tion of allyl chloride in a nonpolar solvent in the presence of a radical reaction inhibitor is dependent on the concentration of chlorine and is described by the sum of kinetic reactions of overall second and third orders. If the concentration $[\text{Cl}_2] > 1.5 \text{ M}$, the main reaction is a reaction involving the participation of two molecules of chlorine and one of olefin. The formation of 1,2,3-trichloropropane proceeds with a negative temperature coefficient; the effective activation energy is $-11.5 \pm 2.3 \text{ kJ/mole}$.

LITERATURE CITED


DIRECT CATALYTIC OXIDATION OF n-BUTANE TO TETRAHYDROFURAN

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The feasibility of partially oxidizing n-butane to tetrahydrofuran in the presence of promoted V-P-O catalyst was demonstrated. Tetrahydrofuran formation was identified by means of chromatography and mass spectrometry. From the relationship between its concentration and reaction temperature tetrahydrofuran could be proposed as a possible intermediate in the transformation of n-butane into maleic anhydride.

From the data on partial catalytic oxidation of n-butane contained in the literature it is clear that maleic anhydride is the only compound to be formed from among the possible oxygen-containing products that keep intact the original number of carbon atoms [1-3]. In the first two references the primary stage of the mechanism is envisaged as dehydrogenation of n-butane to butene and oxidation of the latter to maleic anhydride via the known intermediates (crotonaldehyde, butadiene, furan) [4]. The possibility of tetrahydrofuran being formed is ruled out in such a reaction path.

The present authors proposed in an earlier work [5] a somewhat different n-butane oxidation mechanism, which involved the activation and detachment of hydrogen from the first and fourth carbon atoms and the formation of the hypothetical products 1-butanol, 1,4-butanediol and tetrahydrofuran (THF):

$$\text{CH}_2=\text{CH}_2+\text{O}_2\rightarrow\text{CH}_2=\text{CH}_2+\text{H}_2\text{O}$$

as well as their subsequent conversion into maleic anhydride. Recently published research findings revealed that none of the intermediates suggested in previous reports [1, 2, 5] were discovered under the conditions typically employed for obtaining maleic anhydride (1-2 vol.%...
The formation of dehydrogenation products under specially created conditions has been discussed by Zazhigalov [6]. The highly sensitive TAP method [7], which permits investigations to be carried out when 0.001% oxygen is removed from a monolayer coating, also failed to unearth the proposed intermediates under these conditions. In short, isolation of THF in n-butane oxidation products would throw some light on the maleic anhydride formation mechanism and clarify ways of transforming the hydrocarbon.

It should also be pointed out that tetrahydrofuran is a valuable organic synthesis intermediate product, whose consumption is constantly on the increase [8], and this has dictated the search for new methods of obtaining it [9]. The most promising of those yet suggested must be that developed by Davy McKee which uses maleic anhydride as the starting material [10]. Here the overall scheme for synthesizing tetrahydrofuran can be summarized as follows [Standard Oil (Du Pont) + Davy McKee] [10, 11]:

\[
\begin{align*}
\text{C}_4\text{H}_{10} + \text{O}_2 &\rightarrow \text{C}_4\text{H}_6\text{O}_3 &\rightarrow \text{C}_2\text{H}_5\text{OOCCHCHCOOC}_2\text{H}_5 + \text{H}_2 \\
\text{C}_4\text{H}_6\text{OOCCH}_2\text{CH}_2\text{COOC}_2\text{H}_5 &\rightarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH} &\rightarrow \text{C}_4\text{H}_6\text{O}_3
\end{align*}
\]

Each of the five stages in this THF synthesis requires specific temperature and pressure conditions and a specific catalyst. The direct transformation of n-butane into THF opens up new avenues for obtaining this product.

Scheme (1) shows that only the hydrogen atoms of the CH₂ end groups in n-butane need to be selectively activated in order to obtain THF, just one oxygen molecule then participating in the reaction. To put this process on a practical footing we made use of the fact [12] that with the oxides of certain metals selective activation of the n-butane methyl group hydrogen occurs when it is replaced by D₂. Me-V-P-O catalyst, which is promoted by one of these metals, was therefore used in the reaction. By choosing particular conditions for processing the sample it was possible to obtain a highly dispersed distribution of the promoter oxide (VO)₂P₂O₇ in the basic phase.

When n-butane was oxidized with this catalyst, a peak was found at a point on the product chromatogram which from the retention time could be identified as pertaining to tetrahydrofuran. This was confirmed by mass spectrometry analysis (Fig. 1). The products contained a substance having a mass of 72 (THF) and an accompanying protonated form with a mass of 73. Peaks pertaining to these masses were absent in the control samples containing likely products with a mass of 72 — acrylic acid and butyraldehyde (all samples were neutralized with alkali).

Maleic anhydride (MA) was also found alongside THF in the n-butane oxidation products. As can be seen from the relationships between substance concentrations and reaction temperature (Fig. 2), the MA content was greater than that of THF. This is hardly surprising in view of the fact that the rate at which MA is formed from tetrahydrofuran with V-P-O catalyst is much higher than from n-butane [13]. Under these conditions the maximum THF content was observed at 643-653 K, while MA concentration continued to increase as the temperature rose. The curves describing the dependence of THF and MA concentration on temperature indicate that the formation of the latter may proceed via tetrahydrofuran as intermediate.

The results obtained using the promoted Me-V-P-O catalyst were compared with those from oxidizing n-butane with a V-P-O sample. From Fig. 1 it is evident that a peak corresponding to a mass of 72 was not observed, i.e., THF was not present in the reaction products. The nonpromoted V-P-O catalyst functions at higher temperatures (Fig. 2), where complete conversion of THF into MA might occur. It is also possible that some part might be played here by the specific ability of the additive to activate a CH₃ end group hydrogen in the paraffin molecule.

In summary, the findings show that direct catalytic oxidation of n-butane to THF is possible in principle. THF may serve as an intermediate in the transformation of C₄H₁₀ into maleic anhydride. At the same time, these results do not provide sufficient basis for the assumption that this is the unique reaction route to maleic anhydride. Other parallel paths in its transformation from n-butane are also possible.

**EXPERIMENTAL**

Oxidation of n-butane was carried out in a flow-type apparatus, the products being analyzed chromatographically as they were formed [14]. A working mixture of 1.7 vol.% of n-