PHYSICAL CHEMISTRY

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1962

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Fig. 1

Figure 1: Fig. 1

Abstract

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KINETICS OF THE REACTIONS OF THE TRI-tert-BUTYLPHENOXYL RADICAL WITH CERTAIN HYDROCARBONS

(Presented by Academician V. N. Kondrat’ ev, January 16, 1962)

In the present work we have considered several questions concerning the relation between the reactivity of particles and their structure as applied to reactions of radicals with hydrocarbon molecules:

$$X^{\cdot} + RH \rightarrow XH + R^{\cdot}.$$

Such reactions have recently been the subject of many quantitative investigations. However, most of these studies were carried out for homogeneous gas reactions (1). Analogous investigations in the liquid phase are less systematic and are more qualitative in character (2,3). We investigated the reactivity of molecules of decane, isodecane, toluene, ethylbenzene, and cumene under attack by the tri-tert-butylphenoxyl radical, which, by virtue of its stability, is a convenient object for study (4). On the one hand, because the lifetime of such radicals is sufficiently long in comparison with the duration of most physical experiments and chemical processes, we can operate with them as with ordinary molecules and use them for kinetic studies. On the other hand, the EPR method opens possibilities for investigating the electronic structure of radicals and the distribution of the electron density of the unpaired electron.

Fig. 1. Dependence of $\lg C$ on time in the absence of air.

Tri-tert-butylphenoxyl radicals were prepared by oxidizing the corresponding phenol with lead dioxide in a solution of the hydrocarbon under investigation. In this process, as was shown by us, and also earlier in work (5), the yield of radicals is 96–98% of the phenol. A high degree of purity of the hydrocarbons studied was achieved by careful purification and was monitored by kinetic methods. Thus, for example, the purity of ethylbenzene and cumene was checked by the rate of their oxidation. It turned out that it agrees with the available literature data.

The kinetics of the reactions of the phenoxyl radical with the hydrocarbon were studied by the EPR method. Solutions of radicals in hydrocarbons, in glass ampoules that had been evacuated and sealed beforehand, were placed in the resonator of an EPR spectrometer (6). The reaction rate was followed from the change in the intensity of the EPR signal with time. The study was carried out at different temperatures in the range from 70 to 150°. Ampoules with the reaction mixture were heated by a current of hot air, ⋯

The constancy of the temperature, which was maintained with an accuracy of ±1.0° by an electronic thermostat. To describe the reactions of the phenoxyl radical with hydrocarbons, we proposed the following scheme:

$$\mathrm{PhO}\cdot + \mathrm{RH} \xrightarrow{k_1} \mathrm{PhOH} + \mathrm{R}\cdot, \tag{1}$$

$$\mathrm{PhO}\cdot + \mathrm{R}\cdot \xrightarrow{k_2} \mathrm{PhOR}, \tag{2}$$

where PhO· and R· are, respectively, phenoxyl and alkyl radicals. The validity of this scheme was confirmed by quantitative analysis of the phenol formed as a result of the reaction.

Kinetic treatment of such a scheme leads to the following expression for the rate of disappearance of phenoxyl radicals:

$$-\frac{d(\mathrm{PhO}\cdot)}{dt} = 2k_1(\mathrm{PhO}\cdot)(\mathrm{RH}).$$

Figure 1 presents the dependence of $\lg C$ on time, where C is the concentration of phenoxyl radicals. It is evident from the figure that first-order kinetics with respect to the phenoxyl radical are very well satisfied.

[Figure 2 graph]

Fig. 2. Dependence of $\lg k$ on $1/T$.
1 —isodecane; 2 —*n*-decane; 3 —cumene; 4 —toluene; 5 —ethylbenzene

From the slope of the straight line it is easy to determine the constant k_1; moreover, it was shown that the value of this constant does not depend on the initial concentration of phenoxyl radicals within the range 10^{16}—10^{19} radicals/cm^3. The temperature dependence of the constant k_1 for various hydrocarbons is given in Fig. 2, from which the activation energies of reactions (1) and the corresponding pre-exponential factors can readily be found. The constants were calculated per hydrocarbon molecule.

The data obtained are summarized in Table 1. Analysis of these data shows that comparatively large activation energies are characteristic of the reactions of the radical with hydrocarbons, which is associated with the endothermicity of reaction (1); moreover, they decrease regularly in the series shown, from

n-decane to cumene, with a decrease in the strength of the C—H bond being attacked. The activation-energy values satisfactorily obey the Polanyi—Semenov rule (^{7}) with coefficient $\alpha \approx 1$. The value of A cannot be determined, since the magnitude of the heat effect of reaction (1) is unknown.

[Figure 3 graph]

Fig. 3. Dependence of ΔS_a on the number of methyl groups at the α-carbon atom of the substituent

Analysis of the pre-exponential factors shows that, for the reactions of the phenoxyl radical with the hydrocarbon molecules of the given series, steric effects play a major role. For n-decane the pre-exponential factor is close to the number of binary collisions in the liquid phase (^{8}).

The magnitude of the steric factor in this case is $\rho \simeq 0.1$. Introduction of methyl groups into n-decane lowers the pre-exponential factor by an order of magnitude.

The presence of a phenyl group (in toluene) affects the pre-exponential factor in the same way. Comparison of the pre-exponential factors in the series of the last three alkylaromatic hydrocarbons makes it possible to trace the effect of substitution of the hydrogens at the α-carbon atom of the substituent by methyl groups.

Table 1

Hydrocarbons studied	k_0, $\mathrm{cm^3 \cdot sec^{-1}}$	E, $\mathrm{kcal \cdot mol^{-1}}$
n-Decane	$4.3 \cdot 10^{-11}$	27.5
Isodecane	$3.2 \cdot 10^{-12}$	25.5
Toluene	$9.7 \cdot 10^{-13}$	23
Ethylbenzene	$8.9 \cdot 10^{-15}$	18
Cumene	$8.1 \cdot 10^{-17}$	16.5

As is evident from the data of Table 1, introduction of a methyl group lowers the pre-exponential factor by two orders of magnitude. Figure 3 gives the dependence of the activation entropy ΔS_a, calculated from the basic formula of the theory of absolute reaction rates (^{9}), for this series on the number n of methyl groups at the α-carbon atom of the substituent. The decrease in entropy indicates a decrease in the probability of formation of the activated complex, which is associated with the growth of steric hindrance.

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Received
10 I 1962

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