PHYSICAL CHEMISTRY

Kh. S. Bagdasar' yan, Z. A. Sinitsyna

1965

SovietRxiv

Figure 1

Figure 1: Figure 1

Abstract

Full Text

PHYSICAL CHEMISTRY

Kh. S. Bagdasar' yan, Z. A. Sinitsyna

TWO-QUANTUM PHOTOCHEMICAL REACTION OF DEHYDROGENATION OF ALCOHOLS BY AROMATIC AMINES AT 77°K

(Presented by Academician V. A. Kargin on 17 VII 1964)

Recently Kholmogorov, Baranov, and Terenin (1) discovered a low-temperature photochemical reaction of aromatic amines with alcohols, leading to the formation of alcohol radicals. An analogous reaction in the methanol–indole system was observed by Smoller (2). In these works it was shown, especially convincingly in (1), that the reaction proceeds with the participation of triplet amine molecules. However, a more detailed mechanism of these reactions remained unclear in the cited works.

In our laboratory it was established that the photochemical reaction of aromatic amines in glassy ethanol at 77°K, leading to the formation of ethanol radicals $CH_3\dot{C}HOH$, proceeds at a rate proportional to the square of the light intensity (3). A study of the effect of intermittent illumination showed that the characteristic time of this effect coincides with the lifetime of the amine molecule in the triplet (phosphorescent) state (4). These works left little doubt that the indicated reactions represent an example of "true" two-quantum photochemical reactions, in which the second quantum of light is absorbed by an amine molecule in the triplet state.

Fig. 1. Absorption spectrum of diphenylamine in ethanol at room temperature (experiment No. 6): **1**—before irradiation, **2**—after irradiation at 77°K and subsequent thawing

In all the cited works the chemical process was observed from the EPR spectra of the radicals formed. It is undoubtedly of interest to study these reactions by some final products of the chemical transformation. In the present work, two-quantum photochemical reactions were studied by the formation of molecular hydrogen.

The reaction was carried out in quartz cylindrical vessels 25 mm in diameter and with a wall thickness of 3–5 mm. The reaction vessel had a side arm with a glass partition for connection to a gas chromatograph. By means of a quartz-molybdenum-glass transition the vessel was sealed to a vacuum apparatus, and the solution under study was freed from dissolved air by vacuum treatment. Irradiation of the reaction vessel was carried out in a quartz Dewar of special design, a description of which will be given elsewhere. In all cases glassy solutions transparent at 77°K were used. Gas analysis was carried out

on a Yanak gas chromatograph, whose absolute sensitivity was 0.005 ml of gas under normal conditions. To calculate the quantum yield of the reaction, the number of light quanta incident on the front wall of the reaction vessel was determined using a uranyl oxalate actinometer with various light filters.

Table 1 gives data on the investigation of solutions of diphenylamine in ethanol, methanol, and isopropanol, and of a solution of carbazole in ethanol.

The data obtained make it possible to draw the following conclusions. Of the permanent gases, in all cases only hydrogen is formed. The rate

Table 1

Formation of hydrogen upon irradiation of solutions of amines in alcohols.
Lamp SVDSh-250, light filter UFS-1. Volume of the reaction vessel 2.5 cm^3

Experiment No.	System	Amine concentration, 10^4 mol/l	Irradiation intensity, relative units	Irradiation time, min	Amount of H_2 formed, 10^6 mol
1	Diphenylamine — methanol	5	1	60	4.20
2	Diphenylamine — ethanol	5	1	80	5.25
3	Diphenylamine — ethanol (without filter)	5	1	60	6.60
4	Diphenylamine — ethanol	100	1	60	8.05
5	Diphenylamine — ethanol	100	0.28	150	1.90

Experiment No.	System	Amine concentration, 10^4 mol/l	Irradiation intensity, relative units	Irradiation time, min	Amount of H_2 formed, 10^6 mol
6	Diphenylamine—ethanol	2.5	1	60	6.40
7	Diphenylamine—ethanol	2.5	0.315	165	2.15
8	Diphenylamine—isopropanol	5	1	60	5.35
9	Diphenylamine—isopropanol	5	0.28	150	1.50
10	Diphenylamine—isopropanol	50	1	60	6.80
11	Diphenylamine—isopropanol	50	0.28	120	1.30
12	Carbazole—ethanol	5	1	60	7.10
13	Carbazole—ethanol	5	0.28	140	1.95

of hydrogen formation is proportional to I^n, where $n = 1.8 \pm 0.1$. The quantum yield of hydrogen formation is 0.02 ± 0.005 at $I_0 = 3.3 \cdot 10^{-8}$ einstein/cm^2 · sec. The quantum yield of radical formation $\varphi(R)$ was also estimated by the EPR method at 77° K. For $\varphi(R)$ a value lying within the range 0.01–0.03 was obtained.

It is interesting that, at low amine concentrations, the exposures used give an amount of hydrogen formed several times greater than the amount of amine introduced. For example, at a diphenylamine concentration of $2.5 \cdot 10^{-4}$ mol/l, the amount of hydrogen formed is ~ 10 times greater than the amount of amine introduced. At high amine concentrations (10^{-2} mol/l) the ratio is reversed; however, the quantum yields of hydrogen formation are the same in both cases. It may be assumed that in these reactions there is no simple stoichiometric relation between the yield of hydrogen and the consumption of amine.

To test this assumption, a spectrophotometric study was carried out of a solution of diphenylamine in ethanol ($2.5 \cdot 10^{-4}$ mol/l) at room temperature before irradiation and after irradiation at 77° K followed by warming to room temperature (Fig. 1).

From a comparison of curves 1 and 2 (Fig. 1) it follows that the exposure used by us decreases the concentration of diphenylamine by only 30%. Comparison of this result with the data on the yield of hydrogen (experiment No. 6) leads to the conclusion that the amount of hydrogen formed may exceed the amount of amine consumed by ~ 35 times.

To establish the mechanism of the two-quantum reaction, decisive importance is attached to the study of the effect of intermittent irradiation, since by this

by this method one can establish the lifetime of the intermediate particle. Table 2 gives the data of experiments carried out by this method.

The characteristic lifetime τ was calculated from the formula

$$V_{\text{interr}}/V = \frac{1}{2}\left[1 - \frac{\tau}{\theta}\,\text{th}\,\frac{\theta}{2\tau}\right],$$

derived in the preceding paper (^{4}) (V and V_{interr} are the reaction rates under continuous and intermittent illumination; θ is the illumination interval, equal to the dark interval). The calculated values of τ show a rather large scatter, but the mean value, 2.0 sec, agrees with the value found from the yield of radicals by the EPR method (^{4}).

Table 2

Effect of intermittent illumination in the photolysis of the diphenylamine ($2.5 \cdot 10^{-4}$ mol/l)**—ethanol system**

Experiment No.	Irradiation time, min	θ, sec	Amount of H_2 formed, 10^2 ml	V_{interr}/V	θ/τ	τ, sec
1	180	Continuous illumination	19.0	0.285	1.4	1.35
1	300	1.875	9.0	0.285	1.4	1.35
2	180	Continuous illumination	19.0	0.285	1.4	2.7
2	240	3.75	7.2	0.285	1.4	2.7
3	150	Continuous illumination	10.3	0.375	3.85	1.95
3	300	7.50	7.7	0.375	3.85	1.95

Note. Experiment No. 3 was carried out at a lower light intensity.

For comparison of τ with the phosphorescence lifetime τ_{phosph} of diphenylamine molecules in the triplet state, the latter quantity was measured in various matrices. The specimen under study, immersed in a quartz Dewar with liquid nitrogen, was placed in a light-tight chamber equipped with two photographic shutters. Through one shutter the specimen could be illuminated by the light of an SVDSh-250 lamp through a UFS-1 light filter; through the other shutter the chamber was connected to an FEU-19 photomultiplier. The signal from the photomultiplier, caused by the phosphorescence light, was amplified and fed to an MPO-2 loop oscillograph, which recorded the phosphorescence decay curve. When the oscillograph film was started, the illuminator shutter was simultaneously closed and, with a delay of ~ 0.1 sec, the photomultiplier shutter was opened. Phosphorescence decay curves were obtained for solutions of diphenylamine in ethanol, 3-methylpentane, and a mixture of methylcyclohexane with isopentane. The decay curves for all three solvents practically coincide and give $\tau_{\text{phosph}} = 1.8$ sec*.

Thus, we arrive at the conclusion that $\tau_R = \tau_{H_2} = \tau_{\text{phosph}}$, i.e., the formation of ethanol radicals and hydrogen molecules is limited by one and the same stage—the absorption of a second light quantum by the amine molecule in the triplet state. This conclusion also agrees with the measurement of the quantum yields of hydrogen and ethanol radicals, from which it follows that $\varphi_{(R)} \approx \varphi_{(H_2)}$. The totality of the data obtained makes it possible to state that the reaction studied is a "true" two-quantum sensitized reaction of alcohol dehydrogenation. The consumption of amine is apparently a side process, which proceeds with a quantum yield much smaller than the quantum yield of the dehydrogenation reaction. It is interesting that in papers ([5], [6]), the formation of hydrogen atoms in similar systems was directly detected by the EPR method.

Some experiments carried out in our laboratory showed a great diversity in the photochemical behavior of different systems at 77°K.

Thus, in the naphthalene–ethanol system no formation of hydrogen was detected, whereas in the naphthalene–3-methylpentane system, under the same condi-

* The apparatus for measuring the lifetime was assembled by Yu. V. Kovalev, a member of our laboratory. The indicated measurements were also carried out by him.

···hydrogen is formed, and the reaction rate is proportional to $\sim I^{1.5}$. No formation of hydrogen was detected in the diphenylamine–3-methylpentane system upon illumination with the full light of a PRK-2 lamp.

After work ([3]), a number of studies appeared that present new data on low-temperature reactions with an exponent of I close to 2 and note the role of triplet states for these reactions ([5,7,8]). At the same time, papers ([9,10]) put forward considerations concerning other possible reaction mechanisms for certain systems at 77° K. Further systematic investigations should clarify this new area of photochemistry.

Physical Chemistry Institute
named after L. Ya. Karpov

Received
16 VII 1964

CITED LITERATURE

1. V. E. Kholmogorov, E. V. Baranov, A. N. Terenin, DAN, **149**, 142 (1963).
2. B. Smaller, *Nature*, **195**, 593 (1962).
3. Kh. S. Bagdasar' yan, V. I. Muromtsev, Z. A. Sinitsyna, DAN, **152**, 349 (1963).
4. Kh. S. Bagdasar' yan, Z. A. Sinitsyna, V. I. Muromtsev, DAN, **153**, 374 (1963).
5. V. E. Kholmogorov, E. V. Baranov, A. N. Terenin, DAN, **152**, 1399 (1963).
6. A. K. Piskunov, V. E. Kholmogorov et al., DAN, **154**, 910 (1964).
7. Yu. I. Kozlov, V. I. Muromtsev et al., ZhFKh, **37**, 2800 (1963).
8. V. G. Vinogradova, B. N. Shelimov et al., DAN, **154**, 188 (1964).
9. N. M. Bazhin, N. N. Bubnov, V. V. Voevodsky, *Kinetics and Catalysis*, **5**, 188 (1964).
10. N. N. Bubnov, N. M. Bazhin, V. V. Voevodsky, *Kinetics and Catalysis*, **5**, 357 (1964).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.