S. S. NOVIKOV, V. I. SLOVEVSKII, V. A. TARTAKOVSKII, S. A. SHEVELEV,

A. A. FAINZIL’ BERG

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Abstract

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S. S. NOVIKOV, V. I. SLOVEVSKII, V. A. TARTAKOVSKII, S. A. SHEVELEV,
A. A. FAINZIL' BERG

ON THE QUESTION OF THE EXISTENCE OF THE ACI-FORM OF 1,1-DINITROALKANES AND TRINITROMETHANE

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As is known, in the works of Hantzsch, Ley, Feicht, and others ([1,2]), the idea was advanced that, upon dissolution of 1,1-dinitroalkanes and trinitromethane, as well as some of their salts (for example, mercury and silver salts), in polar solvents, the following equilibrium takes place:

$$RCH(NO_2)_2 \rightleftarrows RC\begin{matrix}/NO_2\\ \backslash NOOH\end{matrix} \rightleftarrows RC\begin{matrix}/NO_2\\ \backslash NOO^-\end{matrix} + H^+. \quad (1)$$

(I) (II) (III)

At the present time, somewhat different schemes of the tautomeric transformations of nitro compounds are generally accepted, namely: scheme (2) ([3]) or (3) ([4]).

$$\begin{array}{ccc} \underset{(I)}{RCH(NO_2)_2} & \rightleftarrows & \underset{(II)}{RC(NO_2)NOOH} \\ & \nearrow\!\searrow \qquad\qquad \nwarrow\!\swarrow & \\ & \underset{(III)}{RC(NO_2)_2^- + H^+} & \end{array} \quad (2)$$

$$RCH(NO_2)_2 \rightleftarrows RC(NO_2)_2^- + H^+ \rightleftarrows RC(NO_2)NOOH \quad (3)$$

(I) (III) (II)

Since the time of Hantzsch it has been accepted that the aci-form II and the anion III are optically identical* and, in the case of 1,1-dinitroalkanes and trinitromethane, have a yellow color ([1,2]). The existence of the aci-form II for

1,1-dinitroalkanes and trinitromethane, as judged by the presence of yellow coloration, is generally acknowledged. As follows from schemes (1)—(3), in aqueous solutions of polynitroalkanes all three forms I—III should coexist.

It should be noted, however, that as early as 1923 Halban (5), discussing the results obtained by Hantzsch, came to the conclusion that in a highly dilute aqueous solution ($0.0001\,N$) there are no nonionized molecules of aci-dinitromethane, and that only an equilibrium exists between true dinitromethane and the ions of the aci-form. However, this point of view was not developed further and at present, in our opinion, has been unjustifiably forgotten. The present work was undertaken as a continuation of our investigations on the study of the dissociation process of 1,1-dinitroalkanes (6) and trinitromethane (7). Let us consider scheme (2) (consideration of schemes (1) and (3) instead of scheme (2) does not introduce any fundamental differences into the course of our subsequent reasoning). The tautomeric equilibrium between I and II at constant temperature and pressure is affected by the different solvation of I and II and by the polar properties of the medium, whereas under the same conditions the electrolytic equilibria between I and III, and II and III, in addition to the polar properties of the medium and different solvation, will also be affected by the pH of the solution. In sufficiently acidic solutions the anion III will pass entirely into the true nitro compound I and the aci-form II, and only the tautomeric equilibrium between I and II will take place. The presence of aci-form II is usually judged by the yellow coloration of solutions (1,2). If this point of view is adhered to, one should expect that upon acidification of the solution the intensity of the yellow coloration will decrease until anions III are present, and then further acidification should not affect the color (provided that the added acid at least will not change the polar properties of the solvent and will not affect, or will affect only very slightly, its solvating capacity). We studied the behavior in media with different pH of the following nitroalkanes: dinitromethane ($K_{\text{dis}} = 2.5 \cdot 10^{-4}$ (20°)) (6), 1,1-dinitroethane ($K_{\text{dis}} = 6.2 \cdot 10^{-6}$ (20°)) (6), and trinitromethane ($K_{\text{dis}} = 6.8 \cdot 10^{-1}$ (20°)) (7). We assumed that upon addition of acid to water the dielectric constant of the solution is probably not less than that of pure water, and that the hydrating capacity of the solution will remain the same at least for acids with concentrations up to $0.2\,N$.

Table 1

Molar extinction coefficients (ε) of 1,1-dinitroethane in aqueous solutions

λ, mμ	$0.1\,N$ KOH ($C =$ 0.0040 g/l)	$0.1\,N$ H_2SO_4 ($C =$ 0.090 g/l)	$0.1\,N$ HCl ($C =$ 0.080 g/l)	$0.1\,N$ CF_3COOH ($C =$ 0.095 g/l)
365	14145	27	22	20

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* Confirmation of this may be, for example, the optical identity of the anion and the aci-form of phenylnitromethane.

λ, mμ	0.1 N KOH ($C =$ 0.0040 g/l)	0.1 N H_2SO_4 ($C =$ 0.090 g/l)	0.1 N HCl ($C =$ 0.080 g/l)	0.1 N CF_3COOH ($C =$ 0.095 g/l)
370	15875	17	18	12
375	16929	11	13	2
380	17606	12	13	7
385	17117	19	25	13
390	15424	12	25	12
395	13016	15	14	10

We found that the yellow color of the solutions disappears completely as soon as the pH reaches the value at which the dissociation of the nitroalkane under study is practically suppressed. It follows from this that the appearance of a yellow color in the case of 1,1-dinitroalkanes and trinitromethane is associated only with the presence of the anion. In this connection it may be noted that, since up to the present time the presence of aci-forms of 1,1-dinitroalkanes and trinitromethane has been judged only from the color, the results of our work cast doubt on the question of their existence. A final solution of this question requires further study.

Table 2

Molar extinction coefficients (ε) of dinitromethane in aqueous solutions

λ, mμ	0.1 N KOH ($C =$ 0.0040 g/l)	0.2 N H_2SO_4 ($C =$ 0.141 g/l)	0.2 N HCl ($C =$ 0.093 g/l)	0.2 N CF_3COOH ($C =$ 0.078 g/l)
345	14576	56	50	101
350	17340	56	46	102
355	19934	55	43	100
360	21394	54	42	98
365	21425	50	40	89
370	19555	45	33	75
375	16397	36	30	59

Table 3

Molar extinction coefficients (ε) of trinitromethane in aqueous solutions

λ, mμ	0.1 N KOH ($C =$ 0.0040 g/l)	5.3 N H_2SO_4 ($C =$ 0.072 g/l)	6.0 N HCl ($C =$ 0.13 g/l)	8.3 N CF_3COOH ($C =$ 2.07 g/l)	16.5 N CH_3COOH ($C =$ 2.10 g/l)
335	10128	22	40	29	78

λ, mμ	0.1 N KOH (C = 0.0040 g/l)	5.3 N H_2SO_4 (C = 0.072 g/l)	6.0 N HCl (C = 0.13 g/l)	8.3 N CF_3COOH (C = 2.07 g/l)	16.5 N CH_3COOH (C = 2.10 g/l)
340	12338	15	38	28	78
345	13848	13	35	26	77
350	14216	13	33	25	76
355	13885	12	30	21	76
360	12338	11	27	18	77
365	10202	8	23	16	78

The results of our experiments are given in Tables 1–3. We judged the intensity of the color from the value of the molar extinction coefficient at the absorption maximum of the anion: dinitromethane, 360–365 mμ; 1,1-dinitroethane, 380 mμ; and trinitromethane, 350 mμ. We found that disappearance of the color occurs for 1,1-dinitroethane already in a medium of 0.1 N acids (see Table 1), for dinitromethane in a medium of 0.2 N acids (see Table 2), and for trinitromethane only in fairly concentrated acids (see Table 3). As is evident from the data of these tables, disappearance of the color depends on the dissociation constant of the nitroalkane studied and on the strength of the acid used for acidification (the fact that sulfuric acid is stronger than hydrochloric acid may be judged, for example, from their acidity function H_0 ([8])).

As one of the confirmations of the existence of the aci-form and of its yellow coloration, Hantzsch cited the following fact ([2]): a 0.0001 N aqueous solution of dinitromethane is ionized, according to electrical-conductivity data—

···by 75%; at the same time the color intensity of this solution proves to be maximal. From this Hantzsch concluded that the remaining 25% of dinitromethane is the aci-form: being, like the anion, colored, it contributes to the color of the solution, as a result of which the color intensity also reaches a maximum.

We have convinced ourselves that these data are incorrect. As calculation shows, in a 0.0001 N aqueous solution dinitromethane, having $K_{\text{diss}} = 2.5 \cdot 10^{-4}$, is indeed dissociated by 77%, which practically coincides with Hantzsch' s data (75%); however, the color intensity of such a solution is by no means maximal, as is clearly seen from the experimental data we obtained (Table 4).

Table 4

Ultraviolet spectrum of a 0.0001 N solution of dinitromethane

λ, mμ	Molar extinction coefficients in aqueous 0.1 N KOH, ε_1	Molar extinction coefficients in water, ε_2	$\varepsilon_2/\varepsilon_1$
350	17514	13537	0.77

λ, mμ	Molar extinction coefficients in aqueous 0.1 N KOH, ε_1	Molar extinction coefficients in water, ε_2	$\varepsilon_2/\varepsilon_1$
355	19810	15521	0.78
360	21409	16525	0.77
365	20938	16221	0.78
370	18631	14494	0.78
375	15256	11950	0.78

From the data of Table 4 it follows that the maximum color intensity is reached only in an aqueous potassium hydroxide medium, where, as is known, we are dealing with the fully ionized salt of dinitromethane. The color intensity of a 0.0001 N solution of dinitromethane in water amounts to 78% of the maximum, i.e., it exactly corresponds to the degree of ionization of dinitromethane in this solution.

Thus, these data confirm that the color of dinitromethane solutions is due only to the presence of the anion, and the intensity of this color can serve as a quantitative measure of the ionization of dinitromethane.

An analogous conclusion is valid for homologs of dinitromethane, as well as for trinitromethane*. It should be noted that in the salts of such compounds as well, the appearance of a yellow color is connected only with ionization of these salts, and not at all with their conversion into the aci-form, contrary to the conclusion of Hantzsch and his school ([1],[2]). Thus we found that the yellow color of aqueous solutions of the mercury salt of trinitromethane can be completely suppressed by addition of a salt with the same cation, for example mercuric nitrate**. The behavior of the mercury salt of trinitromethane has been studied in greater detail in another of our papers ([10]).

The results obtained in our work are, naturally, valid within the limits of accuracy of the investigative method we used. If, for example, the optical density of the solution under study is 0.4, then, knowing the concentration, it is not difficult to calculate that by means of the spectroscopic method one can guarantee the absence of the colored form for gem-dinitroalkanes in an amount greater than 0.1%. For trinitromethane, owing to its greater solubility, this figure is still smaller (0.01%).

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* Andrew and Hammick ([9]), upon acidifying the potassium salt of trinitromethane, obtained a compound with m.p. 50°, which they took to be the aci-form of trinitromethane. The authors gave no evidence in favor of this assumption. Despite repeated attempts, we were unable to reproduce these results.

** To a 0.002 molar solution of the mercury salt of trinitromethane, 0.05 mole $Hg(NO_3)_2$ was added; the color intensity in the region 330–370 mμ was measured on an SF-4 instrument.

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

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