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Abstract

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ON THE DENITROSATION REACTION OF ALIPHATIC-AROMATIC NITROSAMINES

(Presented by Academician M. I. Kabachnik on 29 I 1964)

Aliphatic-aromatic nitrosamines, when acted upon by sulfuric acid of various concentrations, are converted into the salt of the corresponding amine with cleavage of the nitroso group:

$$\mathrm{Ar{-}N}\left(\begin{matrix}\mathrm{Alk}\\ \mathrm{N{=}O}\end{matrix}\right) + 2\mathrm{H}^{\oplus} \rightleftharpoons \mathrm{Ar{-}NH}_2^{\oplus}\mathrm{{-}Alk} + \mathrm{NO}^{\oplus}$$

If electron-acceptor substituents are present in the para position of the aromatic nucleus, then on the spectral absorption curves of solutions of different acidity, in which the denitrosation reaction takes place, an isosbestic point is observed for each arylalkylnitrosamine, indicating that the reaction proceeds without formation of an analytically determinable amount of an intermediate product, for example, the sulfuric acid salt of the starting compound*.

In contrast to this, Zagradnik, kinetically studying the denitrosation of aliphatic nitrosamines, came to the conclusion that, before the cleavage reaction of the nitroso group, an equilibrium is established between the nitrosamine and the conjugate acid; the latter, by eliminating the nitrosonium cation, is then converted into the corresponding amine (^{1}).

Jaffe (^{2}) considers this question somewhat differently, assuming that aliphatic nitrosamines in solutions form with acids not salts, but complexes in which there is a bond of the acid molecules both with the oxygen of the nitroso group and with the nitrogen of the amino group.

Interest in the denitrosation reaction is due to the fact that, on the one hand, this reaction is the reverse of one of the most important reactions in organic chemistry—the diazotization reaction—and, on the other, cleavage of the nitroso group from nitrosoalkylarylamines constitutes the first stage of the well-known Fischer-Hepp rearrangement (^{3}), which has both theoretical and practical significance. Therefore, elucidating the influence of the structure of the starting

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

substances on the rate of the denitrosation reaction is highly timely. To establish this influence, we carried out a kinetic study of the process using examples of substituted phenyl-N-methylnitrosamines having the following substituents in the para position:

$$-\mathrm{OCH_3},\ -\mathrm{CH_3},\ -\mathrm{H},\ -\mathrm{F},\ -\mathrm{Cl},\ -\mathrm{Br},\ -\mathrm{J},\ -\mathrm{C(=O)-C-CH_3},\ -\mathrm{NO_2}.$$

The reaction was studied spectrophotometrically at a temperature of $25 \pm 0.1^\circ$ in the presence of $0.1\,M$ urea in sulfuric acid medium over a concentration range from 20 to 45% ($H_0 = -0.85 \div -2.69$). The presence of an excess of urea was necessary to ensure the irreversibility of the reaction (the initial concentration of nitrosamine was 1.0—$2.0 \cdot 10^{-4}\,M$).

Study of the reaction under these conditions made it possible to show that, just as in the case of denitrosation of aliphatic nitrosamines (^{1}),

* This part of the work was carried out by us jointly with I. Chepchiyansky.

cleavage of the nitroso group from alkyl-arylnitrosamines is catalyzed by acids. This is evidenced by the presence of a rectilinear dependence of $\lg k_1$ on $-H_0$ (Fig. 1). This dependence is determined by the Hammett relation (^{4}):

$$\lg k_1 + H_0 = \mathrm{const},$$

where k_1 is the empirical first-order rate constant, and H_0 is the acidity function.

Fig. 1. Dependence of $\lg k_1$ on the acidity function $-H_0$

Fig. 2. Dependence of $\lg k_1$ on the value of σ for p-substituents. $H_0 = -2.015$

It should be noted that the tangent of the angle of inclination of the straight line for the indicated series of compounds (Fig. 1), as a rule, increases as the donor character of the substituents increases:

Substituents	OCH_3	CH_3	H	F	Cl	Br	J	$COCH_3$	NO_2
$\mathrm{tg}\,\alpha$	1.35	1.53	1.53	1.23	1.15	1.07	1.20	0.97	0.85

which apparently indicates that the role of protons in the denitrosation reaction increases in the same order.

From Fig. 2, constructed on the basis of the same experimental data ($H_0 = -2.015$), it is seen that both electron-donating and electron-accepting substituents increase the rate constant of the reaction. An analogous phenomenon was also observed for denitrosation in media with a different acidity.

This curious fact apparently indicates different mechanisms for the denitrosation reactions of substances with electron-accepting substituents and substances with electron-donating groups. It is possible that in the latter case, in accordance with Jaffé' s views, reaction complexes arise between the nitroso compound and the acid.

The linear character of the dependence of $\lg k_1$ on σ (the values of σ are taken from Jaffé' s work (^{5})) indicates that, for each of the two groups into which all the compounds we investigated should be divided, the Hammett correlation equation (^{4}) is valid. In this connection it is interesting that each group has ρ values of different sign.

According to Bunnett (^{6}), in the study of acid-catalyzed reactions, if water does not participate in the rate-determining step of the process, the value of the empirical "reaction-mechanism criterion" W should be negative; if, however, water participates in this process, its value is positive. Having calculated for the series of compounds studied ···

···the values of W, we found that, by this criterion as well, arylnitrosamines can be divided into two groups. The first includes compounds containing substituents with clearly expressed acceptor properties (n-nitro and n-acetyl groups; $W = +0.11$ and $+1.31$, respectively); the second group includes all the remaining compounds ($0 > W > -4.5$). Thus, we have once again become convinced that the denitrosation mechanisms for the two groups of substances differ from one another: whereas for compounds with electron-donor substituents the water molecule does not take part in the process, for substances of the other group this cannot be asserted.

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