The effect of oxygen on the desulphurisation of organic vapors

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Sulphur can be eliminated from mercaptanes, thioethers, disulfides and thiophene-derivatives by plasma treatment 1) because most C-S-bonds are weaker then C-C- and C-H-bonds and thus are broken preferably. Such processes are of interest for the desulphurisation of petroleum especially when this contains metals and thus is difficult to desulphurise by catalytic techniques.

The plasmadesulphurisation has recently been tested in laboratory scale using pure mercaptanes, thioethers, disulfides, and alkylthiophenes as model compounds 2,3,4). Desulphurisations of 50 - 70 % are achieved on single treatment. The products are unsaturated and saturated hydrocarbons with a fairly large percentage of C_2-compounds. Sulphur is being eliminated either in elementary form or as hydrogen sulfide.

In the plasma treatment of similar sulfoxides and sulfones the desulphurisation is almost quantitative and the yields in g/kWh are about three times as high as in the case of thioethers and alkylthiophenes [5]. Since a conversion of thioethers into sulfoxides or sulfones prior to plasma treatment would not be economically feasible, a plasma treatment of sulphur compounds in the presence of oxygen was tried. For mercaptanes, thioethers and disulfides oxygen causes a strong increase in desulphurisation and in total yield [4]. The desulphurisation of alkylthiophenes is less affected by oxygen addition. As a side effect oxygen addition reduces polymer formation during the plasma treatment.

Since the rate enhancement by oxygen is of practical interest for the desulphurisation of petroleum and for plasma syntheses, a detailed study of this effect was carried out, using di-n-octylthioether and n-pentylthiophene, which both might be considered as representatives for the sulphur compounds in petroleum. As a typical hydrocarbon-n - hexadecane was selected and treated under similar conditions.

All three model compounds are differently affected by oxygen addition. The dialkylthioether shows a moderate increase in gaseous products and a much more pronounced increase in the yield of liquid hydrocarbons (Table 1). Since the formation of new sulphur compounds remains fairly constant the addition of oxygen enhances the degree of desulphurisation and the amount of sulphur being eliminated per kWh.

As expected the influence of oxygen is strongest at low power levels. For example 62 mMole/h oxygen causes an increase in the conversion rate at 40 W from 29 to 76%; at 80 W from 64 to 94%.

As seen from Table 1 the rate enhancement cannot be achieved by trace amounts of oxygen. At low conversion rates there is a fairly linear increase of the yield with added oxygen (Figure 1). When nitrogen is added instead of oxygen the results are similar to those obtained without gas addition.

For pentyl-thiophene oxygen causes a slight increase in the total yield mainly due to the increased production of low molecular weight hydrocarbons. In hexadecane oxygen addition raises the yields of gaseous and liquid hydrocarbons in a similar way.

In all cases the gases are essentially free of SO_2, and CO_2. The liquid products contain a few percent of oxygen, however, show practically no -C-O- and -C=O bands in IR and ^{13}C-NMR. About 20 percent of the oxygen fed into the system is recovered in form of water.

The composition of the gaseous products also changes on oxygen addition. Dioctylthioether produces considerably more C_2H_4 while C_2H_6 and C_2H_2 yields remain practically constant (Table 2). In pentylthiophene oxygen causes a fairly uniform increase in the C_2H_6, C_2H_4, and C_2H_2 production. Hexadecane shows increased C_2H_4 production while the other gases are uneffected.

The different sensitivity to oxygen addition suggests different reaction mechanisms. The rate enhancement is most pronounced for dioctylthioether probably because oxygen surpresses the back reaction of the process

$$R\text{-}S\text{-}R \rightleftharpoons R\cdot + SR\cdot$$

IR and ^{13}C-NMR spectra of the products indicate a prefered attack on the SR-radical probably converting this into a sulfinic acid. As a consequence of the reduced back reaction the C_2H_4 formation through radical fragmention is enhanced. The formation of acetylene which is independant of oxygen probably involves superexcited neutrals 6). In the reaction of hexadecane the increase in total yield and C_2H_4 probably is due to the attack of atomic oxygen causing hydrogen abstraction and subsequent fragmentation of the radicals. In pentylthiophene oxygen addition causes an increase in C_2H_4 and C_2H_2 production and also yields some thiophene aldehyde and its decarbonylation product thiophene. The reaction probably starts by bond rupture and formation of thienyl and butyl radicals. Oxygen attacks the thienyl radical while the remaining butyl radical fragmentates to low molecular weight hydrocarbons. The enhanced C_2H_2-formation could be the consequence of direct attack of oxygen on the thiophene system or of the decomposition of thiophene aldehyde and thiophene.

For the problem of petroleum desulphurisation the present study contributes the following results.

1. All compounds investigated on oxygen addition show increased product formation.

2. The rate enhancement for thioethers is stronger then for thiophene derivatives and hydrocarbons. Thus the desulphurisation of thioether-hydrocarbon mixtures is more effective in presence of oxygen.
3. Oxygen addition enhances especially the yields of ethene and ethine.
4. Plasma reactions which yield large amounts of ethene and ethine often form some polymers. Oxygen addition reduces such polymerisations.

Literature

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Table 1 Effect of oxygen on yields

O_2 mMole/h	0	8	21	42	62	83	125	62 N_2
Dioctylthioether 40 W								
mMole/kWh								
total	113	161	193	217	299	326	354	135
gases	26	33	32	35	48	49	53	15
liquid hydrocarbons	40	60	99	110	160	182	214	50
sulphur compounds	31	49	41	46	59	62	53	56
Pentylthiophene 40 W								
mMole/kWh								
total	177	200	210	217	232	258	275	-
gases	33	49	48	64	71	92	116	-
liquid hydrocarbons	16	29	31	27	25	28	27	-
sulphur compounds	111	109	119	113	119	121	114	-
Hexadecane 80 W								
mMole/kWh								
total	77	-	-	-	123	-	168	-
gases	24	-	-	-	38	-	39	-
liquid hydrocarbons	53	-	-	-	85	-	129	-

Table 2 Effect of oxygen on the yields of C_2-hydrocarbons

O_2 mMole/h	0	8	21	62	125	62 N_2
Dioctylthioether						
mMole/kWh						
C_2H_6	4	3	2	3	3	2
C_2H_4	9	18	21	29	41	12
C_2H_2	13	12	11	15	9	8
Pentylthiophene						
mMole/kWh						
C_2H_6	2	3	3	4	7	-
C_2H_4	26	35	46	52	80	-
C_2H_2	5	11	15	15	39	-
Hexadecane						
mMole/kWh						
C_2H_6	5	-	-	9	5	-
C_2H_4	5	-	-	14	20	-
C_2H_2	14	-	-	16	14	-

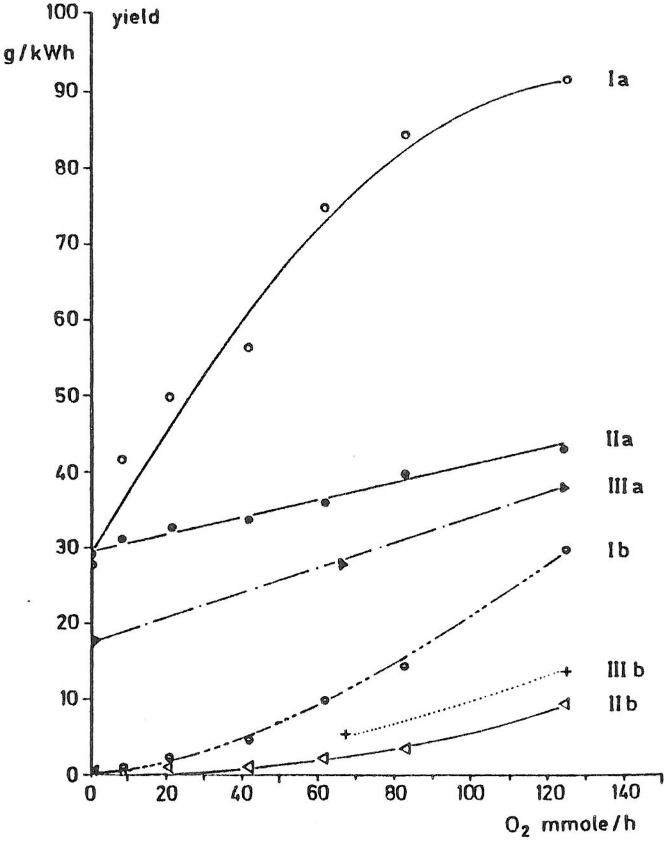

Figure 1

Total yields in the experiments with dioctylthioether (I a), pentylthiophene (II a), and hexadecane (III a), and the corresponding water formation (I b, II b, III b)