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Figure 1

Figure 1: Figure 1

Abstract**Full Text****PHYSICAL CHEMISTRY****I. V. ROZHKOVA****ON THE DEPENDENCE OF THE OXIDIZABILITY OF HYDROCARBONS IN THE LIQUID PHASE ON THEIR STRUCTURE***(Presented by Academician N. N. Semenov, 27 IV 1957)*

N. N. Semenov (^{1,11}), proceeding from the general principles of chain theory, came to the conclusion that the rate of oxidation of hydrocarbons should be determined by the strength of the weakest C–H bond in the molecule. In the present article we attempt to consider the data available in the literature (^{2,4,5}) and our own data (⁶) (see also Fig. 1) on the oxidizability in the liquid phase of hydrocarbons with 7-10 carbon atoms and to compare them with data (^{3,11}) on the strength of the C–H bonds in these hydrocarbons (Table 1).

Fig. 1. Oxidation of paraffin hydrocarbons and toluene ($t_0 = 100^\circ$; $p_0 = 1$ atm). Oxygen absorption on the ordinate axis: oxygen absorption, mole/mole $\cdot 10^4$. 1–*n*-heptane, 2–*n*-octane, 3–*n*-nonane, 4–*n*-decane, 5–2,6-dimethylheptane, 6–2,2,4-trimethylpentane, 7–toluene.

According to the views of representatives of Hinshelwood's school (⁷), in low-temperature oxidation of paraffin hydrocarbons molecular oxygen attacks first of all the middle groups of the chain, which indicates that the weakest C–H bonds are located in the middle of the hydrocarbon molecule; analysis of the equations of V. V. Voevodskii (³) also leads to an analogous conclusion.

The structure of the hydroperoxides of 2-methylhexane, 2,2,4-trimethylpentane, and 2,7-dimethyloctane shows that the experimental data (²) and the existing theoretical ideas (^{3,7}) concerning the location in the molecules of these hydrocarbons of the weakest C–H bonds coincide. With respect to *n*-heptane there is no such agreement; contrary to opinions widespread in the literature, oxidation of the straight paraffin chain begins not at the first (⁸) and not at the middle (^{9,10}), but at the second (²) carbon atom of the chain. The structure of the hydroperoxides of normal octane, nonane, and decane, unfortunately, is as yet unknown.

The dissociation energies of the weakest C–H bonds in normal paraffin hydrocarbons with 7-10 carbon atoms, calculated from the equations

Table 1

Energies of rupture of the weakest C–H bonds and the oxidizability of certain hydrocarbons in the liquid phase

Name of hydrocarbon	Location of the weakest C–H bond (asterisks) and direction of the primary oxygen attack according to K. I. Ivanov (arrows)	Energy of rupture of the weakest C–H bond, kcal/mol	Characterization of oxidizability of the hydrocarbon in the liquid phase
Paraffin hydrocarbons of normal structure	Paraffin hydrocarbons of normal structure	Paraffin hydrocarbons of normal structure	Paraffin hydrocarbons of normal structure
<i>n</i> -Heptane	CH ₃ –CH ₂ – CH ₂ –*CH ₂ – CH ₂ –CH ₂ – CH ₃ ↑	86.64 ^{1 2}	Oxidizes at the same rate as 2,2,4-trimethylpentane and toluene (^{2, 4, 6}), and considerably more slowly than normal octane, nonane, and decane (⁶)
<i>n</i> -Octane	CH ₃ (CH ₂) ₂ – *CH ₂ – *CH ₂ (CH ₂) ₂ CH ₃	86.35 ²	Oxidizes considerably more vigorously than <i>n</i> -heptane, 2,2,4-trimethylpentane, and toluene, and almost the same as normal nonane and decane (⁶)

Name of hydrocarbon	Location of the weakest C–H bond (asterisks) and direction of the primary oxygen attack according to K. I. Ivanov (arrows)	Energy of rupture of the weakest C–H bond, kcal/mol	Characterization of oxidizability of the hydrocarbon in the liquid phase
<i>n</i> -Nonane	CH ₃ (CH ₂) ₃ *CH ₂ –(CH ₂) ₃ CH ₃	86.08 ²	Oxidizes considerably more vigorously than <i>n</i> -heptane, and almost the same as <i>n</i> -octane and <i>n</i> -decane ⁽⁶⁾
<i>n</i> -Decane	CH ₃ (CH ₂) ₃ *CH ₂ *CH ₂ –(CH ₂) ₃ CH ₃	85.92 ²	Oxidizes considerably more vigorously than <i>n</i> -heptane, and almost the same as <i>n</i> -octane and <i>n</i> -nonane ⁽⁶⁾
Paraffin hydrocarbons of iso-structure	Paraffin hydrocarbons of iso-structure	Paraffin hydrocarbons of iso-structure	Paraffin hydrocarbons of iso-structure
2-Methylhexane	CH ₃ CH ₃ – *CH(CH ₂) ₃ CH ₃ ↑	85.95 ²	Oxidizes considerably more readily than <i>n</i> -heptane and 2,2,4-trimethylpentane ⁽⁴⁾
2,2,4-Trimethylpentane	CH ₃ CH ₃ CH ₃ –C–CH ₂ –*CH	84.54 ²	Oxidizes at the same rate as <i>n</i> -heptane and toluene ^(2, 4, 6)
2,6-Dimethylheptane	CH ₃ ↑CH ₃ CH ₃ CH ₃ CH ₃ – *CH(CH ₂) ₃ *CH –CH ₃	84.16 ²	Oxidizes considerably more vigorously than <i>n</i> -nonane ⁽⁶⁾

Name of hydrocarbon	Location of the weakest C–H bond (asterisks) and direction of the primary oxygen attack according to K. I. Ivanov (arrows)	Energy of rupture of the weakest C–H bond, kcal/mol	Characterization of oxidizability of the hydrocarbon in the liquid phase
2,7-Dimethyloctane	$\text{CH}_3 \quad \text{CH}_3 $ $—$ $*\text{CH}(\text{CH}_2)_4\text{CH}—$ CH_3	$ \text{CH}_3$ 84.06 ²	Oxidizes more vigorously than <i>n</i> -decane (⁵)
Aromatic hydrocarbons Benzene	Aromatic hydrocarbons	Aromatic hydrocarbons 99 ³	Aromatic hydrocarbons Practically does not oxidize in the liquid phase (^{2, 5})
Toluene	$\text{H}_2*\text{C}—\text{H}$ attached to a benzene ring	77.5 ³	Oxidizes at the same rate as <i>n</i> -heptane and 2,2,4-trimethylpentane (^{2, 4, 6})

Notes. 1. The energy of rupture of the C–H bond marked with an asterisk is given; the energy of rupture of the C–H bond at the point of attachment of the methyl group is 88.9 kcal/mol. 2. Calculated from the equations of V. V. Voevodskii (³). 3. Experimental data (¹¹).

V. V. Voevodskii's (³), are very close. However, if *n*-octane, *n*-nonane, and *n*-decane (see Fig. 1) are indeed oxidized in the liquid phase almost identically, then *n*-heptane is distinguished by its high resistance to oxidation.

Isoparaffinic hydrocarbons that do not contain a quaternary carbon atom are characterized by the presence of weaker C–H bonds in their molecules than the corresponding normal paraffinic hydrocarbons; in the liquid phase they are oxidized much more readily than the latter (cf. 2-methylheptane and *n*-heptane, 2,6-dimethylheptane and *n*-nonane, 2,7-dimethyloctane and *n*-decane).

However, the very high resistance to oxidation in the liquid phase of paraffinic hydrocarbons that contain a quaternary carbon atom (trimethylpentanes) (^{4,6}) is in complete disagreement with the strength characteristics of the C–H bonds in these hydrocarbons, calculated from the equations of V. V. Voevodskii (³);

these equations do not take into account the “screening” effect of the quaternary carbon atom in isoparaffinic hydrocarbons.

In toluene and benzene, as indicated, the value of the energy of rupture of the weakest C–H bond has been determined experimentally (¹¹); for toluene it is considerably lower than the assumed values of the energies of rupture of the weakest C–H bonds in any paraffinic hydrocarbons. On this basis it would seem that toluene should be oxidized much more readily than the paraffinic hydrocarbons investigated. However, the experimental data (^{2,6}) (see Fig. 1) show that toluene not only is not oxidized more vigorously than paraffinic hydrocarbons, but is considerably more resistant to oxidation in the liquid phase than *n*-octane, *n*-nonane, and *n*-decane, and in this respect is approximately equivalent to the most stable of the paraffinic hydrocarbons investigated—*n*-heptane and 2,2,4-trimethylpentane.

For benzene, on the contrary, the high value of the energies of rupture of the C–H bonds corresponds to an exceptionally high resistance to oxidation in the liquid phase.

Thus, we arrive at the conclusion that the experimental material currently available does not permit one to note regularities between the values of the energies of rupture of the weakest C–H bonds in hydrocarbon molecules and their oxidizability in the liquid phase.

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REFERENCES CITED

1. N. N. Semenov, *Problems of the Oxidation of Hydrocarbons*, Publishing House of the Academy of Sciences of the USSR, 1954, p. 13.
2. K. I. Ivanov, *Intermediate Products and Intermediate Reactions of the Auto-oxidation of Hydrocarbons*, Moscow, 1949.
3. V. V. Voevodskii, DAN, 79, No. 3, 455 (1951).
4. K. I. Ivanov, V. P. Zhakhovskaya, V. K. Saryanova, ed., report at the All-Union Conference on the Oxidation of Hydrocarbons, Publishing House of the Academy of Sciences of the USSR, 1951, pp. 15, 17.
5. N. I. Chernozhukov, S. E. Krein, *Oxidizability of Mineral Oils*, Moscow, 1955.
6. I. V. Rozhkov, E. N. Kornilova, *Chemistry and Technology of Fuels*, No. 12 (1956).
7. C. Cullis, C. Hinshelwood, M. Mulcahy, Proc. Roy. Soc., London, A196, 160 (1949).

8. J. Pope, F. Dykstra, G. Edgar, J. Am. Chem. Soc., 51, 1875, 2203, 2213 (1929).
9. A. Grün, Ber., 53, 955 (1950).
10. M. Mulcahy, Trans. Farad. Soc., 45, 537 (1949).
11. N. N. Semenov, *On Certain Problems of Chemical Kinetics and Reactivity*, Publishing House of the Academy of Sciences of the USSR, 1954.

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