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Mechanism of the benzenediazonium tetrafluoroborate thermolysis in the solid state

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Abstract

The thermolysis of benzenediazonium tetrafluoroborate was studied by thermogravimetry in dynamic mode. The decomposition of $[\mathrm{ArN{\equiv}N}]^+\mathrm{BF_4}^-$ in the solid state with the formation of C_6H_5F, BF_3, C_6H_6, and N_2 starts at $T > 348$ K. The speed of the thermolysis was estimated gravimetrically and by infrared spectroscopy, considering the change of the intensity of the absorption band at $1498\,\mathrm{cm}^{-1}$, which corresponds to fluorobenzene. The maximal rate of thermolysis observes at the 366.5 K. A kinetic scheme, which includes the formation of a neutral complex $[\mathrm{C_6H_5}^{\delta+}\cdots\mathrm{BF_4}^{\delta-}]$, is proposed for the thermolysis of arenediazonium tetrafluoroborate. The decomposition of the complex with the formation of free-radical intermediates explains the chain character of the thermolysis.

Keywords: Benzenediazonium tetrafluoroborate; Solid state; Thermolysis; Chain mechanism

1. Introduction

Due to the presence of the diazo group $-\mathrm{N^+{\equiv}N}$, arenediazonium salts (DAS) are highly reactive and are used in the synthesis of azodyes [1], in preparative synthesis [2], and analytical methods [3]. The basic process which most completely reflects the properties of DAS, is the dediazotization, i.e. the elimination of free nitrogen molecule [4]. The dediazotization occurring during the electrochemical reduction of arenediazonium salts was studied by Elofson and Gadallah [5], who found that the addition of one electron by the DAS cation results in the formation of a diazonium radical, which easily disproportionates with the elimination of free nitrogen and the formation of a phenyl radical:

$$\mathrm{Ar{-}\overset{+}{N}{\equiv}N \overset{+e^-}{\rightleftarrows} Ar{-}N{=}\dot{N};} \tag{1}$$

$$\mathrm{Ar{-}N{=}\dot{N} \rightarrow Ar^{\bullet} + N_2.} \tag{2}$$

Another way to generate electrons for the reduction of DAS consists in the radiolysis of water producing solvated electrons [6]:

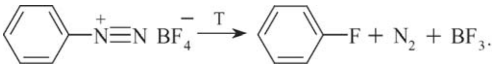
$$\mathrm{H_2O \xrightarrow{\gamma} e^-_{aq} + {}^{\bullet}OH + {}^{\bullet}H + H_2 + H_2O_2;} \tag{3}$$

$$\mathrm{e^-_{aq} + Ar{-}\overset{+}{N}{\equiv}N \rightarrow Ar{-}N{=}\dot{N} \rightarrow Ar^{\bullet} + N_2.} \tag{4}$$

The break of the C–N bond in DAS can also be induced by ultraviolet rays [7]:

$$\mathrm{Ar{-}\overset{+}{N}{\equiv}NX^- \xrightarrow{h\nu} Ar^{\bullet} + N_2 + X^{\bullet}.} \tag{5}$$

One of the main factors that influence the stability of DAS is temperature. The thermolysis of arenediazonium tetrafluoroborate in the absence of solvent leads to the formation of ArF with a good yield (Balz–Schiemann reaction) [8,9]:



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The thermolysis of DAS in solution is enhanced by an increase of the nucleophility of the solvent or by an increase of the electrophilicity of the nitrogen atom in β-position of DAS, which is determined by the nature and position of the substitutes in the phenyl ring [10]. This effect is due to the formation of a complex with a charge transfer between a solvent molecule, which acts as an electron donor (ED), and the nitrogen atom of DAS on which the positive charge is localized. The resulting complex is readily dediazotized [11]:

$$\mathrm{Ar{-}\overset{+}{N}{\equiv}N} + :\mathrm{ED} \rightarrow \mathrm{Ar{-}N{=}N{-}ED^{+}} \rightarrow \mathrm{Ar^{\bullet}} + \mathrm{N_2} + {}^{\bullet}\mathrm{ED}. \tag{7}$$

The influence of the environment on the reaction of the thermal dediazotization in acid methanol solutions was investigated by Bunnett and co-workers [12]. In a nitrogen atmosphere the dediazotization takes place homolytically according to Eqs. (1) and (2), whereas under oxygen the reaction proceeds heterolytically via the formation of an arene-cation:

$$\mathrm{Ar{-}\overset{+}{N}{\equiv}N} \rightarrow \mathrm{Ar^{+}} + \mathrm{N_2}. \tag{8}$$

The presence of strong electron acceptors in the phenyl ring favors the homolytical type of reaction via the intermediate formation of phenyl radicals. The dediazotization of, for example, $C_6F_5{-}N^{+}{\equiv}N$ takes place homolytically and the one-electron reduction by, for example, iodine ions can be the source of tetrafluorinephenyl radicals [13]. The yield of fluorinated arenes is considerably influenced by the nature of the counter-ion. Hence, in the case of tetrafluoroborate of diazonated *o*-aminobenzoic acid, *o*-fluorobenzoic acid is formed with a yield of 19% [14], whereas for hexafluorophosphates the yield increases to 78% [15]. Substitution of the diazo group by fluorine takes place in the case of pyridine-2-*o*-diazonium tetrafluoroborate with a yield of 50% of the fluorine derivative during boiling in petroleum [16].

The Balz–Schiemann reaction has been used for the synthesis of the new antibacterial pyridonecarboxylic acid enoxacine [17], halogen derivatives of thiophenecarboxylates [18], and dimethyl derivatives of metacyclophane [19]. Moreover, drawbacks associated with the classic Balz–Schiemann reaction are eliminated in a series of examples by conducting fluorodediazoniation in ionic liquid solvents, thus opening up a new horizon for a this process [20].

Despite the large number of studies of the dediazotization reaction and its wide application for preparation purposes, its mechanism is not yet explained. In particular, it is not yet known if the reaction proceeds internally or externally spherically, the speed of thermolysis has not been investigated, etc. Moreover, the thermal decomposition of arenediazonium salts was studied for its solutions in most cases [10–12,21,22]. Therefore, in the present work the thermolysis was studied by derivatography with the determination of the gaseous products by an IR spectrometer for the solid samples of arenediazonium tetrafluoroborates. The analysis of the products of the thermolysis as a function of time allowed us to define a chain decomposition of DAS, to propose a reaction scheme and to explain the formation paths of the gaseous products of the Balz–Schiemann reaction.

2. Experimental

Freshly distilled aniline (Linegal Chemicals, analytical grade) was used for the synthesis of benzenediazonium tetrafluoroborate. The diazoniation of aniline was made according to a widely accepted method, described in [9]. IR spectra of the benzenediazonium tetrafluoroborate solid sample, pressed into a pellet together with KBr, were obtained on a Specord M80 spectrophotometer (Carl Zeiss Jena), scanning the region from 4000 to 400 cm^{-1}. Thermogravimetric (TG) and differential thermogravimetric (DTG) measurements were carried out using a microbalance NETZSCH TG 209 in dynamic mode with a heating rate of 2 and 5 K min^{-1} (in the 293–393 K and 393–523 K temperature intervals, respectively) in an inert argon atmosphere. The weights of the samples for analysis were ∼10 mg, the argon flow was 30 cm^3 min^{-1}, and the range of temperature change was from 293 to 523 K. Evolution of the IR absorption spectrum of volatile products of the benzenediazonium tetrafluoroborate thermolysis in the dynamic mode (time interval between next spectrum scanning 23 s) was recorded on a BRUKER IFS66 FTIR spectrophotometer.

3. Results and discussion

Typical differential and integral curves of the mass losses (both with time and elevation of temperature) detected during the heating of the DAS sample in the dynamic mode are shown in Fig. 1. As it indicates results of DTG analysis (Fig. 1a), the decrease of the DAS sample's weight starts at $T > 336$ K and maximal rate of thermolysis observes at the ≈366.5 K. DAS thermolysis finished practically within the 37 min after the start of sample heating (Fig. 1b), that corresponds to reached temperature ≈370 K. However, the thermal decomposition of benzenediazonium tetrafluoroborate starts at 348 K, while an initial minor mass change, which displays as the maximum on DTG curve at 344.4 K, is due, apparently, to the loss of residual water. Previously an analogous peak was observed for the thermolysis of polyaniline [23]. The presence of this peak at 344.4 K cannot be associated with the simple absorption of water, because the loss of moisture should take place already at 303 K (the absorption energy of water molecules is 13–22 kJ mol^{-1} [24]). It is clear that water interacts with DAS molecules via intermolecular hydrogen bonds, the binding energy of which lies in the range 63–75 kJ mol^{-1} [25], which explains the higher temperature.

The hydrogen bonding confirms the IR spectrum of initial DAS in the solid state, which is shown in Fig. 2. The oscillation modes were attributed according to data of work [26]. The valence vibrations of diazo group corresponds the absorption band with maximum at 2290 cm^{-1} while the band at 1080 cm^{-1} can be refers to the BF_4^- ions. There are band at 1640, 1480 and 1420 cm^{-1}, which corresponds to the vibration of benzene ring. The bands at 750 and 700 cm^{-1} can be attributed to the deformation ring-puckering vibrations of C–H bonds in the monosubstituted benzene. The stretching vibrations of O–H bond under the formation of hydrogen bonds (of N···HO type in our case) corresponds wide band in the 3800–2600 cm^{-1} wavelength interval with a maximum at 3430 cm^{-1}, however

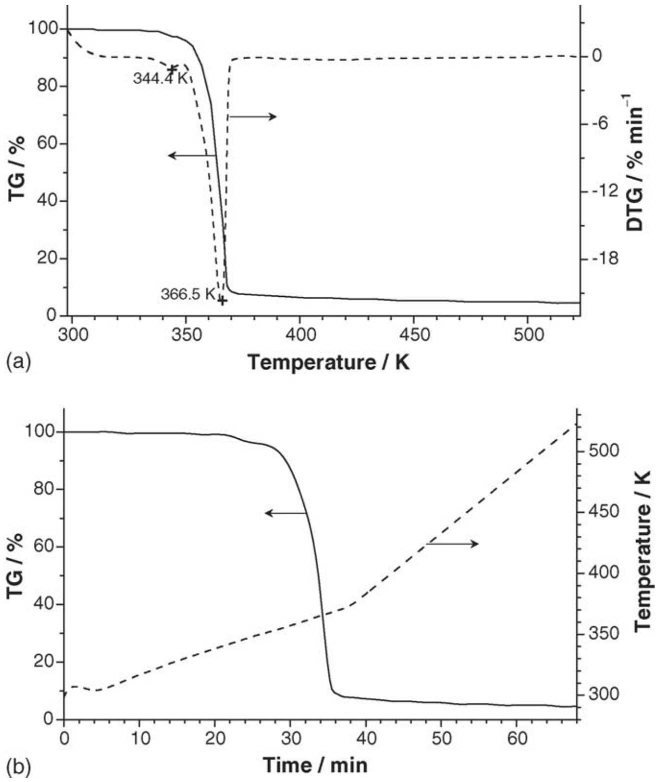


Fig. 1. (a) Integral (—) and differential (- - -) derivatograms of a sample of arenediazonium tetrafluoroborate; b) changes of sample mass (—) and temperature (- - -) with time (sample mass: 11.750 mg; temperature scanning rate: 2 and 5 K min^{-1} before and after the 373 K, respectively).

the valence vibrations of C–H bonds displays also in the same region (maximum of band at 3080–3030 cm^{-1}). Besides, there is the weak smeared band at 935 cm^{-1}, which can be attributed to the O–H deformation vibrations.

The thermolysis of DAS is accompanied by the formation of volatile products, and their accumulation in the gaseous phase can be followed by measuring of the increase of intensity of their absorption bands. During the first 22 min of the sample heating no significant decomposition (Fig. 1b) was observed and no formation of volatile compounds was detected by IR spectroscopy (Fig. 3). The changes in the IR spectrum starting between 26th and 28th min after the beginning of sample heating (Fig. 3).

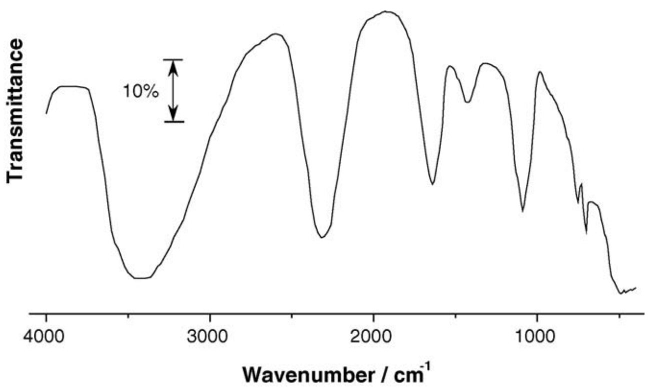


Fig. 2. IR spectrum of benzenediazonium tetrafluoroborate in the solid state.

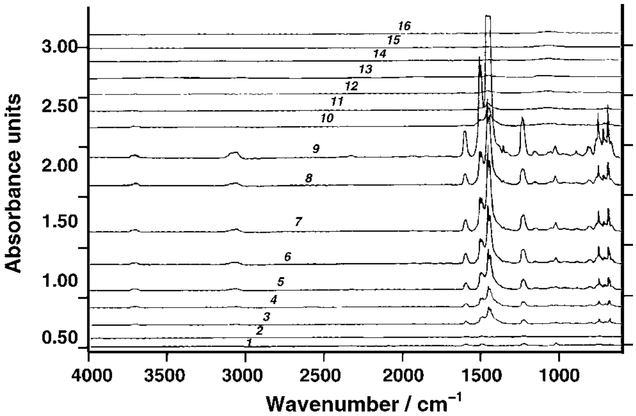


Fig. 3. Dynamics of change of intensity of the IR absorption bands of the volatile products of the thermolysis of DAS. Time intervals after the thermolysis start, s: (1) 1439; (2) 1538; (3) 1677; (4) 1686; (5) 1736; (6) 1776; (7 and 8) 1835; (9) 2053; (10) 2212; (11) 2271; (12) 2410; (13) 2519; (14) 2746; (15) 2866; (16) 2995.

There are the absorption bands at 3059, 1601, 1498, 1236, 1028 and 754 cm^{-1} (Fig. 4) in the IR spectrum, associated with the oscillation modes of benzene and fluorobenzene, which were attributed according to data compiled in a review by Pankratov and Zhelezko [27]. The full dynamics of the formation of gaseous thermolysis products can be seen from Fig. 5.

It should be noticed that, beside the gaseous products, nonvolatile products are formed, which can include dimers resulting from the recombination of free radicals, and also polymeric/oligomeric products, as observed during the electrochemical reduction of diazonium salts [28]. The averaged yield of decomposition with formation of volatile substances is 44.59 %. Therefore, for the construction of the curves of mass losses due to the heating of the particular sample with the total mass of 11.750 mg (Fig. 1), a mass loss equal to 5.240 mg was considered to correspond to a yield of 100 %. The composition of the solid remainder (equal to 55.41 % of the total sample mass) or its thermal decomposition, which takes place at temperatures higher than 373 K, were not investigated by us.

The intensive absorption band at 1498 cm^{-1} (Fig. 4), which corresponds to fluorobenzene, was selected as a reference and from the change of its intensity as a function of time the speed

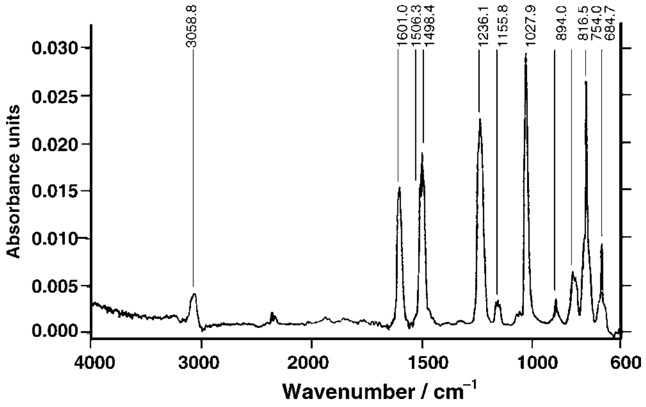


Fig. 4. Absorption IR spectrum of volatile products of the DAS sample thermolysis.

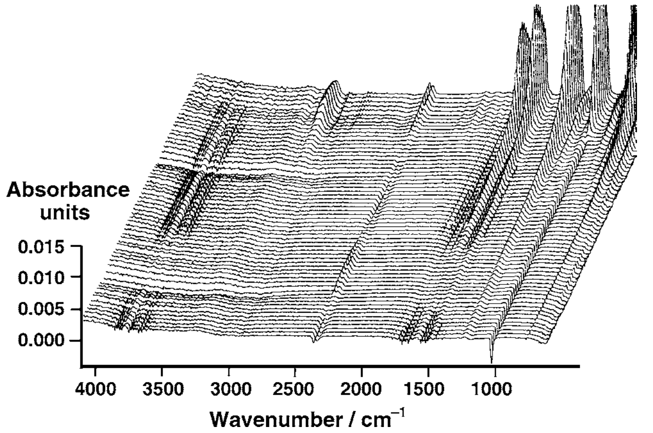


Fig. 5. Evolution of IR absorption spectrum of the volatile thermolysis products when keeping the DAS sample (interval between spectrum scans: 23 s).

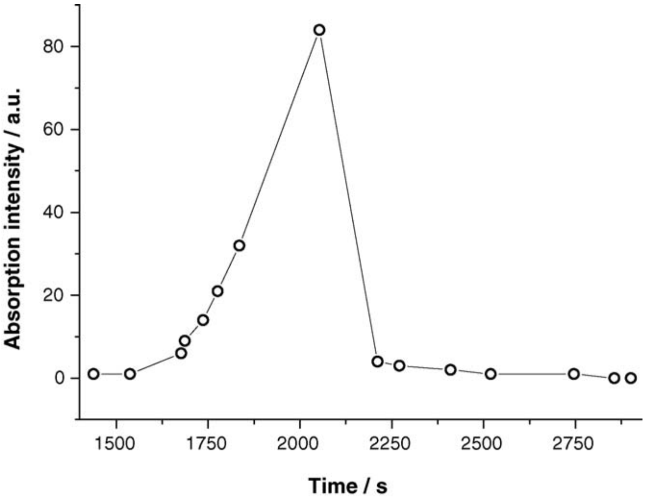
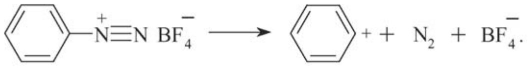


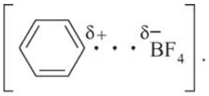
Fig. 6. Change of intensity of the absorption band at 1498 cm^{-1} during the thermolysis of a DAS sample vs. time.

of the thermolysis was estimated (Fig. 6). The intensity of band at 1498 cm^{-1} increases after the ~1540 s of thermolysis. Up to 1740 s the process flows at a constant speed, but is from this moment on self-accelerated. After 2200 s the decomposition and the resulting elimination of gaseous compounds ends, and the intensities of the absorption bands vanish to zero. Such changes of speed are typical for chain reactions. We believe that at the initial stage of the thermolysis of DAS (between 25 and 26 min, when sample destruction is initiated after the water elimination (Fig. 1), and 27–28 min, when the spectra of volatile products were obtained (Fig. 6)) the heterolytical decomposition of the benzenediazo-cation with the formation of a benzene-cation and the elimination of a nitrogen molecule (whose rotation-vibration spectrum is forbidden in IR spectroscopy) takes place:



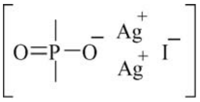
(9)

The benzene and tetrafluoroborate ions are at distance where the forces of electrostatic attraction do not allow them to separate, which may lead to the formation of ion pairs like:



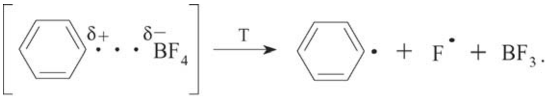
(10)

The probability of the formation of such complexes increases as the thermolysis in the solid state progresses. An ionic transport in glass-like electrolytes takes place by ions from primary formed ionic pairs. For example, during the dissolution of silver iodine in silver phosphate an ionic quadruple is formed:



which in external electric field dissociates to ions that carry the charges and provide the electric conductivity of solid electrolytes [29].

During the initial (induction) period, the basic reaction (9) results in the accumulation of ion pairs (10). At the same time BF_3, and C_6H_5F are eliminated in small quantities, and the formation of ion pairs is conditioned by the kinetics of the competing reaction (6). After the accumulation of a sufficient quantity of ion pairs (10), the latter decompose with the formation of BF_3 and two free-radical particles:

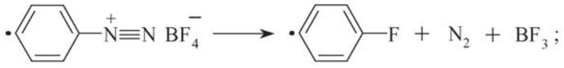


(11)

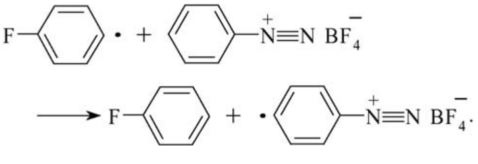
The phenyl radical and the fluorine atom attack the initial arenediazonium salt:

(12)

(13)

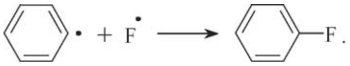


(14)



(15)

The chain starts by the reaction (11). The transformation with the participation of free-radical particles and the formation of at least one product of the reactions (12)–(15) is the continuation of the kinetic chain. The interaction of phenyl radicals and fluorine radicals:



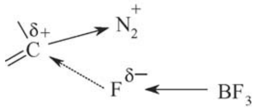
(16)

terminates the chain.

The proposed scheme of chain decomposition of DAS agrees with the acceleration of the thermolysis observed after a induction period. Considering the usual scheme of thermolysis, proposed, for example, by Swain et al., who adopt a heterolytical mechanism of decomposition via the formation of arene cations [30], it is not possible to explain the acceleration of the reaction. The formation of two free-radical particles has been postulated for the photochemical decomposition of arenediazonium chloride [7]. However, this reaction is not a chain reaction, because the possible reactions (12)–(15), the chain continuation reactions, were not considered. The basic product of the reaction, chlorobenzene, was formed as the result of a recombination of arene radicals with chlorine atoms, i.e. by a chain-terminating reaction. A chain mechanism was suggested by Galli for the decomposition of arenediazonium iodine [31], but no experimental proofs were given.

4. Conclusions

The thermolysis of arenediazonium tetrafluoroborate in the solid state is not affected by the interaction of intermediates with the solvent, as observed for the decomposition in solution. The main products of photochemical or thermal decomposition of diphenylamine-4-diazonium salts in ethanol are ethyl ethers, which are formed by a heterolytical break of the C—N bond during the photolysis and a homolytical break of the same bond during the thermolysis [22]. We conclude that at the first stage of the thermolysis a benzene cation is heterolytically formed (9), but this does not consider the attack of the carbon atom by the ions F^- according to the externally spherical mechanism [32]:



The acceptation of a scheme of one-step decomposition (Eq. (6)) is contrary to experimental observations, which indicate a chain mechanism (Fig. 4). For this reason, a stage corresponding to the formation of an uncharged complex (10) was included in the general scheme of the thermolysis. The decomposition of this complex is the origin of a kinetic chain. The yield of the chain decomposition of $Ar–N^+≡N\ BF_4^-$ with the formation of gaseous products was 44.59%. The composition of the solid remainder, which in organic chemistry is called the resinification product, was not studied in the present work.

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