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Chemisorption of Ethane on W(111)

Abstract: Ethane is chemisorbed on W(111) with a sticking probability of ≈0.003. The carbon Auger spectrum at saturation coverage exhibits a two-peak structure similar to that for graphite, while the LEED (low energy electron diffraction) pattern is almost identical to that obtained for an atomically clean surface. Heating the surface to ≈773 K causes desorption of hydrogen and changes the carbon Auger spectrum to a three-peak structure similar to that for tungsten carbide. After annealing, the LEED pattern is affected in different ways depending on the precise conditions, but it may in certain circumstances almost disappear. Exposure to ethylene produces a similar sequence of events. A large kinetic isotope effect is observed with the ratio of the sticking probabilities [$S(C_2H_6)/S(C_2D_6)$, W(111), T = 300 K] being ≈3. A similar ratio is measured for tungsten at T = 2500 K. These data suggest that chemisorption is dissociative in nature, probably involving the reaction $C_2H_6 \rightarrow C_2H_5^* + H \rightarrow$ subsequent steps. Heating of the surface completely dissociates the adsorbed gas, leaving adsorbed carbon and gas phase hydrogen. In analogy with previous work on methane, we believe the large isotope effect suggests that the initial dissociation reaction is dominated by the tunneling of a hydrogen atom through a potential barrier. The implications of this conclusion for other saturated molecules will be discussed.

Introduction

Reactions between molecules in the gas phase often require elevated temperatures and large activation energies. In contrast, the dissociative chemisorption of diatomic molecules frequently occurs with little or no activation energy, as evidenced by rapid adsorption at 300 K or below [1, 2]. Moreover, recent experiments indicate that C_2H_2, C_2H_4, and C_6H_6, for example, are also rapidly adsorbed at room temperature [3–6]. On the other hand, *activated adsorption* seems to be the rule rather than the exception for the saturated hydrocarbons. They typically have small sticking coefficients that increase with increasing temperature [7–9].

Saturated molecules may be classified as having all valence electrons formally involved in covalent single bonds or formally having lone pair electrons. Molecules such as CH_4, C_2H_6, CF_3H, and CF_4 fit into this category. The interaction between undissociated molecules of this type and a clean metal surface is expected to be rather weak since bonding in the usual sense would not be probable. A small distortion of a weakly adsorbed, undissociated molecule would require a large amount of energy, similar in magnitude to that needed for the same distortion in a gas phase molecule. On the other hand, arguments frequently can be presented to indicate that the reaction would be exothermic if the adsorbed molecule were to completely dissociate, leaving adsorbed atoms on adjacent sites (see, for example, [10]). Reactions such as CH_4 (ads) → CH_3 (ads) + H (ads) and C_2H_6 (ads) → C_2H_5 (ads) + H (ads) may also be exothermic or slightly endothermic. Consequently, large activation barriers with widths significantly less than a lattice constant are likely to occur.

In this situation, quantum mechanical tunneling is expected to play a role in the dissociation reaction. The sequence of steps leading to the final product may be initiated by the tunneling of a hydrogen atom through the potential barrier to an adjacent adsorption site. The large kinetic isotope effect (*KIE*) previously reported for methane was interpreted upon this basis [8]. Hydrogen tunnels more readily than deuterium; therefore, the deuterated molecule exhibits a smaller reaction probability [sticking probability (S)] than its protonated counterpart. We expect many saturated molecules (which contain hydrogen) to exhibit large *KIE*, and the investigation of C_2H_6 reported in this paper has been motivated by this expectation.

The generality of *KIE* for saturated molecules is suggested by the following observations. Large *KIE* have been observed at our laboratory for the interaction of both methane and ethane with atomically clean tungsten [8]. Stewart and Ehrlich [7] investigated the *KIE* associated with the reaction of methane with atomically clean rhodium and found it to be large. In the context of a different type of experiment, we have observed a large *KIE*

associated with the reaction of both methane and ethane with a LaB_6-covered rhenium filament and also with a thoriated iridium ion gauge filament [11, 12].

Kinetic isotope effects may originate from several mechanisms [7, 13], and it is difficult to pinpoint the process that is operative in a given situation without detailed calculations. However, most mechanisms predict that the ratio of the reaction rates (k_H/k_D) should decrease with increasing temperature. Behavior of this type is invariably observed for gas phase reactions [13]. In contrast, previously published data for methane, and the data presented in this paper for ethane, indicate that the ratio of the reaction probabilities is relatively independent of temperature. Temperature-insensitive isotope effects ($k_H/k_D \approx$ constant) are believed to indicate a tunneling-dominated step in the dissociative chemisorption reaction. This conclusion is based on *our* lack of success in attempting to explain a temperature-insensitive *KIE* on the basis of other models. It should be noted, however, that a reaction where tunneling makes a contribution will also show a strong temperature dependence if a significant number of particles are going over the barrier rather than through it.

Experimental procedure

The ultra-high-vacuum system shown schematically in Fig. 1 contains ion, cryo, and sublimation pumping capability. The chamber containing the pumps is not shown but is isolated from the LEED-Auger chamber by a valve with large conductance. There are two unique features about this system: one involves the method of exposing surfaces to a given gas; the other is the method for heat-cleaning the sample.

Ethane is first introduced into a closed volume containing a capacitance manometer and a freshly evaporated titanium film. The titanium adsorbs gas from the walls and impurities in the gas supply but does not react with the ethane. Ethane is then introduced into the main chamber with all filaments hot (including sublimation filaments) and the ion pump in the off position. The isolation valve to the main sublimation pump remains in the open position; therefore, the impurity gas concentration is very low for the duration of the experiment. The ethane is subsequently pumped away by a diffusion pump, and Auger (Fig. 2) and LEED spectra (Fig. 3) are obtained. A similar procedure could not be used for C_2H_4 because it reacts with clean titanium. Figure 2 shows Auger spectra for clean tungsten (a) before and (d) after exposure to 2 Pa-s (1.5×10^4 langmuirs, 1 Pa = 7.52×10^{-3} torr) of argon. There is no significant buildup of carbon or other impurities, indicating that the procedure outlined above is effective.

The second unique feature of this system is related to the method used for sample cleaning. The W(111) crystal

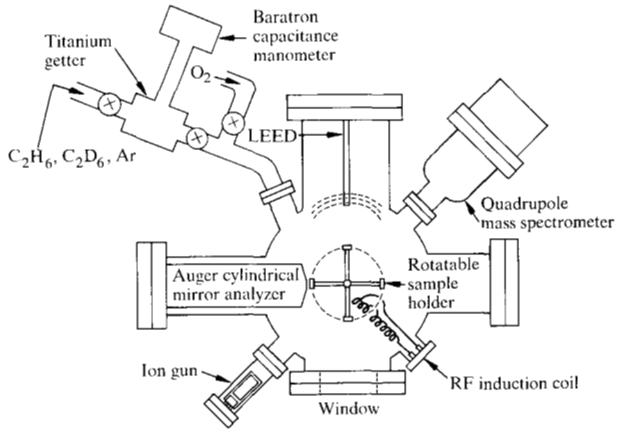
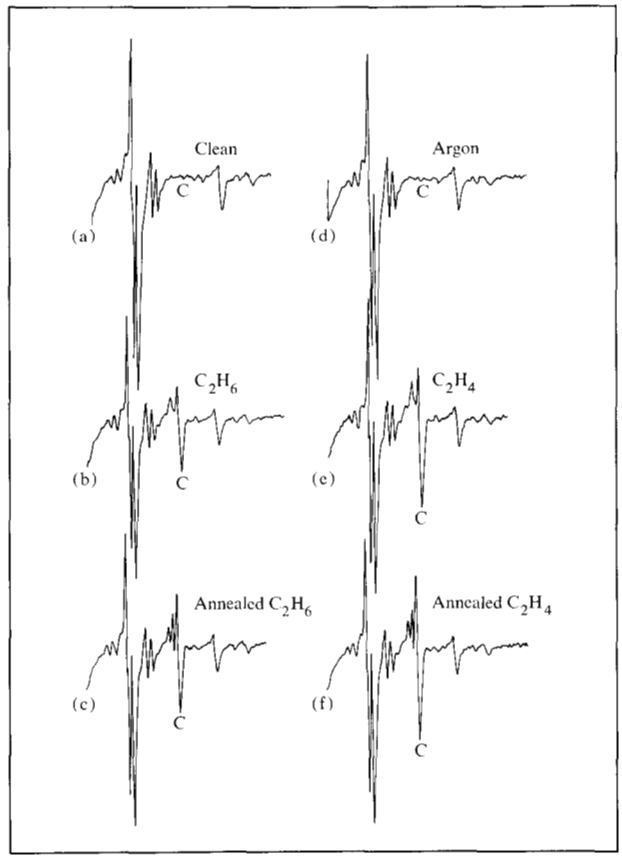


Figure 1 Schematic of ultra-high-vacuum system. The pumping package and an auxiliary diffusion pump are not shown. The manipulator is presented schematically and is designed to show that the sample can be rotated from a position in the center of an rf coil to positions in front of the LEED or Auger chambers (for a more detailed description, see text).

Figure 2 Auger spectra from W(111); (a) clean tungsten; (b) clean tungsten exposed to C_2H_6, 3.3 Pa-s (2.5×10^4 langmuirs); (c) clean tungsten exposed to C_2H_6, 3.3 Pa-s (2.5×10^4 langmuirs), annealed ≈100 s at ≈723 K; (d) tungsten exposed to Ar, 2 Pa-s (1.5×10^4 langmuirs) [This spectrum demonstrates the absence of carbon due to the adsorption of impurity gases under the exposure conditions used in these experiments.]; (e) clean tungsten exposed to C_2H_4, 1.17×10^{-2} Pa-s (88 langmuirs); (f) clean tungsten exposed to C_2H_4, 1.17×10^{-2} Pa-s (88 langmuirs), annealed ≈100 s at ≈723 K.



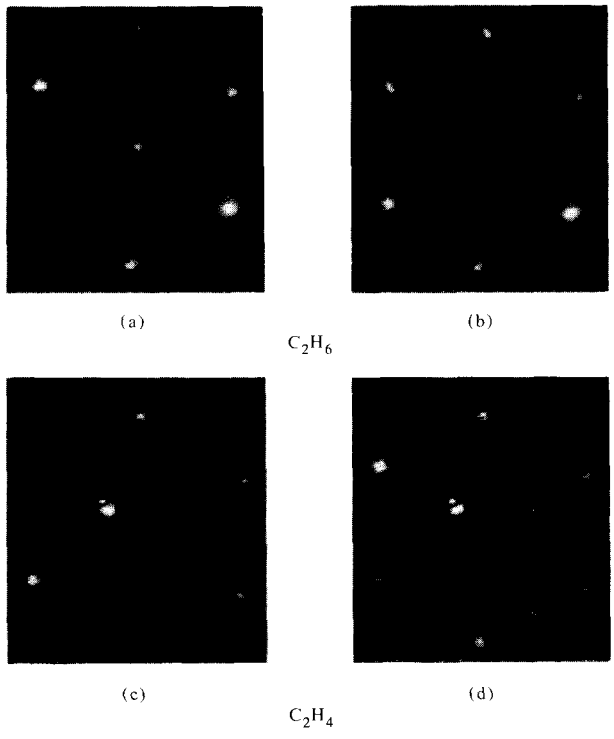


Figure 3 LEED data for W(111) exposed to C_2H_4 and C_2H_6, beam voltage 160 V: (a) clean tungsten; (b) after exposure to C_2H_6, 3.3 Pa-s (2.5×10^4 langmuirs) at ≈300 K; (c) clean tungsten; and (d) after exposure to C_2H_4, 1.33×10^{-2} Pa-s (100 langmuirs) at ≈300 K.

is spot-welded to a 0.01-cm Ta wire (length ≈0.09 cm), which in turn is spot-welded to a 0.20-cm tungsten rod (length ≈5 cm). The top end of the rod-sample configuration is attached to a rotatable manipulator so that the axis is perpendicular to the plane shown in Fig. 1; i.e., it hangs vertically. The sample can be rotated into the center of the coil and its temperature increased to ≈2500 K within a few seconds after application of rf power (≈600 W) to the water-cooled coil. At this temperature, carbon is removed from the surface either by desorption or by diffusion into the bulk. After cleaning, the sample can be rotated to other positions for analysis.

Advantages of this sample-heating procedure include 1) the ease of obtaining any desirable temperature, 2) the insensitivity of the method to sample shape, 3) the uniform temperature obtained over the sample area, 4) the minimal heating of surfaces other than those of the sample (the 0.01-cm Ta wire acts as a thermal barrier), 5) the ease with which several samples can be heated sequentially using the same rf coil, and 6) the fact that the system is easily adapted for temperature programmed desorption.

Results and discussion

Rye and Hansen [14] have shown that ethane is adsorbed on clean, polycrystalline tungsten and have suggested that the initial step is $C_2H_6(g) \rightarrow C_2H_5^* + H^*$. Heating the sample primarily released hydrogen while carbon remained on the surface. Our data for W(111) are consistent with these results. We find that ethane is chemisorbed at room temperature and that the sample, when heated, releases hydrogen.

Plummer et al. [6, 15] have presented convincing arguments indicating that $C_2H_4(g)$ [T = 300 K] reacts with W(100) and W(110) to form C_2H_2 (ads) and H (ads). This is consistent with the results of Rye and Hansen [14], who found that dehydrogenation of C_2H_4 (ads) occurred at an appreciable rate for $T > 200$ K. Demuth and Eastman have also shown that ethylene dehydrogenates to form C_2H_2 (ads) [T = 300 K] on Ni(111) [16].

On the basis of these results, it is intuitively expected that C_2H_6, if chemisorbed, will after a sequence of steps yield C_2H_2 (ads) and H (ads). Our data are consistent with this expectation.

Figure 2 shows Auger spectra for tungsten substrates: (a) clean; (b) after exposure to C_2H_6 [T = 300 K; 3.3 Pa-s (2.5×10^4 langmuirs)]; and (c) after heating the sample with subsequent desorption of hydrogen. The appearance of the carbon peak [(b) and (c)] shows that ethane is adsorbed at room temperature. The carbon structure in (c) is similar to that observed for carbides [17–19] and is almost identical to that found during x-ray photoemission (XPS) excitation of the carbon Auger line in gas phase methane [20, 21]. The methane data are well understood on the basis of calculations by Ortenburger and Bagus [22]. On the other hand, it is not clear how their work is related to Auger structure in carbides. It may be that carbon, in a highly symmetrical environment, always exhibits a three-peak structure similar to those shown in Fig. 2.

The two-peak structure shown in Figs. 2(b) and (e) does *not* resemble similar data obtained for gas phase ethylene or acetylene, but it is vaguely reminiscent of (but not identical to) graphite (see [23] for gas phase data). The lack of resemblance to the acetylene may be caused by lack of resolution in our experiments, but this suggestion remains to be verified. Therefore, these data should not be interpreted as indicating the absence of adsorbed C_2H_2 on the surface.

The carbon Auger spectra obtained after exposure to C_2H_4 [Fig. 2(e)] are identical in most details to those obtained after exposure to C_2H_6 [Fig. 2(b)]. Annealing also produces similar results [compare Figs. 2(c) and 2(f)]. However, at saturation coverage the ratio of the carbon to tungsten intensities (I_C and I_W, respectively) is greater for C_2H_4 than it is for C_2H_6. For example, I_C/I_W (350 eV) for C_2H_4 is ≈3.5 while I_C/I_W (350 eV) for C_2H_6 is ≈2.7. Consequently, the saturation coverage of C_2H_4 is believed to be greater than that of C_2H_6.

Barford and Rye [24] have estimated the saturation coverage of C_2H_4 on W(111) to be 6.7×10^{14} molecules/

cm^2. By assuming that the ratio of Auger peaks is linearly related to carbon concentration, it is estimated (based on Barford's ethylene-data) that the saturation coverage of ethane is $\approx 5 \times 10^{14}$ molecules/cm^2.

Figure 3 shows LEED data taken before and after exposure to both C_2H_6 and C_2H_4. There is no apparent change upon exposure. This result suggests that both gases are either randomly adsorbed or form patches of (1×1) structure. After annealing, the LEED pattern changes (often drastically) but the data are quite dependent on the precise treatment and are not shown in this paper.

In summary, ethane is chemisorbed on W(111) at room temperature; heating to temperatures less than 773 K results in desorption of H_2, the changing of the carbon Auger line from a two-peak to a three-peak structure, and modification of the LEED pattern. These changes almost certainly correlate with the dissociation of a chemisorbed hydrocarbon molecule, possibly C_2H_2 (ads).

It should also be noted that our Auger data are limited by poor resolution and it is believed that the carbon line contained in Fig. 2 has more structure than is evident.

Figure 4 shows the carbon Auger intensity for C_2H_6 and C_2D_6 as a function of exposure, with the slopes being proportional to the reaction probability (sticking probability). Assuming a saturation coverage of 5×10^{14} ethane molecules/cm^2, the data of Fig. 4 lead to the estimate of ≈ 0.003 and ≈ 0.001 for the initial sticking probabilities of C_2H_6 and C_2D_6, respectively. A large kinetic isotope effect is evident since the ratio of the initial (i.e., clean surface) reaction rates is ≈ 3. The *KIE* clearly indicates that the reaction is dissociative in nature. Several mechanisms can produce a *KIE* in a dissociative reaction [13], but we have been unable to postulate a mechanism that would produce a *KIE* of this magnitude for a nondissociative event.

Preliminary experiments on W(100) show that the sticking probability S of C_2H_6 is a factor of 3 to 10 less than that for the W(111) face. This value for W(100) is consistent with estimates based on the published data of Hopkins and Shah [25], who studied work function vs exposure.

The sticking probability of ethane has been measured at high temperature for both polycrystalline tungsten and W(111) and the data are shown in Figs. 5 and 6. (The reader is referred to [8] and [10] for a complete description of the experiment.) Ethane was introduced into a closed volume containing a quadrupole mass spectrometer, a freshly evaporated titanium getter, and the tungsten sample. (The getter eliminates the buildup of impurity gases but does not react with the ethane.)

The initial slope is obtained with the sample saturated with ethane (ethane sticking probability ≈ 0; $T = 300$ K), and the small pressure decrease observed is due to reactions with hot filaments. Upon heating the sample to ≈ 2500 K, the hydrogen is desorbed and the carbon leaves the surface region most probably by diffusing into the bulk material. In any case, Auger spectroscopy shows that the tungsten sample is atomically clean when heated to this temperature under our experimental conditions. Therefore, the change in slope upon heating the sample is directly proportional to the sticking probability of ethane.

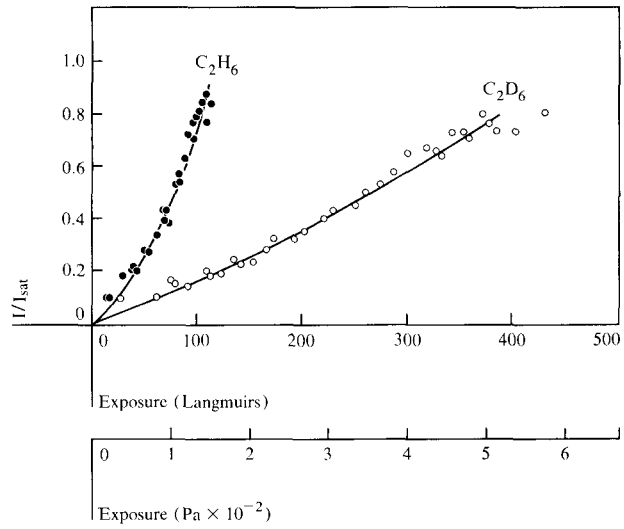


Figure 4 Normalized carbon Auger intensity (I/I_{sat}; 270 eV) as a function of exposure of C_2H_6 and C_2D_6; W(111) substrate; $T = 300$ K. A value of one is obtained for the intensity at saturation.

The obvious difference between the C_2H_6 and C_2D_6 data demonstrates a large kinetic isotope effect. The ratio of the sticking probabilities $[S(C_2H_6)/S(C_2D_6)]$ is ≈ 3.2 for both W(111) and polycrystalline tungsten. The magnitude of this *KIE* is about the same as that measured at room temperature by Auger spectroscopy. This result suggests that the *KIE* is relatively insensitive to temperature, a criterion that has been previously postulated to indicate a reaction dominated by quantum mechanical tunneling of a hydrogen atom through a potential barrier. Therefore, it is probable that this mechanism is operative for the dissociative chemisorption of ethane on tungsten. Finally, it should be emphasized that the interpretation presented here is not based solely on the analysis contained in this paper but is analogous to that presented for CH_4 in [8], where a large quantity of data was available and extensive calculations were performed.

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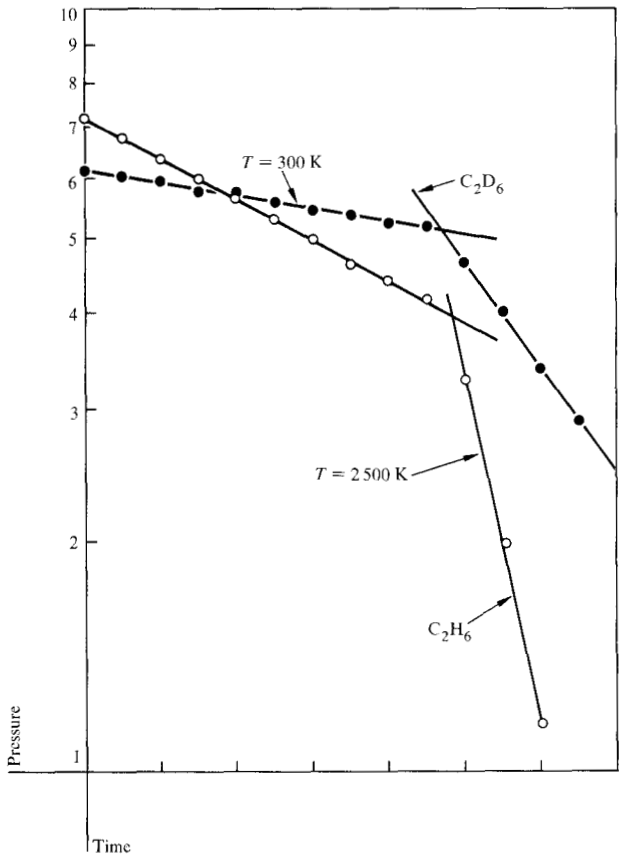

Figure 5 Logarithm pressure vs time for a mixture of C_2H_6 and C_2D_6 contained in a closed volume for ≈1 cm² polycrystalline tungsten sample. The slope of these curves is proportional to the rate at which ethane is reacting with surfaces within the closed volume. The magnitude of the *KIE* is determined by obtaining the ratio of the slope for C_2H_6 to that for C_2D_6. The temperature was changed from 300 K to 2500 K as indicated.

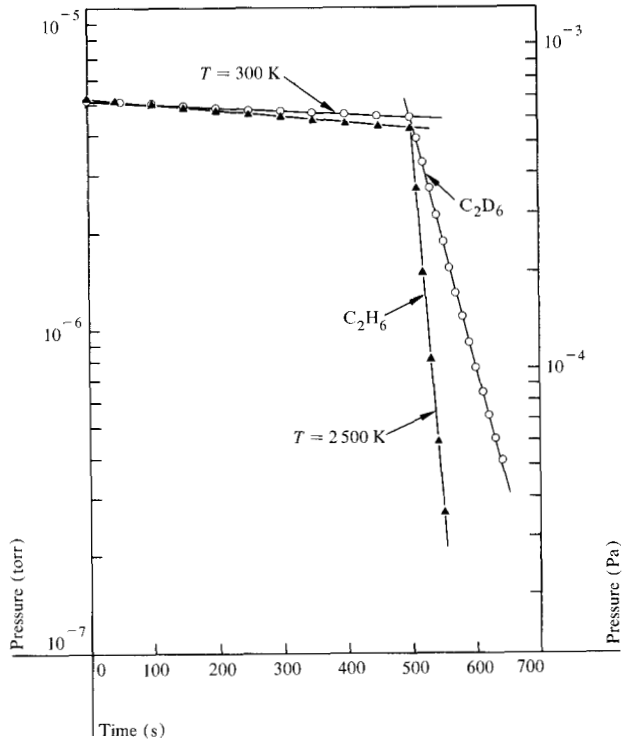

Figure 6 Logarithm pressure vs time for ethane contained in a closed volume for a W(111) crystal. The slope of these curves is proportional to the rate with which ethane is reacting with surfaces within the closed volume. The magnitude of the *KIE* is determined by obtaining the ratio of the slope for C_2H_6 to that for C_2D_6. The temperature was changed from 300 K to 2500 K as indicated. The sample was heated in a vacuum system of small volume by the rf induction method.

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