E. M. GAMUS-CHERNYAVSKAYA, S. Sh. REZNIKOVA, and A. D. STEPukHOVICH

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

E. M. GAMUS-CHERNYAVSKAYA, S. Sh. REZNIKOVA, and A. D. STEPukHOVICH

COMPOSITION OF THE PRODUCTS AND MECHANISM OF THE INITIATED CRACKING OF GASEOUS ALKANES

(Presented by Academician V. N. Kondrat' ev, 7 XII 1959)

The composition of the products of alkane cracking initiated by additions of azomethane has not yet been studied. Although investigation of the kinetics of initiated cracking from measurements of Δp with time, taking into account decomposition of the initiator, makes it possible to conclude that initiation is positive ($^{1-3}$), direct evidence is nevertheless needed for initiation of alkane decomposition, obtained on the basis of studying the composition of the decomposition products of the alkane-initiator mixture. Study of the composition of the products of initiated cracking is also absolutely necessary for elucidating the mechanism of initiated cracking and its differences from the ordinary decomposition of alkanes.

In the present work, the composition of the products of the cracking of propane and butanes initiated by additions of azomethane has for the first time been studied in detail by the method of gas chromatography. Study of initiated cracking by the composition of the products gives indisputable proof that initiation of alkane decomposition occurs to an appreciable extent, which is perhaps the weightiest argument in favor of the radical-chain mechanism of thermal cracking. Thus the conclusions concerning the positive nature of initiation, which were drawn on the basis of purely kinetic data and were not free from objections, are confirmed. At the same time, study of the composition of the products of initiated cracking leads to new conclusions concerning the mechanism of initiated cracking.

A complex vacuum apparatus assembled for the purpose of a comprehensive study of the kinetics and composition of the products of initiated cracking of alkanes was described by us previously (^{4}).

The results of analyses of the products of initiated cracking of propane and butanes, obtained on a chromatographic column and placed in Table 1, show that neither propane (364°, 80 mm, cracking time 10 min) nor butanes (355°, 70–76 mm, cracking time 10 min) decompose by themselves under the conditions of decomposition of the initiator. Introduction of small additions of azomethane

(1-3%) causes cracking of the alkanes to a considerable depth. In the initiated cracking of propane, the paths of dehydrogenation and demethanation are represented; in comparison with ordinary cracking, even at small additions of azomethane (1-3%) the dehydrogenation reaction exceeds the demethanation reaction threefold, whereas in thermal cracking, under approximately analogous conditions with respect to pressure and depth, the dehydrogenation and demethanation reactions proceed equally, or demethanation somewhat predominates. In addition, the yield of methane from the very beginning is almost twice as high as the yield of ethylene. In ordinary cracking of propane, the yields of methane and ethylene remain equal up to very large depths of decomposition. At small additions a high yield of ethane is observed, which is due not only to decomposition of azomethane but also to the reaction of recombination of methyl radicals, which is intensified under the conditions of initiated cracking.

Table 1

Composition of the products of cracking of propane and butanes induced by additions of azomethane
(in volume percent)

P, alkane, mm	P, azomethane, mm	N_2	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}
Propane (364°, 10 min.)	**Propane (364°, 10 min.)**	**Propane (364°, 10 min.)**	**Propane (364°, 10 min.)**	**Propane (364°, 10 min.)**	**Propane (364°, 10 min.)**	**Propane (364°, 10 min.)**	**Propane (364°, 10 min.)**	**Propane (364°, 10 min.)**	**Propane (364°, 10 min.)**	**Propane (364°, 10 min.)**
80.0	–	–	–	–	–	–	–	–	–	100
77.6	2.4 (3%)	3.3	1.5	0.75	0.44	1.65	1.79	90.5	–	–
74.4	5.6 (7%)	4.16	2.6	4.4	2.8	3.51	2.8	79.5	–	–
72.0	8.0 (10%)	7.18	3.1	5.63	3.36	4.2	3.24	73.4	–	–
–	2.2 on average CO_2 (70 mm)	50.0	–	–	–	5.0	–	–	–	–
Butane (355°, 10 min.)	**Butane (355°, 10 min.)**	**Butane (355°, 10 min.)**	**Butane (355°, 10 min.)**	**Butane (355°, 10 min.)**	**Butane (355°, 10 min.)**	**Butane (355°, 10 min.)**	**Butane (355°, 10 min.)**	**Butane (355°, 10 min.)**	**Butane (355°, 10 min.)**	**Butane (355°, 10 min.)**
70.0	–	0	0	0	0	0	–	0	0	100

P, alkane, mm	P, azomethane, mm	N_2	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}
70.0	2.1 (3%)	2.59	0.97	7.46	2.39	2.33	9.72	0.77	1.4	72.64
70.0	2.1 (3%)	2.59	0.97	7.79	2.27	2.33	9.67	0.84	1.1	72.72
–	2.1 on average CO_2 (70 mm)	50.0	–	–	–	50.0	–	–	–	–
Isobutane (355°, 10 min.)	**Isobutane (355°, 10 min.)**	**Isobutane (355°, 10 min.)**	**Isobutane (355°, 10 min.)**	**Isobutane (355°, 10 min.)**	**Isobutane (355°, 10 min.)**	**Isobutane (355°, 10 min.)**	**Isobutane (355°, 10 min.)**	**Isobutane (355°, 10 min.)**	**Isobutane (355°, 10 min.)**	**Isobutane (355°, 10 min.)**
76.0	–	0	0	0	0	0	0	0	0	100
76.0	0.76 (1%)	1.2	1.47	4.44	0.48	0.7	2.2	0.9	1.47	87.63
76.0	2.4 (3%)	2.8	1.6	7.48	0.5	0.75	4.1	1.13	1.5	80.4
76.0	3.8 (5%)	5.2	1.75	8.52	0.7	0.85	6.3	1.1	1.63	72.75
76.0	5.3 (7%)	6.0	1.8	10.76	0.7	1.1	6.35	$\sim$ 1.0	1.64	70.56
76.0	7.6 (10%)	5.9	1.86	11.45	0.7	1.24	6.5	$\sim$ 1.1	1.65	68.72

With an increase in the concentration of azomethane additions (7-10%), the depth of the induced cracking increases, but to a lesser extent than in the region of small additions, and the demethanation reaction begins to predominate more and more. With an increase in the concentration of the additive from 3 to 10%, the yield of ethylene increases by a factor of 7.5, while at the same time the yield of C_3H_6 increases only twofold. The yield of methane still considerably exceeds the yield of ethylene, and the yield of ethane amounts to a fraction somewhat greater than one-half of the nitrogen yield.

These results prove not only the initiating effect of CH_3-radicals on the decomposition of propane, but also indicate, even more clearly than was observed by us in ordinary cracking (4), an intensification of demethanation reactions. When the azomethane concentration is increased in the range 3–10%, the ratio $C_2H_4 : C_3H_6$ increases from 0.25 to 1, i.e., approximately in proportion to the azomethane concentration. The shift toward demethanation is most probably explained by the isomerization reaction of isopropyl radicals, which are formed predominantly at lower temperatures, into propyl radicals. An increase in the yield of $CH_3CH_2—CH_2$-radicals with increasing concentration of CH_3 radicals seems less probable.

The increased yield of CH_4 in comparison with C_2H_4 shows that CH_3 radicals are distributed between propane and azomethane. In the case of decomposition of pure azomethane, a reaction between CH_3 and azomethane with formation of methane undoubtedly also takes place. Consequently, in the azomethane molecule the double bond $N = N$ weakens the $C—H$ bond in the β-position, just as $C—C$ weakens the $C—H$ bond in the methyl group of propylene. On the other hand, the $C—H$ bond in azomethane is less strong than the secondary $C—H$ bond in propane. In light of these data, the decomposition of azomethane is not a true monomolecular reaction, as was also observed by us in studying the kinetics of azomethane decomposition.

The increased yield of ethane is possibly associated with the reaction of addition of CH_3 to azomethane:

$CH_3 + CH_3N = NCH_3 \rightarrow (CH_3)_2N—\dot{N}CH_3$,

with subsequent

with regeneration of azomethane by the reaction

$$\dot{\mathrm{C}}\mathrm{H}_3 + (\mathrm{CH}_3)_2\mathrm{N} - \dot{\mathrm{N}}\mathrm{CH}_3 \rightarrow \mathrm{C}_2\mathrm{H}_6 + \mathrm{CH}_3\mathrm{N} = \mathrm{NCH}_3.$$

This is equivalent to recombination in the volume, in which the azomethane molecule, and not the walls, serves as the mediator. The decomposition of azomethane in a carbon dioxide medium proceeds entirely to nitrogen and ethane. In an alkane medium the decomposition may proceed differently, which is of interest for carrying out initiated cracking.

In the initiated cracking of butane, the same directions and approximately the same product ratios are observed as in ordinary cracking. Paired products are formed in equal yields (somewhat more C_3H_6 is formed than CH_4). The ratio $C_3H_6 : C_2H_4 : H_2$ in initiated cracking (355°, 70 mm, 10 min), equal to $10 : 2.5 : 1$, changes in ordinary cracking (548°, 180 mm, 6 min) and amounts to $9 : 3.5 : 1$ (^{4}). Thus, in the initiated cracking of butane, demethanization predominates even more over the ethane-elimination reaction. This is explained by the fact that lowering the temperature more favors the decomposition of $CH_3\dot{C}HCH_2CH_3$ radicals (decomposition energy 27.7 kcal) than of $CH_3CH_2CH_2\dot{C}H_2$ radicals (decomposition energy 31 kcal), as a result of which partial isomerization of the latter into the former has time to occur.

In ordinary cracking of isobutane, as is known, the dehydrogenation reaction predominates in comparison with the reaction of decomposition into CH_4 and C_3H_6. The ratio iso-$C_4H_8 : C_3H_6 : C_2H_4$ (548°, 180 mm, 6 min) is $7 : 3 : 1$ (^{4}), which is determined by the preferential formation of tertiary isobutyl radicals $(CH_3)_3\dot{C}$ and their subsequent decomposition.

In the initiated cracking of isobutane (355°, 76 mm, 10 min), from the very beginning, with small additions of initiator (3%), the demethanization reaction predominates, and the above ratio is $2 : 6 : 1$. The ratio iso-$C_4H_8 : C_3H_6$ changes from 2.4 in ordinary cracking to 0.26 in initiated cracking, i.e., by a factor of 10. This shift in the directions of decomposition is explained by the fact that, despite the preferential formation of tertiary radicals (upon attack of isobutane molecules by CH_3 radicals), the latter decompose more slowly under the conditions of initiated cracking and partially isomerize into primary isobutyl radicals

$$(CH_3)_3\dot{C} + (CH_3)_3CH \rightleftarrows (CH_3)_3CH + \dot{C}H_2CH(CH_3)_2.$$

The isomerization reaction requires much less isomerization energy (~ 25 kcal), and the decomposition of primary isobutyl radicals proceeds very readily (decomposition energy 3.5 kcal).

As in the case of induced cracking of propane, an increased yield of CH_4 is observed, which is associated with the distribution of CH_3 radicals supplied by the initiator between alkane molecules and the additive owing to competition of the reactions:

$$\dot{C}H_3 + (CH_3)_3CH \rightleftarrows CH_4 + (CH_3)_3\dot{C} \quad \text{(activation energy 7.9 kcal)},$$

$$\dot{C}H_3 + CH_3N = NCH_3 \rightleftarrows CH_4 + \dot{C}H_2N = NCH_3 \quad \text{(activation energy 6.4 kcal)}.$$

With increasing azomethane concentration (1–3%), the initiating effect at first increases rapidly, but with a further increase in the additive (5–7%) the depth of decomposition increases only insignificantly, and in initiated cracking the limit of action of the initiator sets in, which we predicted earlier (^{5}). This proves the effectiveness of initiation by small additions. The limit of action of the initiator is connected with the fact that initiator additives are not only donors but also acceptors of radicals.

On the other hand, with increasing depth of initiated cracking, the retarding action of the cracking products begins to be manifested (^{5}). Experimental data on the initiated cracking of propane and butanes are well described by the equation of self-retarding reactions of Dintses and

growth. A comparison of the initiated cracking of butanes shows that butane is initiated more effectively than isobutane, which is due to the easier decomposition of primary and secondary butyl radicals as compared with tertiary isobutyl radicals. It is noteworthy that the depth of initiated cracking of alkanes, achieved in a somewhat longer time, corresponds to the depths of ordinary cracking, which may be of practical significance, especially in the search for new routes for the chemical processing of associated petroleum gases, off-gases from cracking, and alkanes of higher molecular weight.

The formation of propane in the initiated cracking of isobutane is still difficult to explain, since it is unclear how, in the absence of primary decomposition of isobutane, propyl (or ethyl) radicals arise. It is possible that they are formed by the addition of CH_3 radicals to ethylene. A more thorough study of the kinetics of the initiated cracking of propane and isobutane showed that the curves of their initiated decomposition are similar (percent decomposition—time), and, in particular, that the curves for propane do not have an S-shaped form, otherwise confirming the previous results ([1]).

The rate of initiated cracking of propane and isobutane at a fixed additive decreases with time along a curve analogous to that for the dependence of the rate of self-retarding cracking, with the only difference that the rate curve for initiated cracking approaches the abscissa axis.

The results discussed above lead to the conclusion that it is advisable to carry out experiments on the application of initiated cracking under production conditions in order to determine its prospects as a new technological method.

In conclusion, we express our gratitude to R. V. Kosyreva for the assistance rendered in carrying out the analyses.

Saratov State University
named after N. G. Chernyshevsky

Received
30 XI 1959

REFERENCES CITED

[1] A. D. Stepukhovich, V. V. Tatarintsev, DAN, **94**, 1049 (1954).
[2] A. D. Stepukhovich, E. G. Kaplan, ZhFKh, **30**, 929 (1956).
[3] A. D. Stepukhovich, E. E. Nikitin, ZhFKh, **30**, 1291 (1956).
[4] A. D. Stepukhovich, Dissertation. Moscow, 1958.
[5] A. D. Stepukhovich, ZhFKh, **30**, 556 (1956).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.