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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE MECHANISM OF FORMATION OF SECONDARY PRODUCTS IN HIGH-TEMPERATURE CRACKING OF ETHANE

The present paper is devoted to an investigation of the mechanism of formation of secondary products and, in particular, methane under the conditions of high-temperature cracking of ethane. The experiments were carried out by the previously developed procedure in a flow system with a turbulent reactor ⁽¹⁾. Small amounts of acetylene labeled with radiocarbon C^{14} were added to the initial ethane. The work is a continuation of previous studies, in which the cracking of ethane was investigated by us under analogous conditions with additions, respectively, of radioactive methane ⁽²⁾ and ethylene ⁽³⁾.* Two series of experiments were carried out at temperatures of 800–920° and a pressure of 90 mm Hg, using corundum and quartz, respectively, as heat carriers.

The procedure for carrying out the experiments and analyzing the products has been described in detail earlier ^(2,3).

The first series of experiments (corundum heat carrier) was carried out on a mixture of composition 99.99 + 0.01% C_2H_2 . The specific activity of C_2H_2 was 1.75×10^6 imp/cm³ · sec, and that of the entire initial mixture was 173 imp/cm³ · sec. The second series of experiments (quartz heat carrier) was carried out on a mixture of composition: 99.97% C_2H_6 + 0.03% C_2H_2 . The specific activity of C_2H_2 in this series of experiments was 3.0×10^7 imp/cm³ · sec, and that of the entire mixture was 9100 imp/cm³ · sec. Detailed compositions of the products are given in ⁽³⁾.

Tables 1 and 2 give the specific and partial activities of the products obtained. The partial activities A_i represent the fraction of radioactivity falling on a given component in 1 cm³ of reaction products. The value A_i is equal to the corresponding specific activity multiplied by the fraction of the i -th component in the reaction products. From the data given in the tables it is evident that the specific and partial activities of methane and coke-1 depend substantially on the material of the heat carrier, in contrast to the compositions of the products and the total cracking constant k_1 , on which the heat-carrier material has no noticeable effect. Of greatest interest is the circumstance that, when corundum is used as the heat carrier, the greater part of the radioactivity of C_2H_2 passes into methane (up to 80-90% of the initial amount), coke-1 (10-30%), and, to

a lesser degree, into divinyl (2-3%) (Table 2). The ratio of the specific activity of CH_4 (a_{CH_4}) to the specific activity of C_2H_2 ($a_{C_2H_2}$) in deep experiments approached 1/2, while the ratio $a_{\text{coke}}/a_{C_2H_2}$ was equal to 1 ÷ 2 (Table 1). This indicates that the source of formation of a significant part of CH_4 and all or almost all of coke-1 under the conditions studied was C_2H_2 . The specific and partial radioactivities of coke-2, as well as of the remaining products, including C_4H_6 , were considerably lower than the specific radioactivity of C_2H_2 .

In the experiments using quartz as the heat carrier, the specific activities of coke-1 and methane were, respectively, 2-10 and 20-200 times lower than $a_{C_2H_2}$ (Table 4). The conversion of C_2H_2 into CH_4 and coke-1 in this case

* These investigations made it possible to show the predominantly molecular character of the formation of ethylene from ethane under the conditions considered and to establish the radical character of the reactions forming side and secondary products C_3H_8 , C_4H_{10} , C_3H_6 , and C_4H_8 . The mechanisms of formation of CH_4 , C_4H_6 , C_3H_4 (allene and methylacetylene), and coke remained not fully clarified. The point is that, in investigations (3), the specific activities of C_2H_4 and C_2H_2 in the reaction system were identical, as a result of which it was difficult to draw an unambiguous conclusion as to whether, for example, the source of C_4H_6 is two C_2H_4 molecules or C_2H_2 and C_2H_4 molecules, and also to estimate the role of reactions involving C_2H_4 and C_2H_2 in the formation of CH_4 and coke.

amounted, respectively, to approximately 4.5 and 7% of the initial amount of C_2H_2 at 918 and 873°, and to approximately 15 and 18% at 830° (Table 2). The total fraction of CH_4 formed through C_2H_2 was small and, in the range 830–

Table 1

Specific activities a_i of products of ethane pyrolysis (in imp/cm³ · min)*

Heat-carrier: corundum**	Temperature, °C	Time, sec	a_{CH_4}	$a_{C_2H_4}$	$a_{C_2H_2}$	$a_{C_3H_8}$	$a_{C_3H_6}$	$a_{\text{acetylene}}$	a_{methane}	$a_{C_4H_{10}}$	$a_{C_4H_8}$	$a_{C_4H_6}$	a_{coke}	
													1	2
841	5	0,03413,30			30,30								3,16	34,501,45
847	6,5	0,0536,95			5,77								1,75	18,330,93
886	19	0,0117,30	2,06	0,02382,000,0940,284						0,0631,05			5,60	

Heat-carrier temperature, °C	h, sec	t, sec	$a_{CH_4} \cdot 10^{-3}$	$a_{C_2H_4} \cdot 10^{-3}$	$a_{C_2H_2} \cdot 10^{-3}$	$a_{C_3H_8} \cdot 10^{-3}$	$a_{C_3H_6} \cdot 10^{-3}$	$a_{acetylene} \cdot 10^{-3}$	$a_{benzene} \cdot 10^{-3}$	$a_{C_4H_{10}} \cdot 10^{-3}$	$a_{C_4H_8} \cdot 10^{-3}$	$a_{C_4H_6} \cdot 10^{-3}$	$a_{coke} \cdot 10^{-3}$	$a_{coke} \cdot 10^{-3}$
882	24	0,0242,87	1,23	0,03021,80				3,94					1,96	9,52
893	30	0,0242,87			9,40								1,09	11,502,00
896	34	0,0212,87			7,36								0,79	11,82
Heat carrier: quartz***														
806	2,5	0,071877,7												616
830	6	0,038513		1,42	2903								418	682
828	7	0,04182,8		1,87	3090	2,74	26,00						344	778
834	9	0,06788,2		1,97	1194								135	863
877	22,5	0,01917,0015,801,64	2800	1,92	11,10204	357	1,52	23,7	145	364				
877	24	0,02300,0012,621,77	1628		8,67	125	279	0,96	29,7	112	292			
885	31,5	0,02193,90	1,31	1610	9,45	88,5	191	1,71	17,9	97,0	369			
918	80	0,0146,12	33,151,42	502	1,67	9,85	81,0	117,52,48	14,1	40,2	129			
918	88,3	0,0150,26	23,651,24	595	1,59	9,00	90,0	148,3	10,2	46,0	200			

* The accuracy of determination of the specific activities was 3% (relative).
 ** The specific activity of C_2H_6 in the initial mixture was $1,75 \cdot 10^6$ imp/cm³ · sec.
 *** The specific activity of C_2H_6 in the initial mixture was $3 \cdot 10^7$ imp/cm³ · sec.
 **** Coke-1 represented carbonaceous deposits on the heat carrier. Coke-2—polymeric products deposited in the upper cold part of the reactor.

Table 2

Partial activities A_i of products of ethane pyrolysis (imp/min · cm³ of gas obtained)

Heat-carrier temperature, t , °C	sec	A_{CH_4}	$A_{C_2H_6}$	$A_{C_2H_4}$	$A_{C_2H_2}$	$A_{C_3H_8}$	$A_{C_3H_6}$	$A_{acetylene}$	$A_{C_4H_{10}}$	$A_{C_4H_8}$	$A_{C_4H_6}$	A_{CO_2}	A_{coke-1} (as)
Heat carrier: corundum													
841	0,034	119			5,3							0,9	10,6
847	0,053	103			1,2							1,2	13,4
886	0,0117	5,3	1,3	3,5	46,8	0,07	0,11		0,05	0,13		3,9	
882	0,024	80	0,4	7,5	28,4			0,13				2,2	20,0
893	0,024	72,0			13,0							1,0	23,5
896	0,0217	2,3			25,0							2,4	28,0
Heat carrier: quartz													
806	0,0718	1500		470	5380							126	1393
830	0,0385	1210		222	6000							109	1225
828	0,0418	1380		250	5600	2,7	38					376	1075
834	0,0678	800		525	5500							231	1530
877	0,0194	290	8,1	360	5560	1,85	14,0	15,3	1,6	4,75		283,5	530
877	0,0230	195	5,8	430	6420		17,4	13,7	1,2	7,4		396	670
885	0,0219	290		370	3480		16,2	12,2	20,0	1,2	2,3	194	1220
918	0,0147	250	9,0	430	3660	1,93	28,5	12,9	7	1,2	2,5	220	334
918	0,0150	224	6,3	400	3410	2,23	25,1	22,4	17,8		6,3	344	240

918° amounted to 1-7% of the total amount of CH_4 . The participation of C_2H_2 in coke formation was considerably greater: about 20-50% of the coke was obtained from C_2H_2 . A comparison of the specific activities of CH_4 and of the radical CH_3 shows that formation of that part of CH_4 which is obtained from C_2H_2 does not proceed through the radical CH_3 . The specific activity of CH_3 in the volume can be estimated as follows. Since in (3) it was shown that C_4H_{10} is formed upon recombination of two C_2H_5 radicals, while C_3H_8 is formed from CH_3 and C_2H_5 , $a_{C_2H_5} = \frac{1}{2}a_{C_4H_{10}}$ and $a_{CH_3} = a_{C_3H_8} - a_{C_2H_5}$. From the data of Table 1

it follows that in experiments using quartz as the heat-transfer medium, $a_{CH_4}/a_{CH_3} = 10-20$, i.e., there is a route for obtaining radioactive CH_4 in addition to CH_3 .

From the data on the formation of CH_4 obtained in the present work and in (3), it may be concluded that the amount of CH_4 formed from C_2H_4 and C_2H_2 during cracking of C_2H_6 in the temperature range $800\text{--}920^\circ$ and at a pressure of 100 mm Hg, when quartz is used as the heat-transfer medium, does not exceed 10% of the total amount of CH_4 in the reaction products*.

It should be noted that an increase in methane formation upon adding small amounts of C_2H_2 (4) and C_2H_4 (5) to C_2H_6 was previously observed during cracking of C_2H_6 at lower temperatures.

The first-order rate constant for the overall reaction of consumption of C_2H_2 to form various products (k_2), calculated for experiments using quartz as the heat-transfer medium, was $(18 \pm 2) \text{ s}^{-1}$ and practically did not change with increasing temperature. This may be explained by the large contribution of C_2H_2 consumption in a heterogeneous process limited by transport. In experiments using corundum as the heat-transfer medium, the constant k_2 was determined with considerably less accuracy and was $200\text{--}800 \text{ s}^{-1}$.

Using the value found for k_2 , the rate constant for the formation of C_2H_2 from C_2H_4 (k_3) was calculated:

$$k_3 = \frac{[\text{C}_2\text{H}_2](1 + k_2 t)}{[\text{C}_2\text{H}_4] t}, \quad (1)$$

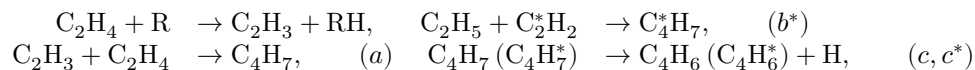
where t is the ratio of the volume of the reaction zone to the volumetric flow rate of the products under the experimental conditions. In experiments with quartz as the heat-transfer medium, the values of k_3 at 830 , 885 , and 920° were, respectively, 0.1 , 0.5 , and 1.8 s^{-1} . The variation of this constant with temperature is described by the formula:

$$k_3 = 4.3 \cdot 10^{15} \exp(84.5 \pm 4 \text{ kcal})/RT \text{ (s}^{-1}\text{)}. \quad (2)$$

When considering the pathways for formation of other products of C_2H_6 cracking, it should be taken into account that the specific activities of all products, including C_4H_6 , allene, and methylacetylene, were tens of times lower than that of C_2H_2 . This indicates that only an insignificant fraction of these compounds was formed with participation of C_2H_2 . Since for all products, except methane and coke, the ratios $a_i/a_{\text{C}_2\text{H}_2}$ and $A_i/A_{\text{C}_2\text{H}_2}$ (a_i and A_i are, respectively, the specific and partial activities of the i -th components) did not depend on the material of the heat-transfer medium, it may be concluded that the formation of these products is homogeneous in character.

The data obtained in the present work agree with the conclusion, made in (3), that under the conditions of C_2H_6 cracking the formation of C_3H_8 and C_4H_{10} occurs by recombination of the radicals CH_3 and C_2H_5 , C_3H_6 —by decomposition of the C_4H_9 radical, and C_4H_8 —by decomposition of the C_4H_9 radical and recombination of C_2H_3 and C_2H_5 . On the basis of (3) and the present work

it should be considered established that the formation of the main amounts of C_4H_6 under the conditions studied occurs with participation of two molecules of C_2H_4 (or radicals formed mainly from C_2H_4). It may be proposed that the formation of C_4H_6 and C_3H_4 (allene and methylacetylene) proceeds according to the scheme:



* Here the formation of CH_4 actually from C_2H_4 and C_2H_2 is meant. The influence of C_2H_4 and C_2H_2 on the rate of CH_4 formation by reactions of the type $C_2H_4 + C_2H_5 \rightarrow C_4H_9 \rightarrow CH_3 + C_3H_6$ has not been taken into account here. The possible influence of reactions of this type in methane formation cannot be evaluated from the ratio of the radioactivities of C_2H_4 , C_2H_2 , and CH_4 :



Molecules containing C^{14} , and the pathways of formation of the principal amounts of labeled products, are marked with an asterisk. In this case, since $a_{C_4H_6} < a_{C_3H_4} \ll a_{C_2H_2}$, it should be assumed that only an insignificant fraction of the corresponding molecules was formed with the participation of C_2H_2 (reactions (b^*) and (f^*)).

In order to decide whether the principal amounts of C_4H_6 are formed by reaction (c) or (d), it is necessary to estimate the concentration of C_2H_3 . If one assumes approximate equality of the rate constants for recombination of two C_2H_3 , two C_2H_5 , and C_2H_5 with C_2H_3 , then, assuming that C_4H_8 is formed mainly by recombination of C_2H_3 and C_2H_5 , we have:

$$\frac{[C_2H_3][C_2H_5](1 + k_{C_4H_{10}} t)}{[C_2H_5][C_2H_5](1 + k_{C_4H_8} t)} \ll \frac{[C_4H_8]}{[C_4H_{10}]} \simeq 0.2 \div 0.5,$$

where $k_{C_4H_8}$ and $k_{C_4H_{10}}$ are the rate constants for the disappearance of C_4H_8 and C_4H_{10} . With

$$(1 + k_{C_4H_{10}} t) \simeq (1 + k_{C_4H_8} t), \quad [C_2H_3]/[C_2H_5] \simeq 0.2 \div 0.5. \quad (3)$$

Assuming that all C_4H_6 is formed by recombination of two C_2H_3 , we obtain:

$$[C_2H_3](1 + k_{C_4H_8} t)/[C_2H_5](1 + k_{C_4H_6} t) \simeq [C_4H_6]/[C_4H_8] = 5 \div 15. \quad (4)$$

Substituting relation (3) into (4), we have:

$$(1 + k_{C_4H_8} t)/(1 + k_{C_4H_6} t) \simeq 30. \quad (5)$$

Since the contact time in the experiments is 0.015–0.05 sec, relation (5) can be fulfilled only at very large values of $k_{C_4H_8}$ (of the order of 200–1000 sec^{-1}) and small values of $k_{C_4H_6}$, which appears unlikely. Thus, the assumption of the predominant formation of C_4H_6 by reaction (d) leads to a contradiction. It is possible, however, that the assumption made concerning equality of the rate constants for radical recombination is not fulfilled, and the recombination of two C_2H_3 for some reason proceeds more than an order of magnitude faster than the recombination of C_2H_3 with C_2H_5 .*

In conclusion, it should be noted that the influence of the surface on the cracking rate has been studied many times. However, the question of which particular processes the surface can influence and what the specific chemical mechanism of this influence is still cannot be considered unambiguously clarified. The use of labeled atoms in the present work made it possible to trace, under C_2H_6 cracking conditions, a clearly expressed dependence of the rate of decomposition of C_2H_2 on the nature of the surface. This rate changes by a factor of 10–20 for different surfaces, and this change is not reflected in the composition of the main products of C_2H_6 cracking or in the rate of the overall conversion of ethane.

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* The assumption that the principal amounts of C_4H_6 are formed by decomposition of C_4H_7 , from which, by reaction (g), allene and methylacetylene are also obtained, likewise leads to difficulty. Under such an assumption, the rate of decomposition of C_4H_7 at the C–C bond must be lower than the rate of its decomposition at the C–H bond, since the content of C_3H_4 in the cracking products is approximately 30 times lower than that of C_4H_6 . It is not excluded, however, that decomposition of C_4H_7 at the C–H bond is facilitated, since it leads to formation of the energetically favorable structure of divinyl.

Note: Figure translations are in progress. See original paper for figures.

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