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A. D. STEPUKHOVICH

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Abstract

Full Text

PHYSICAL CHEMISTRY

A. D. STEPUKHOVICH

ON THE DEPENDENCE OF THE INHIBITION LIMIT IN THE THERMAL CRACKING OF ALKANES ON THE NATURE OF THE INHIBITOR

(Presented by Academician V. N. Kondrat' ev, March 28, 1961)

In 1934 we (^{1}) were the first to discover the inhibiting effect of propylene additions on the rate of thermal cracking of butane. Subsequently, in studying the retarding effect of propylene additions on the rate of thermal decomposition of ethane (^{2}), one of the most interesting phenomena in the field of thermal cracking was discovered—the existence of an inhibition limit for an inhibitor. The essence of this phenomenon is that, as the concentration of the inhibitor is increased, the rate of cracking of alkanes decreases to a certain value, and with further increase in the concentration of the inhibitor it does not change. We called this rate at the inhibition limit the residual rate (^{3}). In our subsequent work it was shown that the phenomenon of an inhibition limit is characteristic of the action of various inhibitors on the decomposition of various alkanes ($^{3-10}$). Similar conclusions were reached in their studies by Steacie and Hinshelwood (^{11,12}), who studied the action of NO on the thermal decomposition of alkanes.

The residual rate of completely inhibited cracking of alkanes was interpreted by us as the rate of a residual chain reaction (^{4}), or, in the limiting case, as the rate of primary decomposition into radicals (^{3,13}). In connection with these studies there arose the question of how various inhibitors act on the rate of thermal cracking of a given alkane. It could be assumed in advance only that if the thermal cracking of an alkane is a homogeneous reaction, and the residual rate at the inhibition limit has the same order of magnitude as the rate of homogeneous initiation of radicals, then different inhibitors should inhibit the radical-chain decomposition of the given hydrocarbon to one and the same limit. Naturally, the difference in the nature of the inhibitors should have been reflected only in the fact that different amounts of inhibitors would be required to attain a given rate of initiation.

Even the first calculations (^{3,14}) showed that the residual rate at the inhibition limit is many times greater than the rate of homogeneous initiation of radicals and, consequently, it cannot be interpreted as the rate of primary dissociation

Figure 1: Dependence of the cracking rate of ethane on inhibitor concentration

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of the hydrocarbon into radicals. This prompted us to turn to the consideration of thermal cracking as a process with heterogeneous initiation of radicals (14,15). With chain initiation on the walls, owing to the facilitated formation of radicals on the surface through simple chemisorption (or even activated adsorption), the initiation rate increased many times and approached the observed residual rate. Moreover, in accordance with experiment, the chain length also decreased, approaching that found from the composition of the products (4,14–16).

With heterogeneous initiation of radicals and homogeneous action of inhibitors, it may be supposed that different inhibitors, by terminating chains in the bulk, reduce the rate of cracking of a given alkane to one and the same value—

values. In an experimental study of the action of various inhibitors on the cracking rate of one and the same alkane, for example of propylene and isobutylene on the rate of thermal decomposition of propane (butane or isobutane), we found that the indicated olefin inhibitors reduce the decomposition rate of the given hydrocarbon practically to one and the same limit (7–9). However, we explained this fact by the similarity in the structure of the inhibitors, whose mechanism of action consists in the abstraction, by active radicals, of H atoms of methyl groups in olefins and the formation of relatively inactive allyl radicals (5,16). The point is that the residual rate at the inhibition limit nevertheless exceeds by several times the rate of heterogeneous initiation of radicals and may be interpreted as the rate of a residual chain reaction with a certain chain length (4,16). In this case, naturally, the inhibition limit must be different for different inhibitors, i.e., it must depend on the nature of the inhibitor.

Almost simultaneously, Hinshelwood and co-workers (17,18) found that still more dissimilar inhibitors (such as NO and propylene) reduce, for example, the rate of decomposition of pentane to the same limit.

Thus, both from our studies and from the work of Hinshelwood and co-workers one may conclude that the inhibition limit is independent of the nature of the inhibitor for a given hydrocarbon. However, these findings are in contradiction with the notion of the residual rate as the rate of a chain reaction. Indeed, relying on the independence of the rate at the inhibition limit from the nature of the inhibitor, Hinshelwood interpreted the residual rate of hydrocarbon decomposition as the rate of a molecular reaction, on which inhibitors, naturally, cannot exert an influence. In their opinion, thermal cracking represents a combination of molecular and chain reactions.

Fig. 1. Dependence of the cracking rate of ethane on the concentration of inhibitors

Relying on the notion that the inhibition limit is independent of the nature of the inhibitor, Voevodsky and co-workers (^{19,20}) proposed a concept according to which the inhibitor suppresses the initiation of radicals on the walls and does not act on chain propagation in the volume, i.e., acts exclusively by a heterogeneous route. The equality of the inhibition limit in the case of different inhibitors in Voevodsky' s concept finds no less simple an explanation than in Hinshelwood' s work, and is associated with the fact that, to block an active center on the surface, one particle of inhibitor of any nature is required. In this case the residual rate can be interpreted only as the rate of initiation, and the chains developing in the volume have a large length (of the order of several hundred links).

Without denying the advantages of this concept in explaining the indicated fact, it should, however, be questioned whether the fact itself is absolute in character. This doubt is based on facts presented in our works, indicating the homogeneous character, in the main, of the action of olefin inhibitors, although NO as a radical may also affect the heterogeneous initiation of chains, and on the view following from these works of the hetero-homogeneous chain character of the residual rate.

In connection with the broad development of studies on the influence of various products of alkane cracking on its course, we were able to put our doubts to the test. In particular, we sought to determine which products inhibit the cracking of ethane, since additions of ethylene do not exert an inhibiting action, while propylene was not detected either in the initial or in the later stages of ethane cracking [16]. In experiments on ethane cracking by the author, E. K. Mogileva and N. S. Sukhova it was shown that small additions of allene and acetylene act as effective inhibitors [16] and at the same time reduce the cracking rate to different limits.

The data on the dependence of the initial rate of ethane cracking (over 10, 30, and 60 sec) on additions of isobutylene, allene, and acetylene at different temperatures (612 and 635°) and initial pressure (10 mm in the case of additions of iso-C_4H_8; 20 mm in the case of additions of C_3H_4 and C_2H_2, and $t = 60$ sec) are presented in Fig. 1. The curves clearly demonstrate that at 612° additions of allene and acetylene slow the cracking rate to different limits. At 635°, in the case of additions of allene and isobutylene, a difference is also observed in the cracking rate at the limit of inhibitor action, lying beyond the possible errors in determining the rate. These results directly prove the dependence of the inhibition limit on the nature of the inhibitor and, at the same time, the radical-chain character of the residual reaction at the limit, which takes place in the volume. It should be noted that even in the case of suppression by an inhibitor of the reaction of chain initiation at the walls, as may occur for the action of NO additions, the independence of the residual rate from the nature of the inhibitor likewise cannot be absolute, if only because of differences in the adsorption properties of the inhibitors or in their reactivity with respect to centers on the surface. In light of this, the coincidence of limits for certain olefins and NO in the case of propane or pentane cannot have absolute significance.

Saratov State University
named after N. G. Chernyshevsky

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CITED LITERATURE

1. A. I. Dintses, A. D. Stepukhovich, D. V. Frost, *Bull. State Chem. Scientific-Research Inst. of High Pressures*, **6**, 4 (1934).

2. A. I. Dintses, D. A. Kvyatkovskii, A. D. Stepukhovich, A. V. Frost, *ZhOKh*, **7**, 1754 (1937).

3. A. D. Stepukhovich, Candidate dissertation, Saratov, 1938.

4. A. D. Stupekhovich, *ZhFKh*, **24**, 513 (1950); *ZhFKh*, **31**, 511 (1957).

5. A. D. Stepukhovich, *DAN*, **89**, 889 (1953); **92**, 213 (1953).

6. A. D. Stepukhovich, A. G. Finkel, *ZhFKh*, **26**, 1413 (1952).

7. A. D. Stepukhovich, E. S. Shver, *DAN*, **89**, 1067 (1953); *ZhFKh*, **27**, 1013 (1953).

8. A. D. Stepukhovich, A. M. Chaikin, *ZhFKh*, **27**, 1737 (1953).

9. A. D. Stepukhovich, G. P. Vorob' eva, *ZhFKh*, **28**, 1361 (1954).

10. A. D. Stepukhovich, L. V. Derevenskikh, *ZhFKh*, **28**, 1413 (1952); **28**, 1720 (1954); **29**, 2129 (1955).

11. L. S. Staveley, *Proc. Roy. Soc. A*, **162**, 557 (1937).

12. E. Hobbs, C. Hinshelwood, *Proc. Roy. Soc. A*, **167**, 447 (1938).

13. A. I. Dintses, *Usp. khim.*, **7**, 404 (1938).

14. A. D. Stepukhovich, *ZhFKh*, **28**, 1882 (1954).

15. I. F. Bakhareva, Candidate dissertation, Saratov, 1954.

16. A. D. Stepukhovich, Doctoral dissertation, Moscow, 1958.

17. F. I. Stubbs, C. Hinshelwood, *Proc. Roy. Soc. A*, **200**, 4158 (1950); **A**

201, 18 (1950).

18. K. U. Ingold, F. I. Stubbs, B. C. Spall, C. Hinshelwood, *Proc. Roy. Soc. A*, **214**, 20 (1952).

19. V. V. Voevodskii, *DAN*, **90**, No. 5 (1953).

20. V. V. Voevodskii, V. A. Poltorak, *DAN*, **91**, No. 3 (1953).

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