Letters to the Editor

Oscillation Fe^{II}—Fe^{III} redox reaction in hydrochloric acid solutions initiated by ultrasonic waves

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We have shown previously[1] that ultrasonic treatment of argon-saturated solutions of HCl results in accumulation of noticeable amounts of Cl_2 over a broad range of HCl concentrations. In the present work, we studied the behavior of 0.1 *M* hydrogen chloride solutions of Fe^{II} (containing ≤1 mol. % Fe^{III}) saturated with either Ar or N_2. Solutions with HCl concentrations ranging from 0.1 to 12.0 mol L^{-1} were studied using an ultrasound generator of the JMT Co. (Japan) operating at 22 kHz. Working solutions were sonicated in glass vessels with an intensity of 5 W cm^{-2} (determined by chemical dosimetry[2]). The concentration of Fe^{III} was recorded by spectrophotometry ($\varepsilon_{\lambda=330\ nm} \approx 2000$) at different time intervals. It was found that a 10-min interval between the measurements is the optimum value. More frequent measurements do not change the patterns of the kinetic curves, whereas measurements at longer intervals preclude the possibility of recording interesting features of the processes occurring in the solutions saturated with N_2.

The experiments showed that under argon, Fe^{II} is oxidized to Fe^{III} over the whole range of HCl concentrations, whereas the concentration of Fe^{III} virtually does not change (Fig. 1, curve *1* and *3*). In the atmosphere of N_2, the Fe^{II}—Fe^{III} system remains inert toward ultrasonic vibrations when the HCl concentrations are <6 mol L^{-1}. When the HCl concentration is ≥6 mol L^{-1}, an Fe^{II}—Fe^{III} redox oscillation process is observed in the atmosphere of N_2 (Fig. 1, curve *2*; Fig. 2). The sonolysis products were found to contain chlorine-containing oxidants, nitrogen oxides, and NH_4^+ ions.

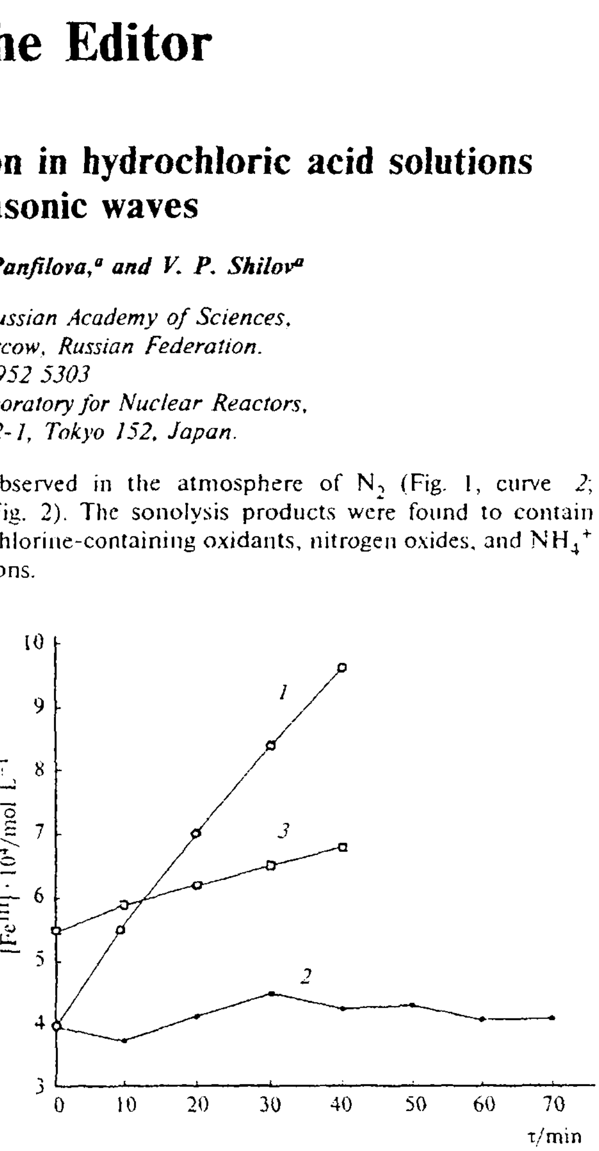

Fig. 1. Kinetic curves for the variation of the Fe^{III} concentration in the solutions: (*1*) [HCl] = 6 mol L^{-1}, Ar; (*2*) [HCl] = 6 mol L^{-1}, N_2; (*3*) [HCl] = 2 mol L^{-1}, Ar.

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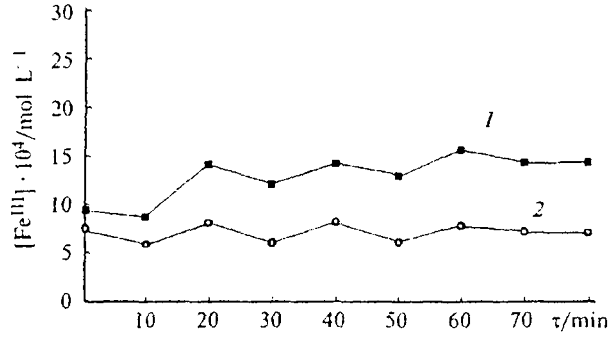

Fig. 2. Kinetic curves for the variation of the Fe^{III} concentration in solutions sonicated under N_2: (*1*) [HCl] = 12 mol L^{-1}; (*2*) [HCl] = 8 mol L^{-1}

It is known[3] that N_2 molecules participate in sonochemical reactions, which result ultimately in the fixing of nitrogen as the products of its oxidation or hydrogenation; these species, in turn, are able to oxidize Fe^{II} or to reduce Fe^{III}. The pattern of the curves presented in Fig. 2 indicates that the initial stage of the process yields mainly reducing agents; for example, these could be active species such as H, NH, and NH_2 and some chloro-substituted ammonia derivatives able to rapidly reduce Fe^{III}. However, the generation of reducing agents by the ultrasonic field does not suffice to make up for their consumption in the reaction with Fe^{III} and other products of sonolysis; finally, oxidants are accumulated in the solution and the direction of the process is reversed. Once a particular concentration of the oxidative species has been attained, the rate of their interaction with Fe^{II} becomes higher than the rate of their generation. After that, consumption of the oxidants starts and their concentration decreases to some critical value at which the process returns to the initial point. The oscillations in the system are damped due to the decrease in the concentration of N_2 in the solution upon its chemical transformations and ultrasonic degassing of the solutions. Apparently, the oscillation process in this system is possible only provided that $[Fe^{II}] >> [Fe^{III}]$.

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Reaction of fullerene C_{60} with diazoacetylcymanthrene: the first C_{60} derivative containing a manganese π-complex

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The synthesis of fullerene derivatives containing an organometallic fragment in an addend is of interest, first of all, from the viewpoint of intramolecular charge transfer. Earlier,[1] we obtained a tricarbonylarenechromium derivative (in the form of a mixture of methanofullerene and fulleroid) by the reaction of C_{60} with a monochromium tricarbonyl complex of diphenyldiazomethane. The present publication reports the synthesis of a fullerene derivative containing a cymanthrenyl fragment (tricarbonylcyclopentadienylmanganese, Cym) by a similar reaction from diazoacetylcymanthrene (**1**)[2] (Scheme 1).

The reaction of C_{60} with an equimolar amount of diazo ketone **1** in boiling toluene for 14 h affords a low-polar product **2** (R_f = 0.8, yield 8%, 20% with respect to the consumed C_{60}, 1 : 2 toluene—hexane as the eluent) and a more polar compound **3** (R_f = 0.4, yield 8.5%, 22% with respect to the consumed C_{60}). The degree of conversion of C_{60} is 37%. The products were isolated from the reaction mixture by chromatography on SiO_2 (100/160 μm): product **2** was eluted following the recovered C_{60} with a 1 : 4 toluene—hexane mixture, and product **3** was eluted with a 1 : 1 toluene—hexane mixture. IR spectra ($CHCl_3$) suggest the presence of an

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