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> CHEMICAL KINETICS AND CATALYSIS

Superacids as Catalysts of the Oxidation of Inorganic Substrates

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Abstract—The oxidation of sulfur dioxide, nitrogen dioxide, carbon monoxide, etc., in anhydrous trifluoroacetic acid (TFA) at room temperature was observed. The oxidative ability of anhydrous TFA in reactions with inorganic substances was shown to be related to molecular oxygen dissolved in it. The dissolved molecular oxygen endowed TFA with the properties of a superacid with $pK_a \approx -12$. Mechanisms of active oxygen reactions with inorganic substrates were suggested.

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INTRODUCTION

The catalytic activity of fluorine-containing superacids such as HF-SbF₅, FSO₃H, and FSO₃H-SbF₅ in hydrocarbon transformations is usually related to the high mobility of protons capable of forming carbonium ions [1]. It was found in [2] that anhydrous trifluoroacetic acid (TFA) also exhibited the properties of superacids. It was suggested that this was related to dissolved molecular oxygen in an active state different from the ground triplet state. We therefore deemed it interesting to study the chemical nature of active oxygen dissolved in TFA in more detail and find out if high oxidative activity is a general property of classic superacids. In this work, we studied the oxidation of a wide range of inorganic substances in anhydrous TFA as compared with their similar transformations in fluorosulfonic acid (FSA), one of the strongest superacids.

EXPERIMENTAL

The oxidation of sulfur(IV) oxide was studied at room temperature by passing a flow of SO_2 at a rate of 20 ml/min through anhydrous TFA or FSA (100 ml) in a bubbler. Experiments were continued until SO_2 began to get through the reactor, as was established from changes in the color of an aqueous solution of potassium bichromate. Sulfur(VI) oxide formed was determined gravimetrically. For this purpose, a solution sample (20 ml) was taken from the bubbler, a 20% solution of Ba(NO₃)₂ was added to it in excess, and the mixture was heated at 50°C for 20 min. Heating was necessary for the destruction of Caro's acid anhydride and its dimers, which we found to be the primary products of the oxidation of SO₂ in TFA; these substances did not form precipitates with barium nitrate. The BaSO₄ precipitate was separated from the solution, washed with distilled water, dried until its weight ceased to change, and weighed [3]. With fluorosulfonic acid, sulfur contained in FSA itself was taken into account.

Transformations of nitrogen(IV) oxide were studied similarly. The reaction was considered complete when NO₂ appeared at the exit from the system. The presence of nitrate(V) ions in the reaction mixture was established by the "brown ring" reaction [4]. The amount of nitrogen(V) oxide formed was estimated from the amount of nitrogen(IV) oxide absorbed until it began to flow through the reactor unchanged. Experiments with the oxidation of SO₂ and NO₂ were performed so as to attain 100% conversion of the initial substrate into compounds with higher oxidation degrees.

The oxidation of CO was also conducted at room temperature. Carbon monoxide prepared by treating formic acid with concentrated H_2SO_4 was bubbled through anhydrous TFA. The distillation of anhydrous TFA with absorbed CO was accompanied by the evolution of carbon dioxide, which reacted with a solution of barium nitrate to form a white BaCO₃ precipitate. During distillation, CO₂ evolved was not completely absorbed by the solution of barium nitrate. We were therefore unable to determine the degree of substrate conversion in this reaction.

Parallel experiments with TFA were always performed after removing dissolved oxygen by oxalic acid admixtures until the absence of oxidizers was established by the "benzene ring" reaction with potassium iodide. Several oxidation experiments were also performed with glacial acetic acid.

RESULTS AND DISCUSSION

The suggestion was made in [5] that peroxide groups could form in TFA. For this reason, we first experimentally checked this hypothesis. All qualitative reactions for peroxide groups in TFA were, however, indicative of their absence. It follows that the oxidative ability of TFA was related exclusively to active oxygen dissolved in it. The reactivity of this active oxygen was demonstrated in reactions of TFA with many substances capable of redox transformations, including chromium(III) chloride and carbon(II), sulfur(IV), nitrogen(II), and nitrogen(IV) oxides.

Chromium(III) compounds can be oxidized to chromium +6 derivatives under the action of oxidative melts and in aqueous solutions, always with the formation of oxo compounds. In acid media, oxidation to chromium(VI) can only be caused by strong oxidizers. Mixing equal volumes of TFA and an aqueous solution of $CrCl_3$ caused green solution coloration to change into blue, which was evidence of the formation of the CrO_5 peroxo complex. As has been mentioned, TFA does not contain peroxo groups. It was therefore the interaction of Cr^{3+} with dissolved active oxygen (*O₂) that was responsible for the formation of the CrO_5 peroxo complex,

Importantly, no such peroxo complex was formed under the action of molecular oxygen in the triplet state. It follows that active oxygen in TFA is a stronger oxidizer than potassium bichromate.

The oxidation of sulfur dioxide in the absence of a catalyst is a very slow reaction. Performing oxidation requires the transition of oxygen into an active state.

Trifluoroacetic acid absorbs SO_2 in an 8.8 : 1 molar ratio. The resulting reaction mixture contains peroxo groups and sulfur(VI), whereas sulfur(IV) is completely absent,



The presence of peroxo groups and sulfur(VI) corresponds to the formula unit of Caro's acid anhydride (SO_4) . Indeed, hydrolysis under weak heating gave H_2SO_4 and H_2O_2 ,

$$\begin{array}{c} O & O \\ O & O \\ O & O \end{array} + H_2O \longrightarrow \begin{array}{c} O & O \\ O & O \\ O & O \end{array} + H_2O \longrightarrow \begin{array}{c} O & O \\ O & O \end{array} + H_2O \longrightarrow \begin{array}{c} O & O \\ O & O$$

These results directly prove the presence of dissolved active oxygen in TFA; this oxygen is consumed to oxidize SO_2 . The question arises of whether this consumption can be compensated for by absorbing molecular oxygen. After the oxidation of sulfur(IV) to sulfur(VI) was complete, when all dissolved oxygen was used up, a flow of air was passed through TFA. After this, the oxidation of sulfur(IV) resumed. It follows that a virtually unlimited amount of SO_2 can be oxidized by alternating the saturation of TFA with air oxygen and oxidation. Trifluoroacetic acid can therefore be considered a catalyst of the oxidation of SO_2 in the presence of dissolved molecular oxygen.

The role played by trifluoroacetic acid as a catalyst of oxidation is the activation of oxygen dissolved in it. It was shown in [6] that fluorine-containing compounds formed very strong complexes with molecular oxygen. The formation of these complexes changes the electronic configuration of the dioxygen molecule, likely into that of the reactive singlet state. The resulting electronic configuration of the oxygen molecule corresponds to its singlet state, which may be the reason for the anomalously strong oxidizing properties of oxygen in TFA and the strength of bonds between dissolved oxygen and TFA molecules.

All superacids contain fluorine atoms. It is therefore logical to assume that they can also dissolve molecular oxygen with its transition into the active state. Fluoro-sulfonic acid HF \cdot SO₃ is the strongest among all acids known; its p K_a equals –13.5. It is most extensively used as a superacidic catalyst. The only direct proof of the presence of dissolved active oxygen in it would be the oxidation of SO₂ to SO₃, because the reduction of molecular oxygen contained in fluorosulfonic acid changes the degree of oxidation of the central atom and thereby destroys superacid molecules.

We found that the behavior of FSA differed from that of TFA by the absence of peroxo groups and a much larger (by a factor of 4) amount of absorbed and converted SO₂. The larger solubility of SO₂ in FSA compared with FTA is related to donor–acceptor and dative interactions between sulfur and oxygen atoms of a neighboring molecule, which results in the formation of trimers and polymers (SO₃)_n very characteristic of sulfur(VI) oxide. Possibly, it is the higher concentration of SO₂ in HF · SO₃ that explains the absence of peroxo compounds as intermediate oxidation products,

$$SO_2 + SO_4 \longrightarrow 2SO_3$$
.

The hypothesis of the stabilization of active singlet oxygen in fluorine-containing superacids allows us to consider two variants of their interaction with substrates after one-electron oxidation and the formation of ion-radical pairs or charge transfer complexes:

$$A + *O_{2} \cdot F - R \longrightarrow \left[A^{+} \cdot \underbrace{O_{2}^{\cdot} \cdot F - R}_{2}\right],$$
$$\left[A^{+} \cdot \underbrace{O_{2}^{\cdot} \cdot F - R}_{2}\right] \xrightarrow{1} A^{+} \cdot + O_{2}^{\cdot} \cdot F - R$$
$$\xrightarrow{2} AO_{2} + \underbrace{F - R}_{2}$$

If the interaction energy between the $O_2^{\overline{}}$ radical anion and fluorine-containing fragments is higher than the energy of its interaction with radical cation A^{+} , charge separation occurs, and the radical cation goes out of the complex (path 1). Its further transformations depend on its intrinsic nature and medium acidity [7]. However, if the interaction energy between $O_2^{\overline{1}}$ and fluorine-containing fragments is lower than that between $O_2^{\overline{1}}$ and

 A^{+} , the charges combine and the formation of oxygen-containing substrates occurs (path 2). Indeed, it was shown in [2] that the products of methylphenylcyclopropane transformations in oxygenated TFA were 1-(butenyl)-4-(3-phenylbutyl)-benzene dimers with a 97% degree of conversion. After part of the oxygen was removed, the same products were formed, but the conversion decreased to 70%. This leads us to conclude that the reaction with methylphenylcyclopropane in TFA follows path 1.

As with sulfur dioxide, the oxidation of NO_2 in anhydrous TFA involves the formation of nitrogen(V) peroxo compounds, which decompose under the action of water and when heated to produce nitric acid. Calculations show that the number of active oxygen molecules that participate in the oxidation of NO_2 is much larger (O_2 : TFA = 1 : 12) than with the oxidation of SO₂ (1 : 17). This is likely related to a lower ionization potential of NO_2 (9.78 eV) compared with SO₂ (12.34 eV). The oxidation of substances with still larger ionization potentials, for instance, carbon monoxide (14 eV), also occurs in anhydrous TFA. In the latter reaction, no peroxide compounds were detected in the reaction mixture. To summarize, superacids can effect the catalytic oxidation of sulfur and nitrogen dioxides and carbon monoxide at as low as room temperature. Their oxidative action is caused by molecular oxygen dissolved in them in the form of active singlet O_2 molecules. Trifluoroacetic acid, which is not a superacid formally, is capable not only of dissolving and strongly binding substantial amounts of molecular oxygen but also of activating it.

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