# Reports of the Academy of Sciences of the USSR

A. V. Finkelshtein, Z. M. Kuzmina

1964

SovietRxiv

## Abstract

## Full Text

**Reports of the Academy of Sciences of the USSR**

1964. Volume 158, No. 1

## CHEMISTRY

A. V. Finkelshtein, Z. M. Kuzmina

# THE INFLUENCE OF THE STRUCTURE OF CERTAIN NITROBENZENE DERIVATIVES ON THE CATALYTIC REDUCTION OF THE NITRO GROUP

*(Presented by Academician A. A. Balandin, 4 IV 1964)*

The study of the catalytic hydrogenation of aromatic nitro compounds to amino derivatives in the liquid phase at atmospheric pressure and low temperatures has been carried out since 1871 (*1*). At the same time, the number of works on this question is comparatively small, and they are devoted mainly to the selection of catalysts, the study of the reaction mechanism, and the influence of the medium on its course. The influence of the nature and position of a substituent in the aromatic nucleus on the catalytic reduction of the nitro group has scarcely been studied systematically.

In the present work an attempt is made at a quantitative evaluation of the influence of the nature and position of a substituent in nitrobenzene derivatives on the reactivity of the nitro group in the catalytic reduction reaction in the presence of a nickel contact.

## Experimental data and their discussion

The objects of the investigation were carefully purified nitrobenzene, *m*-nitrotoluene, *p*-nitrotoluene, *o*-nitrophenol, *p*-nitrophenol, *o*-nitroaniline, and *p*-nitrophenetole.

Hydrogenation was carried out at a temperature of 20° and a hydrogen pressure of 750 mm Hg. Ethyl alcohol served as the solvent. The reaction was carried out in a jacketed duck-shaped vessel with vigorous shaking (1440 one-way oscillations per minute), which ensured that the process proceeded in the kinetic region. The constancy of the temperature in the vessel and in the gas burettes was maintained by an ultrathermostat of type I-8. Skeletal nickel of type W-5 served as the catalyst.

Figure 1

Figure 1: Figure 1

**Fig. 1.** Kinetic curves of catalytic hydrogenation of *o*-nitrophenol (1), *o*-nitroaniline (2), *p*-nitrotoluene (3)

The amounts of nitro compound, catalyst, and solvent in each experiment were 2.1 mmole, 1 g, and 60 ml, respectively. In our experiments all nitro compounds were reduced to the corresponding aniline derivatives. Some results are shown in Fig. 1.

It is seen from Fig. 1 that the rate of reduction of *o*-nitrophenol, *o*-nitroaniline, and *m*-nitrotoluene in the presence of the catalyst used by us is constant during the greater part of the course of the process (an appreciable decrease in the rate is observed only at the very end of the process). An analogous course of reduction was also observed for the other nitro compounds.

The hydrogenation rate constants, calculated in the usual way from the main part of the kinetic curve (at $t = 20^\circ$, $p = 750$ mm Hg), are given in Table 1.

As is evident from the data in Table 1, the reactivity of the nitro group in the process studied depends on the chemical nature and position of the substituent in the aromatic nucleus. In accordance with the data presented in Table 1, the substituents ($R$) of the investigated substances of the type $RC_6H_4NO_2$ can be arranged, according to the value of the rate constant of catalytic hydrogenation of the nitro group, in the following series:

$$o\text{-}OH > o\text{-}NH_2 > n\text{-}OC_2H_5 > m\text{-}CH_3 >$$

$$> H > n\text{-}CH_3 > n\text{-}OH.$$

**Table 1**

| Substance | $k$, mmol/min | Substance | $k$, mmol/min |
|---|---|---|---|
| *n*-Nitrophenol | 0.125 | *n*-Nitrophenetole | 0.182 |
| *n*-Nitrotoluene | 0.154 | *o*-Nitroaniline | 0.200 |
| Nitrobenzene | 0.172 | *o*-Nitrophenol | 0.250 |
| *m*-Nitrotoluene | 0.176 | | |

Comparison of the latter with the literature data(2) showed that in the indicated series the meta- and para-substituents are arranged in the order of decreasing Hammett substituent constants. At the same time, we had previously(3) established that a linear relationship is observed between the Hammett constants and the shift of the electronic absorption spectra of certain aromatic compounds observed upon changing the solvent ( “solvatochromic effect” ).* This prompted us to attempt to correlate the hydrogenation rate constants with the magnitude of the “solvatochromic effect” ($\Delta\nu_{1,2}$).

For this purpose, ultraviolet absorption spectra were recorded for the compounds listed above in two solvents.

The spectra were recorded by the usual method on an SF-4 spectrophotometer. Carefully purified ethanol and normal heptane served as solvents. The magnitude of the “solvatochromic effect” ($\Delta\nu_{1,2}$) was determined as the difference between the frequencies corresponding to the maxima of the K absorption bands in heptane and ethanol. The values of $\Delta\nu_{1,2}$ found by us for seven nitro compounds are given in Fig. 2.

As follows from Fig. 2, the dependence between the logarithm of the hydrogenation rate constant and the magnitude of the “solvatochromic effect” for the ortho-, meta-, and para-substituted nitrobenzene derivatives investigated by us is linear and is interpreted by the equation

$$\lg k = -0.46 - 1.8 \cdot 10^4 \Delta\nu_{1,2}.$$

The small range of investigated compounds naturally precludes any broad generalizing conclusions, but nevertheless, in our opinion, it permits the possibility of estimating the reactivity of aromatic nitro compounds in catalytic reduction reactions from spectral data.

The existence of a dependence between $\lg k$ and $\Delta\nu_{1,2}$ also provides some basis for the following considerations.

The magnitude of the “solvatochromic effect” $\Delta\nu_{1,2}$ is determined by the energy of interaction** of the molecule of the dissolved substance in the ground and nonequilibrium excited state with the molecules of the first and second solvents.

As already noted above, the interaction in question is of a universal nature and does not cause radical changes in the structure of the molecules of the dissolved substance, i.e., it does not lead to dissociation, etc. Indeed (see Fig. 3)

$$hc\nu_1 = E_1^* - E_1 = E^* - W_1^* - E + W_1,$$

---

* It should be especially noted here that we mean only those spectral shifts that are due to the difference in the universal interaction between the molecules of the dissolved substance and the molecules of different solvents.

** We neglect the interaction between molecules of the dissolved substance, since dilute solutions were used for recording the UV spectra.

Figure 2 and Figure 3

Figure 2: Figure 2 and Figure 3

$$hc\nu_2 = E_2^* - E_2 = E^* - W_2^* - E + W_2,$$

and therefore,

$$\Delta\nu_{1,2} = \nu_1 - \nu_2 = \frac{(W_2^* - W_1^*) - (W_2 - W_1)}{hc}.$$

The stabilization energy ($W$), in turn, depends on the properties and structure of the molecules of the solvent and the dissolved substance. But since for all the substances we studied $\Delta\nu_{1,2}$ was determined for one and the same pair of solvents, the observed differences in this quantity for compounds of the type $RC_6H_4NO_2$ have as their cause only those changes in $W$ that are produced by the difference in substituents ($R$) in their chemical nature or position relative to the nitro group.

**Fig. 2.** Dependence between the rate constant and the "solvatochromic effect" for compounds of the type $RC_6H_4NO_2$.
1 –$R = OH$; 2 –$NH_2$; 3 –$OC_2H_5$; 4 –$CH_3$; 5 –$H$;
*a* –ortho, *b* –meta, *c* –para

**Fig. 3.** Scheme of electronic levels in vapors and solutions, *a* –vapors, *b* and *c* –solutions in the first and second solvent

At the same time, the differences in the rate constants for reduction of the nitro derivatives studied are due to changes in the activation energy of the process as a result of the action of the same substituents on the reaction center, since all substances were hydrogenated under identical conditions and the reaction center underwent identical changes in all cases.

What has been said may serve as some confirmation of the earlier assumption[3] concerning the existence of a relationship between the change in the energy of interaction of the molecules of a dissolved substance with the medium and the change in the activation energy of certain reactions, provided that they are caused by one and the same change in the structure of the molecule.

Siberian Technological Institute
Krasnoyarsk

Received
31 III 1964

## REFERENCES CITED

1. M. Zaitsev, *J. prakt. Chem.*, **2**, 418 (1871).
2. V. A. Palm, *Uspekhi khimii*, **30**, 1069 (1961).
3. A. V. Finkel' shtein, V. L. Pogrebnaya, S. V. Luk' yanchuk, *ZhFKh*, No. 8 (1964).

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