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PHYSICAL CHEMISTRY

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Fig. 1.

Figure 1: Fig. 1.

Abstract

Full Text

PHYSICAL CHEMISTRY

G. P. Safonov, V. Ya. Shlyapintokh, S. G. Entelis

CRYSTALLOLUMINESCENCE AND ITS USE FOR STUDYING THE KINETICS OF AMINE ACYLATION

(Presented by Academician V. N. Kondrat'ev, April 6, 1964)

Recently there has been a great increase in interest in studying the kinetics and mechanism of reactions between amines and acid chlorides. This is due chiefly to the fact that the process of interaction of dicarboxylic acid dichlorides with diamines underlies one of the new methods for obtaining high-molecular-weight substances—the method of interfacial polycondensation.

Condensation and polycondensation reactions, as was recently discovered, are accompanied by luminescence^(1,2). In the search for new methods of studying the kinetics of these reactions, we investigated the nature of the glow and its connection with the mechanism and kinetics of acid chloride reactions with amines. As a model we chose the reaction of acylation of aniline by benzoyl chloride, the kinetics of which has been studied comparatively well^(3,4). The reaction was carried out in diethyl ether. Luminescence was measured on a photometric setup with an FEU-33 photomultiplier (spectral sensitivity range 350–610 m μ), connected into a photon-counting circuit. The limiting sensitivity of the setup was 20–40 photons per second on the photocathode surface.

Fig. 1.

The reaction was carried out in a glass vessel 1 (Fig. 1), equipped with a thermostating jacket 2. In conducting the experiment, 1 ml of a solution of aniline in ether was placed in the reaction vessel. An ethereal solution of benzoyl chloride (1 ml) was placed in the thermostated vessel 5, located above the reactor, with which vessel 5 was connected by a bent capillary 3. Through the capillary, the benzoyl chloride solution was transferred into the reaction vessel by excess pressure of dry nitrogen. To prevent evaporation of the ether, the capillary was connected to the reaction vessel by means of a polyethylene coupling 4 with a slit through which the excess nitrogen was released.

Fig. 2

Figure 2: Fig. 2

Reagents. Aniline of grade *r* was purified by the method of ⁽⁵⁾. Diethyl ether was dried over metallic sodium and distilled with a dephlegmator. Benzoyl chloride was distilled three times in vacuum. Benzanilide was obtained by the reaction of aniline with benzoyl chloride, carried out in ether, was thoroughly washed with warm water, recrystallized three times from ethanol, and dried in vacuum to constant weight.

Kinetic measurements showed that the glow in the reaction of aniline with benzoyl chloride appears after a certain "induction period." At the same time, the chemical interaction begins immediately after mixing the reagents, as is seen from the formation of aniline hydrochloride—the side product of the reaction. The characteristic kinetic curves of the glow

are shown in Fig. 2. It is evident from them that the maximum intensity of the luminescence and the magnitude of the induction period vary regularly with changes in the concentrations of the reagents. The column in the figure shows the magnitude of the standard light signal from a radioactive phosphor, corresponding to 800 photons incident on the photocathode in 1 sec.

Fig. 2. Kinetic curves of the luminescence accompanying the acylation reaction of aniline; 21.6°, aniline concentrations in mole/liter: 1 —0.220; 2 —0.158; 3 —0.138.

The investigation carried out showed that the observed luminescence arises not in the reaction, as had been assumed earlier ⁽¹⁾, but in the process of crystallization of the poorly soluble reaction product—benzanilide—and, consequently, is crystalloluminescence. This conclusion is based on the following experimental facts.

- 1) Luminescence in the reaction is observed only in those solvents in which the solubility of benzanilide is low (ethyl, diisopropyl, and dibutyl ethers, toluene, benzene, dichloroethane). The reaction in alcohols and dimethylformamide proceeds without formation of a benzanilide precipitate and is not accompanied by luminescence.
- 2) Introducing benzanilide into the solution before mixing the reagents leads to a shortening of the induction period.
- 3) Rapid cooling of the reacting mixture causes a sharp increase in the intensity of the luminescence.
- 4) Luminescence of the same spectral composition,* as in the reaction, arises upon crystallization of pure benzanilide caused by cooling its saturated solution in ethanol or by adding a precipitant.
- 5) Control experiments in which the reaction between aniline and hydrogen

Fig. 3

Figure 3: Fig. 3

chloride was carried out in diethyl ether showed that crystallization of aniline hydrochloride is not accompanied by luminescence.

Thus it was established that the induction period is the time required to reach an amide concentration sufficient for crystallization to begin. Obviously, the duration of the induction period τ must depend on the rate of the chemical transformation and on the magnitude of the concentration of the reaction product—benzanilide—required for crystallization to begin.

The kinetic scheme of the process of *N*-acylation is known from the literature. This is a second-order reaction in which, from a molecule of aniline A and benzoyl chloride B, a molecule of benzanilide C is formed:

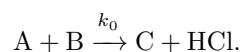
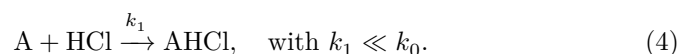


Fig. 3. Anamorphoses of equation (1): $a -14^\circ$; $b -26.5^\circ$.

* The spectral composition of the luminescence was determined using a set of light filters.

Hydrogen chloride reacts rapidly with aniline, giving aniline hydrochloride



To bind the hydrogen chloride, the initial concentration of aniline was taken to be twice as large as the concentration of the acid chloride.

The expression for the rate of formation of benzanilide has the form:

$$\frac{d[C]}{dt} = -\frac{d[B]}{dt} = k_0[A][B] = 2k_0[B]^2,$$

from which it is easy to obtain the dependence of the induction-period magnitude on the initial concentration of the reagents

$$\tau = \frac{2[C]_\tau}{A_0 k_0 [A_0 - 2[C]_\tau]} \quad (1)$$

or

$$\frac{1}{A_0 \tau} = \frac{k_0 A_0}{2[C]_\tau} - k_0, \quad (1')$$

Fig. 4. Comparison of solubility values of benzanilide C_0 with C_{0k} values obtained from measurements of induction periods.

Figure 4: Fig. 4. Comparison of solubility values of benzanilide C_0 with C_{0k} values obtained from measurements of induction periods.

where $[C]_\tau$ is the critical concentration of benzanilide at the moment crystallization begins. In the coordinates $[\frac{1}{A_0\tau}; A_0]$, the curve for equation (1') is straightened. The intercept cut off on the ordinate axis is equal to k_0 , and on the abscissa axis to $2[C]_\tau$.

For verification of equation (1), several series of experiments were carried out at various temperatures. In the experiments, the initial concentrations of the reagents were varied and the durations of the induction periods were determined. The corresponding experimental dependences are shown in Fig. 3. The points lie satisfactorily on a straight line. By processing the data obtained by the least-squares method, the values of k_0 and $[C]_\tau$, given in Table 1, were found.

Table 1

$t, ^\circ\text{C}$	$10^2 k_0, \text{l/mol} \cdot \text{sec}$	$10^2 [C]_\tau, \text{mol/l}$
6.5	2.0	1.4
10.0	3.3	1.9
14.0	3.6	2.2
20.0	5.8	3.1
26.5	9.2	3.7

The values obtained for the rate constants of benzoylation of aniline in diethyl ether are close to the values indicated in the literature for other solvents.

Solvent	Toluene	Chlorobenzene	Bromobenzene	Benzene
$10^2 k_0, \text{l/mol} \cdot \text{sec}$ at 25°	5.55	5.99	7.22	7.5

Data on the reaction of benzoyl chloride with aniline in ether are absent from the literature.

Fig. 4. Comparison of solubility values of benzanilide C_0 with C_{0k} values obtained from measurements of induction periods.

In Fig. 4, the values C_{0k} , obtained from kinetic experiments at various temperatures, are compared with the values $[C]_0$, where $[C]_0$ is the solubility of benzanilide determined by direct measurements. The values $[C]_0$ are 1.75 times smaller. This means that at the moment crystallization begins the solution is supersaturated. As can be seen from Fig. 4, at different temperatures the supersaturation proves to be approximately the same. Owing to this, from the kinetic

experiments it is possible to determine not only the values of the activation energy of the reaction, but also the heat of solution of benzanilide. From the kinetics, for the heat of solution the value $\Delta H_{\text{sol}} = 8.3$ kcal/mol was obtained; from direct solubility measurements it was found that $\Delta H'_{\text{sol}} = 7.0$ kcal/mol, $\Delta S = 17.0$ cal/mol · deg. The activation energy is 12.2 kcal/mol.

The results presented confirm the correctness of the assumption that the glow in the reaction under study arises during crystallization of a poorly soluble product.

Usually, the use of luminescent methods for studying kinetics is based on the existence of a proportional relationship between the intensity of the glow and the rate of the process in which excited particles are formed. However, in reactions in which, during the experiment, a precipitate accumulates that attenuates the intensity of the glow, it is not possible to use intensity measurements to determine kinetic parameters. The method described above does not require measurements of glow intensity, and a change in the transparency of the solution does not hinder its application. It is possible to measure photometrically the kinetics of a reaction that is not itself accompanied by luminescence. The glow arises in the accompanying physical process of crystallization. Kinetic information is obtained by measuring the time interval from the beginning of the reaction to the moment at which the glow appears. The glow is a kind of marker indicating that a certain concentration of the reaction product has been reached in the system. In this case, the magnitude of the glow intensity and its reproducibility in parallel experiments are of no significance.

Although crystalloluminescence has long been known, it has always been observed only in the formation of ionic crystals, such as, for example, NaCl, NaBr, KCl, KJ, As₂O₃, BaBrO₃. Luminescence during the formation of molecular crystals has been discovered in the present work, not only during the crystallization of benzanilide, but also during the formation of crystals of *p*-iodobenzamide, eosin, uranine, and 9,10-dibromoanthracene.

In the present work, crystalloluminescence was used to study the kinetics of a chemical process. However, measurements of crystalloluminescence can also be applied to the investigation of the crystallization processes themselves and of the energy levels of the crystals formed.

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