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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Effect of Solvent Nature on the Reaction of Metallic Iron with Benzoic Acid in a Bead Mill

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Abstract—Results of an experimental study of the influence exerted by the solvent nature on the reaction rate, achieved degree of acid expenditure, selectivity with respect to salts of iron(II) and (III), and phase state of the reaction mixture in a single-stage reaction of iron with benzoic acid and atmospheric oxygen in the presence of a stimulating iodine additive are presented.

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Iron(III) and (II) benzoates are rather widely used in various industries [1–11].

Commonly, these salts are obtained by one of the following three methods: (i) exchange interaction of iron salts and mineral acids with sodium benzoate or by a direct reaction of an iron oxide with benzoic acid in the temperature range 125–260°C in the presence of an organic dispersing agent [12]; (ii) reaction of benzoic acid with the metal nitrate in the presence of an inert organic solvent, followed by addition to the reaction mixture of ammonia and(or) amine, and(or) tetraalkylammonium hydroxide at a temperature of 20–40°C and pressure of $(1–50) \times 10^5$ N m^{-2} [13]; and (iii) direct electrosynthesis [14]. These methods require certain auxiliary substances and rather severe conditions and yield by-products that need utilization. Moreover, some of these methods cannot be performed in a single stage.

It was of interest to obtain iron benzoates in a single-stage process in accordance with the stoichiometric overall equations (HA stands for carboxylic acid)

$$2Fe + 4HA + O_2 \rightarrow 2FeA_2 + 2H_2O, \quad (1)$$

or

$$4Fe + 12HA + 3O_2 \rightarrow 4FeA_3 + 6H_2O, \quad (2)$$

i.e., with atmospheric oxygen as an oxidizing agent, crushed iron or its alloys (including those of waste origin) as a reducing agent, and also an organic solvent and iodine (the latter as a stimulating additive). By now, iron(II) and (III) formates and acetates have been synthesized by this method [15–18]. The process occurs in a single technological stage to give the target product mainly in the form of a suspension easily separated by filtration. The filtrate containing dissolved products of conversion of the stimulating additive and iron salts is recycled and thereby requires neither separation, nor repeated utilization.

The overall processes (1) and (2) are heterogeneous, complex, and multistage. Their principal stages are the following [19–22]:

$$Fe + I_2 \rightarrow FeI_2, \quad (3)$$

$$2FeI_2 + 4HA + O_2 \rightarrow 2FeA_2 + 2I_2 + 2H_2O, \quad (4)$$

and(or)

$$4FeI_2 + 12HA + 3O_2 \rightarrow 4FeA_3 + 4I_2 + 6H_2O, \quad (5)$$

and also [17, 18]

$$4FeA_2 + O_2 + 4HA \rightarrow 4FeA_3 + 2H_2O, \quad (6)$$

$$Fe + 2FeA_3 \rightarrow 3FeA_2. \quad (7)$$

Together, stages (3) + (4), (3) + (5) or (3) + (4) + (5) constitute cyclic processes of consumption and formation of iodine, and just this circumstance is the reason why it is used as a catalyst.

The main purpose of the liquid phase is the transport function. The place where the basic stages occur is the iron surface onto which the reactants are de-

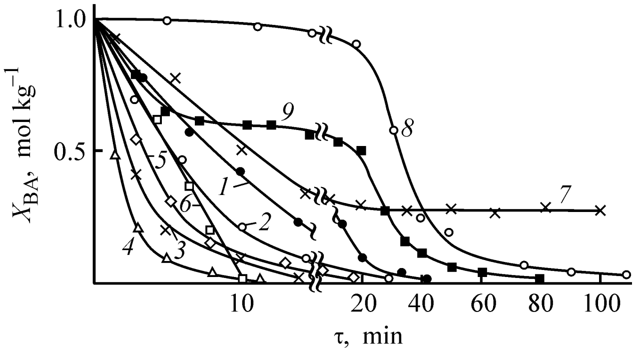

Fig. 1. Kinetic curves of benzoic acid consumption for formation of iron salts at varied nature of a solvent in the liquid phase of the charge. Reactor: vertical bead mill with a four-blade stirrer rotating at 1560 rpm; mass of beads 200 g; 1 : 1 mass ratio of beads to the liquid phase of the charge; charge: crushed cast iron 60 g, iodine 0.03 mol kg^{-1} liquid phase; temperature 60 ± 2°C. (X_{BA}) Concentration of benzoic acid and (τ) time. Solvent: (*1*) dimethylformamide, (*2*) 2 : 3 (*v*/*v*) mixture of dimethylformamide and butanol, (*3*) *n*-butanol, (*4*) chlorobenzene, (*5*) bromobenzene, (*6*) ethyl cellosolve, (*7*) toluene, (*8*) petroleum spirit, and (*9*) ethylbenzene.

livered by means of adsorption. The solid products formed on the surface should be removed into the solution bulk to preclude full passivation of the surface by their deposits. Their desorption cannot play any significant part in systems of this kind. Considerably more important is their dissolution or mechanical removal (scraping, scuffing, stripping). The role of the solvent is also important. On the whole, the solvent nature should largely determine the competitive ability of reactions (3)–(7) and, consequently, that of (1) and (2), as well as the selectivity with respect to the iron(II) and (III) salts and the heterophase state of the final reaction mixture, which may either facilitate or hinder its separation and product recovery. In this study, an attempt was made to evaluate the effect of the solvent nature on the reaction of iron with benzoic acid in a bead mill.

EXPERIMENTAL

The experiment was performed in a vertical bead mill with a high-speed (1440 and 1560 rpm) blade stirrer whose shaft was connected to that of a 0.5-kW motor. The stirrer case was made of stainless steel and had a wall thickness of about 10 mm. The blades and the shaft of the stirrer were made of st.45 or stainless steel. In both cases, their working life was rather short (1–2 months), which was predetermined by their involvement in the redox process under consideration as a source of reacting iron. To preclude rapid wear, the case and bottom of the bead mill were protected with an inserted steel shell and a well-fit false bottom with a foot bearing for the blade stirrer. As a grinding agent served glass beads 0.8–3.1 mm in diameter, both individually and together with powdered reduced iron, sieved fractions of crushed cast iron, and fragmented steel shavings with the maximum linear particle size of 5 mm. The mass ratio between the glass beads and ground iron and(or) its alloys was widely varied.

The bead mill was equipped with a reflux condenser and heat supply via a liquid bath that could be moved along the longitudinal axis of the reactor. The course of the process was monitored by sampling, with the content of carboxylic acid and its iron(II) and (III) salts determined. The monitoring results were used to plot the corresponding kinetic curves.

The reagents were charged in various orders. Most frequently, glass beads, solvent, and carboxylic acid were charged first and then agitation was switched on and thereby a solution of carboxylic acid was prepared. Occasionally, this solution was prepared preliminarily and then batched into the reactor. After that, ground iron or iron alloys and the catalyst were charged and air was fed into the reactor for bubbling. The bubbler was fabricated in an elastic version to preclude its disintegration upon contact with moving beads or heavy particles of iron or its alloys.

It was found that, without iodine, the process begins, but rapidly terminates at acid conversions not exceeding 2–3%. Therefore, if the chosen temperature mode was to be strictly maintained (in the range 15–90°C), the stimulating additive was introduced at the instant when the system reached the working temperature.

Figure 1 shows kinetic curves of benzoic acid consumption for the process performed in various solvents. The role of the solvent is manifested not only in different rates of acid consumption, but also in the existence of the period of self-accelerated development (e.g., in petroleum spirit), intermediate self-deceleration (in ethylbenzene), self-termination (in toluene), and self-resumption of the process (in ethylbenzene), in its selectivity with respect to iron(II) and (III) salts, and in the manner in which the selectivity varies in the course of the process.

In all of the solvents chosen, the amounts of iodine used for stimulation were completely soluble. Therefore, the maximum concentrations of iodine were determined only by its close. At the same time, its running concentrations were 10–20 times lower than the maximum values. This indicated that, in the course of the process, the main part of iodine

Solubility of benzoic acid and its iron salts and of iron(II) iodide in the solvents used at 17 ± 1°C

Solvent of the liquid phase	Solubility, mol kg^{-1}			
	benzoic acid	iron(III) benzoate	iron(II) benzoate	iron(II) iodide* [21]
Formamide	1.712	0.041	<0.0011	–
Dimethylformamide	4.398	0.412	0.0375	0.57
n-Butanol	2.058	0.110	0.0087	0.24
2 : 3 (*v*/*v*) mixture of dimethylformamide and *n*-butanol	3.607	0.281	0.0158	–
Ethyl cellosolve	2.724	0.183	0.0274	0.41
Petroleum spirit	0.028	0.008	<0.0003	0.0004
Toluene	0.817	0.083	<0.0003	0.0009
Ethylbenzene	0.559	0.062	<0.0003	0.0005
Chlorobenzene	0.581	0.082	<0.0003	–
Bromobenzene	0.623	0.029	<0.0003	–
Water	0.145	0.013	0.0007	>2.08

* At 29 ± 1°C.

being introduced was in the form of FeI_2, which was confirmed by direct analysis.

The acid must also be to some extent soluble in the solvent used (see table), but this extent remains unknown. The process could also be performed in dimethylformamide, in which the solubility of benzoic acid exceeds 4 mol kg^{-1}, and in petroleum spirit, in which the solubility is more than 100 times lower and the main part of the acid charged into the reactor remained in the solid phase in the course of the process. The conclusion that the solubility of the acid is not a key factor is also confirmed by the fact that the rate and time characteristics of the process depend on the initial content of the acid in the charge not only in a rather complicated way, but also not too strongly (Figs. 2, 3). In addition, clear requirements to the role played by the solubility of salt products in the liquid phase could not be formulated. At a high solubility of the metal iodide, there appears an important mass-exchange pathway to disintegration and removal of its surface deposits from iron. In this case, reactions (4) and (5) partly pass into solution, i.e., into homogeneous conditions. The FeA_2 and FeA_3 salts being accumulated are first present in solution and then, beginning at a certain instant of time, form independent solid phases. The solid phase of green FeA_2 appears first, which correlates with its poorer solubility, compared with FeA_3. As a direct experiment demonstrated, transformations of dissolved and suspended salt products into components of surface deposits on the metal are unlikely.

At the same time, at a poor solubility of iron(II) iodide in the liquid phase used (e.g., in petroleum spirit), reactions (4) and (5) will be predominantly

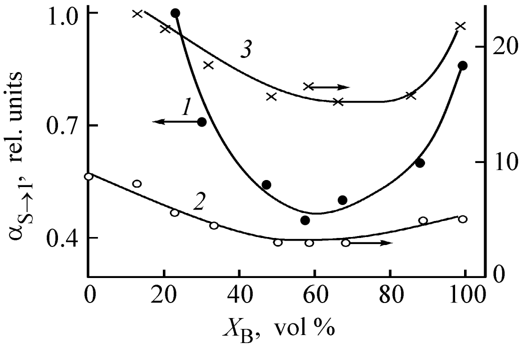

Fig. 2. Conversion α of benzoic acid in a single-stage reaction with fragmented iron in the presence of iodine vs. the content X_B of *n*-butanol mixed with dimethylformamide as a solvent of the liquid phase. Dosage: benzoic acid in accordance with its solubility at 21°C and iodine 0.125 mol kg^{-1}; 4 : 1 mass ratio of the liquid phase and reduced iron; mass of the liquid phase 200 g; temperature 60 ± 1°C; rotation rate of the blade stirrer of the vertical bead mill 1560 rpm. (*1*) ($\alpha_{S\to 1}$) Conversion at the selectivity with respect to the iron(III) salt approaching 100% and remaining so till the end of the process; (*2*, *3*) (τ_α) time in which (*2*) 50% and (*3*) 100% conversion of benzoic acid is reached.

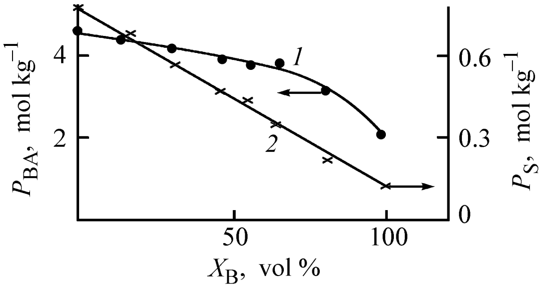

Fig. 3. Solubility of (*1*) benzoic acid (P_{BA}) and (*2*) iron(III) benzoate (P_S) vs. the content X_B of *n*-butanol in a mixture with dimethylformamide as a solvent. Temperature (°C): (*1*) 21 and (*2*) 18.

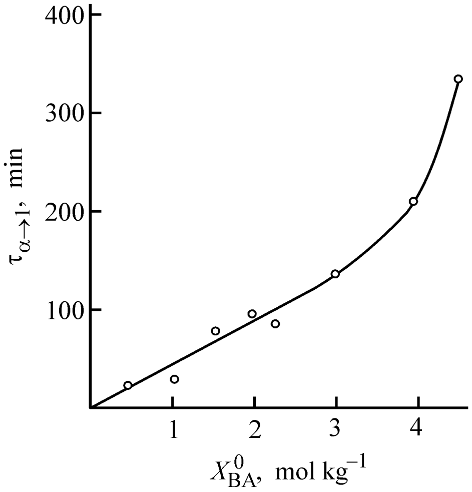

Fig. 4. Time $\tau_{\alpha\to 1}$ in which a virtually quantitative conversion of benzoic acid mainly into the iron(III) salt is reached vs. the initial concentration X^0_{BA} of the acid in a 2 : 3 (*v*/*v*) mixture of dimethylformamide and butanol, taken as the liquid phase for the reaction of 30 wt % (relative to the liquid phase) crushed cast iron with benzoic acid at 60°C in the presence of 0.075 mol kg^{-1} of a stimulating iodine additive and bubbling with air. Reactor: vertical bead mill with a four-blade stirrer rotating at 1550 rpm; 1 : 1 mass ratio of beads and the liquid phase charge; air expenditure for bubbling 2.2 l min^{-1} kg^{-1} liquid phase.

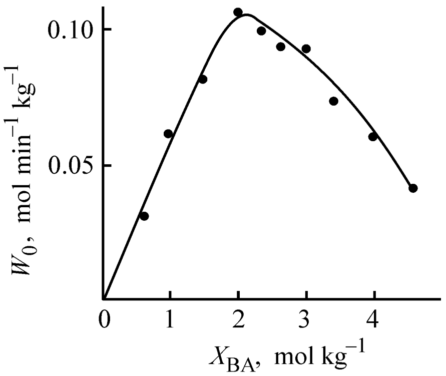

Fig. 5. Initial rate W_0 of the conversion of benzoic acid into iron salts vs. the initial content X_{BA} of benzoic acid in the liquid phase of the system. Process conditions the same as those for Fig. 4.

heterogeneous, and FeA_2 and FeA_3 remaining on the surface can well be transformed into important components of the surface deposits on iron. Mechanical methods for disintegration and removal of surface deposits become the most important in this case. Because both these variants have been implemented in practice, with the process rates and durations being comparable, there is no good reason to prefer one of them.

The following circumstance appeared to be the most important in this regard: the viscosity of the system grows as the product is accumulated both in solution and as a suspension, with the increase being self-accelerated in deep stages. This leads to a synchronous decrease in the operation efficiency of the bead mill, to the point of complete loss of its working capacity. The results obtained demonstrate that this occurs when iron salts are accumulated in a total amount of 1.2–1.5 mol kg^{-1}. Consequently, the maximum content of the acid in the charge, determined with account of the fact that its whole amount can be converted into salts, must not exceed 3.6–4.5 mol kg^{-1}. However, this does not mean that just these initial concentrations of the acid will be optimal (Figs. 2, 4, 5), because the corresponding dependences are complicated. For example, the solubilities of benzoic acid and iron(III) benzoate substantially fall as the content of *n*-butanol in the mixed solvent increases (Fig. 3), whereas the time in which a 50% or >98% conversion of benzoic acid into iron salts is reached passes through a minimum at a 60–65% content of *n*-butanol in the mixed solvent. Consequently, it is better that the solubility of the final product in the liquid phase used should not be too high, so that the product would accumulate in the form of a suspension. In this case, the viscosity grows more slowly and the product itself can be easily isolated by simple filtration.

Comparison of the data in Figs. 4 and 5 shows that the manner in which the process duration increases with the initial content of benzoic acid is associated not only with the pronounced differences in the viscosities of the reaction mixtures in deep-conversion stages, but with the fact that the initial rates pass through a maximum as functions of the content of the acid. At the beginning of the process, the viscosity of the liquid phase will also grow with the content of benzoic acid. However, this increase is incomparable with the rise in the viscosity of the reaction mixture, observed as the acid expenditure for salt formation becomes quantitative.

Experiments with different solvents revealed variants in which the reaction mixture becomes, in the course of the process, a glue-like viscous mass that entraps glass beads and solid particles of the metal. In these cases, the process is always doomed to self-termination because of the complete loss of working capacity by the bead mill. This is a rather rare phenomenon for benzoic acid (e.g., in toluene; Fig. 1, curve *7*). By contrast, this situation is one of the most frequently occurring for butyric acid.

However, not any self-termination of the process is due to a strong thickening of the reaction mixture or to its transformation into a glue-like mass. As an example can serve curve *9* in Fig. 1. Whose intermediate portion is associated with blocking of the metal surface by surface deposits of salt products, which becomes weaker in the course of time and self-resumption of the process occurs.

In some cases, self-termination of the process was observed in systems in which products were mostly accumulated as suspended solid phases, and no noticeable decrease in the operation efficiency of the bead mill was observed in the course of their accumulation. For example, self-termination occurred in water (not shown in Fig. 1, the corresponding kinetic curve is similar to curve *7*) by the 85th–90th minute, with no self-resumption observed in the following 150 min. This self-deceleration also occurred because of the blocking of the iron surface by a mixture of benzoates of iron(II) (green) and iron(III) (brown). An inspection of unreacted particles of cast iron revealed a greenish-gray deposit on their surface. The filtered-off precipitate of the salt products had the same coloration.

The nature of the solvent used strongly affects the accumulation kinetics of iron(II) and (III) salts and, consequently, the achievable selectivity with respect to the target product. This can be illustrated by the example of the mixed solvent used in this study, with varied ratio of dimethylformamide and *n*-butanol in the solvent (Fig. 2, curve *1*). The conversion on reaching and exceeding which the selectivity with respect to iron(III) salt tends to unity passes through a minimum. This minimum is observed at a content of *n*-butanol within the range 50–70% and acid conversions into the product of about 50%. It is this range of alcohol contents in the mixed solvent that should be regarded as the most interesting, although the solubility of benzoic acid in this region is substantially lower than 4 mol kg^{-1} (at 21°C).

The solubility of both the acid and iron(III) salt in dimethylformamide is considerably higher (Fig. 3). It additionally increases as temperature is raised. In dimethylformamide, the process can be brought virtually to complete expenditure of the acid for salt formation, provided that its initial concentration does not exceed 5.5 mol kg^{-1}. However, the 100% selectivity with respect to the iron(III) salt cannot be reached neither in the end, nor in the course of the process. It was found that it is impossible to obtain products in the solid phase in this medium: at so large initial contents of benzoic acid, the final reaction mixture is something intermediate between a poorly flowable paste and a glue-like mass that does not release the solid phase neither under rapid cooling, nor in the case of natural or artificially decelerated cooling. A similar pattern is observed in all the other cases when the content of *n*-butanol in the mixed solvent is smaller than 20 vol %.

The iron(III) salt can be selectively obtained at the instant of virtually quantitative consumption of the acid with such solvents as *n*-butanol, petroleum spirit, butyl acetate (not shown in Fig. 1) and the above-mentioned mixtures of dimethylformamide and *n*-butanol. The kinetic curve of iron(II) salt accumulation in these solvents passes through a weak maximum lying close to the ordinate axis and further approaches the abscissa axis and virtually runs into it. In such solvents as dimethylformamide, formamide (not shown in Fig. 1; the process is slower than that in dimethylformamide, but goes to completion and shows no self-termination), and water, iron(II) and (III) salts are always accumulated in comparable amounts.

The nature of the solvent used strongly affects, through the dynamics of variation of the phase state of the reaction mixture, the operation efficiency of the bead mill. This, in turn, is transformed to a certain extent to the apparent efficiency of the stimulating additive used and, consequently, affects its optimal amount, which is far from being the same in different solvents.

CONCLUSIONS

(1) The liquid phase predetermines the type of the kinetic curve of consumption of benzoic acid in its reaction with metallic iron in a mechanically activated process: quantitative characteristics of its separate portions, duration of the process as a whole, occurrence of autoacceleration and autodeceleration, self-termination and self-resumption, and selectivity with respect to iron(II) and (III) salts, and also the dynamics of their variation in the course of the process.

(2) At the instant of virtually quantitative consumption of benzoic acid, a selectivity for iron(III) benzoate that tends to 100% is provided by use of such solvents as white spirit, *n*-butanol, butyl acetate, and some mixtures of *n*-butanol and dimethylformamide, in which case a significant amount of the target salt is accumulated in the solid phase in the form of a suspension.

(3) The complete dissolution of the acid in the solvent for the liquid phase, used in the study, is not

a necessary condition for rapid and, a fortiori, quantitative and selective course of the redox process of the given type.

(4) The least favorable variant, as far as the rate and extent of the process, its selectivity for salts, and their isolation from the reaction mixture are concerned, was obtained with a solvent composed of dimethylformamide and its mixtures with up to 20% *n*-butanol (by volume). In this case, non of the salts is accumulated and the reaction mixture turns into a viscous glue-like system.

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