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Atomic Hydrogen-Driven Halogen Extraction from Si(100): Eley-Rideal Surface Kinetics

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Abstract: The interaction of atomic hydrogen with halogen-terminated Si(100) surfaces was studied by Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD) mass spectroscopy. Efficient removal of surface halogen has been observed when the halogen-terminated Si(100) surface was exposed to atomic hydrogen at a substrate temperature, $T \leq 630$ K. The reaction rate constants for halogen extraction on the Si(100) surface follow the trend $k_I > k_{Br} > k_{Cl}$. In addition, the halogen extraction kinetics are found to be first order in both the surface coverage of halogen and in the atomic hydrogen flux. Studies of the temperature dependence of the halogen extraction rate show the activation energies for the extraction of Cl and Br are 2.1 ± 0.2 and 1.6 ± 0.2 kcal mol^{-1}, respectively. The extremely low activation energy for the reaction demonstrates that the H-extraction process follows an Eley-Rideal reaction mechanism where the surface reaction is mainly driven by the high internal energy of incident atomic hydrogen instead of thermal excitation from the Si(100) solid surface.

I. Introduction

Surface chemical processes on silicon surfaces often occur as a result of the thermally activated decomposition and/or desorption of adsorbates. An alternate method to induce surface chemistry is to use an active gas-phase species containing either excess kinetic or internal energy, producing surface reactions which occur via pathways not accessible by thermally accommodated adsorbates. Atomic hydrogen is a promising reactant for this type of surface chemical reaction due to its excess potential energy (52 kcal mol^{-1} compared to $^1/_2H_2(g)$). Recently, the abstraction of adsorbates induced by incoming H atoms from the gas phase has been reported on both metal and semiconductor surfaces.[1-6] These observations suggest that a new class of surface chemical reaction may be initiated using the high internal energy of hydrogen atoms. This paper is concerned with the abstraction of halogen adsorbate atoms using atomic hydrogen.

Surface chemistry involving both hydrogen and halogen species on Si has been addressed in connection with the epitaxial growth of silicon via chemical vapor deposition (CVD) using, for example, halosilanes and hydrogen: $SiX_4 + 2H_2 \rightarrow Si + 4HX$.[7,8] The *individual* interactions of H and halogen molecules with the Si(100) surface have been studied using various surface science techniques.[9-16] Surface reactions of these adsorbates with Si substrates are likely to produce volatile silicon-containing species at elevated temperatures due to the formation of strong covalent bonds with silicon. In CVD processes, the reactions of atoms or radical species with surfaces must also be considered. The present work is thus directed toward the study of surface reactions using gas-phase hydrogen atoms as one of the reactants. In this paper it will be demonstrated that the abstraction of halogen adsorbates from the Si(100) surface can be efficiently induced by incident atomic hydrogen from the gas phase. Halogen abstraction by atomic H occurs essentially without thermal accommodation of the atomic H on the surface. Since thermal activation from the solid surface is of minor importance for the removal of halogen by atomic H, the H-induced extraction reaction may also provide new approaches for the production of epitaxial thin films at low substrate temperatures.

In this study, the measurement of halogen extraction has been made by Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD) mass spectroscopy. The results indicate that removal of surface halogen is quite effective at low Si(100) substrate temperatures, where temperatures as low as 300 K have been employed. The reaction rate constants of atomic H-induced halogen extraction on the Si(100) surface follow the trend $k_I > k_{Br} > k_{Cl}$. In addition, the reaction kinetics are first order in both the surface coverage of halogen and in the atomic hydrogen flux. Studies of the temperature dependence of the reaction rate for Br and Cl show the activation energy for the extraction process is 1.6 ± 0.2 and 2.1 ± 0.2 kcal mol^{-1}, respectively. The extremely low activation energy for the reaction demonstrates that the H-extraction process follows an Eley-Rideal (ER) reaction mechanism,[1-5,17] where the surface reaction is mainly driven by the high internal energy of atomic hydrogen instead of by the thermal excitation from the Si(100) solid surface.

II. Experimental Section

The ultrahigh vacuum system (with a base pressure of 1×10^{-10} Torr) and Si(100) crystal preparation have been described previously;[10,18,19]

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selected aspects will be summarized here. The system is equipped with Auger electron spectroscopy (AES), an argon ion sputtering gun, a collimated and calibrated microcapillary array doser,[18] and a multiplexed quadrupole mass spectrometer (QMS) with capabilities for both random flux and line-of-sight detection.[20] Heating of the Si(100) crystal (15 × 15 × 1.5 mm; p-type; B-doped; 10 Ω·cm) is provided by a Honeywell programmable temperature controller used to drive a feedback circuit to control the power to the crystal.[21]

For the adsorption of molecular species, a calibrated multicapillary doser was used to deliver the gas molecules onto the Si(100) surface, giving carefully controlled absolute adsorbate exposures.[18] For dosing of H atoms onto the prepared surface, a tungsten-spiral filament (wire diameter = 0.25 mm; spiral radius = 1 cm, T = 1800 K) with line-of-sight exposure to the crystal surface was used to produce atomic hydrogen during H_2 exposure. The characteristics of molecular hydrogen dissociation by a hot tungsten filament have been examined previously.[22,23] The atomization rate of molecular hydrogen on a hot tungsten filament (T = 1800 K) is linearly dependent on the H_2 pressure at $P(H_2) < 1 \times 10^{-6}$ Torr.[22,23] However, owing to the uncertainties in determining the absolute flux of atomic hydrogen, the exposures of atomic hydrogen are given by the H_2 exposures in Langmuir (L) [1 L = 10^{-6} Torr·s], uncorrected for ion gauge sensitivity.

Surface cleanliness and the relative surface coverages of the adsorbed halogens were measured by AES. All the AES data reported here were obtained by averaging at four or more positions on the prepared surface. However, an electron stimulated desorption (ESD) effect was observable during AES measurements (electron beam energy = 3 kV; crystal current = 3.0 μA) for all the halogen adsorbates studied in this work. Since the ESD cross sections for all three halogen adsorbates are independent of coverages (as measured by ourselves), all AES measurements were made using a standardized time schedule instead of extrapolating the AES signal to that at Auger measurement time zero. This procedure permits accurate measurements of the relative rates of halogen abstraction by atomic hydrogen.

TPD measurements were made with a shielded, differentially pumped quadrupole mass spectrometer (QMS). Data acquisition with the multiplexed QMS has been described previously.[19] The QMS was equipped with a small conical, axially oriented aperture (diameter = 5 mm), for efficient collection of desorbing species from the center of the crystal. During line-of-sight desorption measurements, the crystal was accurately and reproducibly placed 2 mm away from the aperture. In addition, the aperture was negatively biased (−100 V) to prevent spurious electrons from escaping from the mass spectrometer (electron energy = 70 eV) which could possibly cause electron-stimulated effects on the prepared surface.

The Cl- and Br-terminated Si(100) surfaces were prepared by chemisorption of molecular chlorine and bromine onto the Si(100) surface at $T \leq 300$ K, while the I-terminated surface was prepared by chemisorption of methyl iodide at room temperature. The research grade bromine (99.95%) and methyl iodide (99+%) were further purified by numerous freeze–pump–thaw cycles, and the chlorine (99.999%) and hydrogen (99.9995%) were used directly. No contamination of the gases was observed with mass spectrometry.

III. Results and Discussion

Dissociative adsorption of halogen molecules or halogen-containing species on the Si(100)–(2 × 1) surface, followed by the evolution of silicon halide species via thermal excitation, has been studied[12,13,16] and reinvestigated by our group.[10,11] At halogen coverages ≤1 ML, thermal desorption of halogens and/or silicon halides are only observable at $T \geq 700$ K. However, at halogen coverages higher than 1 mL, evolution of silicon halides can be detected at desorption temperatures lower than 700 K. To avoid the chemical complexity possibly introduced at halogen coverages >1 ML, all the following experiments were performed at coverages ≤1 ML, and dosing of atomic H onto the prepared surfaces was carried out at Si(100) substrate temperatures ≤630 K. Thorough studies have been done on all three halogen adsorbates, but mainly the results with bromine will be shown here for the purpose of clarity.

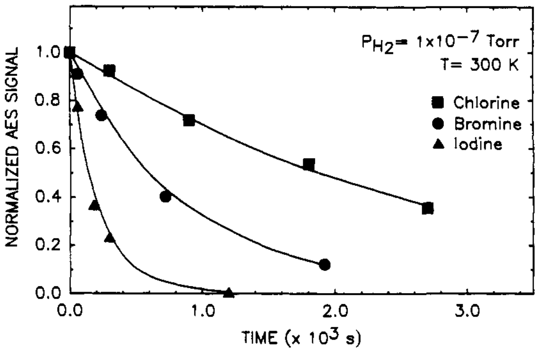

Figure 1. Depletion of three different halogen adsorbates on the Si(100) surface by atomic hydrogen at 300 K. The H_2 pressure was kept constant (1×10^{-7} Torr) throughout the experiments. The solid lines are calculated based on the first-order rate law discussed in the text.

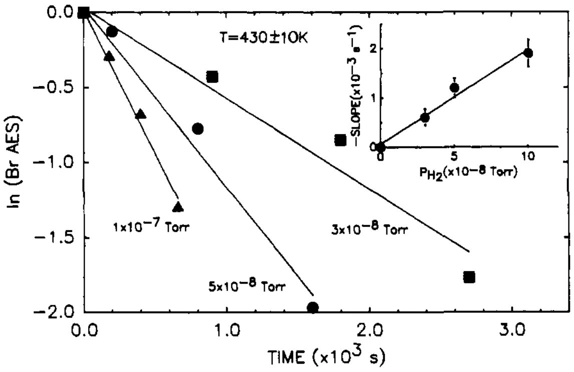

Figure 2. The dependence of bromine extraction rate on the atomic hydrogen flux, F_H, which is expressed in terms of H_2 pressure $P(H_2)$. The main figure is a semilogarithmic plot of the fractional coverage of Br versus reaction time with T = 430 K and at three different $P(H_2)$. The inset shows the linear relationship between the Br extraction rate and H_2 pressure.

Data for the extraction of adsorbed halogen species on Si(100) by atomic hydrogen at 300 K are shown in Figure 1. The experiments were performed by using the same H flux (the same H_2 pressure and W filament temperature during dosing), so the relative extraction reaction rate constant, k, for different halogen adsorbates can be obtained. The AES spectra were taken after each H exposure. The characteristic AES signals used for data analysis are Cl(LMM) at 181 eV, Br(MNN) at 55 eV, and I(MNN) at 511 eV. The intensities of all AES signals are normalized to the intensity at zero reaction time, and, therefore, each data point represents the relative surface coverage at reaction time t.

Two important features may be seen in Figure 1. First, the exponential behavior of halogen removal, as shown by the fitted solid lines in Figure 1, indicates that the extraction process is first order in the surface coverage of halogen, θ, based on simple chemical reaction kinetics

$$R = -\mathrm{d}\theta/\mathrm{d}t = k(F_H)^n\theta \quad (1)$$

or

$$\theta_t = \theta_0 \exp[-k(F_H)^n t] \quad (2)$$

where R is the reaction rate, θ is the fractional coverage of halogen species on the surface, k is the rate constant for the extraction reaction, F_H is the flux of the hydrogen atoms impinging onto the surface, and n is the order of dependence of reaction rate on F_H, which will be shown to be unity later in this paper. As shown from eq 2, a constant F_H yields an exponential decay of halogen coverage with respect to reaction time for first-order reaction kinetics in the surface halogen coverage. A second observation from Figure 1 is that the rate of halogen extraction on the Si(100) surface follows the trend $k_I > k_{Br} > k_{Cl}$, and analysis of the data

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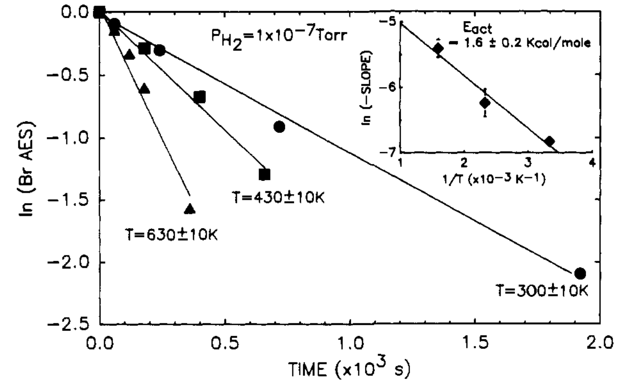

Figure 3. The dependence of bromine extraction rate on the Si(100) substrate temperature. The main figure is a semilogarithmic plot of the fractional coverage of Br versus reaction time with $P(H_2) = 1 \times 10^{-7}$ Torr and three different substrate temperatures. The inset is the Arrhenius plot for the extraction reaction which gives an $E_{act} = 1.6 \pm 0.2$ kcal mol^{-1}.

based on the first-order reaction kinetics (eq 1 and 2) gives the relative reaction rates at 300 K for the three adsorbates: $k_I = 5.0k_{Br} = 12.4k_{Cl}$. A similar trend has also been observed from the gas-phase studies for the reaction of atomic H with methyl halides.[24,25]

The dependence of extraction rate on the atomic hydrogen flux, F_H, was studied by observing the changes in reaction rate while varying the H_2 pressure, $P(H_2)$, during H dosing at constant substrate temperature. Figure 2 shows the effect of H_2 pressure on the bromine extraction rate at a constant Si(100) substrate temperature of 430 ± 10 K. The results are shown in a semilogarithmic plot of the fractional coverage of the adsorbate versus reaction time. With a constant F_H, the semilogarithmic plot gives a straight line with a slope which is proportional to the negative of the rate constant k, and the proportionality depends on the reaction order, n, of the atomic hydrogen flux, F_H. The straight line fits at each different H_2 pressure are a result of fitting using the least-squares method. As seen in Figure 2, the extraction rate linearly increases with increasing H_2 pressure and hence with F_H.[22,23] Therefore, as shown in the inset of Figure 2, the linear dependence of extraction rate on $P(H_2)$ gives direct evidence for the first-order dependence of the extraction rate on the flux of atomic hydrogen. The same results were also obtained for the Cl- and I-terminated Si(100) surfaces. The H-induced halogen extraction reaction is thus first order in both the surface coverage of the halogen adsorbate and the flux of atomic hydrogen.

The effect of crystal temperature on the halogen extraction rate was also studied. The data shown in Figure 3 are presented as a semilogarithmic plot of the fractional coverage of bromine versus reaction time, and the negative of the slope of each plot obtained at different temperature is proportional to the corresponding reaction rate constant, k. The temperature dependence of the bromine extraction rate can therefore be determined from the slopes obtained at different substrate temperatures. The small increase in the extraction rate with a large increase in Si(100) substrate temperature indicates that a low activation energy is involved in the extraction process.

The activation energy via the thermal excitation of the solid surface has been estimated from the temperature dependence of the rate constant, k, assuming the atomic H-driven halogen extraction reaction rate follows Arrhenius kinetics. Analysis of the Arrhenius plot (as shown in the inset of Figure 3) gives $E_{act} = 1.6 \pm 0.2$ kcal mol^{-1} for the H-induced extraction of bromine from the Si(100) surface. Similar studies with chlorine gave $E_{act} = 2.1 \pm 0.2$ kcal mol^{-1}. The temperature dependence of the iodine extraction rate was not studied here because of the unknown chemical effect from the co-adsorbed CH_x species left on the surface after the adsorption of CH_3I. The observed low activation energies for the extraction process (1.6–2.1 kcal mol^{-1}) indicate that the thermal excitation of the Si(100) surface is of minor importance in determining the halogen extraction rate.

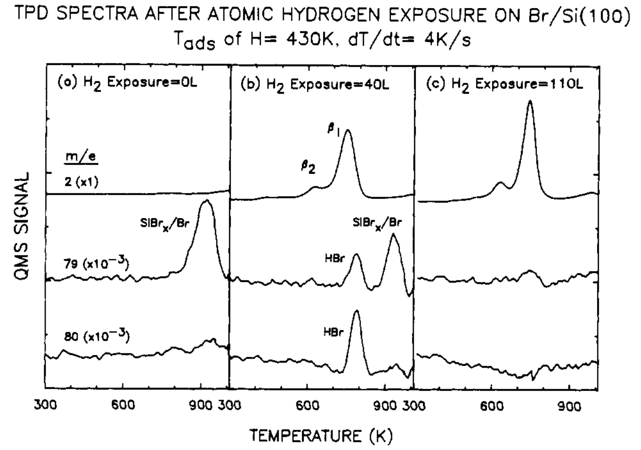

Figure 4. Series of TPD spectra taken after the Br-terminated Si(100) was exposed to different atomic hydrogen exposures at a substrate temperature of 430 K. The spectra were taken with a heating rate of 4 K s^{-1}.

Removal of the halogen adsorbate from the Si(100) surface could occur according to two different surface reaction mechanisms involving attack by atomic H: mechanism 1, halogen extraction by formation and desorption of hydrogen halides; mechanism 2, etching of the halogen-terminated Si(100) surface via the formation of halogen-substituted silane compounds.

Although we are not able to directly identify the H-induced reaction products in this apparatus during exposure to atomic H, mechanism 1 is favored for the following reasons.

(1) Etching of the Si(100) surface by atomic hydrogen is known to be more efficient at low temperatures (maximum rate observed in the temperature range of 320–360 K)[26-28] and high hydrogen coverages.[9,26-29] This is due to the need to achieve high hydrogen coverages to cause the breaking of the Si–Si bonds and the formation of higher surface hydrides, SiH_2 and SiH_3. However, studies of the temperature dependence of the halogen extraction rate (see Figure 3) show an opposite dependence on temperature. Therefore, a different reaction mechanism from the silicon etching process has to be responsible for the H-induced extraction of halogen.

(2) The first-order reaction kinetics in both the surface coverage of halogen and the atomic hydrogen flux indicates that the stoichiometry of the reaction intermediate in the rate-determining step must have a 1:1 ratio of hydrogen to halogen. On the other hand, for the removal of halogen via the formation of a halosilane (SiH_3X), more complicated chemical kinetics may be expected.

The slight effect of thermal excitation of the Si(100) surface on the removal rate of halogen by atomic hydrogen means that the driving force for halogen extraction must reside in the high internal energy of atomic hydrogen. As a matter of fact, mechanism 1 is the so called Eley–Rideal (ER) mechanism, where one of the reactants enters the transition state directly from the gas phase without equilibrating at the surface prior to reaction. The ER reaction mechanism has been known for atomic H-induced surface reactions on metal substrates[3-5,17] and was also proposed recently for H-atom-induced desorption of H_2 from the monohydride phase of Si(100).[1,2] A recent study[5] of the extraction of Cl adsorbed on the Au(111) surface by atomic hydrogen, using resonance enhanced multiphoton ionization (REMPI) laser spectroscopy and molecular beam scattering techniques, detected the production of HCl in its first vibrational excited level ($v = 1$), and this product is evolved with an $E_{act} = 1.6$ kcal mol^{-1}. The low activation energy resembles our results for the H-atom ex-

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traction of halogens from Si(100).

Further support for the ER reaction mechanism comes from investigations using TPD mass spectroscopy. These studies help differentiate various desorption products as a result of different surface reactions, generally under equilibrium conditions. Figure 4 shows series of TPD spectra taken after the Br-terminated Si(100) was exposed to different atomic hydrogen exposures at a substrate temperature of 430 K. Figure 4a shows the results of the thermal desorption for Br/Si(100) without exposing the prepared surface to the atomic hydrogen. The only detectable desorption products are $SiBr_x$ and/or Br.[11] With a medium H exposure on the same prepared Br/Si(100) surface, the corresponding TPD spectra (Figure 4b) show the desorption of HBr,[30] in addition to the desorption of β_2-H_2, β_1-H_2,[9] $SiBr_x$, and/or Br. Notice that the temperature-programmed desorption of HBr is only observable in the temperature range of the β_1-H_2 desorption from the monohydride phase of Si(100), above 720 K. With a high atomic H exposure, the prepared Si(100) surface then becomes almost free of bromine as a result of the extraction process (see Figure 3), and the corresponding TPD spectra (Figure 4c) show mainly the β_2- and β_1-H_2 desorption.

Thermal desorption of HBr occurring in the same temperature range of the monohydride β_1-H_2 desorption provides important information relevant to the H-induced extraction reaction. First of all, no desorption of HBr under thermal equilibrium conditions is observed in the temperature range from 300 to 720 K. Similar results have also been observed for other halogen adsorbates.[10,11] *This indicates that this efficient removal of halogen adsorbates by atomic hydrogen at $T \leq 720$ K cannot be explained as a result of thermal desorption of the hydrogen halide under equilibrium conditions.* In the other words, during the extraction process, the incoming hydrogen atom is not thermally accommodated on the surface before reacting with the surface halogen adsorbate, and the extraction reaction therefore occurs at low temperatures where the Langmuir–Hinshelwood process $H(a) + X(a) \rightarrow HX(g)$ does not occur. Secondly, the temperature range of HBr thermal desorption is nearly coincident with that of β_1-H_2 desorption from the monohydride phase, suggesting that excitation of the monohydride Si–H bond is required for the desorption of HBr in this second surface reaction channel.

IV. Conclusions

A surface reaction driven by collisions with gas-phase atomic hydrogen has been demonstrated on the halogen-terminated Si(100) surfaces. The extraction of adsorbed halogens on the Si(100) surface by atomic hydrogen has been shown to proceed via an Eley–Rideal reaction mechanism. The extraction kinetics are found to be first order in both the surface coverage of halogen and in the atomic hydrogen flux. In addition, the reaction rate constants follow the trend $k_I > k_{Br} > k_{Cl}$. The extremely low activation energy (1.6 – 2.1 kcal mol^{-1}) for the extraction process indicates that the thermal excitation of the Si(100) solid surface is of minor importance in controlling the halogen extraction kinetics.

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Registry No. Si, 7440-21-3; H, 12385-13-6; I_2, 7553-56-2; Br_2, 7726-95-6; Cl_2, 7782-50-5; HI, 10034-85-2; HBr, 10035-10-6; HCl, 7647-01-0.

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(30) Desorption of HBr is confirmed by comparing the mass spectrometer fragmentation ratio, Br^+ ($m/e = 79$)/HBr^+ ($m/e = 80$). Our measurements from the results of TPD show the ratio of $Br^+/HBr^+ \simeq 0.50$, which is in good agreement with the value from the literature (0.45 is obtained from: *Atlas of Mass Spectral Data*; Stenhagen, E., Abrahamsson, S., McLafferty, F. W., Eds.; Interscience: New York, 1969; Vol. I, p 104).

A New Type of Oxyhalogen Oscillator: The Bromite–Iodide Reaction in a Continuous Flow Reactor[1]

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Abstract: The reaction between bromite and iodide ions in a flow reactor shows two steady states and sustained oscillations in pH, redox potential, and $[I^-]$. The oscillatory behavior is extremely sensitive to the inflow ratio $[BrO_2^-]/[I^-]$, the flow rate, the initial pH of the input solutions, and the stirring rate. Batch experiments suggest that the system behaves in several respects like the analogous chlorite–iodide oscillator. The bromite–iodide system, however, is also a pH oscillator and is the first oxyhalogen oscillator to oscillate in the neutral and basic pH range.

Introduction

Chemical reactions involving halogen species have played a dominant role in the study of homogeneous liquid-phase oscillating chemical reactions. The first discoveries of periodic behavior in chemical solutions of nonbiological origin, the Bray[2] and Belousov–Zhabotinskii[3] (BZ) reactions, occurred with reactions of iodate and bromate, respectively. With the exception of the highly unstable OX^- and $OX^\cdot$ species, halogen and oxyhalogen species with every existing oxidation state from −1 to +7 have been utilized as starting reagents in chemical oscillators.

Among the oxyhalogen-based oscillators, bromate and chlorite ions have played particularly central roles. Bromate is the key species in the Belousov–Zhabotinskii reaction, undoubtedly the most familiar and most widely studied of the chemical oscillators. It also serves as the starting point for many other oscillating reactions, most of which may be thought of as derived from the "minimal bromate oscillator",[4] which consists of bromate, bromide, and a metal catalyst in a continuous flow reactor (CSTR). Chlorite ion was used in the first deliberately designed chemical

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