NATURE OF THE INDUCTION PERIOD IN THE CHEMILUMINESCENT REACTION OF $W(CO)_6$ AND XeF_2

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The chemiluminescence (CL) and gas evolution in the redox reaction of $W(CO)_6$ and XeF_2 in toluene has an induction period (IP) [1]. In the present work, we studied the effect of the reaction concentrations, temperature, and reaction products on the IP.

EXPERIMENTAL

The samples used were prepared and purified according to reported procedures: XeF_2 [2], WF_6 [3], CO_2 [4], and HF [6]. Pure-grade $W(CO)_6$ was purified by sublimation thrice in vacuum. The samples of toluene and argon were purified according to our previous procedures [7].

The solution of $W(CO)_6$ and XeF_2 were prepared by dissolving weighed samples of the solids in toluene directly before the experiments carried out in an argon atmosphere. Aliquots of the gaseous reagents were introduced into the reactor using a syringe directly into the reaction solution (10.1 μℓ) or with the argon stream bubbled through the solution. The CL [7] and amount of gas evolved using a gas burette were measured during the reaction.

In order to measure the rate constants for the decomposition of XeF_2 and WF_6, a sample of the solid sample and an aliquot of gaseous samples where dissolved in water at 298 K. Then, in the case of WF_6, the change in the concentration of fluoride ions, which result from hydrolysis, was measured potentiometrically using an F-selective electrode. The kinetics for the decomposition of XeF_2 in toluene containing $3 \cdot 10^{-3}$ M water was studied relative to the decrease in $[XeF_2]$ measured by iodometric titrations.

RESULTS AND DISCUSSION

At room temperature and initial $W(CO)_6$ concentration $\leqslant 10^{-3}$ M and concentrations of $XeF_2 \leqslant 3 \cdot 10^{-3}$ M, the IP (40-60 min) is significantly greater than the time for the major reaction (~1 min) (Fig. 1, curves 1 and 2). The IP may be decreased by increasing the reagent concentrations and solution temperature such that the reaction (as well as the CL and gas evolution) proceeds with a marked rate immediately after mixing of the reagents. The length of the IP depends linearly on these reaction parameters (Fig. 2, curves 1 and 2), i.e., an acceleration of the formation of the reaction products reduces the IP.

A number of stable reaction products, namely, CO_2, CO, Xe, HF, and WF_6, were tested as possible accelerators. Only WF_6 affects the IP. The introduction of the remaining products (up to $2.2 \cdot 10^{-2}$ M) into the reaction mixture does not alter the reaction kinetics. The preliminary introduction of WF_6, which had been synthesized independently, into a toluene solution $W(CO)_6$ leads to the onset of emission and gas evolution upon the subsequent addition of XeF_2 without an IP (Fig. 1, curves 3 and 4). Variation of the amount of introduced WF_6 showed that the minimal concentration of this compound necessary for the reaction of $W(CO)_6$ and XeF_2 without an IP is $2 \cdot 10^{-5}$ M (Fig. 3, curve 1). Thus, the formation of very small amounts of WF_6, which acts as a unique "release mechanism," is sufficient for a significant acceleration of the reaction (i.e., the elimination of the IP).

The above results were obtained for identical batches of solvent, containing a strictly determined limited amount of water. Failure to maintain this condition leads to irreproducibility in the length of the IP. Ths significant dependence of the kinetics of the reaction of $W(CO)_6 + XeF_2$ on the presence of moisture in the solution is clearly seen upon the introduction of water vapor with the argon stream prior to the addition of XeF_2 into the solution

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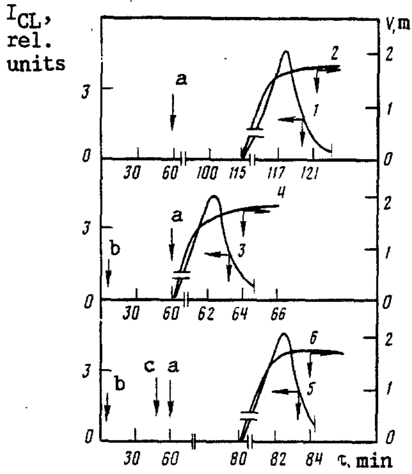

Fig. 1

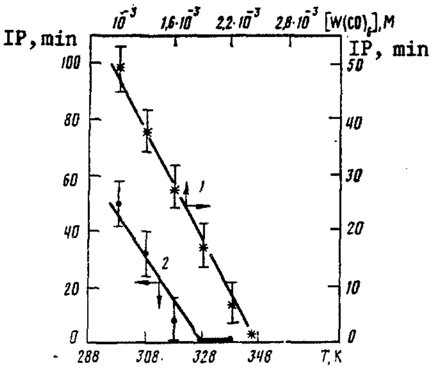

Fig. 2

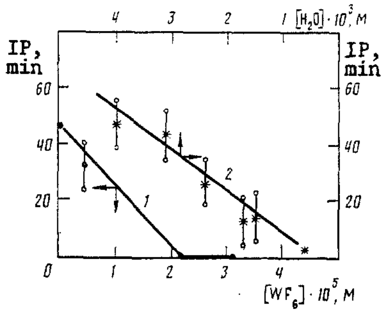

Fig. 3

Fig. 1. The effect of added WF_6 and H_2O on the IP for the appearance of CL (1, 3, 5) and the onset of gas evolution (2, 4, 6) in the reaction of $W(CO)_6$ and XeF_2 in toluene at 298 K. $[W(CO)_6]_0 = 10^{-3}$ M, $[XeF_2]_0 = 3\cdot10^{-3}$ M. The zero moment corresponds to the complete dissolution of the sample of $W(CO)_6$. The arrows indicate the moments of introduction: a) XeF_2 solution, b) $[WF_6]_0$ gas = $(2\cdot10^{-5}$ M), c) water vapor with the argon stream bubble through the solution.

Fig. 2. Dependence of the length of the IP in the reaction of $W(CO)_6 + XeF_2$ in toluene on the concentration of the starting reagents (1) and the solution temperature (2). 1) 298 K $[XeF_2] = 3[W(CO)_6]$, 2) $[XeF_2]_0 = 3\cdot10^{-3}$ M and $[W(CO)_6]_0 = 10^{-3}$ M.

Fig. 3. Effect of the concentration of added WF_6 (1) and H_2O (2) on the IP of the reaction of $W(CO)_6 + XeF_2$. $[XeF_2]_0 = 3\cdot10^{-3}$ M, $[W(CO)_6]_0 = 10^{-3}$ M, 298 K. WF_6 and water were introduced as aliquots using a microsyringe.

of $W(CO)_6$ containing WF_6. In this case, CL begins not immediately after the addition of XeF_2 (Fig. 1, curve 5), as in the analogous experiment without the introduction of water (Fig. 1, curve 3). The length of the IP increases proportionately to the water content in the reaction mixture of $W(CO)_6$ and XeF_2 (Fig. 3, curve 2). These results indicate an inhibiting effect of water due to its reaction with WF_6, leading to the "removal" of WF_6 from the solution.

In the system studied, water may react not only with WF_6 but also with XeF_2. Thus, we measured the rate constants for decomposition of the following compounds in water at 298 K: $(1.3 \pm 0.3)\cdot10^{-2}$ sec^{-1} for WF_6 and $(4.5 \pm 0.2)\cdot10^{-4}$ sec^{-1} for XeF_2. The rate constant for the decomposition of XeF_2 in toluene containing $3\cdot10^{-3}$ M water was found to be $(1.7 \pm 0.2)\cdot10^{-4}$ sec^{-1}. These data indicate the predominance of the reaction of H_2O with WF_6 in comparison with the hydrolysis of XeF_2.

Since XeF_2 decomposes at a significant rate even in dried toluene, it was of interest to establish the effect of the products of this decomposition on the IP. The addition of aliquots of a solution obtained after 15 h decomposition when $[XeF_2]_0 = 3\cdot10^{-3}$ M to the system of $W(CO)_6 + XeF_2$ does not affect the IP. However, decomposition in a solution with $[XeF_2]_0 = 3\cdot10^{-2}$ M proceeds without an IP. On the other hand, the reaction in this case is significantly less than in a parallel experiment without additive. This behavior indicates a different mechanism for the elimination of the IP. Support for this hypothesis lies in the lack of a noticeable effect for toluene solutions of XeF_2 decomposed in a Teflon reactor rather than a glass vessel. Thus, the observed change in the kinetics of the reaction of $W(CO)_6 + XeF_2$ upon the addition of the products of the prolonged decomposition of XeF_2 is attributed to compounds, which are formed with the participation of the walls of the glass reactor and this effect on the IP is usually not operative under the ordinary conditions for carrying out this reaction.

CONCLUSIONS

1. The length of the induction period of the reaction of $W(CO)_6$ and XeF_2 in toluene is proportional to the reagent concentrations and temperature.

2. Only WF_6 among the various products (CO_2, C, HF, Xe, and WF_6) accelerated the reaction. The presence of water in toluene inhibits this reaction due its reaction with WF_6.

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KINETICS OF THE DISPROPORTIONATION OF N-ARYLHYDROXYLAMINES AT DIFFERENT HYDROGEN PARTIAL PRESSURES

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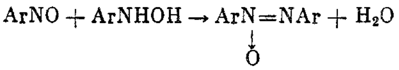
In previous work [1], we showed that the rate of the conversion of N-arylhydroxylamines, ArNHOH, into the corresponding aromatic amines, $ArNH_2$, is independent of the hydrogen pressure in the range from 0.1 to 1.0 MPa, which indicates the following disproportionation reaction [2]:

$$2ArNHOH \rightarrow ArNO + ArNH_2 + H_2O \tag{1}$$

Carrying out the disproportionation of ArNHOH in an inert gas atmosphere gives ArNO, which reacts with ArNHOH to form an azoxybenzene [3, 4].



$$ArNO + ArNHOH \rightarrow Ar\underset{\underset{O}{\downarrow}}{N}{=}NAr + H_2O \tag{2}$$

We undertook a study of the kinetics of the disproportion of ArNHOH upon the partial and complete replacement of H_2 by an inert gas. For this purpose, the reaction kinetics was investigated in a mixture of the inert gas and hydrogen with 0.1 MPa total pressure in the system.

Figures 1 and 2 show that the rate of conversion of ArNHOH in the segment representing a sufficiently high hydrogen content decreases only slightly, while the rate sharply drops in the range of $\bar{p}_{H_2}$ from 400 to 150 hPa and, at $\bar{p}_{H_2} < 150$ hPa, becomes virtually equal to the rate of ArNHOH conversion in a nitrogen atmosphere. At $\bar{p}_{H_2} < 400$ hPa, there is a sharp increase in the content of oxygen-containing compounds (Fig. 1b).

Such a dependence of the distribution of the reaction products indicates a change in the nature of the reactions proceeding on the surface of the heterogeneous catalyst. Upon carrying out the reaction in a system with a sufficiently high hydrogen content, ArNO is hydrogenated to give ArNHOH rather than undergoing reaction (2). Hence, oxygen-containing compounds are virtually lacking in the $\bar{p}_{H_2}$ range from 1000 to 400 hPa. A transition occurs in the range from 400 to 150 hPa. Since nitroso and azoxy compounds are adsorbed on the catalyst to a greater extent than ArNHOH [5] and, thereby, hinder the conversion of ArNHOH to $ArNH_2$, the decrease in the rate of the conversion of ArNHOH with decreasing $\bar{p}_{H_2}$ is attributed to the formation of these intermediate oxygen-containing compounds.

With increasing $\bar{p}_{H_2}$, there is a gradual transition to a region, in which the hydrogenation of ArNO to ArNHOH occurs before its reaction with ArNHOH to form an azoxy compound and, at $\bar{p}_{H_2} > 0.1$ MPa, the rate of ArNHOH conversion, as shown in our previous work [1], is independent of $\bar{p}_{H_2}$.

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