Kinetic regularities of conversion of ozone complexes with arenes

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The kinetic regularities of conversion of ozone complexes with several substituted benzenes (ArX = C_6H_5Me, C_6H_5Et, $C_6H_5CHMe_2$, $C_6H_5CMe_3$, C_6H_5F, C_6H_5Cl, *m*-BrC_6H_5Me, and $C_6H_5CH_2Cl$) were studied by spectrophotometry. The rate of consumption of $ArX \cdot O_3$ in a CH_2Cl_2—ArX solution obeys the kinetic equation $W = k_0[ArX \cdot O_3] + k_1[ArX \cdot O_3][ArX]$. The values of the rate constants k_0 and k_1 for the complexes studied were determined at −60÷0 °C.

Key words: ozone, aromatic hydrocarbons, ozone complexes; reaction mechanism, rate constants; ozonolysis.

Ozone forms π-complexes with arenes $ArX \cdot O_3$, which are sufficiently stable at low temperatures and whose absorption maxima lie in the range from 340 to 540 nm.[1,2] It has been shown previously[3] that the consumption of the $C_6H_5CHMe_2 \cdot O_3$ and $C_6H_5Cl \cdot O_3$ complexes in the presence of cumene and chlorobenzene occurs simultaneously by first- and second-order reactions. In this work, the effect of the structure of the complexes on the kinetics of their decomposition was studied.

Experimental

The kinetics of transformation of $ArX \cdot O_3$ was studied by spectrophotometry, measuring the optical density of the complex in the liquid phase over time. Experiments were carried out at −60÷0 °C in a 1-cm thermostated quartz cell provided with an attachment with a bubbler and a thermocouple. The cell containing 1.5 mL of a solution of substrate ArX (0.5—10 mol L^{-1}) in CH_2Cl_2 was placed into the cell chamber of an SF-26 spectrophotometer and thermostated to the specified temperature. A cooled ozone-oxygen mixture (40 mL min^{-1}, 1—2 % O_3) was introduced into the cell to accumulate $ArX \cdot O_3$. When the concentration of $ArX \cdot O_3$ in the solution reached the specified value, the introduction of the gas mixture was stopped. The change in the optical density of $ArX \cdot O_3$ was recorded automatically at 377—383 nm (Fig. 1).

Toluene (**1**), ethylbenzene (**2**), cumene (**3**), *tert*-butylbenzene (**4**), fluorobenzene (**5**), chlorobenzene (**6**), *m*-bromotoluene (**7**), benzyl chloride (**8**), and methylene chloride were purified by the known procedures.[4]

Results and Discussion

It is established that at $[ArX \cdot O_3]_0 \ll [ArX]_0$ ($[ArX \cdot O_3]_0$ and $[ArX]_0$ are the initial concentrations of aromatic hydrocarbon and the complex, respectively) the consumption of $ArX \cdot O_3$ obeys a first-order law in the whole temperature range and the range of concentrations of the reagents studied (see Fig. 1). The effective constants *k'* were determined from the semilogarithmic

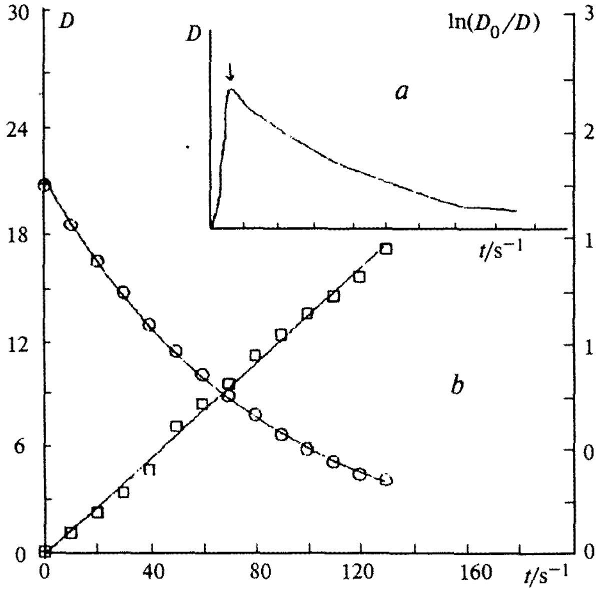

Fig. 1. *a*, Kinetic curves of accumulation and consumption of *m*-$MeC_6H_4Br \cdot O_3$ ($[m\text{-}MeC_6H_4Br \cdot O_3]_0$ = 5.5 mol L^{-1}, −30 °C), the moment when the introduction of ozone is stopped is indicated by the arrow; *b*, kinetic curve of consumption of *m*-$MeC_6H_4Br \cdot O_3$ and its semilogarithmic anamorphosis (*1, 2*).

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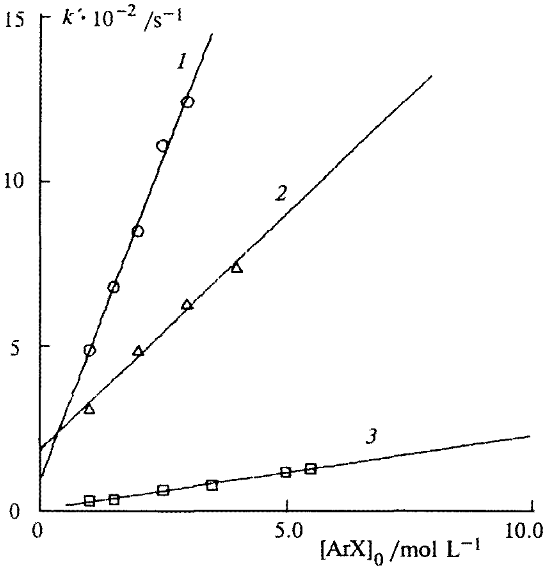


Fig. 2. Dependence of the effective first-order rate constant k_0 of consumption of the complex on the concentration of aromatic hydrocarbon(−30 °C): *1*, cumene; *2*, toluene; *3*, *m*-bromotoluene.

anamorphoses of the kinetic curves of consumption of $\mathrm{ArX \cdot O_3}$. Under the conditions studied, the k' values depend linearly on the concentration of ArX (Fig. 2):

$$k' = a + b[\mathrm{ArX}], \tag{1}$$

where a/s^{-1} and $b/\mathrm{L\ mol^{-1}\ s^{-1}}$ are the empirical constants. The a and b values at various temperatures are presented in Table 1.

Therefore, the rate equation for the consumption of the complex takes the form:

$$W = -\mathrm{d}[\mathrm{ArX \cdot O_3}]/\mathrm{d}t = a[\mathrm{ArX \cdot O_3}] + b[\mathrm{ArX \cdot O_3}][\mathrm{ArX}]. \tag{2}$$

Table 1. Kinetic parameters of consumption of $\mathrm{ArX \cdot O_3}$ in $\mathrm{CH_2Cl_2}$

T/°C	ArX	(*a*) k_0 /s^{-1}	(*b*) k_1 /L mol^{-1} s^{-1}
−47	$\mathrm{C_6H_5Cl}$	$(1.46\pm1.06)\cdot10^{-4}$	$(8.12\pm1.66)\cdot10^{-5}$
−30	—	$(8.33\pm1.40)\cdot10^{-4}$	$(8.52\pm7.40)\cdot10^{-5}$
−10	—	$(3.75\pm0.59)\cdot10^{-3}$	$(3.14\pm0.13)\cdot10^{-3}$
0	—	$(3.76\pm1.36)\cdot10^{-3}$	$(7.72\pm0.32)\cdot10^{-3}$
−30	$\mathrm{C_6H_5F}$	$(9.14\pm0.57)\cdot10^{-4}$	$(4.83\pm1.20)\cdot10^{-4}$
−30	$\mathrm{C_6H_5CH_2Cl}$	$(9.62\pm1.12)\cdot10^{-4}$	$(2.94\pm0.60)\cdot10^{-3}$
−30	m-$\mathrm{MeC_6H_4Br}$	$(1.99\pm0.11)\cdot10^{-3}$	$(2.31\pm0.32)\cdot10^{-3}$
−30	$\mathrm{C_6H_5Me}$	$(1.90\pm0.30)\cdot10^{-2}$	$(1.40\pm0.10)\cdot10^{-2}$
−30	$\mathrm{C_6H_5Et}$	$(2.63\pm0.21)\cdot10^{-2}$	$(1.25\pm0.11)\cdot10^{-2}$
−60	$\mathrm{C_6H_5CHMe_2}$	$(2.56\pm0.28)\cdot10^{-3}$	$(9.82\pm0.75)\cdot10^{-4}$
−47	—	$(5.18\pm0.38)\cdot10^{-3}$	$(6.50\pm0.20)\cdot10^{-3}$
−30	—	$(1.02\pm0.41)\cdot10^{-2}$	$(3.86\pm0.19)\cdot10^{-2}$
−30	$\mathrm{C_6H_5CMe_3}$	$(5.04\pm1.20)\cdot10^{-3}$	$(7.02\pm3.20)\cdot10^{-3}$

An increase in the k' value as the concentration of ArX increases can be explained in terms of a scheme that takes into account the reaction of the complex with the substrate along with its transformation according to the first-order law:

$$\mathrm{ArX \cdot O_3} \xrightarrow{k_0} \mathrm{P_0}, \tag{a}$$

$$\mathrm{ArX \cdot O_3} + \mathrm{ArX} \xrightarrow{k_1} \mathrm{P_1}, \tag{b}$$

where k_0/s^{-1}, $k_1/\mathrm{L\ mol^{-1}\ s^{-1}}$ and $\mathrm{P_0}$, $\mathrm{P_1}$ are the rate constants and the products of the corresponding stages.

It follows from the scheme that the rate of consumption of the complex can be described by Eq. (2) at $k_0 = a$ and $k_1 = b$, and the effective first-order rate constant k' is equal to

$$k' = W_{\mathrm{ArX \cdot O_3}}/[\mathrm{ArX \cdot O_3}] = k_0 + k_1[\mathrm{ArX}]. \tag{3}$$

The relative contribution of reactions (a) and (b) to the overall process depends on the nature of ArX, its concentration, and the temperature. At high concentrations of ArX, the consumption of $\mathrm{ArX \cdot O_3}$ in the reaction with the substrate is the predominant route of the transformation of the complex. For example, $W_1/W_0 \approx 11$ for the cumene complex at −30 °C and $[\mathrm{C_6H_5CHMe_2}]_0 = 3$ mol L^{-1}.

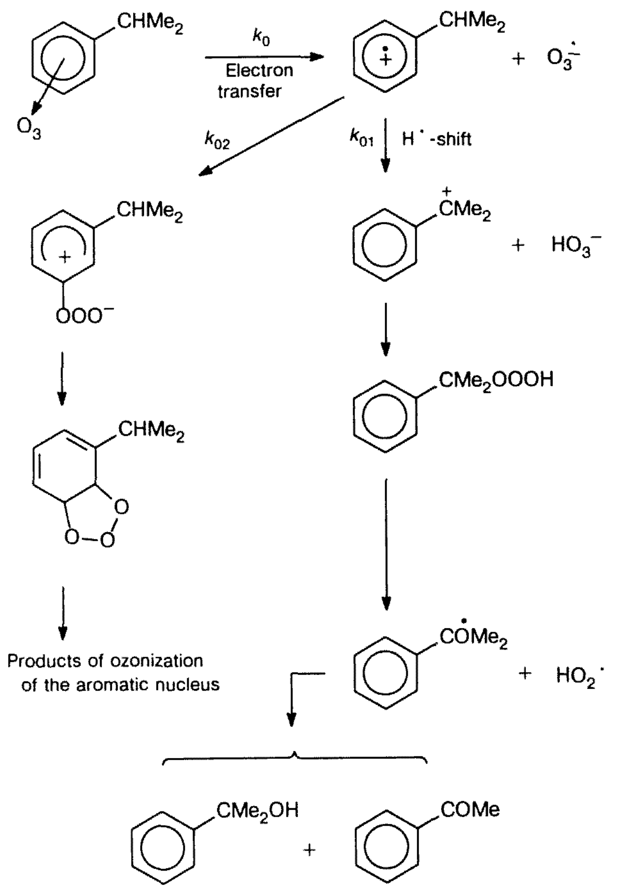
The activation parameters of the transformation of the complexes of $\mathrm{O_3}$ with cumene and chlorobenzene were calculated from the data in Table 1 (see Table 2). The pre-exponential factors A_1 are the same as those in the reactions of ozonolysis of aromatic compounds and olefins.[5] At the same time, the A_0 value is anomalously low, which is likely related to the polar nature of the irreversible decomposition of $\mathrm{ArX \cdot O_3}$.

The products of oxidation of both the side chain and the aromatic nucleus are formed from the complexes of $\mathrm{O_3}$ with alkyl-substituted benzenes. Thus, cumene hydrotrioxide, cumene hydroperoxide, dimethylphenylcarbinol, acetophenone, and ozonides formed due to the decomposition of the cumene complex have been found.[3,6,7] Their formation can be explained in terms of the mechanism suggested by W. A. Pryor[6,7] (Scheme 1).

Table 2. Activation parameters of transformation of $\mathrm{ArX \cdot O_3}$

Parameter	$\mathrm{C_6H_5Cl \cdot O_3}$	$\mathrm{C_6H_5CHMe_2 \cdot O_3}$
A' (E'/kcal mol^{-1})	$(6.88\pm1.92)\cdot10^{8}$ (11.60 ± 2.78)	$(3.44\pm0.68)\cdot10^{6}$ (8.72 ± 1.35)
A_0 (E_0/kcal mol^{-1})	$(7.08\pm1.55)\cdot10^{4}$ (8.89 ± 1.21)	(186.2 ± 19.10) (4.74 ± 0.24)
$\Delta S_0^{\neq}$/kcal mol$^{-1}\cdot$K^{-1}	−37.93	−49.74
A_1 (E_1/kcal mol^{-1})	$(3.71\pm1.15)\cdot10^{8}$ (13.44 ± 3.03)	$(7.94\pm0.55)\cdot10^{9}$ (12.58 ± 0.71)

Scheme 1



In this scheme, an electron transfer is the key stage, which results in the formation of aromatic radical cation $ArH^{\cdot +}$ and radical anion $O_3^{\cdot -}$, which transform subsequently to the ion pair and hydrotrioxide. The mechanism of formation of hydrotrioxide due to the intracage recombination of the ion pair ($R^+ + HO_3^-$) has been suggested by S. W. Benson on the basis of the thermochemical calculations.[8] Another channel of the transformation of radical cations and anions is the formation of the products of ozonization of the aromatic nucleus. No hydrotrioxides are formed from complexes of halogen-substituted benzenes, therefore, the reaction occurs only to the aromatic nucleus. This mechanism is evidenced by a high negative value of the constant (ρ) in the correlation $\log k_0 = (-2.02\pm0.36) - (2.14\pm1.20)\sigma_{\mathrm{I}}$, $r = 0.906$ (for σ_{I} see Ref. 9), the low values of the activation entropy $\Delta S_0^{\neq} = -49.7$ and -37.9 for the complexes with cumene and chlorobenzene at −30 °C (see Table 2), and a very noticeable effect of the polarity of the medium on k_0.[10]

The reaction of $ArX \cdot O_3$ with ArX can occur at both the aromatic ring and the side chain. The relative contribution of these reactions to the overall process is likely to depend on the nature of ArX. The aromatic nucleus is attacked in the case of fluorobenzene and chlorobenzene. According to the literature data, for the reactions of C_6H_5Me, $C_6H_5CD_3$, and $C_6D_5CD_3$ with $C_6H_5Me \cdot O_3$, $C_6H_5CD_3 \cdot O_3$, and $C_6D_5CD_3 \cdot O_3$ $k_{\mathrm{I}} = 1.4 \cdot 10^{-2}$, $1.4 \cdot 10^{-2}$, and $1.2 \cdot 10^{-2}$ mol^{-1} L s^{-1} (−30 °C),[11] respectively; hence, the reaction directed at the side chain is insufficient for toluene. However, this route can play a noticeable role for alkylbenzenes with the weak C—H bond in the alkyl substituent. For example, the rate constants k_{I} differ substantially (see Table 2) for cumene and *tert*-butylbenzene with equal induction constants of substituents ($\sigma = -0.197$), which can be explained by the easiness of the attack of a weak C—H α-bond in isopropylbenzene. The dependence of $\log k_{\mathrm{I}}$ on the bond strength is shown in Fig. 3.

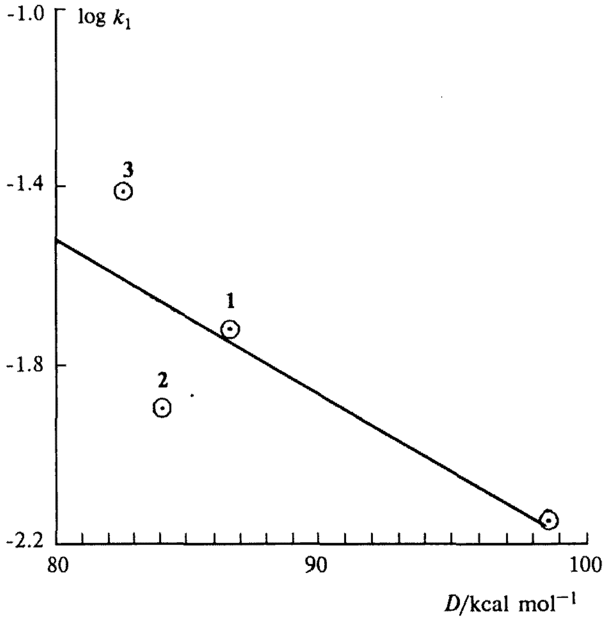


Fig. 3. Dependence of $\log k_{\mathrm{I}}$ on the C—H bond strength (D). The values of D are taken from Ref. 12. The numbers of the points correspond to the numbers of the compounds in the text.

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