

Kinetics and Stoichiometry of the Reaction of Ozone with Fullerene C₆₀ in a CCl₄ Solution

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Abstract—The stoichiometry (1 : 1) and the numerical value of the rate constant of the reaction of a fullerene with ozone ($1.2 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$) at 0°C were determined. A kinetic study of the reaction revealed the presence of an active impurity in high-purity samples. Suggestions as to the structure of this impurity were proposed based on the rate constant of its reaction with ozone. In contrast to simple aromatic compounds, the reaction of the fullerene with the first molecule of ozone dramatically (by several orders of magnitude) decreased the reactivity of the other C=C bonds in the molecule.

INTRODUCTION

Presently, one of the most rapidly developing branches of chemical physics is associated with the discovery and study of fullerenes, a new allotropic modification of carbon [1–4]. Among the reactions of fullerenes, the interaction with ozone has attracted considerable attention since the early steps into the chemistry of these compounds [5–8]. The functionalization of the fullerene molecule was the main goal of studies on this reaction [5, 6]. Monoxides, polyoxides, various oxygen-containing functional groups in the ground state [6, 7] or excited states [9], and aggregation products [6] were detected in the reaction products. Mechanistic studies of this reaction are difficult to perform because the structure and properties of the fullerene molecule are unusual and both the parent compound and the reaction products are sparingly soluble. Therefore, the mechanism of an attack of ozone on the fullerene molecule, the composition of products formed at the first step of the reaction, and the number of ozone molecules capable of participating in the subsequent steps remain unknown. As a rule, the degree of reaction and the participation factors of the solvent and concomitant oxygen in the reaction were not monitored in the relevant studies. The reaction rate was qualitatively evaluated in toluene solutions (toluene is a compound reactive toward ozone [10]). Kheifets and Pavlov [11] published quantitative kinetic data obtained with the use of a solvent (CCl₄) inert to ozone; they were the first to determine the rate constants of this reaction. They recognized four steps, which differed in rates and corresponded to the consecutive addition of several ozone molecules to the fullerene molecule, in the course of the reaction of ozone with a fullerene. However, at first glance, the reported reaction rate constants seemed too high and untypical of aromatic conjugation systems [12]. Moreover, Kheifets and Pavlov [11]

reported no stoichiometric data, whereas the subdivision of the reaction into particular steps seems problematic in the absence of these data. The results of a stoichiometric and kinetic study of the reaction of a fullerene with ozone are given below; these results were correlated with previously published data.

EXPERIMENTAL

Starting compounds. Ozone was synthesized from oxygen in an electric discharge. Fullerene C₆₀ (certified purity of 99.9%) was prepared at the Razuvaev Institute of Organoelement Chemistry, Russian Academy of Sciences (Nizhni Novgorod). The fullerene was additionally analyzed by HPLC (Hewlett-Packard 1050 Series chromatograph; UV detection, 333 nm; column, 250 × 4.6 mm; stationary phase, C₁₈; eluant, CHCl₃–PhCH₃–MeOH (1 : 1.1 : 1.3); eluted as a single peak) and elemental analysis (O and H contents were lower than 0.1%). Chemically pure CCl₄ was additionally treated with a flow of ozonated oxygen for 30 min to decompose possible active impurities.

The procedure of kinetic measurements was described previously [13]. The reaction was performed in a bubbling reactor under standard conditions (the ozone concentration in a gas mixture at the reactor inlet was $[\text{O}_3]_0 = 2.5 \times 10^{-6} \text{ mol/l}$; the gas (O₂ + O₃) flow rate was $v_g = 0.1 \text{ l/min}$; the solution volume in the reactor was $V = 20 \text{ ml}$; the bubbler was a Schott filter no. 2; the bubble diameter was ~1 mm). Our previous broad experience allowed us to consider diffusion limitations as insignificant under the specified conditions.

RESULTS AND DISCUSSION

Reaction stoichiometry. The reaction of the fullerene C₆₀ with ozone in a CCl₄ solution occurred relatively rapidly. As can be seen in Fig. 1, about a half

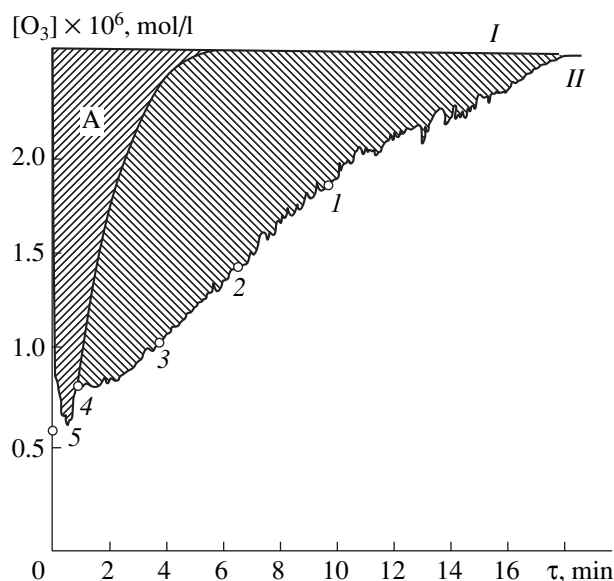


Fig. 1. The time dependence of the concentration of ozone at the reactor (I) inlet and (II) outlet. The numerals indicate points used for calculating the rate constants given in the table.

of the ozone amount that entered the reactor with a gas flow was absorbed upon passing an ozone–oxygen mixture ($[O_3] = 2.5 \times 10^{-6}$ M; $v_g = 0.1$ l/min; 0°C) through a solution of the fullerene (F) (20 ml; $[F] = \sim 11 \times 10^{-5}$ M) placed in the bubbling reactor. The area restricted below by the curve of ozone concentration in the gas mixture at the reactor outlet (Fig. 1, curve II) and above by the line that represents the ozone concentration at the reactor inlet as a function of time (curve I) (shaded area in Fig. 1) is equivalent to the consumption of ozone in the reaction. A comparison of the ozone consumption with the amount of the fullerene used in the experiment allowed us to draw a conclusion on the stoichiometric coefficient of the reaction. The ozone consumption in moles was equal to the number of moles of the fullerene introduced into the reactor. Thus, we believe that the stoichiometric coefficient of the reaction under the conditions of our experiments was equal to unity (0.92 by area and 1.05 with consideration for the unreacted fullerene in solution). As follows from the model [13], the difference between ozone concentration levels at the reactor inlet ($[O_3]_0$) and outlet ($[O_3]_g$) characterizes the rate of the reaction in solution. Thus, data shown in Fig. 1 allowed us to conclude that the reactivity of reaction products dramatically decreased after the addition of an ozone molecule to the fullerene molecule. Judging from the character of absorption, the reactivity decreased by a few orders of magnitude, although 29 potentially reactive centers remained in the molecule. This fact to some extent contradicts previous findings on the reaction of ozone with simple aromatic compounds. In particular, it was found [12] that after the addition of the first molecule of ozone to benzene or

naphthalene, the following molecules added much more easily. This effect is due to the high consumption of energy for overcoming the aromatic conjugation at the first step and to the absence of this consumption at the subsequent steps. To explain this different fullerene behavior, it should be taken into account that the primary product of the reaction of ozone with fullerene is an oxide, which exhibits a very strong electronegative inductive effect; it is likely that this effect exceeds the weakening of conjugation. The reactions of simple aromatic compounds with ozone yield other products (aldehyde groups, oxy groups, or aromatic ring opening) and hence have other consequences.

Kinetics of ozone addition to the fullerene. On passing a flow of an ozone-containing gas through a fullerene solution, the color of the solution gradually changed from light violet to brownish, which is due to the color of reaction products. The products were deposited on the reactor walls for ~ 1 day, and the solution took on a violet, although weaker, color tone again. It is evident that a small amount of unreacted fullerene was retained in the system. The shape of the experimental function $[O_3]_g = f(\tau)$ (τ is the reaction time) suggests that a small portion of the fullerene used in the experiments exhibited a much higher reactivity toward ozone than the bulk. In Fig. 1, region A, in which this active impurity primarily reacts, is separated from the shaded area. The reaction rates were evaluated in experiments with different initial ozone and fullerene concentrations. The reaction was found to obey a bimolecular law, and the experimental data were linearized on the coordinates of the equation

$$\frac{[O_3]_0 - [O_3]_g}{[O_3]_g} = \text{const}[F],$$

as required by the mathematical model [14]. This is illustrated in Fig. 2. In addition to the evaluation of the reaction stoichiometry, data shown in Fig. 1 are also valuable for the calculation of the reaction rate and other kinetic parameters. Indeed, in an experiment, the feed rate (v_g) of a gas mixture to the reactor, the ozone concentrations in a gas flow at the reactor inlet and outlet ($[O_3]_0$ and $[O_3]_g$, respectively), and the rate of ozone consumption ($v_g([O_3]_0 - [O_3]_g)$) are known at every point in time. The solution volume (V) in the reactor and the initial fullerene concentration in solution were specified by experimental conditions. The current fullerene concentration $[F]$ was calculated by subtracting the portion that corresponded to the ozone consumed in the reaction from the total area over the curve of $[O_3]_g = f(\tau)$ (see [14] for more detail). These data allowed us to calculate the reaction rates and rate constants for a few arbitrarily chosen points in the experimental curve. The main points of the calculation were as follows:

(1) The rate of the reaction in solution is

$$w_{\text{sol}} = k[O_3]_{\text{sol}}[F]; \quad (1)$$

(2) According to a material balance equation, the amount of ozone consumed per unit time is equal to the product $v_g([O_3]_0 - [O_3]_g)$; relating this to a unit volume of the solution, we obtain

$$v_g([O_3]_0 - [O_3]_g)/V; \quad (2)$$

(3) The experimental conditions were chosen so that the rate of ozone dissolution was much higher than the rate of chemical reaction. This allowed us to consider that the concentration of ozone in the solution is proportional to its concentration in the gas phase: $[O_3]_{sol} = \alpha[O_3]_g$, where α is the solubility factor. The solubility of ozone in CCl_4 under the experimental conditions was measured previously [15]. Equating (1) and (2) with the replacement of $[O_3]_{sol}$ by $\alpha[O_3]_g$ in Eq. (1) gives the equation

$$k = \frac{v_g([O_3]_0 - [O_3]_g)}{V\alpha[O_3]_g[F]}.$$

Substitution of known and experimentally determined terms into Eq. (3) allowed us to calculate the rate constants for different fullerene conversions. The table summarizes the results of this calculation.

The data presented in the table and Fig. 2 suggest that the reaction obeyed a bimolecular law during the observation time (except for the first minute). A comparison of the results with published constants [11] demonstrated that the addition of the first molecule of ozone to the fullerene (this addition is the essence of the test reaction) was slower by one order of magnitude than that according to Kheifets and Pavlov [11] (cf. $k = 1.2 \times 10^3$ and $2.9 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$). It is our opinion that this difference may be due to the presence of an active impurity in the fullerene used. The guaranteed high purity of the product and the absence of data on the reaction stoichiometry allowed Kheifets and Pavlov [11] to consider the step of rapid ozone addition as the main reaction, whereas the third step of the process observed by Kheifets and Pavlov [11] was the main reaction (cf. $k = 1.2 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ (table) and $k_3 = 1.5 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ [11]).

The presence of an active impurity in the parent fullerene was supported by data in both Fig. 1 and the table (the lowest row). For clarity, data in the table are presented in reverse order with respect to reaction time, from the end to the beginning. This demonstrates more clearly that an amount (~7% based on added ozone) of a substance that is more reactive than the major portion of the fullerene taken was present in the sample. We can draw inferences concerning the nature of this product. Judging from the rate constant ($k = 8.8 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$), ozone reacted with a conjugated double bond similar to $C=C$ in tetraphenylbutadiene or divinylbenzene [14, pp. 85 and 175]. The detection of impurities that are structurally different from the fullerene in considerable amounts was unexpected because the parent fullerene was of high-purity grade (higher than 99% according to HPLC and elemental analysis data). We found in addi-

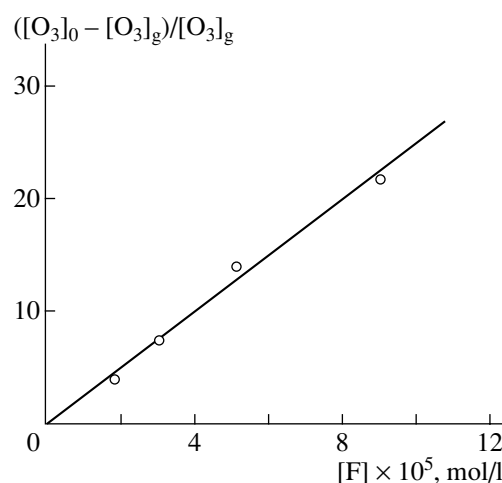


Fig. 2. The plot of $\frac{([O_3]_0 - [O_3]_g)}{[O_3]_g}$ against the concentration of the fullerene. The linear character corresponds to a bimolecular law.

tional experiments that the above impurity was accumulated in the test solution from the crystalline fullerene, which was taken in large excess to prepare a saturated solution. When this excessive fullerene was used for preparing a new portion of solution, "rapid" initial portions disappeared from the kinetic curve. The amounts of the detected impurity were ~0.7 wt % on the basis of the total amount of fullerene used in the experiment (including the undissolved substance). Although this value is low, it is noticeably higher than the allowable values based on the expected purity (99.9%). The above impurity was present in the samples used by different authors (at least by us and Kheifets and Pavlov [11]); consequently, it was reproducible. Its activity in the reaction with ozone was also stable. This can be seen from a comparison of the reaction rate constants obtained in this work ($k = 8.8 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$) and published by Kheifets and Pavlov [11] ($k_1 = 2.9 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$). Therefore, the reaction of this impurity with ozone can be confused with the first step of the reaction $F + O_3 \rightarrow \text{products}$, and erroneous conclu-

Rate constants (k) at different residual concentrations of the fullerene in solution

Entry	τ , s	$[F] \times 10^5$, mol/l	$[O_3]_g \times 10^6$, mol/l	$k \times 10^{-3}$, $\text{l mol}^{-1} \text{ s}^{-1}$
1	582	1.8	1.8	0.97
2	372	3.0	1.4	1.2
3	210	5.1	1.05	1.3
4	48	9.0	0.8	1.1
5	0	11.0	0.58	88

Note: $V = 20 \text{ ml}$, $v_g = 0.1 \text{ l/min}$, $[O_3]_0 = 2.5 \times 10^{-6} \text{ M}$, 0°C , $\alpha = 2.1$.

sions can be drawn with respect to both reaction rates and product compositions.

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