Acid-catalysed radical chain reaction of quinoneimine with hydroquinone

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Trichloroacetic acid in as low concentrations as ~10^{-6} mol dm^{-3} increased the rate of a chain reaction between *N*-phenyl-1,4-benzoquinonemonoimine and 2,5-di-*tert*-butylhydroquinone in chlorobenzene by a factor of 2 to 3.

Quinoneimine reacts with hydroquinone by a chain mechanism.[1,2] This reaction, which is analogous to quinone reactions with hydroquinones, is characterised by very long chains of several thousand steps at room temperature. The additives of trichloroacetic acid in extremely low concentrations of ~10^{-6} mol dm^{-3} dramatically accelerated the reaction.

Free-radical reactions with the participation of quinones are of great interest in chemistry and biology. Acids, which occur as impurities or result from reactions in chemical and biochemical systems, can affect both the rate and the direction of reactions. In this context, the effects of acids on processes with the participation of quinones are of paramount importance.

The reaction of *N*-phenyl-1,4-benzoquinonemonoimine (QMI) with 2,5-di-*tert*-butylhydroquinone (H$_2$Q) consists in the reduction of QMI and the oxidation of H$_2$Q. The reaction products are 4-hydroxydiphenylamine (H$_2$QMI) and 2,5-di-*tert*-butyl-1,4-quinone (Q):

The reaction kinetics was studied by spectrophotometry. The quinonemonoimine was determined by absorption in the visible region (ε = 2995, 1631 and 563 dm^3 mol^{-1} cm^{-1} at λ = 450, 500 and 526 nm, respectively). The measurements were continuously performed on a Specord UV-VIS spectrophotometer in a thermostatted (298.2±0.1 K) quartz cell with an optical path length of 1.0 cm. Argon was a bubbling gas; chlorobenzene, which was purified as described previously,[2] was used as a solvent. The quinonemonoimine was prepared by the oxidation of 4-hydroxy-

Figure 1 Accelerating effect of CCl$_3$COOH on the consumption of quinone-imine in the chain reaction with hydroquinone. Initial concentrations, mol dm^{-3}: (*1*)–(*3*) [QMI]$_0$ = [H$_2$Q]$_0$ = 2×10^{-4}; (*1a*)–(*3a*) [QMI]$_0$ = 1×10^{-4}, [H$_2$Q]$_0$ = 6×10^{-5}. Trichloroacetic acid concentration, ×10^6 mol dm^{-3}: (*1*), (*1a*) 0; (*2*), (*2a*) 2.94; (*3*), (*3a*) 8.82. Chlorobenzene, 298.2 K.

diphenylamine with PbO$_2$ and purified by liquid chromatography on SiO$_2$.

Figure 1 demonstrates the effect of CCl$_3$COOH on the reaction kinetics. It can be seen that the addition of the acid in a concentration of ~10^{-6} mol dm^{-3} increased the initial reaction rate by a factor of 2 to 3. The effect of the acid was studied at constant initial QMI and H$_2$Q concentrations of (1–8)×10^{-4} and (0.6–4)×10^{-4} mol dm^{-3}, respectively. The concentration of CCl$_3$COOH was varied within the range 0–8.8×10^{-6} mol dm^{-3}.

The reaction of QMI with H$_2$Q occurs *via* a complex chain mechanism (completely reversible chain reaction[2]). Products strongly affect the kinetics because the rate of radical generation increases as the products are accumulated (the reversibility of chain termination steps accelerates the reaction). On the other hand, the inhibiting effect of products on the rate of a forward reaction becomes stronger because chain-propagating steps are reversible.[2,3] To minimise the role of products, the reaction kinetics was studied by measuring the initial rates w_{QMI} when the effect of products can be neglected. The values of w_{QMI} were determined by the treatment of the kinetic curve of QMI consumption using the equation

$$\ln (a + \ln [QMI]) = b + ct,$$

where *a*, *b* and *c* are empirical constants. In this case,

$$w_{QMI} = c[QMI]_0(\ln [QMI]_0 + a).$$

Figure 2 indicates that w_{QMI} is an almost linear function of the acid concentration. This is an unexpected result because in the absence of the acid the reaction occurs by the mechanism given below with quadratic chain termination (rate constants of elementary steps at 298.2 K, dm^3 mol^{-1} s^{-1}).[2]

QMI + H$_2$Q → HQMI· + HQ·,	k_1 = 3.22×10^{-3}	(1)
QMI + HQ· → HQMI· + Q,	k_2 = 3.47×10^7	(2)
HQMI· + H$_2$Q → H$_2$QMI + HQ·,	k_3 = 1.65×10^7	(3)
HQMI· + HQMI· → H$_2$QMI + QMI,	k_4 = 8×10^8	(4)
HQMI· + HQ· → H$_2$QMI + Q (QMI + H$_2$Q)	k_5 = 8×10^8	(5)
HQ· + HQ· → H$_2$Q + Q·	k_6 = 8×10^8	(6)

In this reaction scheme, HQMI· denotes semiquinone radicals, which are formed from QMI on the addition of a hydrogen atom. These can be either 4-hydroxydiphenylaminyl or 4-anilinophenoxyl radicals, which are considered indistinguishable for simplicity.

At long chains, the reaction rate is highly sensitive to the rate of radical generation. Thus, an accelerating effect of acids in the chain radical reactions of oxidation of organic compounds with oxygen in the presence of hydroperoxides (specially added or accumulated in the course of reaction) is due to the acid catalysis of radical hydroperoxide decomposition. That is, the acid participates in the step of chain initiation.[4] In this context, the hypothesis that additional acid-catalysed radical formation is responsible for the acceleration of the reaction of QMI with H$_2$Q was first considered.

If this is true, it should be assumed that two acid molecules participate in the elementary event of radical formation in order to explain the experimental linear dependence of w_{QMI} on [CCl$_3$COOH] (see Figure 2). Indeed, at $k_4 = k_5 = k_6$, the following relation can be derived based on the above mecha-
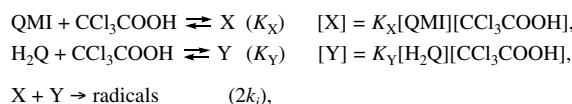
Figure 2 Initial rate of the reaction of QMI with H_2Q as functions of CCl_3COOH concentration. QMI and H_2Q concentrations, $\times 10^4$ mol dm^{-3}: (*1*) 1 and 0.6; (*2*) 2 and 2; (*3*) 4 and 4, respectively.

nism ($\alpha = k_3/k_2 = 0.48$ at 298.2 K):

$$\frac{\frac{[QMI]}{[H_2Q]} + \alpha + \alpha^2\frac{[H_2Q]}{[QMI]}}{[QMI]^2[H_2Q]^2}\, w_{QMI}^2 = \frac{k_1 k_3^2}{k_4} + \frac{k_3^2}{2k_4}\frac{w_i}{[QMI][H_2Q]}. \quad (1)$$

If protonated QMI and H_2Q molecules participate in the radical generation

$$QMI + CCl_3COOH \rightleftarrows X \quad (K_X) \qquad [X] = K_X[QMI][CCl_3COOH],$$
$$H_2Q + CCl_3COOH \rightleftarrows Y \quad (K_Y) \qquad [Y] = K_Y[H_2Q][CCl_3COOH],$$

$$X + Y \rightarrow radicals \qquad (2k_i),$$

then $\quad w_i = 2k_i K_X K_Y [QMI][H_2Q][CCl_3COOH]^2.$

In this case, equation (1) takes the form

$$\frac{\frac{[QMI]}{[H_2Q]} + \alpha + \alpha^2\frac{[H_2Q]}{[QMI]}}{[QMI]^2[H_2Q]^2}\, w_{QMI}^2 = G = \frac{k_1 k_3^2}{k_4} + \frac{k_3^2 k_i K_X K_Y}{2k_4}[CCl_3COOH]^2.(2)$$

At constant concentrations of QMI and H_2Q,

$$w_{QMI}^2 = const_1 + const_2[CCl_3COOH]^2,$$
$$\text{and } w_{QMI} \sim [CCl_3COOH],$$

which is consistent with experimental data. Note that the same relationship between w_{QMI} and $[CCl_3COOH]$ can also be derived on the assumption that radicals are additionally generated by the reaction between one of the components with the other doubly protonated component.

The results shown in Figure 3, where experimental data are treated in the G – $[CCl_3COOH]^2$ coordinates of equation (2), indicate that equation (2) cannot adequately describe the experimental data. Thus, the action of the acid is more complex, and it is not limited by the participation only at the step of radical
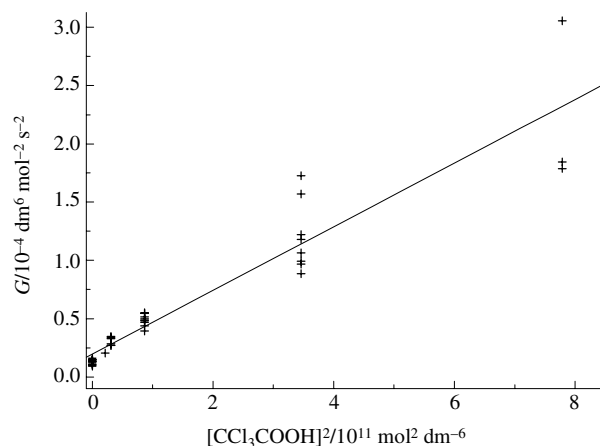
Figure 3 Experimental data plotted on the coordinates of equation (2). Chlorobenzene, 298.2 K, bubbling Ar.

formation.

Even rough preliminary estimations, which can be derived from data in Figure 3, are of interest:

$$k_1 k_3^2 / k_4 = (1.96 \pm 0.44) \times 10^3 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-2},$$
$$k_3^2 k_i K_X K_Y / k_4 = (2.79 \pm 0.16) \times 10^{14} \text{ dm}^{12} \text{ mol}^{-4} \text{ s}^{-2},$$
$$\text{hence } k_i K_X K_Y / k_1 = (1.42 \pm 0.4) \times 10^{11} \text{ dm}^6 \text{ mol}^{-2}$$
$$\text{and } k_i K_X K_Y = (4.6 \pm 1.3) \times 10^8 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}.$$

These data suggest that the radical formation under the action of the acid is highly effective.

Thus, a strong accelerating effect of trichloroacetic acid on the chain reaction of a quinonemonoimine with hydroquinone was found. Undoubtedly, the acid acts as a catalyst because its long accelerating effect manifests itself at very low concentrations, which are lower than the initial reactant concentrations by two orders of magnitude. The effect of the acid is complex. The acid not only increases the rate of radical formation but also participates in other steps of the chain reaction.

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