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Abstract

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ON THE COMPOSITION OF THE PRODUCTS AND THE KINETICS OF BUTANE CRACKING INITIATED BY ADDITIONS OF ETHYLENE OXIDE

(Presented by Academician A. V. Topchiev, January 8, 1960)

It has long been found that propane, butane, isobutane, and pentane ([1,2]), when introduced into the zone of decomposing ethylene oxide and not decomposing by themselves at 400°, undergo decomposition. In some studies the catalytic effect of decomposing ethylene oxide on the thermal decomposition of ethylene, ethyl ether, acetaldehyde, and other compounds ([3]) was also shown. On the other hand, study of the pyrolysis of ethylene oxide showed that decomposition occurs with the participation of radicals ([4,5]). These facts provided grounds for discussing a radical-chain mechanism for the influence of ethylene oxide on the thermal decomposition of organic molecules ([4]). Although the question of the mechanism of ethylene oxide decomposition has been touched upon in numerous works ([6–11]), it cannot be regarded as clarified. Nevertheless, as a result of A. I. Terenin' s investigations of the triplet excited state of molecules ([12]), it is probable that, at least, photochemical decomposition and, apparently, also thermal decomposition of ethylene oxide proceed by a biradical mechanism ([8]).

In the present work we studied the initiating effect of additions of ethylene oxide on the cracking of butanes. Only isolated experiments in this direction are known ([2]). The study of the composition of the products and the kinetics of butane cracking initiated by additions of ethylene oxide was carried out by a static method in a high-vacuum apparatus representing a combination of three consecutively connected parts: a kinetic apparatus for studying butane cracking from the change in pressure, an apparatus for separating the cracking products by chromatographic method, and an apparatus for burning hydrogen and methane and determining CO ([14]).

Results on the study of the composition of the products ($t = 10$ min.) and the kinetics of initiated cracking of butanes at 450°C, initial mixture pressure

Table 1

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Composition of the products of initiated cracking of butanes (450°, $P_{\text{mixture}} =$ 200 mm, $t = 10$ min.)

	Butane	Butane	Butane	Butane	Isobutane	Ethylene oxide
	Additions of ethylene oxide (vol. %)	Additions of ethylene oxide (vol. %)	Additions of ethylene oxide (vol. %)	Additions of ethylene oxide (vol. %)	Additions of ethylene oxide (vol. %)	450°, 40 mm
	1	3	5	10	10	450°, 40 mm
CO	0.25	0.47	0.82	1.75	1.5	50.84
H_2	0	0.61	0.62	0.88	6.02	11.86
CH_4	1.52	5.0	6.8	7.3	4.51	27.12
C_2H_4	1.73	2.72	3.26	4.4	0.9	1.52
C_2H_6	1.47	3.0	3.5	4.61	1.1	7.28
C_3H_6	1.37	5.0	6.6	7.6	4.02	–
C_3H_8	0.36	0.43	0.45	0.76	1.75	1.36
C_4H_8	0	0.57	0.62	0.76	5.89	–
C_4H_{10}	93.4	82.2	77.3	71.9	74.29	–
Percent decomposition	6.5	17.8	22.7	28.1	25.7	
Chain length	12.4	17.6	12.6	7.3	7.2	

hydrocarbon and oxide, equal to 200 mm Hg, in the ethylene oxide concentration range of 1-10%, are given in Table 1 and in Figs. 1-3.

The data on the composition of the products presented in Table 1 show that small additions of ethylene oxide cause significant cracking of butanes, which practically does not occur at 450° in the absence of the oxide. At the same time, the products of the initiated cracking of butanes contain all the products characteristic of the thermal cracking of butanes at higher temperatures (550-600°). Small additions of the oxide (1-3%) act most effectively. With a subsequent increase in the concentration of the additive, the percentage decomposition increases less and less. Thus, when the concentration of the oxide is increased from 1 to 3%, the percentage decomposition increases from 6.5 to 17.8, i.e., almost

Fig. 1. Effect of additions of ethylene oxide on the extent of decomposition of butanes. Concentration of C_2H_4O: a–1%, b–3%, v–5%, g–iso-$C_4H_{10} + 10\%$, d –n-$C_4H_{10} + 10\%$.

Fig. 2. Effect of additions of ethylene oxide on the rate of initiated cracking of butane: a–1% additive, b–3%, v–5%, g–10%.

proportionally to the concentration of the additive, but with a further increase of the additive from 5 to 10% the percentage decomposition increases only from 22.7 to 28.1. Consequently, saturation sets in in the initiating action, and one should expect a limiting degree of initiation, which was predicted by one of us (13) and was clearly observed experimentally by us in the case of butane cracking initiated by additions of azomethane.

With an addition of oxide equal to 10%, the decomposition reaches approximately 30% (other conditions being equal, the extent of initiated cracking of isobutane is lower than that for butane). The decomposition of ethylene oxide itself cannot explain either such a deep decomposition of the butanes or the complete composition of the products, since pure ethylene oxide, on decomposition, gives small amounts of H_2, CH_4, C_2H_4, C_2H_6, and C_3H_8 (see Table 1).

In the initiated cracking of butane, the ratios of the yields of paired products customary for thermal cracking at higher temperatures are observed (CH_4—C_3H_6, C_2H_6—C_2H_4, and H_2—C_4H_8); however, at a low initiator concentration (1%) the directions of demethanation and deethanization are equal, in contrast to ordinary cracking. With an increase in the concentration of ethylene oxide (3-5%), the demethanation reaction begins to predominate, as occurs in ordinary cracking. This curious fact indicates that, under the influence of the initiator, during cracking there occurs a shift toward demethanation, which was observed in ordinary

cracking of butanes. The observed shift is most probably explained by the hypothesis of isomerization of butyl radicals into secondary butyl radicals (14).

The increased yields of CH_4, C_2H_6, and H_2, compared with ordinary cracking, are explained by decomposition of the oxide. The average chain length, determined from the ratio of the sum of olefins to carbon monoxide, at first increases with increasing additive, passes through a maximum, and then again falls to the limit that was also observed in ordinary cracking.

A similar picture is observed in the initiated cracking of isobutane, with preservation of the predominance of the decomposition pathways characteristic of ordinary cracking (14). The somewhat overestimated yield of H_2, CH_4, and C_2H_6 is associated with decomposition of the oxide.

The results of studying the kinetics of the initiated cracking of butanes from the change in pressure in the reaction zone, taking into account decomposition of the oxide, are presented in Figs. 1-3.

The curves for the dependence of the degree of decomposition (X) of the butanes

Fig. 3. Effect of the degree of initiated cracking of butane on the monomolecular rate constant: *a*—1% additive, *b*—3%, *v*—5%, *g*—10%.

Figure 2: Fig. 3. Effect of the degree of initiated cracking of butane on the monomolecular rate constant: *a*—1% additive, *b*—3%, *v*—5%, *g*—10%.

on time (Fig. 1) show that the initiating effect depends on the concentration of ethylene oxide and is well approximated by a dependence expressing saturation in the initiating action:

Fig. 3. Effect of the degree of initiated cracking of butane on the monomolecular rate constant: *a*—1% additive, *b*—3%, *v*—5%, *g*—10%.

$$X = b\left(1 - e^{-aT_0}\right), \tag{1}$$

in which a and b are certain constants, and T_0 is the concentration of oxide and X is the degree of decomposition (expressed in mm Hg).

The initial rate of initiated cracking of butane

$$\left(W = \frac{\Delta P}{P\Delta t} \cdot 100\right)$$

increases with increasing initiator concentration and, in each individual case, rapidly decreases with time, reaching a certain limiting value practically independent of the initial concentration of the additive (Fig. 2). The rate curves for initiated cracking are analogous to the curves of self-retarding or inhibited ordinary cracking obtained by us earlier $^{(15)}$.

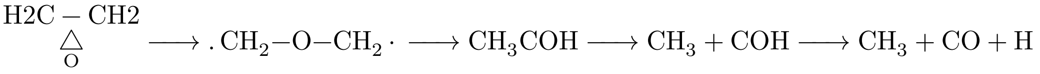
The kinetics of initiated cracking, like that of ordinary cracking, has the character of a process self-retarded by the products and is described by the equation $^{(16)}$ for self-retarding reactions of Dainton and Frost:

$$\frac{1}{t}\ln\frac{1}{1-X} = k_0 + \beta\frac{x}{t}$$

(Fig. 3).

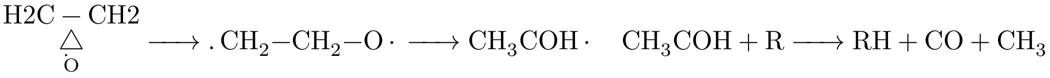
The mechanism and kinetics of butane cracking initiated by additions of ethylene oxide can be interpreted within the framework of the theory, proposed by one of us, of the dual action of additives $^{(13,14,17)}$, in which not only the initiating but also the inhibiting properties of ethylene oxide are taken into account.

The initiating properties of ethylene oxide apparently reduce to decomposition reactions involving biradicals:



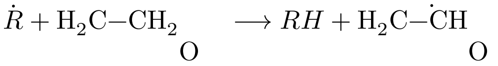
$$\underset{O}{\overset{H2C - CH2}{\triangle}} \longrightarrow .\,CH_2{-}O{-}CH_2\cdot \longrightarrow CH_3COH \longrightarrow CH_3 + COH \longrightarrow CH_3 + CO + H \qquad (I)$$

or



$$\underset{\dot{O}}{\overset{H2C - CH2}{\triangle}} \longrightarrow .\,CH_2{-}CH_2{-}O\cdot \longrightarrow CH_3COH\cdot \quad CH_3COH + R \longrightarrow RH + CO + CH_3 \qquad (II)$$

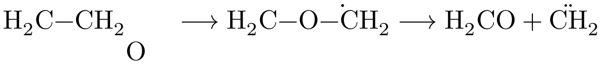
The inhibiting properties are possibly associated with the reaction



$$\dot{R} + \underset{O}{H_2C{-}CH_2} \longrightarrow RH + \underset{O}{H_2C{-}\dot{C}H} \qquad \text{(III)}$$

in which the radical of cyclic structure is less active, tending toward dimerization (or polymerization).

However, if the role of $\dot{R}$ in reaction (III) is played by a methylene radical, formed, for example, by the reaction



$$\underset{O}{H_2C{-}CH_2} \longrightarrow H_2C{-}O{-}\dot{C}H_2 \longrightarrow H_2CO + \ddot{C}H_2 \qquad \text{(IV)}$$

then, entering into reaction with ethylene oxide, it can give a CH_3-radical capable of developing chains.

On the basis of experimental data on the kinetics of decomposition and the corresponding radical-chain scheme of initiated cracking, in which we neglected the inhibiting action of the oxide and of the products on the decomposition, we calculated the rate constant for the decomposition of ethylene oxide ($450^\circ,\ K_0 = 0.20\ \text{min}^{-1}$) and the activation energy of the decomposition, which proved to be 51.2 kcal/mol, in good agreement with the values of 52 kcal and 50 kcal found in previous studies on the decomposition of the oxide (^{1,7}).

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