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Abstract

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STUDY OF THE KINETICS OF RECOMBINATION OF TRIPHENYLMETHYL RADICALS BY THE METHOD OF ELECTRON PARAMAGNETIC RESONANCE

(Presented by Academician V. N. Kondrat' ev, 23 V 1958)

Studying the kinetics of the dissociation of hexaphenylethane from the rate of absorption of oxygen and nitric oxide (^{1}), Ziegler and co-workers drew attention to the fact that the activation energy for the decomposition of hexaphenylethane into radicals (18-20 kcal) considerably exceeds the heat of its dissociation (11-12 kcal). This means that the reverse reaction of recombination of triphenylmethyl radicals must proceed with an activation energy equal to the difference between the activation energy of dissociation and the heat of dissociation of hexaphenylethane (6-8 kcal).

With the aid of the method of electron paramagnetic resonance (EPR) it proved possible to verify this conclusion by directly measuring the rate of dimerization of triphenylmethyl radicals in solution. For this purpose, a sealed capillary with a toluene solution of hexaphenylethane, heated to 100°, was rapidly cooled to the temperature of the experiment in a thermostated liquid placed in the resonator of an EPR spectrometer. In this way it was possible to obtain appreciable supersaturated concentrations of triphenylmethyl radicals and to measure the rate of their recombination. Special experiments showed that, when a thin-walled capillary with an internal diameter of about 1 mm was used, the temperature of the solution in the capillary was established in the first seconds. The measurements were carried out on an EPR spectrometer with high-frequency modulation of the magnetic field. A solution of hexaphenylethane was obtained by shaking a solution of triphenylchloromethane in toluene with zinc dust until the reaction for chlorine disappeared. The concentration of hexaphenylethane prepared in this way was determined gasometrically from the amount of nitric oxide absorbed. The concentration of triphenylmethyl radicals during the reaction was measured by the ratio of the integral intensities of the EPR signals of the solution taken and of a solution of diphenylpicrylhydrazyl of known concentration. Measurement of the rate of dimerization was carried out in the interval from -64 to $-9°$. The rapid change of the signal at $-9°$ was recorded by cinematographic filming of the oscilloscope screen. In Fig. 1 two kinetic curves of recombination of triphenylmethyl radicals at $-64°$ and $-35°$ are shown. It is seen from the figure that

Fig. 1. Kinetics of dimerization of triphenylmethyl radicals in toluene. 1 —at temperature −64°; 2 —at temperature −35°

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Fig. 2. Temperature dependence of the equilibrium constant for dissociation of hexaphenylethane in toluene

Figure 2: Fig. 2. Temperature dependence of the equilibrium constant for dissociation of hexaphenylethane in toluene

the rate of recombination increases noticeably with increasing temperature.

Fig. 1. Kinetics of dimerization of triphenylmethyl radicals in toluene. 1 —at temperature −64°; 2 —at temperature −35°.

The kinetics of radical recombination, taking the reverse reaction into account, obeys the kinetic equation:

$$\frac{d[R]}{dt} = -k_2[R]^2 + k_1\left(\frac{a-[R]}{2}\right), \tag{1}$$

where $[R]$ is the concentration of radicals, k_2 is the rate constant of radical recombination, k_1 is the rate constant of dissociation of hexaphenylethane, and

$$\frac{a-[R]}{2}$$

is the concentration of undissociated hexaphenylethane (a is the amount of NO absorbed). Expressing $k_1 = k_2K$ (K is the equilibrium constant of the reaction $2(\mathrm{C_6H_5})_3\mathrm{C}leftarrows(\mathrm{C_6H_5})_3\mathrm{C}-\mathrm{C}(\mathrm{C_6H_5})_3$), one can determine k_2 from equation (1). From the equilibrium concentration of radicals in the interval from +60 to −50°, the equilibrium constant for the dissociation of hexaphenylethane in toluene was determined. Figure 2 gives the temperature dependence of the equilibrium constant in the coordinates $\lg K$ versus $1000/T$. Calculation by the least-squares method gives the following value of $\lg K$:

$$\lg K = 4.944 - \frac{11200}{4.576T}$$

(K in mol/l).

Fig. 2. Temperature dependence of the equilibrium constant for dissociation of hexaphenylethane in toluene

Fig. 3. Temperature dependence of the dimerization rate constant of triphenylmethyl radicals in toluene

Figure 3: Fig. 3. Temperature dependence of the dimerization rate constant of triphenylmethyl radicals in toluene

The value of the equilibrium constant and ΔH (11.2 kcal) agree very well with values determined by other methods (2). The rate constant of radical recombination could be calculated either by integrating equation (1) or directly from equation (1), determining $d[R]/dt$ by graphical differentiation of the kinetic curves. The second approach proved more convenient, since it made it possible to avoid uncertainty in the choice of the initial concentration $[R]_0$, associated with the lowering of the temperature at the initial moment of the reaction. Constancy of the constant during the reaction served as a criterion for the correctness of kinetic equation (1) and, simultaneously, for constancy of the temperature during the reaction. Figure 3 gives the temperature dependence of the dimerization rate constant. It can be seen that the Arrhenius dependence is well fulfilled. The rate constant found is described by the following formula:

$$k_2 = 3.85 \cdot 10^7 e^{-\frac{6950 \pm 500}{RT}} \ (\mathrm{l} \cdot \mathrm{mol}^{-1} \mathrm{sec}^{-1}).$$

Fig. 3. Temperature dependence of the dimerization rate constant of triphenylmethyl radicals in toluene

Thus, as a result of the direct determination of the rate of dimerization of triphenylmethyl radicals, there was confirmed not only the very fact of the existence of an activation energy in this reaction, but also its magnitude, coinciding with the difference between the activation energy of dissociation and the energy of rupture of the C–C bond in hexaphenylethane.

It should be noted that, despite the considerable inertness of the $(C_6H_5)_3C\cdot$ radicals, which distinguishes them from radicals of other types, for example alkyl radicals, the magnitude of the activation energy of their dimerization fits satisfactorily

into the general dependence of the activation energy on the heat effect of the reaction, $E = 11.5—0.25Q$ (^{3}), which is satisfied for most radical reactions.

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