Hydrogen Abstraction from *n*-Butyl Formate by H[•] and HO₂[•]

Wassja A. Kopp, Raymond T. Langer, Malte Döntgen, and Kai Leonhard*

Lehrstuhl für Technische Thermodynamik (LTT), RWTH Aachen, 52062 Aachen, Germany

E-mail: Kai.Leonhard@ltt.rwth-aachen.de

*To whom correspondence should be addressed

Abstract

The combustion chemistry of esters has been elucidated in the past through the study of smaller formates and acetates. Hydrogen abstraction from the fuel as an initiation step is mostly modeled based on estimations for similar abstractions from non-oxygenated hydrocarbons. This study reports computed *ab-initio* rates for abstractions by $\text{H}^\bullet$ and $\text{HO}_2^\bullet$ radicals from the recently proposed biofuel candidate *n*-butyl formate. The energies are evaluated with a double hybrid density functional that performs especially well for barrier heights (B2KPLYP/aug-cc-pvtz). Hindered rotation of $\text{HO}_2^\bullet$ with respect to *n*-butyl formate is treated using accurate eigenvalue summation and shows large influence on the rates. Transition states at the γ and δ positions are still influenced by the formate group. The abstraction from the γ carbon by $\text{HO}_2^\bullet$ is slowest, although proceeding over the lowest barriers, due to the important influence of transition state entropies. A comparison with smaller esters and *n*-butanol shows that estimated rates deviate within one order of magnitude from the *ab-initio* computations for similar groups in *n*-butyl formate.

Keywords: Hindered Rotor, Ester Conformers, Biofuel ignition, TAMkin

Introduction

Current biofuels used in diesel and homogeneous charge compression ignition (HCCI) engines often contain various large ester molecules.¹ In order to control their combustion and to reduce pollutants, one needs to know the combustion chemistry of these molecules.² Recent modeling has concentrated on smaller model compounds to learn about the basic combustion features of the various larger esters. Four small alkyl esters — methyl and ethyl formate (MF resp. EF) and methyl and ethyl acetate — have been studied by Westbrook *et al.*¹ Their approach reduces the number of different hydrogen abstraction rates to five (per abstracting radical) by treating groups with the same neighbors equally. This approach has then been extended by Yang *et al.* to larger alkyl esters — ethyl propanoate, methyl butanoate and

methyl *iso*-butanoate — all of which are $C_5H_{10}O_2$ isomers.³ A fourth $C_5H_{10}O_2$ isomer, *n*-butyl formate (BF), has been recently proposed as a biofuel itself. Subsequent studies on BF by Lee *et al.* revealed interesting low-temperature chemistry and highlighted the role of hydrogen abstraction reactions from the fuel.⁴ Despite their importance, hydrogen abstraction rates for BF as well as for the smaller esters are mostly based on estimations. Since BF contains groups present as well in EF or *n*-butanol, the model of Lee *et al.*⁴ used rates from these fuels that in turn have mostly been derived from non-oxygenated hydrocarbons. For example, the butanol data used in the model of Sarathy *et al.*⁵ for abstraction by $H\cdot$ radicals is based on the analogy to hydrocarbons⁶ while the data for abstraction by $HO_2\cdot$ radicals is based on *ab-initio* calculations from Zhou *et al.*⁷

Hydrogen abstraction in a general context has attracted a lot of interest. In the literature various methods have been studied to compute rate constants theoretically. Chan and Radom obtained rate constants from B2KPLYP barriers for hydrogen abstraction by a chlorine atom.⁸ Vandeputte *et al.* studied five hydrogen abstractions from alkanes and alkenes by a methyl radical with different methods and obtained best agreement with experiment using the Eckart tunneling correction and 1D hindered rotor (HR) about the forming bond.⁹ Hydrogen abstraction by H atoms from hydrocarbons and oxygenated hydrocarbons has been studied by Sumathi, Carstensen and Green where the existence of a moiety that is nearly constant with respect to different neighbored groups has been proposed. Rate rules have been derived from that.¹⁰ This approach has later been extended to hydrogen abstraction by methyl and hydrogen radicals from oxygenated hydrocarbons including smaller formates.¹¹

Hydrogen abstraction by $H\cdot$ radicals has been computed by Huynh, Lin and Violi¹² for the BF structural isomer methyl butanoate. The ignition behavior of methyl butanoate has been modeled extensively¹² to be used as a model for biodiesel, but, due to missing low temperature chemistry, methyl butanoate autoignition characteristics have turned out to be not similar to typical biodiesel behavior.¹³ The Huynh study reports barriers for abstraction by $H\cdot$ radicals computed at the BH&HLYP/cc-pVTZ level that are rather low compared

to unimolecular decomposition steps (e.g. 30 kJ/mol average barrier height for abstraction by $\text{H}^\bullet$ radicals compared to 290 kJ/mol being the lowest unimolecular decomposition height on BH&HLYP/cc-pVTZ level). The hydrogen abstraction reactions are therefore important initiation steps.

In this study we use double hybrid density functional theory (B2KPLYP¹⁴) to evaluate the energies of BF geometries obtained from the B3LYP functional and compute hydrogen abstraction rates for the lowest energy conformation. Abstraction by $\text{H}^\bullet$ radicals has been shown to dominate fuel consumption in low-pressure flames of MF.¹⁵ Abstraction by $\text{HO}_2^\bullet$ radicals was shown to be important in intermediate temperature shock tube ignition of e.g. *n*-butanol.¹⁶ We therefore compute rates for hydrogen abstraction from BF by $\text{H}^\bullet$ and $\text{HO}_2^\bullet$ radicals. Our computations extend the size of investigated formates, contribute to a refined BF mechanism¹⁷ and allow for a comparison with similarly structured alkyl esters.

Methods

The skeleton of BF consists of the seven first row atoms $\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-\text{C}=\text{O}$. We use dihedral angles defined for each set of four consecutive atoms of the skeleton to describe the conformations. For each dihedral angle we performed relaxed torsional scans. The gaussian program suite version 03 has been used throughout all of the electronic structure calculations.¹⁸ From the scan of one dihedral angle we obtained minima that we used as starting points for the scan of the next dihedral angle as well as for full optimization of the resulting minimum structure.

In order to obtain starting points for transition state (TS) structure optimization, we scanned the potential energy of the respective bond being formed during the reaction. From the maximum showing up in the scan, a subsequent optimization converged to the desired TS. The direction of the vibration eigenvector corresponding to the imaginary frequency indicated that the found TS really corresponds to the hydrogen abstraction reaction. In the

TS the dihedral angles corresponding to hindered rotation of HO_2 with respect to BF have been scanned, but the intramolecular dihedral angles of the BF backbone in the TSs have not been scanned. The two intermolecular dihedral scans are described below.

Figure 1: Lowest energy BF conformation with numbering of dihedral angles, carbon (grey), oxygen (red) and hydrogens (white). Here, the HO_2 radical abstracts hydrogen no. 3 from the δ carbon. The two axes (O–O axis and reaction axis) around which hindered rotation is computed in this study are shown.

The frequencies — that play an important role in thermochemistry and kinetics — have been obtained with the B3LYP functional because the standard deviation of such frequencies from experimental ones is even lower than the deviation of frequencies obtained with MP2 from experimental ones.¹⁹ Rate constant computations require knowledge of the frequencies for the computation of free enthalpies $G = H - TS$. Scaling factors (for B3LYP, 6-311+G(d,p)²⁰) to reproduce experimental thermochemical data at 600 K for the B3LYP functional amount to 0.9953 for enthalpies and to 1.0046 for entropies. We therefore decided to leave the frequencies unchanged. In order to do the normal mode analysis in a minimum, the geometries should of course be obtained with the same method as the frequencies. There-

fore we used the B3LYP functional with TZVP (triple- ζ valence polarizable) basis set for all geometry optimizations, scans and frequency calculations. We applied an ultrafine grid for DFT integration (99 radial shells and 590 angular points per atom) and tight convergence criteria for optimization (maximum force $< 1.5 \times 10^{-5}$ a.u.). In contrast, throughout the scans gaussian03 standard settings were used.

Single point energies for reactants, TSs and products have been evaluated on the optimized geometries with a computationally more demanding double hybrid functional. Modern fifth-rung density functionals improve the exchange-correlation energy using a second-order perturbation term (PT2) for the correlation in addition to the hartree-fock (HF) exchange term in standard hybrid functionals.²¹ These functionals can be improved for the calculation of barriers. In the B2KPLYP functional, the two fractions of the exchange HF and the correlation PT2 part have been adjusted to yield more accurate barrier heights. Indeed, for a test set of 38 hydrogen transfer reactions, this functional yields barrier heights with a root-mean squared (rms) error of 3.6 kJ/mol. For databases with hydrogen bonded systems, B2KPLYP performs even better.¹⁴ The functional is therefore well applicable to the $\text{BF} + \text{H}^\bullet / \text{HO}_2^\bullet$ case. Since this functional is not implemented in gaussian03, we mixed the PT2 term with the other terms by adding 0.42 times the second-order energy (E2) term to the self consistent field energy (as described in the original B2KPLYP paper¹⁴ in footnote 47). We applied the aug-cc-pVTZ basis set to compute the B2KPLYP energies because the developers of that functional found barriers obtained with diffuse quadruple- and quintuple- ζ basis sets essentially indistinguishable from those obtained with diffuse triple- ζ basis sets.

A comparison of various tunneling methods applied to hydrogen abstraction by CH_3 radicals showed that Eckart tunneling outperforms both the Wigner as well as the Skodje & Truhlar tunneling methods.⁹ The underestimation of the tunneling effect by zero-curvature methods partly compensates the overestimation of the reaction rate by non-variational transition state theory (TST).⁹ Therefore in this study reaction rates have been determined using

conventional TST for ideal gases according to

$$k_{\text{TST}}(T) = \frac{k_{\text{B}}T}{h} \frac{Q_{\text{TS}}}{Q_{\text{Reac}}} \exp\left(-\frac{\Delta E_{\text{B}} + \text{ZPE}}{k_{\text{B}}T}\right) \quad (1)$$

with Q_i being the partition function of the TS or the reactants (Reac) and $\Delta E_{\text{B}} + \text{ZPE}$ being the energy barrier including zero-point energy. Then this classical rate is multiplied with the tunneling factor $\kappa(T)$ corresponding to tunneling along an unsymmetrical eckart-shaped potential (also called Zero-Curvature Tunneling, ZCT).

$$k(T) = \kappa(T) \cdot k_{\text{TST}}(T) \quad (2)$$

For reactions with $\text{H}^\bullet$ radicals the corresponding IVTST-0 option in polyrate2008 has been used.²² For reactions with $\text{HO}_2^\bullet$ radicals, unsymmetrical eckart corrections have been used as they are implemented in the TAMkin package²³ that can also treat hindered rotation properly which is described in the following.

TSs for reactions with $\text{HO}_2^\bullet$ radicals contain two hindered rotation modes for each hydrogen abstraction that occur neither in the reactants nor in the products. In the following we apply a nomenclature that consists of two parts: i for a carbon atom and ij for a certain hydrogen atom which is bound to the carbon atom i . The indices $i = \alpha, \beta, \gamma, \delta, \text{f}$ and $j = \{12, 13\}; \{9, 10\}; \{6, 7\}; \{2, 3, 4\}; \{16\}$, i.e. an appropriate number that depends on i , can be found in Figure 1. Thus ij denotes an arbitrary hydrogen atom of BF whereas αj refers to $\alpha 12$ as well as $\alpha 13$. The first mode, rotation around the reaction axis (RA), corresponds to the dihedral angle DRA_{ij} : $\text{O}_{\text{outer}} - \text{O}_{\text{inner}} - i - i'$, where i is the carbon atom to which the abstracted hydrogen ij is bound to and i' is an arbitrary neighbored carbon atom or in the case of $ij = \text{f}16$ one of the neighbored oxygen atoms (O_{carb} or O_{ester}). The fourth atom can be chosen arbitrarily since no absolute values will be used. The second mode refers to rotation around the O—O axis that changes the dihedral angle DHO2_{ij} :

$\text{H}_{\text{term}}-\text{O}_{\text{outer}}-\text{O}_{\text{inner}}-ij$. These modes have been treated explicitly as hindered rotations. Further torsional modes (i.e. intramolecular torsions in BF) have not been modeled as hindered rotations but rather treated harmonically around the equilibrium position based on the BF lowest energy conformation that we have determined before. Nevertheless, coupling can link the two intermolecular modes investigated (DRA and DHO2) to each other and to the torsional intramolecular modes in BF. An exact treatment of coupled degrees of freedom is in principle possible and has been described in the literature, but has so far been limited to systems of 4 to 6 atoms.^{24,25} Approximate methods have been applied to larger systems but still require knowledge of all reactant conformations and of all transition state conformations. This can be a challenging task as has been demonstrated for abstraction from the γ -carbon of *n*-butanol with 262 transition state conformations.²⁶ The conformations can then be taken into account approximately, e.g. via a rotational-conformer distribution partition function²⁷ or by multi-structural interpolation schemes between low-temperature and high-temperature hindered rotor limits.²⁸ For intramolecular modes the contributions to the free energy difference between the TS and the reactants will partially cancel. For the two intermolecular torsions DRA and DHO2 in turn this will not be the case. Therefore we can include a great part of torsional anharmonicity by focusing on these two modes. This gives a feasible approach to determine abstraction rates for each BF hydrogen including hindered rotor effects. The partition function for each hindered rotator has been obtained from accurate eigenvalue summation while the eigenvalues have been obtained from solutions to the Schroedinger Equation containing the torsional potential from the previously described dihedral scans.

A fourier series has been fitted to the potential points computed in the dihedral scans. The size of the series has been varied for all the sites and modes to get the best compromise between low deviation and avoidance of oscillations. The vibrational partition function of the TS has been multiplied with the partition functions of the hindered rotors and divided by the corresponding harmonic oscillator (HO) partition functions. The frequencies for the

eliminated HOs have been derived from the curvature in the minimum of the torsional scan as recommended by Ghysels *et al.*²³ Then again reaction rates have been derived according to eq 2. All these steps have been performed with the python package TAMkin.²³

The uncertainty of the calculated rates is site-specific and discussed at the end of the results and discussion section.

Results & Discussion

The conformations of BF²⁹ have been determined (as described in the methods section) from the 19 minima of the torsional scans. Of these minima, 18 have a mirror counterpart each. The energies of the conformations have been evaluated both at B3LYP/TZVP and B2KPLYP/aug-cc-pVTZ levels of theory. For both methods, the lowest energy conformation turned out to be D1,D2,D3,D4 $\approx 180^\circ, \pm 60^\circ, 180^\circ, 0^\circ$ (cf. Table 1 for dihedral definition). The order of the conformations with respect to their energies is the same for both methods. Conformations for which D4 $\approx 180^\circ$ are more than 10 kJ/mol higher in energy than those for which D4 $\approx 0^\circ$.

Table 1: Definition of dihedral angles D1,D2,D3,D4 via atom labels (cf. Figure 1 for atom labels). The axis, which is defined by Atom 2 and Atom 3 represents the axis of rotation.

Dihedral Angle	Atom 1	Atom 2	Atom 3	Atom 4
D1	carboxylic oxygen	f	ester oxygen	α
D2	f	ester oxygen	α	β
D3	ester oxygen	α	β	γ
D4	α	β	γ	δ

Internal rotations of gas-phase *n*-alkanes can be well described within an uncoupled scheme.³⁰ A similar investigation of oxygenated hydrocarbons shows that the uncoupled model can still describe well the conformational behavior of e.g. ethers and alcohols.³¹

We compare the conformational behavior of BF to the one of *n*-butanol because the

long alkyl chain here is most similar. Despite that, the conformational behavior of the two substances is different. Differences affect mostly the dihedral angle D3 and arise from the carboxylic oxygen (O_{carb}) that pulls electrons from the formate carbon making it the only positively charged carbon of the molecule. Thus when the positively charged and more extended formate group C–H end approaches the also positively charged hydrogens of the other groups, more repulsion arises in comparison to the single –H end in *n*-butanol. The D3 dihedral angle value therefore increases from $\approx 60^\circ$ for *n*-butanol to values for BF between $87^\circ < D3 < 89^\circ$ if D4 is in *cis*-conformation (mainly the formate carbon is repelled) or even to $100^\circ < D3 < 130^\circ$ if D4 is in *trans*-conformation (where the formate carbon and hydrogen are repelled).

Furthermore, some conformations that are reported for *n*-butanol³² could not be optimized at all in the BF case or only for one orientation of the O–(C=O)–H end. The two conformations with $D2 \approx 180^\circ$ or 60° and $D3 \approx 60^\circ$, $D4 \approx -60^\circ$ appear only with the *trans* position of D4 that is energetically much higher (see above). In addition, the conformations with $D2, D3, D4 \approx 60^\circ, -60^\circ, 60^\circ$ (that are similar to the stable *n*-butanol gg'g conformation³²) are not stable at all since the positive ends of the molecule repel each other. Similar conformations of the radical $(\text{CH}_2)_4\text{O}(\text{CHO})$, however, are stable as is discussed below.

The various conformations will affect the thermochemistry of BF, e.g. the heat capacity is increased since with rising temperature, higher energy conformational states will get more populated leading to an additional heat consumption. Concerning the reaction rates, we expect that part of that influence will cancel since the same conformations will be similarly present in the TSs. This is not true for the two hindered rotations of $\text{HO}_2^\bullet$ with respect to the molecule that are uniquely present in the TSs and are later shown to have large influence. All following rate computations are based on the BF lowest energy conformation.

For the unsymmetrical Eckart tunneling correction one needs the potential energies of reactants, TS and products, in particular the BF radicals. The radicals have been optimized after the proper hydrogen was deleted from the minimum energy BF conformation. The

special case for δ radicals to form a metastable ring has been evaluated; but since the corresponding electronic reaction energy both at B3LYP and B2KPLYP level exceeds the energy of the linear radical conformations by 22 kJ/mol, we used the linear fuel radical conformations throughout. The reaction energies of $\text{BF} + \text{H}^\cdot / \text{HO}_2^\cdot$ yielding $\text{H}_2 / \text{H}_2\text{O}_2$ and the corresponding radical are listed in Table 2 and Table 3. The reaction energy is defined by $\Delta E_{\text{R}} = E_{\text{BF}^\cdot} + E_{\text{H}_2 / \text{H}_2\text{O}_2} - E_{\text{BF}} - E_{\text{H}^\cdot / \text{HO}_2^\cdot}$ and the barrier is defined by $\Delta E_{\text{B}} = E_{\text{TS}} - E_{\text{BF}} - E_{\text{H}^\cdot / \text{HO}_2^\cdot}$. The reaction energy difference between abstraction by $\text{H}^\cdot$ and $\text{HO}_2^\cdot$ amounts constantly to 63.35 kJ/mol in electronic energy and to 69.1 kJ/mol when ZPE is included.

Table 2: Barrier heights and reaction energies for $\text{BF} + \text{H}^\cdot$ reaction, imaginary frequency and length of formed and broken bonds obtained from B3LYP/TZVP geometries and frequencies (cf. Supporting Information) and B2KPLYP/aug-cc-pVTZ energies (+ZPE: ZPE corrected).

Hydrogen No. (cf. Figure 1)	ΔE_{B} [$\frac{\text{kJ}}{\text{mol}}$]	$\Delta E_{\text{B}} + \text{ZPE}$ [$\frac{\text{kJ}}{\text{mol}}$]	ΔE_{R} [$\frac{\text{kJ}}{\text{mol}}$]	$\Delta E_{\text{R}} + \text{ZPE}$ [$\frac{\text{kJ}}{\text{mol}}$]	ν_{im} [$i \text{ cm}^{-1}$]	H $\cdots$ H [$\text{\AA}$]	H $\cdots$ C [$\text{\AA}$]
$\delta 2$	50.73	43.96	2.12	-11.13	1192	0.927	1.366
$\delta 3$	51.17	44.38	2.12	-11.18	1199	0.926	1.367
$\delta 4$	52.19	45.59	3.42	-9.61	1200	0.923	1.367
$\gamma 6$	44.21	36.83	-9.21	-22.51	1218	0.953	1.327
$\gamma 7$	40.53	33.28	-9.21	-22.51	1176	0.965	1.320
$\beta 9$	45.71	38.27	-4.64	-17.10	1224	0.951	1.336
$\beta 10$	45.98	38.66	-4.64	-17.10	1238	0.957	1.330
$\alpha 12$	42.96	35.88	-11.79	-23.47	1268	0.990	1.295
$\alpha 13$	44.12	36.9	-11.79	-23.47	1276	0.985	1.302
f16	45.50	38.55	-12.61	-19.75	1339	0.989	1.314

Table 3: Barrier heights and reaction energies for BF + HO₂ reaction, imaginary frequency and length of formed and broken bonds obtained from B3LYP/TZVP geometries and frequencies (cf. Supporting Information) and B2KPLYP/aug-cc-pVTZ energies (+ZPE: ZPE corrected).

Hydrogen No. (cf. Figure 1)	ΔE_B [$\frac{\text{kJ}}{\text{mol}}$]	$\Delta E_B + \text{ZPE}$ [$\frac{\text{kJ}}{\text{mol}}$]	ΔE_R [$\frac{\text{kJ}}{\text{mol}}$]	$\Delta E_R + \text{ZPE}$ [$\frac{\text{kJ}}{\text{mol}}$]	ν_{im} [$i \text{ cm}^{-1}$]	O $\cdots$ H [$\text{\AA}$]	H $\cdots$ C [$\text{\AA}$]
$\delta 2$	88.84	75.04	65.48	57.97	1633	1.158	1.389
$\delta 3$	84.99	72.99	65.48	57.92	1627	1.147	1.411
$\delta 4$	93.68	80.00	66.77	59.49	1637	1.151	1.393
$\gamma 6$	61.71	50.59	54.14	46.59	1672	1.155	1.398
$\gamma 7$	66.72	54.90	54.14	46.59	1678	1.153	1.397
$\beta 9$	83.92	69.26	58.71	52.00	1660	1.161	1.387
$\beta 10$	86.82	72.36	58.71	52.00	1687	1.167	1.379
$\alpha 12$	74.00	61.38	51.56	45.63	1695	1.149	1.397
$\alpha 13$	73.79	60.86	51.56	45.63	1692	1.148	1.399
f16	80.28	66.90	50.75	49.35	1556	1.145	1.407

Since barriers for abstracting hydrogens even of the same group can differ both in energy and entropy, we investigated all 10 hydrogens of BF.²⁹ The TS data in Table 2 show that with decreasing distance from the formate group, the TSs become earlier. So, corresponding to the Hammond postulate,³³ the reaction energies get more exothermic (except for the formate group). The imaginary frequencies rise from 1192 to 1276 (or even 1339 $i\text{cm}^{-1}$ for the formate group) due to the larger curvature at the barrier. Compared to the literature methyl butanoate barrier heights (from the older BH&HLYP hybrid functional and the smaller cc-pVTZ basis set),¹² the BF barrier heights are $\sim 50\%$ larger.

Reaction Rates for hydrogen abstraction from BF by H $\cdot$ are computed based on the TS information (B2KPLYP energies) presented above. The parameters for the modified Arrhenius expression for the rate $k(T) = A \cdot T^n \cdot \exp(-\frac{E_a/R}{T})$ in units $\frac{\text{cm}^3}{\text{mol}\cdot\text{s}}$ fitted to the computed data can be found in Table 4. The rates for abstraction of different hydrogens from the same carbon are reported individually as well as summed up. The maximum deviation of the fit from the computed rates between 600 and 2000 K remains below 7%.

Table 4: Arrhenius parameters of BF + H $\cdot$ hydrogen abstraction from BF groups.

	$A[\frac{\text{cm}^3}{\text{mol}\cdot\text{s}}]$	n	$E_a[\frac{\text{J}}{\text{mol}}]$
$\delta 2$	1.1730E+05	2.5649	31626
$\delta 3$	1.0334E+05	2.5771	31911
$\delta 4$	1.3118E+05	2.5754	33289
δ	1.153E+06	2.43	33815
$\gamma 6$	1.5896E+05	2.5509	24890
$\gamma 7$	2.5556E+05	2.4743	22190
γ	6.143E+05	2.46	23987
$\beta 9$	1.2209E+05	2.5642	26273
$\beta 10$	1.2314E+05	2.5911	26507
β	9.039E+06	2.13	30464
$\alpha 12$	7.3851E+04	2.5973	23355
$\alpha 13$	5.3686E+04	2.6253	24107
α	1.065E+06	2.35	26124
f16	8.4314E+04	2.6570	25648

Frequently, reaction barriers and rates are estimated based on the corresponding bond dissociation energies or based on the corresponding reaction energies using Evans-Polanyi-like relationships^{34 35 36}. The calculated barriers for hydrogen abstraction by H $\cdot$ radicals correlate well both with bond dissociation energies (BDEs), cf. Table 5, and with the corresponding heat of reactions. The trend of the barriers can be described by $\Delta E = 0.55 \cdot \Delta E_{\text{R_H}} + 49.4\text{kJ/mol} = 0.62 \cdot \text{BDE} - 208.5\text{kJ/mol}$. The energies predicted by the correlation with BDEs deviate from the calculated ones by -0.6/+3.9 kJ/mol (cf. Figure 2) while those predicted by the correlation with ΔE_{R} deviate by -2.5/+3.3 kJ/mol (cf. Figure 3). These deviations are of similar magnitude as standard deviations of model chemistry predictions like CBS-QB3.

Table 5: C–H bond dissociation energies of BF from Vranckx *et al.*¹⁶

C–H bonds	BDE butyl formate [$\frac{\text{kJ}}{\text{mol}}$]
f	411
α	406
β	414
γ	409
δ	420
$\delta 4$	421

Figure 2: Barriers for $\text{H}^\bullet$ and $\text{HO}_2^\bullet$ as function of the bond dissociation energy. Based on the data points linear regression was performed.

Barriers for abstraction by $\text{HO}_2^\bullet$ radicals as calculated in this study do not correlate so well neither with BDEs (cf. Figure 2) nor with the corresponding heat of reactions (cf. Figure 3). Maximum deviations are especially large ($-5.8/+13.1$ kJ/mol) for abstraction from the γ -site. The trends including barriers at all sites read $\Delta E = 1.29 \cdot \Delta H_r + 5.1 \text{ kJ/mol} = 1.45 \cdot \text{BDE} - 517.6 \text{ kJ/mol}$. If the γ site is excluded, the trends read $\Delta E = 0.96 \cdot \Delta H_r + 26.8 \text{ kJ/mol} = 1.08 \cdot \text{BDE} - 362.4 \text{ kJ/mol}$ and the maximum deviations reduce to $-4.2/+6.3$ kJ/mol. This shows that the special behavior with $\text{HO}_2^\bullet$ at the γ -site is not related to the abstraction site so that the activation energy would correspond to the site-specific energies. It is rather influenced by the energy-lowering hydrogen bonded type interactions to the formate group.

Figure 3: Barriers for $H^\bullet$ and $HO_2^\bullet$ as function of the electronic reaction energy. Based on the data points linear regression was performed.

Abstraction by $HO_2^\bullet$ leads, in contrast to abstraction by $H^\bullet$, to two intermolecular hindered rotations per abstraction site that are described in the following.

Figure 4: Diagrams of the two scanned internal coordinates (DHO2 and DRA) in $\text{BF} + \text{HO}_2$ TSs. Both start in the same rotational minimum. While the shape of the DRA potentials differs with the abstracted hydrogen, there is a uniform pattern in the DHO2 potentials.

Hydrogen abstraction by HO_2 radicals is more complicated since the radical can approach the molecule in different more or less favorable orientations. The detailed potential energy scans with the allowed energy levels for the one-dimensional hindered rotations connecting these orientations are given in the Supporting Information. The characteristic data of the rotational potential energy profiles are collected in Table 6.

Table 6: Potential energy of $\text{H} \cdots \text{O}-\text{O}-\text{H}$ rotation in the TSs relative to the lowest energy orientation (cf. Fig 4).

E [$\frac{\text{kJ}}{\text{mol}}$]	0° Max.	2 nd Min.	180° Max.
$\delta 2$	42	2	24
$\delta 3$	41	0	23
$\delta 4$	41	3	26
$\gamma 6$	35	4	33
$\gamma 7$	48	5	42
$\beta 9$	31	0	25
$\beta 10$	43	0	24
$\alpha 12$	35	4	35
$\alpha 13$	35	4	35
f16	33	0	30

Hindered rotation of the terminal hydrogen (H_{term}) of $\text{HO}_2^{\cdot}$ around DHO2_{ij} has the same form in each TS of this study. Two minima at $\text{DHO2}_{ij} = 90^\circ(\pm 10^\circ)$ and $270^\circ(\pm 10^\circ)$ are separated by two maxima (cf. Fig 4). The rotational barriers are higher for this rotation mode than for the DRA_{ij} modes i.e. rotation of the $\text{O}-\text{H}$ tail. The highest maximum arises mostly from rotation of the H_{term} into the plane formed by the oxygen atoms of $\text{HO}_2^{\cdot}$ and the hydrogen to be abstracted (corresponding to $\text{DHO2}_{ij} = 0^\circ$ or *cis*-position of $ij-\text{O}-\text{O}-\text{H}$). This barrier varies between 30 to 50 kJ/mol in excess of the TS barrier height. The other maximum on the opposite side showed excess energies from 20 to 40 kJ/mol. The energy levels up to the energy maxima are grouped in 6 to 8 pairs. Energy levels above the lower maximum are denser and of roughly equidistant spacing up to the higher maximum, above which the levels are spaced similar as in a free rotor. There is no such uniformed pattern for the potentials resulting from scans of DRA_{ij} .

In the lowest BF conformation the carbon atoms α , β , γ , δ lie approximately in the same plane ($\text{D1} \approx 180^\circ$, 'alkyl-plane'), which will be used as a reference to illustrate the locations of the hydrogen atoms as well as the change of the conformation of the heavy atoms. As depicted in Figure 1. positive sense of rotation, i.e. increase of a dihedral angle, is defined by the axis intersecting the inner atoms and pointing away from BF.

Abstraction from the δ -carbon atom can take place at three distinct locations since the conformation of lowest energy is not a symmetrical one.

Hydrogen atom $\delta 2$ (Figure 1) is located opposite to the formate group (*trans*-position of dihedral angle D: $\delta 2 - \delta - \alpha - \text{O}_{\text{ester}} \approx 180^\circ$). The DHO2_ $\delta 2$ rotation mode couples strongly to the DRA_ $\delta 2$ rotation mode between the maximum and the second lowest minimum of the potential (DHO2_ $\delta 2 = 0 \dots 100^\circ$). During the DHO2_ $\delta 2$ rotation mode, the outer oxygen (O_{outer}) moves from the side of the molecule to the back between the two other δ -carbon hydrogens ($\delta 4$, $\delta 3$) that leads to a large variation in DRA_ $\delta 2$ of $\pm 150^\circ$.

Hydrogen atom $\delta 3$ is placed at the same side of the molecule as the formate group, between the hydrogens $\beta 6$ and $\gamma 9$ (all atoms lie above the alkyl plane, Figure 1). Through the gap between $\beta 6$ and $\gamma 9$ the H_{term} of the $\text{HO}_2^\bullet$ radical can interact with the ester oxygen (O_{ester}) of the formate group slightly bending the molecule, i.e. α and β are pulled above the alkyl plane. This leads to the lowest reaction energy barrier (of 85 kJ/mol) at the δ -carbon. If this interaction is not present because the $\text{HO}_2^\bullet$ is rotated away from the formate group, the reaction barrier height increases to 93 kJ/mol. The interaction causes a strongly curved minimum in the DRA_ $\delta 2$ rotation mode.

The third hydrogen $\delta 4$ is placed in the alkyl plane (*gauche*-position in dihedral angle D: $\delta 4 - \delta - \alpha - \text{O}_{\text{ester}} \approx 60^\circ$). The barrier for abstraction of this hydrogen amounts to 94 kJ/mol and is the highest of the BF+ $\text{HO}_2^\bullet$ barriers. Rotating the O_{outer} (DRA_ $\delta 4$ mode) out of the minimum lets the radical interaction with one γj -hydrogen change to the other $\gamma j'$ -hydrogen at negligible higher energy after overcoming a small barrier less than 1 kJ/mol while crossing the alkyl plane. Rotating the H_{term} (DHO2_ $\delta 4$) onto the opposite side yields a second minimum of essentially the same energy.

Figure 5: Scan steps for hindered rotation of HO_2 abstracting the $\text{H } \gamma_7$

Figure 6: Potential energy surface for the hindered rotor scan of DHO2_γ7 dihedral. The letters correspond to the pictures in Fig 5. The two different colors correspond to the different rotational senses in which the scans have been performed both starting at structure (a).

The lowest energy barriers for hydrogen abstraction by $\text{HO}_2^\bullet$ from BF occur at the γ -carbon. This is obviously due to an energetically favorable interaction with the formate group.

For the abstraction of $\gamma 6$, there are two BF conformers possible. The barrier for abstraction of hydrogen amounts to 75 kJ/mol if the H_{term} interacts with the O_{ester} and to 62 kJ/mol if it interacts with the O_{carb} . There are two reasons why we compute the rate constant based on the latter TS: One reason is that the interaction with the O_{carb} yields the lowest energy TS. The other reason is that rotation around DRA_γ6 starting at the higher energy TS containing the interaction with the O_{ester} quickly disrupts the interaction and finally ends up in the lowest energy TS by interaction with the O_{carb} . The corresponding interaction with the O_{carb} in the lowest energy TS leads to a BF conformer that is not the lowest one in the absence of the radical. This conformation is maintained when the H_{term} is rotated away from the formate group.

For $\gamma 7$, the H_{term} can interact with O_{carb} and thereby attracts the formate group. This changes the BF conformer (D3 decreases from 180° to about 120°) and results in a low

barrier of 67 kJ/mol.

Dependent on the rotational sense different conformations emerge in course of the DHO2_ γ 7 scan due to the interaction between the H_{term} and the O_{carb}. In the case of decreasing DHO2_ γ 7 the H_{term}, though being rotated out of the torsional minimum (cf. Fig 5(a)), initially remains bound (cf. Fig 5(b), 5(c)). In this region of the scan the DHO2_ γ 7-rotation couples strongly with the DRA_ γ 7 rotation, so that the O_{outer} is rotated by 90°. Thereby the H_{term} stays orientated to the formate group until the distance between the formate group and the O–H tails becomes too large and the interaction is finally disrupted (DHO2_ γ 7 $\approx$ 220°) (cf. Fig 5(d)). This interaction results in a lower potential energy between 180° and 360°.

Rotation in opposite sense (increasing DHO2_ γ 7) disrupts the hydrogen bond at Δ DHO2_ γ 7 = 60° which finally yields the higher energy conformation at DHO2_ γ 7 = 250° (cf. Fig 5(e)). Further rotation leads to an interaction between the H_{term} and O_{ester} at DHO2_ γ 7 = 330° and a higher potential energy from 250 to 360° (cf. Fig 5(f)).

In the non-hydrogen bound regime between 180 and 220° the conformations resulting from the scans in both directions are of similar energy although their DRA_ γ j values differ by 180° since the scan decreasing the DHO2_ γ 7 dihedral couples to the DRA_ γ 7 mode as previously described.

In order to describe the DHO2_ γ 7 rotation within our decoupled scheme, we combine the points of lowest energy from both scans (as can be seen in Fig 6) to a continuous potential of lowest energy along all DHO2_ γ 7 values.

In the TS for abstracting β 10, the HO₂ does not interact with the formate group leading to a high barrier (87 kJ/mol) of abstraction. The barrier for abstracting the other hydrogen β 9 is 3 kJ/mol lower. Here, rotation of the H_{term} (DHO2_ β 9) couples strongly with the rotation of the O_{outer} (DRA_ β 9) and slightly with the formate group rotation (D3).

In the α TSs, the H_{term} of HO₂ interacts with the O_{carb} (O_{carb}) while the BF part remains in the lowest energy reactant conformation. Rotating the O_{outer} away (increasing DRA_ α j) breaks the interaction with the O_{carb} and yields a second (higher) minimum by interaction

of the H_{term} and the O_{ester} . Further rotation lets the H_{term} again attract the O_{carb} , slightly turning the formate group, yielding the lowest energy TS again.

Rotation of the H_{term} ($DHO2_aj$) couples strongly to the rotation of the O_{outer} 8. Starting with the H_{term} located between O_{carb} and the O_{outer} (cf. Fig 7(a)), decrease of $DHO2_aj$ yields a different result than increasing orientation. Both orientations disrupt the interaction between the O_{carb} and the hydrogen.

Figure 7: Scan steps for hindered rotation of HO_2 abstracting an α H

Figure 8: Potential energy surface of the hindered rotor scan of DHO2_ αj dihedral. Coupling leads to several possible paths of local minimum energy (different colors). The letters correspond to the pictures in Fig 7. The two different colors correspond to the different rotational senses in which the scans have been performed both starting at structure (c).

For decreasing DHO2_ αj , initially the O_{outer} is rotated away from the formate group in a positive rotational sense yielding a less favorable interaction with the other α -carbon hydrogen ($\alpha j'$, cf. Fig 7(b)). Due to the repulsion between O_{outer} and O_{carb} the distance between the formate group and the radical increases. Further decrease of DHO2_ αj finally pushes the O_{outer} – H_{term} tail to the side of the O_{ester} where the H_{term} again starts interacting with the O_{carb} (cf. Fig 7(c)). For this orientation, the movement comes out at the starting point after 360°, but there is a jump in the potential.

For increasing DHO2_ αj disruption of the initial interaction between the H_{term} and the O_{carb} pushes the O_{outer} in direction of the O_{ester} (decreasing DRA_ αj). After 360° rotation, the lowest energy TS from which the motion started is not reached again since the O_{outer} has been rotated away due to coupling (cf. Fig 7(d)).

To describe the DHO2_ αj rotation within our decoupled scheme, we again combine the points of lowest energy from both scans (as can be seen in Fig 8) to a continuous potential of lowest energy along all DHO2_ αj values. To fit both rotation directions into one potential,

we kept the two maxima that showed up with increasing dihedral angle and chose as second lowest minimum the one where the O_{outer} has flipped (cf. Fig 7(c)), thus minimizing the potential energy.

Abstraction of the formate group hydrogen f16 by HO₂ proceeds over a barrier of 80 kJ/mol; the hindered rotations are smooth with little coupling. From this HR treatment we deduced rate constants using TST as described in the method section.

Arrhenius expressions have been fitted to the computed rates, both with hindered rotor treatment (HR) and without (HO) (cf. Table 7). The maximum deviation of the fit from the computed rates between 600 and 1900K remains below 10%.

Table 7: Arrhenius parameters of BF + HO₂ hydrogen abstraction from BF groups.

	HO $A[\frac{\text{cm}^3}{\text{mol}\cdot\text{s}}]$	HR $A[\frac{\text{cm}^3}{\text{mol}\cdot\text{s}}]$	HO n	HR n	HO $E_a[\frac{\text{J}}{\text{mol}}]$	HR $E_a[\frac{\text{J}}{\text{mol}}]$
$\delta 2$	1.6262E-02	8.1468E+00	4.2478	3.5785	63521	67409
$\delta 3$	7.8915E-04	2.3365E+00	4.1782	3.4571	60919	67281
$\delta 4$	2.6313E-02	1.1949E+01	4.2672	3.6013	68524	70601
δ	3.6527E-02	1.1464E+01	4.9734	4.3011	60813	62971
$\gamma 6$	3.7680E-03	4.0238E-03	3.8713	4.0528	41808	45199
$\gamma 7$	2.4703E-03	7.7712E-02	4.0115	3.7599	44453	50893
γ	1.8109E-01	4.3301E-02	4.1586	4.5201	41486	42978
$\beta 9$	9.9898E-03	8.4884E+00	4.2631	3.6071	58235	61682
$\beta 10$	2.2939E-02	1.1092E+01	4.3001	3.5946	60913	64048
β	2.7582E-02	7.6348E+00	4.9467	4.3528	54505	56473
$\alpha 12$	1.7295E-03	8.8597E-01	4.1768	3.6792	49780	56991
$\alpha 13$	1.5195E-03	3.2595E-01	4.1900	3.7998	49189	56120
α	1.3835E-02	2.8360E-01	4.6382	4.5421	45644	49805
f16	7.4953E-02	1.3855E-01	4.1540	4.2100	57181	54358

In order to derive an uncertainty factor for our computed rates, we apply eq 3³⁷ to the logarithm of the rate from TST formulation. The exponential of the resulting Δz yields the computational uncertainty factor. We can thereby assess analytically the uncertainties arising within TST using the HO model for the vibrations. For a general property z the

uncertainty Δz depends on the parameters x_i as:

$$\Delta z = \sqrt{\sum_i^n \left| \frac{\partial z}{\partial x_i} \Delta x_i \right|^2} . \quad (3)$$

The property of interest here is the reaction rate from the TST formulation according to eq 1. We split the logarithm of the rate into the individual translational, rotational and vibrational contributions of the TS and the reactants as

$$\begin{aligned} \ln k = & \ln \frac{k_B T}{h} + \ln q_{\text{rot_TS}} \cdot q_{\text{trans_TS}} - \sum_{\text{Reac}} \ln q_{\text{rot_Reac}} q_{\text{trans_Reac}} - \sum_i^{n_{\text{TS}}} \ln \left(1 - \exp \left(-\frac{\nu_i}{k_B T} \right) \right) \\ & + \sum_j^{n_{\text{Reac}}} \ln \left(1 - \exp \left(-\frac{\nu_j}{k_B T} \right) \right) - \frac{\Delta E_B}{k_B T} + \frac{E_{\text{ZPE_TS}}}{k_B T} - \frac{E_{\text{ZPE_Reac}}}{k_B T} . \end{aligned} \quad (4)$$

E_{ZPE_i} refers to the zero point energy of the species that can be obtained from proper differences of the columns in Tables 2 respectively 3. We neglect any uncertainty in the translational and rotational partition function q_{trans} and q_{rot} but rather concentrate on frequencies ν_i (in the formulas already scaled by hc ; the total number of frequencies for a species is named by n_{TS} or n_{Reac}) and energies. From $\frac{\partial \ln k}{\partial x_i}$ follow the individual sources of uncertainty evaluated for a temperature of 1000 K which often occurs in combustion processes. The corresponding standard deviations Δx_i for the various properties have been obtained from the literature as described below.

RMS errors for vibrational frequencies can be obtained from the comparison by Merrick *et al.*²⁰ of vibrational frequencies obtained from B3LYP DFT with several Pople basis sets to experimental frequencies. The TZVP basis set in our study has not been examined in the comparison; we therefore take the values from the smaller 6-311+G(d,p) basis set. For “low” frequencies ($\nu < 1000 \text{ cm}^{-1}$) it is meaningful to obtain the rms error from reciprocal frequencies, so we apply the uncertainty of $1.3\text{E-}04 \text{ cm}^{-1}$ to frequencies below 1000 cm^{-1} . For “high” frequencies above 1000 cm^{-1} , we apply the value of 35 cm^{-1} . The total vibrational

uncertainty arising from the frequencies within the HO approximation is weighted for high frequencies with

$$\begin{aligned}
\nu_i : \quad \frac{\partial \ln k}{\partial \nu_i} &= \frac{\partial}{\partial \nu_i} \ln \left(1 - \exp \left(-\frac{\nu_i}{k_B T} \right) \right) \\
&= \frac{1}{1 - \exp \left(-\frac{\nu_i}{k_B T} \right)} \left(-\exp \left(-\frac{\nu_i}{k_B T} \right) \right) \left(-\frac{1}{k_B T} \right) \\
&= -\frac{1}{k_B T \left(1 - \exp \left(-\frac{\nu_i}{k_B T} \right) \right)}
\end{aligned} \tag{5}$$

and for low frequencies with

$$\begin{aligned}
\frac{\partial \ln k}{\partial \frac{1}{\nu_i}} &= \frac{1}{1 - \exp \left(-\frac{\nu_i}{k_B T} \right)} \left(-\exp \left(-\frac{\nu_i}{k_B T} \right) \right) \left(-\frac{1}{k_B T} \right) \left(\frac{1}{\nu_i} \right)^2 \\
&= \frac{1}{k_B T} \frac{1}{1 - \exp \left(-\frac{\nu_i}{k_B T} \right)} \nu_i^2
\end{aligned} \tag{6}$$

The corresponding uncertainties in $\ln k$ vary between 0.2469 and 0.2564 for the 10 hydrogen abstraction rates by $\text{HO}_2^\bullet$ and between 0.2375 and 0.2405 for the 10 hydrogen abstraction rates by $\text{H}^\bullet$.

The least-squares fit of zero-point vibrational energies (ZPVEs) by Merrick *et al.*²⁰ yields a rms error of 0.36 kJ/mol per vibration. The ZPE contribution to $\ln k$ as a function of frequency reads

$$\frac{\partial \ln k}{\partial E_{\text{ZPE}}} = \pm \frac{1}{k_B T} \tag{7}$$

$$\Delta E_{\text{ZPE}} = \Delta \nu \frac{hc N_A}{2} = 0.36 \text{ kJ/mol} \tag{8}$$

where $+$ is the transition state and $-$ are the reactants.

The derivative with respect to the electronic energy barrier height yields

$$\Delta E_B : \frac{\partial \ln k}{\partial \Delta E_B} = -\frac{1}{k_B T} \tag{9}$$

The uncertainty in the barrier height amounts to 3.6 kJ/mol (see methods section) giving rise to an uncertainty of 0.4330. Thus the total uncertainty in $\ln k$ within the HO-TST

framework varies between 0.6616 and 0.6653 for the 10 hydrogen abstraction rates by $\text{HO}_2^\bullet$, corresponding to a factor 1.94. Uncertainty for abstraction by $\text{H}^\bullet$ varies between 1.9065 and 1.9086 for all sites.

Additional uncertainty arises both from our neglect of reaction path curvature in the tunneling treatment and from our neglect of variational effects in the transition state theory treatment. Both effects have been considered in a recent study on hydrogen abstraction from the α -carbon of 1-butanol by $\text{HO}_2^\bullet$.³⁸ Their maximum influence in the temperature interval from 500 K to 2000 K amounts to a factor of 1.56 (curvature) and 0.73 (variational effects).

The neglect of coupling between the two intermolecular modes (DRA, DHO2) and to the internal rotations of BF will lead to an underestimation of the reaction rate with $\text{HO}_2^\bullet$ as is indicated by a comparison with 1-butanol calculations.²⁶ The approximate multistructural treatment for 1-butanol + $\text{HO}_2^\bullet$ yields maximal ratios of anharmonic to harmonic rates of 30 respectively 146 for abstraction from the α resp. γ -carbon of 1-butanol. The comparison for these sites of our HR treatment to HO for BF yields ratios of 7 respectively 3. One could therefore conclude that especially the rate for abstracting a γ hydrogen may be highly underestimated although the anharmonic behavior of BF will differ from that of 1-butanol. This would in turn both contradict to the close agreement at 500 K of our computation with the model of Sarathy *et al.*⁵ and overcompensate at 2000 K where our computation is a factor 5 slower than the model. At the β and δ abstraction sites, our computed rate constants already exceed the modeled ones. This difference will even increase through multistructural effects. Our computations thus correct estimations for $\text{BF} + \text{HO}_2^\bullet$ based on 1-butanol in the right direction while the real rate constants are likely to be even higher.

In order to discuss the results of the present work a comparison with the reaction rate data of similar molecules will be performed. Due to the structural similarity of MF, EF and *n*-butanol to BF, their reaction rates will be compared to the results for BF.

Westbrook *et al.*¹ examined four similar alkyl ester fuels including MF and EF. By treat-

ing groups with similar neighbors equally, the complexity of the reaction mechanism was reduced. For MF we refer to the work of Dooley *et al.*¹⁵ who improved on the work of Westbrook *et al.*¹ and other studies about MF. The EF data have been taken from propane and methyl cyclohexane and been scaled by factors of 2 and 4 to fit the flame speciation data.¹ The propane values in turn are based on rate constant rules described in the iso-octane mechanism by Curran *et al.*³⁹ The rates reported in this study for BF are more similar to the corresponding MF rates than to the EF rates. The butanol data have been taken from the extensive work of Sarathy *et al.*⁵ Therein the abstraction rates of H $\cdot$ radicals are taken from hydrocarbons⁶ and updated to consider the effect of the hydroxyl-group based on the work of Sivaramakrishnan *et al.*⁴⁰ on ethanol. Furthermore the abstraction rates of HO $_2\cdot$ radicals are taken from *ab-initio* calculations performed by Zhou *et al.*⁷ As stated above, the butanol rate constants are derived from alkane rates. We therefore include *n*-butane in our comparison for abstraction by H $\cdot$ from Healy *et al.*⁶ as well as for abstraction by HO $_2\cdot$ from Carstensen *et al.*⁴¹ and Healy *et al.*⁶

Figure 9: Illustration of H abstraction rates by $H^\bullet$ radicals. The curves in Fig 9(a) refer to the abstractions at different carbon atoms of BF and the following graphs (Fig 9(b) to Fig 9(f)) compare the rates of the five BF groups to the corresponding rates for butane⁶, n -butanol⁵, MF¹⁵ and EF¹.

From Fig 9(a) it can be seen that the abstraction by a $H^\bullet$ radical at the γ site is highest over the whole temperature range. While at high temperatures the differences between rates

become very small they differ much stronger at low temperatures.

The influence of low temperatures can be seen best for abstraction at the formate group (cf. Fig 9(f)). While the slopes of all three curves are similar at high temperatures, the difference between the EF, MF and BF rate increases with decreasing temperature. This is due to the stronger decreasing slope of EF and also MF compared to BF. The BF rate for the formate group is lowest over the whole temperature region, but still similar to the MF rate. The EF rate exceeds both rates by a factor up to 10. At low temperatures the BF rate is the lowest for all abstraction sites except for abstraction at the α carbon (cf. Fig 9(e)). Since the BF rates are smaller than the EF rates (except for abstraction at the β carbon at high temperatures, cf. Fig 9(d)) it can be concluded that the influence of the formate group is damped in BF. A possible reason for the damping is the longer alkyl chain attached to the formate group.

For the β , γ and δ position the corresponding butanol + $\text{H}^\bullet$ rates have a similar slope as the BF rates (cf. Fig 9(d), 9(c), 9(b)), but exceed them always by a factor of 2 to 9. Again the increasing difference between two curves (BF and *n*-butanol) can be observed (cf. Fig 9(c), 9(d)). For the γ position the rates diverge even more below 800 K. Sarathy *et al.* have noted that the effect of the O–H group disappeared at the β site, so hydrocarbon rate rules have been used.⁵ The butanol rate for abstraction from the β position does not match the computed rate for BF. With increasing distance to the O–H group resp. formate group the differences between *n*-butanol and BF decreases. Since for abstraction at the δ position the rates of *n*-butanol and BF are still not the same, it can be concluded that the influences of the groups have a different range or the error of the applied hydrocarbon rate rules causes the difference.

Abstraction by $\text{H}^\bullet$ radicals from the γ position is similar for *n*-butanol and *n*-butane, with a higher rate constant than for BF at all considered temperatures. Abstraction from the δ position by $\text{H}^\bullet$ is similarly slower for BF than for *n*-butane.

Figure 10: Illustration of H abstraction rates by HO_2 radicals. The curves in Fig 10(a) refer to the abstractions at different carbon atoms of BF and the following graphs (Fig 10(b) to Fig 10(f)) compare the rates of BF groups to the corresponding rates for butane^{6 41}, *n*-butanol⁵, MF¹⁵ and EF¹.

The groups of BF interact differently with HO_2 than with $\text{H}^\bullet$ radicals. Especially at high temperatures, for HO_2 , abstraction from the γ group is the slowest process while the fastest

is abstraction from the formate group (cf. Fig 10(a)). For $\text{H}\cdot$, it is vice versa (cf. Fig 9(a)).

A comparison for abstraction by $\text{HO}_2\cdot$ radicals with the reaction rate data of similar molecules (that we already used for the discussion of abstraction by $\text{H}\cdot$ radicals) shows more similarity of the computed rates with the estimated ones (cf. Fig 10(b) to 10(f)). For several groups, the rates for BF and EF or *n*-butanol are equal at intermediate temperatures. Especially abstraction from the formate group of BF and EF is nearly identical, while the rate constant for MF is much lower (one to two orders of magnitude cf. Fig 10(f)). The rates of the formate and α group of EF deviate up to a factor of 3 from the corresponding BF rates. For the more different β group, the agreement is still good both with the *n*-butanol and the scaled EF values. At high temperatures, the BF rate is approx. twice as large as the *n*-butanol rate, while the deviation increases with lower temperatures to a factor of five.

The δ group shows the same behavior with slightly less deviation (cf. Fig 10(b)). Abstraction by $\text{HO}_2\cdot$ radicals from *n*-butane has also been studied by Carstensen *et al.*⁴¹ via computational methods. Abstraction from the δ position of BF is nearly as fast as from *n*-butane in the Healy model; the *n*-butane calculations yield even higher rate constants. Finally, abstraction from the γ group has the same rate for BF and *n*-butanol at 500 K; up to 2000 K the BF rate is 5 times slower (cf. Fig 10(c)). The *n*-butane constant from the model of Healy *et al.*⁶ is similarly larger than the computed rate constants for BF as can be seen for butanol. The rate constant from Carstensen for *n*-butane in turn is even larger (0.5 to 1 order of magnitude) than the Healy model. For the *n*-butanol + $\text{HO}_2\cdot$ rate computation an overall uncertainty of 2.5 has been postulated.⁵ Furthermore, since interaction of the $\text{HO}_2\cdot$ radical with the formate group is also present in β , γ and δ TSs, a kinetic behavior of BF different from that of *n*-butanol is not surprising.

The influence of hindered rotation on the rate is large in the whole temperature region. The temperature-averaged ratio of HR to HO treatment is close to the maximum ratio. While the effect amounts to a factor of 2.5 to 3 for TSs $\delta 2$, $\delta 4$, $\gamma 6$, $\gamma 7$ and $\beta 10$, it is

significantly higher for the formate group TS. At the α -carbon and the other β -carbon TS, hindered rotation introduces a factor of 6. The largest effect of hindered rotation occurs at the δ -carbon hydrogen with the lowest barrier ($\delta 3$). The computed reaction rates confirm that hindered rotation has a large effect on the reaction rate of BF with $\text{HO}_2^\bullet$ radicals. This has been anticipated from the fact that the hindered rotations of the $\text{HO}_2^\bullet$ radical in the TS are not present in the reactant state and thus do not cancel in the rate formulation. The differences in the HR to HO ratios are linked to the structures of the different TSs. For example, TS $\delta 3$ enables a hydrogen-bond between the hydrogen of the $\text{HO}_2^\bullet$ radical and the O_{ester} and thus has the lowest barrier at the δ carbon.

The effect of hindered rotation on the entropy in this study always increases the rate. The effect on the enthalpy in turn depends on the temperature and the nature of the TS and is mostly smaller than the effect on the entropy. Since entropy differences enter the TST rate exponent linearly while energy differences decay with $1/T$, these differences have a large impact on the rates. This is especially apparent in abstraction from the γ carbon atom that has the lowest barrier heights. Despite this, the abstraction rates from γ by $\text{HO}_2^\bullet$ are the lowest rates compared to abstraction from all the other groups because their low-entropy barriers lead to high free energy barriers with increasing temperature. This can still be affected by multistructural effects as explained above, but once more shows that relative rates in combustion chemistry can in general not be evaluated based on barrier heights alone.

Conclusion

This first computational study on the reaction of $\text{H}^\bullet$ and $\text{HO}_2^\bullet$ with *n*-butyl formate provides rates for hydrogen abstraction from various structural alkyl ester sites. Of particular interest is abstraction from the γ site, not treated in former studies on smaller esters, where the lowest barrier heights occur. These barriers result in the fastest rates for abstraction by $\text{H}^\bullet$

radicals. An analogous conclusion for abstraction by $\text{HO}_2^\bullet$ is misleading, because of the more complex transition states. The special arrangement enabling the energy-lowering interaction results concurrently in a low barrier entropy and makes the abstraction by $\text{HO}_2^\bullet$ from the γ site the slowest process at the temperatures studied (500 K to 2000 K). The transition states show that in case of $\text{HO}_2^\bullet$, the formate group can influence the whole transition states till the δ group (cf. Fig 1). All of the computed abstraction rates by $\text{H}^\bullet$ radicals show that analogies to estimations for smaller alkyl formates lead to rates that are mostly too fast. The computed abstraction rates by $\text{HO}_2^\bullet$ radicals underline the importance of a proper hindered rotor treatment. The correction for hindered rotation to the rate amounts to a factor of 2 to 8 over all the combustion relevant temperature range. The resulting rates are used in the first combustion mechanism for *n*-butyl formate¹⁷ and we expect that the rates computed in this study will be useful for further development of alkyl ester modeling.

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Supporting Information Available

As supporting material we include a document with hindered rotation profiles for all the transition states with $\text{HO}_2^\bullet$ and the corresponding gaussian03 files listed in the document. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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