DECOMPOSITION OF PEROXOBENZOIC ACID IN BENZENE CATALYZED BY TRANSITION METAL 2,4-PENTANEDIONATES

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The decomposition of peroxobenzoic acid in benzene was studied, and catalytic effects of Fe(III), Mn(III), Co(II), Co(III), and Cr(III) on the reaction rate and the composition of the reaction mixture were investigated. An analogous experiment carried out in perdeuterobenzene and determination of the distribution of deuterium in the reaction products provided evidence for the participation of the solvent in peroxobenzoic acid decomposition.

Autoxidations of hydrocarbons, aldehydes and ketones in the liquid phase are processes in which peroxocompounds are formed as unstable intermediates. The autoxidation of benzaldehyde[1] involves the intermediate formation of peroxobenzoic acid, which either reacts with another molecule of benzaldehyde[2] or decomposes[3] to yield the end product, benzoic acid.

In studying the autoxidation of benzaldehyde our interest was centred on the fate of the peroxobenzoic acid. This question has received much study in the past. The older literature contains mainly studies on the stability of peroxobenzoic acid and its solutions in various solvents under a variety of conditions[4,5]. The decomposition of peroxobenzoic acid was studied by Kirmse and Horner[6], who proposed a free radical chain mechanism for this reaction, in contrast to Goodman and coworkers[7] who considered the same reaction, under the same conditions, to proceed by an ionic mechanism.

Of special relevance to our investigation are studies dealing with peroxobenzoic acid decomposition in organic solvents. Cohen and Edwards[8] studied this reaction in benzene and 1-butanol in the presence of 2,2-diphenyl-1-picrylhydrazyl. A free radical chain mechanism, involving the interaction with the last-mentioned compound, was proposed for the reaction in benzene, but no evidence for such a mechanism was found in 1-butanol. Tokumaru and Simamura studied the non-catalyzed decomposition of peroxobenzoic acid in alcohols[9], ethers[10], and aliphatic and aromatic hydrocarbons[11]. An important finding from these studies is that the solvents participate in the reaction, the reaction rate being sensitive to the nature of the solvent employed. From results of kinetic studies and product analyses it was concluded that the reaction proceeded by a free radical chain mechanism. The most important of papers dealing with the peroxobenzoic acid decomposition in acetic acid is the study of Heertjes and coworkers[12], which provides a comparison of the course and the reaction products of the non-catalyzed decomposition and the reaction catalyzed by Co(II) and Co(III) ions. Unlike the Japanese authors, Heertjes and coworkers detected oxygen, in addition to carbon dioxide, in the reaction products.

EXPERIMENTAL

Chemicals

Peroxobenzoic acid was prepared from dibenzoyl peroxide and sodium ethoxide[13]. Benzene (Lachema) and perdeuterobenzene were analytical grade. Fe(III), Mn(III), Co(II), Co(III) and Cr(III) 2,4-pentanedionates were prepared following a published procedure[14].

Apparatus

The main part of the apparatus was a thermostatted reaction vessel designed so as to allow samples to be withdrawn without disturbing the protective atmosphere. The volume changes were measured by means of a thermostatted burette connected to the vessel. The vessel, mounted in a shaking device, was placed in a dark box.

Procedure

The vessel was filled, in an atmosphere of nitrogen, with a solution of peroxobenzoic acid, and was vigorously shaken (3—5 vibrations per second). The gas volume change was recorded, and samples of the reaction mixture were analyzed for peroxobenzoic acid content.

Analytical Methods

The variation in the peroxobenzoic acid concentration was followed by iodometric titration. The carbon dioxide content was determined by reaction with $Ba(OH)_2$, whose excess was titrated with oxalic acid. The ultraviolet spectra were taken on an SP 800 B spectrophotometer (Unicam, Cambridge), and mass spectra were recorded on an LKB 8500 spectrometer. Thin layer chromatography (TLC) was carried out on Silufol UV 254 plates (heptane-ethanol, 5 : 1).

RESULTS AND DISCUSSION

Reaction Products

The peroxobenzoic acid decomposition was studied in the same manner as the benzaldehyde autoxidation in benzene solution[15]. The reaction was carried out without a catalyst addition, and with additions of Co(III), Co(II), Fe(III), Mn(III) and Cr(III) 2,4-pentanedionates. The kinetics were followed by measuring the decrease in peroxobenzoic acid content by iodometric titration, and by determining the volume of evolved gas. The results are summarized in Table I.

The volumetric determination and GLC analysis showed that the evolved gas was a mixture of carbon dioxide and oxygen, indicating that the peroxobenzoic acid decomposition does not proceed by a simple reaction mechanism.

Analysis of the reaction mixture by means of TLC allowed the reaction products to be detected and isolated. Identification of the products was accomplished by comparing the R_F-values, and ultraviolet and mass spectra with the corresponding standards. The analysis established the presence of benzoic acid, biphenyl, benzoic phenyl ester, and dibenzoyl peroxide. In addition, the reaction mixture contained a product X, which we were not able to identify definitely. From the R_F-value and the reaction with KI on a thin layer it may only be inferred that this product is peroxobenzoic phenyl lester. Table II gives a summary of the quantitative composition of the final reaction mixture. Benzoic acid, in the form of sodium salt,was determined by weighing. Approximate contents of other compounds were determined by using TLC and the standards.

TABLE I

Effect of transition metal 2,4-pentanedionates on the rate of peroxobenzoic acid decomposition. 100 ml of benzoic acid solution in benzene, 298 K; complex concentrations 1 . 10^{-3} mol dm^{-3}; $[N_2]$ = saturated

Value	No add.	Co(II)	Co(III)	Mn(III)	Cr(III)	Fe(III)
Time, s	Peroxobenzoic acid concentration, mol dm^{-3}					
0	0·120	0·114	0·115	0·121	0·150	0·132
900	—	0·054	0·050	0·008	—	—
1 800	—	0·018	0·016		0·072	—
2 700	—	0·005	0·003		—	—
3 600	0·118				0·045	0·115
5 400	—				0·026	—
7 200	—				0·014	0·099
10 800	—				0·002	0·092
18 000	0·112					0·082
Evolved gas, ml	12	45	57	65	—	52
CO_2 content %	—	12·7	15·1	8·9	—	9·8

The composition of the reaction mixture and the volume of the evolved gas vary little from one catalyst to another. The benzoic acid content is always higher than 80%. No phenol, even in traces, was proved in the reaction mixture; the method used for its detection was the reaction with diazobenzidine carried out on a thin layer.

Decomposition of Peroxobenzoic Acid in Perdeuterobenzene

Tokumaru and Simamura have studied the decomposition of peroxobenzoic acid in various solvents, and proposed a free radical chain mechanism for this process, involving free radicals originating from the solvent[9-11]. In order to study the participation of solvent in peroxobenzoic acid decomposition, we used perdeuterobenzene in place of benzene.

The peroxobenzoic acid decomposition in $2 . 10^{-1}$ mol dm^{-3} solution in perdeuterobenzene under a nitrogen atmosphere was catalyzed by an addition of Co(III) tris(2,4-pentanedionato)complex ($1 . 10^{-3}$ mol dm^{-3}) at 25°C. The reaction products were isolated by means of TLC, and the distribution of deuterium was deduced from mass spectra. As simple compounds were involved, it was possible to identify the mass spectra by comparison with tabulated data.

The highest molecular peak found for benzoic acid was at $m/e = 122$, corresponding to undeuterated benzoic acid. Similarly, the mass spectrum of dibenzoyl peroxide showed a peak at $m/e = 242$ due to the undeuterated compound, no peak being observed at a higher m/e. The secondary splitting gave rise to a peak at $m/e = 77$, characteristic of undeuterated phenyl. The mass spectrum of biphenyl exhibited a single molecular peak at $m/e = 159$, indicating the presence of the C_6H_5—C_6D_5

TABLE II

Composition of the reaction mixture on decomposition of all of the peroxobenzoic acid. 100 ml of peroxobenzoic acid solution in benzene ($2 . 10^{-1}$ mol dm^{-3}); [Co(III) 2,4-pentanedionate] = $1 . 10^{-3}$ mol dm^{-3}; 298 K; [N_2] = saturated

Reaction product	Product content of the reaction mixture %
Benzoic acid	80—90
Biphenyl	5—8
Benzoic phenyl ester	2—6
Dibenzoyl peroxide	1—2
Product X	2—4
Water	traces

molecule. This compound was isotopically pure, and the occurrence of the undeuterated biphenyl ($m/e = 154$) and perdeuterated biphenyl ($m/e = 164$) was smaller than 0·5%. The mass spectrum of benzoic phenyl ester showed molecular peaks at $m/e = 198$ and $m/e = 203$, characteristic of undeuterated product and a product with one deuterated phenyl, respectively. Comparison of the peak intensities indicated that the proportion of the deuterated derivative was 50 – 70%. Since the peak at $m/e =$ $= 105$, arising from the primary splitting to C_6H_5CO, was unchanged, and two peaks at $m/e = 77$ and $m/e = 82$ appeared, attributed to phenyl and perdeuterated phenyl, respectively, it is clear that the perdeuterated phenyl binds to C_6H_5CO to form the ester.

Decomposition Kinetics

The rate of peroxobenzoic acid decomposition in benzene has been measured at various concentrations of Co(III) tris(2,4-pentanedionato)complex as catalyst. Linearity of plots of log $[C_6H_5COOH]$ against time (Fig. 1) indicates that at a constant catalyst concentration the peroxobenzoic acid decomposition is first order in peroxobenzoic acid. The decomposition rate is thus described by the equation

$$-d[C_6H_5CO_3H]/dt = k_{exp}[C_6H_5CO_3H] = (k_0 + k_1\,[Cat]^n)\,[C_6H_5CO_3H]\,,$$

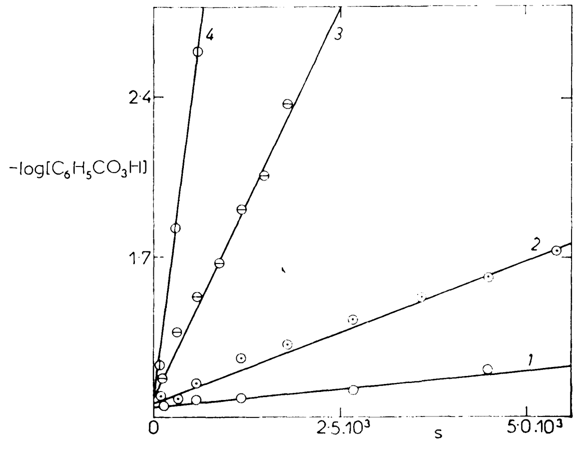

FIG. 1

Effect of Co(III) tris(2,4-pentanedionato)complex on the rate of peroxobenzoic acid decomposition. 100 ml of 0·13 mol dm^{-3} solution of peroxobenzoic acid in benzene; [Co(III) 2,4-pentanedionate]: *1* 5 . 10^{-4} mol dm^{-3}; *2* 1·3 . 10^{-3} mol dm^{-3}; *3* 3 . 10^{-3} mol dm^{-3}; *4* 5 . 10^{-3} mol . . dm^{-3}; $T = 298$ K; $[N_2]$ = saturated where k_0 is the rate constant of the non-catalyzed reaction, and k_1 is the rate constant of the catalyzed reaction.

The rate constant k_0 was evaluated as $1 . 10^{-5}$ s^{-1}. Plotting $\log(k_{exp} - k_0)$ against log [Cat] yielded $k_1 = 4 . 10^1$ (formal dimension: mol$^{-1,85}$ l^{1,85} s^{-1}) and $n = 1{\cdot}85$.

The rate of the non-catalyzed reaction is apparently negligible compared with the rate of the catalyzed reaction. The non-integral order with respect to the catalyst concentration indicates that the catalyzed reaction is of complex nature. It is likely that this reaction involves the substitution of peroxobenzoic acid into the catalyzing complex, which substantially complicates the reaction mechanism.

The apparent activation energy of the catalyzed reaction, calculated from the rate constants of peroxobenzoic acid decomposition at 25°C, 35°C at a constant Co(III) tris(2,4-pentanedionato)complex concentration of $5 . 10^{-4}$ mol dm^{-3}, is 85 kJ mol^{-1}.

The experimental results lead to the conclusion that the decomposition of peroxobenzoic acid in benzene is catalyzed by transition metal 2,4-pentanedionates, the catalytic activity decreasing in the order Mn(III) > Co(II) = Co(III) > Cr(III) ≫ ≫ Fe(III). The rate of the non-catalyzed reaction is negligible compared with the rate of the catalyzed reaction.

The peroxobenzoic acid decomposition yields benzoic acid as the main product with oxygen and carbon dioxide evolved in the gas phase. The reaction mixture contains small concentrations of several other compounds. The relative amounts of the reaction products depend to some extent on the nature of the catalyst.

Analysis of products of peroxobenzoic acid decomposition has provided definite evidence that the solvent participates in the process. The formation of most of the products might be explained in terms of some of the published free radical chain mechanisms. The structure of the biphenyl formed, however, which has exclusively the composition C_6H_5—C_6D_5, can hardly be rationalized on the assumption of a free radical chain mechanism. Another feature irreconcilable with a free radical chain mechanism is the absence of phenol from the reaction products.

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