styrene, b) gas–liquid chromatography shows that aldehydes, but not styrene oxides, are formed when styrene polyperoxides break down in an inert atmosphere, either in chlorobenzene solution or in a mixture with styrene itself [3, 11]. The formation of olefin oxides in these systems could be accounted for if the dioxetanes are assumed to participate in epoxidation processes, a possibility already pointed out in [7]. Olefin epoxidation by dioxetanes might also be possible in norbornene oxidation by singlet oxygen if the conditions were such that the rate of oxidation by triplet-state oxygen were vanishingly low [13].

CONCLUSIONS

1. Formation of chemiluminescence emitters during the liquid-phase oxidation of olefins by molecular oxygen can proceed through peroxide radical disproportionation or through the breakdown of intermediate molecular oxidation products.

2. A study of the kinetics of these processes has shown that the second of these two possibilities is realized through dioxetanes and polymeric peroxides formed by chain reactions in the oxidation process.

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THE ELECTROCHEMICAL REDUCTION OF 2-OXY-4,6-DIMETHYLPYRIMIDINE ON PLATINUM AND RHODIUM ELECTRODES

L. A. Taran, V. S. Gromakov, Yu. P. Kitaev

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Electrochemical methods can be used to obtain significant information concerning the mechanism and kinetics of pyrimidine ring reduction, and the effect of adsorption processes and the medium pH on the reduction itself. The present work was a study of the electrochemical reduction of 2-oxy-4,6-dimethylpyrimidine (I) on solid electrodes, and of the effect of the nature of the metal and the acidity of the solution on the reduction process. Only the polarography of (I) on the dropping mercury electrode has been discussed in the literature [1].

EXPERIMENTAL

Potentiostatic polarization curves were developed on a rotating disk electrode with an apparent surface area of 0.28 cm^2, working at pH 0.8 (0.4 N H_2SO_4) and pH 3.0 (acidified 0.4 N Na_2SO_4 solution). The i vs φ

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR.

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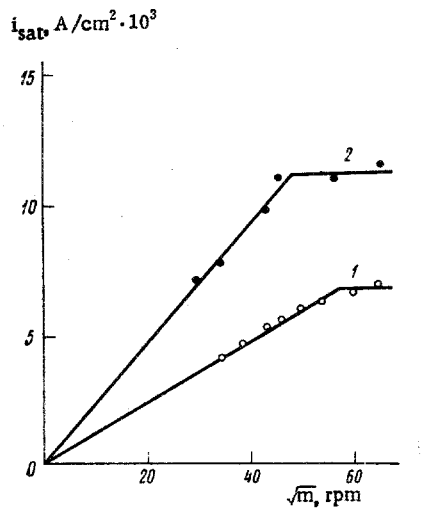


Fig. 1

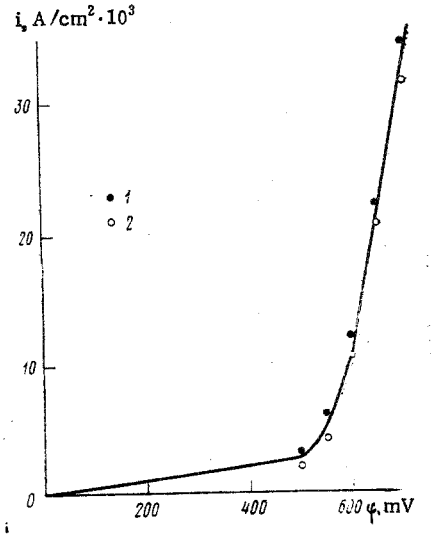


Fig. 2

Fig. 1. Variation of the saturation current with the rate of rotation of platinum (1), and rhodium (2), electrodes, at $C_6H_8N_2O \cdot HCl$ concentrations of $5 \cdot 10^{-3}$ and $8.3 \cdot 10^{-3}$ M.

Fig. 2. Potentiostatic polarization curve obtained with the rotating copper disk electrode (m = 2000 rpm) in the following solutions: 1) 0.4 N H_2SO_4; 2) 0.4 N H_2SO_4 + $5 \cdot 10^{-3}$ M $C_6H_8N_2O \cdot HCl$.

curves were developed from current measurements with a 30 sec time lag. Potentials were varied over the interval from +90 to −30 mV, measurements being relative to a reversible hydrogen electrode in the working solution. The cathodes were Pt/Pt and Rh/Rh electrodes. The platinum electrode was platinized for 5 min in a 3% chloroplatinate solution at i_k = 50 mA/cm^2, and then subjected to cathodic−anodic activation at potentials in the 0-1.5 V range (φ_r). The Rh electrode was prepared from a disk Pt electrode which was first coated with Rh by a 30 min reduction in a sulfate bath [2] at i_k = 1 mA/cm^2 and then covered by Rh-black by a 5 min reduction in a 0.4% $RhCl_3$ solution at i_k = 15 mA/cm^2. Cathodic−anodic activation was carried out at potentials in the 0-1.2 V range. Reproducibility of the electrode surface state was checked through integrated potentiodynamic background curves developed over the region of hydrogen potentials, and through determination of true surface areas [3]. The difference between surface areas in parallel experiments was never more than 10%.

Experiments were carried out in a cell with divided electrode spaces, working out of contact with the air at 20 ± 1°C. Potentials were measured relative to a reversible hydrogen electrode in the working solution (φ_r). Preliminary electrolysis and determination of the effect of the solution pH on the rate of reduction of (I) were carried out on stationary Pt/Pt and Rh/Rh electrodes with 17 cm^2 apparent surface area, working under galvanostatic conditions with an optimal current of 80 mA. Compound (I) was taken in the form of the chlorohydrate ($C_6H_8N_2O \cdot HCl$) at an initial concentration of 0.2 M; changes in the concentration during the course of the electrolysis were followed by polarographic analysis.

Buffer solutions covering the range from pH 0.8 to pH 8.8 were used here. The solutions were kept agitated by a magnetic stirrer. The electrolysis products were identified in 0.4 N H_2SO_4 solution. The solution was neutralized with $Ba(OH)_2$ at the end of the electrolysis (absence of reduction waves on the polarographic curve). The $BaSO_4$ formed here was filtered off and the water evaporated in vacuum. The product obtained was recrystallized, first from ethanol and then from a THF−ethyl acetate mixture. Final purification was through sublimation.

DISCUSSION OF RESULTS

Polarographic curves obtained with Pt and Rh electrodes in solutions of pH 0.8 showed a plateau, corresponding to a saturation current, whose length was proportional to the depolarizer concentration and the square root of the rate of rotation of the electrode (m). This indicates that the saturation current was diffusional in nature. The effect of the stirring rate on the value of the saturation current can be seen from Fig. 1. Saturation current plateaus did not appear on the polarograms obtained with the Pt/Pt and Rh/Rh electrodes in solutions of pH 3.0. Over the presaturation current region φ_r = 70-30 mV , a plot of the polarographic data gave

TABLE 1

Solution pH	Electrode: platium, reaction order	platium, b, mV	rhodium, reaction order	rhodium, b, mV
0,8	0,26	42	0	46
3,0	0,0	48	0	50

TABLE 2

Solution	Solution, pH	Electrode: rhodium, k, h^{-1}	Electrode: platium, k, h^{-1}
Sulfuric acid	0.8	0,64	0,66
Citric acid with added KCl	3,3	0,68	0,64
The same	5.1	0,60	0,68
Boric acid	8.8	0,45	0,45

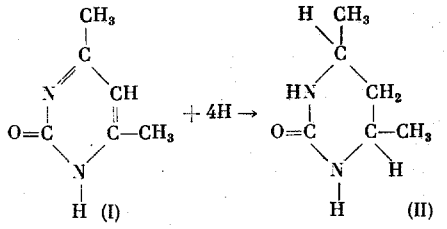
parallel linear curves in semilogarithmic coordinates. The reaction order was determined by developing logarithmic current strength vs $C_6H_8N_2O \cdot HCl$ concentration relations at fixed potentials. The results obtained, together with Tafel slopes, are given in Table 1.

The data obtained here indicated that the electrode reaction was close to being a zero-order process, apparently proceeding in the potential region where the electrode surface is completely covered by the adsorbate. The fact that the reaction rate was independent of the depolarizer concentration while the saturation current was diffusional in nature would imply that the reduction of (I) proceeds through an electrocatalytic mechanism in which the intrinsic electrochemical step is hydrogen ion discharge according to the scheme

$$H_3O^+ + e \rightleftarrows H_{ads} + H_2O \quad \text{(acid solutions)}$$
$$H_2O + e \rightleftarrows H_{ads} + OH^- \quad \text{(alkaline solutions)}$$

The adsorbed hydrogen formed hydrogenates the organic molecules, as was shown by special experiments in which electrolysis was carried out on a Cu electrode which carried only an insignificant amount of adsorbed surface hydrogen [4]. There was no evidence of the reduction of (I) here, the polarization curves for background and electrolyte coinciding (Fig. 2). It is true that the reduction of (I) does occur on the Hg electrode whose surface is also free of adsorbed hydrogen, but only at much higher negative potentials where there is a direct transfer of electrons to the molecules through an electrochemical mechanism.

On the Pt and Rh electrodes, the adsorbed hydrogen resulting from the electrochemical stage in the reaction reduces (I) to 2-oxo-4,6-dimethyl-1,3-diazacyclohexane (II)



Compound (II) was a white crystalline substance with mp 243-245°C. Found: C 56.49; H 9.45; N 22.25%. $C_6H_{12}N_2O$. Calculated: C 56.22; H 9.44; N 21.86%. IR spectrum (ν, cm^{-1}): 1670 (C=O), 3075, 3220 (NH).

The effect of the solution pH on the rate of reduction of (I) on the Pt and Rh electrodes was studied by constructing kinetic curves showing the logarithm of the depolarizer concentration plotted against the time of electrolysis, following the procedure suggested in [5]. Galvanostatic electrolysis (i = 80 mA; initial concentration, 0.2 M) on a stationary electrode (S_{app} = 17 cm^2) with magnetic stirring gave data leading to linear plots whose slopes gave, in turn, the value of k, the apparent rate constant with an accuracy of ± 0.08 h^{-1} (Table 2).

In order to prevent the electrolyte from becoming alkaline because of the loss of hydrogen ions during electrolysis, HCl was added to the buffer solutions of pH 3.3 and 5.1. It can be seen from Table 2 that the rate of reduction of (I) was constant over the interval from pH 0.8 to pH 5.1, and independent of the nature of the metal catalyst, at least to within the limits of experimental error. Although the reaction rate fell off somewhat in the more alkaline solutions (pH 8.8), this might reflect a decrease in the accuracy of measurement because of the high ohmic resistance of the solution itself.

The fact that neither the acidity of the solution nor the nature of metal catalyst had any effect on the electrochemical reduction of (I) could be due to the unique character of adsorption processes carried out under these conditions.

The authors would like to thank V. S. Reznik for his help in this work.

CONCLUSIONS

1. The reduction of 2-oxy-4,6-dimethylpyrimidine in aqueous buffer solutions and on electrodes with low hydrogen-overvoltage (Pt and Rh) proceeds through an electrocatalytic mechanism leading to the formation of 2-oxo-4,6-dimethyl-1,3-diazacyclohexane.

2. The fact that neither the solution pH nor the nature of the metal had any effect on the reduction rate could be due to peculiarities in the adsorptional behavior of the 2-oxy-4,6-dimethylpyrimidine.

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THE PHOTOCHEMISTRY OF THE ALIPHATIC NITROCOMPOUNDS

COMMUNICATION 9. THE FLASH PHOTOLYSIS OF THE α-POLYNITROALKYLSULFIDES AND α-POLYNITROALKYLSULFONES

E. M. Maksyutov and V. I. Slovetskii

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The properties of the α-polynitroalkylsulfides $RSC(NO_2)_2R'$ (I) and α-polynitroalkylsulfones $RSO_2C(NO_2)_2R'$ (II) are radically different from those of the usual organic sulfides and sulfones. The accumulation of NO_2 groups of the α-C atom increases the tendency of these compounds to undergo $C_{NO_2}-S$ bond heterolysis under mild attack from both nucleophilic and electrophilic reagents [1]. On the other hand, the thermal gas-phase decomposition of (I) and (II) follows first-order reaction kinetics and proceeds through homolytic rupture of the C–N bond [2]. In other words, different bonds are broken in heterolysis and thermal decomposition. The literature contains no information on the photochemistry of either (I) or (II). The present work was a study of the photochemistry of (I) and (II) in various solvents, at 20°C and at lower temperatures as well.

EXPERIMENTAL

Solutions of (I) and (II) were studied by flash photolysis and rapid kinetic spectroscopy [3]. With a energy of 440-875 J to the exciting lamp, we estimated [4] that more than 10^{18} quanta of exciting radiation from the 240-390 nm region of the spectrum fell on the reaction cell in each flash. Compounds (I) and (II) resemble the polynitroalkanes [5], showing wide absorption bands in the UV spectrum. The first, more intense, of these bands ($\varepsilon \sim 10^4$) appears in the neighborhood of 210 nm, with a second, less intense, band at ~280 nm. The number of molecules of (I) and (II) present in the reaction cell during an experiment was of the order of $\sim 10^{16}$. The measured quantum yields for the photodecomposition of analogous compounds range from ~0.35 to 0.5 [6]. The solutions were irradiated at 20°C, and at temperatures in the neighborhood of the freezing point, working in the low-temperature system described in [7]. Excitation was carried out over the 220-600 nm range, the flash energy being held constant to within ±4%. The hermetically sealed cylindrical quartz cell had a length of 1.75 cm. The initial concentration of (I) and (II) in the solutions chosen for irradiation varied from 10^{-3} to 10^{-4} mole/liter. The stability of these solutions were checked spectrophotometrically. Each solution proved to be stable over the time required for carrying out an experiment. Preparative photolysis of $p\text{-}NO_2\ PhSC(NO_2)_3$ (Ib) was carried out in a cylindrical quartz cell, 3 cm in length, with 20-60 min exposure to the entire emission from a DRT-220 lamp. The initial concentration of (Ib) in these solutions was $\sim 4 \cdot 10^{-1}$ mole/liter. The concentrations of (I) and (II), both in the original and in the irradiated solutions, was determined spectrophotometrically from the absorption of the polynitroalkane anions formed by treating the solutions with standard

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.

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