Catalytic Functionalization of Saturated Hydrocarbons using Sulphur Dioxide

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The heterogeneous reaction of adamantane with sulphur dioxide on supported metal and oxide catalysts gave mainly adamantanone with yields of up to 38%. The reaction of butanes on supported metal catalysts gave 5-methyl-2,3-dithiacyclopent-4-enethione. Both systems were studied in the temperature range 300—450 °C.

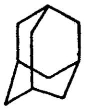
THE complete degradation of hydrocarbons into CO, CO_2, and H_2O is strongly favoured by thermodynamics under all circumstances when oxygen and hydrocarbons react. Nevertheless, by a proper choice of catalysts and conditions, many intermediate (partial) oxidation or dehydrogenation products are obtained in good yield. The most important of these products possess the same carbon skeleton as the starting hydrocarbons, and may be described as products of C–H bond attack or hydrogen-abstraction, or products of oxygen addition to unsaturated systems. In many cases, these compounds undergo further oxidation with C–C bond rupture, leading step by step to oxides of carbon. The selectivity for primary products decreases with high conversion levels throughout a complex network of successive and competitive reactions.

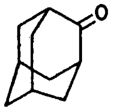
Adams *et al.*[1] had found that sulphur dioxide could be used in several oxidation reactions with much better results, in terms of yield and selectivity, than with air or oxygen. For example, but-2-ene gave butadiene with up to 85% selectivity. However, conversion and selectivity were much lower with alkanes, especially n-alkanes. Similarly, carbon dioxide has been used by Lee *et al.*[2] as a hydrogen acceptor in the dehydrogenation reactions of alkanes and coke removal on Cr_2O_3–Al_2O_3 and V_2O_5–Al_2O_3 catalysts with fairly good conversions and selectivities [reactions (1) and (2)].

$$C_nH_{2n+2} + CO_2 \rightleftharpoons C_nH_{2n} + CO + H_2O \quad (1)$$

$$C + CO_2 \rightleftharpoons 2CO \quad (2)$$

On the basis of these studies, adamantane (I) was chosen as the model alkane because it is believed to be strain free [3] and hence less likely to undergo complete oxidation. The establishment of a catalytic route to adamantanone (II) is desirable, as functionalized adamantanes are useful precursors in organic synthesis and have found uses in medicine.[4] The well known synthetic method [5] for obtaining (II) uses concentrated sulphuric acid and its utility suffers from the fact that charring of adamantane occurs and polymeric substances form. Isobutane was included in the present studies as it is the simplest molecule with a tertiary carbon.


(I)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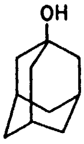
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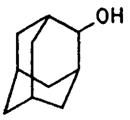
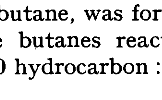

(IV)

RESULTS

The reaction of (I) with sulphur dioxide on supported metal catalysts and oxide catalysts was investigated in the temperature range 300—450 °C. The main product (II) was obtained in up to 38% yield. Comox 471, the commercial cobalt molybdate–alumina desulphurization catalyst, was found to be the most efficient catalyst. The results are outlined in Table 1.

The reactions of isobutane, isobutene, and n-butane with sulphur dioxide on a variety of supported metal catalysts and oxide catalysts were studied in the temperature range 300—450 °C and a rate of flow of 5 cm^3 min^{-1}. Several runs were done using hydrocarbon : SO_2 ratios of 0.5, 1.0 and 2.0 [‡] in which the best results in terms of conversion and selectivity were obtained using a ratio of 1.0. The optimum reaction temperature was 350—400 °C. A small amount of isobutyl alcohol and some hydrogen sulphide were produced but the major product was a yellow-orange solid. The pure compound was obtained by separation from sulphur by column chromatography, followed by recrystallization from cyclohexane, ether, or carbon tetrachloride yielding yellow-orange needles, m.p. 35—37 °C (lit., 40 °C). From elemental analysis, mass, i.r., u.v., and n.m.r. spectroscopy the compound was identified as 5-methyl-2,3-dithiacyclopent-4-enethione (V) (trithione).[6-8] The compound was desulphurized over Raney nickel in an atmosphere of hydrogen, at a flow rate of 8 cm^3 min^{-1}, at 100 °C, and the expected product, isobutane, was formed.



(V)

The results of the butanes reaction at the optimum temperature and a 1.0 hydrocarbon : SO_2 ratio are given in Table 2.

DISCUSSION

Several postulates have been advanced concerning the nature of the oxygenated intermediate on the surface, for example, the hydroperoxide intermediate advanced by

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[‡] By volume at room temperature.

TABLE 1

Reaction products (%) of adamantane–SO_2

Temp. (°C)	Catalyst	Gas compos.	Rate of flow ($cm^3 min^{-1}$)	(I)	(II)	(III)	Others [c]
200	2% Pd–Al_2O_3	SO_2	6.0	100			
250	2% Pd–Al_2O_3	SO_2	6.0	100			
300	2% Pd–Al_2O_3	SO_2	6.0	98.6	1.4		
350	2% Pd–Al_2O_3	SO_2	6.0	98.3	1.7		
400	2% Pd–Al_2O_3	SO_2	5.0	98.0	2.0		
450	2% Pd–Al_2O_3	SO_2	5.0	96.4	3.6		
300	2% Pd–Al_2O_3	SO_2–air (3 : 1)	6.0	73.1	10.3	16.6	
350	2% Pd–Al_2O_3	SO_2–air (3 : 1)	6.0	99.3	0.5	0.2	
400	2% Pd–Al_2O_3	SO_2–air (3 : 1)	6.0	81.0	9.9		9.1
300	1% Pd–1% Cu–Al_2O_3	SO_2	5.0	99.9	0.1		
350	1% Pd–1% Cu–Al_2O_3	SO_2	5.0	99.8	0.2		
400	1% Pd–1% Cu–Al_2O_3	SO_2	5.0	97.4	2.6		
450	1% Pd–1% Cu–Al_2O_3	SO_2	5.0	97.1	2.9		
300	2% Cu–Al_2O_3	SO_2	5.0	99.9	0.1		
340	2% Cu–Al_2O_3	SO_2	5.0	96.3	3.5	0.2	
400	2%Cu–Al_2O_3	SO_2	5.0	90.5	8.9	0.6	
450	2%Cu–Al_2O_3	SO_2	5.0	92.6	7.4		
300	2% Ni–Al_2O_3 [a]	SO_2	5.0	99.9	0.1		
350	2%Ni–Al_2O_3 [a]	SO_2	5.0	89.5	10.3	0.2	
400	2% Ni–Al_2O_3 [a]	SO_2	5.0	87.4	12.6		
450	2% Ni–Al_2O_3 [a]	SO_2	5.0	89.9	10.1		
300	2% Co–Al_2O_3	SO_2	5.0	99.9	0.1		
350	2% Co–Al_2O_3	SO_2	5.0	92.6	7.4		
400	2% Co–Al_2O_3	SO_2	5.0	87.6	12.4		
450	2% Co–Al_2O_3	SO_2	5.0	90.4	9.6		
300	Comox 471	SO_2	5.0	99.9	0.1		
350	Comox 471	SO_2	5.0	62.0	38.0		
400	Comox 471	SO_2	5.0	84.8	15.2		
450	Comox 471	SO_2	5.0	66.0	34.0		
400	Comox 471	SO_2	8.0	97.0	3.0		
400	5% Ni–Al_2O_3	SO_2	8.0	95.6	4.4		
400	5% Ni–Al_2O_3	SO_2	8.0	92.6	7.4	<0.1	
350	2% Ni–Al_2O_3 [b]	SO_2	5.0	99.1	0.9		
400	2% Ni–Al_2O_3 [b]	SO_2	5.0	92.2	7.8		
350	2% Ni–SiO_2	SO_2	6.0	100			
400	2% Ni–SiO_2	SO_2	5.0	99.9		<0.1	
450	2% Ni–SiO_2	SO_2	5.0	18.9	24.3	56.8	
350	Bismuth molybdate (Bi–Mo 2 : 1)	SO_2	5.0	100			
400	Bismuth molybdate (Bi–Mo 2 : 1)	SO_2	5.0	100			
450	Bismuth molybdate (Bi–Mo 2 : 1)	SO_2	5.0	98.4	1.6		
500	Bismuth molybdate (Bi–Mo 2 : 1)	SO_2	5.0	94.0	5.6	0.4	

[a] Chloride salt. [b] Nitrate salt. [c] Incomplete combustion and cracking products.

TABLE 2

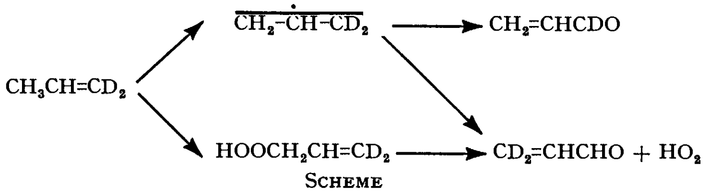
Reaction products (%) of butanes–SO_2 [a]

Catalysts	Reactants	Conversion [b]	Product (V) selectivity [c]	Gas phase		
				n-Butane	Isobutane	Isobutene
2% Pd–Al_2O_3	Isobutane–SO_2	Low	Good		100	Trace
Sulphur–glass wool	Isobutane	Very low	Good		100	
Powdered sulphur–freshly reduced 2% Pd–Al_2O_3	Isobutane	Low	Good		81.7	18.3
2% Pd–Al_2O_3	Isobutene–SO_2	Medium	Good			100
Comox 471	Isobutene–SO_2					100
Glass wool	Isobutene–SO_2					100
Sulphur–glass wool	Isobutene	Low	Good			100
2% Pt–Al_2O_3	Isobutene–SO_2	Low	Good			100
2% Ni–Al_2O_3	Isobutene–SO_2	Medium-high	Poor			100
2% Pd–Al_2O_3	n-Butane–SO_2	Very low	Good	100	Trace	Trace
Sulphur–glass wool	n-Butane	Extremely low	Good	100		

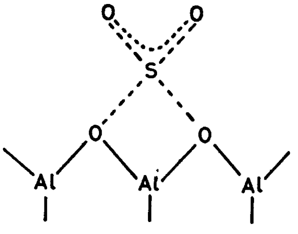
[a] Semi-quantitative results are outlined because a small amount of a carbon–sulphur condensate formed on the catalyst and inner walls of the reactor. (Low, poor <30%; medium *ca.* 50%; high, good >70%.) [b] Conversion is based on the amount of product (solid and gaseous) formed on passing a certain volume of hydrocarbon through the reactor, *i.e.*, GHSV. [c] Selectivity is based on the amount of product (V) formed relative to the total.

Margolis[9] [reaction (3)]. In addition, Hall[10] proposed a competing reaction *via* a π-allyl intermediate for the oxidation of propene on Rh–α-Al_2O_3 (Scheme). In the case of the alkanes, it is not clear whether oxidative dehydrogenation with subsequent conversions that coincide with those of alkenes take place, or whether there are other conversion paths.

$$CH_2{=}CHCD_3 + O_2 \longrightarrow CH_2{=}CH{-}CD_2OOD \longrightarrow CH_2{=}CHCDO + D_2O \quad (3)$$


Scheme

It is evident that the concentration of the supported metal catalyst within the tested range and the nature of the salt used in the preparation of the catalyst did not dramatically affect the results obtained from the adamantane–SO_2 reaction. The reaction is not promoted by the support alone, as was evidenced by blank experiments. Al_2O_3 was found to be a better support than silica, with regard to conversion and selectivity. It was found that when adamantan-1-ol–SO_2 were reacted on 2% Ni–Al_2O_3, under the same reaction conditions used for adamantane (350 °C and a flow rate of 4.0 cm^3 min^{-1}) it was converted into 97.4% adamantane (I) and 2.6% adamantanone (II). This result would indicate that the mechanism is similar to that advanced by Geluk and Schlatmann [5] for the case of sulphuric acid oxidation of (I). The oxidation of (I) to (III) by sulphuric acid is followed by a 1,2 hydride shift to give adamantan-2-ol (IV) *via* the reversible interchange between the tertiary and secondary adamantyl cations. Compound (IV) gives (II) either by further oxidation with sulphuric acid or by disproportionation in which (I) is also formed.



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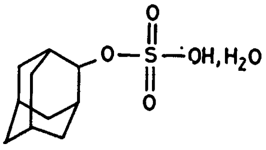


(VII)

The question of whether SO_2 adsorbs and forms a surface sulphite or sulphate which reacts with (I) in a manner similar to its reaction with sulphuric acid is supported by the results of Habgood *et al.*[11] The adsorption of SO_2 on a variety of aluminas was studied and a sulphate-like structure (VI) was postulated, involving two lattice oxygens and the adsorbed SO_2 molecule, on the basis of i.r. studies. The main interaction of SO_2 with the catalyst leads to the formation of surface sulphites and sulphates as was also observed by Schoonheydt and Lunsford [12] on MgO, by Low *et al.*[13] on CaO, and Blyholder and Cagle [14] on evaporated Fe and Ni films in the temperature range 300—550 °C. Sulphur dioxide anions (SO_2^-) have been reported by Ono *et al.*[15] to form an alumina. An intermediate molecular complex between SO_2 and butene in the adsorbed state to which a sulphone-like structure has been ascribed was shown by Förster and Seeleman [16] to be involved in the zeolite isomerization of butenes upon addition of SO_2. Further, Smith and Williams [17] had found that an adamantanesulphonic acid monohydrate (VII) formed on reacting (I) with hydrogen peroxide $-SO_2-O_2$ in solution (Hostapon process).

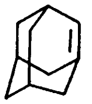
On the basis of the above mentioned reported observations and in the light of the present results the reaction sequence (4)—(6) is suggested. The presence of H_2S and elemental sulphur among the reaction products seems to support this sequence. The above mentioned sequence would imply that the formation of a molecular complex between the adsorbed SO_2 and adamantane plays a significant role in this reaction. It is premature at this stage to give some insight into the precise nature and structure of this complex. However, the involvement of adamantene (VIII) in the formation of the molecular complex may be excluded as the expected adamantene dimers (IX) [18,19] were not isolated.

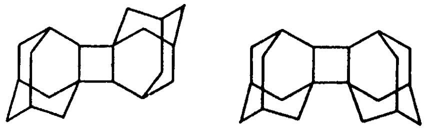
$$3C_{10}H_{16} + SO_2^* + H_2O \longrightarrow 3C_{10}H_{16}O + H_2S \quad (4)$$

$$2H_2S + SO_2^* \longrightarrow 3S + 2H_2O \quad (5)$$

$$C_{10}H_{16}O + S^* \longrightarrow C_{10}H_{14}O + H_2S \quad (6)$$

* Surfaces species.

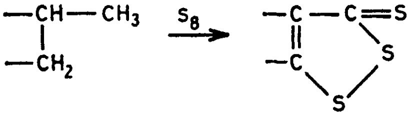

(VIII)


(IX)

The conversion was found to be better on the less noble metals which parallels the ease of formation of oxides and sulphides. Mixed oxide catalysts proved to be the most efficient catalysts. The major advantage of the heterogeneous method of synthesizing (II) used in this work is that (I) can be separated from the products and then recycled over the catalytic bed leading to a higher yield with minimum loss due to charring.

In the reaction of butanes with SO_2 on supported metals the reactivity decreases in the order isobutene > isobutane > n-butane, and the activity of the various supported metal catalysts decreases in the order Ni > Pt > Pd, as expected [20] from the order of cracking of butanes on metals. The lower yield on Pt is expected [21] since the decomposition of SO_2 on Pt occurs at a higher temperature than on Pd, and the conversion of n-butane to isobutene is expected to be less than that for isobutane.[22] The reaction between SO_2 and C_4 hydrocarbons is not a thermal reaction and Comox 471 (cobalt molybdate) proved to be inactive.

In contrast to the adamantane–SO_2 reaction, it seems that the mechanism involved in the butanes–SO_2 reaction is similar to that proposed by Haag and Miale [23] for the reaction of alkanes with carbonyl sulphide on MgO and SiO_2. The alkene was shown to be the major product. That is, the abstraction of a hydrogen atom by a surface sulphur species with the formation of a free radical which in turn gives the alkene. Further, Ashmawy [24] has investigated the propane–SO_2 system over Pd–Al_2O_3 in the temperature range 550—600 °C and propane : SO_2 ratios of 6.0 and 3.0. Propane converts into propene in only 20% selectivity at 52% conversion. It is apparent from the present work that the reaction, at 350—400 °C and a hydrocarbon : SO_2 ratio of 1.0, does not stop at the isobutene stage but



progresses further to give (V). It is known [25] that trithiones are generated preferentially in the presence of sulphur if there is a three-carbon system present in the skeleton. It is interesting to note that the amount of sulphur dioxide present in the feed can be critical. Mann and Yao [26] have observed that a small amount of SO_2 in the feed acted as a modifier enhancing both conversion and selectivity in the formation of methacrolein by the oxidation of isobutane over copper oxide. A larger amount poisoned the catalyst rendering it inactive.

EXPERIMENTAL

The flow system used was of the fixed catalyst bed type (1.5 g in a Pyrex tube 6 mm i.d.) over which the hydrocarbon and SO_2 were passed. Adamantane was volatilized into the gas stream by heating at 80 °C. The supported metal catalysts were prepared by impregnating the support with the metal salt at the required concentration. These were $PdCl_2$, chloroplatinic acid, $Cu(NO_3)_2,3H_2O$, $CuCl_2,2H_2O$, $Ni(NO_3)_2,6H_2O$, $NiCl_2,6H_2O$, and $CoCl_2,6H_2O$. The support A-type Al_2O_3, and Comox 471 (cobalt molybdate on alumina industrial catalyst) were supplied by Laporte Industries Ltd. Bismuth molybdate (Bi : Mo 2.0) was prepared by the method of Adams *et al.*[27] Raney nickel was prepared using nickel–aluminium alloy by the method of Vogel.[28] The supported metals were reduced *in situ* in an atmosphere of hydrogen heated and maintained at 350 °C for at least 12 h.

The adamantane reaction products were separated using a Perkin-Elmer F11 gas chromatograph fitted with either 20 m or 50 Apiezon-L capillary columns, a 4 m silicon nitrile fluid on Chromosorb W column, or a 4 m silicon gum rubber on Chromosorb G column. For the butanes–SO_2 reaction, product (V) was preparatively separated from sulphur on a column (30 × 2.5 cm) of silica gel (Whatmann S.G. 40), elution being carried out with carbon disulphide. The hydrocarbons in the gas phase were separated either on a 4 m 10% Carbowax 1430 on Chromosorb W column or a 16 ft acetonylacetone on Celite column.

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