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Abstract

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Comparative Study of the Kinetics of the Reactions of Conversion of Various Hydrocarbons into Acetylene in an Electric Discharge in a Static System

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The electrocracking of methane to acetylene has been studied many times previously*. The expediency of applying this method for the synthesis of acetylene was demonstrated. As for homologues of methane and olefins, their conversion has been carried out mainly under conditions of low-temperature forms of discharge (silent and glow), when acetylene either is not formed at all, or its production is associated with large energy expenditures, or else a mixture of hydrocarbons was subjected to cracking (^{4}). Thus, the literature contains almost no data that would make it possible to compare the kinetics and energetics of electrocracking of different hydrocarbons. The present communication is devoted to this question.

Experimental Part

Procedure. The process was carried out under static conditions, using a glow discharge and chiefly a high-voltage arc discharge at pressures of 35 and 70 mm Hg, currents of 100 and 300 mA, and distances between the electrodes of 15 and 50 mm. The main part of the apparatus was a reactor (a 5-liter flask) with two brass electrodes having internal water cooling. The working procedure has been described in greater detail previously (^{1}). At the end of an experiment, a gas sample was taken with a mercury pump and analyzed for the contents of: C_2H_2 —with an alkaline solution of mercuric cyanide; C_2H_4—with a 67% solution of sulfuric acid activated with silver oxide; C_3H_6—with an 87% solution of sulfuric acid.

Hydrogen was burned over copper oxide at 250°. Methane, ethane, and propane were determined from the residue after combustion of hydrogen. In the kinetic calculations, two principal reaction pathways were taken into account:

$$\text{Hydrocarbon} \begin{array}{l} \xrightarrow{K_1} \quad C_2H_2 + H_2 \\ \xrightarrow{K_2} \quad C + H_2 \end{array}$$

Fig. 1

Figure 1: Fig. 1

The total rate constant for the decomposition of hydrocarbons was determined from the first-order equation

$$K_1 + K_2 = \frac{1}{\tau} \ln \frac{1}{1-\Delta},$$

where Δ is the overall degree of conversion of the hydrocarbon, equal to the ratio of the amount of decomposed hydrocarbon to its initial amount.

* A detailed list of references may be found in article ([1]). See also ([2,3]).

Figure 1 presents changes in the concentration of acetylene in the products of the conversion of methane and ethylene as a function of the discharge-burning time (curves 1, 2), and also as a function of the energy consumption, expressed in kilowatt-hours per cubic meter of acetylene, reduced to normal conditions (curves 3, 4). Experimental conditions: reactor volume 5 l; initial pressure 70 mm Hg, current 100 mA, distance between electrodes 50 mm.

As can be seen, acetylene at first accumulates; then, at long reaction times, a decrease in the concentration of C_2H_2 is observed owing to its decomposition into the elements. The same character of the curves is observed under other experimental conditions, and also for the homologs of methane and ethylene, with the sole difference that the value of the maximum concentration changes, as does the reaction time corresponding to the maximum.

Fig. 1. Dependence of the concentration of acetylene during the cracking of methane and ethylene on the discharge-burning time (1, 2) and on the energy consumption per unit volume of acetylene (kWh per 1 m^3 C_2H_2) (3, 4). 1, 3 —methane; 2, 4 —ethylene.

Table 1 presents the principal characteristics of the process under various experimental conditions.

Comparison of the acetylene concentrations obtained with the theoretically possible ones indicates that, under the specified conditions, the principal direction of the process is cracking to acetylene. Ethylene amounts to only 10–15% of the acetylene content. Decomposition of the hydrocarbon into the elements is a side reaction, which becomes stronger on going from methane to propane and still more to propylene, i.e., to hydrocarbons less rich in hydrogen. In the case of the indicated hydrocarbons, acetylene concentrations were obtained that considerably exceed the maximum concentrations in the cracking of methane (for example, for propylene by a factor of 1.5). It is furthermore very important that the maximum concentrations correspond to substantial utilization of the initial hydrocarbon (the degree of cracking is on average equal to 80%).

Another very important characteristic of electrocracking is the energy consumption referred to 1 m^3 C_2H_2 (α). The change in energy consumption as a function of acetylene concentration can be followed, for certain conditions of cracking of methane and ethylene, from curves 3 and 4 in Fig. 1. As can be seen, in the initial period of acetylene accumulation the energy consumption changes little. For the other hydrocarbons studied and under other experimental conditions, the character of the curves remains the same. Table 2 gives values of the energy consumption for the initial period of the reaction. As can be seen, in the indicated series of hydrocarbons the energy consumption is in all cases comparatively small; it is maximal for methane, decreases substantially for ethane and propane, and still more for ethylene and propylene. If one takes into account that the energy consumption in the industrial carbide method of producing acetylene is approximately 12 kWh/m^3, then the advantage of electrocracking becomes obvious; carrying it out in a flow-type enlarged installation will make it possible to reduce the energy consumption still further.

The same Table 2 gives the value of the thermochemical efficiency of the discharge (η), which makes it possible to estimate what part of the total discharge energy is the energy thermochemically necessary for the production of ···

Table 1

Main indices of the electrocracking of methane, ethane, propane, ethylene, and propylene, obtained under different discharge-combustion conditions

Hydrocarbon	Electrode distance, mm	Current, mA	Pressure, mm Hg	Maximum concentration of C_2H_2, vol. %	Total cracking, % of the corresponding maximum concentration	Sums (average) of the constants ($K_1 + K_2$) ($sec^{-1} \cdot 10^4$) of the hydrocarbon decomposition rate	Energy efficiency of the discharge $\varphi = \frac{(K_1 + K_2)P_H}{W}$
CH_4	15	100	37	17.8	85	57	5
CH_4	15	100	70	18.2	96	72	8
CH_4	15	300	35	20.2	95	166	6
CH_4	15	300	70	19.0	94	140	7
CH_4	50	100	35	17.4	95	258	8

Hydrocarbon	Electrode distance, mm	Current, mA	Pressure, mm Hg	Maximum concentration of C_2H_2, vol. %	Total cracking, % of the corresponding maximum concentration	Sums (average) of the constants $(K_1 + K_2)$ $(\text{sec}^{-1} \cdot 10^4)$ of the hydrocarbon decomposition rate	Energy efficiency of the discharge $\varphi = \frac{(K_1 + K_2)P_H}{W}$
CH_4	50	100	70	17.8	93	302	12
CH_4	50	300	35	19.0	90	845	10
CH_4	50	300	70	16.2	88	702	11
C_2H_6	15	100	37	–	–	84	6
C_2H_6	15	100	70	–	–	69	7
C_2H_6	15	300	35	24.4	90	207	6
C_2H_6	15	300	70	19.4	75	114	6
C_2H_6	50	100	35	23.2	91	412	10
C_2H_6	50	100	70	21.2	80	279	10
C_2H_6	50	300	35	20.4	83	1000	10
C_2H_6	50	300	70	19.4	75	535	8
C_3H_8	15	100	37	26.6	85	99	6
C_3H_8	15	100	70	22.6	73	85	8
C_3H_8	15	300	35	24.2	80	157	5
C_3H_8	15	300	70	20.8	76	115	5
C_3H_8	50	100	35	23.8	80	355	8
C_3H_8	50	100	70	20.6	87	207	7
C_3H_8	50	300	35	22.0	70	585	7
C_3H_8	50	300	70	18.4	68	538	7
C_2H_4	15	100	37	28.4	85	135	7
C_2H_4	15	100	70	27.4	87	94	9
C_2H_4	15	300	35	29.2	80	251	6
C_2H_4	15	300	70	24.6	75	131	5
C_2H_4	50	100	35	30.2	86	535	12
C_2H_4	50	100	70	27.6	82	322	11
C_2H_4	50	300	35	27.8	82	1050	10
C_2H_4	50	300	70	24.0	75	700	7
C_3H_6	15	100	37	30.8	90	120	7
C_3H_6	15	100	70	26.8	85	72	8

Hydrocarbon	Electrode distance, mm	Current, mA	Pressure, mm Hg	Maximum concentration of C_2H_2, vol. %	Total cracking, % of the corresponding maximum concentration	Sums (average) of the constants $(K_1 + K_2)$ $(\text{sec}^{-1} \cdot 10^4)$ of the hydrocarbon decomposition rate	Energy efficiency of the discharge $\varphi = \frac{(K_1 + K_2)P_H}{W}$
C_3H_6	15	300	35	28.2	85	216	5
C_3H_6	15	300	70	23.0	82	135	–
C_3H_6	50	100	35	28.2	86	422	9
C_3H_6	50	100	70	25.4	83	307	9
C_3H_6	50	300	35	25.0	80	830	6
C_3H_6	50	300	70	19.8	70	536	6

···of producing a given amount of acetylene. The high value of the thermochemical efficiency of the discharge, reaching 0.4–0.5, distinguishes the electrocracking of hydrocarbons from other endothermic reactions in a discharge. An explanation of this may be given by assuming a chain mechanism for the electrocracking reaction, by analogy with thermal cracking, for which chain kinetics is considered proven. It may be assumed that only the initial stage of the reaction—namely the formation of radicals and atoms—occurs in this case by electron impact. The further development of the chains takes place through thermal activation of the individual links of the process.

Consideration of the value of the sum of the kinetic constants (Table 1) for different hydrocarbons shows that, under identical experimental conditions, they

Table 2

Hydrocarbon	Energy consumption in kWh per 1 m^3, $[C_2H_2] \leq$ 3-5%	Energy consumption in kWh per 1 m^3, $[C_2H_2] \leq$ 10-12%	Heat effect in kWh per 1 m^3 C_2H_2 for the reaction: hydrocarbon $\rightarrow C_2H_2 + H_2$	Thermochemical coefficient of useful action of the discharge (η)
CH_4	9.6	12.7	4.7	0.27
C_2H_6	5.8	8.2	3.8	0.47
C_3H_8	6.6	9.4	3.7	0.38
C_2H_4	3.5	4.8	2.2	0.45
C_3H_6	4.6	6.4	2.7	0.41

have close values. However, the sum $K_1 + K_2$ increases on going to higher currents, and also when the distance between the electrodes is increased. In other words, on going to a more powerful discharge, the crackability of all hydrocarbons increases, and moreover to an equal extent for all hydrocarbons.

If the initial rate of cracking is expressed as $(K_1+K_2)P_\mathrm{n}$ (under the assumption of first kinetic order), where P_n is the initial pressure of the hydrocarbon, and this rate is referred to a unit of power, it turns out that the quantity obtained, or the "energy efficiency of the discharge" (4)* , remains approximately constant for all hydrocarbons, irrespective of the experimental conditions (Table 1). The individual deviations that occur are not regular in character and are apparently due to random causes. This important result may be interpreted to mean that the rate of conversion of hydrocarbons in a glow arc depends not on the structure of the hydrocarbon, but on the energy supplied to the discharge.

In conclusion, we note that the data obtained indicate the possibility of applying to the electrocracking of the hydrocarbons studied the technological scheme developed for methane cracking. In this case, advantages should be expected both with respect to acetylene yields and with respect to a reduction in energy consumption, as compared with those obtained in methane cracking.

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* For more detail on energy efficiency, see (3, 5).

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