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# Mechanism of the $1-C_4H_9 + O$ reaction and the kinetics of the intermediate $1-C_4H_9O$ radical

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The 1-C<sub>4</sub>H<sub>9</sub> + O reaction has been investigated in two quasi-static reactors with different detection systems. From a time-resolved measurement of OH formation by laser induced fluorescence (T = 295 K, p = 21 mbar, bath gas: He) an inverted vibrational state distribution for OH X<sup>2</sup>II (v = 0, 1, 2) was observed. By using Fourier transform infrared spectroscopy, relative product yields of  $0.55 \pm 0.08$  for  $1-C_4H_8$ ,  $0.397 \pm 0.05$  for HCHO and  $0.053 \pm 0.02$  for  $C_3H_7$ CHO were determined (T = 298 K, p = 2 mbar, bath gas: He). The results are explained in terms of the formation and subsequent decomposition of an intermediate chemically activated  $1-C_4H_9O$  radical and a competing abstraction channel leading directly to OH +  $1-C_4H_8$ . A modeling by statistical rate theory based on *ab initio* results for the stationary points of the potential energy surface of  $C_4H_9O$  allows the quantitative description of the product branching ratios. From this modeling, threshold energies of  $E_{06} = 55 \pm 6$  and  $E_{07} = 88 \pm 6$  kJ mol<sup>-1</sup> for the  $\beta$ -C–C and the  $\beta$ -C–H bond dissociation, respectively, in  $1-C_4H_9O$  are obtained. For the 1,5 H atom shift, a most probable value of  $E_{05} = 40 \pm 5$  kJ mol<sup>-1</sup> follows from a comparison of our quantum chemical results with data from the literature.

## 1. Introduction

The reactions of alkoxyl radicals have been extensively studied in recent years because of their crucial role in atmospheric chemistry and in combustion systems<sup>1-15</sup> (for a review of earlier work, see *e.g.* refs. 14–16). Whereas for small alkoxyl radicals under tropospheric conditions the bimolecular reaction with O<sub>2</sub> to form carbonyl compounds and HO<sub>2</sub> dominates,<sup>17–19</sup> the unimolecular decomposition and isomerization channels become important at elevated temperatures.<sup>4</sup> For sufficiently large alkoxyl radicals, isomerizations, in particular 1,5-isomerizations *via* six-member transition states, efficiently compete with the decomposition steps and the H abstraction by O<sub>2</sub>.<sup>17–20</sup> The simplest radical exhibiting this feature is 1-butoxyl, 1-C<sub>4</sub>H<sub>9</sub>O. Therefore, it can serve as a prototype for the kinetic behaviour of the higher alkoxyl radicals.

Alkoxyl radicals can be generated by the reaction of alkyl radicals with oxygen atoms. Accordingly, in the course of the reaction

$$1-C_4H_9 + O \rightarrow \text{products} \tag{1}$$

1-butoxyl radicals are formed intermediately, probably in competition to H abstraction:

$$1-C_4H_9 + O \rightarrow 1-C_4H_8 + OH$$
(1a)

$$1-C_4H_9 + O \rightarrow 1-C_4H_9O \tag{1b}$$

Therefore, the final product branching of reaction (1) to a large part reflects the competition between the unimolecular

reaction channels of the 1-butoxyl radical:

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O

 $\rightarrow$  CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH(')OH ( $\rightarrow$ ···) (2)

- $\rightarrow$  CH<sub>3</sub>CH<sub>2</sub>CH(<sup>•</sup>)CH<sub>2</sub>OH ( $\rightarrow$  ···) (3)
- $\rightarrow$  CH<sub>3</sub>CH(<sup>•</sup>)CH<sub>2</sub>CH<sub>2</sub>OH ( $\rightarrow$  ···) (4)
- $\rightarrow$  'CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH ( $\rightarrow$ ···) (5)
- $\rightarrow$  CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>(') + HCHO (6)

$$\rightarrow$$
 H<sup>•</sup> + CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO (7)

The 1-C<sub>4</sub>H<sub>9</sub>O radicals formed in reaction (1b) are highly excited, with an average energy of ~400 kJ mol<sup>-1</sup>. Consequently, their kinetics has to be described in terms of the specific rate coefficients  $k_i(E)$  for the reactions (i = 2-7). A comparison with results from thermal experiments, if available, and quantum chemical calculations can be accomplished by unimolecular rate theory.<sup>21–23</sup>

In the present study, we report on the experimental determination of the relative product yields for reaction (1). A model capable of describing the basic findings in a quantitative way was developed. The results of quantum chemical calculations at different levels are related to the experimental observables by statistical rate theory. In this way, the branching ratios for reactions (1a) and (1b) as well as for reactions (2)–(7) can be determined, and reasonable threshold energies for the unimolecular reactions of  $1-C_4H_9O$  are obtained.

#### 2.1. Experimental arrangements

Two different arrangements were used in order to identify and quantify the primary products of the  $O + 1-C_4H_9$  reaction, experimentally realized by the simultaneous photolysis of the precursors  $SO_2$  ( $SO_2 \rightarrow O + SO$ ) and  $1-C_4H_9I$  ( $1-C_4H_9I \rightarrow 1-C_4H_9 + I$ ) combined with different spectroscopic methods and time resolution.

2.1.1. UV-laser photolysis cell with laser induced fluorescence (LIF). The experimental set-up is shown schematically in Fig. 1. The flowing mixture of  $SO_2-C_4H_9I$  highly diluted by He was photolyzed in a quasi-static reaction vessel by an excimer laser at 193 nm, allowing the total exchange of the reaction mixture between two photolytic laser pulses. The OH radicals in the vibrational state v = 0, 1, 2 were detected by the pump/probe technique via the  $A^2\Sigma^+ \leftarrow X^2\Pi$  transition in the wavelength region of 306.4–318.5 nm by saturating the transitions to the electronically excited states and measuring the fluorescence. (Saturation reduces the dependence of the LIF signal on the fluctuations of the laser fluence.) By the variable time delay between the photolysis laser pulse and the probe laser a time resolution of 0–400 µs was achieved. For details of the detection system see for example ref. 24.

2.1.2. UV-laser photolysis cell with FTIR spectrometer. In a vacuum-tight stainless steel sphere (volume: 4 l) the mixture of  $SO_2 + C_4H_9I$  partly diluted by Ar was photolyzed by an excimer laser at 193 nm (Lambda Physik EMG 102). Typical operation conditions were: laser beam profile of 6 mm × 20 mm, laser energy of 10-60 mJ, repetition rate of 0.5-3 Hz. Perpendicular to the laser beam a multiple pass mirror system of the White type (40 traversals, 8 m optical path) was coupled to an FTIR spectrometer for the optical absorption measurements [Bruker IFS 66; MCT (Hg/Cd/Te) detector]. For species identification and quantification, the spectral region  $(600-5000 \text{ cm}^{-1})$  and spectral resolution  $(0.11-4 \text{ cm}^{-1})$  were selected according to the lowest spectral interference and the accuracy by the number of scans (20-500). To give some examples: the simultaneous detection of the main products HCHO/C<sub>3</sub>H<sub>7</sub>CHO was achieved around 1745 cm<sup>-1</sup>, the search for the absent product C<sub>2</sub>H<sub>4</sub> in the presence of the main product  $1-C_4H_8$  around 950 cm<sup>-1</sup>, both with a spectral resolution of 1 cm<sup>-1</sup>. The detection sensitivity of  $C_2H_4$ (signal-to-noise ratio of 3, 500 scans) was  $5 \times 10^{-5}$  mbar  $(2 \times 10^{-12} \text{ mol cm}^{-3})$ . The reaction vessel was equipped with a gas handling system, pressure transducers, heaters, and a pumping device. Details will be published elsewhere.

In order to estimate the concentrations of the  $1-C_4H_9$  radicals and the O atoms formed by photolysis at 193 nm the absorption coefficients of  $1-C_4H_9I$  and SO<sub>2</sub> were measured by



Fig. 1 Experimental arrangement.

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a UV-spectrometer (Cary 5 UV-VIS-NIR Spectrophotometer, Varian)  $[\epsilon(1-C_4H_9I) = 53.2 \text{ m}^2 \text{ mol}^{-1}; \epsilon(SO_2) = 240 \text{ m}^2 \text{ mol}^{-1}$ , see also ref. 25;  $\lambda = 190-195 \text{ nm}; p = 1-6 \text{ mbar}; T = 295 \text{ K}$ ]. The IR absorption coefficients of the reactants and the products were determined by the standard procedures (absorbance vs. concentration) for authentic samples in the wavelength region of minimal spectral interferences (see below).

The chemicals were of commercial grade [He ( $\geq$ 99.995%), SO<sub>2</sub> ( $\geq$ 99.98%), Messer Griesheim; 1-C<sub>4</sub>H<sub>9</sub>I (>99%), 1-C<sub>4</sub>H<sub>8</sub> (>99%) Merck; 1-C<sub>3</sub>H<sub>7</sub>CHO ( $\geq$ 99%), Fluka].

### 2.2. Experimental results

2.2.1. Formation of OH radicals by reaction (1a) as detected by LIF. In order to elucidate the mechanism of the primary attack in the  $C_4H_9 + O$  reaction the population of the different vibrational states of the primarily formed OH radical has been studied: a thermal distribution of OH would point to a complex formation of  $C_4H_9O$  with statistically controlled decomposition  $C_4H_9O \rightarrow C_4H_8 + OH$ ; a highly non-thermal distribution would point to a direct route *via* abstraction along  $O + C_4H_9 \rightarrow C_4H_8 + OH$ . Time-resolved measurements were performed in order to estimate the contribution of collisional relaxation to the measured population.

The formation of OH radicals in the ground and the first and second excited vibrational states (v = 0, 1, 2) was measured as a function of the reaction time for highly diluted mixtures, as displayed in Fig. 2. The measured signal intensities were converted to relative concentrations via the known Einstein coefficients found in the literature.<sup>26,27</sup> In the absence of one reaction partner, SO2 or C4H9I, respectively, no OH formation was detected. As can be deduced from Fig. 2, the excited states v = 1, 2 are highly populated with a nonthermal distribution (see the Discussion) with a maximum at a reaction time of around 50  $\mu$ s. The ground state (v = 0) exhibits the maximum at around 100 µs. This later maximum is explained by the relaxation of the excited states after 50 µs to the ground state, which is also semi-quantitatively reflected by the reduction of OH(v = 1, 2) between 50 and 100 µs and the increase of OH(v = 0). The relaxation times for the processes  $OH(v = 1) + He \rightarrow OH(v = 0) + He$  and OH(v = 1)+ SO<sub>2</sub>  $\rightarrow$  OH(v = 0) + SO<sub>2</sub> have been reported recently by Hippler et al.28



**Fig. 2** The reaction 1-C<sub>4</sub>H<sub>9</sub> + O: Formation of the OH radical in the vibrational states v = 0, 1, 2 as observed by LIF (p = 21.4 mbar; T = 294 K;  $[1-C_4H_9I]_0 = 2.2 \times 10^{-10}$  mol cm<sup>-3</sup>;  $[SO_2]_0 = 7.0 \times 10^{-10}$  mol cm<sup>-3</sup>; estimated concentrations:  $[1-C_4H_9]_0 = 5.2 \times 10^{-12}$  mol cm<sup>-3</sup>,  $[O]_0 = 7.2 \times 10^{-11}$  mol cm<sup>-3</sup>).

0,2

0,1

Absorbance 0'0

-0,1

-0,2

3000

For the simulation of the influence of secondary reactions on the primary product formation, a rate coefficient for reaction (1) was needed. An approximate value was estimated from three different experimental approaches in our laboratory: (1) from the time-resolved profiles of OH(v = 0, 1, 2), (2) from the competition between the reaction  $O + C_4H_9$ and the reference reaction  $1-C_4H_9 + 1-C_4H_9 \rightarrow 1-C_4H_8$  $+ C_4H_{10}$ /hydrocarbons<sup>29</sup> via the variation of the  $[O]_0/[C_4H_9]_0$  ratio and (3) from the fast flow reactor studies of the reaction  $O + 2-C_4H_9$  and the mixed reaction O $+ (1C_4H_9 + 2-C_4H_9)$ . All three values were centered in the range of  $(2-3) \times 10^{14}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> with a weighted average value of  $(2.4 \pm 0.6) \times 10^{14}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. A more quantitative direct determination of  $k_1$  is under way.

The population inversion of the vibrational states of OH in other alkyl radical + oxygen atom reactions has been observed by Leone *et al.*<sup>30</sup> using the infrared chemiluminescence of OH (X<sup>2</sup> $\Pi$ , v = 1-5) at low pressure. As the v = 0state is not accessible by this method, the population of the v = 0 state was deduced by a surprisal analysis. The experiments gave a non-thermal distribution of OH(v = 0-5) for the reactions O + C<sub>2</sub>H<sub>5</sub>, O + 1-C<sub>3</sub>H<sub>7</sub> and O + 2-C<sub>3</sub>H<sub>7</sub>.

2.2.2. Formation of final products of reaction (1) as detected by FTIR. In Fig. 3 the difference FTIR absorption spectra are given for the reaction system at small and high conversions with the assignment of the reaction products indicating the spectral regions for a quantitative concentration measurement via the absorbance. A search has been carried out for the possible products C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>5</sub>OH, with a negative result. In Fig. 4 the relative calibrated concentrations of the main products 1-C<sub>4</sub>H<sub>8</sub>, HCHO and C<sub>3</sub>H<sub>7</sub>CHO are shown as a function of the depletion of the radical precursor  $1-C_4H_0I$  consumed by photolysis. Spectra were taken after every group of 500 laser pulses where the decrease of product formation at the end of an experiment was due to a decrease in laser pulse energy. In order to estimate the influence of the secondary photolysis of the aldehydic products on the primary product yield, samples of the aldehydes of comparable concentrations were photolyzed separately, leading to negligible changes in the branching ratios. The C<sub>3</sub>H<sub>7</sub> radical is a co-product of reaction (6), and therefore the reaction  $C_3H_7$ + O needs to be considered. As we have studied the reaction of oxygen atoms with the homologous alkyl radicals CH<sub>3</sub>,  $C_2H_5$  and  $C_3H_7$  for product formation like 1- $C_4H_9$  the contribution of the additional HCHO formation via  $O + C_3H_7$ could be estimated  $(O + C_3H_7 \rightarrow OH + C_3H_6/HCHO$  $+ C_2H_5/C_2H_5CHO + H$ ). In order to quantify the uncertainties of the branching ratios, modeling studies of the

HCHO: CO stretch

1-C<sub>4</sub>H<sub>8</sub>: CH<sub>2</sub>wag 965 - 1018 cm<sup>-1</sup>

871 - 958 cm<sup>-1</sup>

1-C<sub>4</sub>H<sub>9</sub>I: CH deform 1174 - 1200 cm<sup>-1</sup> 1229 - 1275 cm<sup>-1</sup>

1743 - 1748 cm

1-C<sub>3</sub>H<sub>7</sub>CHO: CH stretch 2695 - 2735 cm<sup>-1</sup> \_1

2794 - 2819 cm

2500



2000

1500

1000



**Fig. 4** The reaction 1-C<sub>4</sub>H<sub>9</sub> + O: Formation of the stable reaction products as a function of the photolyzed radical precursor 1-C<sub>4</sub>H<sub>9</sub>I (p = 1.0 mbar; T = 293 K;  $[1-C_4H_9I]_0/[SO_2]_0 = 3/4$ ;  $[1-C_4H_9]_0/[O]_0 = 1/5.8$ ).

primary and the various secondary reactions were performed. These substantiated the assignment of the main primary product channels with the following uncertainties:  $1-C_4H_8$  (0.55  $\pm$  0.08), HCHO (0.397  $\pm$  0.05),  $C_3H_7$ CHO (0.053  $\pm$  0.02). The overall reaction scheme comprises the reactions of the labile species O, OH, H,  $C_3H_7$ ,  $C_4H_9$ , the precursors SO<sub>2</sub>,  $1-C_4H_9I$ , and the products  $1-C_4H_8$ , HCHO,  $C_3H_7$ CHO, where the rate coefficients were taken from recent reviews or estimated.<sup>31,32</sup>

## 3. Modeling of the product branching

#### 3.1. Quantum chemical calculations

For the modeling of the branching ratios by statistical unimolecular rate theory, the vibrational frequencies and rotational constants of the 1-butoxyl radical and the transition states for reactions (2)–(7) are required as well as the corresponding threshold energies. The geometric data and frequencies have been obtained by *ab initio* calculations at MP2/6-31G\* level, and the results are shown in Table 1. The energetic parameters stem in part from ref. 4 and in part from quantum chemical calculations carried out in the present work. All *ab initio* calculations were performed using the GAUSSIAN 94 program package.<sup>33</sup> In recent studies,<sup>4,7,9–13</sup> the capability of different theoreti-

In recent studies,<sup>4,7,9–13</sup> the capability of different theoretical methods was tested to predict reliable energetic parameters for  $\beta$ -bond dissociation reactions of alkoxyl radicals. A modified G2(MP2) approach<sup>7,9,10</sup> is employed in the present work to characterize the  $\beta$ -decomposition reactions and the 1,5isomerization step, which are the dominating unimolecular reaction channels of 1-C<sub>4</sub>H<sub>9</sub>O.<sup>3,4</sup> The original G2(MP2) procedure<sup>34,35</sup> is modified insofar as the equilibrium geometries, transition structures and harmonic frequencies are calculated at the MP2(fc)/6-31G\* level, an alteration that is discussed in more detail in refs. 7 and 9. The threshold energies at 0 K follow from the classical barrier heights [obtained as the energy differences from the G2(MP2) model] by adding the differences of the vibrational zero-point energies scaled by a factor of 0.9646 as recommended by Pople *et al.*<sup>36</sup> The results are included in Table 2.

The threshold energy of the 1,5 H atom transfer obtained by our G2(MP2)-like procedure agrees with results from different DFT methods<sup>3,4,11</sup> and a BAC-MP4 calculation<sup>4</sup> within 6 kJ mol<sup>-1</sup>. Also the agreement with a thermal activation energy of 41 kJ mol<sup>-1</sup> determined by a relative measurement<sup>1</sup> is reasonable, and, consequently, a value of  $40 \pm 5$  kJ mol<sup>-1</sup> can be recommended for this threshold

**Table 1** Harmonic wavenumbers  $v_i$  (scaled by 0.9427)<sup>36</sup> and rotational constants A, B and C as obtained from the *ab initio* calculations (MP2/6-31G\*)

	$v_i$ /cm <sup>-1</sup>	A, B, $C/cm^{-1}$
1-C <sub>4</sub> H <sub>9</sub> O	106, 114, 179, 246, 374, 406, 489, 719, 824, 889, 972, 978, 1036, 1050, 1102, 1200, 1233, 1264, 1288, 1332, 1371, 1389, 1395, 1463, 1470, 1475, 1483, 2848, 2898, 2911, 2926, 2928, 2953, 2983, 3010, 3012	0.6638, 0.06742, 0.06412
TS(2)	2126i, 87, 105, 185, 244, 376, 433, 617, 724, 842, 887, 923, 995, 1046, 1092, 1114, 1136, 1218, 1244, 1284, 1332, 1368, 1389, 1454, 1468, 1475, 1482, 2458, 2895, 2920, 2927, 2956, 2961, 2975, 3010, 3013	0.6952, 0.06636, 0.06360
TS(3)	2215i, 97, 147, 238, 261, 416, 672, 708, 807, 856, 926, 957, 1018, 1076, 1102, 1107, 1131, 1157, 1240, 1254, 1279, 1363, 1389, 1455, 1473, 1477, 1498, 1954, 2905, 2928, 2934, 2960, 2993, 3012, 3016, 3016	0.4151, 0.08542, 0.07940
TS(4)	2408i, 141, 205, 229, 355, 514, 594, 740, 822, 889, 929, 956, 991, 1060, 1103, 1135, 1174, 1205, 1240, 1262, 1321, 1343, 1383, 1457, 1462, 1466, 1490, 1773, 2888, 2913, 2935, 2959, 2975, 2992, 2995, 3022	0.3299, 0.1097, 0.09197
TS(5)	2141i, 162, 306, 383, 436, 482, 645, 803, 831, 874, 919, 934, 1009, 1049, 1098, 1137, 1157, 1206, 1230, 1255, 1306, 1329, 1340, 1429, 1452, 1459, 1470, 1529, 2866, 2917, 2924, 2935, 2968, 2979, 2989, 3060	0.2357, 0.1589, 0.1071
TS(6)	551i, 67, 86, 147, 245, 320, 365, 579, 707, 745, 870, 888, 890, 1011, 1083, 1147, 1188, 1223, 1280, 1310, 1380, 1448, 1465, 1472, 1477, 1484, 1644, 2789, 2846, 2931, 2933, 2982, 3018, 3024, 3028, 3125	0.6171, 0.06157, 0.05852
TS(7)	1630i, 97, 105, 222, 248, 341, 510, 560, 617, 731, 851, 876, 950, 1026, 1034, 1114, 1147, 1226, 1260, 1289, 1344, 1363, 1388, 1449, 1468, 1474, 1480, 1630, 2780, 2923, 2927, 2934, 2978, 3003, 3013, 3015	0.4963, 0.07725, 0.07332

energy. For the  $\beta$ -C–C bond dissociation, the modified G2(MP2) barrier height agrees with results from DFT<sup>4,10,11,13(a)</sup> and BAC-MP4<sup>4,11</sup> computations within  $\pm 8$  kJ mol<sup>-1</sup>. The barrier obtained from corrected MP4 calculations,<sup>4</sup> however, is lower by *ca*. 10 kJ mol<sup>-1</sup> and those from CBS calculations<sup>3,13(a)</sup> are lower by *ca*. 10–20 kJ mol<sup>-1</sup>. For the  $\beta$ -C–H bond dissociation, the barrier heights at BAC-MP4 and B3LYP/6-311+G(2d,p) level<sup>4</sup> exceed those from our G2(MP2) calculations by ~12 kJ mol<sup>-1</sup> and ~3 kJ mol<sup>-1</sup>, respectively.

For reactions (5), (6) and (7), the agreement between the activation parameters from DFT-B3LYP<sup>3,4</sup> and from the more expensive G2(MP2) and BAC-MP4<sup>4</sup> calculations is reasonable. Therefore, a geometry optimization at MP2/6-31G\* level (or higher) combined with a DFT-B3LYP<sup>37,38</sup> or a G2(MP2) energy calculation should allow for a reasonable description of the unimolecular reactions of alkoxyl radicals. We note that for the two  $\beta$ -bond dissociation reactions (6) and (7), the most product-like transition structures were obtained by the DFT calculations and the least product-like at the MP2/6-31G\* level.<sup>3,4</sup> This is discussed in detail in ref. 9 for the case of C<sub>2</sub>H<sub>5</sub>O.

In Section 4, the adequacy of the threshold energies will be verified by a comparison of the predicted branching ratios with our experimental results.

**Table 2** Threshold energies at T = 0 K as obtained from quantum chemical calculations and the resulting high-pressure limiting Arrhenius parameters for T = 300 K based on the data from Table 1 and the reaction path degeneracies given in the text

Reaction	$E_{0i}/\text{kJ} \text{ mol}^{-1}$	Method	$lg(A_{\infty}/s^{-1})$	$E_{\infty}/\mathrm{kJ} \mathrm{mol}^{-1}$
(2)	105.0 <sup>a</sup>	MP-SAC2	13.55	107.3
(3)	103.6 <sup>a</sup>	MP-SAC2	13.05	104.7
(4)	70.79 <sup>a</sup>	MP-SAC2	12.57	70.91
(5)	43.76	G2(MP2)	12.06	42.68
(6)	60.96	G2(MP2)	13.76	64.16
(7)	83.22	G2(MP2)	13.52	85.64
<sup>a</sup> Ref. 4.				

## 3.2. Statistical unimolecular rate theory

The branching ratios between the different unimolecular reaction channels of  $1-C_4H_9O$  under our experimental conditions can be expressed in terms of the respective low-pressure limiting rate coefficients for chemical activation:<sup>21-23</sup>

$$\frac{r_m}{r_n} = \frac{k_{0m}}{k_{0n}} \tag{8}$$

Here,  $r_j$  is the rate of reaction for channel j and

$$k_{0j} = \int_{E_{0,\min}}^{\infty} k_j(E) F^{\rm ss}(E) \, \mathrm{d}E \tag{9}$$

with the normalized steady-state distribution for  $1-C_4H_9O$ 

$$F^{\rm ss}(E) = \frac{F(E)}{\sum_{i} k_i(E)} \left[ \int_{E_{0,\min}}^{\infty} \frac{F(E) \, dE}{\sum_{i} k_i(E)} \right]^{-1}$$
(10)

and the specific rate coefficients  $k_i(E)$ . Here  $E_{0, \min}$  denotes the lowest threshold energy among the different unimolecular channels *i*. The nascent distribution of the 1-butoxyl radicals, F(E), is approximated by<sup>21</sup>

$$F(E) = \frac{W_{1-C_{4}H_{9}O}(E - E_{0}^{ar}) \exp[-(E - E_{0}^{ar})/k_{B}T]}{\int_{0}^{\infty} W_{1-C_{4}H_{9}O}(\varepsilon) \exp(-\varepsilon/k_{B}T) d\varepsilon}$$
(11)

where  $k_{\rm B}$  is Boltzmann's constant, *T* the temperature,  $W_{1-C_4H_9O}$ the sum of states for 1-C<sub>4</sub>H<sub>9</sub>O and  $E_0^{\rm ar}$  the threshold energy for the reaction 1-C<sub>4</sub>H<sub>9</sub>O  $\rightarrow$  1-C<sub>4</sub>H<sub>9</sub> + O. The specific rate coefficients follow from RRKM theory as<sup>21–23,39</sup>

$$k_{i}(E) = \frac{L_{i} W_{i}(E - E_{0i})}{h \rho_{1-C_{4}H_{9}O}(E)}$$
(12)

where h is Planck's constant,  $\rho_{1-C_4H_9O}$  the density of states of 1-C<sub>4</sub>H<sub>9</sub>O,  $E_{0i}$  the threshold energy for channel i and  $W_i$  the sum of states of the corresponding transition state. Symmetry effects are explicitly expressed in terms of reaction path degeneracies  $L_i$ . The energy E is counted from the vibrational



Fig. 5 Schematic energy diagram for the formation and subsequent unimolecular reaction of  $1-C_4H_9O$ .

ground state of  $1-C_4H_9O$ , and some of the relevant quantities are illustrated in Fig. 5. The thermochemical limit  $E_0^{ar}$  is approximated by the difference of the heats of formation at 298 K for  $1-C_4H_9 + O$  and  $1-C_4H_9O$ . The following values (in kJ mol<sup>-1</sup>) have been used:  $1-C_4H_9$ , 80.9;<sup>40</sup> O, 249.2;<sup>41</sup> and  $1-C_4H_9O$ , 62.8;<sup>41</sup> it follows that  $E_0^{ar} = 392.9$  kJ mol<sup>-1</sup>. By adding the mean energy of the distribution function F(E), an average excitation energy of 407.0 kJ mol<sup>-1</sup> is obtained for the nascent  $1-C_4H_9O$  population.

The sums and densities of states were exactly counted,<sup>42</sup> using the molecular parameters from Section 3.1. The conservation of total angular momentum was taken into account.<sup>43</sup> From the thermal rotational distribution of  $1-C_4H_9$  at 300 K and the orbital angular momentum caused by the capture process,  $1-C_4H_9 + O$ , an average rotational excitation of  $\langle J \rangle \approx 60$  follows for the nascent  $1-C_4H_9O$  population.<sup>44,45</sup> Accordingly, all sums and densities of states were calculated for J = 60. It should be noted, however, that due to the tight transition states in this system, the branching ratios are virtually independent of the rotational excitation.

For the reaction path degeneracy  $L_i$ , we used a value of 1 for reaction (6) and 2 for all other reactions; however, some remarks regarding these numbers are necessary. The general approach to determining reaction path degeneracies was reviewed in ref. 46, and a thorough representation of this topic can also be found in ref. 22. The situation is quite clear in the case of reactions (2), (6) and (7). By considering all permutations between like atoms in the 1-butoxyl radical and the corresponding transition state and by correlating the mutually accessible configurations, the above values are obtained in a straightforward manner. It is unimportant whether the trans or the gauche conformation of the 1-butoxyl radical is considered as the reactant equilibrium structure or whether the torsions are treated as hindered rotations. For these reactions, the  $1-C_3H_7$  group simply acts as a spectator. The situation becomes more complex for reactions (3)-(5). Because the overall symmetry numbers for the 1-butoxyl radical as well as for the transition states are unity, the reaction path degeneracy is the ratio of the respective numbers of optical isomers:<sup>22</sup>

$$L_i = \frac{m_i}{m_{1-C_4H_9O}}$$

The transition states 3–5 are asymmetric, and hence  $m_i = 2$ . For the 1-butoxyl radical, however,  $m_{1-C_4H_9O} = 1$  in the *trans* and  $m_{1-C_4H_9O} = 2$  in the *gauche* conformation. Accordingly, the reaction path degeneracies are 2 and 1, respectively. Because both conformations differ in energy by only ~3 kJ mol<sup>-1</sup> (ref. 47), they are comparably populated even at room temperature. At this point, the approximate character of the concept of reaction path degeneracy becomes obvious. In an exact treatment, the full hindered rotor phase space of the 1butoxyl radical would have to be sampled in calculating the density of states. Because these hindered rotations disappear in the cyclic transition states, a formal value of  $L_i = 2$  would result.<sup>22</sup> We used this value as an approximation in the case of reactions (3)–(5), even though we calculated the density of states for harmonic torsional vibrations. We note that the branching between reactions (2), (6) and (7) is not influenced by this choice.

## 4. Discussion

The specific rate coefficients computed with the parameters from Tables 1 and 2 are shown in Fig. 6. The resulting lowpressure limiting rate coefficients for the unimolecular channels and the relative branching fractions are contained in Table 3. Among the reactions of  $1-C_4H_9O$ , the  $\beta$ -C–C bond dissociation dominates with a fractional contribution of ~70% followed by the  $\beta$ -C–H bond split with ~18%. The isomerization steps on the whole contribute with ~12%, where nearly one half can be assigned to the 1,5 H shift. Though the latter reaction has the lowest threshold energy, its specific rate coefficients fall below those of the decomposition channels at high excitation energies because of the tightness of the cyclic transition state (*cf.* Fig. 6).

In characterizing the product yields, it is important to consider the fate of the carbon-centered radicals that follow from the isomerization steps (2)–(5). Apart from subsequent isomerizations, including the reverse reactions to  $1-C_4H_9O$ , the most important consecutive steps of these species are the  $\beta$ -C–C bond dissociation reactions, which would lead to the following stable products: H<sub>2</sub>CCHOH for reaction (2), H<sub>2</sub>CCHCH<sub>2</sub>OH



Fig. 6 Nascent distribution of  $1-C_4H_9O$  and specific rate coefficients for reactions (2)–(7); threshold energies from Table 2. For the dissociation reactions, the breaking bond is given.

**Table 3** Low-pressure limiting rate coefficients and relative branching fractions  $Y_i$ 

Reaction	$k_{0i}/s^{-1}$	$Y_i^{\ a}$	$Y_i^{\ b}$	$Y_i^c$	Exp.
(1a)		0.0	0.55	0.55	0.55
(2)	$9.9 \times 10^{10}$	0.030	0.014	0.011	
(3)	$3.5 \times 10^{10}$	0.011	0.005	0.004	
(4)	$1.0 \times 10^{11}$	0.030	0.014	0.011	
(5)	$1.9 \times 10^{11}$	0.057	0.026	0.021	
(6)	$2.3 \times 10^{12}$	0.692	0.310	0.354	0.397
(7)	$6.0 \times 10^{11}$	0.180	0.081	0.049	0.053

<sup>*a*</sup> Reaction (1a) neglected. <sup>*b*</sup> Relative branching fraction of reaction (1a) set equal to the experimental  $1-C_4H_8$  yield (see text). <sup>*c*</sup> Recommended values  $E_{06} = 55$  kJ mol<sup>-1</sup> and  $E_{07} = 88$  kJ mol<sup>-1</sup> used. Stable species that we did observe, and that can be attributed at least in part to the isomerization channels, are 1- $C_3H_7CHO$  and 1- $C_4H_8$ . Butyraldehyde, which is the product of reaction (7), can also be formed as a result of reaction (2) by a  $\beta$ -O-H bond split of the  $\alpha$ -hydroxy-1-butyl radical. The energetically favourable decomposition path of this radical, however, is the  $\beta$ -C-C bond dissociation as mentioned above. Accordingly, the O-H bond split plays only a minor role, and the fractional contribution of this reaction route to the production of 1- $C_3H_7$ CHO should be negligible and by far below its hypothetical maximum value of  $Y_2/(Y_2 + Y_7) \approx 0.14$  (cf. Table 3). Therefore, the observed butyraldehyde yield is solely attributed to reaction (7).

1-Butene can result from an OH split-off from  $CH_3CH_2CH \cdot CH_2OH$ , which is the product of reaction (3). However, there is again an energetically favoured parallel channel leading to  $H_2CCHCH_2OH + CH_3$ . Anyway, reaction (3) alone would result in a 1-butene yield of at most ~1%, as becomes obvious from Table 3, and hence the observed yield of 55% cannot be explained by unimolecular isomerization/decomposition steps of the intermediate  $C_4H_9O$  radical. Apparently, there is a direct route leading from  $1-C_4H_8 + OH$  [reaction (1a)] with a fractional contribution of ~55% to the overall reaction. The nature of this route is not quite clear; however, some evidence for a direct meta-thesis will be given below.

The third stable product detected, HCHO, can be unambiguously attributed to the  $\beta$ -C–C bond dissociation of 1-C<sub>4</sub>H<sub>9</sub>O, reaction (6). Consequently, with the premises just stated, the observed ratio [HCHO]/[1-C<sub>3</sub>H<sub>7</sub>CHO] reflects the branching between reactions (6) and (7), a correspondence that can be used to verify in part the results of our quantum chemical calculations.

Inspection of Table 3 reveals that, based on the data of Tables 1 and 2, the relative contributions of reactions (6) and (7) are predicted in the correct order of magnitude if a fractional contribution of 0.55 for reaction (1a) is assumed. However, the predicted branching ratio between the C-C and the C-H bond dissociation is  $k_{06}/k_{07} = Y_6/Y_7 = 3.8$  (cf. Table whereas the experimental value is [HCHO]/[1-3),  $C_3H_7CHO$  = 7.5. Normally, equilibrium geometries and vibrational frequencies calculated by ab initio methods are much more reliable than the corresponding energies and, moreover, uncertainties in the energies have a much stronger influence on the calculated rate coefficients. Therefore, we used the threshold energies  $E_{06}$  and  $E_{07}$  as varying parameters and fitted the ratio  $k_{06}/k_{07}$  to the experimental value of [HCHO]/[1-C<sub>3</sub>H<sub>7</sub>CHO], leaving the frequencies unchanged. The calculated ratio can be increased from 3.8 to the observed value of 7.5 by decreasing  $E_{06}$  and/or increasing  $E_{07}$ . By keeping  $E_{07} = 83.22$  kJ mol<sup>-1</sup> fixed, the experimental ratio is obtained with  $E_{06} = 49.96$  kJ mol<sup>-1</sup>, and by keeping  $E_{06} = 60.06$  kJ mol<sup>-1</sup> fixed, the experimental set of  $E_{00} = 220$  kJ 60.96 kJ mol<sup>-1</sup> fixed, an optimum value of  $E_{07} = 93.39$  kJ mol<sup>-1</sup> resulted. If both  $E_{06}$  and  $E_{07}$  are simultaneously varied within this range, a branching ratio of 7.5 is always obtained for a difference  $E_{07} - E_{06} \approx 33$  kJ mol<sup>-1</sup>. This leads us to the following most likely values for the threshold energies:  $E_{06} =$  $55 \pm 6$  kJ mol<sup>-1</sup> and  $E_{07} = 88 \pm 6$  kJ mol<sup>-1</sup>. The relative product yields obtained by using these values are also contained in Table 3. The agreement with the experimental branching fractions is good.

As is outlined in Section 2.2, an inverted vibrational distribution is observed for OH. For the sake of comparison, we estimated the relative populations of the vibrational levels in the statistical limit, using a simple phase-space model<sup>48</sup> with the molecular data for  $1-C_4H_8$  from ref. 49 and for OH from ref. 50. We obtained relative populations of 1,  $5.5 \times 10^{-2}$ ,  $2.5 \times 10^{-3}$  and  $9.2 \times 10^{-5}$  for the vibrational states  $v_{\rm OH} = 0$ , 1, 2 and 3, respectively, which is clearly different from the distribution observed. This indicates that reaction (1a) probably is a direct abstraction process.<sup>51</sup>

## 5. Conclusions

The 1-C<sub>4</sub>H<sub>9</sub> + O reaction is likely to proceed *via* two parallel channels, which contribute nearly equally to the overall reaction. One is probably a direct abstraction channel leading to 1-C<sub>4</sub>H<sub>8</sub> and OH, and the second is an association process resulting in a chemically activated 1-butoxyl radical. Under low-pressure conditions, the latter essentially undergoes  $\beta$ -C-C and  $\beta$ -C-H bond dissociation. Isomerization products are not observed. The branching between these channels can be described by statistical rate theory using results from quantum chemical calculations. In this way, reliable threshold energies can be obtained.

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