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A. B. TSENTsIPER, E. N. EREMIN, and N. I. KOBOZEV

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Abstract

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A. B. TSENTsIPER, E. N. EREMIN, and N. I. KOBOZEV

ON THE INFLUENCE OF HYDROGEN AND ARGON ON THE ELECTROCRACKING OF METHANE AND ETHYLENE

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The question of the influence of hydrogen on the electrocracking of methane has been discussed repeatedly in the literature. Some authors believed that hydrogen hinders the deposition of carbon ([1]). S. S. Vasil' ev ([2]) considered that under some conditions hydrogen activates cracking, while under others it retards it. According to D. Koller ([3]), in the presence of hydrogen the overall degree of conversion of methane increases. Meanwhile, this question is important both for practical purposes and for understanding the mechanism of electrocracking; therefore we carried out a study in which the influence of hydrogen on the process was compared with the influence of chemically inert argon. The influence of hydrogen and argon on the electrocracking of ethylene and other hydrocarbons was also studied.

Experimental Part

The work was carried out under static conditions in an apparatus described earlier ([5]). The degree of conversion (Δ) was determined from the change in pressure, on the assumption that decomposition of the hydrocarbon proceeds mainly in two directions:

$$\text{Hydrocarbon} \begin{cases} \nearrow \mathrm{C_2H_2} + \mathrm{H_2}, \\ \searrow \mathrm{C} + 2\mathrm{H_2}, \end{cases}$$

which are characterized by the same change in volume. The procedure of the experiment was as follows: at a specified partial pressure of the hydrocarbon, hydrogen or argon was added up to a certain total pressure, equal to 50 or 150 mm Hg. Then the discharge was switched on periodically for various intervals of time (τ). After each switching-on and cooling of the reactor, the pressure was measured. The current in all experiments was 300 mA. Gas analysis was carried out at the end of the experiment, when the degree of conversion had reached approximately 50%.

Figure 1: Change in the rate of overall conversion of methane and ethylene with time upon dilution with hydrogen and argon.

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Figure 1 presents the dependences of the average rates of decomposition of methane and ethylene, as well as of their mixtures with hydrogen and argon, on time. At hydrocarbon pressures equal to 40 mm Hg, the decomposition rates of methane and ethylene are of the same order. As can be seen, the addition of argon or hydrogen retards the cracking of both hydrocarbons to approximately the same degree, and the more strongly, the higher the partial pressure of the added gas. Thus, at a total pressure of 150 mm Hg the rate of decomposition of the hydrocarbons decreases by approximately a factor of two. When the pressure of the initial hydrocarbon is lowered to 10 mm Hg and without an additive, methane cracks much more slowly than ethylene (by approximately a factor of 50). In this case, upon dilution of ethylene with hydrogen or argon, the already noted effect of cracking inhibition is observed. If, however, the gases are added to methane, a sharp activation of the process is observed, and the cracking rate of methane approaches the rate of ethylene decomposition under these conditions. It is characteristic that during activation

the process changes, as does the external appearance of the discharge. If at $P = 40$ mm Hg the discharge in an atmosphere of pure hydrocarbon or in a mixture with argon or hydrogen burns with a yellow, slightly smoky flame, then at $P = 10$ mm Hg in methane the discharge has a bluish glow, changing to intense yellow only when hydrogen or argon is added. In the case of ethylene at this pressure the discharge burns with a yellow flame.

Fig. 1. Change in the rate of overall conversion of methane $(A,)$ and ethylene $(A', ')$ with time upon dilution with hydrogen and argon. Δ is the degree of conversion of the hydrocarbon, corresponding to the time of burning of the discharge τ.

Figure	Curve No.	Partial pressure (in mm): hydrocarbon	Partial pressure (in mm): hydrogen	Partial pressure (in mm): argon	Figure	Curve No.	Partial pressure (in mm): hydrocarbon	Partial pressure (in mm): hydrogen	Partial pressure (in mm): argon
A, A'	1	40	0	[10]	$, '$	1	10	0	40
A, A'	2	40	0	[110]	$, '$	2	10	0	140
A, A'	3	40	10	[–]	$, '$	3	10	40	0

Figure	Curve No.	Partial pressure (in mm): hydrocarbon	Partial pressure (in mm): hydrogen	Partial pressure (in mm): argon	Figure	Curve No.	Partial pressure (in mm): hydrocarbon	Partial pressure (in mm): hydrogen	Partial pressure (in mm): argon
A, A'	4	40	110	[–]	$,'$	4	10	140	0
A, A'	5	40	0	0	$,'$	5	10	0	0

The points of intersection of the kinetic curves with the dashed line correspond to conversion of the hydrocarbon by 15-18%.

Thus, activation of methane cracking is observed when the total pressure of the methane itself is increased, and also as a result of the addition of hydrogen and, to an even greater extent, argon. Activation of the process was also observed during a single experiment under the following conditions: the initial methane pressure was 50 mm Hg, the current strength 50 mA, and the distance between the electrodes 28 mm. At first the discharge burned with a pale-yellow flame at electrodes covered with a smoldering glow. However, some time after the beginning of the experiment localization of the discharge was observed between incandescent points on the carbonaceous deposits that had formed on the electrodes. The weak glow of the flame then changed to an intense yellow and soon

the cracking rate increased tens of times. If, however, the experiment was begun with electrodes initially covered with deposits or other resinous substances, the cracking rate was significant at once, and the discharge burned with a sooty yellow flame. It is characteristic that neither at higher nor at lower pressures was any acceleration observed in the course of cracking. In the first case the discharge was active irrespective of the state of the electrode surface; in the second case the slight increase in current density due to partial localization of the discharge was apparently insufficient for the discharge to become active.

Thus, activation of the electrocracking of methane may be caused by quite different factors (an increase in pressure, an increase in current, localization of the discharge between hot spots) and is evidently due to the transition of the discharge from a low-activity glow discharge to a more chemically active one—an arc discharge. The latter is characterized by large values of molecular temperature, the positive role of which in the electrocracking of hydrocarbons has been noted previously ([3],[6]). In expressing general considerations on the mechanism of the chemical action of the discharge, one may suppose that, by electronic activation, only processes having significant activation energies (rupture of C—C and C—H bonds) take place. Further chain development of the process proceeds

with the participation of the radicals and atoms formed and requires thermal activation, i.e., relatively high temperatures. The concept of a chain mechanism of the process is confirmed by the high values obtained for the thermal coefficient (0.4–0.6) for the cracking of hydrocarbons ([5]).

All the foregoing, in our opinion, convincingly proves the absence of any specific influence of hydrogen on the intensity of electrocracking of hydrocarbons.

Moscow State University
named after M. V. Lomonosov

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