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Comments on the mechanism of the vapour-phase catalytic synthesis of thiophenes

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A study of the synthesis of thiophene from the reaction of butanol and CS_2 over potassium-promoted Cr_2O_3/γ-Al_2O_3 has been performed by examination of the reactivity of model intermediates. This study indicates that the reaction path involves successive dehydrogenation, O/S exchange and dehydroheterocyclization.

Keywords: thiophene synthesis, heterogeneous catalyst, vapour phase, chromia–alumina

1. Introduction

The sulfur-containing C_4 heterocycle, thiophene, is widely used as a feedstock in the chemical industry [1] and is produced on an industrial scale (1000 tonne p.a.) via two heterogeneous catalytic processes [2–4]. The first involves the reaction of C_{4+} alcohols or carbonyls with CS_2 over alkali-promoted chromia–alumina [2]. The second is based upon the reaction of an α,β-unsaturated aldehyde with H_2S over an alkali-promoted alumina [3,4]. However, to date there is no consensus of opinion regarding the mechanism of these reactions, nor indeed upon the reaction pathway by which the linear (partially or wholly) saturated oxygenate is converted into heterocyclic product. Indeed, while previous work has demonstrated the successful conversion of alkanes, alkenes, dienes, oxygenates, thiols and organic disulfides into thiophene, attempts to utilise such methods for the synthesis of substituted thiophenes, in particular the unfavoured electrophilic group 3-substituted variants, have encountered process problems and resulted in significantly lower yields [5]. Hence it is clear that this matter requires attention to establish the absolute pathway and nature of the active surface for the reaction in order to develop improved catalysts. In this letter we present the first systematic analysis of the reactivity of various cited reaction intermediates and from these data, propose a reaction pathway for the process.

2. Experimental

All reactions were performed in a fixed-bed microreactor described elsewhere [5]. This entailed passing a vaporised stream of organic reagent (all Analar grade ex Aldrich) and CS_2 (Aldrich 99.9%) in N_2 at a molar ratio $1:1.5:80$, organic$:CS_2:N_2$, and total STP GHSV of 12000 h^{-1}, over 1.0 g of 7.5% K_2CO_3, 11% Cr_2O_3/γ-Al_2O_3 (an industrial thiophene synthesis catalyst), from 300 to 500 °C. The reaction stream was scrubbed to remove H_2S and other sulfur residues prior to analysis by on-line GC using a diatomite CLQ 80–100 mesh on 5% PEG column, with carbon mass balance of 98–100% for all data quoted, based upon conversion of organic.

3. Results and discussion

To determine the “key initial step” of the thiophene synthesis reaction the matrix of possible reactions was established (figure 1). From this matrix it is apparent that there are four possible initial reactions that butanol can undergo:

(a) *O/S exchange.* A surface mediated or gas-phase heteroatom atom exchange to yield butanethiol, as proposed by Azizian and Pizey [6].

(b) *Dehydration.* Acid/base catalysed or thermal reaction to form butene, which has been used as a feedstock in previous commercial processes and is further suggested as a possible intermediate via microscopic reversibility in HDS [5,9].

(c) *α-, β- or δ-C–H dehydrogenation.* Via vapour-phase or surface thiolative dehydrogenation using S^{2-}_{ads} to produce one of the isomers of butenol which can undergo keto–enol tautomerisation and secondary dehydrogenation to form butenal, the “crotonized” intermediate suggested by Barrault et al. [3,4].

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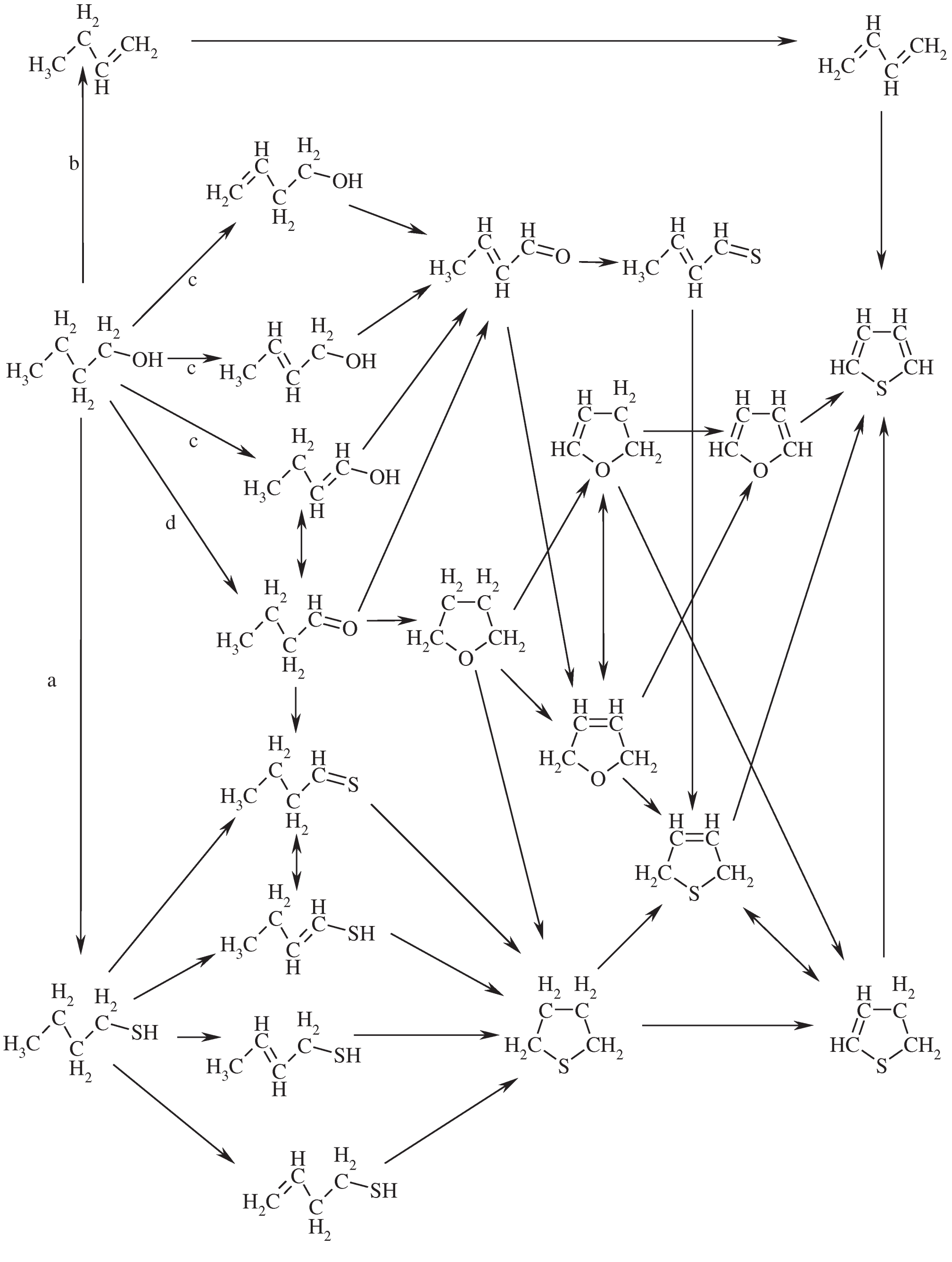


Figure 1. Thiophene synthesis pathways.

(d) *OH dehydrogenation*. Similar to (c), but reaction occurs at the weakly acidic OH functional group to produce butanal, which again may exhibit keto–enol equilibrium or also undergo secondary dehydrogenation.

The reactivity of each of these intermediates was examined and compared to that of butanol (figure 2). These show heterocycle yield decreases in the order

$$\text{but-1-enol} > \text{butanal} > \text{butanol} \gg \text{butanethiol} > \text{2-methylbutene}.$$

Given that oxygenate feeds produced significantly higher yields than non-oxygenates, it was clear that heteroatom retention is critical for efficient reaction and that O/S exchange only occurs a late stage in the reaction. In addition, the significant improvement in yields observed for butenol and butanal indicated that selectivity was further enhanced by the presence of unsaturation, whether carbonyl or skeletal, within the oxygenate. These results contrast with those of Azizian and Pizey [6], who have claimed similar reactivities for butanol and butanethiol and claim the latter to be a key reaction intermediate.

Secondly, the sequence of O/S exchange, secondary dehydrogenation and cyclisation were studied. In this the reactivities of but-2-enal, tetrahydrothiophene (THT) and furan were examined, giving the results in figure 2. It was

Table 1
Apparent activation energies.[a]

Feed	Butanol	Butanal	Butenol	Butenal	Furan	THT[b]	2MB[c]
Apparent E_{act} (kJ mol^{-1})	51.0	42.6	28.6	21.2	101.9	129.4	54.0

[a] After the method of Thomas and Thomas [7].
[b] Tetrahydrothiophene.
[c] 2-methylbutene.

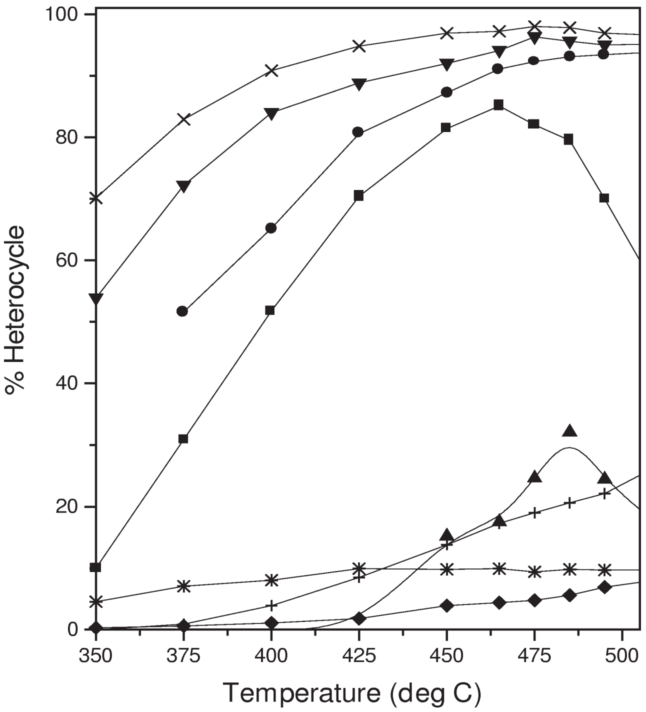
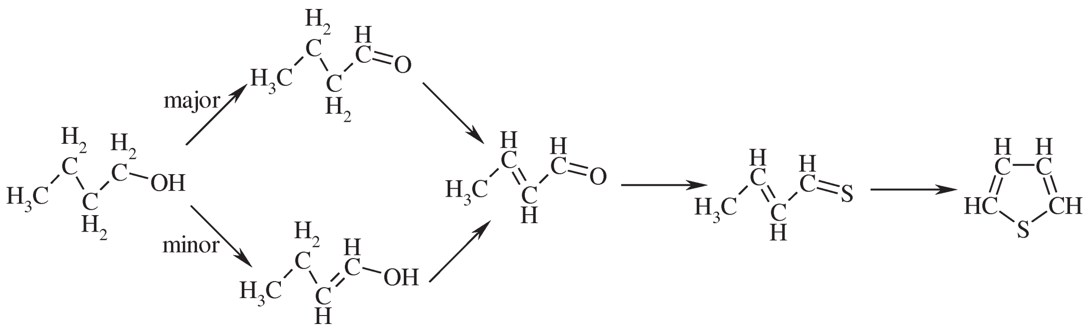


Figure 2. Thiophene yield profiles. Reaction conditions: 1 : 1.5 : 80, organic : CS_2 : N_2, GHSV = 12000 h^{-1}. All samples taken after 15 min equilibration at each temperature. *Note*: 2-methylbutene was used in reaction since it is a liquid at room temperature. Thiophene yields from: (■) butanol, (•) butanal, (▼) but-2-enol, (×) but-2-enal, (▲) butanethiol, (+) tetrahydrothiophene, (♦) furan, (∗) 2-methylbutene (to 3-methylthiophene).

clear that the unsaturated aldehyde was both highly active and selective, with a peak yield of 98 mol% thiophene, the highest yield obtained within this study. This contrasts with the results obtained for furan and THT. The former produced thiophene in a very selective reaction but with low activity, while the latter showed a higher activity but with lower selectivity. The results obtained differ to those of Fenno et al. [10] who synthesised thiophene from furan over alkali-exchanged zeolites, and with Commarieu et al. [11] and Azizian and Pizey who both have employed THT in thiophene synthesis procedures. Indeed, the latter have claimed that cyclisation of the thiol occurs prior to dehydrogenation to heteroaromatic, in contrast to the findings of this study. However, in addition to the absolute yields recorded, the almost identical temperature response profiles of butanol, butanal, butenol and butenal strongly indicate a common reaction mechanism in operation. The observed increases in yields for these molecules reflect their relative positions in the pathway, with concomitant decreasing possibilities of side reactions. Conversely, the manifestly divergent temperature responses of furan, 2-methylbutene, butanethiol and THT indicate that whilst the conversion of these materials to thiophene is possible, the reaction pathways followed are different.

These points are further reflected in the apparent activation energies for the various intermediates (table 1) with the butanol displaying the highest activation energy barrier and butenal the lowest for the linear oxygenates. The activation energies of non-oxygenates and also furan are higher, in agreement with their non-participation within the major reaction pathway. Comparison of E_{act} values also shows that the conversion of alcohol (saturated and unsaturated) to the aldehyde has a lower energy barrier (ca. 8 kJ mol^{-1}) than the conversion of saturates to unsaturates (ca. 22 kJ mol^{-1} for both alcohol and aldehyde). This is consistent with α-C–H dehydrogenation as the rate-limiting step of the reaction, with dehydrogenation of the alcohol presumably being facilitated by donation of the weakly acidic alcoholic $H^{\delta+}$ to a surface site or secondary active species. Moreover, it suggests that there is minimal keto–enol tautomerisation within the system to help overcome the energy barrier to α-C–H abstraction. From these observations we propose the reaction pathway shown in scheme 1.

This involves two successive dehydrogenation steps, followed by O/S of the aldehyde and dehydroheterocyclisation to product. The initial divergence to either aldehyde or unsaturated alcohol reflects the differences in E_{act} values discussed. This duality has been observed experimen-



Scheme 1.

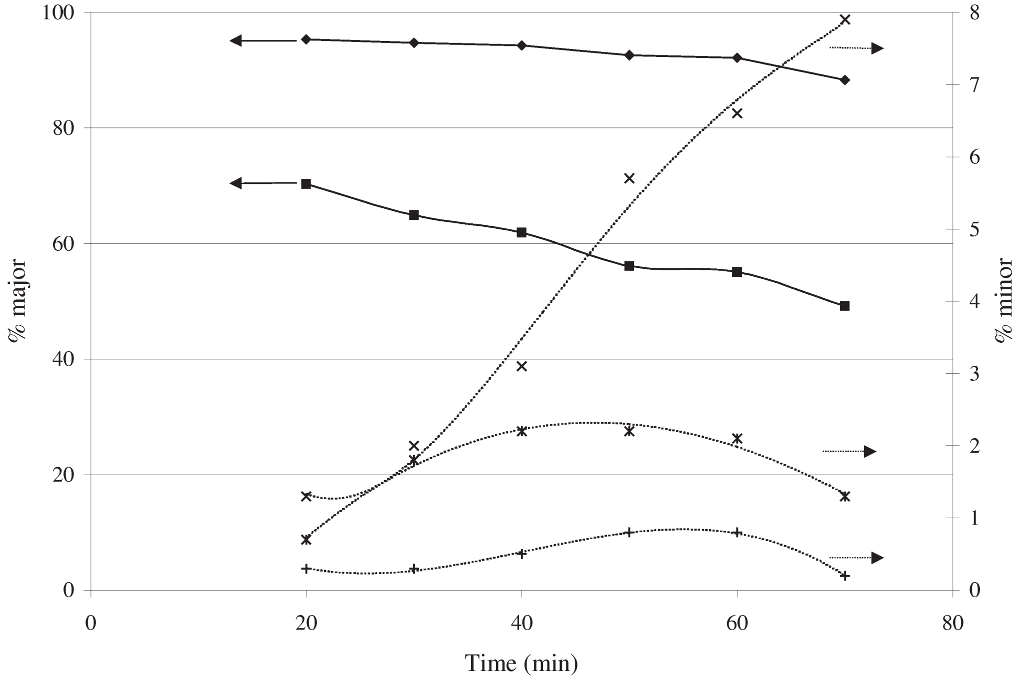


Figure 3. Reactivity of pre-sulfided surface. Conditions as described in text. (♦) Conversion, (■) thiophene, (×) butanal, (∗) butenal, (+) butenol.

tally [5], where the reaction of butanol upon a pre-sulfided surface (treated for 1 h at 475 °C with 1 ml of CS_2 and then reaction commenced in the absence of co-fed CS_2). Analysis of the product stream revealed the presence of butanal, butenol and butenal (in addition to thiophene, see figure 3) as S^{2-}_{ads} was depleted and thiophene yields decreased. Moreover, the proportion of butanal was consistently higher indicating it to be the major initial reaction product and that dehydrogenation of the carbon skeleton is likely to occur only on sulfided sites. These observations and pathway are consistent with the work of Barrault et al. [3] who propose a "crotonized" intermediate as being necessary for reaction. The conversion of butenal to butenethial, or butenethial to thiophene has not been rigorously tested due to the instability of the unsaturated thiocarbonyl. However, work by March [8] concerning the synthesis of unsaturated thials from aldehydes and H_2S supports this claim since cyclisation of an α-hydroxy-thiol (the other possible mercapto-addition product) via an intra-molecular dehydration–cyclisation would produce equimolar quantities of water as a by-product which has been well documented as being a poison to the catalyst [5].

The evaluation of this pathway is particularly useful from a catalytic perspective since it indicates that dehydrogenation "function", facilitated by S^{2-}_{ads}, to be an important pre-requisite for efficient catalysis. This both enables specific design requirements for future materials to be proposed and also helps account for the difficulties encountered in synthesis of substituted thiophenes where α-H abstraction is sterically or chemically hindered.

Acknowledgement

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