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STUDY OF THE AUTOOXIDATION OF ALKYL AND HALOGEN DERIVATIVES OF 1,1-DIPHENYLETHANE AND ISOPROPYLBENZENE

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In previous works (1−5) it was shown that the autooxidation of 1,1-diphenylethane and some of its alkyl derivatives gives the corresponding hydroperoxides. In continuation of these works, it was of interest to carry out studies on obtaining hydroperoxides of halogen derivatives of aryl hydrocarbons, and also a more detailed study of the autooxidation process itself for the initial aryl hydrocarbons and halogen derivatives in relation to their structure. The aim of the present work was to study the influence of aryl and alkyl radicals, as well as of halogens, on the rate of the autooxidation process. For the study, compounds of the following structure were selected

$$R - C_6H_4 - C(H)(CH_3)_2 \quad \text{and} \quad C_6H_5 - C(H)(R_1) - C_6H_4 - R_2;$$

$$R = H,\ Cl,\ Br,\ J; \quad R_1 = CH_3,\ C_2H_5,\ n\text{-}C_3H_7; \quad R_2 = H,\ CH_3,\ C_2H_5,\ \text{iso-}C_3H_7,\ \text{tert.-}C_4H_9,$$

as well as Cl, Br, J.

In addition, for comparison, 9-methylfluorene was also studied:

9-methylfluorene structure

$$C{-}CH_3,\ C{-}H$$

Compounds of this structure were obtained by various methods. Isopropylbenzene was prepared from the technical product by careful purification. The following hydrocarbons were synthesized by known methods: 1,1-diphenylethane (1−3), 1,1-diphenylpropane (4), 1,1-diphenyl-*n*-butane (5), and alkyl derivatives of 1,1-diphenylethane (methyl, ethyl, isopropyl, and tert-butyl) (5). 9-Methylfluorene was prepared by an organomagnesium synthesis from fluorenone and methyl iodide, followed by reduction of the carbinol. The halogen derivatives of isopropylbenzene were obtained by the following methods. *p*-Chloroisopropylbenzene

Fig. 1 and Fig. 2 graphs

Figure 1: Fig. 1 and Fig. 2 graphs

was obtained from chlorobenzene and isopropyl bromide with anhydrous aluminum chloride as catalyst. *p*-Bromoisopropylbenzene was obtained by direct bromination of isopropylbenzene (6). *p*-Iodoisopropylbenzene was obtained from *p*-nitroisopropylbenzene via the corresponding diazo compound (7).

Halogen derivatives of 1,1-diphenylethane were obtained by condensation of styrene with the corresponding halobenzenes by the method that was developed —

developed in the laboratory for 1,1-diphenylethane (2,3). However, the yields of the halo derivatives of 1,1-diphenylethane proved to be somewhat lower (50–55%) than the yield of the hydrocarbons.

The substances listed were purified in the proper manner, as required for the autoxidation process.

Our investigations of autoxidation were carried out in an alkaline medium under the optimum conditions developed in our laboratory for 1,1-diphenylethane (2,3), namely: a 5% solution of caustic soda was added to the substance being oxidized, calculated as 0.05% pure caustic soda and 1% water by weight of the product taken. To avoid an induction period, the hydroperoxide of the substance being oxidized was also added, either in pure form or as a concentrate, in an amount of 0.5% by weight of the sample. The experiments were conducted in small reactors of 50 ml volume made of ordinary chemical glass; air was introduced by means of a capillary tube (immersed in the substance being oxidized) at a rate of 25–30 ml per minute. Samples of 30 g were taken for the experiment. The rate of autoxidation was determined by the iodometric method from the amount of hydroperoxide formed. The experiments were carried out at 80, 90, and 100°.

Fig. 1. Rate of hydroperoxide formation during autoxidation: **1**—isopropylbenzene, **2**—1,1-diphenylethane, **3**—9-methylfluorene, **4**—1,1-diphenylpropane, **5**—1,1-diphenyl-*n*-butane

Fig. 2. Rate of hydroperoxide formation during autoxidation: **6**—1-phenyl-1-*p*-tolylethane, **7**—1-phenyl-1-*p*-ethylphenylethane, **8**—1-phenyl-1-*p*-isopropylphenylethane, **9**—1-phenyl-1-*p*-tert.-butylphenylethane

From the results shown in Fig. 1 for 90° (curves 1, 2, and 3), it is evident that isopropylbenzene is oxidized faster than 1,1-diphenylethane, but 9-methylfluorene, which is isomeric with the latter, is oxidized at the initial stage at a higher rate than both preceding hydrocarbons. Consequently, the accumulation of phenyl residues at the tertiary C atom retards autoxidation, which at first glance seems unclear.

Figure 3 and Figure 4: kinetic curves of hydroperoxide accumulation during autoxidation.

Figure 2: Figure 3 and Figure 4: kinetic curves of hydroperoxide accumulation during autoxidation.

It is known (8) that phenyl radicals exert a positive influence on the autoxidation process, especially in monoaryl hydrocarbons. Evidently, when two phenyl radicals are located at the tertiary C atom, then, in our view, the retardation of the autoxidation of 1,1-diphenylethane occurs because of steric hindrance arising in the free-radical process of autoxidation. According to modern concepts of this process, the bulky peroxide radical $(C_6H_5)_2CH_3COO\cdot$ must interact with the hydrogen of the tertiary C atom of the starting hydrocarbon $(C_6H_5)_2CH_3C{-}H$, where the hydrogen is also considerably shielded by phenyl residues. Confirmation of these considerations may be provided by known data (9,10), showing that during autoxidation of triphenylmethane its hydroperoxide is not formed, but only triphenylmethyl peroxide. In light of the proposed assumption concerning the role of steric hindrance, the data on the acceleration of the autoxidation of 9-methylfluorene, in which, owing to bonding of the phenyl ···

radicals and their orientation in one plane, steric hindrance is weakened, but the positive influence of phenyl residues on the autoxidation process is retained. The specificity of 9-methylfluorene consists only in the fact that, in the course of autoxidation, the extent of its conversion into the hydroperoxide remains low, owing to the low thermal stability of the hydroperoxide itself, which we have obtained in pure crystalline form and are at present studying in detail.

The results presented in Fig. 1 (curves 4, 5) show that 1,1-diphenylpropane and 1,1-diphenyl-*n*-butane are oxidized to the corresponding

Fig. 3. Rate of formation of hydroperoxides during autoxidation: **1**—isopropylbenzene, **10**—*p*-chloroisopropylbenzene, **11**—*p*-bromoisopropylbenzene, **12**—*p*-iodoisopropylbenzene

Fig. 4. Rate of formation of hydroperoxides during autoxidation: **2**—1,1-diphenylethane, **13**—1-phenyl-1-*p*-chlorophenylethane, **14**—1-phenyl-1-*p*-bromophenylethane, **15**—1-phenyl-1-*p*-iodophenylethane

hydroperoxides even more slowly than 1,1-diphenylethane. We likewise explain the retardation of the autoxidation of these hydrocarbons by the increase in steric hindrance at the tertiary C atom as a result of lengthening of the aliphatic chain.

Figure 2 gives data on the autoxidation of para-alkyl derivatives of 1,1-diphenylethane at 90°, from which it is seen that 1-phenyl-1-*p*-tolylethane and 1-phenyl-1-*p*-tert-butylphenylethane (curves 6, 9) are oxidized at the same rate as 1,1-diphenylethane. However, 1-phenyl-1-*p*-ethylphenylethane and 1-phenyl-1-*p*-isopropylphenylethane (curves 7, 8) are oxidized somewhat faster, which is evidently connected with partial oxidation at the site of these alkyls to the corresponding hydroperoxides, as shown in the work of K. S. Grigor' eva (^{11}). Thus, these data show that radicals located in one of the benzene rings of 1,1-diphenylethane in the para position do not exert a substantial influence on the rate of autoxidation. These observations, in comparison with the preceding ones, confirm that structural factors (the presence of alkyl and aryl radicals) exert a particularly strong influence when they are varied at the tertiary C atom at which, according to the accepted view (^{12}), the autoxidation process occurs. Moreover, in our opinion, the influence of these structural factors is due to steric hindrance.

Figure 3 gives data on the autoxidation of para-halo derivatives of isopropylbenzene at 90°, from which it is seen that halogens exert a negative influence on the autoxidation process and, in terms of their retarding action, are arranged in the series: Cl $<$ Br $<$ I. Meanwhile, from the data presented in Fig. 4 it is seen that halogens in the para position in one of the benzene rings of 1,1-diphenylethane exert a positive influence on the process of autoxidation, i.e., para-halo derivatives of 1,1-diphenylethane are oxidized more rapidly to the corresponding hydroperoxide, and in their

with respect to their accelerating effect, the halides are arranged in the reverse order J $>$ Br $>$ Cl.

The observed difference in the influence of halides in derivatives of monoaryl (isopropylbenzene) and diaryl (1,1-diphenylethane) hydrocarbons on the autoxidation process can be explained by the dual character of halides when they participate, on the one hand, in electronic displacements and, on the other, in conjugation effects. In our case, the order of the retarding influence of halides in isopropylbenzene is evidently explained by the decrease in the activity of free radicals and in the mobility of hydrogen at the tertiary C atom, owing to the weakening of the polarizing influence of the halides in the order Cl $>$ Br $>$ J. A similar order of retarding influence of halides, as is known, is also observed in the polymerization of vinyl halides and para-halostyrenes.

The activating influence of halides in halogen derivatives of 1,1-diphenylethane can probably be explained by the polarizability of the halides and their participation in conjugation of double bonds. In our case, in the presence of two benzene nuclei, conjugation of the unsaturated bonds of the ring through the tertiary C atom occurs; moreover, halides in such a system exert a positive influence in such an order that the greater the polarizability of the halide, the greater its positive influence on autoxidation. An analogous regularity is observed in the polymerization of 2-halo-substituted butadiene-1,3, in which there is a conjugated system of double bonds.

In addition to the results set forth above, we have obtained data on the autoxidation of all the listed compounds at 80 and 100°, and at present their analytical treatment is being carried out.

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