# On the Mechanism of the Reaction between Ozone and Alcohols: Ozonation Kinetics of Butanol-1 and Its Esters in CCl$_4$

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**Abstract**—The ozonation kinetics of butanol-1, tributyl borate, butyl acetate, and butyl trichloroacetate was studied in the temperature range from –20 to 45°C. The reactivity of the α-methylene group of the *n*-butyl moiety decreases in going from the alcohol to its trichloroacetic ester. In butyl trichloroacetate, this group is deactivated to such an extent that the kinetic parameters of the ozonation of this ester are comparable to the parameters observed earlier for *n*-butane. This decrease in reactivity is due the fact that the preexponential factor in the rate constant of the initial formation of an ozone–substrate complex decreases on passing from the alcohol to its esters. The activation energy of this process is constant within the error of data processing. It is concluded that the high reactivity of alcohols toward ozone is due to the initial formation of the ozone–substrate complex involving the hydroxyl group of the latter.

Reactions of ozone with organic compounds are used in fine organic synthesis and in industry [1–6]. The data obtained by various researchers on the alcohol ozonation mechanism suggest that ozone primarily attacks the α-CH bond, the weakest bond in the substrate [7–13]. The reaction obeys the bimolecular rate law. Some deviations from this law are observed however, which are commonly explained by assuming the formation of a labile intermediate complex between ozone and the substrate at the initial stage of the reaction [7, 12, 13].

All alcohols except tertiary ones react with ozone much more rapidly than the structurally related hydrocarbons, their formal precursors. The high reactivity of the alcohols can be explained by the activating effect of the hydroxyl group on the α-CH bond of the substrate. Another plausible explanation is the initial formation of an ozone–substrate complex involving the OH group of the substrate. Presumably, this interaction orients the reacting species in a favorable way and thus facilitates their further conversion. For example, the phenol ozonation kinetics is most consistent with the process scheme that includes the formation of a complex between ozone and the phenolic hydroxyl group at the initial stage in the reaction [14, 15].

In order to elucidate the effect of the hydroxyl group on the reactivity of primary alcohols toward ozone, we studied the ozonation kinetics of butanol-1 (**Ia**), butyl acetate (**Ib**), tributyl borate (**Ic**), and butyl trichloroacetate (**Id**) between –20 and 45°C.

$$CH_3(CH_2)_3OX \ (\textbf{I}), \quad \text{where} \ \ X = H \ (\textbf{a}), \ COCH_3 \ (\textbf{b}),$$

$$B(O(CH_2)_3CH_3)_2 \ (\textbf{c}), \quad \text{and} \ \ COCCCl_3 \ (\textbf{d}).$$

Comparing the reactivities of the α-methylene groups of the butyl moieties in this series of compounds is interesting as such because ester ozonation data are absent in the literature.

## EXPERIMENTAL

Butanol-1 and butyl acetate were reagent-grade. Tributyl borate was synthesized from butanol-1 (reagent grade) and boric acid (special purity grade) using a standard procedure [16] immediately before kinetic measurements. Butyl trichloroacetate was obtained from *n*-butanol and trichloroacetic acid (reagent grade) using a similar procedure.

Ozone was produced from oxygen under electric discharge conditions. Before being fed into the ozone generator, oxygen was dried with Mg(ClO$_4$)$_2$.

The solvent was CCl$_4$ (reagent grade). Prior to performing the reaction, it was treated with an ozone–oxygen mixture (~10% O$_3$) for 30 min for decomposing the possible active impurities, held over calcium chloride, and distilled.

Ozonation was carried out in a temperature-controlled bubbler under steady-state conditions ([O$_3$]$_0$ = $6 \times 10^{-5}$–$5 \times 10^{-4}$ mol/l, oxygen feed rate of $v$ = 0.1 l/min, solution volume of 30 ml, Schott filter no. 2 as the disperser). The substrate conversion in all experiments did not exceed 0.1%. The reaction rate was derived from the difference between the inlet and outlet ozone concentrations in the gas mixture ([O$_3$]$_0$ – [O$_3$]$_g$). A detailed description of these kinetic measurements is
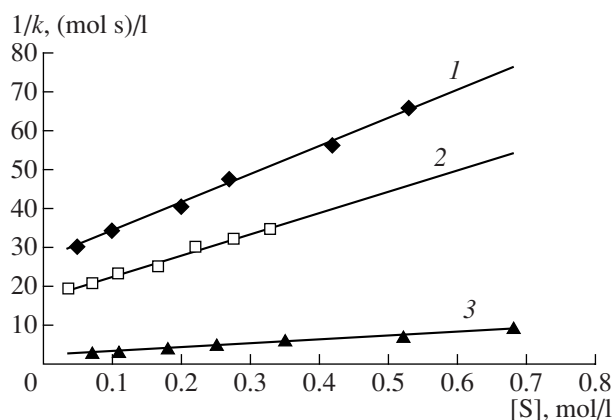
**Fig. 1.** $1/k_{eff}$ versus the substrate concentration at 20°C: (*1*) butyl acetate, (*2*) tributyl borate, and (*3*) butanol-1.

presented elsewhere [2]. The ozone uptake rate was determined as

$$v_g([O_3]_0 - [O_3]_g), \qquad (1)$$

where $v_g$ is the flow rate of the gas mixture. The ozone consumption rate due to the reaction taking place is

$$V_s k[O_3]_s[S], \qquad (2)$$

where $V_s$ is the volume of the solution, $k$ is the rate constant of the reaction, [S] is the substrate concentration in the solution, and $[O_3]_s$ is the ozone concentration in the solution.

Under steady-state conditions, expression (1) is equal to expression (2). At the same time, the ozone concentration in the solution is proportional to the ozone concentration in the gas phase: $[O_3]_s = \alpha[O_3]_g$, where $\alpha$ is the solubility coefficient (Henry's coefficient). Hence, we obtain the following expression for the rate constant of the reaction:

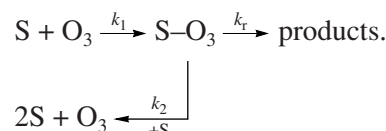$$k = \frac{v_g([O_3]_0 - [O_3]_g)}{V_s \alpha[O_3]_g[S]}. \qquad (3)$$

This calculation technique was described in greater detail in an earlier publication [17]. The main error in this method of rate constant determination comes from the error in the gas flow rate measurements (±3 ml/min or ±3%). The ozone concentration in the gas phase was measured with an accuracy of ±0.5%. Under these conditions, the expected error in the calculated rate constant is ±3.1%.

A static method [2, 18] was also used in the study of the ozonation kinetics. The reaction was performed in the temperature-controlled sample cell of a spectrophotometer. An ozone–oxygen mixture was passed through the sample cell with a substrate solution until the necessary $O_3$ concentration in the solution ($1.7 \times 10^{-5}$–$6.8 \times 10^{-4}$ mol/l) was reached. The blank in the reference cell was a solution containing the same substrate concentration. The substrate and ozone concentrations in the sample cell were chosen so that the substrate was

at least in 100-fold excess over ozone. After the necessary $O_3$ concentration was reached, the sample cell was sealed hermetically and the ozone consumption rate in the cell was monitored spectrophotometrically. Using this procedure, we determined the monomolecular ozone disappearance rate constant ($k_{mono}$). From the dependence of $k_{mono}$ on the substrate concentration, it is possible to determine the stoichiometry of the reaction and the ozonation rate constant at the given temperature.

## RESULTS AND DISCUSSION

For all substrates, we found that the rate constant (Eq. (3)) decreases with an increasing substrate concentration. This situation in ozonation was also observed in earlier studies. Earlier, we suggested the following reaction scheme to explain this behavior [19]:

$$S + O_3 \xrightarrow{k_1} S\text{–}O_3 \xrightarrow{k_r} \text{products.}$$
$$2S + O_3 \xleftarrow[{+S}]{k_2}$$

It is assumed here that ozone initially forms a complex with the substrate ($k_1$). This complex can either be converted into reaction products ($k_r$) or decompose back into the initial compounds ($k_2$). The effective rate constant depends on the substrate concentration in the following way:

$$k_{eff} = \frac{k_1 k_r}{k_r + k_2[S]}.$$

It is most convenient to process the kinetic data in terms of $1/k_{eff}$ as a function of [S]:

$$\frac{1}{k_{eff}} = \frac{1}{k_1} + \frac{k_2[S]}{k_1 k_r}. \qquad (4)$$

This dependence is expected to be linear.

Indeed, for butanol-1 and its acetic and boric esters, the results of the measurements are linearizable well in the $1/k_{eff}$ versus [S] coordinates ($r^2 = 0.98$–$0.99$). Figure 1 shows the corresponding straight lines for these three substrates at 20°C. From these lines, it is possible to calculate $k_1$ and $k_2/k_r$ for each of the three substrates. In the same way, these quantities were determined for several temperatures between –20 and 45°C.

The molecule of the boric ester, as distinct from the other substrates, has three *n*-butanol groups. For this reason, the effective concentration was taken to be 3[S] in data processing for this substrate. This was dictated by the necessity of comparing the reactivities of one *n*-butanol group in the series of compounds examined. Upon the substitution of 3[S] for [S] in Eqs. (3) and (4), the values of $k_1$ and $k_2/k_r$ 3 decrease by a factor of 3. Hereafter, all kinetic data for tributyl borate ozonation refer to one *n*-butyl group.
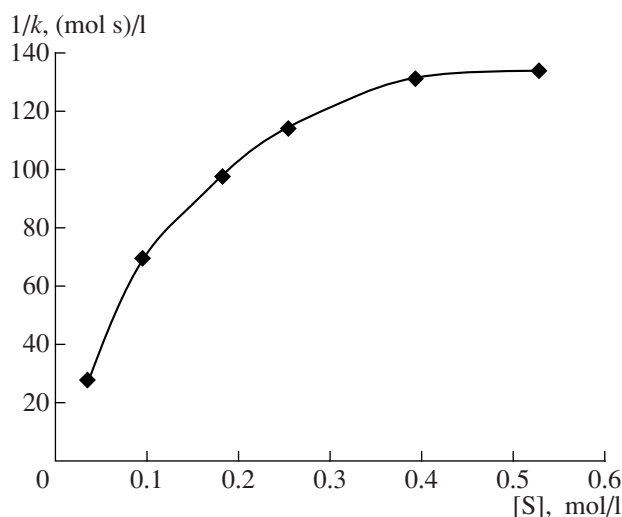
**Fig. 2.** $1/k_{eff}$ as a function of the butyl trichloroacetate concentration at 20°C.
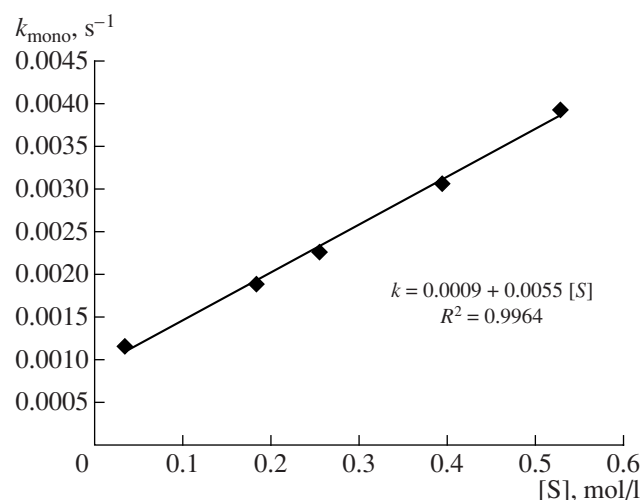


**Fig. 3.** $k_{mono}$ for ozone consumption as a function of the butyl trichloroacetate concentration at 20°C.

The isothermal rate constants obtained for butyl trichloroacetate using the bubbling technique are in conflict with the kinetic scheme presented above. The dependence of $1/k_{eff}$ on [S] for this substrate is plotted in Fig. 2. This dependence is inconsistent with the above kinetic scheme. For this reason, we carried out a kinetic study of butyl trichloroacetate ozonation in $CCl_4$ using the static method. Figure 3 shows the dependence of the monomolecular rate constant of ozone consumption in the reaction medium ($k_{mono}$) on the substrate concentration at 20°C.

It is clear from Fig. 3 that, firstly, the reaction is first-order with respect to the substrate. Secondly, the rate of ozone consumption in ester ozonation is comparable with the ozone decomposition rate in the absence of a substrate ($k_0 = 0.0009$). It is this fact that accounts for the overestimated $k_{eff}$ values at low trichloroacetate concentrations and for the shape of the curve shown in Fig. 2. If, for each concentration of the trichloroacetate, we define $k_{eff}$ as $k_{mono}/[S]$, the $1/k_{eff}$ versus [S] curve for

this ester will coincide with the curve plotted in Fig. 2. In further discussion of the results obtained for butyl trichloroacetate, we will present both data collected by the static method and data calculated from the dependence of $k_{mono}$ on [S].

The table lists kinetic parameters for the ozonation of all of the four substrates in $CCl_4$.

Clearly, the rate constant of the initial formation of the ozone–substrate complex, $k_1$, decreases in the order butanol > tributyl borate > butyl acetate > butyl trichloroacetate. This is not accompanied by any significant change in $k_2/k_r$. For butyl trichloroacetate, $k_2/k_r$ could not be determined experimentally. It is likely that $k_1$ for this substrate is so small that the ozonation rate is limited by the first reaction step alone. Because of this, the observed bimolecular rate constant for butyl trichloroacetate is equal to $k_1$ throughout the possible range of its concentrations.

Thus, the rate constant of the initial formation of the substrate–ozone complex, $k_1$, decreases sharply on

Kinetic parameters of the ozonation of butanol-1 and its esters in $CCl_4$

| Substrate | $k_1$ (20°C), l $mol^{-1}$ $s^{-1}$ | $\log A$ [l $mol^{-1}$ $s^{-1}$] | $\Delta E_a$, kcal/mol |
|---|---|---|---|
| Butanol-1 | $0.420 \pm 0.020$ | $6.60 \pm 0.47$ | $9.00 \pm 0.40$ |
| Tributyl borate* | $0.058 \pm 0.004$ | $5.60 \pm 0.14$ | $9.10 \pm 0.20$ |
| Butyl acetate | $0.037 \pm 0.003$ | $5.30 \pm 0.25$ | $8.95 \pm 0.35$ |
| Butyl trichloroacetate | $0.00550 \pm 0.00018$ | $5.50 \pm 0.21$ | $10.20 \pm 0.50$ |
| Substrate | $k_2/k_r$ (20°C), l $mol^{-1}$ | $\log A$ [l mol] | $\Delta E_a$, kcal/mol |
| Butanol-1 | $4.10 \pm 0.20$ | $5.90 \pm 0.60$ | $6.50 \pm 0.30$ |
| Tributyl borate* | $3.20 \pm 0.15$ | $5.20 \pm 0.19$ | $6.20 \pm 0.23$ |
| Butyl acetate | $2.70 \pm 0.13$ | $5.50 \pm 0.17$ | $6.25 \pm 0.25$ |

* The kinetic parameters of tributyl borate ozonation refer to one *n*-butyl group.
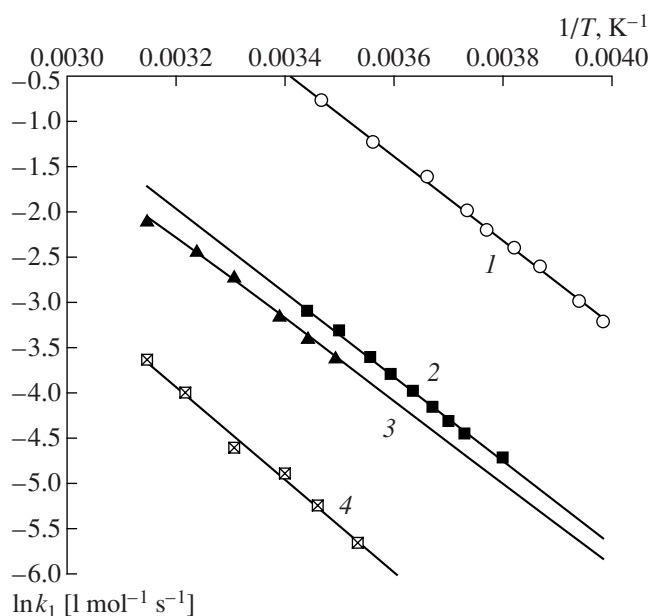
**Fig. 4.** Arrhenius plots of $k_1$ for the ozonation of (*1*) butanol-1, (*2*) tributyl borate, (*3*) butyl acetate, and (*4*) butyl trichloroacetate.



**Fig. 5.** Arrhenius plots of $k_2/k_r$ for the ozonation of (*1*) butanol-1, (*2*) tributyl borate, and (*3*) butyl acetate.

passing from butanol to its esters. This fact may be due both to the disappearance of the hydroxyl group and to the negative inductive effect of the ester groups. The true cause of the effect can be determined by comparing the Arrhenius parameters of the ozonation reactions.

Figure 4 shows the Arrhenius plots of $k_1$ for the four substrates. The same plots for $k_2/k_r$ are presented in Fig. 5. The corresponding Arrhenius parameters are listed in the table.

On passing from butanol-1 to its esters, the preexponential factor of $k_1$ decreases by one order of magnitude. The activation energies for butanol and its boric and acetic esters can be taken to be equal within the error of data processing. A noticeable increase in the activation energy (by 1–2 kcal/mol) is observed only on passing to butyl trichloroacetate. In general, the kinetic parameters of the ozonation of this ester are close to those of the ozonation of the hydrocarbons *n*-propane and *n*-butane [3, 4]. It is likely that, owing to its strong negative effect, the trichloroacetate group deactivates the α-CH bond in the molecule of the ester and, as a consequence, the ozonation behavior of the ester is similar to that of the above hydrocarbons.

The formal Arrhenius parameters for $k_2/k_r$ vary only slightly from one substrate to another. The difference does not exceed the error of linear extrapolation in the $\ln k_2/k_r$ versus $1/T$ coordinates.

Thus, the most significant fact is that the preexponential factor of the rate constant of the initial substrate–ozone complex formation, $k_1$, decreases by one order of magnitude on passing from butanol-1 to its esters. The preexponential factors for all three esters are
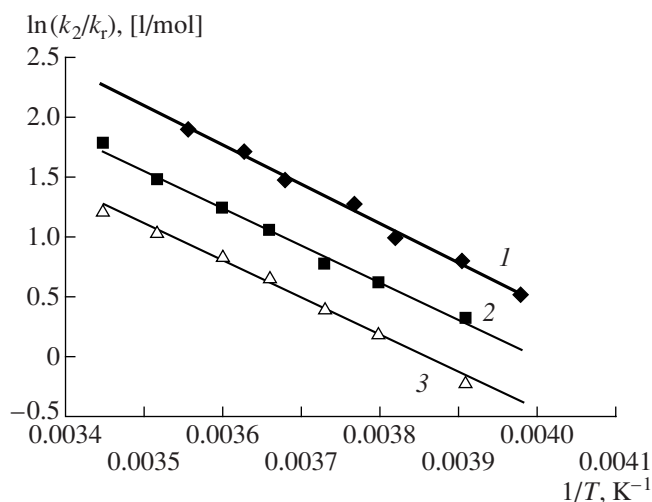
similar and lie within the error of data processing. At the same time, the inductive effects of the ester groups in the substrates are obviously different. The strongest electron-accepting properties are shown by the trichloroacetate group. As a consequence, the kinetic parameters of the reaction between butyl trichloroacetate and ozone are similar to the parameters observed for *n*-butane. Since there is no appreciable difference between the activation energies for the three other substrates, the decrease in $k_1$ on passing from the alcohol to its esters can be attributed to the absence of the hydroxyl group in the latter, which has an effect on the preexponential factor. The results obtained in this study support the hypothesis that the initial formation of the complex between ozone and the alcohol involves the hydroxyl group of the latter. The observed kinetic effect of this interaction can be due both to the transition state geometry changing in a favorable way for further conversions and to the concentration of ozone near the methylene groups of the substrate. In both cases, there would be changes in the preexponential factor of $k_1$, and this was actually observed in our experiments.

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