SULFOXIDATION OF SATURATED HYDROCARBONS, INITIATED BY OZONE AND NITROGEN DIOXIDE

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The sulfonation of saturated hydrocarbons with a mixture of SO_2 and O_2 (sulfoxidation) is a convenient method for the one-step preparation of alkylsulfonic acids. The reaction is a chain reaction,

$$RH + {}^1/_2O_2 + SO_2 \rightarrow RSO_3H$$

and UV and γ radiation, as well as chemical initiators (peroxides, ozone, azo compounds, etc.), are used to initiate it [1].

The reaction of N_2O_4 with O_3 was used as the initiating system in the present paper, which previously had practically not been used for the initiation of chain processes. It is known that this reaction is an efficient source of active free radicals [2] at 25°C, $k_1 = 2.9 \cdot 10^4$ liter/mole·s, and $K = 3 \cdot 10^{-4}$ mole/liter [3]

$$N_2O_4 \overset{K}{\rightleftarrows} 2\dot{N}O_2$$

$$O_3 + \dot{N}O_2 \rightarrow \dot{N}O_3 + O_2$$

The formed peroxide radicals $\dot{N}O_3$ can react rapidly with the hydrocarbon

$$\dot{N}O_3 + RH \rightarrow \dot{R} + HNO_3$$

The reaction

$$\dot{N}O_3 + \dot{N}O_2 \rightarrow N_2O_5$$

proceeds in parallel at high speed. Reaction (3) is reversible, but the rate constant of the decomposition is low: at 20° in the liquid phase it is $(3 \pm 1) \cdot 10^{-5}\ s^{-1}$ [4]. Consequently, N_2O_5 can be considered to be a stable product under our experimental conditions.

In order to realize reaction (2), the experiments were run at a low N_2O_4 concentration in the starting mixture (1 vol.%). The half-life of reaction (1) is $\tau_{(1)} \sim 0.1$-0.2 s, and the contact time of the reactants in the reactor is ~20 s. Consequently, the initiation rate will be approximately equal to the rate of feeding the O_3 into the solution: $W_i \approx 1.3 \cdot 10^{-5}$ mole/liter·s. In the absence of $\dot{N}O_2$, $W_i' \approx k_4[RH][O_3]$, where $[O_3]$ is the O_3 concentration in the solution

$$RH + O_3 \rightarrow \dot{R} + H\dot{O} + O_2$$

Assuming that $[RH] \approx 5$ mole/liter, $k_4 \approx 10^{-2}$ liter/mole·s, and $[O_3] \approx 10^{-5}$ mole/liter [5, 6], we obtain $W_i' \sim 5 \cdot 10^{-7}$ mole/liter·s. As a result, the addition of $\dot{N}O_2$ to the reaction mixture, with the other conditions kept constant, can increase the initiation rate by more than one order of magnitude, provided $k_2[RH] \gg k_3[\dot{N}O_2]$. But the increase in the sulfoxidation rate should be equally as great, since a linear termination of the chains occurs under the experimental conditions [7]. The experimental results are given in Table 1.

As follows from Table 1, the selectivity of the process in RSO_3H shows little change when N_2O_4 is added. Here the reaction rate increases by 3-5 times, i.e., an acceleration of the reaction is actually observed. The difference between experiment and calculation is explained by the approximate nature of estimating the effect. Previously we had shown that the sulfoxidation proceeds at a constant rate in the initial period [8].

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TABLE 1. Effect of Initiation Method on Yield (%) of Sulfonic Acids at 20°C

Hydrocarbon	Initiation reaction	Yield of "oil" g/h	Oil		Organic phase	
			RSO_3H	H_2SO_4	RSO_3H	H_2SO_4
n-Octane	$O_3 + RH$	0,63	94,5	5	1,3	0,4
"	$O_3 + \dot{N}O_2$	2,52	97,0	3	1,7	0,7
n-Decane	$O_3 + RH$	0,25	82,0	8	1,6	0,2
"	$O_3 + \dot{N}O_2$	0,65	74,0	11	1,9	0,3
n-Hexadecane	$O_3 + RH$	0,12	80	11	3,4	0,4
"	$O_3 + \dot{N}O_2$	0,65	85	11	5,4	0,6

EXPERIMENTAL METHOD

The experimental procedure was described in [8]; the rate of feeding the SO_2, O_2 (3% O_3), and N_2O_4 into the reactor was respectively 6.0, 3.0, and 0.1 liter/h; the volume of the hydrocarbon was 30 ml; the temperature was 20° and the reaction time was 1 h.

The reaction products, namely monosulfonic acids, disulfonic acids (~2%), and H_2SO_4, separate out during reaction as an oil, which settles on the bottom of the reactor. The concentrations of the sulfonic acids and H_2SO_4 in the oil and in the organic phase were determined by potentiometric titration [8]. Nitrogen-containing compounds (nitroalkanes, nitro esters) were not detected in the reaction products.

CONCLUSIONS

The effect of nitrogen dioxide on the yield of products obtained in the ozonized sulfoxidation of saturated hydrocarbons was studied. The addition of 1% nitrogen dioxide to the gas mixture leads to an increase of 3-5 times in the conversion rate.

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