

Displacement of Metal Atoms from Salts by Hydrogen and the Role of This Reaction in Chain Processes

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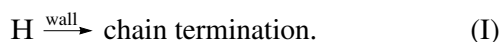
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Abstract—The interaction of hydrogen atoms with a variety of alkali metal and alkaline-earth metal salts results not only in the recombination of these atoms but also in the displacement, into the gas phase, of free radicals ($\text{CaCl}^*(A^1P_{1/2}, B^2S^+)$ and $\text{CaF}^*(A^2P)$) and metal atoms, including their excited species, which are detected spectroscopically. Transmission spectra indicate that the NaCl surface undergoes metallization when treated with a high-frequency discharge and a rarefied hydrogen flame. Combustion is affected by the gas-phase hydrogen atoms involved in the chain reaction and by the varying composition and properties of the surface. The concentration of Na atoms over the NaCl surface at 770 K is 10^9 – 10^{11} cm^{-3} in a stream of H atoms at 1 Torr and in the $2\text{H}_2 + \text{O}_2$ flame at 4 Torr. The concentration of sodium atoms in the $^2P_{3/2}$ and $^2P_{1/2}$ excited states is $\sim 5 \times 10^6$ – $5 \times 10^8 \text{ cm}^{-3}$. The role of the discovered reactions in combustion, pyrolysis, and plasma chemistry is discussed.

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Reaction mixtures containing free atoms and radicals are usually in contact with solid surfaces' such as reactor walls, the surface of the solids placed into the reactor for some purpose, and the surface of the solid reaction products (which are often dispersed in the reaction volume). For a long time, the heterogeneous reactions of atoms and radicals in chain processes were commonly viewed as recombination or even as



Although heterogeneous chain propagation in unbranched-chain and degenerate branched-chain reactions were admitted by Semenov [1], these reactions have never been included in reaction networks or taken into consideration in data processing. The properties and functions of the surface have been assumed to be invariable.

However, it was established by kinetic analysis and spectroscopic studies (see [2] and later publications in this area, e.g., [3–8]) that, in developed chain combustion, part of the adsorbed atoms react with molecular gas-phase components and thus participate in chain propagation. For example, it was directly demonstrated that, at the $\text{H}_2 + \text{O}_2$ combustion temperature, adsorbed hydrogen atoms react with gas-phase dioxygen and the rate of this heterogeneous reaction is close to the combustion rate [4, 5]. Furthermore, the adsorbed atoms and atomic groups whose reactions with gas-phase components determine combustion kinetics were directly identified [6]. It was demonstrated by IR emission spectroscopy that the deuterium–oxygen flame in a reactor whose walls are covered with adsorbed hydro-

gen atoms contains H_2O_2 and H_2O [9]. The formation of these compounds, as well as the lowering of the first autoignition limit of the D_2 – O_2 mixture in the presence of adsorbed H atoms, is due to heterogeneous chain propagation, whose initial step is the observed reaction between adsorbed hydrogen atoms and gas-phase O_2 . These results are in good agreement with the data reported in [3, 4]. The changes caused by this type of reaction in the properties of the surface and in the role of the surface in the chain process are reversible. Therefore, if the experiment is performed with due carefulness and the experimental procedure and process conditions are invariable, the measurements will be quantitatively reproducible. At the same time, as was demonstrated by spectroscopic and chemical methods, the reactions between hydrogen atoms and the surface often result in metal atoms passing to the gas phase, as in the case of the combustion of H_2 with O_2 over NaCl or KCl [9]. Obviously, these heterogeneous reactions are irreversible. They cause other “anomalies” in H_2 combustion, including the termination of combustion at pressures slightly above the first autoignition limit (P_1), even though the reactant concentrations are still above the limiting values measured in the same experiments [10]. As is demonstrated below, the alkali metal causes spatial chain termination, and that is why alkali metal salts are effective in fire fighting [11].

The mechanism of the formation of metal atoms in the ground and excited states upon the interaction between the chain process and salt surface has not been elucidated as of yet. It was assumed in an earlier study

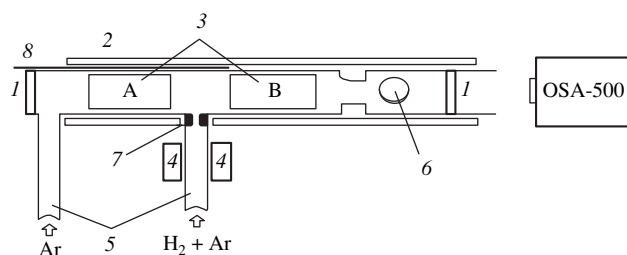
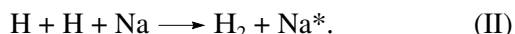


Fig. 1. Schematic of reactor I: (1) optical window, (2) heater, (3) lined cylinder, (4) high-frequency discharger, (5) gas inlet, (6) vacuum branch, (7) nozzle, and (8) thermocouple.

[12] that the reaction yielding excited sodium atoms in the combustion space is



However, below we present data demonstrating that this mechanism cannot account for the observed phenomenon. The surface excitation of atoms has not been considered in the literature.

The purpose of this study is to see whether metal atoms can be forced out of other salts, including salts with divalent anions. Furthermore, we will estimate the concentration of displaced metal atoms in the combustion of hydrogen over a NaCl surface. The mechanism and role of this reaction in the chain process will be discussed.

EXPERIMENTAL

Measurements were performed in a vacuum setup [9] under static and jet flow conditions at mixture pressures of 0.5 to 10 Torr and temperatures of 460 to 850 K. Reactor I (Fig. 1) was a furnace-heated quartz cylinder of diameter 4 cm and length 30 cm containing a thin-walled quartz cylinder with an outer diameter of 3.9 cm and length of 4 cm. A salt was deposited from its solution onto the inner surface of the smaller cylinder, or a single crystal of the salt was placed in the cylinder. The design of reactor I allowed the position of this cylinder relative to the side inlet to be varied when it was required to choose the homogeneous or heterogeneous channel of the interaction between the salt and gas-phase atoms [9]. The pressure limit P_1 was measured in reactor II, which was 3.5 cm in diameter and 20 cm in length. A salt was deposited from aqueous solution onto the inner surface of this reactor, and the reactor was then pumped. Both a stoichiometric $\text{H}_2 + \text{O}_2$ flame and a high-frequency discharge generated in an $\text{H}_2 + \text{Ar}$ mixture were used to produce hydrogen atoms. Radiation from electronically excited species was detected with an OSA-500 optical spectroscopic analyzer. Reactions were conducted in the 3% $\text{H}_2 + \text{Ar}$ mixture and in the stoichiometric mixture $2\text{H}_2 + \text{O}_2$. Hydrogen, oxygen, and argon were reagent grade, and the salts NaCl, NaF, Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7$, Na_2SO_4 ,

NaNO_3 , KCl, KBr, CsI, CaCl_2 , and CaF_2 were special-purity grade. Spectra were studied using optical NaCl, KBr, and CsI single crystals (Perkin-Elmer). Excited Na, K, and Cs atoms were detected as radiation at 589, 766.5 and 770, and 852 nm, respectively. Na atoms in the ground state were detected by atomic absorption spectroscopy using a sodium lamp (589 nm). Gas pressure in the reaction zone was measured with a VDG-1 sensor. The reactor was pumped to 5×10^{-3} Torr using a 2-RVN-5D fore pump. Residual pressure was measured with a VIT-2 vacuum gauge. Gas flow rates were controlled with RRG-1 flow regulators.

RESULTS AND DISCUSSION

According to emission spectroscopic data, hydrogen atoms generated both in the high-frequency discharge and in the $2\text{H}_2 + \text{O}_2$ flame react with alkali and alkaline-earth metal salts to yield metal atoms in the gas phase. In some cases, we detected the excited species CaCl^* ($A^1P_{1/2} - X^2S^+$ at $\lambda = 625\text{--}610$ nm and $B^2S^+ - X^2S^+$ at $\lambda = 600\text{--}590$ nm) and CaF^* ($A^2P - X^2S^+$ at $\lambda = 629\text{--}590$ nm), which were identified by their vibronic structures [13]. Thus, hydrogen atoms not only recombine but also displace metal atoms and acid residues.

The signals from divalent fragments are several times more intense than the signals from alkali metals. When the cylinder is placed downstream of the side inlet, the radiation from the excited metal atoms is 7–10 times as intense as in the case when the flowing H atoms do not pass through the cylinder. Therefore, the observed radiation is mainly due to heterogeneous reactions between hydrogen atoms and the salt surface rather than homogeneous reactions. This is also indicated by the fact that the slope of the Arrhenius plot of the logarithm of integrated radiation intensity (ϵ) is 2–3 times smaller for a metal than for the vapor of its salt.

The value of ϵ is much larger for an NaCl single crystal than for NaCl powder. Therefore, the smaller the amount of defects on the crystal surface, the stronger the temperature dependence of radiation intensity.

The concentration of emitting Na^* species was estimated using the relationship

$$E \approx \int_V \{S n_0(x, y, z) / R^2(x, y, z)\} dV(x, y, z), \quad (1)$$

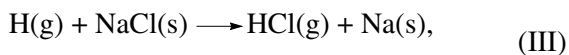
where the integrand is the fraction of radiation that is emitted by the volume element dV and gets into the entrance slit of area S , R is the distance between this volume element and the entrance slit, and n_0 is the number of emitting species in this volume element per second.

The mean value of n_0 was estimated taking into account that the sensitivity of the OSA-500 instrument is 2400 quanta per count. R_m was 33 cm and S was 0.015 cm^2 . The mean E value was estimated from the

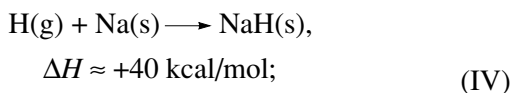
observed mean intensity of the Na *D*-line, which was ~20 counts for the NaCl surface in a 3% H₂ + Ar stream at 0.7 Torr and ~2000 counts for the 2H₂ + O₂ flame at 6 Torr (data were accumulated over 32 ms at 770 K). For these values, Eq. (1) gives Na* concentrations of ~5 × 10⁶ and ~5 × 10⁸ cm⁻³ for H atoms from the gas discharge and flame, respectively.

The spatial distribution of the intensity of sodium *D*-line emission from the end of reactor I in contact with flowing H atoms was studied, and it was found that the radiation is mainly localized at the reactor walls. Therefore, the excited sodium atoms are knocked out of the solid surface. Furthermore, when gas-discharge H atoms react with the salt surface, the intensity of the Na* signal decreases by one order of magnitude as the total pressure is increased from 1 to 2 Torr, although all of the H₂ is dissociated at these pressures. This finding and the localization of radiation at the salt surface indicate that reaction (II) [12] cannot account for the appearance of sodium atoms in the reactor space. Indeed, the rate of this reaction must increase in proportion to squared gas-discharge pressure, while the deactivation rate decreases linearly with increasing pressure.

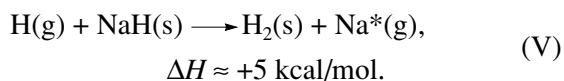
Obviously, the transfer of Na atoms to the reactor space must change the composition and properties of the salt surface. Electron- and photon-stimulated desorption from NaCl and KCl surfaces was studied [14, 15], and it was demonstrated that, if the energy of the bombarding particles exceeds the band gap of the crystal, halogen atoms will pass to the gas phase, resulting in a partially metallized surface even at room temperature. Based on the above results, the desorption data [14, 15], and the thermochemistry of the reaction [16], the mechanism of the excitation of sodium atoms can be represented as



$$\Delta H \approx +10 \text{ kcal/mol};$$



$$\Delta H \approx +40 \text{ kcal/mol};$$



$$\Delta H \approx +5 \text{ kcal/mol}.$$

Our Na* emission intensity data calculated as a function of total pressure are in agreement with this mechanism.

Thus, the above data suggest that, entering into a heterogeneous reaction with gas-phase atoms, the surface can emit atoms in both ground and excited states.

Upon long-term treatment with H atoms generated in the gas discharge or hydrogen flame, the surface of NaCl turns violet, indicating that it changes its composition during hydrogen combustion. In air, the color disappears in a few tens of seconds. The absorption spectrum of a NaCl single crystal colored by a hydrogen

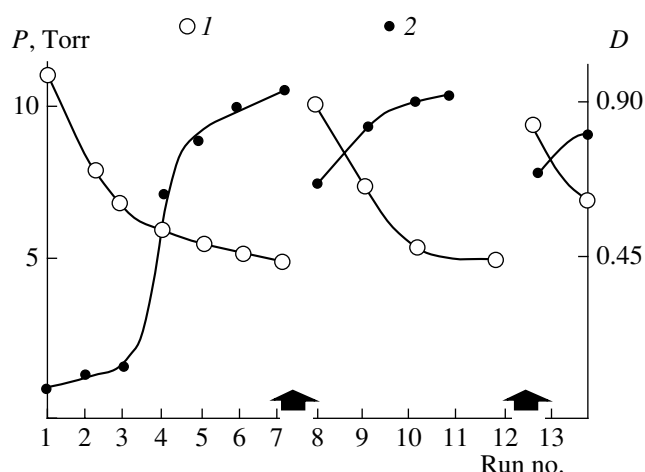


Fig. 2. Variation of (1) the autoignition pressure of the 2H₂ + O₂ mixture (*P*) and (2) the absorbance due to the sodium atoms (*D*) under jet flow conditions (gas flow rate 0.2 cm³/min). The points represent data obtained after successive 10-s flame treatments of the surface, and the arrows mark the admission of atmospheric air into the reactor followed by pumping to 5 × 10⁻³ Torr. The first point refers to the fresh NaCl surface. *T* = 770 K.

flame shows a band at 654–606 nm due to sodium clusters with a characteristic size of 45–70 nm [17]. This finding is evidence of surface metallization and is in agreement with stimulated desorption data [14, 15].

The concentration of Na atoms in the ground state was determined by the discrete absorption method [18] as applied to the measurement of sodium vapor pressure [19]. At 770 K, the concentration of sodium atoms over the NaCl surface was ~10⁹ cm⁻³ for the 3% H₂ + Ar stream at 0.7 Torr and ~10¹¹ cm⁻³ for the 2H₂ + O₂ flame at 6 Torr. These concentrations indicate that a considerable proportion of H atoms react with the surface to displace metal atoms into the gas phase. In essence, this process is the loss of active species, because the displaced metal atoms do not participate in chain propagation.

According to our measurements, the minimum autoignition pressure of the 2H₂ + O₂ mixture flowing over an initially fresh salt surface decreases progressively with each admission of the combustible mixture and can be reversibly increased by admitting air followed by pumping reactor I (Fig. 2), as in the case of static combustion. This flame treatment of the surface raises the concentration of Na atoms, indicating an increase in the degree of surface metallization. As is clear from Fig. 2, the rate of the heterogeneous loss of active species is lower on the flame-treated surface than on the air-treated surface. This may be due to the direct substitution reaction $\text{H(g)} + \text{NaH(s)} \longrightarrow \text{HNa(s)} + \text{H(g)}$, which is not a chain termination step. Upon the admission of humid air, the metallized surface reacts

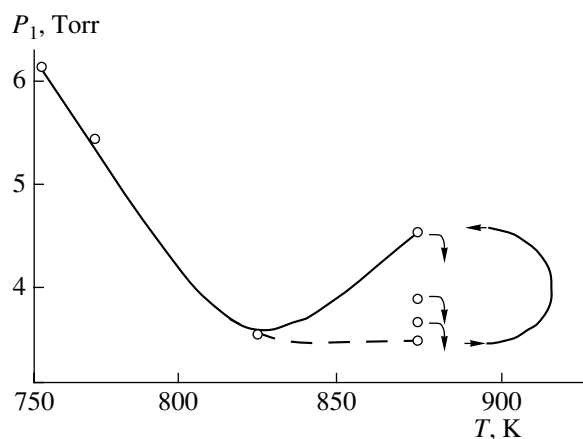
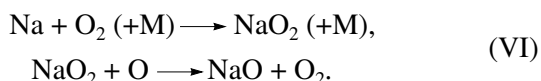


Fig. 3. Temperature dependence of P_1 under static conditions for autoignition over the NaCl surface. The vertical arrows show the decrease in P_1 caused by 10-min flame treatments of the surface for the 3% H_2 + Ar mixture at 2 Torr. The horizontal arrows show the increase in P_1 caused by a single admission of atmospheric air followed by pumping to 5×10^{-3} Torr.

with water vapor to yield NaOH, whose chain-terminating effect is strong.

A similar situation is observed under static conditions (reactor II). The temperature dependence of P_1 for this reactor is plotted in Fig. 3. The fact that P_1 increases with temperature is usually explained by the increase in the NaCl vapor pressure and, accordingly, in the rate of spatial chain termination involving NaCl molecules. However, treating the surface with a high-frequency discharge reduces P_1 , whose initial value is reversibly restored by the air treatment and subsequent pumping of reactor II (Fig. 3). An increase in the degree of surface metallization reduces P_1 . At the same time, it causes an increase in Na concentration and, accordingly, in the rate of homogeneous chain termination through the following sequence of reactions [20]:



Our data point to the following two factors in the interaction between the H_2 flame and NaCl surface:

The first is the effective chain termination through the interaction between H atoms and the surface, which yields Na atoms, which do not participate in chain branching. This enhances the homogeneous chain termination involving Na atoms. The above-mentioned self-deceleration of combustion near P_1 [10] can be explained by these reactions of Na atoms.

The second factor is the metallization of the surface treated with hydrogen atoms (chain propagators). This treatment causes a decrease in the chain termination rate. The mechanism of this process invites further investigation.

Thus, the data reported here, as well as the results of earlier studies [1–10, 21–23], demonstrate that, in chain combustion in the presence of a solid salt, the heterogeneous recombination of atoms and radicals is accompanied by heterogeneous chain propagation and, in some cases, by the transfer of metal atoms and anions from the salt lattice to the gas phase. The gas-phase reactions of these species and the changes in the chemical properties of the surface affect both the combustion kinetics as a whole and the spectral composition of the flame.

Earlier [21–23], it was demonstrated by analysis of some publications chosen as examples that the observed chain combustion data cannot be explained without allowing for the variation of surface properties during combustion and for heterogeneous chain propagation. Taking into account these factors is also necessary when studying the spectral composition of a flame. For example, the radiation from alkali metal atoms during combustion in reactors that have not been purified by a special procedure may be misinterpreted as some anomaly of gas-phase combustion [24].

Note that the chemical modification of the surface under the action of the chain reaction, as well as heterogeneous chain propagation, is possible only during ignition and combustion after an induction period, because the main role in these processes is played by active intermediates, namely, atoms and free radicals. Provided that the experimental conditions and procedure are precisely reproduced, the state of the surface will be the same before each experiment and, therefore, the results of these experiments will be quantitatively reproducible. This explains the fact that, in the experiments described in detail in Semenov's monograph [1], the way the induction period (τ) varies with initial pressure (P_0), as well as the constancy of oxygen partial pressure at the first autoignition limit in a wide range of O_2 mole fractions in the kinetically controlled region of chain termination, is absolutely consistent with the theory of isothermic branched-chain processes [1, Tables 44, 46]. In this connection, note that Aleksandrov and Kozlov's statement that experimental data for the combustion of detonating gas below 0.38 Torr are distorted by the valve lubricant [25] is groundless and contradicts numerous facts. In the above-mentioned Semenov experiments [1, Tables 44, 46], the detonating gas pressure was 0.06–0.15 Torr and τ was up to 0.6 s. In the immediate vicinity of the first autoignition limit, which appears in Semenov's equations, τ is as long as tens of seconds. If the observed autoignition limit, O_2 mole fraction, or τ had been significantly distorted by a hypothetical inhibitor or some other factor, none of the regularities described in the monograph would have taken place under these conditions. The quantitative agreement between the data reported by Semenov [1] and the theory of isothermic chain reactions is further evidence that there were no distorting factors in those experiments. The discrepancies between the earlier equations and experimental data for developed isothermic combustion, which were discovered and explained by

Semenov and his colleagues [1, 2], are due to heterogeneous chain propagation.

A wrong interpretation has been suggested by Aleksandrov and Kozlov [25] for the data that were obtained using an unlubricated setup [26] and proved the correctness of the standard procedure. Indeed, if the ratio of the cross-sectional area of the reactor to that of the outlet tube, the distance between the tube and the valve, and the value of P_1 are taken into account, it will be clear that the largest possible contribution of the valve to chain termination (diffusion-controlled loss of atoms) does not exceed 0.5%. Therefore, contrary to the statement made by Aleksandrov and Kozlov [25], even if the valve surface had been modified, this modification would have been unable to affect the chain termination rate, because chain termination takes place on the reactor surface.

It was demonstrated (see, e.g., [22, 26]) that the inference as to the distorting effect of the lubricant [25] stems from the authors' own negligence: they inadequately pumped the reactor after the relubrication of the valves. This follows directly from data presented in their subsequent papers and in Aleksandrov's dissertation [27]. For example, it is clear from oscillograms presented in their publications that the gas pressure in the closed reactor increased, although the number of moles of gas in the isothermal H_2 oxidation decreased monotonically. The solvent vapor that was released by the lubricant distorted the reaction kinetics and the readings of the differential pressure gauge. Furthermore, it was demonstrated that computational equations used by Aleksandrov and Kozlov [25] contain mistakes leading to negative concentration values [22].

Aleksandrov and Kozlov (see [25] and other publications of these authors) ignore the results of Semenov's classical experiments on the combustion of hydrogen and phosphorus at 0.1 Torr and lower pressures. These results also indicate that, if the experiment is correctly conducted, the presence of lubricant vapor will be ruled out and no distortions will arise from use of a lubricant in the vacuum system. Denying the possibility of heterogeneous chain propagation, Aleksandrov and Kozlov slur over numerous data obtained in the last two decades, including the IR spectroscopic identification of adsorbed atoms and radicals, the observation of the participation of these species in heterogeneous chain propagation [4–6], and data concerning isothermic combustion localized at the surface under conditions of kinetically controlled heterogeneous chain termination [28]. In their recent publication [25], Aleksandrov and Kozlov, who have long denied heterogeneous chain propagation, again refer to their results dating from the early 1980s and try to ascribe the distorting effect of the solvent vapor that they failed to remove to the correct experimental procedure that has been used by many researchers in the elaboration and development of the theory of branched-chain processes.

Furthermore, Aleksandrov and Kozlov [25] refer incorrectly to an article in *Gorenje i vzryv* (1972, p. 646) when discussing heterogeneous chain propagation. That article deals with pulsed combustion rather than heterogeneous chain propagation.

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