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THE ROLE OF ACIDITY IN THE KINETICS OF AROMATIC COMPOUND NITRATION

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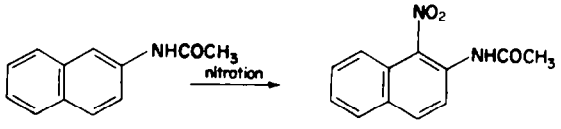
Abstract—Colorimetric method was used for investigation of the nitration rate in the solutions $HNO_3 + H_2O$, $HNO_3 + CH_3COOH + H_2O$, $HNO_3 + H_2SO_4 + H_2O$, $HNO_3 + HClO_4 + H_2O$. A mechanism of nitration of aromatic compounds based on a system of protolytic equilibria is proposed.

IN the work of Minc *et al.*[1-4]—based on the investigation of cathodic polarization and Raman spectra of nitric acid solutions—it was concluded that an increase of medium acidity* caused weakening of the HO—NO_2 bond and it was suggested that the HO—NO_2 molecule is the nitrating agent in the absence of nitronium ions (NO_2^+). This point of view is opposed to that of Ingold *et al.*[5] who state that the nitric acid molecule under similar conditions cannot be the nitrating agent. The present work is an investigation of the problem by means of nitration kinetics.

The colorimetric method used in this work enabled the concentration of a coloured nitroderivative formed during nitration to be determined. An important problem was the selection of an aromatic compound which would fulfil the following experimental requirements: (a) one-step nitration with a measurable rate in all investigated solutions, (b) a colourless compound with a coloured nitroderivative, (c) good solubility of both in the investigated solutions, (d) agreement with Lambert-Beer's law.

After preliminary experiments, N-acetyl-2-naphthylamine (ArH) was chosen. It is nitrated to the 1-nitro-N-acetyl-2-naphthylamine ($ArNO_2$)



In order to determine the $ArNO_2$ concentration on the basis of extinction measured, the validity of Beer's law was tested. The Lambert-Beer's law in the form

$$\log \frac{I_0}{I} = E = \varepsilon hc$$

* Acidity is considered as a function of the strength and concentrations of all acids and bases in the solution.

[1] S. Minc, *Bull. Acad. Polon. Sci.* Cl. III, **1**, 333 (1953).
[2] S. Minc and S. Jasielski, *Roczniki Chem.* **28**, 109 (1954).
[3] S. Minc and Z. Kecki, *Roczniki Chem.* **30**, 935 (1956).
[4] S. Minc, Z. Kecki and S. Osiecki, *Bull. Acad. Polon. Sci.* Cl. III, **5**, 343 (1957).
[5] C. K. Ingold *et al. J. Chem. Soc.* 2441 (1950).

expresses the proportionality between the extinction E and concentration c only on condition that the extinction coefficient ε and the length of the absorbing path h remain constant (the latter was fulfilled in the photocolorimeter construction). The constancy of ε was tested as follows: ArH was introduced into the nitrating mixture and after completion of the reaction the solution was diluted with the same nitrating mixture in suitable proportions to obtain $ArNO_2$ solutions in various concentrations. The dependence of the extinction on the $ArNO_2$ concentration (expressed in arbitrary units) is given in Fig. 1. The absolute concentration of $ArNO_2$ was about $2 \cdot 10^{-3}$

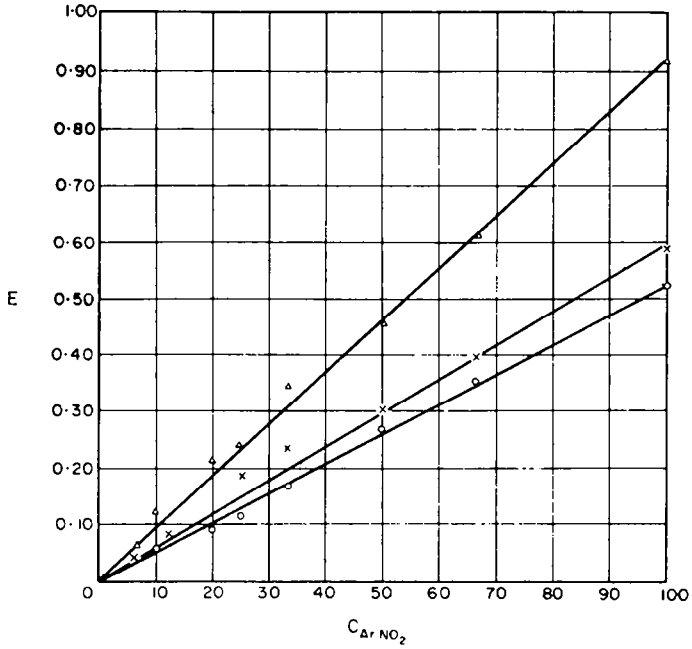


FIG. 1. Test of validity of the Beer's law. Dependence of the extinction E on the $ArNO_2$ concentration in solutions: △ HNO_3 7·0 M + H_2O, ○ HNO_3 3·1 M + H_2SO_4 4·9 M + H_2O, × HNO_3 5·8 M + $HClO_4$ 5·0 M + H_2O.

mole/l. The results show the extinction coefficient as constant during the investigation. The differences in the slope could arise from the initial concentration difference and from the dependence of ε on the medium, but does not preclude the application of Lambert-Beer's law to every mixture under investigation.

Measurement of the reaction rate

The nitrating mixture was introduced into one cell of photo-colorimeter. ArH was added to a portion of the same nitrating mixture, the solution introduced into the second cell of the colorimeter and the extinction readings taken at regular time intervals and when the extinction value became constant all the dissolved ArH was assumed nitrated. On the basis of Lambert-Beer's law it was possible to determine the fraction of ArH nitrated in times t_1, t_2 etc. If ε and h are constant, then

$$\frac{E_t}{E_\infty} = \frac{c_t}{c_\infty}$$

where E_t and E_∞ are the extinctions at times t and t_∞, respectively; c_t/c_∞ is the fraction of ArH nitrated in the time t. In some cases t_∞ was of the order of several hours.

Determination of the reaction order

In all the solutions investigated the nitric acid greatly exceeded the ArH concentration and thus, the first order reaction was to be expected. It was checked by means of the fractional life method

$$t_{1/n} \sim \frac{1}{a^{s-1}}$$

where $t_{1/n}$ is the fractional life time ($n = 1, 2, 3, 4, \ldots$), a is the initial reactant concentration, s is the reaction order. The fractional life times are: (a) proportional to a for the

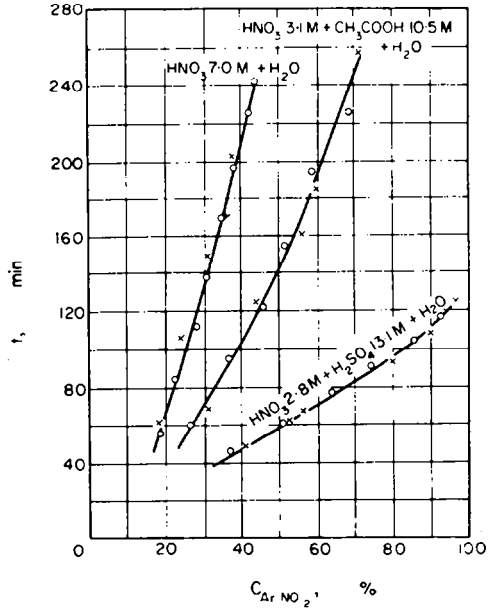


FIG. 2. Determination of the reaction order by means of the fractional life method. ×—initial ArH concentration = a, ○—initial ArH concentration = $2a$.

zero order reactions, (b) independent of a for the first order reactions, (c) inversely proportional to a for the second order reactions.

The dependence of $ArNO_2$ concentration on the nitration time was determined in two parallel series, one having the initial ArH concentration equal to a and the other to $2a$. The results given in Fig. 2 show the fractional life time to be independent of the initial concentration of ArH. Thus the reaction is of the first order.

Calculation of the reaction rate constant

In the equation for the first order reaction

$$\ln \frac{a}{a - c_t} = k_1 t$$

the nitration was assumed complete, thus the initial ArH concentration equalled the final $ArNO_2$ concentration, $a = c_\infty$. Then

$$2{\cdot}303 \log \frac{1}{1 - c_t/c_\infty} = k_1 t$$

Since $c_t/c_\infty = E_t/E_\infty$ the expression of the rate constant is

$$k_1 = -\frac{2{\cdot}303}{t} \log (1 - E_t/E_\infty)$$

In the course of each nitration it was possible to make about 10 measurements and each nitrating solution was examined twice. Thus the values k_1 given in Table 1 are the average of 14–20 measurements. The average error was estimated to be ± 7 per cent.

TABLE 1. NITRATION RATE CONSTANTS IN THE INVESTIGATED SOLUTIONS
($c_{ArH} = 1{\cdot}4 \times 10^{-3}$ mole/l.)

No.	Concentration, mole/l.					$\xi = \frac{\Sigma[HX]}{[H_2O]}$	Rate constant $10^5 k_1$ sec^{-1}	Medium
	HNO_3	CH_3COOH	H_2SO_4	$HClO_4$	H_2O			
1	4·0	—	—	—	48·7	0·08	1·9	
2	6·3	—	—	—	44·8	0·14	3·9	$HNO_3 + H_2O$
3	10·0	—	—	—	37·7	0·26	4·5	
4	3·1	10·5	—	—	17·7	0·77	7·7	$HNO_3 +$
5	2·9	13·6	—	—	8·2	2·01	11·7	$CH_3COOH +$
6	5·4	12·5	—	—	5·5	3·26	13·0	H_2O
7	3·0	15·3	—	—	—		16·9	
8	3·1	—	4·9	—	38·0	0·21	3·7	
9	3·2	—	7·7	—	30·0	0·36	4·4	$HNO_3 +$
10	3·0	—	9·7	—	25·0	0·51	4·7	$H_2SO_4 +$
11	2·8	—	13·1	—	15·2	1·05	20·3	H_2O
12	2·8	—	14·9	—	7·9	2·24	46·1	
13	6·2	—	4·8	—	31·8	0·35	5·0	
14	6·1	—	10·0	—	14·8	1·09	10·8	
15	3·2	—	—	2·8	43·0	0·14	5·1	
16	2·8	—	—	7·2	32·3	0·31	6·2	$HNO_3 +$
17	6·0	—	—	3·4	29·2	0·32	5·1	$HClO_4 +$
18	5·8	—	—	5·0	30·2	0·36	5·9	H_2O
19	0·9	—	—	8·7	32·2	0·30	2·9	
20	2·7	—	14·6	P_2O_5 0·8	5·4	3·50	102·6	$HNO_3 + H_2SO_4 + P_2O_5 + H_2O$

DISCUSSION

According to Ingold *et al.*[5] in the nitrating mixture which does not allow the formation of NO_2^+ ions because of too great water concentration, the nitrating agent is the $H_2NO_3^+$ ion. Ingold based his conclusion on a sudden great change of the nitration rate constant k_1 caused by only a small concentration change of the nitration mixture components. He maintains that nitric acid is a base in relation to H_2SO_4 or $HClO_4$, water is a base in relation to HNO_3, H_2SO_4 and $HClO_4$. Water causes hydration and dissociation of the acids beginning with the strongest one. When the concentration of the strong acid exceeds that of free water, the acid excess reacts with nitric acid to form the $H_2NO_3^+$ ions, the nitrating agent.

Preliminary analysis of the results in Table 1 are apparently in agreement with Ingold's. A function ξ can be formed, defined as the ratio of the sum of all acid concentrations [HX] (including HNO_3) to the water concentration, $\xi = \Sigma[HX]/[H_2O]$. Nitric acid is included because it is both an acid and a base.[6]

Fig. 3 shows the dependence of k_1 on ξ. A sudden increase of k_1 takes place at the value $0{\cdot}70 < \xi < 1{\cdot}00$.

According to Ingold[5] one can calculate that the 2-phenylethylsulphonic acid nitrated showed the sudden increase of k_1 at the value $0{\cdot}36 < \xi < 0{\cdot}44$. In the

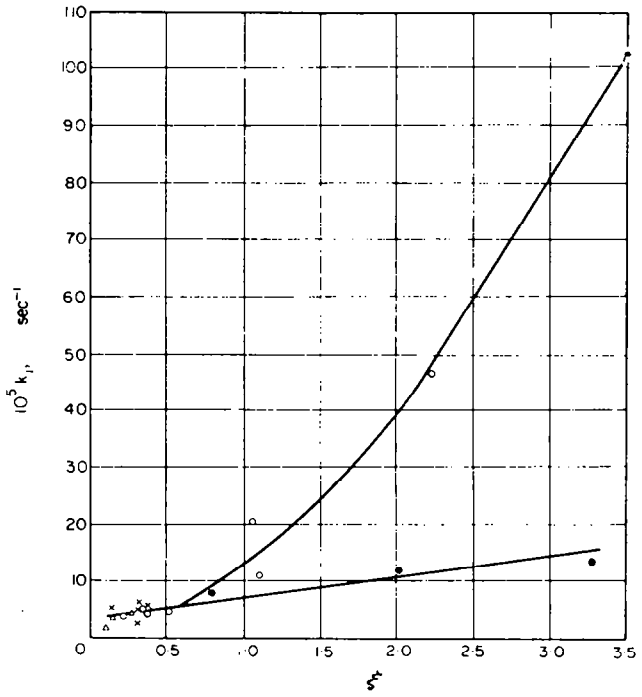


FIG. 3. Dependence of the nitration rate constant on the function

$$\xi = \frac{\Sigma[HX]}{[H_2O]}$$

△ $HNO_3 + H_2O$, ● $HNO_3 + CH_3COOH + H_2O$,
○ $HNO_3 + H_2SO_4 + H_2O$, × $HNO_3 + HClO_4 + H_2O$,
* $HNO_3 + H_2SO_4 + P_2O_5 + H_2O$.

nitration of N-acetyl-2-naphthylamine, if the $H_2NO_3^+$ ion were the nitrating agent formed according to Ingold at the value $\xi = 0{\cdot}4$, a k_1 change would occur in the same range of ξ.

Secondly, during nitration with $HNO_3 + CH_3COOH + H_2O$ mixture, the $H_2NO_3^+$ ion cannot be formed as acetic acid is a base in relation to HNO_3. Nevertheless, an increase of k_1 was observed although not so sudden as in the case of H_2SO_4, but nevertheless pronounced.

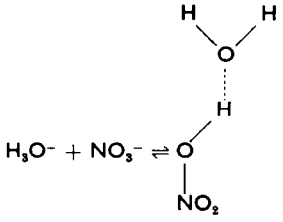
A better explanation of the experimental facts and not contrary to Ingold's hypotheses is that an increase of acid concentration and at the same time a decrease

[6] C. K. Ingold and D. J. Millen, *J. Chem. Soc.* 2612 (1950).

of water concentration in the nitrating medium results in the following reactions: First by the dehydration of H_3O^+ ions

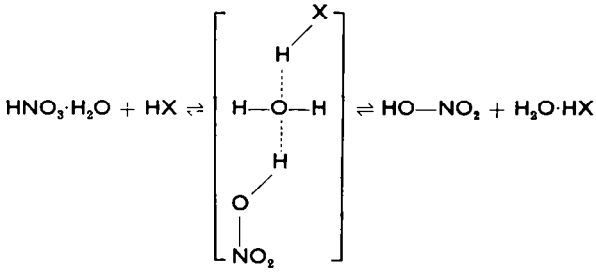
$$(H_3O^+)\cdot(nH_2O) + nHX \rightleftharpoons (n+1)\,H_3O^+ + nX^- \tag{1}$$

followed by depressed dissociation of HNO_3



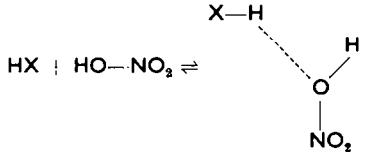
(2)

A further increase of acid concentration causes the dehydration of HNO_3



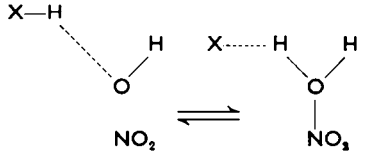
(3)

The final stage is the dehydration of the acid HX and its interaction with $HO—NO_2$ as a base



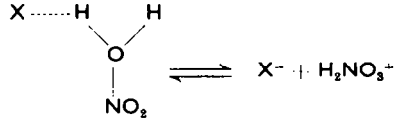
(4)

when the HX is a strong enough acid, it follows



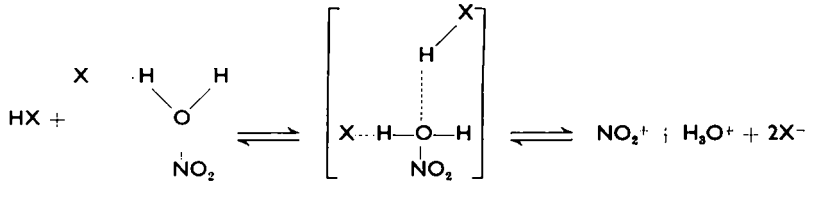
(4a)

and if there was a possibility of solvation, dissociation results



(4b)

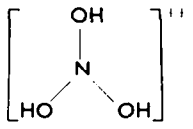
the last stage leads to the nitronium ion formation



(5)

This scheme is based on Brønsted's protolytic reactions. It is considered[7] that the initial stage of a protolytic reaction is the formation of a hydrogen bond between an acid and a base. A complete proton transfer and the following dissociation into ions depends on the presence of a solvating agent and does not always take place. In the protolytic scheme hydrogen bonding is essential and the introduction of a proton into the nitric acid molecule causes a gradual polarization and weakening of the HO—NO_2 bond that leads finally to a break down of the bond and to the formation of NO_2^+ ion solvated by X^- ions. A similar conclusion was drawn in previous work[3,4] from the changes in Raman spectrum of the solutions and it should be stressed that the changes depended on the acidity of the medium.

An objection to this hypothesis is the assumption that two oxygen atoms in the nitric acid molecule do not take part in the hydrogen bond formation, but if they did, the NO_2^+ ion formation according to the equation



$$+ 2X^- \rightleftharpoons NO_2^- + H_3O^+ + 2X^-$$

would not be possible, yet the existence of NO_2^+ ion has been proved.[8]

Further support for the proposed mechanism may be found in the bond length difference between the oxygen and nitrogen atoms in the HNO_3 molecule: the N—OH bond, $r = 1{\cdot}405$ Å, is much longer than both N—O bonds, $r = 1{\cdot}206$ Å,[9,10] so the oxygen atom of OH is bound more weakly to the nitrogen and the hydrogen bond formation is therefore easier.

The sudden change in the nitration rate constant

The activation energy of nitration is the smaller, the weaker the HO—NO_2 bond. It also depends on the ease with which the proton detaches from the nitrated ArH. The possibility of hydrogen bond formation between the acid and ArH by the substituents or even π-electrons[7,11] must be taken into account. Hetherington and Masson[12] mentioned the role of interaction between ArH and the acid in nitration. It seems obvious that the sudden change of k_1 sets in when the thermal motion energy approaches the activation energy arising from the given nitration conditions. It is also obvious that the k_1 change will occur in an acidity range characteristic of any given ArH. Furthermore, if the acidity is too great, the proton detachment from ArH can be more difficult in some cases. Thus, the optimum concentration range of the nitrating mixture is adequate in one of the (2) to (5) stages in the protolytic scheme, depending on the properties of the nitrated ArH.

The $H_2NO_3^+$ ion could be the nitrating agent but its presence in the nitrating solution is not necessary and its existence has not yet been optically proved. Ingold stated that the $H_2NO_3^+$ ion spectrum could not be identified, like the H_3O^+ ion, the

[7] A. I. Šatenštejn, *Usp. Khim.* **24**, 377 (1955).
[8] C. K. Ingold *et al.*, *J. Chem. Soc.* 2504 (1950); *Ibid.* 2552 (1950); *Ibid.* 2576 (1950).
[9] L. R. Maxwell and V. M. Mosley, *J. Chem. Phys.* **8**, 738 (1940).
[10] D. J. Millen and J. R. Morton, *J. Chem. Soc.* 1523 (1960).
[11] W. G. Schneider, *Hydrogen Bonding*. Papers of Symposium at Ljubljana 1957, p. 55. Pergamon Press (1959).
[12] J. A. Hetherington and I. Masson, *J. Chem. Soc.* 105 (1933).

frequency of proton exchange was so high that formation of definite vibration levels was prevented. This argument cannot be accepted as then no spectrum would be observed in the $HNO_3 \cdot H_2O$ system, since by the proton exchange the H_2O molecule would pass into the H_3O^+ ion just as frequently as the HNO_3 into the NO_3^-. Nevertheless, the spectrum of $HNO_3 \cdot H_2O$ was observed and in the liquid state it consisted of the spectra of HNO_3 and H_2O molecules, whereas in the solid state there were observed in the spectrum the NO_3^- and H_3O^+ bands[13,14] and thus the identification of the H_3O^+ ion spectrum was achieved.[14,15]

It is well known[16] that compounds such as BF_3, $AlCl_3$ accelerate nitration. They cannot cause the formation of $H_2NO_3^+$ ions, but instead may weaken the HO—NO_2 bond by attracting the OH-oxygen electrons and can cause the NO_2^+ formation in accordance with the protolytic scheme.

Urbański and Hackel[17] investigated the O-nitration kinetics of starch and observed that nitration takes place in the absence as well as in the presence of NO_2^+ ions. The nitration rate increases continuously when passing from the solutions without NO_2^+ ions to the solutions in which the NO_2^+ ions can be formed. Except for the NO_2^+ ion they assume the nitrating agent could be the HO—NO_2 molecule in accordance with the protolytic scheme.

Finally, the effect of dehydrating agents on the nitration kinetics will be discussed. Martinsen[18] pointed out that an addition of P_2O_5 to the $HNO_3 + H_2SO_4 + H_2O$ mixture did not change the nitration rate constant to any extent. In the protolytic scheme P_2O_5 would favour the dehydration of H_3O^+ stage (1) and of HNO_3 molecules stage (3). Furthermore, P_2O_5 would form phosphoric acid thus increasing the acidity of the medium.

The k_1 was measured in a $HNO_3 + H_2SO_4 + H_2O$ solution after addition of P_2O_5 (No. 20 in Table 1) and a considerable increase of k_1 corresponding to the increase of ξ value (Fig. 3) was observed.

The ξ function might have been an important property for the nitration process as a value defining the medium acidity if it contained not only the concentrations but also the strength of acids and bases. In its present form it has a limited significance only.

EXPERIMENTAL

The reagents used were: nitric acid, $d = 1{\cdot}39$; sulphuric acid, $d = 1{\cdot}84$; perchloric acid, $d = 1{\cdot}54$; glacial acetic acid; acetic acid anhydride; phosphorous pentoxide; all commercial grades and used without further purification.

The acid sum concentration in the solutions was determined by acidimetric analysis; the concentration of nitric acid—by nitrometric method; the concentration of water—by density measurements.

Acetic acid anhydride was used to prepare a nonaqueous solution of $HNO_3 + CH_3COOH$ (No. 7 in Table 1).

N-acetyl-2-naphthylamine, m.p. 133°, dissolved in a mixture of acetic acid with water (1:1) was a basic solution of ArH, with concentration of $2{\cdot}8 \times 10^{-2}$ mole/l. This solution was added to the nitrating mixtures in a ratio of 1:20. Thus the concentration of ArH in the nitrating mixtures was $1{\cdot}4 \times 10^{-3}$ mole/l.

The extinction measurements were carried out by a Pulfrich photocolorimeter with a vertical

[13] A. Simon and M. Weist, *Z. Anorg. Chem.* **268**, 301 (1952).
[14] D. E. Bethell and N. Sheppard, *J. Chem. Phys.* **21**, 1421 (1953).
[15] R. C. Taylor and G. L. Vidale, *J. Amer. Chem. Soc.* **78**, 5999 (1956).
[16] A. V. Topčiev, *Nitrovanie uglevodorodov i drugich organičeskich soedinenij*. Moskva (1956).
[17] T. Urbański and J. Hackel, *Tetrahedron* **2**, 300 (1958).
[18] H. Martinsen, *Z. Phys. Chem.* **59**, 605 (1907).

light path. Cylindrical glass cells were used. The length of the absorbing path was 10 mm constant. A blue filter (470 mμ) was applied for all the measurements. An iron ring sealed in glass was placed in the cell and moved vertically with an electromagnet to mix the nitrating solution. It did not disturb the light path. The temperature was kept constant at 20 $\pm$ 2°.

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