Kinetics and Stoichiometry of the Reaction between Ozone and C_{70} Fullerene in CCl_4

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Abstract—The kinetics and stoichiometry of the reaction between C_{70} fullerene and ozone have been studied. The reaction obeys a bimolecular rate law. The stoichiometric coefficients of the reaction are 1 : 12 to 1 : 22, depending on reaction conditions. The rate constant at 22°C is 5×10^4 l mol^{-1} s^{-1} for the first stage of fullerene conversion and $(0.8–0.6) \times 10^4$ l mol^{-1} s^{-1} for the subsequent stages. Since the stages differ in terms of reaction rate, the original C_{70} molecules are first involved in the reaction, whereas, at the subsequent stages, all molecules are involved with equal probabilities, irrespective of the number of preceding reaction events in which they have participated.

Fullerene chemistry is a rapidly progressing interdisciplinary area between chemistry, physics, and materials science. Most studies in fullerene chemistry have dealt with fullerene separation [1] and molecular structure [2–5], the synthesis of new compounds and materials using fullerenes [6–8], the introduction of functional groups or heteroatoms into fullerene molecules [6, 8], and the replacement of conventional additives (oxidation inhibitors [9], conducting components [7], etc.) in commercial materials. Ozone is among the reagents frequently used in fullerene modification. It reacts readily with fullerenes to form oxides, ketones, and other products [10–15].

In all of the above cases, it is appropriate and sometimes necessary to control the conversion and the rates of the reactions involving fullerenes and other reagents, primarily because fullerene molecules contain many reaction sites (C=C groups) interlinked through a system of conjugated bonds. These sites are often capable of adding many reactant molecules (at least 5 O atoms [6] and up to 26 Cl atoms [16]); hence, the kinetics of the reaction should be known to achieve a desired extent of the reaction. However, there have been only a few publications on this subject. Up to now, only the kinetics of the reaction between ozone and C_{60} fullerene have been studied [17–19]. Essentially different rate constants have been reported for this reaction, although the authors have proceeded from the same basic assumptions. For instance, according to our earlier data [18], the reaction of ozone with C_{60} proceeds in several steps, the addition rate of the first molecule being one order of magnitude higher than that of the second molecule. According to other authors [19], the

reaction rate increases as the ozonation products build up in the system. Since the primary reaction product is fullerene monoozonide [20], it is believed that the first step of C_{60} ozonization is indeed more rapid than the subsequent steps. The kinetics of the reactions between ozone and fullerenes other than C_{60} were not studied previously, although these fullerenes could be expected to show essentially different reactivities because of the difference in molecular structure. In this work, we report our experimental study of the stoichiometry and kinetics of the reaction between ozone and C_{70} fullerene and compare the results to the corresponding data for the reaction between C_{60} fullerene and O_3.

EXPERIMENTAL

Starting compounds. Ozone was prepared from oxygen in an electric discharge. C_{70} fullerene (92%) was synthesized at the Institute of Macromolecular Compounds, Russian Academy of Sciences. The purity of fullerene was determined by HPLC on a Hewlett Packard 1050 chromatograph equipped with a UV detector ($\lambda = 333$ nm) and a 250×4.6 mm column packed with a C_{18} stationary phase. The eluent was a $CHCl_3$–$PhCH_3$–MeOH (1.0 : 1.1 : 1.3) mixture. Elemental analysis was also used. The chromatogram showed two peaks due to C_{70} (92%) and C_{60} (8%). According to the elemental analysis data, the O and H contents were at most 0.1 at %.

CCl_4 (reagent grade) to be used as the solvent was treated with flowing ozonized oxygen for 30 min to decompose any possible active impurities.
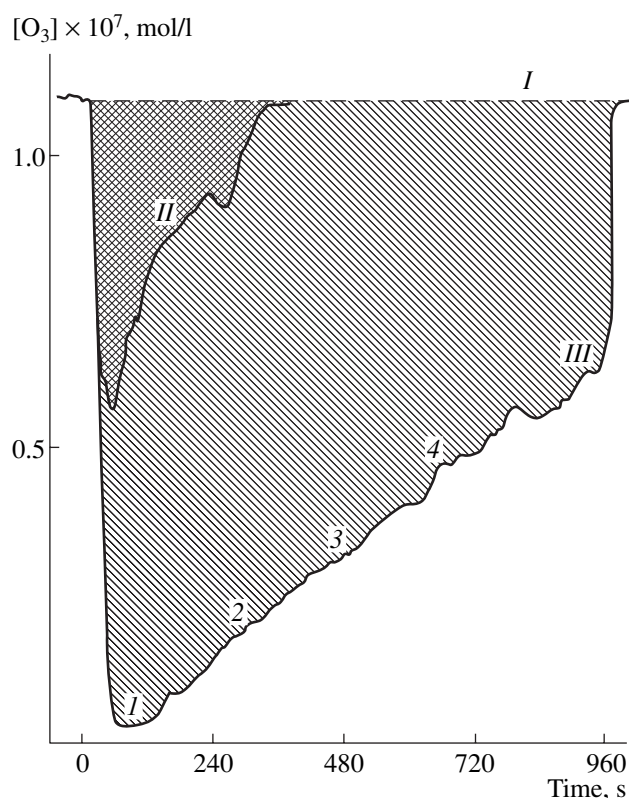
Ozone concentration at the reactor (*I*) inlet and (*II*, *III*) outlet in the course of the reaction between ozone and the fullerenes (*II*) C_{60} and (*III*) C_{70}. (*1–4*) Data points used in the calculation of the rate constants presented in the table.

Kinetic measurements are described elsewhere [21]. The reaction was carried out in a bubble reactor under conditions such that the diffusion limitations could be neglected ([O_3] = 1.1×10^{-7} mol/l; oxygen feed rate, 0.1 l/min; the volume of solution in the reactor, 20 ml; Schott filter No. 2 as the disperser; bubble diameter, ~1 mm).

RESULTS AND DISCUSSION

Reaction stoichiometry. As the ozone-containing gas was passed through a fullerene solution, the brown solution gradually faded but was not completely discolored even when the reaction was complete. It is likely that the reaction products were also colored. The reaction of C_{70} fullerene with ozone in CCl_4 is rather fast. The figure illustrates ozone consumption by solutions of the fullerenes C_{60} (curve *II*) and C_{70} (curve *III*) taken in equivalent amounts. As the ozone–oxygen mixture ([O_3] = 1.1×10^{-7} mol/l; flow rate, 100 ml/min; 0°C) is passed through the fullerene solution (20 ml; [F] $\approx$ 7.2×10^{-4} mol/l) in the bubbler, C_{60} consumes about half the ozone fed, whereas C_{70} consumes more than 90% of the ozone. The hatched areas in the figure, which are bounded below by the outlet ozone concentration curves (curves *II* and *III*) and above by the inlet

ozone concentration line (line *I*), are proportional to the amount of ozone consumed by C_{60} and C_{70}, respectively.

A comparison between the ozone consumption and the amounts of fullerenes loaded into the reactor showed that C_{60} and C_{70} take up different amounts of ozone at the fast addition stage. As was mentioned in an earlier paper [18], although the C_{60} molecule has a great number of reactive sites, its reactivity decreases by 1–2 orders of magnitude upon the addition of one ozone molecule. Therefore, the stoichiometric coefficient of this reaction is 1. As can be seen in the figure, a C_{70} molecule is capable of adding as many as 12 ozone molecules, and, as will be shown below, the rate of this process is markedly higher than the rate of the reaction between C_{60} and ozone. The fullerene molecules have many centers capable of reacting with ozone. These include all conjugated C=C bonds of the framework, and it is, therefore, not surprising that a great number of ozone molecules can be added. It would be expected that, in the limiting case of all framework multiple bonds reacted with ozone, the number of consumed O_3 molecules is 35. The fact that the reaction ceases at earlier stages indicates that an added ozone molecule exerts an electronegative inductive effect on the adjacent multiple bonds. Such effects were observed not only for reactions involving C_{60} fullerene but also for reactions of simpler compounds, for example, divinylbenzene [21, p. 86].

The number of ozone molecules added to one C_{70} molecule varied between 12 to 22, depending on the fullerene concentration and temperature.

Ozone addition kinetics. Experiments carried out at various initial concentrations of the starting reactants and an analysis of ozone consumption by the reaction system (see below) showed that the interaction between C_{70} and ozone, as well as most reactions between ozone and other substrates, obey a bimolecular rate law. As follows from our model of the process [21, p. 60], the difference between the inlet and outlet ozone concentrations in the gas mixture is a measure of the reaction rate in the solution. The smaller this difference and the higher the ozone concentration at the reactor outlet, the lower the reaction rate. As can be seen in the figure, the outlet ozone concentration increases rapidly at the end of the observation period (~16 min), after the consumption of 12 equivalents of O_3. This run of the consumption curve indicates that the substrate's capability for adding ozone decreases by more than one order of magnitude in spite of the 23 potentially reactive sites remaining in the fullerene molecule C_{70}. This behavior of the reaction resembles the behavior of ozone reacting with C_{60} fullerene (which was studied earlier), with the difference that the latter reaction is slowed down once one ozone molecule is added. The causes of this deceleration have been discussed above.

Examination of the curvature of the ascending portion of curve *III* revealed three successive characteristic

periods: a short (~1.5-min) initial period corresponding to the addition of one equivalent of O_3, a longer period in which the other 11 equivalents of ozone are added, and a final period defined by the ascending portion of the consumption curve. The rate constants were calculated for the four most characteristic points of curve *III*. The calculation procedure, which is described in [18], was based on the following reasoning. The following data are known at each time point: the gas feed rate (v_g); the inlet and outlet ozone concentrations in the gas flow ($[O_3]_0$ and $[O_3]_g$, respectively); and the ozone consumption rate (v_{O_3}), which is equal to $v_g([O_3]_0 - [O_3]_g)$. The solubility of ozone in CCl_4 (κ) under the experimental conditions was measured earlier [22]. The volume of solution in the reactor (V) and the initial fullerene concentration are specified by the experimenter. The current fullerene concentration ($[F]$) can be calculated by subtracting, from the total area above the $[O_3]_g = f(\tau)$ curve, the part of this area that corresponds to the amount of ozone consumed in the reaction (see [21] for details). The ozone consumption rate,

$$w_{sln} = Vk[O_3]_{sln}[F], \qquad (1)$$

is equal to the rate at which ozone as a gas mixture is fed into the reactor (v_{O_3}).

The experimental conditions were chosen so that the rate of ozone dissolution was much higher than the rate of the chemical reaction. Therefore, the ozone concentration in the solution was proportional to the ozone concentration in the gas phase: $[O_3]_{sln} = \kappa[O_3]_g$. Equating w_{sln} with v_{O_3} and replacing $[O_3]_{sln}$ with $\kappa[O_3]_g$ in Eq. (1), we obtain

$$
\begin{aligned}
k &= \frac{v_g([O_3]_0 - [O_3]_g)}{V\kappa[O_3]_g[F]_\tau} \\
&= \frac{2 \times 10^{-3}(1.08 - 0.022) \times 10^{-7}}{0.02 \times 1.7 \times (6.0 \times 10^{-5}) \times (0.022 \times 10^{-7})} \quad (2) \\
&= 5 \times 10^4 \quad 1\ mol^{-1}\ s^{-1}.
\end{aligned}
$$

Here, k is the rate constant, v_g is the gas feed rate (l/s), $[O_3]_0$ is the ozone concentration at the inlet of the reactor, $[O_3]_g$ is the ozone concentration at the outlet of the reactor, V is the reactor volume, κ is the solubility (Henry) coefficient, and $[F]_\tau$ is the concentration of the reactive sites of fullerene in the solution at the time point τ.

The rate constants at various C_{70} conversions (points 1–4 in the figure) were calculated by substituting known and experimentally measured terms into Eq. (2). The calculated data are presented in the table.

Examination of the data presented in the table shows that the first ozone molecule adds to the fullerene molecule 6–8 times more rapidly than the subsequent molecules. Taking into account the multistep nature and the complicated stoichiometry of the reaction, one can conclude that the reaction obeys a bimolecular rate law. This is indicated by the above experimental data for different initial fullerene and ozone concentrations and by the shape of the $[O_3]_g = f(\tau)$ curve. Indeed, the fullerene concentration decreases during the reaction, the concentration of dissolved ozone increases, and all these changes affect the reaction rate according to the bimolecular kinetic law. As is clear from the data presented in the table, the addition rate somewhat decreases with an increase in the number of ozone molecules added to fullerene. As in the addition of the first molecule, this is likely due to the inductive effect of the oxygen-containing functional groups that form upon the incorporation of ozone into the fullerene molecule.

In conclusion, let us analyze the probability distribution between ozone attacking initial fullerene molecules and ozone attacking molecules that have already participated in some reaction events. It is well known that many polyconjugated and aromatic compounds, which are close relatives of the fullerenes, react with ozone in another way. In particular, it was noted that, after the addition of one ozone molecule to benzene or naphthalene, subsequent molecules add much more readily [21, p. 175]. Only complete ozonation products are present in the reaction mixture along with the starting compound, whereas no intermediates are observed. This effect is due to the high energy required for overcoming the aromatic conjugation at the first stage and the absence of such an energy barrier at the subsequent stages. In the case of C_{70}, the aromatic conjugation in the framework is likely to be not very strong. This follows from the similarity of the rate constants of the C_{70}–ozone reaction and the reactions involving unconjugated C=C bonds in alkenes. It is this fact that determines the specific time distribution of reaction products in this system. Owing to the great difference between the rate constants of the first and second stages, ozone initially adds to fresh C_{70} molecules. At the second stage, all products are involved in the reaction with nearly equal probabilities, irrespective of the number of ozone molecules already added.

Rate constants at various residual concentrations of fullerene reactive sites in the solution

Point no.	τ, s	$[F]_\tau \times 10^4$, mol/l	$k \times 10^{-4}$, l mol^{-1} s^{-1}
1	40	7.2	5
2	252	3.6	0.8
3	438	2.1	0.7
4	630	1.03	0.6

Note: $V = 20$ ml, $v_g = 0.1$ l/min, $[O_3]_0 = 1.1 \times 10^{-7}$ mol/l, $T = 22°C$, and $\kappa = 1.7$.

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