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Polymer of Intrinsic Microporosity Induces Host-Guest Substrate Selectivity in Heterogeneous 4-Benzoyloxy-TEMPO Catalysed Alcohol Oxidations

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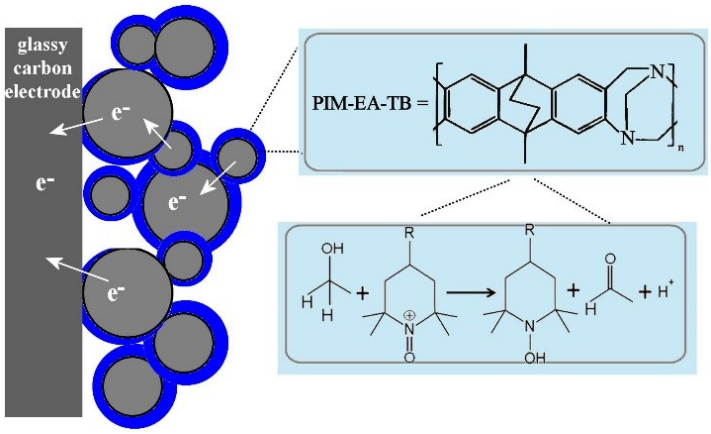
Abstract

The free radical 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4B-TEMPO) is active as an electrocatalyst for primary alcohol oxidations when immobilised at an electrode surface and immersed into aqueous carbonate buffer solution. In order to improve the catalytic process, a composite film electrode is developed based on (i) carbon microparticles of 2-12 μm diameter to enhance charge transport and (ii) a polymer of intrinsic microporosity (here PIM-EA-TB with a BET surface area of 1027 m^2g^{-1}). The latter acts as a highly rigid molecular framework for the embedded free radical catalyst with simultaneous access to aqueous phase and substrate. The resulting mechanism for the oxidation of primary alcohols is shown to switch in reaction order from first to zeroth with increasing substrate concentration consistent with a kinetically limited process with competing diffusion of charge at the polymer layer-electrode interface (here the "LEk" case in Albery-Hillman notation). Reactivity optimisation and screening for a wider range of primary alcohols in conjunction with DFT-based relative reactivity correlation reveals *substrate hydrophobicity* as an important factor for enhancing catalytic currents. The PIM-EA-TB host matrix is proposed to control substrate partitioning and thereby catalyst reactivity and selectivity.

Keywords: carbon microspheres, membrane, fuel cell, biofuel, mesoporosity, voltammetry.

Graphical abstract:



1. Introduction

Green catalytic and electro-catalytic processes are of considerable interest for sustainable chemical processes [1]. Controlling molecular electrocatalyst reactivity within a microporous host environment (here the host is a highly rigid polymer of intrinsic microporosity, PIM [2]) offers opportunities for (i) improved selectivity due to host – substrate interactions, (ii) increased reactivity due to modified catalyst – substrate interaction, and (iii) control over catalyst density and co-catalyst effects. Electrocatalysis in conventional non-rigid polymer films has been well studied [3,4] but is mechanistically complex with many kinetic sub-cases depending on (i) the transport of reactants and products, (ii) the control of pH, (iii) the transport of charge via coupled electron hopping with concomitant ion diffusion, (iv) the chemical rate constants, and (v) additional partitioning effects between the bulk reagent phase and the electrocatalytic layer or film. Here the case of a polymer of intrinsic microporosity (PIM) [2] acting as a highly rigid host environment for the electrocatalytically active free radical 4-benzoyloxy-TEMPO is investigated more closely.

The free radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) is commonly used as a stable redox catalyst that mediates alcohol hydroxyl group oxidation to aldehydes and in some cases to carboxylic acids [5,6]. Hydroxyl group oxidation is a fundamentally important reaction with a broad range of applications in synthetic bio-transformations [7,8,9], radical initiated polymerisation reactions [10], in sensors [11], and in complex catalyst systems for bio-fuel cells [12]. It is of interest to develop modified substrates with TEMPO permanently immobilised [13]. TEMPO is activated by undergoing a one-electron oxidation to $TEMPO^{+}$. This process can be initiated either by sacrificial chemical oxidants [14] or by an applied

electrochemical potential [15, 16]. The TEMPO catalysed oxidation of primary alcohol groups proceeds via overall two-electron oxidation of the alcohol requiring two equivalents of $TEMPO^+$. Most studies have reported that TEMPO exhibits good selectivity towards primary alcohol oxidations in alkaline conditions (to aldehydes or to carboxylates [17,18]), but there are also more complex examples of secondary alcohols being oxidized to ketones [19] and examples of novel multi-catalyst multi-step oxidations [20].

In terms of the catalytic mechanism, there is good evidence for the key reaction step involving the transfer of hydride (= two electrons) from the primary alcohol to $TEMPO^+$. For example, it has been reported that adding a stoichiometric amount of chemical oxidant to TEMPO in the presence of an excess amount of alcohol results in a complete conversion to TEMPOH (the two-electron reduced form of $TEMPO^+$) and the aldehyde [21]. This indicates that under the right conditions one molecule of $TEMPO^+$ can oxidise one molecule of alcohol directly to the aldehyde. In the corresponding electrochemical mechanism TEMPO regeneration occurs with a comproportionation reaction with $TEMPO^+$ and TEMPOH quickly forming two molecules of TEMPO (see Figure 1). The rate of comproportionation is reported to be relatively rapid in alkaline conditions [22].

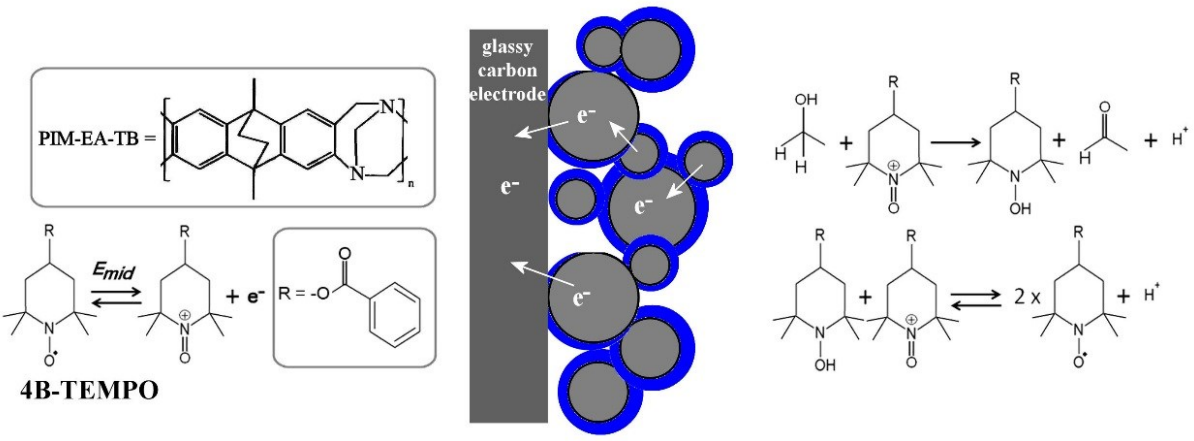


Figure 1. Scheme showing (i) the PIM-EA-TB molecular structure, (ii) 4B-TEMPO structure and reactivity, and (iii) a cartoon of the composite film with electrocatalyst embedded in PIM-EA-TB on carbon microspheres.

The immobilisation of TEMPO catalysts on the electrode surface is of considerable interest [23] and porous polymer substrates can be practical and versatile catalyst hosts. Polymers of intrinsic microporosity (PIMs [24,25]) provide a new generation of highly rigid microporous materials with (i) excellent processability, (ii) highly rigid pore structures in which guest catalyst molecules can be readily embedded, (iii) good access of solvent and substrate to the catalyst through rigid pores, and (iv) robustness towards corrosion. In our previous work the poly-amine structure PIM-EA-TB [26] (synthesised based on a Tröger's base reaction [27,28,29]) has been employed to electrochemically grow palladium lamellae [30], to act as a host for molecular Fe(II)-porphyrinato electrocatalyst [31], and to protect gold nanoparticles [32] and fuel cell catalysts [33]. Recently we have demonstrated proof-of-concept for the immobilisation of the molecular electrocatalyst 4-benzoyloxy-TEMPO (or 4B-TEMPO) into a porous PIM-EA-TB host film for the electrocatalytic oxidation of saccharides [34]. Major limitations in this electrocatalytic process were observed due to low overall currents caused by a thick polymer film and a limited reactive interface. Therefore, in this study (i) a three-dimensional electrocatalyst film based on carbon microspheres is developed to increase the reactive interface, (ii) the film thickness and catalyst loading are investigated as process optimisation parameters, and (iii) substrate concentration and chemical properties are considered as parameters in the overall reaction scheme. It is shown that a wide range of primary alcohols are electrocatalytically oxidised in aqueous carbonate buffer at pH 10.3. As a new feature, the partitioning (accumulation) of more hydrophobic substrates into the PIM-EA-TB host film is identified as a key step in enhancing the heterogeneous electrocatalytic oxidation process. In order to dissect molecular electronic *versus* host-partitioning effects, an approximate DFT model of the reaction is proposed.

2. Experimental Details

2.1. Chemical Reagents

4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl benzoate (4-benzoyloxy-TEMPO), perchloric acid, dimethylformamide (DMF), sodium hydroxide, sodium bicarbonate, D-(+)-glucose, sorbitol, methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, benzyl alcohol, 3-pyridinemethanol, 4-pyridinemethanol, 1,3-propandiol, 1,4-dimethanolbenzene and glassy carbon microsphere (2-12 μm diameter) were purchased from Sigma-Aldrich, TCI Chemicals, or Fisher Scientific and used without further purification. PIM-EA-TB was prepared following a literature protocol [35]. Solutions were prepared with filtered and deionized water of resistivity 18 MΩ cm at 22 ^{o}C from a Thermo Scientific water purification system.

2.2. Instrumentation

A potentiostat system (Metrohm micro-Autolab II) was employed with a conventional three-electrode cell configuration: a Pt wire as counter electrode, a KCl-saturated calomel electrode (SCE, Radiometer, Copenhagen) as reference, and a glassy carbon electrode (BAS) with a diameter of 3 mm as the working electrode.

2.3. Electrode Preparation

PIM-EA-TB was dissolved in dimethylformamide (DMF) acidified with perchloric acid (ca. 0.5% by volume) to make up a stock solution with a concentration of 30 mg cm^{-3}. 4B-TEMPO stock solution was prepared with 28 mg cm^{-3} in pure DMF. 50 μL of PIM stock solution was mixed with 5 μL of 4B-TEMPO stock solution, and an additional 45 μL of DMF was added with 36 mg of solid glassy carbon microspheres. The suspension was

homogenised by gentle shaking or with a short burst of ultrasound. Next, 0.5 μL of the resulting mixture was pipetted onto the glassy carbon disc electrode. The DMF was left to evaporate in a fume hood, and the electrode was used for electrochemical measurements as soon as the DMF evaporated. The final composition of the composite film on the electrode contains ca. 0.75 μg of 4B-TEMPO, 7.5 μg of PIM, and 180 μg of glassy carbon micro-particles. Figure 2 shows typical scanning electron micrographs. Pre-conditioning potential cycles (ten cycles between 0.3 V and 0.9 V vs. SCE with a scan rate of 10 mVs^{-1}) prior to voltammetric measurements were necessary to generate reproducible redox peaks.

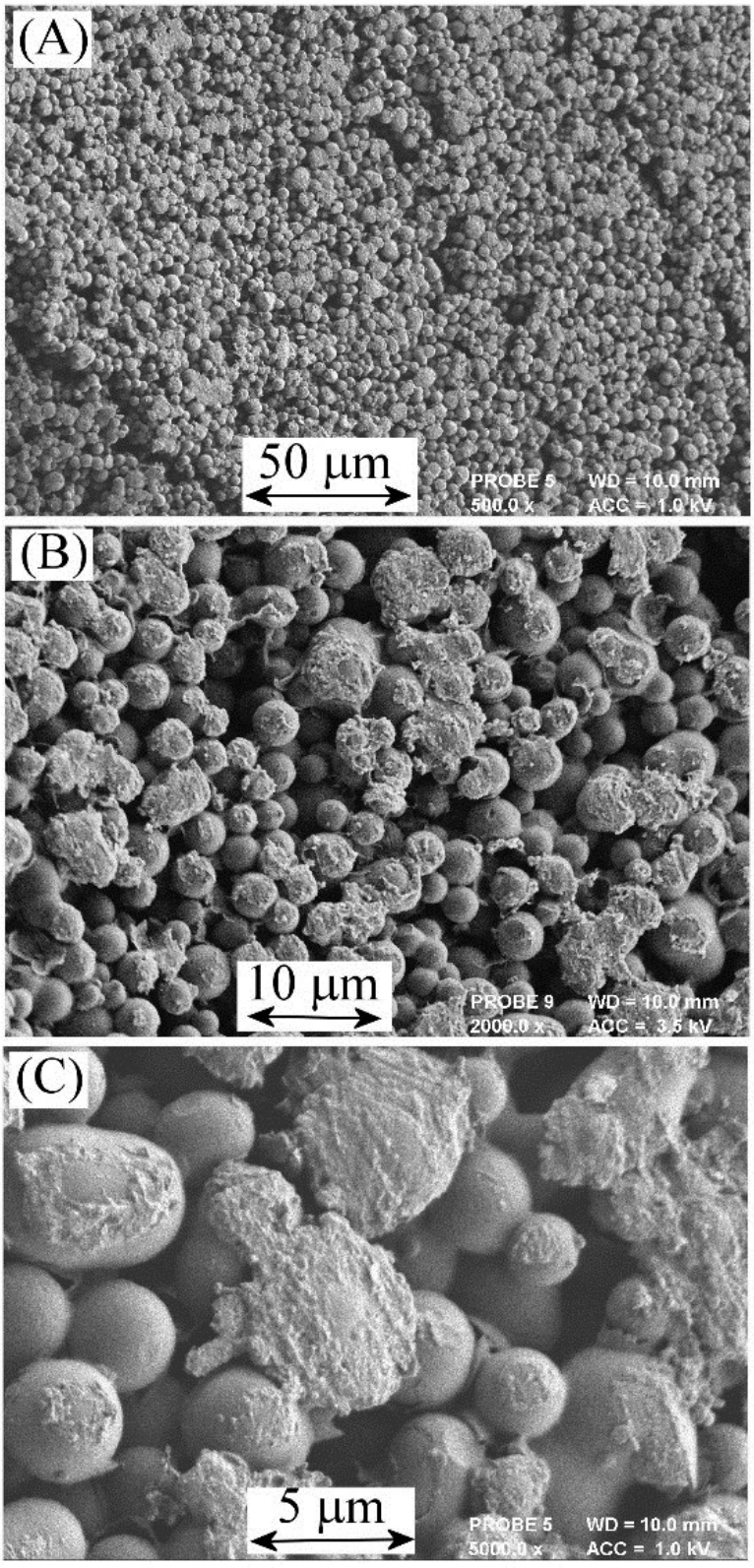


Figure 2. SEM images for the composite film made of 0.75 µg 4B-TEMPO immobilised in 7.5 µg PIM-AT-TB with 180 µg carbon microparticles giving a porous film of approximately 50 µm thickness on a 3 mm diameter glassy carbon electrode. The thickness of the PIM-EA-TB layer around each carbon microparticle is estimated to be 50 nm.

2.4. Density Functional Theory (DFT) Calculation of Kinetic Barriers

The reaction between oxidised 4B-TEMPO$^+$ cation, $NaCO_3^-$ anion and various primary alcohols was examined using DFT calculations. Calculations were performed with Gaussian09 suites of code [36] and protocol rB3LYP/6-311++G(d,p)/SCRF= (cpcm,solvent=water)/ temperature=298.15 (see ESI for full computational details). The nature of all the stationary points as minima or transition states was verified by calculations of the vibrational frequency spectrum. All transition states were characterized by normal coordinate analysis revealing precisely one imaginary mode corresponding to the intended reaction. As expected, the oxidation of alcohols to aldehydes by 4B-TEMPO$^+$ is highly thermodynamically favoured (by $\leq$ -200 kJmol^{-1}, see Table S1 in Supporting Information). Calculations also revealed the key hydride transfer step to occur via a cyclic transition state, with an activation barrier low enough for the reaction to happen readily at room temperature. Table 1 shows the calculated free enthalpy barriers of this transition state for a series of alcohols. Figure 3 illustrates the proposed reaction mechanism. A two-electron transfer occurs formally as hydride transfer from the primary alcohol to the TEMPO$^+$ oxygen.

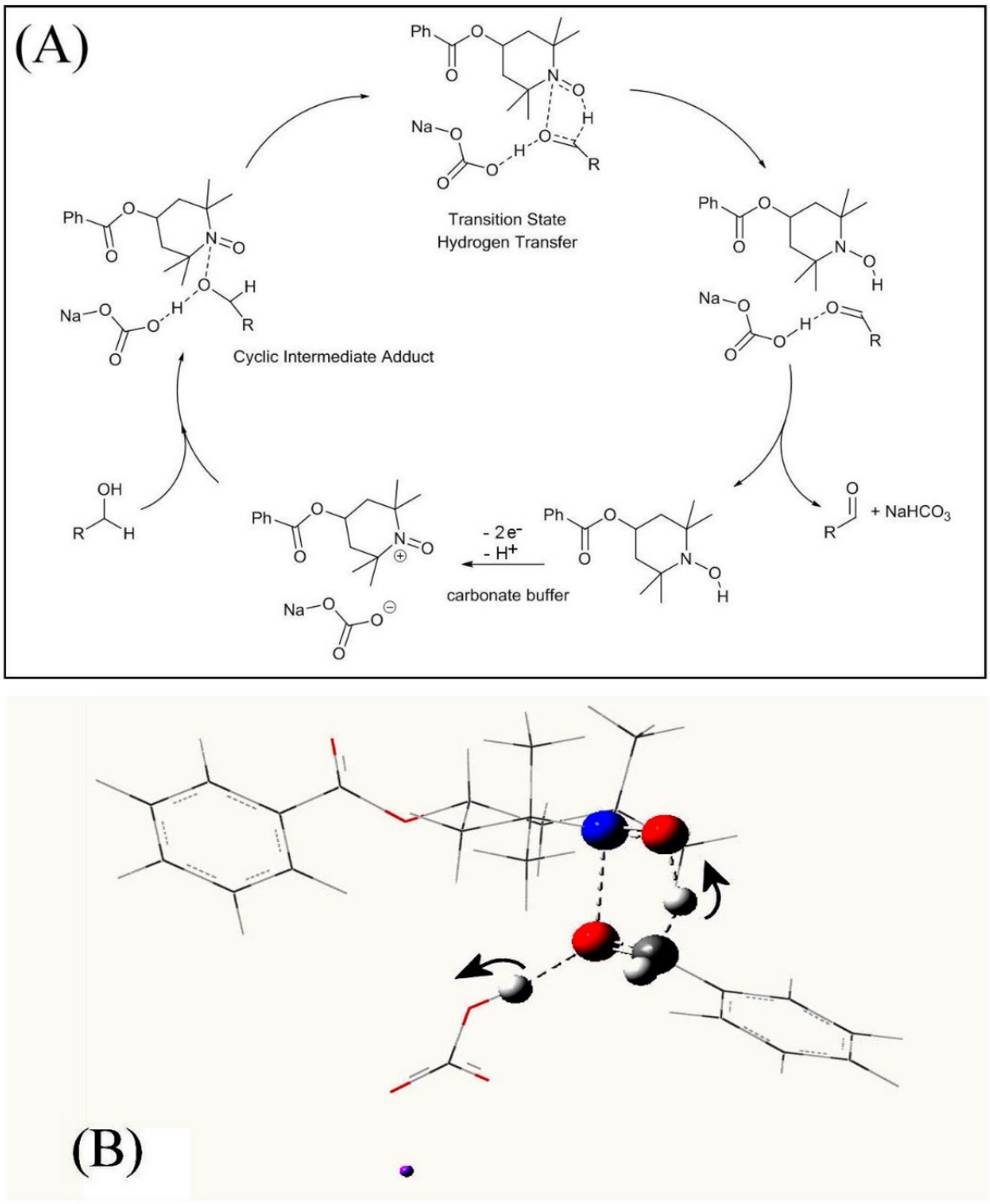


Figure 3. (A) Postulated reaction mechanism with cyclic transition state for the hydride transfer. (B) Molecular structure of DFT calculated transition state for the hydrogen transfer step between benzyl alcohol and 4B-TEMPO$^+$ (red: oxygen, blue: nitrogen, grey: carbon, white: hydrogen, purple: sodium; light blue: displacement vectors of the TS imaginary frequency). Image obtained with GaussView 5.0.8.

A summary of the calculated kinetic transition state barriers in kJ mol^{-1} is given in Table 1. For molecules with multiple primary alcohol moieties, only one calculation was performed. Additionally, octanol-water partitioning constant data ($logP_{OW}$) are included in this table in order to interpret and compare with experimental kinetic data (*vide infra*).

Table 1. Summary of DFT calculation results in terms of the approximate activation barrier for the rate limiting hydride transfer process converting a primary alcohol to an aldehyde. Additional data for the logarithm of the octanol-water partion coefficient ($logP_{OW}$ [37]) are included.

	Substrate	**$log(P_{OW})$**	**DFT Free enthalpy barrier / $kJmol^{-1}$**
(i)	α-D-glucose	-2.5	19.0
(ii)	D-sorbitol	-2.0	11.2
(iii)	1,3-propanediol	-1.07	18.5
(iv)	methanol	-0.72	15.2
(v)	ethanol	-0.31	20.3
(vi)	propan-1-ol	0.34	19.9
(vii)	butan-1-ol	0.78	20.1
(viii)	pentan-1-ol	1.65	18.8
(ix)	hexan-1-ol	1.94	19.0
(x)	4-pyridine-methanol	0.06	13.6
(xi)	3-pyridine-methanol	0.03	14.4
(xii)	1,4-benzenedimethanol	0.67	9.42
(xiii)	benzylalcohol	1.26	13.1

3. Results and Discussion

3.1. Reactivity of 4B-TEMPO Embedded in PIM-EA-TB/Carbon Microsphere Films I.: Charge Transport

The effect of glassy carbon microparticles of nominal 2 to 12 μm diameter on the electrochemical reactivity of 4B-TEMPO immobilized at a 3 mm diameter glassy carbon electrode is dramatic. Figure 4A shows cyclic voltammetry data for 4B-TEMPO deposited on

its own, when embedded into PIM-EA-TB, and when embedded into PIM-EA-TB with glassy carbon microparticles. The current increased by an order of magnitude with the presence of microparticles, consistent with an increase in surface area, as well as improved flow of electrons and electrolyte through the film (see scheme in Figure 1).

In Figure 4B and 4C the effect of scan rate is compared with/without carbon microparticles and further important effects are observed. In the 4B-TEMPO – PIM-EA-TB film (Figure 4B) a reversible oxidation – reduction redox process is seen at ca. E_{mid} = +0.63 V vs. SCE. The charge under the oxidation and the reduction peaks is scan rate dependent with a decrease observed at faster scan rate. The double logarithmic plot of estimated peak charge versus scan rate in Figure 4B shows a slope of approximately -1/2, which is consistent with a diffusion controlled charge transport process within the 4B-TEMPO – PIM-EA-TB film. In contrast, a similar plot of data for the 4B-TEMPO – PIM-EA-TB – carbon microparticle film shows a transition from semi-infinite diffusion to thin film behaviour (finite diffusion or complete film electrolysis) at a scan rate of approximately v_{trans} = 20 mVs^{-1} (Figure 4C). The approximate "transition time" for complete electrolysis in this film is therefore given by dimensional analysis as $\tau = \frac{RT}{v_{trans}F} \approx 1s$ (with the gas constant, R, the absolute temperature, T, the Faraday constant, F, the film thickness, δ, and the charge diffusion coefficient, D). Transport of charges in the film may be dominated either by inter-molecular hopping of electrons (starting at the electrode surface) or by ion diffusion (from the solution phase).

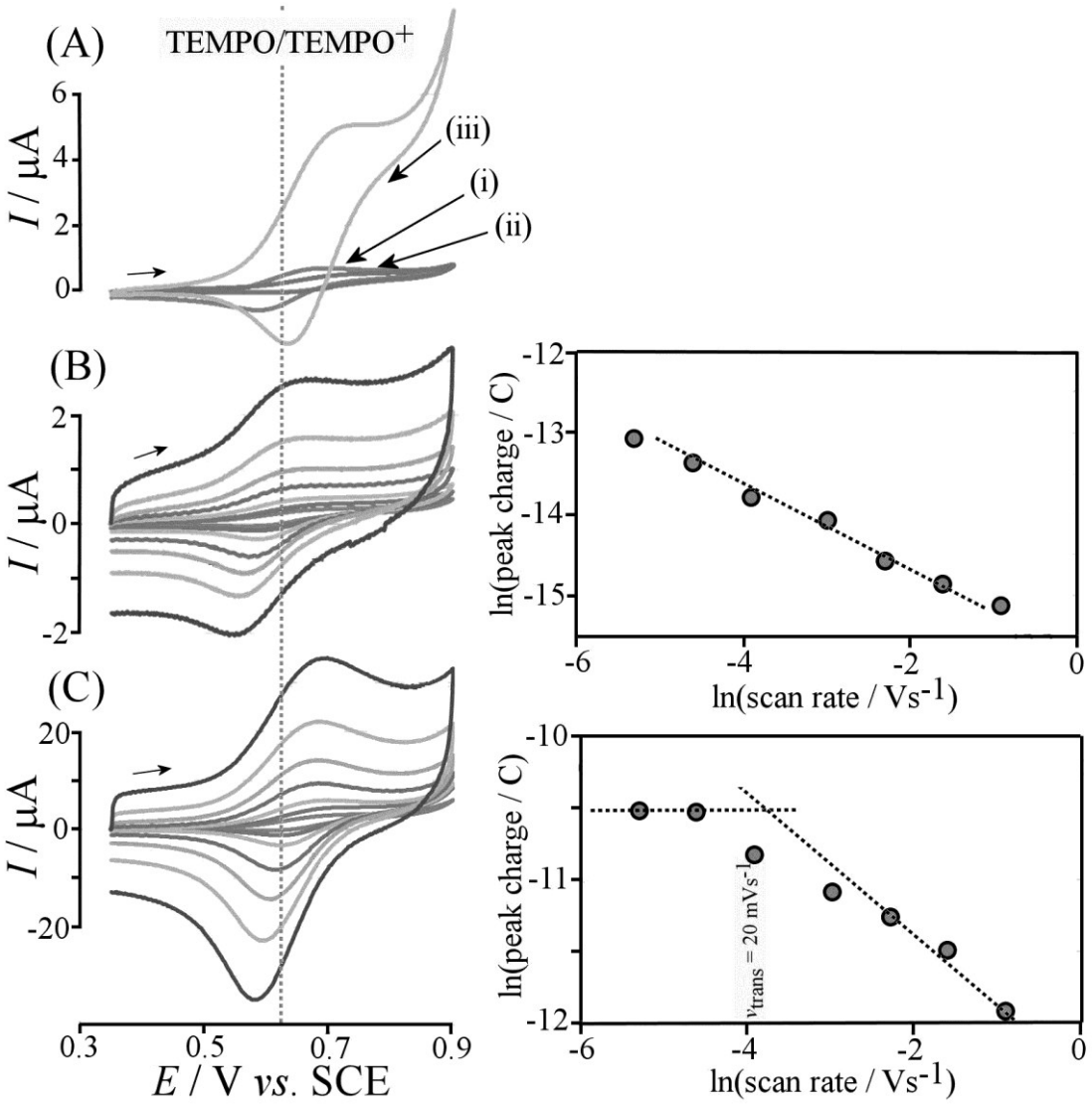


Figure 4. (A) Cyclic voltammograms (scan rate 10 mVs^{-1}; in 0.1 M carbonate buffer pH 10.3) for (i) 0.75 µg of 4B-TEMPO immobilised on a 3 mm diameter glassy carbon electrode, (ii) immobilised within 7.5 µg PIM-EA-TB, and (iii) immobilised in 7.5 µg PIM-EA-TB + 180 µg carbon microparticles. (B) Cyclic voltammograms (scan rates (i) 5, (ii) 10, (iii) 20, (iv) 50, (v) 100, (vi) 200, and (vii) 400 mVs^{-1}) for 0.75 µg 4B-TEMPO. Inset shows peak charge versus scan rate. (C) As before for 7.5 µg 4B-TEMPO. Inset shows peak charge versus scan rate.

The transport of charges in the composite film is likely to be complicated in particular with the amount of 4B-TEMPO in the film affecting the overall mechanism of the process. Assuming a diffusion-dominated charge propagation mechanism, it is possible to estimate the apparent diffusion coefficient from $\tau = \frac{\delta^2}{\pi D}$ as $D \approx 10^{-15}$ m^2s^{-1} (based on $\delta \approx 50$ nm, see Figure

2), which is consistent with typical charge hopping processes [38]. This rate of charge hopping is considerably slower when compared to substrate diffusion in the film and therefore one of the rate limiting factors in the catalytic reaction (*vide infra*).

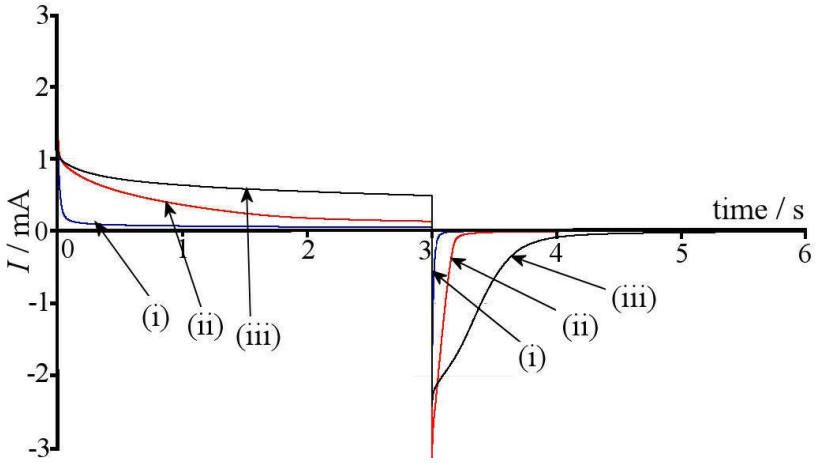


Figure 5. Chronoamperometry data for the oxidation (0.9 V vs. SCE) and back-reduction (0.0 V vs. SCE) of (i) 0.0, (ii) 0.75, and (iii) 7.5 μg of 4B-TEMPO immobilised in 7.5 μg PIM-EA-TB with 180 μg glassy carbon microparticles (2-12 μm diameter) immersed in 0.1 M carbonate buffer pH 10.3.

Further complexity in the charge transport is revealed in chronoamperometry data (Figure 5). The applied potential was initially stepped up to an oxidation potential of +0.9 V vs. SCE followed by a step down to 0.0 V vs. SCE. Without 4B-TEMPO (trace i) only short charging currents are recorded. With 0.75 μg 4B-TEMPO immobilised, oxidation of 4B-TEMPO occurs within a couple of seconds. The back-reduction appears to be somewhat faster (see trace ii) and associated with less charge. For 7.5 μg 4B-TEMPO immobilised in 7.5 μg PIM-EA-TB (see trace iii) the oxidation appears to be slower, but the back-reduction again occurs within a one second period and with a shape more typical of a moving reaction boundary than that of a Cottrellian diffusion process. The excess anodic current (also visible as background anodic current in cyclic voltammetry data, see Figure 4) and asymmetry in oxidation and

reduction rate for high loadings are currently not fully understood, but the 4B-TEMPO oxidation response appears chemically reversible and stable enough for electro-catalytic processes to be driven. The role of the PIM-EA-TB host film in the transport of cations, anions, and reagents will require further more quantitative study.

3.2. Reactivity of 4B-TEMPO Embedded in PIM-EA-TB/Carbon Microsphere Films II.: Glucose Oxidation

The oxidation of glucose can serve as an important model system to assess the electrocatalytic activity of immobilised 4B-TEMPO. In a recent study it has been shown that this process is feasible, but it occurred only with relatively low catalytic efficiency [34]. Here the effect of introducing the glassy carbon microparticles on the electrocatalytic current is investigated.

First the effect of pH on 4B-TEMPO is studied. Figure 6A shows typical cyclic voltammetry data and a decrease in peak current when changing the pH of the carbonate buffer from 9.3 to 10.3 and to 11.3. This trend could be due to the pH affecting charge transport. It is known that TEMPO catalysts in homogeneous solution produce higher catalytic currents in more alkaline conditions, however when immobilised additional detrimental effects are possible. This is demonstrated in Figure 6D where the effect of glucose concentration and pH are summarised. The plot shows a typical increase in catalytic current (see Figure 6C) with glucose concentration but also a loss of activity when the solution is too alkaline. This can be attributed to either slower charge transport or loss of catalyst due to side reactions as suggested by Green *et al.* [18]. A solution pH of 10.3 appears to be a good compromise and is therefore used for most of the experiments performed in this study.

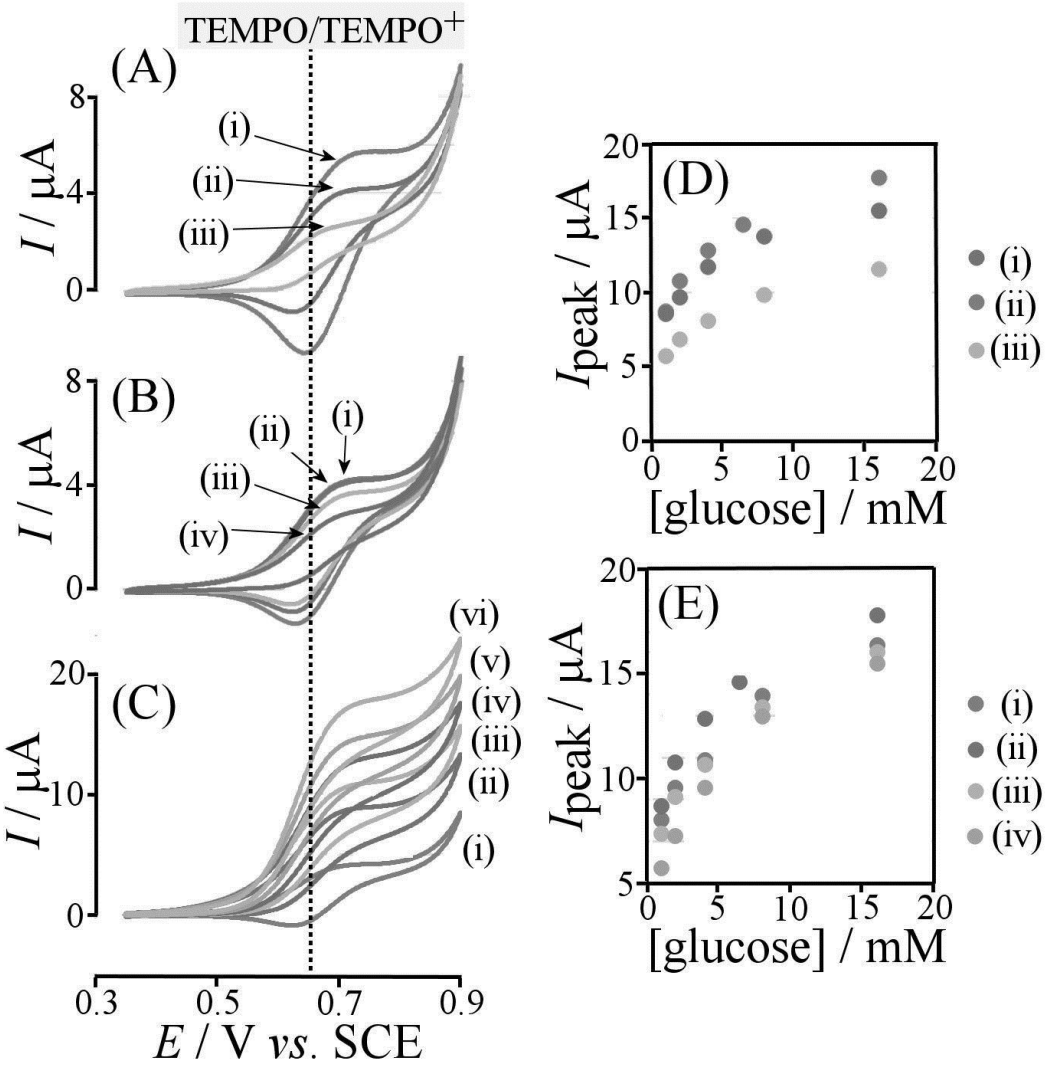


Figure 6. (A) Cyclic voltammograms (scan rate 10 mVs^{-1}; in 0.1 M carbonate buffer with pH (i) 9.3, (ii) 10.3, and (iii) 11.3) for 0.75 µg 4B-TEMPO + 7.5 µg PIM-EQA-TB + 180 µg carbon microparticles immobilised on a 3 mm diameter glassy carbon disk electrode. (B) As above but at pH 10.3 in (i) 0.05, (ii) 0.1, (iii) 0.2, and (iv) 1.0 M carbonate buffer. (C) As above in 0.1 M carbonate buffer at pH 10.3 with addition of (i) 0, (ii) 1, (iii) 2, (iv) 4, (v) 8, and (vi) 16 mM glucose. (D) Plot of peak currents versus glucose concentration at pH (i) 9.3, (ii) 10.3, and (iii) 11.3. (E) Plot of peak current versus glucose concentration at pH 10.3 for (i) 0.05, (ii) 0.1, (iii) 0.2, and (iv) 1.0 M carbonate buffer.

The effect of adding carbon microparticles into the catalyst film is significant with typically an order of magnitude increase in glucose oxidation current. The additional effect of ionic strength is demonstrated in Figure 6B and 6E. Charge transport appears impeded with

increasing ionic strength (or buffer concentration) possibly due to the higher concentration of CO_3^{2-} dianion in the catalyst film affecting charge hopping rates. Measurements in the presence of glucose suggest that a good compromise is reached at 0.1 M carbonate buffer. The effect of the glucose concentration on the catalytic current appears to be similar under all conditions, suggesting a "saturation" of the reactive film and switch to zeroth order kinetics at a substrate concentration higher than 16 mM (*vide infra*). Next, the effect of the 4B-TEMPO concentration in the catalytic film is investigated.

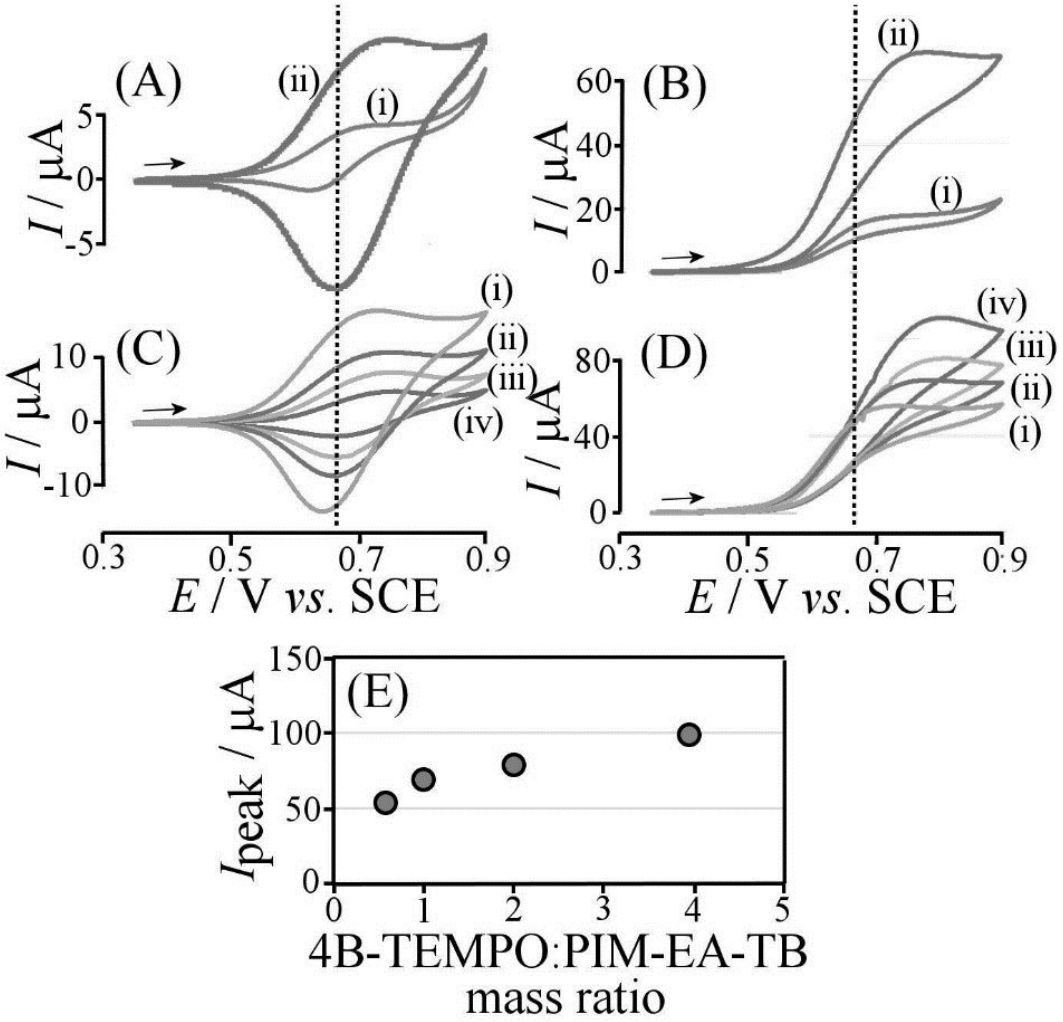


Figure 7. (A) Cyclic voltammograms (scan rate 10 mVs^{-1}; in 0.1 M carbonate buffer pH 10.3) with 7.5 μg PIM-EA-TB and 180 μg carbon microparticles and with (i) 0.75 μg 4B-TEMPO and (ii) 7.5 μg 4B-TEMPO at a 3 mm diameter glassy carbon electrode. (B) As above but with 16 mM glucose. (C) As above but with 0 mM glucose, with 7.5 μg 4B-TEMPO, and with (i) 12.7, (ii) 7.5, (iii) 3.7, and (iv) 1.9 μg PIM-EA-TB. (D) As above but

with 16 mM glucose. (E) Plot of the peak current versus 4B-TEMPO:PIM-EA-TB mass ratio indicating that a lower 4B-TEMPO concentration lowers the catalytic efficiency.

Figure 7 shows that increasing the amount of 4B-TEMPO by 10 times (with the amount of PIM-EA-TB and carbon microparticles fixed) increases both the Faradaic current in the absence of glucose (Figure 7A) and the catalytic current in the presence of glucose (Figure 7B) significantly. The amount of 4B-TEMPO in the film is therefore effective in increasing the catalytic current. Reducing the amount of PIM-EA-TB (with a fixed amount of 4B-TEMPO and carbon microparticles in the film) has a less dramatic effect. Catalytic glucose oxidation currents can be increased with lower PIM-EA-TB loading (Figure 7C), but the electrode also becomes unstable probably due to absence of a sufficiently rigid PIM framework and loss of catalyst due to crystallisation or leaching out into the solution phase. A 4B-TEMPO:PIM-EA-TB mass ratio of approximately 1:1 results in stable currents and therefore a good compromise.

3.3. Reactivity of 4B-TEMPO Embedded in PIM-EA-TB/Carbon Microsphere Films III.: Primary Alcohol Oxidation

Figure 8A shows cyclic voltammograms in the presence of different types of primary alcohols: (i) 4 mM ethanol, (ii) 4 mM glucose, (iii) 4 mM 3-pyridinemethanol, and (iv) 4 mM benzyl alcohol. The catalytic current changes significantly depending on the chemical identity of the substrate used indicating that the rate limiting process here has to do with the properties of the substrate and the kinetics of the catalytic reaction step. The plot in Figure 8B shows that for all substrates a transition from first order to zeroth order in substrate reaction order occurs when going from low to high substrate concentrations. The concentration where the switch occurs is close to 1 mM for ethanol but much higher for benzylalcohol. The fact

that the switch occurs can be explained based on competition of charge transport and catalytic reaction rate (*vide infra*) and changes for individual substrate molecules suggest an effect based on the chemical reaction rate rather than based solely on transport effects and/or local pH.

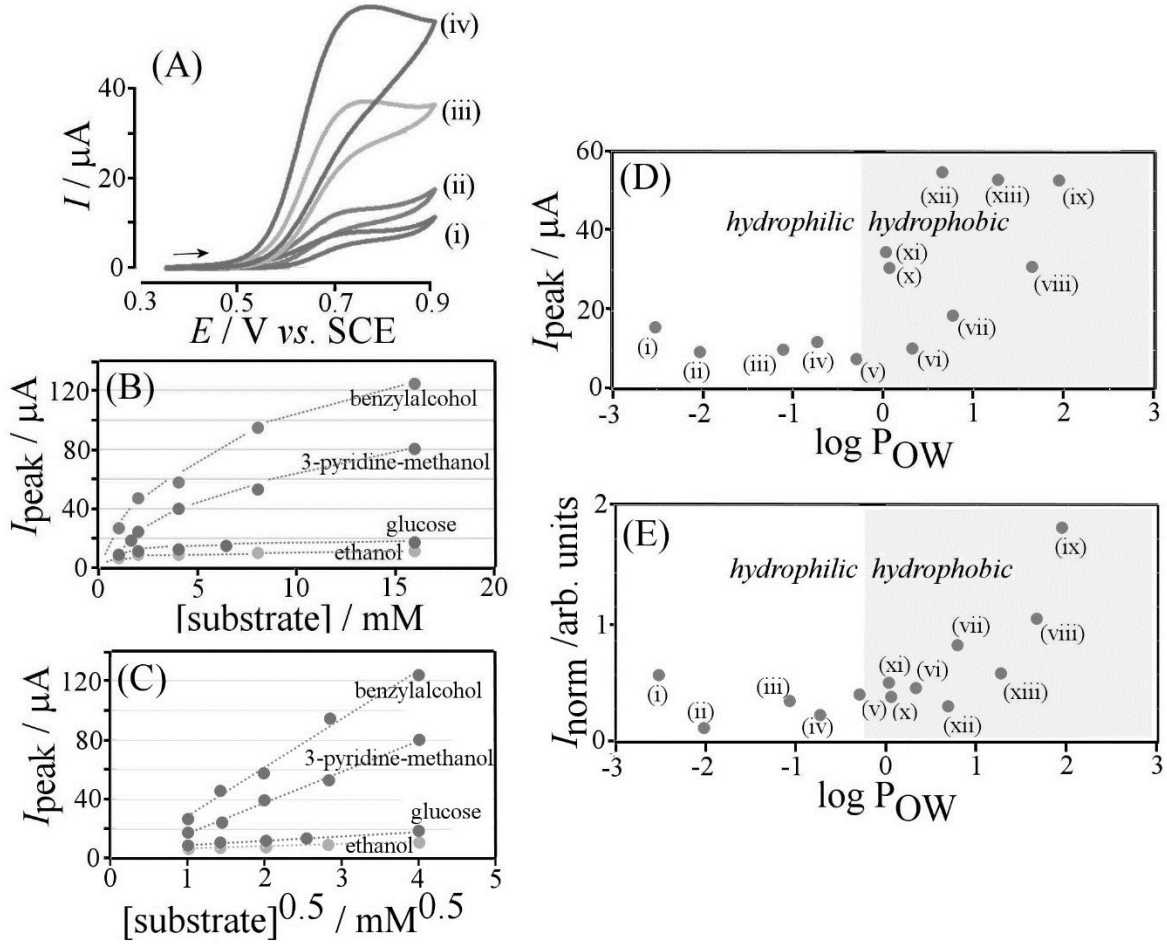


Figure 8. (A) Cyclic voltammograms (scan rate 10mVs^{-1}; in 0.1 M carbonate buffer pH 10.3) with 0.75 µg 4B-TEMPO + 7.5 µg PIM-EA-TB + 180 µg carbon microparticles on a 3 mm diameter glassy carbon electrode in the presence of (i) 4 mM ethanol, (ii) 4 mM glucose, (iii) 4 mM 3-pyridine-methanol, (iv) 4 mM benzyl alcohol. (B) Plot of peak current versus substrate concentration. (C) Plot of peak current versus square root of substrate concentration. (D) Plot of peak current versus log P_{OW} (octanol-water partitioning coefficients) for 4 mM of (i) glucose, (ii) sorbitol, (iii) 1,3-propanediol, (iv) methanol, (v) ethanol, (vi) 1-propanol, (vii) 1-butanol, (viii) 1-pentanol, (ix) 1-hexanol, (x) 4-pyridine-methanol, (xi) 3-pyridine-methanol, (xii) 1,4-benzene-dimethanol, and (xiii) benzylalcohol. (E) Plot of the normalised

peak current (the peak current divided by the square root of the Arrhenius factor $exp\frac{-E_A}{RT}$ with the DFT kinetic activation barrier E_A) versus log P_{OW}.

The plot in Figure 8C demonstrates that for most substrates in good approximation a square root dependence of the peak current on the substrate concentration is observed, which can be interpreted based on a model introduced by Albery and Hillman [3] to dissect the mechanistic cases for a thin film immobilised catalyst and partitioning of the substrate. The square root dependence of the current on substrate is indicative of a process that is governed by competing charge diffusion in the catalyst film and the chemical rate of the catalytic reaction. The transport of the partitioned substrate towards the reaction zone is fast and not rate limiting. As a result of this the process occurs at the interface of the thin film catalyst and the electrode surface (denoted "LEk" case [3]) with a current that is depend on the square root of the substrate bulk concentration as well as on the square root of the second order rate constant for the catalyst reacting with the substrate.

A further important rate limiting factor could be the partition coefficient of the substrate into the PIM-EA-TB catalyst film, which can be correlated directly to the octanol-water partition coefficients. A plot of the catalytic current with substrate concentrations fixed at 4 mM versus the logarithmic octanol-water partition coefficient (see Figure 8D) shows a clear correlation in particular for a given class of substrates such as the n-alkyl alcohols. However, the distinct reactivity of different primary alcohols causes a considerable spread of data points. In order to better reveal the PIM-EA-TB host effect, the approximate activation barrier for the 4B-$TEMPO^+$ reaction with primary alcohols has been calculated by DFT methods (see Experimental). This then allows catalytic peak currents to be normalised to minimise the effect of the bimolecular rate constant (for this catalytic case – "LEk" – and

only in first approximation, normalisation can be achieved by dividing the peak current by the square root of the Arrhenius factor $exp\frac{-E_A}{RT}$, see Table 1). The resulting plot in Figure 8E shows a systematic effect of the $\log P_{OW}$ (or hydrophobicity) of the substrate on the electrocatalytic currents. It can therefore be assumed that partitioning of the substrate into the PIM-EA-TB host occurs thereby increasing locally the substrate concentration and selectively enhancing the electrocatalytic process.

4. Conclusion

It has been shown that a PIM-EA-TB composite with glassy carbon microparticles can be employed as a three-dimensional electrode with good access of solution phase and substrate to the active catalyst site. In this case a 4-benzolyoxy-TEMPO catalyst was employed to study the oxidation of primary alcohols to aldehydes in a carbonate buffer at pH 10.3 and novel reactivity patterns were observed. Catalytic activity followed the analytical model consistent with the substrate reacting near the electrode-film interface. Factors that limit the catalytic process in the film were identified as the kinetic rate constant of catalysis, partitioning of the substrate into the film and the substrate concentration. Concentration of catalyst and the rate of electrochemical charge hopping were assumed to be constant and independent of substrates present. Removal of the effect of the catalytic rate constant (here estimated with an appropriate DFT model) allowed a clear demonstration of the PIM-EA-TB film selectivity towards hydrophobic substrates.

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20th September 2015

SUPPORTING INFORMATION

Polymer of Intrinsic Microporosity Induces Host-Guest Substrate Selectivity in Heterogeneous 4-Benzoyloxy-TEMPO Catalysed Alcohol Oxidations

Sunyhik D. Ahn [1], Adam Kolodziej [1], Richard Malpass-Evans [2], Mariolino Carta [2], Neil B. McKeown [2], Stephen D. Bull [1], Antoine Buchard [1], and Frank Marken*[1]

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DFT Calculations

Computational details

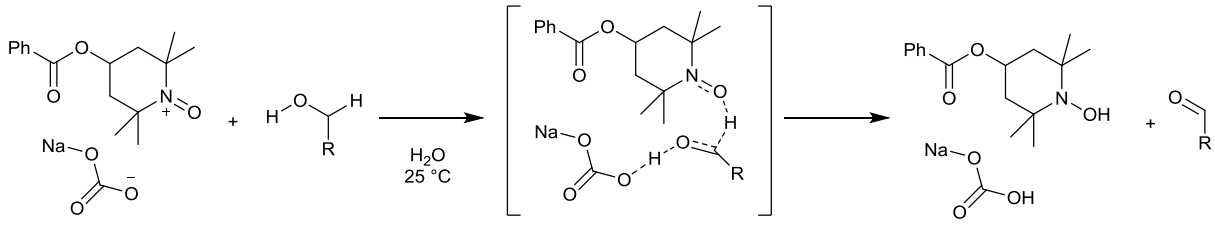
All calculations employed the following protocol: rB3LYP/6-311+G(d,p)/SCRF= (cpcm,solvent=water)/ temperature=298.15.

The B3LYP functional is a hybrid of exact (Hartree-Fock) exchange with local and gradient-corrected exchange and correlation terms, as first suggested by Becke.[1] In B3LYP,[2] the exchange is provided by Becke 88 exchange functional[3] and the correlation is provided by the correlation functional of Lee, Yang and Parr (LYP),[4] with some local correlation expression of Vosko, Wilk, and Nusair.[5] The calculations were all carried out using a self-consistent-reaction-cavity continuum solvation model to account for the reactions conditions (in water). Implementation of the self-consistent-reaction-cavity continuum solvation model has recently been enhanced to allow efficient evaluation of first and second energy derivatives, following an earlier suggestion of the method.[6] The split-valence triple ζ with polarization *and* diffuse functions 6-311+G(d,p) basis set was selected to account for potential ions and nonbonding interactions, while allowing the models to scale up to the maximum size of 73 atoms, and an associated maximum of 1071 basis functions.

All geometries were fully optimized without any symmetry or geometry constrains. In addition, frequency calculations were carried out to check their nature: all stationary points as minima and characterised by no imaginary mode, whereas transition states were characterized by precisely one imaginary mode corresponding to the intended reaction. In one case (benzylalcohol), this was augmented by an intrinsic reaction coordinate (IRC) calculation,[7] which also confirmed the identity of the reaction. Free energies were calculated within the harmonic approximation for vibrational frequencies. Only the most stable conformational isomers are reported for all intermediates.

All calculations were performed using the Gaussian09 suite of codes.[8] The authors would also like to acknowledge the use of the EPSRC UK National Service for Computational Chemistry Software (NSCCS) at Imperial College London, as well as the High Performance Computing (HPC) facilities (Aquila cluster) at the University of Bath, in carrying out this work.

Computed free enthalpies reaction path between oxidised 4B-TEMPO$^+$ cation, $NaCO_3^-$ anion and various primary alcohols



Thermodynamics of the reaction between oxidised 4B-TEMPO$^+$ cation, $NaCO_3^-$ anion and various primary alcohols was examined using DFT. The key hydride transfer step was also calculated and was found to occur via a cyclic transition state. For α-D-glucose, the oxidation to glucono-δ-lactone was found to be kinetically and thermodynamically favoured compared to the formation of the aldehyde. For D-sorbitol, which features two stereochemically different primary alcohols, only one set of calculation was performed. Full coordinates for all

stationary points, together with computed free enthalpies and vibrational frequency data, are also available via the corresponding Gaussian 09 output files, stored in the digital repository (DOI number will be available as soon as the article is accepted for publication, and the data made public): http://figshare.com/s/da93054a467911e5b18c06ec4bbcf141

Table S1. Summary of DFT calculation results in terms of the approximate activation barrier for the two-electron transfer process converting a primary alcohol to an aldehyde and the overall thermodynamics of the reaction between 4B-TEMPO$^+$ cation, $NaCO_3^-$ anion and a primary alcohol.

	System	*Transition state* $\Delta(\Delta G^{TS}_{298.15K})$ *(kJ mol^{-1})*	*Free enthalpies of formation* $\Delta(\Delta G_{298.15K})$ *(kJ mol^{-1})*
(i)	α-D-glucose	19.0	-271.6
(ii)	D-sorbitol	11.2	-221.8
(iii)	1,3-propanediol	18.5	-225.2
(iv)	methanol	15.2	-199.2
(v)	ethanol	20.3	-230.8
(vi)	propan-1-ol	19.9	-229.0
(vii)	butan-1-ol	20.1	-231.4
(viii)	pentan-1-ol	18.8	-230.8
(ix)	hexan-1-ol	19.0	-230.8
(x)	4-pyridine-methanol	13.6	-226.4
(xi)	3-pyridine-methanol	14.4	-233.1
(xii)	1,4-benzenedimethanol	9.4	-243.1
(xiii)	benzylalcohol	13.1	-241.4

Table S2. List of all computed structures and their computed free enthalpies.

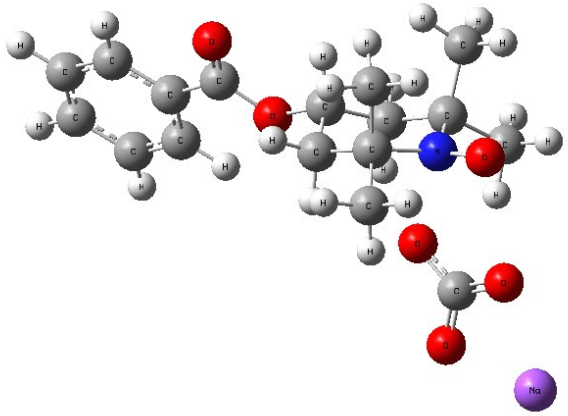
System	*G (Hartree)*
[4B-TEMPO$^+$][$NaCO_3^-$]	-1329.535876
4B-TEMPOH	-903.893483
$NaHCO_3$	-426.918515
α-D-glucose	-687.258413

$TS_{(i)}$	-2016.787043
glucono-δ-lactone	-686.085721
D-sorbitol	-688.451248
$TS_{(ii)}$	-2017.98286
$aldehyde_{(ii)}$	-687.259617
1,3-propanediol	-269.584476
$TS_{(iii)}$	-1599.113323
β-hydroxypropionaldehyde	-268.394131
methanol	-115.742804
$TS_{(iv)}$	-1445.272891
formaldehyde	-114.542556
ethanol	-155.046871
$TS_{(v)}$	-1484.57499
acetaldehyde	-153.858659
propan-1-ol	-194.345048
$TS_{(vi)}$	-1523.87334
propanal	-193.156152
butan-1-ol	-233.643376
$TS_{(vii)}$	-1563.171613
butanal	-232.455382
pentan-1-ol	-272.941932
$TS_{(viii)}$	-1602.470647
pentanal	-271.753712
hexan-1-ol	-312.240396
$TS_{(ix)}$	-1641.769034
hexanal	-311.052167
4-pyridine-methanol	-362.837382
$TS_{(x)}$	-1692.368094
pyridine-4-aldehyde	-361.647486
3-pyridine-methanol	-362.83647
$TS_{(xi)}$	-1692.366875
pyridine-3-aldehyde	-361.649129
1,4-benzenedimethanol	-461.32215
$TS_{(xii)}$	-1790.854441
p-(hydroxymethyl)benzaldehyde	-460.138628
benzylalcohol	-346.781922
$TS_{(xiii)}$	-1676.312829
benzaldehyde	-345.59773

Optimized geometries and computed free enthalpies

Full coordinates for all the stationary points, together with their 3 lowest calculated vibrations and their computed Free Gibbs Energy are reported below.

[4B-TEMPO$^+$][NaCO$_3^-$]



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H	-2.50888800	2.32372100	-0.53291400
H	-4.18854100	1.82407200	-0.78616500
C	-3.36348800	1.29635600	1.13602000
H	-4.16584300	0.59401900	1.35883300
C	-3.87155500	-0.80191400	-1.21554600
H	-4.65221400	-0.41830800	-1.87508900
H	-4.33463900	-1.03061200	-0.25834800
H	-3.48146200	-1.72377300	-1.64912800
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H	-3.20498600	1.05279800	-3.07058100
H	-2.01573600	-0.25426900	-3.10413100
H	-1.53639400	1.36548700	-2.54962600
C	-1.49376000	-0.44430200	1.15275700
C	-2.04262300	0.85726000	1.75231200
H	-1.30767100	1.64880400	1.61093500
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C	-2.32048500	-1.67716400	1.58355100
H	-2.14152600	-1.83823200	2.64834700
H	-3.39275100	-1.55549400	1.44599000
H	-1.99347400	-2.56744500	1.04469600
C	-0.04111400	-0.66920500	1.57704500
H	-0.01941700	-0.76565200	2.66488100
H	0.35498900	-1.58890800	1.14619300
H	0.58485600	0.16874500	1.28184700
O	-0.99859300	-1.28365600	-0.99340500
O	-0.31180100	1.39755500	-0.53340000
C	0.81024000	1.28255700	-1.19775600
O	1.14219900	0.17652200	-1.74286700
O	1.55592500	2.32020300	-1.27760000
Na	3.12398700	1.11463000	-2.56233900
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C	-5.01245700	2.86256200	1.92543600
O	-5.91637700	2.14817400	1.53715700

C	-5.21846000	4.16555100	2.62026200
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H	-3.56206500	6.77261200	4.04184300
H	-7.79329600	6.13267900	3.65547900
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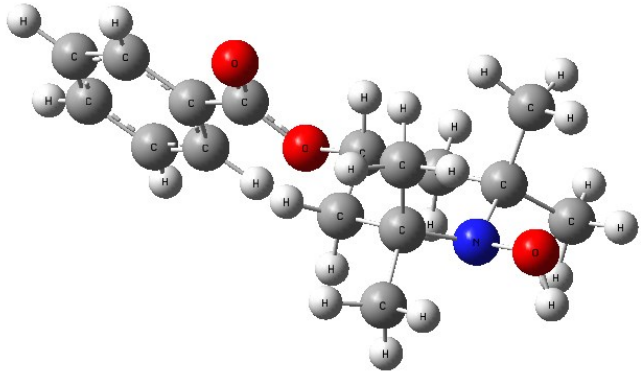
Sum of electronic and thermal Free Energies= -1329.535876

Frequencies -- 21.4099 24.0671 32.5798

4B-TEMPOH



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H	-0.03723900	2.24281100	1.13019600
C	-1.64300000	-0.20890400	1.47853700
H	-2.69059200	0.05891000	1.63973700
H	-1.04010100	0.43173300	2.12090300
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H	-3.36618300	-0.27202600	-0.67594900
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H	-2.17367000	-0.74741800	-1.90077500
C	1.28600400	-0.03062200	-0.02783700
C	1.22001700	1.45196500	-0.45501700

H	1.23359800	1.51067400	-1.54799200
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C	1.63302900	-0.16730000	1.47233800
H	2.67427400	0.12672700	1.62907200
H	1.01689100	0.45820800	2.11714800
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H	2.16439000	-0.69318500	-1.90869500
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H	0.77211100	7.33427900	-3.26300800
H	-1.47625500	9.03090900	-0.01839700
H	-0.28203900	9.29971500	-2.17714300

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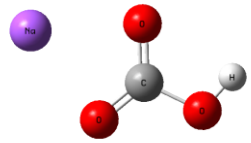
$NaHCO_3$



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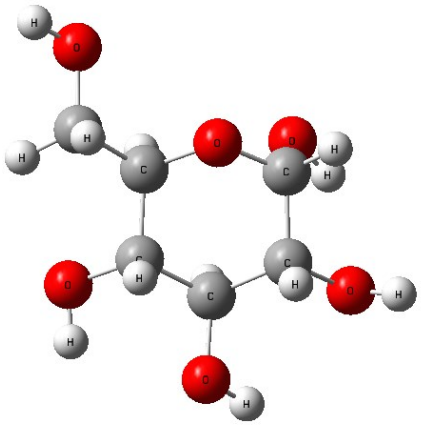
α-D-glucose



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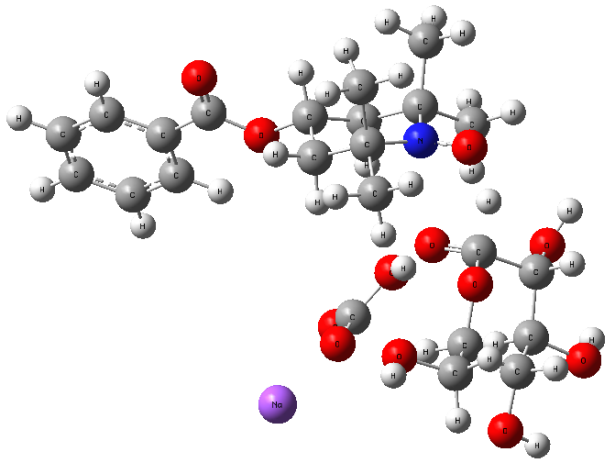
Sum of electronic and thermal Free Energies= -687.258413

Frequencies -- 64.2491 93.9269 107.7401

$TS_{(i)}$



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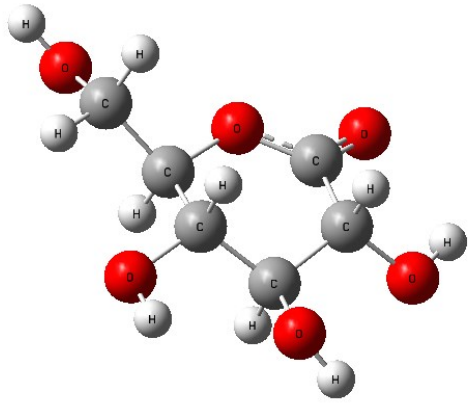
H	-3.99044423	1.18465714	-0.98666081
C	-3.33251599	0.93189332	1.05492684
H	-4.23623156	0.40222356	1.35330270
C	-4.03940781	-1.51799377	-0.84607573
H	-4.73690442	-1.21082943	-1.62824226
H	-4.56783319	-1.46544488	0.10303828
H	-3.75524801	-2.55526453	-1.03318682
C	-2.32984453	-0.56324708	-2.37854911
H	-3.12205750	-0.10297185	-2.97308466
H	-2.15949999	-1.56930254	-2.76334674
H	-1.41728558	0.01379103	-2.49358487
C	-1.72021490	-1.00885649	1.47667685
C	-2.11243965	0.43990401	1.81745583
H	-1.27030365	1.09801125	1.59172122
H	-2.29907006	0.49506493	2.89284253
C	-2.70538635	-2.03878636	2.07842598
H	-2.56483954	-2.04822444	3.16152509
H	-3.75130295	-1.81191715	1.88528233
H	-2.48798535	-3.03926521	1.69939226
C	-0.33018630	-1.30084255	2.04488443
H	-0.36427186	-1.12871743	3.12277666
H	-0.04761907	-2.34193982	1.88073500
H	0.42034967	-0.64837095	1.60767042
O	-1.03461951	-2.14060160	-0.50186984
H	0.15205067	-1.68971098	-0.95273070
H	0.80087728	1.72853530	0.29527456
O	1.03279381	2.37494317	0.99435117
C	1.11934896	3.63734365	0.45729661

O	0.89286738	3.77658592	-0.77346518
O	1.42289760	4.54932696	1.26449112
Na	1.33959021	6.11309014	-0.53748767
O	-3.50963871	2.32917472	1.42785609
C	-4.75578955	2.83849051	1.42111946
O	-5.74156943	2.19480379	1.11776243
C	-4.78845493	4.27162977	1.83082580
C	-3.62654655	4.97795936	2.16893962
C	-6.03008103	4.91857420	1.87309212
C	-3.71086805	6.31594836	2.54532985
H	-2.66616805	4.48114344	2.13679617
C	-6.11011649	6.25537028	2.24993013
H	-6.92239491	4.36489084	1.60931174
C	-4.95037534	6.95575681	2.58655745
H	-2.81028970	6.85925477	2.80668644
H	-7.07336346	6.75097907	2.28132799
H	-5.01255637	7.99739367	2.88040681
O	0.31858298	0.26725139	-0.69792421
C	2.34255459	-1.14825294	-0.84155344
O	0.86305888	-0.78719197	-2.69540155
C	3.31710738	-0.14450270	-1.47449391
H	2.53472902	-2.14473452	-1.24795050
O	2.58750732	-1.11973788	0.55389906
C	1.66956919	0.21510915	-3.33869197
C	3.13983196	-0.04626580	-2.98623170
H	3.12909558	0.84097469	-1.02877668
O	4.67184426	-0.52518077	-1.24037783
H	2.38053801	-1.98045315	0.93268176
H	1.37910045	1.20956845	-2.98001163
H	3.44823851	-1.00256801	-3.43079438
O	3.93101958	1.01523256	-3.51956897
H	4.80228716	-0.57021422	-0.28487017
H	4.83728906	0.88168299	-3.21500403
C	0.89854859	-0.71782487	-1.25816551
C	1.42829689	0.13813458	-4.83334129
H	1.50688574	-0.90688328	-5.15634920
H	2.20376140	0.72125850	-5.33928255
O	0.13065168	0.66449791	-5.12669878
H	0.00392602	0.63641187	-6.08098749

Sum of electronic and thermal Free Energies= -2016.787043

Frequencies -- -781.0142 10.5135 13.4475

glucono-δ-lactone



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0 1
 H                  0.14700100   -1.48939800   -0.95570700
 C                  0.80167000   -0.62493500   -1.11454600
 H                  0.79342400   -0.36622200   -2.17771700
 C                  2.22071500   -0.99466400   -0.73475800
 C                  2.85673700   -1.97168900   -1.72645800
 H                  2.83175200   -0.08911900   -0.68771900
 C                  4.17326300   -2.50291800   -1.17173700
 H                  2.18154300   -2.82061800   -1.90187500
 C                  3.90065100   -3.22758900    0.13774400
 H                  4.86005500   -1.66678200   -0.99432700
 H                  3.27324200   -4.10548100   -0.08099300
 O                  2.17316900   -1.52943600    0.62762300
 O                  3.06254300   -1.25464400   -2.93529000
 H                  3.61132600   -1.81046200   -3.50450500
 O                  4.71334200   -3.37381700   -2.16073400
 H                  5.63547200   -3.55795100   -1.94736600
 O                  5.12368400   -3.62919000    0.72010400
 H                  4.95900900   -3.80598900    1.65692100
 O                  0.39293800    0.48410000   -0.31500500
 H                 -0.51347300    0.71054200   -0.54944200
 C                  3.08428300   -2.38007500    1.11544000
 O                  3.19353800   -2.53389500    2.31008200

Sum of electronic and thermal Free Energies=          -
686.085721
Frequencies --    43.4758            91.2732
101.8430
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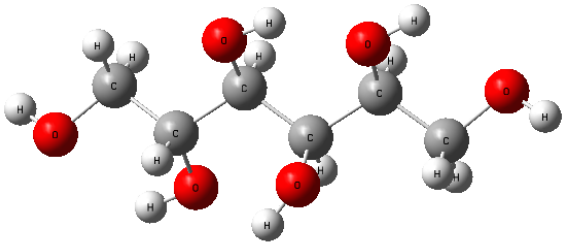
D-sorbitol



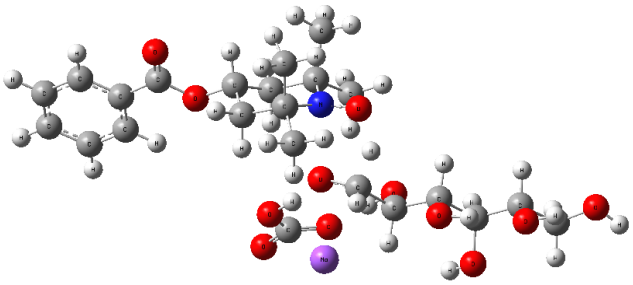
0 1

H	-3.09072300	0.68197100	-1.49327100
C	-3.14594000	0.60441500	-0.40145600
H	-3.13979600	1.60720200	0.03314700
C	-1.96220500	-0.19987200	0.11649200
C	-0.62028600	0.43262300	-0.26818200
H	-2.02536000	-0.23898000	1.21216600
C	0.57178300	-0.49392400	0.05771900
H	-0.60831100	0.58181700	-1.35856000
C	1.90771700	0.09902900	-0.39140900
H	0.42600500	-1.40451500	-0.53233700
H	1.84070000	0.26746700	-1.47451700
C	3.08942700	-0.82171200	-0.12607300
H	3.18726100	-1.00386100	0.94634700
H	2.94144600	-1.77651500	-0.64280100
O	-1.99742500	-1.52787200	-0.41480400
H	-2.91491600	-1.82440800	-0.34912700
O	-0.56567800	1.69184700	0.39991500
H	0.36353300	1.97379700	0.40370500
O	0.65173500	-0.82404100	1.44768600
H	-0.01352400	-1.49464900	1.63730300
O	2.11708700	1.36263400	0.26289000
H	3.00298200	1.66584600	0.02427700
O	4.24850100	-0.14322000	-0.63318200
H	5.03530100	-0.52133100	-0.22749900
O	-4.32525500	-0.11745100	-0.01248300
H	-5.07929400	0.22763900	-0.50155200

Sum of electronic and thermal Free Energies= -688.451248

Frequencies -- 33.3009 53.7106 77.8325

$TS_{(ii)}$



0 1

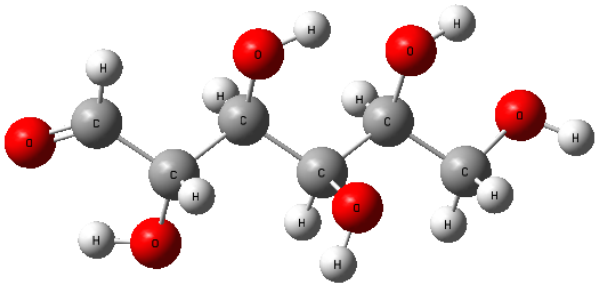
N	-0.02992569	-1.98037590	0.73700707
C	0.91634211	-1.93718506	1.93187076
C	2.19645117	-1.19203309	1.51377846
H	1.96415453	-0.12955341	1.41227306
H	2.93025541	-1.30417798	2.31536412
C	2.77908977	-1.68380828	0.19435979
H	3.15069261	-2.70390977	0.28137792
C	1.20550162	-3.38095644	2.40460340
H	1.74733041	-3.32957173	3.35141836
H	1.81344086	-3.95534113	1.70921059
H	0.27049514	-3.91791506	2.57621221
C	0.25274514	-1.18868709	3.09458489
H	0.94516558	-1.19873637	3.93885114
H	-0.66879721	-1.67949917	3.40901247
H	0.04366753	-0.15649540	2.82521020
C	0.45940766	-2.31631027	-0.66729821
C	1.76459012	-1.54618477	-0.93064718
H	1.53257229	-0.48720350	-1.06406886
H	2.19431276	-1.91516803	-1.86528926
C	0.65216512	-3.84565753	-0.79509043
H	0.79435395	-4.08177934	-1.85206070
H	1.51555544	-4.22901280	-0.25529600
H	-0.23954806	-4.37114454	-0.44817653
C	-0.60355652	-1.89081319	-1.68198661
H	-0.20010579	-2.05566330	-2.68377373
H	-1.50882625	-2.49095927	-1.58020433
H	-0.86488084	-0.84230841	-1.56936327
O	-1.23902249	-2.24627154	0.98883223
H	-1.92451356	-1.03827118	0.98526800
C	-1.81083166	0.20130630	0.98421216
H	-2.01367977	0.39305420	2.05409540
O	-0.57427789	0.36894816	0.60792900
H	0.22827522	1.55830316	-0.30667358

O	0.84490438	2.23723742	-0.67942723
C	0.28309695	2.85832287	-1.75154038
O	-0.88656347	2.50850575	-2.10652892
O	0.96808749	3.73880982	-2.31550836
Na	-0.79709524	4.04762374	-3.90895427
O	3.91083204	-0.84118413	-0.17120860
C	5.14137412	-1.20722005	0.23221059
O	5.36516004	-2.21186929	0.87942310
C	6.19368285	-0.24670289	-0.20796848
C	5.88751431	0.92079542	-0.91964493
C	7.52682285	-0.53366403	0.11185537
C	6.90648732	1.78811529	-1.30489796
H	4.85877607	1.14613150	-1.16681887
C	8.54227221	0.33432746	-0.27678498
H	7.75398602	-1.43745486	0.66322188
C	8.23333346	1.49667003	-0.98559025
H	6.66567419	2.69088163	-1.85406785
H	9.57213658	0.10656782	-0.02779795
H	9.02438197	2.17357378	-1.28769393
C	-2.96197027	0.75842822	0.10015590
C	-4.28575689	0.02639498	0.36427805
H	-3.08757397	1.80384156	0.42823586
C	-5.42979566	0.53874439	-0.53652054
H	-4.14259617	-1.03425606	0.10572239
C	-6.71505821	-0.27035606	-0.36140043
H	-5.10166116	0.37904968	-1.56844856
H	-6.47722751	-1.31330417	-0.60984286
C	-7.84118905	0.18973284	-1.27505013
H	-8.10549012	1.22526674	-1.04993245
H	-7.52534513	0.11662910	-2.32175484
O	-2.69526153	0.70566251	-1.28049101
H	-1.96799948	1.33600689	-1.50218119
O	-4.56032564	0.15594690	1.75944813
H	-5.49352116	-0.07764144	1.88834901
O	-5.72164798	1.92552244	-0.33048794
H	-5.02253080	2.44444126	-0.74263109
O	-7.14323000	-0.20699279	1.01063384
H	-8.00178405	-0.64713494	1.06343422
O	-8.95085812	-0.68427136	-1.01662190
H	-9.75866298	-0.26597926	-1.33134796

Sum of electronic and thermal Free Energies= -2017.982860

Frequencies -- -648.0093 10.1783 13.0527

Aldehyde$_{(ii)}$



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0 1
 C                    -3.24579100    0.55818300   -0.07498900
 H                    -3.25051800    1.58785300    0.31061100
 O                    -4.15347100    0.12023500   -0.75111000
 C                    -2.05173400   -0.30000600    0.28047600
 C                    -0.73742700    0.37207000   -0.17552500
 H                    -2.02481900   -0.36281600    1.37844400
 C                     0.48514700   -0.51543200    0.14459000
 H                    -0.77525700    0.48678700   -1.26832600
 C                     1.77675000    0.07548500   -0.42661000
 H                     0.32334400   -1.46976100   -0.36487300
 H                     1.64651200    0.16201300   -1.51358200
 C                     2.99897000   -0.78981900   -0.15994000
 H                     3.15103600   -0.89825500    0.91630000
 H                     2.85925800   -1.78029000   -0.60730200
 O                    -2.17571700   -1.58828400   -0.28260900
 H                    -3.01812100   -1.60201400   -0.76545400
 O                    -0.69802100    1.64363200    0.46135300
 H                     0.21818200    1.96221600    0.40765200
 O                     0.63005100   -0.72447500    1.55270200
 H                     0.23629900   -1.57104200    1.78564500
 O                     1.97564000    1.38807600    0.12474100
 H                     2.84564400    1.69423800   -0.16362700
 O                     4.10978300   -0.11042900   -0.76338000
 H                     4.92682400   -0.44184900   -0.37706800

Sum of electronic and thermal Free Energies=          -
687.259617
Frequencies --    43.9126            52.5485
79.2415
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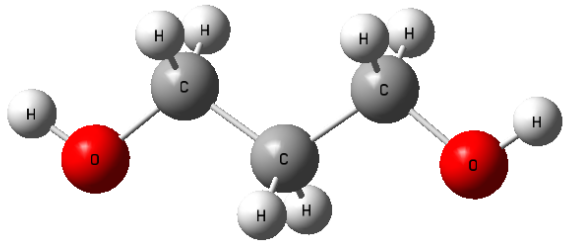
1,3-propanediol



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0 1
 H                 -1.29246400    1.13014800   -0.88695900
 C                 -1.26414900    0.48577200    0.00017500
 H                 -1.29277900    1.12975900    0.88757000
 C                  0.00001500   -0.36074600    0.00023700
 C                  1.26408300    0.48579500   -0.00040200
 H                 -0.00025400   -1.00786300   -0.88291100
 H                  0.00022900   -1.00719800    0.88386100
 H                  1.29241000    1.12950200   -0.88802100
 H                  1.29278900    1.13043000    0.88650900
 O                  2.39260900   -0.40172600   -0.00024400
 H                  3.19642200    0.12898700    0.00294400
 O                 -2.39256100   -0.40172600   -0.00024900
 H                 -3.19642100    0.12892200    0.00089700

Sum of electronic and thermal Free Energies=          -
269.584476
Frequencies --    94.3101           111.3358
194.8428
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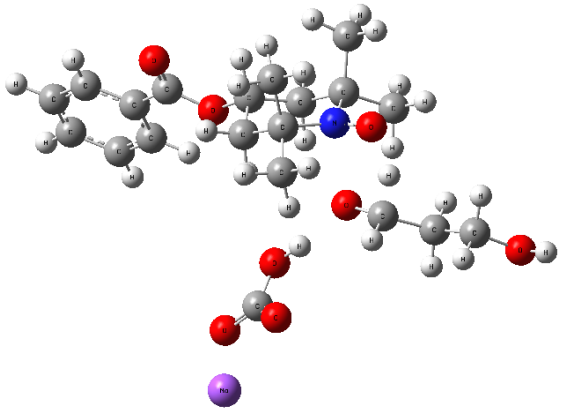
$TS_{(iii)}$



0 1

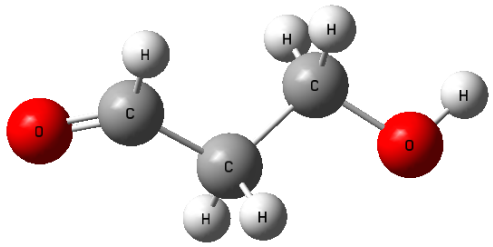
N	-1.66389627	-1.76562343	0.53341116
C	-0.83589203	-1.32449713	1.73768638
C	0.48928211	-0.72267162	1.23926391
H	0.29199693	0.25532447	0.79504606
H	1.13780629	-0.57555932	2.10573286
C	1.18988346	-1.58729132	0.19813973
H	1.52731674	-2.53050752	0.62622775
C	-0.61081966	-2.53839080	2.66845771
H	-0.17691696	-2.17874900	3.60389948
H	0.06747987	-3.28328035	2.25769785
H	-1.56250453	-3.02103954	2.89794649
C	-1.61118914	-0.26316276	2.52889326
H	-1.00057150	0.03253310	3.38472192
H	-2.55279811	-0.66084269	2.90903427
H	-1.80723920	0.61593882	1.91959632
C	-1.04108381	-2.48965595	-0.65547572
C	0.29085313	-1.80569930	-1.00841210
H	0.07981556	-0.83718534	-1.46786432
H	0.80362779	-2.42360521	-1.74968971
C	-0.85391208	-3.98202720	-0.29775275
H	-0.55886868	-4.51823212	-1.20216464
H	-0.08678035	-4.15797429	0.45334254
H	-1.79447398	-4.40637421	0.05823978
C	-1.98618859	-2.40596414	-1.85800349
H	-1.52523146	-2.93974435	-2.69181945
H	-2.94524538	-2.87831966	-1.64287930
H	-2.14742383	-1.37029922	-2.14591084
O	-2.87774271	-2.02827096	0.77237009
H	-3.58883313	-0.92106034	0.35537376
C	-3.50480200	0.21498101	-0.14947635
H	-3.85089770	0.82097536	0.71163156
O	-2.22951227	0.29891045	-0.41647735
H	-1.23220068	1.76054325	-0.43719773
O	-0.54585730	2.43706190	-0.64347446
C	-0.79823072	3.59451601	0.04779716
O	-1.81483764	3.63629920	0.79117123
O	0.02639287	4.52544830	-0.12992800

Na	-1.25540300	5.87765005	1.35817577
O	2.37095763	-0.89018769	-0.29421166
C	3.53622073	-1.07258646	0.35421928
O	3.65456441	-1.78454991	1.33265831
C	4.65899623	-0.31141353	-0.26487234
C	4.47902381	0.49507574	-1.39641796
C	5.92912734	-0.41748499	0.31605005
C	5.56062505	1.18462063	-1.93821834
H	3.49883243	0.57962512	-1.84609629
C	7.00724152	0.27305063	-0.22827461
H	6.05824820	-1.04257032	1.19069411
C	6.82425925	1.07500523	-1.35623687
H	5.41804324	1.80729247	-2.81369487
H	7.98800836	0.18722514	0.22472536
H	7.66432566	1.61316487	-1.78039345
C	-4.50691499	0.21771076	-1.31309961
C	-5.92051435	-0.11987097	-0.86633118
H	-4.18423433	-0.48143783	-2.08782749
H	-4.50316256	1.22061679	-1.75722899
H	-5.96570202	-1.14758603	-0.48540269
H	-6.23531868	0.55341527	-0.05936165
O	-6.79488178	0.02491230	-1.99583803
H	-7.69256119	-0.18095835	-1.71338088

Sum of electronic and thermal Free Energies= -1599.113323

Frequencies -- -667.6296 11.7018 15.9985

β-hydroxypropionaldehyde

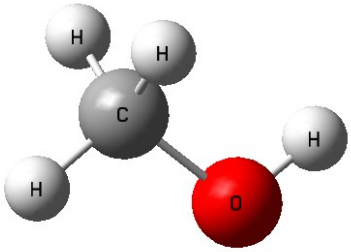


0 1

C	-1.40714100	0.24521800	0.27051100
H	-1.43042300	1.13890600	0.92530800
O	-2.41291300	-0.10490000	-0.30910000
C	-0.08478900	-0.46654700	0.19151400
C	1.06823200	0.47447900	-0.15339200
H	-0.15128900	-1.29079400	-0.52111500
H	0.10708800	-0.88361700	1.18974300
H	0.96449300	0.83859100	-1.18153600
H	1.06497800	1.34077600	0.51868500
O	2.28394400	-0.26596400	-0.00654900
H	3.01909000	0.30415300	-0.25769200

Sum of electronic and thermal Free Energies= -
268.394131
Frequencies -- 71.0509 99.7268
240.4475

Methanol

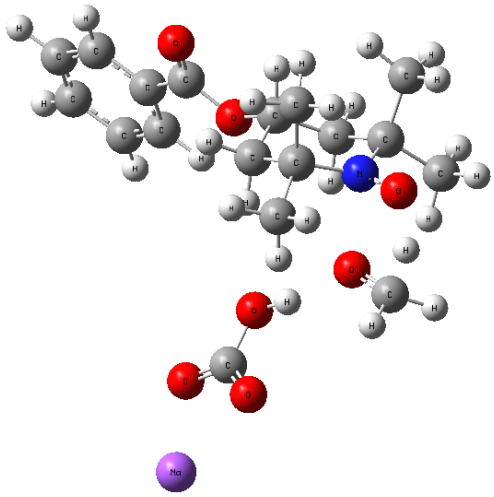


0 1

O	0.51406100	1.25708500	-0.04900800
H	0.18960900	2.16330200	-0.07218900
C	1.94454500	1.29023000	-0.01106700
H	2.28501300	0.25504700	0.01653100
H	2.36094100	1.77388800	-0.90085600
H	2.31291200	1.80574400	0.88197100

Sum of electronic and thermal Free Energies= -
115.742804
Frequencies -- 293.3583 1020.5372
1068.7647

TS(iv)



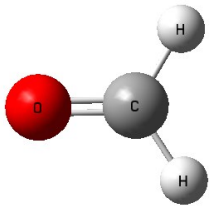
0 1

N	-1.73729643	-0.98208951	-0.15170375
C	-2.78448817	-0.25827242	-0.98732760
C	-3.12171286	1.07961518	-0.30577388
H	-2.28522740	1.76887077	-0.43871151
H	-3.99218103	1.50534735	-0.81009823

C	-3.39477180	0.94416001	1.18798024
H	-4.30613207	0.37785065	1.37684132
C	-4.03029810	-1.15972988	-1.14232934
H	-4.69683706	-0.70520058	-1.87857826
H	-4.59473502	-1.28221155	-0.22006242
H	-3.74129731	-2.14680231	-1.50794894
C	-2.21667394	0.01009011	-2.38731047
H	-2.97175487	0.54878462	-2.96365048
H	-1.99522274	-0.92124700	-2.90992804
H	-1.31597005	0.61793808	-2.33441313
C	-1.80824022	-1.04965296	1.36811927
C	-2.19537387	0.34033155	1.90175096
H	-1.34395914	1.01370843	1.78104398
H	-2.40329638	0.24999531	2.97080689
C	-2.82267531	-2.13793000	1.78704251
H	-2.74298557	-2.28854850	2.86582086
H	-3.85627748	-1.87835553	1.56709416
H	-2.58829740	-3.08296650	1.29353369
C	-0.43444833	-1.44477171	1.92565240
H	-0.50753492	-1.48057449	3.01469409
H	-0.13454314	-2.43338509	1.57606921
H	0.32315304	-0.71560838	1.64713569
O	-1.16583549	-1.96514409	-0.72099296
H	0.04080177	-1.52645113	-1.07545950
C	0.82298456	-0.52719465	-1.04036510
H	1.01818357	-0.38191859	-2.11593397
O	0.10585979	0.36698735	-0.43056246
H	0.12875242	2.14354544	-0.59364400
O	0.04399279	3.10762563	-0.41865682
C	0.67477298	3.82339837	-1.40515309
O	1.23103692	3.18745932	-2.33982554
O	0.63748528	5.07229575	-1.27871239
Na	1.91920103	5.28180042	-3.27034121
O	-3.58212641	2.26980567	1.76492982
C	-4.81884975	2.79924651	1.76715147
O	-5.79394109	2.22893240	1.31736234
C	-4.85536173	4.15635648	2.38453501
C	-3.70626636	4.77257441	2.89758157
C	-6.08515544	4.82404332	2.44437088
C	-3.79124028	6.04216382	3.46308863
H	-2.75517345	4.25916815	2.85277578
C	-6.16590044	6.09262700	3.01001630
H	-6.96776878	4.34010606	2.04535506
C	-5.01886700	6.70331389	3.52022695
H	-2.90027001	6.51580597	3.85853009
H	-7.11985274	6.60505986	3.05316828
H	-5.08156029	7.69193203	3.96059051
H	1.66670166	-0.96769797	-0.48231361

Sum of electronic and thermal Free Energies= -
1445.272891
Frequencies -- -879.7001 12.5394
17.7314

Formaldehyde

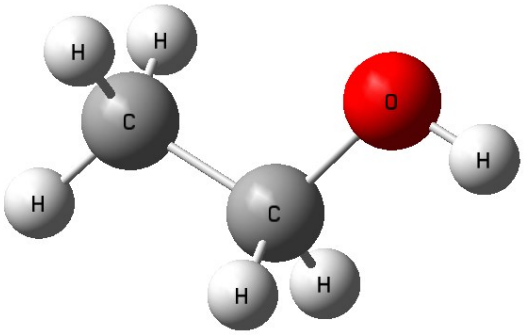


0 1

C	0.53129500	0.00000000	0.00001300
O	-0.67677200	0.00000000	-0.00001200
H	1.11320700	-0.93848500	-0.00001000
H	1.11320000	0.93848900	0.00002900

Sum of electronic and thermal Free Energies= -
114.542556
Frequencies -- 1212.4112 1257.0317
1525.5498

Ethanol



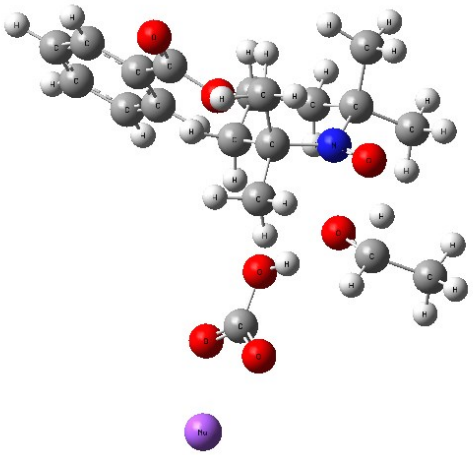
0 1

C	-0.71722800	0.13189900	-0.00508100
C	0.79932800	0.12190900	0.01213100
H	-1.09932300	1.15613400	-0.00493500
H	-1.09948200	-0.38096700	-0.89160100
H	-1.10661100	-0.37849200	0.87977700

H	1.17409200	-0.90837300	0.02357300
H	1.17403100	0.62690500	0.91027100
O	1.27098600	0.80138700	-1.16413000
H	2.23421600	0.79578900	-1.15435700

Sum of electronic and thermal Free Energies= -155.046871
Frequencies -- 234.2138 271.5139 415.8191

$TS_{(v)}$



0 1

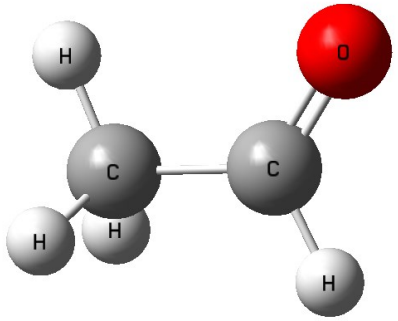
N	-1.73259000	-0.99349400	-0.14173100
C	-2.78234700	-0.26781200	-0.97987500
C	-3.11846200	1.07415300	-0.30671300
H	-2.27989300	1.76037100	-0.44246700
H	-3.98709900	1.49783500	-0.81593900
C	-3.39419200	0.94799100	1.18679100
H	-4.30398800	0.38011400	1.37824500
C	-4.02675100	-1.17330100	-1.12554200
H	-4.69516000	-0.72448500	-1.86345900
H	-4.58953100	-1.29080100	-0.20180200
H	-3.73641000	-2.16200500	-1.48551400
C	-2.22198800	-0.00667700	-2.38394700
H	-2.98876700	0.51147000	-2.96361700
H	-1.98602400	-0.94001800	-2.89628600
H	-1.33293700	0.61809900	-2.33980400
C	-1.80474300	-1.04246200	1.38110500
C	-2.19316000	0.35133800	1.90266400
H	-1.34281100	1.02504500	1.77527900
H	-2.39815200	0.26877500	2.97290700
C	-2.81984900	-2.12885200	1.80516100
H	-2.74445200	-2.26818700	2.88563500
H	-3.85289300	-1.87392600	1.57823100
H	-2.58075600	-3.07807700	1.32216100
C	-0.43456200	-1.42915500	1.94612200

H	-0.51364000	-1.46888700	3.03461400
H	-0.12308100	-2.41317700	1.59392200
H	0.31480400	-0.69104600	1.67171000
O	-1.16612000	-1.97354300	-0.70495800
H	0.06871800	-1.49961600	-1.12581400
C	0.81394400	-0.50682300	-1.16315100
H	0.83410900	-0.34179600	-2.25884000
O	0.12974300	0.37202600	-0.47939900
H	0.15656800	2.13175700	-0.55168500
O	0.07272300	3.09206200	-0.34593900
C	0.70887700	3.84029700	-1.30269500
O	1.26918800	3.23738500	-2.25726800
O	0.67354600	5.08468200	-1.13387100
Na	1.96354700	5.34595600	-3.12000000
O	-3.58540400	2.27590500	1.75644200
C	-4.82456300	2.80001600	1.75797400
O	-5.79704400	2.22447300	1.30928600
C	-4.86721000	4.15765500	2.37359400
C	-3.72117000	4.77939700	2.88680700
C	-6.10009500	4.81971400	2.43251500
C	-3.81224000	6.04889500	3.45157600
H	-2.76772600	4.27029800	2.84283500
C	-6.18691600	6.08820300	2.99743900
H	-6.98035100	4.33146100	2.03355500
C	-5.04292700	6.70440100	3.50785900
H	-2.92364900	6.52680900	3.84722400
H	-7.14325300	6.59621800	3.04000900
H	-5.11037600	7.69289800	3.94779100
C	2.15797600	-0.99323000	-0.61688700
H	2.08072800	-1.31245300	0.42362400
H	2.88816700	-0.17857300	-0.66962600
H	2.53504400	-1.82719500	-1.21490900

Sum of electronic and thermal Free Energies= -1484.574990

Frequencies -- -645.6511 13.7550 17.9374

Acetaldehyde



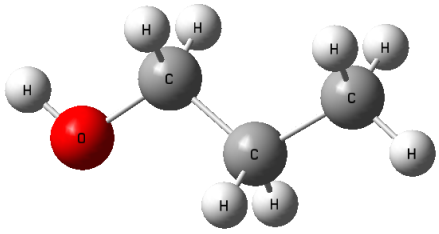
0 1

C	0.39127600	0.06982900	0.00152100

O	1.41164100	0.25142800	-0.63012400
H	-0.00378700	0.87542000	0.65135100
C	-0.41387000	-1.19126800	-0.01722200
H	-1.43448400	-0.95938500	-0.34049600
H	0.02904200	-1.94001900	-0.67377500
H	-0.49260200	-1.58068300	1.00358400

Sum of electronic and thermal Free Energies= -153.858659
Frequencies -- 157.8476 512.4939 779.3632

Propan-1-ol

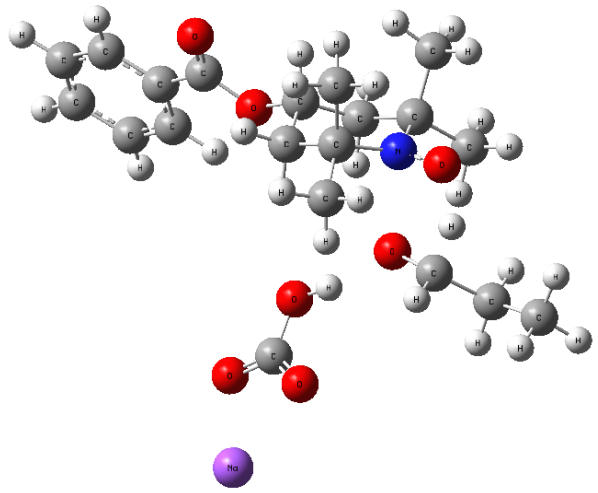


0 1

H	0.12437400	-1.44283500	-1.22733300
C	0.77031600	-0.55669300	-1.27009400
H	0.83919200	-0.23918000	-2.31821500
C	2.15285900	-0.89082100	-0.73278100
C	2.82824400	-2.01646600	-1.52172600
H	2.06120600	-1.17566200	0.32090500
H	2.77106800	0.01280400	-0.76589200
H	2.24093200	-2.93889300	-1.48054400
H	2.95187100	-1.74597800	-2.57485600
H	3.81920500	-2.23540100	-1.11677900
O	0.20941900	0.49893300	-0.47214400
H	-0.65983600	0.71791900	-0.82437500

Sum of electronic and thermal Free Energies= -194.345048
Frequencies -- 122.9096 229.2642 246.3204

$TS_{(vi)}$



0 1

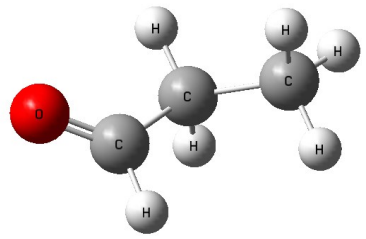
N	-1.68882000	-0.93952900	-0.18174900
C	-2.75649000	-0.22626900	-1.00743200
C	-3.10991500	1.10557900	-0.32294300
H	-2.28320800	1.80582800	-0.46011100
H	-3.98880200	1.51853500	-0.82324000
C	-3.37286800	0.96482400	1.17151900
H	-4.27111900	0.37972800	1.36528400
C	-3.98638100	-1.15182800	-1.15030600
H	-4.66832800	-0.70932000	-1.87959400
H	-4.53949700	-1.28630000	-0.22309700
H	-3.68166700	-2.13255100	-1.52015700
C	-2.21130500	0.05387100	-2.41382200
H	-2.99183700	0.56130900	-2.98459500
H	-1.96181600	-0.87168600	-2.93380500
H	-1.33369300	0.69479100	-2.37197800
C	-1.74917600	-0.99960200	1.34102700
C	-2.15671600	0.38401500	1.87472100
H	-1.31848500	1.07243000	1.74538800
H	-2.35234300	0.29124700	2.94587700
C	-2.74240500	-2.10589500	1.76551900
H	-2.65623500	-2.25113400	2.84440000
H	-3.78144800	-1.86743800	1.54826500
H	-2.49083400	-3.04758000	1.27417100
C	-0.36848100	-1.36676100	1.89344400
H	-0.43865600	-1.41533200	2.98219300
H	-0.04278200	-2.34287100	1.53213400
H	0.36643600	-0.61431700	1.61867800
O	-1.11074700	-1.90723200	-0.75519800
H	0.11400200	-1.41315600	-1.17969000
C	0.84108400	-0.40443300	-1.22005000
H	0.84918200	-0.23535200	-2.31692200
O	0.14850200	0.45829400	-0.52636500
H	0.15717100	2.21848700	-0.58967500
O	0.06677400	3.17745300	-0.38001600
C	0.70163100	3.93336000	-1.33162400

O	1.26637900	3.33763900	-2.28811100
O	0.66069700	5.17671800	-1.15670400
Na	1.95455600	5.45019900	-3.14114000
O	-3.58371000	2.28483300	1.75257000
C	-4.83261300	2.78508700	1.76916700
O	-5.79696700	2.19685500	1.31938500
C	-4.89735000	4.13314700	2.40356300
C	-3.76209700	4.76549100	2.92769900
C	-6.14092600	4.77405400	2.47127600
C	-3.87448600	6.02421200	3.51240600
H	-2.80044500	4.27269600	2.87714900
C	-6.24896700	6.03202400	3.05568700
H	-7.01283000	4.27774900	2.06400500
C	-5.11575100	6.65863200	3.57735000
H	-2.99426900	6.51011200	3.91694800
H	-7.21350000	6.52368300	3.10492000
H	-5.19981500	7.63875000	4.03289700
C	2.20460700	-0.87537200	-0.69417400
C	2.80223100	-2.01141400	-1.52736000
H	2.11057900	-1.17495400	0.35251500
H	2.87608500	-0.00771600	-0.71208700
H	2.18032000	-2.91052600	-1.47944300
H	2.89437500	-1.72519200	-2.57979200
H	3.79980500	-2.27721100	-1.16885500

Sum of electronic and thermal Free Energies= -1523.873340

Frequencies -- -652.1178 14.0802 17.2948

Propanal



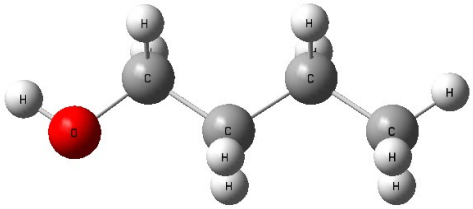
0 1

C	0.77868300	-0.24084500	0.29190700
O	1.82288600	-0.03284800	-0.29064800
H	0.69949000	-1.09935000	0.99030200
C	-0.46819600	0.58481000	0.15311900
H	-0.62563800	1.07589200	1.12286800
H	-0.30292900	1.36314600	-0.59513300
C	-1.69717700	-0.27764000	-0.17921900
H	-2.59622400	0.34095100	-0.19918300
H	-1.59169600	-0.75432800	-1.15677300
H	-1.84595900	-1.06148100	0.56825600

Sum of electronic and thermal Free Energies= -193.156152

Frequencies -- 85.0977 208.7055 328.1847

Butan-1-ol



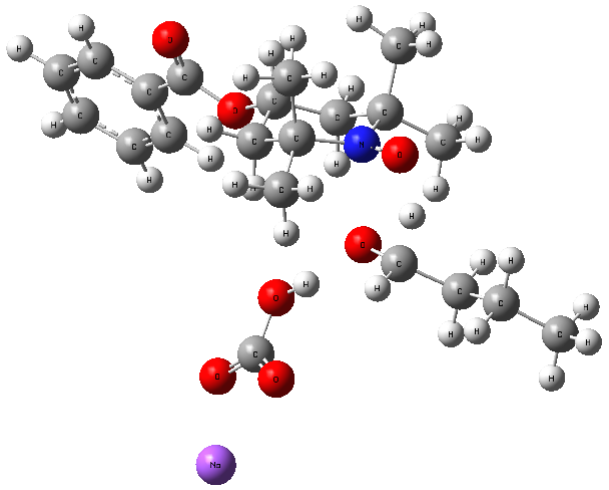
0 1

H	0.13867000	-1.38097900	-1.23411900
C	0.79020500	-0.50000300	-1.29221600
H	0.84126600	-0.18656600	-2.34252400
C	2.17969600	-0.84018700	-0.77790700
C	2.84561700	-1.97094000	-1.57072900
H	2.10584600	-1.12372200	0.27860200
H	2.80399300	0.05994400	-0.82319900
C	4.24530000	-2.31615500	-1.05369800
H	2.21184200	-2.86471400	-1.53026500
H	2.90814100	-1.68597200	-2.62761800
H	4.91252700	-1.45049500	-1.11357300
H	4.21110800	-2.63745500	-0.00792300
H	4.69526000	-3.12464500	-1.63642800
O	0.25080200	0.56296900	-0.48833300
H	-0.63076600	0.77358900	-0.81410800

Sum of electronic and thermal Free Energies= -233.643376

Frequencies -- 105.5198 111.7281 184.4976

$TS_{(vii)}$



0 1

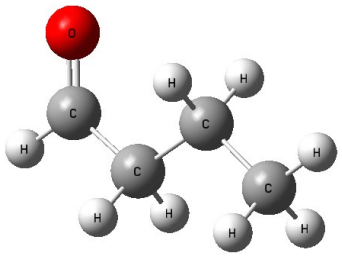
N	-1.66381080	-0.91333682	-0.19405355
C	-2.74259616	-0.20981880	-1.01366526
C	-3.10722037	1.11691380	-0.32508645
H	-2.28853787	1.82603906	-0.46476288
H	-3.99271730	1.52138206	-0.82061661
C	-3.36176684	0.97047477	1.17026237
H	-4.25220417	0.37455243	1.36682922
C	-3.96297493	-1.14840985	-1.15306411
H	-4.65294457	-0.71190744	-1.87840738
H	-4.51037792	-1.29106685	-0.22372049
H	-3.64907056	-2.12489390	-1.52644384
C	-2.20668375	0.07881506	-2.42189536
H	-2.99557757	0.57788066	-2.98855925
H	-1.94849981	-0.84294706	-2.94436413
H	-1.33650606	0.72997608	-2.38276872
C	-1.71708653	-0.97668625	1.32890713
C	-2.13595425	0.40191299	1.86671905
H	-1.30541071	1.09896580	1.73408575
H	-2.32532239	0.30564190	2.93869174
C	-2.69743248	-2.09354354	1.75575240
H	-2.60445023	-2.24031280	2.83385053
H	-3.73984054	-1.86477902	1.54427694
H	-2.43914970	-3.03161714	1.26100762
C	-0.33042907	-1.33128012	1.87459754
H	-0.39550324	-1.38357808	2.96349306
H	0.00372256	-2.30300166	1.50919279
H	0.39572281	-0.57075900	1.59877707
O	-1.07905321	-1.87437499	-0.77175345
H	0.13948812	-1.36677436	-1.20104486
C	0.85553613	-0.35105841	-1.24255299
H	0.85588997	-0.17775538	-2.33845916
O	0.15656791	0.50283569	-0.54309379
H	0.15044547	2.26293925	-0.60725733
O	0.05440220	3.22158549	-0.39822228
C	0.68554957	3.98051572	-1.34991449

O	1.25257477	3.38752492	-2.30675094
O	0.63921035	5.22365666	-1.17475613
Na	1.93456133	5.50223464	-3.15846557
O	-3.58587496	2.28669776	1.75490038
C	-4.84122827	2.77036201	1.77983028
O	-5.80014326	2.17073237	1.33346224
C	-4.92067508	4.11543739	2.41879441
C	-3.79210526	4.75961429	2.94294120
C	-6.17178630	4.74098808	2.49129435
C	-3.91860276	6.01469353	3.53259128
H	-2.82464789	4.27871480	2.88865379
C	-6.29388072	5.99546757	3.08038186
H	-7.03847495	4.23562473	2.08405032
C	-5.16731440	6.63381985	3.60220190
H	-3.04356264	6.50970354	3.93731757
H	-7.26419504	6.47523848	3.13321400
H	-5.26234125	7.61116605	4.06153547
C	2.22611354	-0.80770590	-0.72342425
C	2.83521887	-1.94684198	-1.54690908
H	2.14303862	-1.10124319	0.32689295
H	2.89338834	0.06427421	-0.75260292
C	4.24022922	-2.33763019	-1.07917953
H	2.17760779	-2.82280860	-1.49700102
H	2.87276437	-1.65130509	-2.60229196
H	4.93015978	-1.49095646	-1.15215630
H	4.23088060	-2.66917474	-0.03608910
H	4.64763596	-3.15239278	-1.68425824

Sum of electronic and thermal Free Energies= -1563.171613

Frequencies -- -647.5673 13.4047 16.6928

Butanal



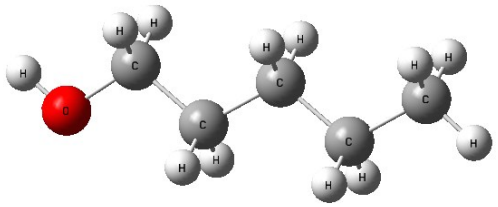
0 1

C	1.56444700	0.40942800	-0.00002300
O	2.04146200	-0.70670000	0.00000900
H	2.23261800	1.29400700	-0.00004800
C	0.09738300	0.72823500	0.00001600
H	-0.07892900	1.37903700	0.86881000
H	-0.07903900	1.37911700	-0.86869300
C	-0.84652000	-0.47281200	-0.00000600

H	-0.63656500	-1.09503400	-0.87552400
H	-0.63662300	-1.09508800	0.87549000
C	-2.32049400	-0.05756200	-0.00000400
H	-2.97469100	-0.93335500	-0.00018800
H	-2.56372000	0.54043400	0.88376200
H	-2.56364700	0.54074800	-0.88357800

Sum of electronic and thermal Free Energies= -232.455382
Frequencies -- 81.7025 170.3411 193.4654

Pentan-1-ol



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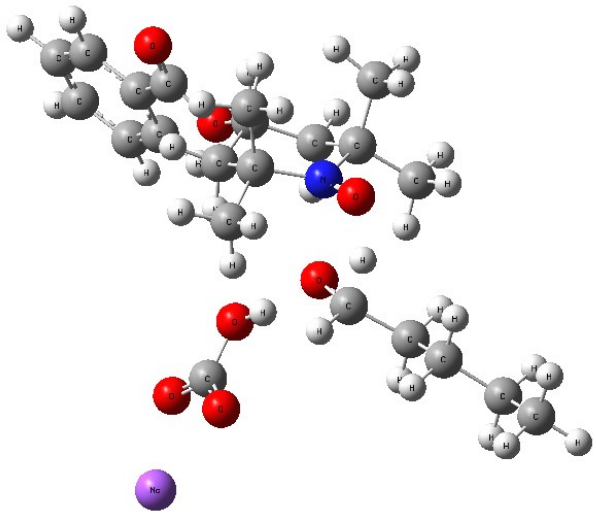
H	0.17753600	-1.26884300	-1.28542300
C	0.81523600	-0.37758800	-1.33952600
H	0.84647400	-0.04760700	-2.38549800
C	2.21688000	-0.70423700	-0.84981900
C	2.88852300	-1.81145300	-1.67004900
H	2.16107100	-1.00507500	0.20289600
H	2.82539300	0.20677800	-0.88911000
C	4.30249500	-2.15055200	-1.18411000
H	2.27003300	-2.71743600	-1.63640100
H	2.93403800	-1.50933400	-2.72413300
C	4.97236300	-3.25726400	-2.00371300
H	4.92109000	-1.24561300	-1.21778000
H	4.25797500	-2.45207200	-0.13067400
H	4.39324800	-4.18533100	-1.96115800
H	5.06148900	-2.97007500	-3.05638300
H	5.97767700	-3.47508500	-1.63218400
O	0.27201500	0.66521200	-0.51193500
H	-0.61677200	0.86837000	-0.82249200

Sum of electronic and thermal Free Energies= -272.941932
Frequencies -- 74.4472 90.9876 135.1843

TS(viii)



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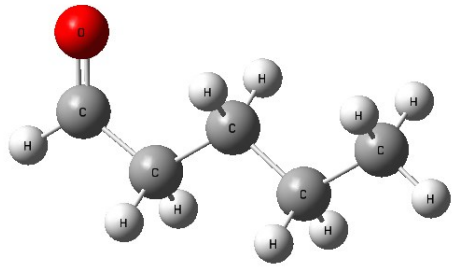
N	-1.61831788	-0.86393991	-0.23337248
C	-2.71683161	-0.17457996	-1.03832274
C	-3.10236817	1.13846511	-0.33476455
H	-2.29903028	1.86480135	-0.47498179
H	-3.99987596	1.52955841	-0.81932392
C	-3.34127161	0.97354412	1.16121567
H	-4.21759546	0.35763940	1.35930242
C	-3.91934852	-1.13601274	-1.17757584
H	-4.62376173	-0.70622215	-1.89296260
H	-4.45608918	-1.29923678	-0.24547319
H	-3.58882658	-2.10209434	-1.56352357
C	-2.19755866	0.13762105	-2.44778003
H	-3.00134695	0.62394171	-3.00451734
H	-1.92291743	-0.77375949	-2.97995367
H	-1.34170195	0.80756945	-2.40925958
C	-1.65906981	-0.94259336	1.28906157
C	-2.09859106	0.42331721	1.84247941
H	-1.28221518	1.13664887	1.70843479
H	-2.27693666	0.31447273	2.91513458
C	-2.61602029	-2.08066539	1.71308503
H	-2.51002993	-2.23710996	2.78861274
H	-3.66417777	-1.86739037	1.51418270
H	-2.34665169	-3.00889414	1.20585469
C	-0.26209031	-1.27736398	1.82092482
H	-0.31788583	-1.34138127	2.90969732
H	0.08682725	-2.23924744	1.44346736
H	0.44817658	-0.50123024	1.54720691
O	-1.01786727	-1.80680211	-0.82485839
H	0.18667588	-1.26975188	-1.25728361
C	0.88130475	-0.23887358	-1.29377798
H	0.86975697	-0.05454249	-2.38778168
O	0.17020612	0.59322735	-0.58050773

H	0.13582328	2.35339937	-0.63943763
O	0.02937971	3.31078871	-0.42934213
C	0.65774414	4.07684681	-1.37727535
O	1.23205243	3.49034851	-2.33374544
O	0.60157734	5.31918083	-1.19939275
Na	1.90180830	5.60971957	-3.18054863
O	-3.58847188	2.27935394	1.75970615
C	-4.85515248	2.73092429	1.80824690
O	-5.80525037	2.11218991	1.36914403
C	-4.95929141	4.06626428	2.46374921
C	-3.84089474	4.73039362	2.98475758
C	-6.22396543	4.66115079	2.55647557
C	-3.99091858	5.97456110	3.59175774
H	-2.86300951	4.27320098	2.91473464
C	-6.36952277	5.90498641	3.16250426
H	-7.08269130	4.14049262	2.15164586
C	-5.25305946	6.56313188	3.68143970
H	-3.12375346	6.48490173	3.99438417
H	-7.35027265	6.36098720	3.23091141
H	-5.36640227	7.53206126	4.15425320
C	2.26501754	-0.67174357	-0.78892518
C	2.89569337	-1.78298781	-1.63348400
H	2.19355082	-0.98309222	0.25701924
H	2.91081872	0.21637741	-0.80744825
C	4.31400371	-2.15418527	-1.18550204
H	2.26010827	-2.67692629	-1.59440360
H	2.92205099	-1.47119025	-2.68562326
C	4.94177007	-3.26697034	-2.03018086
H	4.94964566	-1.26137407	-1.22699400
H	4.28973752	-2.46371401	-0.13369061
H	4.34500117	-4.18347539	-1.98152297
H	5.01141088	-2.97222374	-3.08224312
H	5.95104659	-3.50836242	-1.68481817

Sum of electronic and thermal Free Energies= -1602.470647
Frequencies -- -653.1468 12.4667 14.9361

Pentanal



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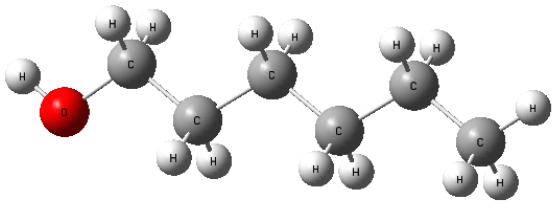
C	2.21464800	0.23166300	0.00014400

O	2.47455000	-0.95394900	-0.00020100
H	3.03640600	0.97590000	0.00051900
C	0.83392300	0.82079400	0.00009400
H	0.78524200	1.49382700	0.86851700
H	0.78541600	1.49369600	-0.86844800
C	-0.32025600	-0.17868900	0.00011600
H	-0.23496800	-0.83077900	-0.87603500
H	-0.23512000	-0.83048300	0.87651300
C	-1.69383000	0.50222100	-0.00033800
H	-1.77354900	1.15625300	0.87625000
H	-1.77340700	1.15516400	-0.87775400
C	-2.85514100	-0.49567900	0.00017500
H	-3.82041300	0.01814800	-0.00105300
H	-2.82051300	-1.14207700	-0.88261900
H	-2.82155200	-1.13991500	0.88456900

Sum of electronic and thermal Free Energies= -271.753712

Frequencies -- 74.4347 108.5048 138.7138

Hexan-1-ol



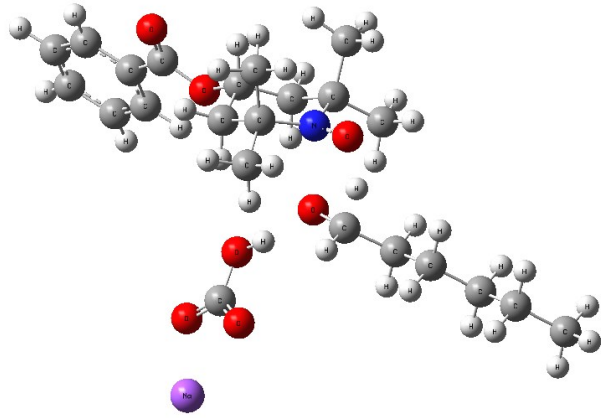
0 1

H	0.20077300	-1.21384800	-1.32092600
C	0.83283800	-0.31743500	-1.35116400
H	0.86358300	0.03921500	-2.38836900
C	2.23576800	-0.64744800	-0.86755400
C	2.91650700	-1.72723900	-1.71674000
H	2.18015100	-0.97711200	0.17648400
H	2.83790500	0.26852100	-0.88079400
C	4.33096800	-2.07098700	-1.23643900
H	2.30266600	-2.63684800	-1.71011500
H	2.96201600	-1.39454000	-2.76144500
C	5.01950300	-3.14853900	-2.08163500
H	4.94584900	-1.16162700	-1.24107900
H	4.28681400	-2.40536800	-0.19182900
H	4.40498100	-4.05708600	-2.07673600
H	5.06266900	-2.81444600	-3.12548800
C	6.43242400	-3.48627000	-1.59631500
H	6.89466000	-4.25775800	-2.21875500
H	7.08044600	-2.60421100	-1.62361500
H	6.41791700	-3.85464100	-0.56545300
O	0.28153900	0.70055200	-0.49838100

H	-0.60751600	0.90689200	-0.80607800

Sum of electronic and thermal Free Energies= -312.240396
Frequencies -- 60.6464 70.4785 102.0035

$TS_{(ix)}$



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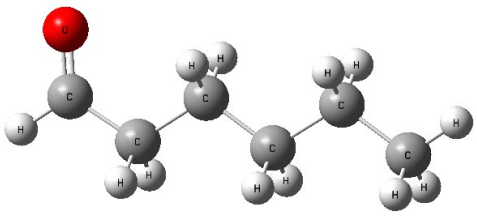
N	-1.59730459	-0.84590063	-0.23796034
C	-2.70691486	-0.16798445	-1.03718908
C	-3.10451335	1.13963360	-0.33013676
H	-2.31053271	1.87550869	-0.47359068
H	-4.00898231	1.52067462	-0.80977500
C	-3.33394684	0.97045897	1.16684093
H	-4.20234525	0.34460963	1.36855307
C	-3.89905142	-1.14277541	-1.17307349
H	-4.61082858	-0.72015553	-1.88543341
H	-4.43051722	-1.31299947	-0.23922736
H	-3.55907681	-2.10465862	-1.56130254
C	-2.19701544	0.15215967	-2.44829615
H	-3.00880275	0.62943162	-3.00123499
H	-1.91347707	-0.75518274	-2.98268434
H	-1.34920623	0.83244928	-2.41256530
C	-1.63144368	-0.92776519	1.28432859
C	-2.08192309	0.43308586	1.84138862
H	-1.27349940	1.15469158	1.70361364
H	-2.25373773	0.32147752	2.91482230
C	-2.57591144	-2.07549180	1.71042603
H	-2.46273618	-2.23366932	2.78497020
H	-3.62695937	-1.87091189	1.51776463
H	-2.30105623	-3.00002056	1.19940377
C	-0.22930450	-1.25014909	1.81028175
H	-0.28034915	-1.31637316	2.89915459
H	0.12722383	-2.20811736	1.42998316
H	0.47259497	-0.46694321	1.53509482
O	-0.98751522	-1.77984622	-0.83412864
H	0.20793787	-1.22668438	-1.27092800
C	0.89094838	-0.18778282	-1.30579336

H	0.87345863	0.00111634	-2.39892478
O	0.17332251	0.63341887	-0.58652527
H	0.11706819	2.39264527	-0.65529578
O	0.00225155	3.35021840	-0.45015715
C	0.62090760	4.11685283	-1.40403808
O	1.19665275	3.53056325	-2.35974048
O	0.55527490	5.35953605	-1.23177829
Na	1.85462158	5.65200323	-3.21318657
O	-3.59335416	2.27298050	1.76734731
C	-4.86571394	2.70715147	1.82690212
O	-5.81119745	2.07469985	1.39747113
C	-4.98250614	4.04204725	2.48113258
C	-3.86857660	4.72387745	2.98863768
C	-6.25478060	4.61844966	2.58598205
C	-4.03050959	5.96720138	3.59431844
H	-2.88482405	4.28106933	2.90903681
C	-6.41225409	5.86148398	3.19064222
H	-7.10998977	4.08423443	2.19151899
C	-5.30017693	6.53734186	3.69604425
H	-3.16674055	6.49129167	3.98643630
H	-7.39887040	6.30309920	3.26844752
H	-5.42279869	7.50571072	4.16768917
C	2.28080356	-0.60848877	-0.80743456
C	2.92931786	-1.69206182	-1.67441797
H	2.21316019	-0.94266524	0.23170998
H	2.91263284	0.28972614	-0.80649646
C	4.34608114	-2.06240611	-1.22173643
H	2.30065316	-2.59158686	-1.66477971
H	2.96210314	-1.35184252	-2.71737019
C	5.00496665	-3.14043424	-2.08999030
H	4.97468982	-1.16239073	-1.22605759
H	4.31425231	-2.40799500	-0.18029853
H	4.37368676	-4.03742188	-2.09087152
H	5.04232684	-2.79209322	-3.12939820
C	6.41664127	-3.51124080	-1.62580217
H	6.85795993	-4.28093286	-2.26543305
H	7.08040454	-2.64078038	-1.64626525
H	6.40646204	-3.89584760	-0.60082839

Sum of electronic and thermal Free Energies= -1641.769034

Frequencies -- -656.6594 11.0467 13.7874

Hexanal



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 C                  -2.83909900    0.26626900   -0.00002900
 O                  -3.13051000   -0.91203700   -0.00007400
 H                  -3.64078200    1.03214800   -0.00011800
 C                  -1.44317500    0.81885500    0.00010600
 H                  -1.37700400    1.49043800   -0.86827400
 H                  -1.37710300    1.49021700    0.86865800
 C                  -0.31576400   -0.21091700    0.00002800
 H                  -0.41928900   -0.85993700    0.87632500
 H                  -0.41944500   -0.85995800   -0.87623300
 C                   1.07526600    0.43296600   -0.00007300
 H                   1.17438300    1.08443100   -0.87794100
 H                   1.17439200    1.08473900    0.87756600
 C                   2.21703300   -0.58944400    0.00013000
 H                   2.11744400   -1.24027200    0.87732600
 H                   2.11739500   -1.24071500   -0.87672900
 C                   3.60590800    0.05599100   -0.00008900
 H                   4.39632900   -0.69993700    0.00011900
 H                   3.74836000    0.68615800   -0.88387200
 H                   3.74838800    0.68666100    0.88333000

Sum of electronic and thermal Free Energies=          -
311.052167
Frequencies --    51.6675            92.3742
109.3351
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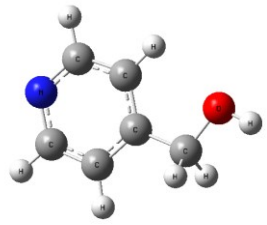
4-pyridine-methanol



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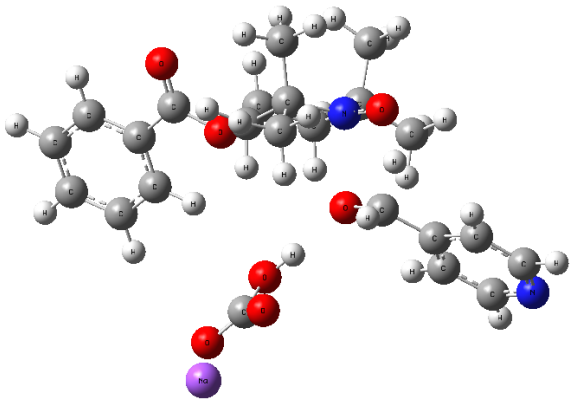
0 1
 H                   2.10476900   -1.25121500   -0.88386100
 C                   1.89013600   -0.63768500    0.00008200
 H                   2.10478000   -1.25095800    0.88420400
 C                   0.42726300   -0.27338400    0.00004400
 C                  -0.54273900   -1.28097100   -0.00001100
 C                  -1.88685800   -0.92870700   -0.00002900
 H                  -0.25994700   -2.32809400   -0.00004900
 H                  -2.65074100   -1.70062100   -0.00011000
 C                  -0.01769600    1.04762300    0.00005000
 H                   0.68767200    1.86744900    0.00006400
 N                  -2.32320500    0.34029300   -0.00002900
 C                  -1.38933900    1.29840100    0.00001800
 H                  -1.75117300    2.32271700    0.00001100
 O                   2.69071700    0.54124200   -0.00010100
 H                   3.61673600    0.27707200   -0.00017000
```

Sum of electronic and thermal Free Energies= -362.837382
Frequencies -- 40.3611 171.6305 209.5152

$TS_{(x)}$



0 1

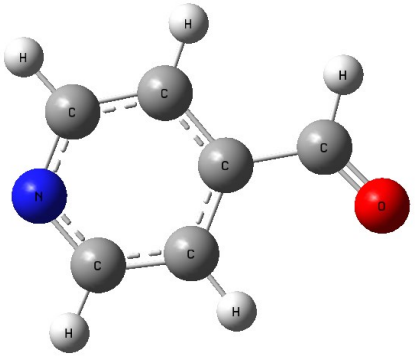
N	-1.18429787	-1.96362189	0.81404786
C	-0.24558060	-1.58271606	1.95649834
C	0.98912793	-0.87763535	1.36867414
H	0.70283134	0.12095011	1.03273162
H	1.72485901	-0.76699275	2.16841253
C	1.60220130	-1.62248477	0.18834800
H	2.02732061	-2.57636948	0.49842061
C	0.13307806	-2.85971518	2.74296837
H	0.65555199	-2.55692591	3.65273920
H	0.79092132	-3.53052633	2.19479775
H	-0.76506506	-3.40803907	3.03303238
C	-0.97015665	-0.63533705	2.92093297
H	-0.28085752	-0.38817540	3.73076759
H	-1.84794849	-1.11062286	3.35979679
H	-1.26517126	0.28467907	2.42211422
C	-0.67177153	-2.56874893	-0.48864170
C	0.58254917	-1.79459930	-0.92719082
H	0.27889490	-0.80605481	-1.27851992
H	1.03506841	-2.32663902	-1.76750792
C	-0.38764237	-4.07372378	-0.27148049
H	-0.19723461	-4.52806055	-1.24597538
H	0.47851935	-4.26887221	0.35658438
H	-1.25756470	-4.56473133	0.16851945
C	-1.75361990	-2.44507324	-1.56547784
H	-1.36736284	-2.88569001	-2.48685981
H	-2.65783876	-2.98600611	-1.28510274
H	-1.99758317	-1.40260214	-1.75001090
O	-2.36339814	-2.26770654	1.14494323
H	-3.13574782	-1.15387824	0.87108000
C	-3.10308289	0.02635923	0.47427709

H	-3.39581206	0.51859452	1.42207719
O	-1.86060664	0.16920066	0.10584985
C	-4.20581875	0.10949554	-0.55412686
C	-5.53044723	-0.16630691	-0.19860699
C	-6.52842798	-0.05243181	-1.15990844
H	-5.78505220	-0.46711949	0.81215972
H	-7.56097007	-0.26787121	-0.90110544
C	-3.96103511	0.50022687	-1.87157820
H	-2.95704378	0.74662206	-2.19276645
H	-0.92203589	1.68246079	0.01814865
O	-0.27934890	2.39135951	-0.21124381
C	-0.56559525	3.53051245	0.49910005
O	-1.55205329	3.51043949	1.28282886
O	0.19891014	4.50574605	0.29548052
Na	-1.09711672	5.77001016	1.85343182
O	2.68762997	-0.82959443	-0.37345104
C	3.92507181	-0.99310319	0.13109234
O	4.18366485	-1.76400226	1.03488463
C	4.93502735	-0.13022148	-0.54581774
C	4.59371532	0.73467765	-1.59400783
C	6.26394112	-0.19916723	-0.10860960
C	5.57431975	1.51869606	-2.19607247
H	3.56802009	0.79040813	-1.93308075
C	7.24070256	0.58625470	-0.71243664
H	6.51822897	-0.86985263	0.70250437
C	6.89702847	1.44597029	-1.75727213
H	5.30699815	2.18599224	-3.00709863
H	8.26740406	0.52913035	-0.37027293
H	7.65812589	2.05773478	-2.22810716
C	-5.02920522	0.58763407	-2.76070853
H	-4.85638541	0.89456517	-3.78831271
N	-6.29833194	0.31607883	-2.42912213

Sum of electronic and thermal Free Energies= -1692.368094

Frequencies -- -666.3965 14.0479 16.0470

pyridine-4-aldehyde



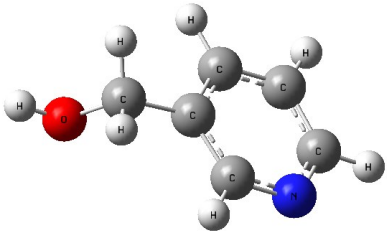
0 1

C	1.98480100	0.47197400	-0.00005100
H	2.26395000	1.54158400	0.00001600
O	2.83686600	-0.39235500	-0.00002800
C	0.52350800	0.20529900	-0.00001500
C	-0.37522400	1.27275700	0.00005500
C	-1.74104900	0.99341100	0.00008100
H	-0.02520800	2.29884700	0.00009300
H	-2.46514200	1.80185900	0.00014100
C	0.01663400	-1.09744700	-0.00005800
H	0.68467000	-1.94942100	-0.00011100
C	-1.36224300	-1.26941600	-0.00003000
H	-1.78984600	-2.26686500	-0.00006400
N	-2.23455800	-0.24952000	0.00003700

Sum of electronic and thermal Free Energies= -361.647486

Frequencies -- 102.8452 214.2763 224.6443

3-pyridine-methanol



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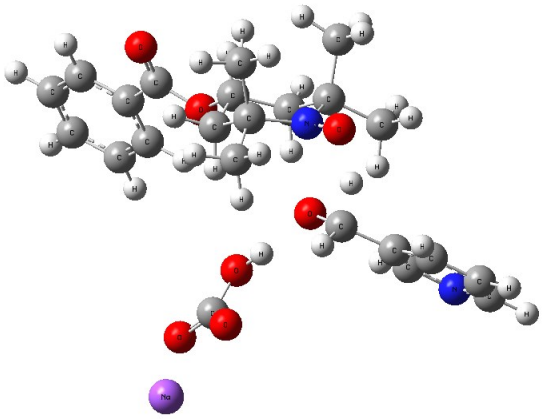
C	-0.43905000	-0.05154000	0.27962200
C	0.22339000	1.17586900	0.20240900
C	1.59221600	1.19441600	-0.04218900
C	2.25712500	-0.02035700	-0.20051000
H	-0.32545300	2.10199700	0.33617300
H	2.13892400	2.12736300	-0.10544100
H	3.32610700	-0.04002300	-0.39052100
C	-1.92278000	-0.13278400	0.51382100
H	-2.19090300	-1.12916800	0.88037800
H	-2.22436400	0.60340400	1.26663600
O	-2.59413500	0.13577000	-0.73142000
H	-3.54378000	0.14087100	-0.56323300
C	0.32541200	-1.20756600	0.10602000
H	-0.15229500	-2.18239300	0.16384300
N	1.64385200	-1.20806300	-0.12735900

Sum of electronic and thermal Free Energies= -362.836461

Frequencies -- 33.1788 141.2385 250.0479

TS$_{(xi)}$



0 1

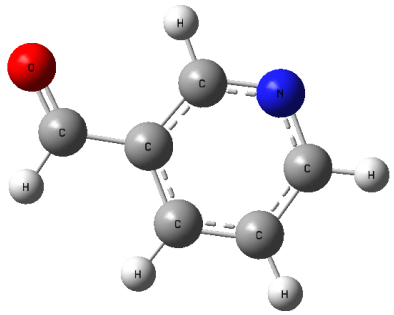
N	-1.19103130	-1.96615172	0.83076490
C	-0.24653693	-1.58248960	1.96745453
C	0.98464383	-0.87683502	1.37316748
H	0.69604018	0.12142999	1.03838447
H	1.72450385	-0.76563871	2.16905338
C	1.59191777	-1.62170879	0.18985718
H	2.01925699	-2.57526876	0.49787796
C	0.13739454	-2.85791973	2.75384285
H	0.66349842	-2.55350204	3.66099463
H	0.79365931	-3.52855729	2.20346024
H	-0.75874281	-3.40711317	3.04844617
C	-0.96834378	-0.63456729	2.93334168
H	-0.27471431	-0.38099535	3.73753058
H	-1.84118882	-1.11193241	3.37973916
H	-1.27107760	0.28170285	2.43216870
C	-0.68477747	-2.56985032	-0.47501594
C	0.56650672	-1.79455885	-0.92019122
H	0.25971248	-0.80629538	-1.26938687
H	1.01502198	-2.32603832	-1.76303483
C	-0.39802909	-4.07455940	-0.25934073
H	-0.21034956	-4.52879161	-1.23441235
H	0.47047738	-4.26852873	0.36590509
H	-1.26579627	-4.56661190	0.18376122
C	-1.77229903	-2.44725197	-1.54639251
H	-1.39127066	-2.88953615	-2.46917029
H	-2.67529424	-2.98706037	-1.26002840
H	-2.01634142	-1.40454620	-1.73043160

O	-2.36698833	-2.27024739	1.16815533
H	-3.14803140	-1.14294309	0.89193350
C	-3.11220506	0.02526596	0.48407959
H	-3.40205969	0.53498504	1.42408088
O	-1.86601451	0.16394097	0.11607381
C	-4.20949070	0.10353722	-0.55059512
C	-5.53239356	-0.20582490	-0.22075835
C	-6.51910420	-0.09476002	-1.19297627
H	-5.78410751	-0.53073880	0.78407822
C	-6.15228496	0.32617320	-2.47075780
H	-7.55311700	-0.33089996	-0.97254157
H	-6.89817008	0.41792750	-3.25459671
C	-3.95419973	0.53013721	-1.85734301
H	-2.94312237	0.80420477	-2.13983656
H	-0.93215049	1.67309234	0.03762763
O	-0.28890579	2.38296123	-0.19046393
C	-0.57465001	3.52247019	0.51855963
O	-1.56143592	3.50443220	1.30212471
O	0.19068376	4.49726909	0.31466517
Na	-1.10425768	5.76369486	1.87065460
O	2.67412478	-0.82839776	-0.37787616
C	3.91439447	-0.99182960	0.11941620
O	4.17842870	-1.76268645	1.02170959
C	4.92040739	-0.12895505	-0.56344041
C	4.57293229	0.73608361	-1.60948896
C	6.25191334	-0.19809377	-0.13423326
C	5.55000196	1.52006030	-2.21733461
H	3.54523680	0.79194496	-1.94243328
C	7.22514434	0.58724710	-0.74384546
H	6.51099007	-0.86888796	0.67527513
C	6.87531709	1.44711656	-1.78650981
H	5.27788991	2.18747662	-3.02666755
H	8.25387818	0.52994021	-0.40786885
H	7.63365035	2.05882375	-2.26185990
N	-4.89447161	0.64120209	-2.80438987

Sum of electronic and thermal Free Energies= -1692.366875

Frequencies -- -604.0426 14.1027 16.4750

pyridine-3-aldehyde



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0 1
 C                 -1.97102600    0.47616300   -0.00015400
 H                 -2.25241000    1.54614600   -0.00045700
 O                 -2.82789900   -0.38710700   -0.00045100
 C                 -0.51679300    0.21956100    0.00047900
 C                  0.38614900    1.28640800    0.00029800
 C                  1.74795300    1.00887700   -0.00008800
 H                  0.02503300    2.30954500    0.00064000
 C                  2.15133400   -0.32455300   -0.00052100
 H                  2.48535800    1.80141600   -0.00009200
 H                  3.20760800   -0.57471200   -0.00090100
 C                 -0.00492800   -1.08607000    0.00062800
 H                 -0.68828400   -1.92910200    0.00111800
 N                  1.29853600   -1.36268000   -0.00007900

Sum of electronic and thermal Free Energies=          -
361.649129
Frequencies --   106.2602           213.2619
227.3386
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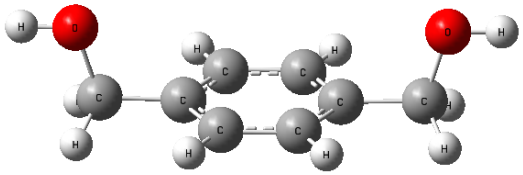
1,4-benzenedimethanol



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0 1
 H                 -3.30551900   -0.88770500   -0.79725900
 C                 -2.91610100    0.00019500   -0.28815200
 H                 -3.30547900    0.88871200   -0.79620400
 C                 -1.41042300    0.00021100   -0.32220200
 C                 -0.69658700   -1.20268700   -0.32538400
 C                  0.69654100   -1.20269700   -0.32537000
 H                 -1.23470100   -2.14495000   -0.33517500
 C                  1.41042000    0.00018000   -0.32220000
 H                  1.23463500   -2.14497400   -0.33516300
 C                 -0.69657200    1.20306400   -0.32471600
 H                 -1.23465500    2.14534900   -0.33397700
 C                  0.69659500    1.20304600   -0.32472800
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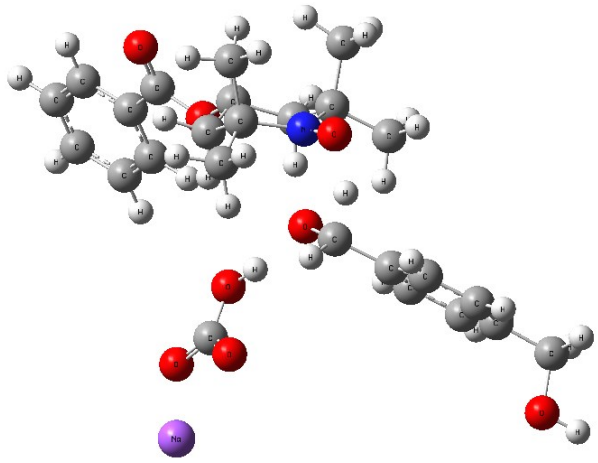
H	1.23468700	2.14532700	-0.33404200
C	2.91610500	0.00009900	-0.28814600
H	3.30545000	-0.88788300	-0.79716400
H	3.30553100	0.88853700	-0.79630400
O	3.34265600	-0.00058000	1.09031100
H	4.30703800	-0.00048500	1.10280900
O	-3.34263400	-0.00061200	1.09032000
H	-4.30701800	-0.00086100	1.10283000

Sum of electronic and thermal Free Energies= -461.322150
Frequencies -- 36.9114 41.5948 80.1540

TS$_{(xii)}$



0 1

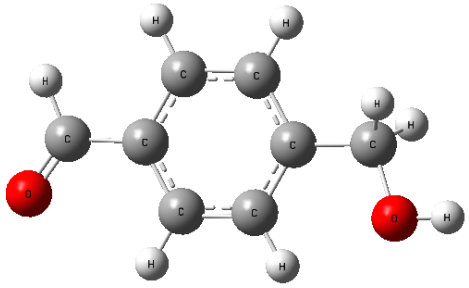
N	-1.78748322	-1.02928314	-0.12684910
C	-2.82383189	-0.28771090	-0.97298549
C	-3.13249393	1.06468681	-0.30769553
H	-2.28304628	1.73488607	-0.45205356
H	-3.99657722	1.49910220	-0.81577742
C	-3.40442081	0.95345859	1.18771632
H	-4.32387231	0.40347768	1.38448175
C	-4.08496924	-1.17274447	-1.10406464
H	-4.74371483	-0.72108410	-1.84883908
H	-4.64988849	-1.26403821	-0.17881313
H	-3.81477745	-2.17203242	-1.45023581
C	-2.25921772	-0.05610988	-2.37924963
H	-3.01531824	0.47109007	-2.96449030
H	-2.04300140	-1.00066604	-2.87927568
H	-1.35792775	0.55088434	-2.34195108
C	-1.86327174	-1.06881188	1.39713252
C	-2.21453848	0.33852743	1.90726190
H	-1.34707775	0.98784778	1.77007910
H	-2.41995918	0.27072518	2.97838285
C	-2.90985250	-2.12491525	1.82295374
H	-2.82448406	-2.27257221	2.90150568

H	-3.93665811	-1.83424189	1.61208454
H	-2.70766662	-3.07857567	1.33203128
C	-0.50563274	-1.49859612	1.95953367
H	-0.57714236	-1.50592147	3.04924139
H	-0.24006438	-2.50373403	1.63056581
H	0.27405876	-0.80336811	1.66133264
O	-1.21394249	-2.00180477	-0.68194910
H	0.06761845	-1.51936400	-1.07889880
C	0.77339593	-0.51616983	-1.11762522
H	0.80467212	-0.38023299	-2.21715734
O	0.06827874	0.36724730	-0.45605381
C	2.11373684	-0.96434953	-0.57924682
C	2.80262880	-2.00674788	-1.21359961
C	4.04717490	-2.42102169	-0.75026751
H	2.35789061	-2.49896522	-2.07335433
C	4.63928207	-1.80346284	0.35851790
H	4.56311124	-3.23514889	-1.24907153
C	2.70519541	-0.34297303	0.52457715
H	2.18589841	0.47311077	1.01248913
H	0.13655482	2.11919868	-0.63391462
O	0.05923837	3.09547432	-0.51831317
C	0.79884984	3.74403913	-1.47386991
O	1.42754333	3.04816383	-2.31572643
O	0.78098966	4.99890402	-1.41860870
Na	2.26426134	5.04914260	-3.28652828
O	-3.57302357	2.28893455	1.74565305
C	-4.80977472	2.81970528	1.77041173
O	-5.79530940	2.24343046	1.35245634
C	-4.83228526	4.18463821	2.36997647
C	-3.66964006	4.81504408	2.83281812
C	-6.06373538	4.84549403	2.46434320
C	-3.74309869	6.09174167	3.38366073
H	-2.71712816	4.30751630	2.76013734
C	-6.13293910	6.12094797	3.01560774
H	-6.95676330	4.35076854	2.10354608
C	-4.97244659	6.74573798	3.47590026
H	-2.84193919	6.57661230	3.74050383
H	-7.08823496	6.62775237	3.08635494
H	-5.02604172	7.73980855	3.90505925
C	3.95242967	-0.75945519	0.98615465
H	4.39852614	-0.26645590	1.84416538
C	5.99975041	-2.22962101	0.84149068
H	6.08837188	-2.05700995	1.91932177
H	6.15199593	-3.29703493	0.64912224
O	7.00049548	-1.46082165	0.14062485
H	7.86651385	-1.74190932	0.45866863

Sum of electronic and thermal Free Energies= -1790.854441

Frequencies -- -504.2676 10.0898
13.6678

p-(hydroxymethyl)benzaldehyde

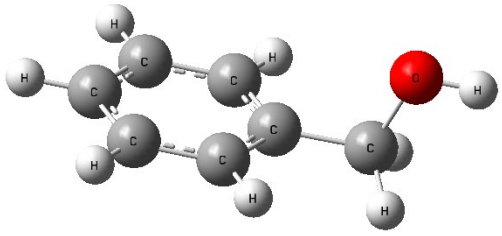


0 1

C	2.97193500	0.15470300	-0.02437900
H	3.44715800	1.15403500	-0.05732400
O	3.66288300	-0.85018100	-0.00844600
C	1.50093000	0.17472300	-0.00297400
C	0.83435800	1.40841600	-0.02554400
C	-0.55327200	1.45539800	-0.00984200
H	1.40870900	2.32841800	-0.06009900
C	-1.30267700	0.27281900	0.03390800
H	-1.06016500	2.41434400	-0.03323700
C	0.75156200	-1.00930600	0.03619000
H	1.26761700	-1.96219700	0.05179400
C	-0.63612700	-0.95971200	0.05471200
H	-1.21463200	-1.87349800	0.08384900
C	-2.80847600	0.36096900	0.07909700
H	-3.11168000	0.75312600	1.05877800
H	-3.15086700	1.07584700	-0.67894500
O	-3.38748800	-0.92319400	-0.14170300
H	-4.33869500	-0.85112800	-0.01063200

Sum of electronic and thermal Free Energies= -460.138628
Frequencies -- 32.8562 88.2345
158.0517

benzylalcohol



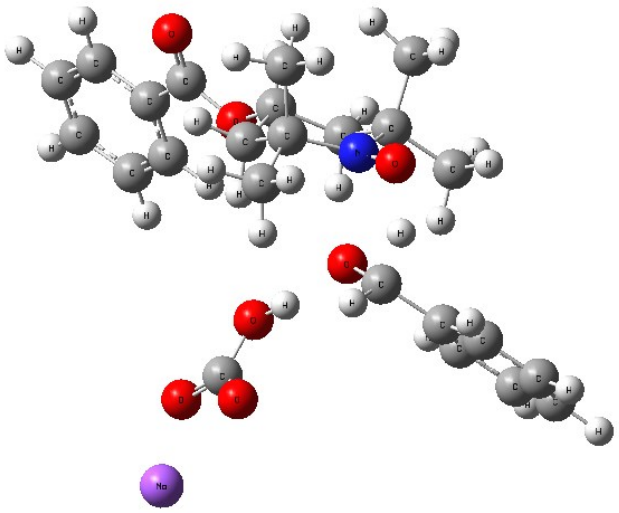
0 1

C	-1.61828200	-1.20700200	0.08064000
C	-0.24539800	-1.20458300	-0.16471700

C	0.45565100	0.00006200	-0.28888500
C	-0.24549300	1.20464300	-0.16462500
C	-1.61838200	1.20693000	0.08070600
C	-2.30750300	-0.00006900	0.20440900
H	-2.14947000	-2.14796000	0.17078500
H	0.28601900	-2.14546100	-0.26535000
H	0.28582700	2.14558300	-0.26517500
H	-2.14964600	2.14784100	0.17090900
H	-3.37549000	-0.00012400	0.39138500
C	1.94336300	0.00013000	-0.52337700
H	2.23533700	-0.88779900	-1.09408900
H	2.23531800	0.88829300	-1.09372700
O	2.61083900	-0.00011500	0.75576200
H	3.56165200	-0.00012500	0.59426100

Sum of electronic and thermal Free Energies= -346.781922
Frequencies -- 39.1635 140.7064 256.8473

TS$_{(xiii)}$



0 1

N	-1.74411569	-1.01752043	-0.14091791
C	-2.79721531	-0.29248897	-0.97912400
C	-3.12663922	1.05248609	-0.30925605
H	-2.28838692	1.73633866	-0.45576176
H	-3.99906167	1.47416624	-0.81359343
C	-3.39139134	0.93550772	1.18745939
H	-4.30268467	0.37313401	1.38785791
C	-4.04141737	-1.20090121	-1.10976191
H	-4.71492261	-0.75532664	-1.84482937
H	-4.59723950	-1.31417485	-0.18156676
H	-3.75316206	-2.19091553	-1.46773727
C	-2.24547000	-0.04304729	-2.38823283

H	-3.01919489	0.46335064	-2.96889606
H	-2.00601696	-0.98031588	-2.89154962
H	-1.36136319	0.58919900	-2.35573240
C	-1.81236705	-1.06110871	1.38363935
C	-2.18948225	0.33673354	1.90127429
H	-1.33579928	1.00469394	1.76813985
H	-2.39168186	0.25900653	2.97238217
C	-2.83622326	-2.13856933	1.81166235
H	-2.74131414	-2.29001303	2.88889135
H	-3.86953498	-1.86570367	1.60868179
H	-2.61964870	-3.08596663	1.31490200
C	-0.44374433	-1.46475818	1.93856976
H	-0.50799618	-1.47327973	3.02871221
H	-0.16086872	-2.46479612	1.60851179
H	0.32047983	-0.75475963	1.63516497
O	-1.16549932	-1.98566185	-0.69961452
H	0.10376667	-1.48727698	-1.11153253
C	0.79326855	-0.47239798	-1.15458157
H	0.81005728	-0.33127943	-2.25396101
O	0.07867712	0.39510643	-0.48265186
C	2.14661711	-0.90141803	-0.63217096
C	2.84272821	-1.93039205	-1.28132502
C	4.10267699	-2.32538597	-0.83880305
H	2.39360625	-2.42410900	-2.13813402
C	4.68750939	-1.69373385	0.26134126
H	4.62846772	-3.12469120	-1.34933970
H	5.66897686	-1.99872555	0.60652989
C	2.74148918	-0.27044726	0.46483624
H	2.21403043	0.53731911	0.95817210
H	0.13890873	2.15449019	-0.52782682
O	0.06199270	3.11490191	-0.32000495
C	0.70903982	3.85899964	-1.27281800
O	1.26973509	3.25243290	-2.22478779
C	4.00414392	-0.66402615	0.90874949
H	4.45728637	-0.16209070	1.75674306
O	0.68220772	5.10348216	-1.10313503
Na	1.97389181	5.35579418	-3.08890047
O	-3.57296469	2.26748735	1.74966690
C	-4.81041164	2.79641224	1.75611865
O	-5.78813025	2.22049170	1.31967307
C	-4.84331040	4.15944239	2.35997498
C	-3.69043008	4.78287310	2.85547081
C	-6.07382439	4.82535746	2.42502169
C	-3.77240154	6.05800423	3.40880483
H	-2.73884392	4.27076701	2.80665646
C	-6.15152691	6.09943200	2.97854469
H	-6.95932353	4.33570700	2.03961447
C	-5.00072743	6.71737672	3.47123029
H	-2.87857095	6.53736100	3.79064754
H	-7.10603139	6.61045247	3.02593458

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 H                  -5.06105815    7.71030625    3.90211552

Sum of electronic and thermal Free Energies=          -
1676.312829
Frequencies --  -509.3113              11.2832
16.3118
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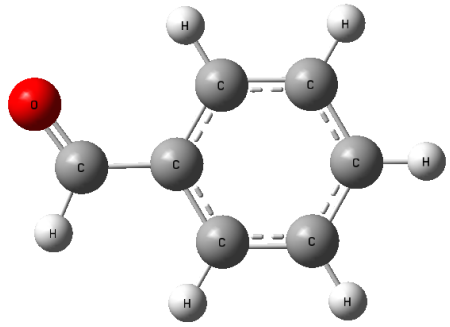
benzaldehyde



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0 1
 C                  2.21719100   -0.23747500   -0.00008200
 C                  1.72517500    1.06782600   -0.00011700
 C                  0.34984600    1.28695100   -0.00004400
 C                 -0.53565400    0.20111000    0.00013500
 C                 -0.03409100   -1.10969900    0.00017700
 C                  1.33759300   -1.32586700    0.00005000
 H                  3.28739500   -0.41029100   -0.00017400
 H                  2.40988700    1.90757600   -0.00022800
 H                 -0.04252900    2.29863700   -0.00009200
 H                 -0.72813700   -1.94176100    0.00029000
 H                  1.72836000   -2.33667200    0.00006200
 C                 -1.98660000    0.46389900    0.00027300
 O                 -2.85409700   -0.39170700   -0.00040900
 H                 -2.26295800    1.53569000    0.00106100

Sum of electronic and thermal Free Energies=          -
345.597730
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Frequencies --   113.0074            217.5631
235.0124
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