. J. Cvetanović, J. Chem. Phys. 23, 1375 (1955).
- ²⁶K. Yamaguchi and T. Fueno (private communication).
- ²⁷H. Melville and B. G. Gowenlock, *Experimetal Methods in Gas Reactions* (MacMillan, London, 1964), Chap. I, pp. 14–17.
- ²⁸D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics (Plenum, New York, 1969), pp. 77-83.
- ²⁹K. Kleinermanns and A. C. Luntz, J. Phys. Chem. 85, 1966 (1981).
- ³⁰J. D. Lambert, Vibrational and Rotational Relaxations in Gases (Oxford University, Oxford, 1977), Chap. 4, pp. 83-114.

¹E. Hirota, J. Phys. Chem. 87, 3375 (1983).