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Acid catalysis of the radical decomposition of tetraphenylhydrazine

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Acids considerably accelerate the decomposition of tetraphenylhydrazine into free radicals, as found using radical scavengers.

Homolytic bond cleavage in the presence of acids with the formation of free radicals is of particular interest. A few reactions of this type are known presently because they are difficult to study experimentally and the relevant data are difficult to interpret. Nevertheless, the above acid-catalysed reactions can play an important role, for example, if they initiate subsequent chain reactions.

Thus, the reaction of *N*-phenyl-1,4-benzoquinoneimine with 2,5-di-*tert*-butylhydroquinone in chlorobenzene was found to occur by a radical chain mechanism with very long chains (several thousands of units at room temperature).[1,2] This reaction was initiated by tetraphenylhydrazine (TPH), which generated active diphenylaminyl radicals $Ph_2N\cdot$ on decomposition. It was of interest to examine the effect of acids on the radical decomposition of tetraphenylhydrazine in the context of the kinetics of chain reactions in quinone–hydroquinone systems, as well as of acid-catalysed homolysis of *N*-nitrosodiphenylamine[3] and a hydroperoxide.[4]

In this work, the kinetics of radical decomposition of tetraphenylhydrazine under the action of trichloroacetic acid with the use of *N*,*N*′-diphenyl-1,4-phenylenediamine (DPPDA) as a radical scavenger. The radical decomposition of tetraphenylhydrazine was studied previously.[2,5–9]

The course of the reaction was monitored by spectrophotometry. *N*,*N*′-Diphenyl-1,4-phenylenediamine is converted into intensely coloured quinonediimine $Ph–N=C_6H_4=N–Ph$ (QDI) in the reactions with free radicals

$$TPH \rightarrow R\cdot,$$
$$R\cdot + DPPDA \rightarrow RH + QDIH\cdot,$$
$$QDIH\cdot + R\cdot(+\ QDIH\cdot) \rightarrow QDI + RH(+\ DPPDA),$$

where QDIH· is the 4-anilinodiphenylaminyl semiquinone radical $Ph–N^{\cdot}–C_6H_4–NH–Ph$, which is formed from DPPDA. In the course of experiments, the absorbance at an absorption band maximum of QDI ($\lambda = 450$ nm, $\varepsilon = 6.495\times10^3$ dm^3 mol^{-1} cm^{-1} at 364.2 K) was continuously measured. The experiments were performed in a thermostatted quartz reactor cell (8.5 ml; optical path length of 2.0 cm) on a Specord UV–VIS spectrophotometer. Argon was a bubbling gas; chlorobenzene purified in accordance with a published procedure[2] was used as a solvent.

Tetraphenylhydrazine was synthesised by the oxidation of diphenylamine with $KMnO_4$ in acetone;[10] the purity of the resulting TPH was no worse than 99.5%. Trichloroacetic acid was recrystallised from methanol, washed with methanol, toluene, and hexane and then dried in a vacuum.

Figure 1 demonstrates the effect of CCl_3COOH additives on the absorbance at $\lambda = 450$ nm. It can be seen that the rate of increase of the absorbance increased with acid concentration; in this case, the time τ taken to completely consume DPPDA taken in deficiency ($[TPH]_0 > [DPPDA]_0$) was shortened.

The absorbance A_{max} after the consumption of DPPDA (at the point τ in time when the curves are sharply flattened out) also depends on the acid concentration: the higher $[CCl_3COOH]_0$, the greater A_{max}. The spectra were measured in the course of reaction at regular intervals to find the reason for higher values of A_{max} in the presence of an acid. These experiments demonstrated that, in the presence of CCl_3COOH, QDI in a mixture with its protonated form $QDIH^+$ was accumulated. The greater the acid concentration, the higher the relative fraction of $QDIH^+$. The protonated form exhibits a broad absorption band in the visible region with a maximum at a shorter wavelength than that of QDI. The molar absorption coefficient of $QDIH^+$ at $\lambda = 450$ nm is somewhat higher than ε_{QDI}. After the complete consumption of DPPDA, coloured products of the reaction between unreacted TPH and CCl_3COOH are accumulated. The absorption spectra of these products (measured in the presence of TPH and the acid and in the absence of DPPDA) exhibited a broad band at $\lambda_{max} \sim 540$ nm (the solution became pink). This band overlaps the absorption band of QDI (if it is present in solution). Because of this, the absorbance at $\lambda = 450$ nm in Figure 1 slowly increased after attaining the area with A_{max} (after time τ).

Taking into account the dependence of the molar absorption coefficient (and A_{max}) on the acid concentration, the time τ of consumption of DPPDA taken in deficiency rather than the kinetics of absorbance changes was used for calculating the apparent rate constant k_a of radical formation in the decomposition of TPH. The treatment of the experimental curves using the

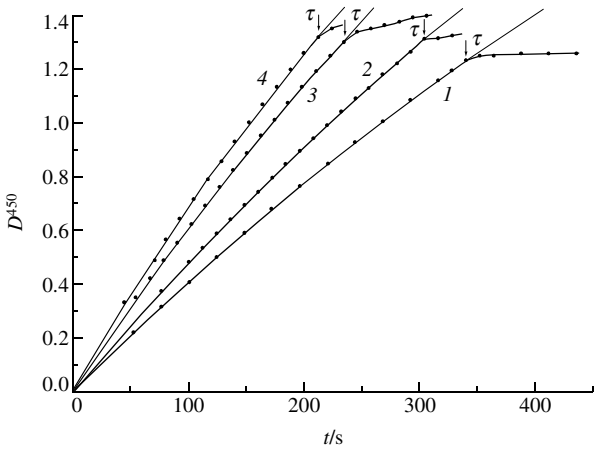

Figure 1 Time dependence of the absorbance at $\lambda = 450$ nm in the decomposition of TPH (3.08×10^{-4} mol dm^{-3}) in the presence of DPPDA (9.35×10^{-5} mol dm^{-3}) at different CCl_3COOH concentrations (10^3 mol dm^{-3}): (*1*) 0, (*2*) 0.70, (*3*) 1.65 and (*4*) 2.20. Chlorobenzene, 364.2 K.

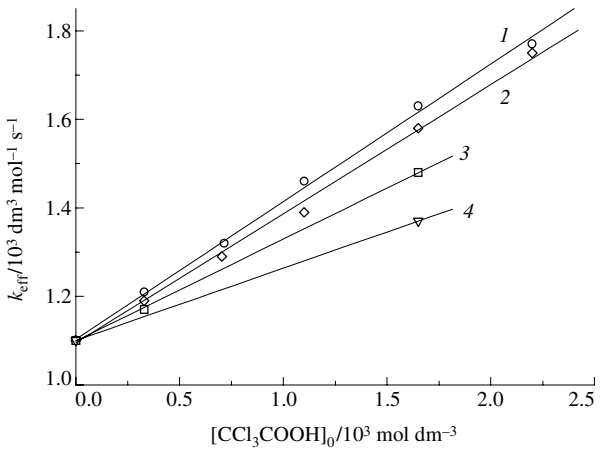

Figure 2 k_a as a function of CCl_3COOH concentration. TPH concentration (10^4 mol dm^{-3}): (*1*) 1.54, (*2*) 3.08, (*3*) 6.16 and (*4*) 9.24. Chlorobenzene, 364.2 K.

equation

$$D = D_\infty(1 - e^{-kt}),$$

(where D_∞ and k are empirical parameters) demonstrated that this equation adequately approximates experimental data up to the inflection points of A^{450} curves (this fact is indicative of the high efficiency of radical scavenging). Taking into account this circumstance and using the experimental values of τ, the apparent rate constant k_a was calculated by the equation

$$k_a = -\frac{1}{\tau}\ln\left(1 - \frac{[\mathrm{DPPDA}]_0}{0.95[\mathrm{TPH}]_0}\right),$$

where $e = 0.95$ is the probability of radical escape into the bulk on TPH decomposition in chlorobenzene.[2] It is believed that e remained unchanged in the presence of an acid.

Figure 2 indicates that k_a linearly increases with the acid concentration. At the same time, an increase in the TPH concentration results in a decrease in k_a. Thus, the real reaction mechanism is complicated, and the simplest mechanism

$$\mathrm{TPH} \xrightarrow{k_1} \mathrm{R}\cdot,$$

$$\mathrm{TPH} + \mathrm{HA} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{X} \xrightarrow{k_3} \mathrm{R}\cdot + \mathrm{HA}$$

can be used only at infinitely small TPH concentrations. To extrapolate correctly experimental data to [TPH] → 0 and formally describe the process at finite TPH concentrations, the above scheme is supplemented with the following reaction:

$$\mathrm{X} + \mathrm{TPH} \xrightarrow{k_4} \text{Inactive products.}$$

Then, assuming that the concentration of X is small and quasi-steady-state, [X] is expressed as follows:

$$[\mathrm{X}] = \frac{k_2[\mathrm{TPH}][\mathrm{HA}]}{k_{-2} + k_3 + k_4[\mathrm{TPH}]}.$$

In this case, the rate of TPH decomposition is

$$v_{\mathrm{decomp}}^{\mathrm{TPH}} = k_1[\mathrm{TPH}] + k_3[\mathrm{X}] = \left(k_1 + \frac{k_2k_3}{k_{-2} + k_3}\frac{[\mathrm{HA}]}{1 + \frac{k_4}{k_{-2} + k_3}[\mathrm{TPH}]}\right)[\mathrm{TPH}],$$

whence it follows that

$$k_a = k_1 + a\frac{[\mathrm{HA}]}{1 + b[\mathrm{TPH}]}, \qquad (1)$$

where $a = \dfrac{k_2k_3}{k_{-2} + k_3}$ and $b = \dfrac{k_4}{k_{-2} + k_3}$.

Equation (1) is consistent with experimental data; it suggests the linear dependence of k_a on [HA] at $[\mathrm{TPH}]_0$ = const and a decrease in k_a with $[\mathrm{TPH}]_0$ at [HA] = const. Equation (1) can be rearranged to

$$\frac{[\mathrm{HA}]}{k_{\mathrm{eff}} - k_1} = \frac{1}{a} + \frac{b}{a}[\mathrm{TPH}]. \qquad (2)$$

Figure 3 illustrates the treatment of experimental data on the coordinates of equation (2). The slope and the intercept of the straight line gave the following values:

$$\frac{1}{a} = \frac{k_{-2} + k_3}{k_2k_3} = 2.53\pm0.1 \text{ mol s dm}^{-3}$$

$$(a \approx K_2k_3 = 0.395\pm0.02 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}),$$

$$\frac{b}{a} = \frac{k_4}{k_2k_3} = (3.6\pm0.24)\times10^3 \text{ s}$$

$$[b = (1.42\pm0.12)\times10^3 \text{ dm}^3 \text{ mol}^{-1}].$$

Unfortunately, additional independent experiments are required for obtaining detailed information on the reaction mechanism. It is believed that $k_3 > k_1$ because only in this case small acid additives can result in a considerable increase in k_a. Thus, the energy of dissociation of complex X into radicals is lower than that of free TPH.

In conclusion, note that the rate of radical formation from tetraarylhydrazines in the presence of acids was not measured previously. In this work, this was done with the use of direct radical scavenging. The homolytic decomposition of TPH is significantly accelerated under the action of acids. It is likely that acids exert a catalytic effect on the radical decomposition; however, it is strongly complicated because of the participation of the acid in complexation with parent and formed nitrogen-containing compounds. This was supported by experiments with 4-*n*-pentadecylhydroxybenzenesulfonic acid, when the reaction was considerably accelerated at an acid concentration of ~ 10^{-6} mol dm^{-3}.

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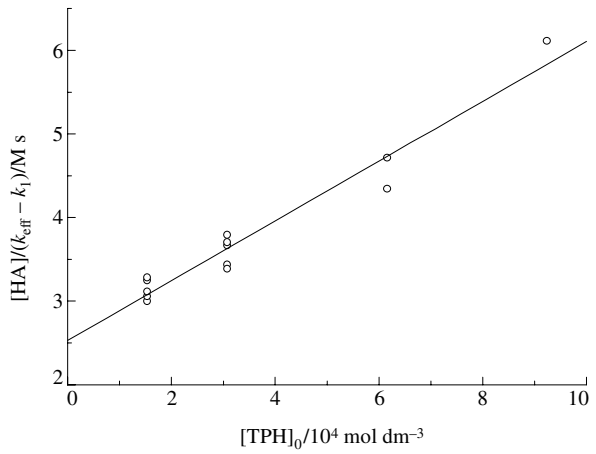

Figure 3 The experimental data shown in Figure 2 on the coordinates of equation (2).

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