ON REACTION RATE CONSTANTS $Cl + CH_3I, C_3F_7I, CF_3I$

EGU General Assembly 2011

Igor Larin, Alexandr Spasskiy, and Elen Trofimova

Institute for energy problems of chemical physics RAS (IEPCP RAS) 119334, Moscow, Leninskii pr., 38, bldg. 2. Russia

IEPCP RAS

Abstract

Method of resonance fluorescence (RF) has been used to measure the reaction rate constants of chlorine atoms with CH_3I (k_I), CF_3I (k_{II}) and C_3F_7I (k_{III}) in flow reactor at 295 K. It has been obtained that k_I = $(0.9\pm0.15)\times10^{-11}$ $cm^3 molecule^{-1} s^{-1}$; k_{II} = $(7{,}4\pm0.6)\times10^{-13}$ $cm^3 molecule^{-1} s^{-1}$; k_{III} = $(5{,}2\pm0.3)\times10^{-12}$ $cm^3 molecule^{-1} s^{-1}$. It was experimentally proved that under our experimental conditions reaction of chlorine atom with CH_3I occurs on the surface of the reaction vessel, while reaction of chlorine atom with CF_3I and C_3F_7I are homogeneous.

1

Introduction

Last years reactions of chlorine atoms with iodine containing hydrocarbons both natural and anthropogenic origin became a topic of many works. Natural source of these substances are biomass oceans, as well as photochemical processes occurring in sea water. Anthropogenic source is the use of these substances in the industry and as fire-fighting product. Some contribution gives also the combustion of biomass and the cultivation of rice fields.

Chlorine atoms in the marine atmosphere are generated by heterogeneous processes of chlorine-containing particles (NaCl, HCl, $ClONO_2$) with N_2O_5 and ozone resulting in weakly bonded Cl_2 molecules, HOCl and $ClNO_2$ which dissociate under action of UV radiation with a formation of chlorine atoms. As a result the concentration of chlorine atoms in the atmosphere under this conditions can be as high as 10% of the concentration of OH radicals. Because the reaction rate constants for Cl atoms often are considerably higher than for OH radicals, no wonder that the studying the reactions of chlorine atoms with halogen-containing hydrocarbons attracts attention, taking into account the role of these chemicals in changing ozone layer and climate.

This work is devoted to measurement of the reaction rate constants of chlorine atoms with CH_3I, which annual emission in the atmosphere (mainly from ocean) accounts 1.5 megatonnes, and also the same for reaction of chlorine atoms with CF_3I and C_3F_7I which (albeit in much smaller quantities) are emitted in the atmosphere by industry.

2

Methods & approaches

Experiments carried out in the flow reactor shown in Fig. 1.

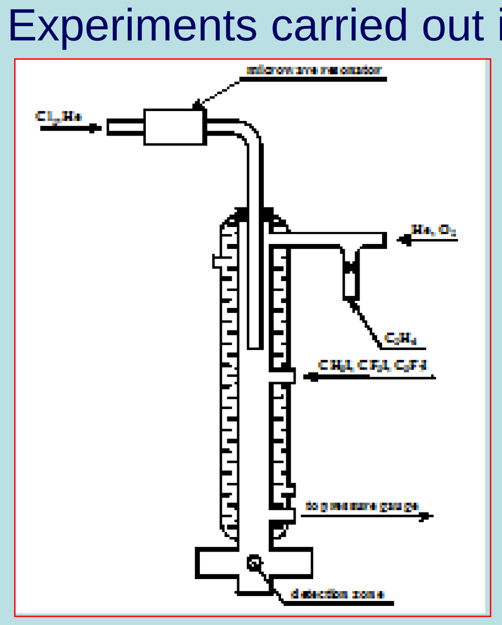


Fig.1.

The reactor was a quartz cylinder with an internal diameter of 1.7 cm. The reactor surface was covered with a fluorocarbon f-32 I to decrease the rate of heterogeneous loss of atoms and radicals. Oxygen, helium and ethan has been entered into the reactor through side holes. Also through side entrance CH_3I, CF_3I, and C_3F_7I are supplied

Cl_2 are synthesized through oxidation of HCl by $KMnO_4$, purified by distillation-temperature and kept in glass bottles. Cl_2 with He are coming through resonance lamp to get Cl atoms. CF_3I or CH_3I, C_3F_7I are kept in glass isolated from light cylinders and through the valve of fine adjustment entered into the reactor in mixture with helium and oxygen. Flow rate has been determined by measuring the pressure drop in a calibrated vessel. Ethane has been used to calibrate absolute sensitivity of the system to chlorine atoms.

When measuring the reaction rate constants by RF the signals of iodine atoms and chlorine atoms have been measured in the registration zone shown in Fig. 2 together with a source of resonance radiation and an ionization counter used for registration of the reemitted resonance radiation. Experiments run at the room temerature and under pressure of some mm Hg.

3

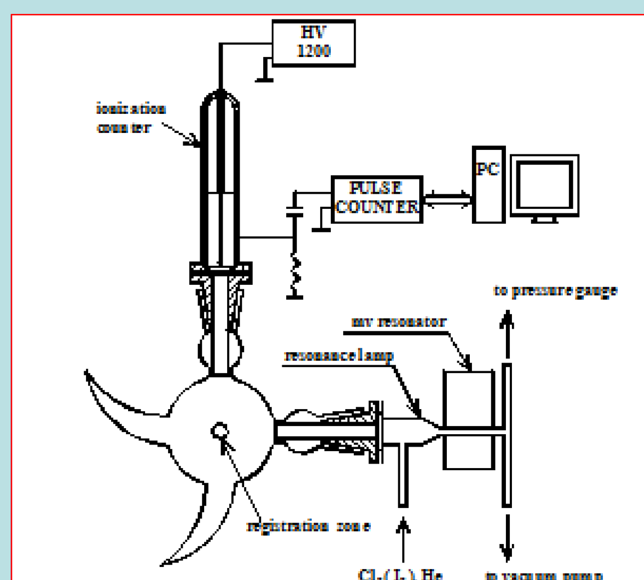


Fig.2.

Chlorine atoms are generated by a discharge frequency of 254 MHz, in a mixture Cl2:He (1:10000). RF system for registration of chlorine atoms included a resonance lamp emitting a Cl resonance line 118.9 nm and photoionization counter filled with a mixture of Ar and NO and running within a range of 117-134 nm.

To calibrate absolute sensitivity to atoms of chlorine we used a titration with help of C_2H_6. Ethan added to the flow of chlorine atoms until RF signal of chlorine atoms are not dropped to zero. The results showed that Cl atoms concentration is proportional to the flow of molecular Cl_2 via reactor. Signal to noise ratio of 2 was obtained at concentrations $[Cl] \approx 1\cdot10^{10}$ $atom\cdot cm^{-3}$.

Iodine atom RF registration system included iodine resonance lamp emitting a resonance radiation at 178.3 nm and ionization chamber described above. Calibration of the absolute sensitivity to iodine atoms were produced by titration of a known number of I_2 by oxygen atoms produced in microwave discharge in mixture of 4% O_2 in He. The concentration of oxygen atoms far exceeded the concentration of initial molecular iodine, that allows to transform whole initial I_2 in iodine atoms. This source allowed to get a certain amount of I atoms and transport them to the distance specified by heterogeneous loss of O atoms.

4

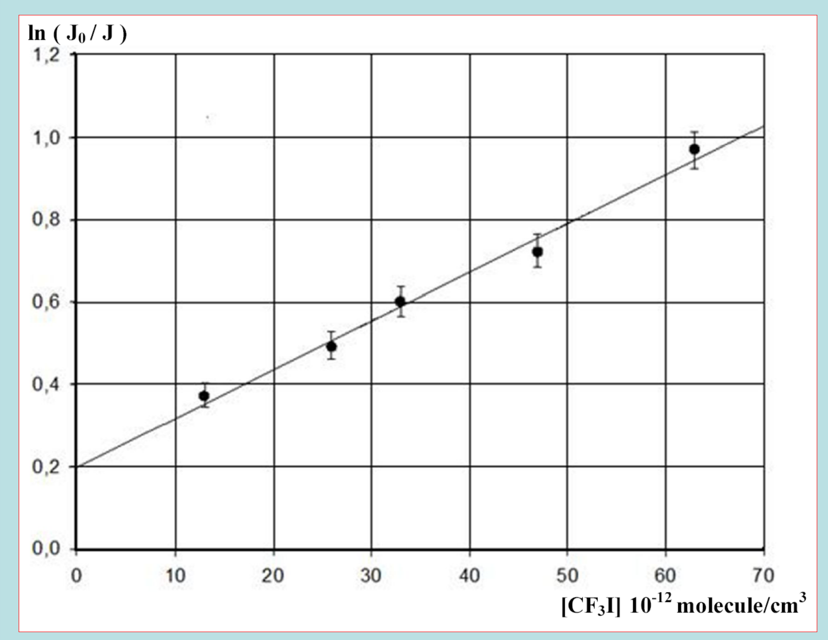
Results

Reaction $Cl + CH_3I \rightarrow$ products

The experiment was that through the moving nozzle chlorine atoms enter into the reactor at a certain distance from the zone registration where they react with excess iodide methane mixed with helium or oxygen. Changing the position of the nozzle relative to the registration area, we can change the contact time τ. So registering a change in the concentration of chlorine atoms, we can watch the kinetics of the reaction. Taking into account a possibility of the interaction of Cl atoms with reactor wall the reaction rate constant can be written in the following way :

$$\ln\frac{[Cl_0]}{[Cl(\tau)]} = k_I[CH_3I]\tau + k_w\tau.$$

Here $[Cl_0]$ – concentration of Cl when $[CH_3I] = 0$,
kw – rate of the loss of Cl atoms on the reactor wall (s^{-1}),
τ – contact time equals z/v_0 (z – distanes between point of entering Cl atoms and the registration zone , v_0 – linear velocity of the gas stream).
The results obtained are shown in Fig.3. $\ln(J_0/J)= \ln([Cl_0]/[Cl(\tau)])$.



The data in Fig. 3 results in $k_I=(0.9\pm0.15)\times10^{-11}$ $cm^3 molecule^{-1} s^{-1}$.
This value is higher than any literature data for the reaction and below we explain a possible reasons for that.

Reaction $Cl + CF_3I \rightarrow$ products

Measuring the reaction rate constant in this case was similar to that described above for the reaction of chlorine atoms with CH_3I. The data obtained are presented in Fig. 4. Using formulas

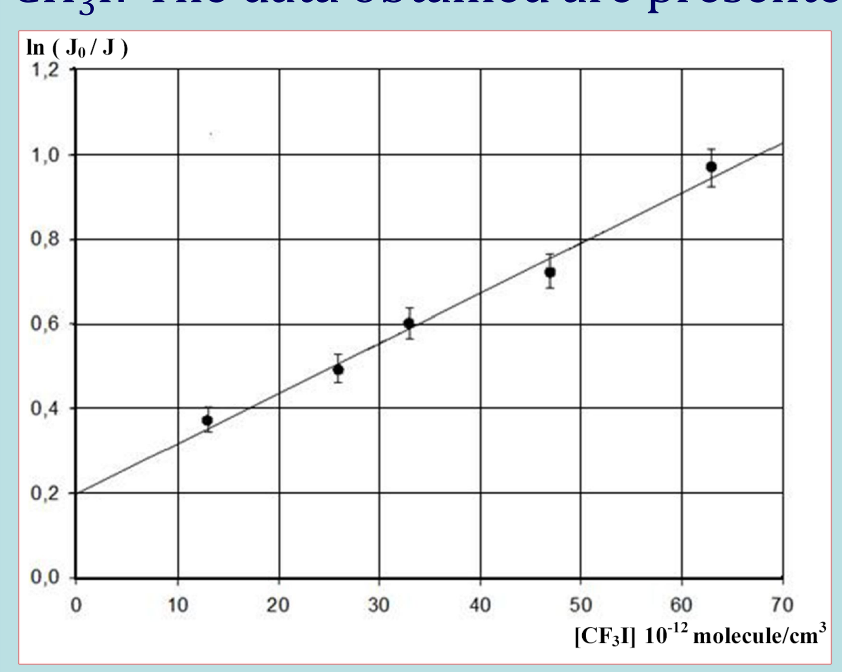


Fig. 4.

$$\ln\frac{J_0}{J} = k_{II}[CF_3I]\tau + k_w\tau$$

(all notations as above)
one can get for k_{II}

k_{II} $(7{,}4\pm0.6)\times10^{-13}$ $cm^3 molecule^{-1} s^{-1}$.

5

Reaction $Cl + C_3F_7I \rightarrow$ products

All procedure under measuring the reaction rate constant in this case was as before. Experiments run at 295 K and pressure 1.5 torr. Data obtained are presented in Fig. 5. Using these data and expression
$\ln\frac{J_0}{J} = k_{III}[C_3F_7I]\tau + k_w\tau$
one can get for k_{III}
$k_{III}=(5{,}2\pm0.3)\times10^{-12}$ $cm^3 molecule^{-1} s^{-1}$

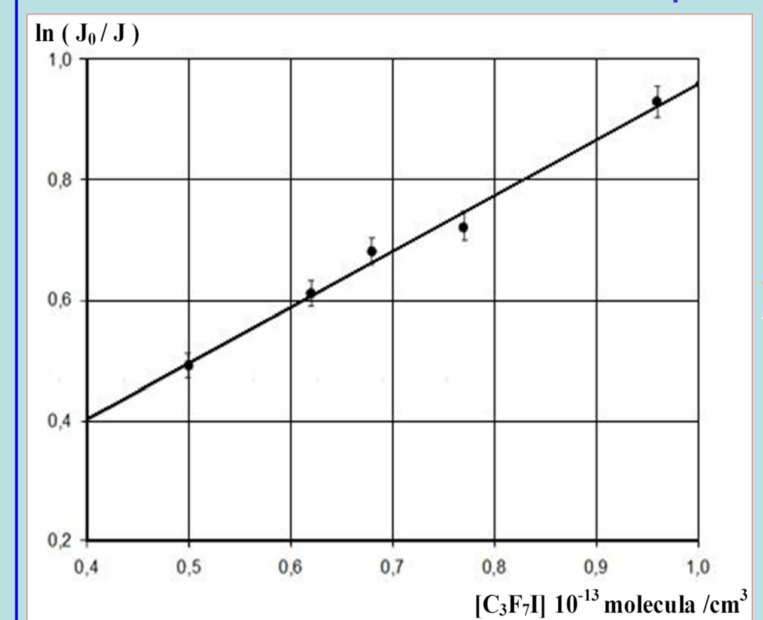


Fig. 5.

Discussion

As it was said above k_I is larger than anyone hitherto reported for the reaction of chlorine atoms with iodomethane. We assumed that reactions might take place on the reactor wall. To see whether the reaction occurs in the gas phase or on the reactor surface, we used the method suggested in the work Orkin, V.L., Khamaganov, V.G., and Larin I.K., Int.J.Chem.Kinet., 1993, vol. 25, p. 67.

It was shown that solving diffusion equation for concentration of the active particles in flow reactor with their loss in volume and on the wall, you can get the theoretical dependence $k/k_{obs}=f(\lambda^2)$ for various ratio $\alpha=k_{het}/(k_{het}+k_{hom})$, where k–real rate constant, k_{obs}–observed one, λ^2 characterizes effective rate of change of active particles concentration in the experiment, and can be found experimentally. Fig. 6 shows a dependence $k/k_{obs}=f(\lambda^2)$ for α=0-1 calculated for the conditions of the experiments described above. So α≈1 means mostly heterogeneous character of the reaction and α≈0 –homogeneous one. Points 1 in Fig. 6 relates to reaction of Cl atoms with CH_3I and points 2 and 3 - to the reaction of Cl atoms with CF_3I and C_3F_7I.

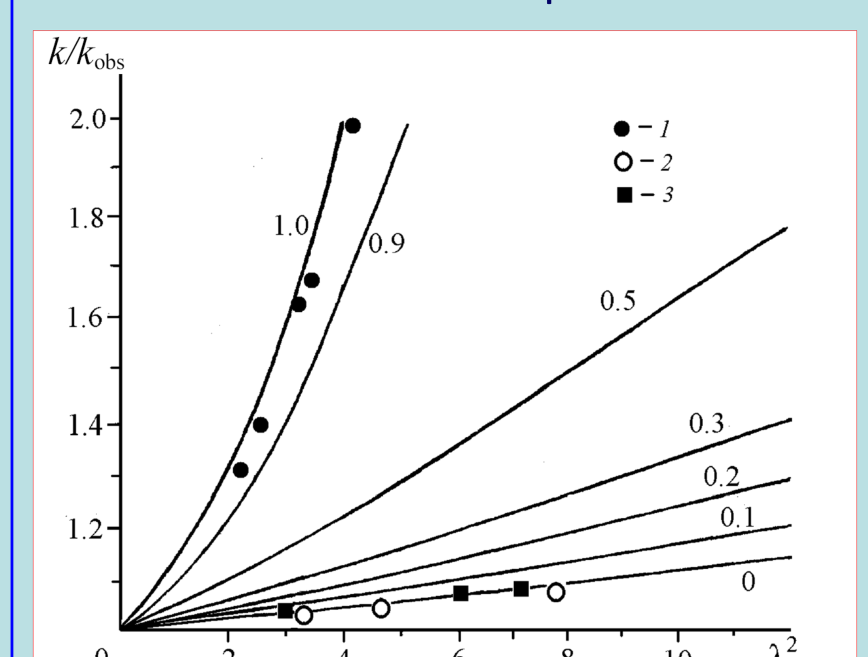


Fig. 6.

This analysis allows to conclude that under conditions of our experiments the reaction $Cl+CH_3I \rightarrow$ products run mainly on the wall and so the rate constant of the reaction characterizes just this sort of reaction.

6