Nitration of Anthraquinone in Nitric Acid

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1-Aminoanthraquinone, an important intermediate for dyes and pigments, has been previously manufactured industrially by the mercury catalyzed sulphonation of anthraquinone followed by ammonolysis of the resulting sulphonic acid. To avoid the pollution problems inherent in this process, in particular the mercury contamination of the product and effluents, the obvious route of nitration (1, 2), followed by reduction of the 1-nitro-anthraquinone, has been studied. In the following, the kinetic and reaction engineering results of the nitration of anthraquinone in nitric acid will be discussed.

Experimental kinetic studies.

When anthraquinone is added to concentrated nitric acid, 1-nitro-anthraquinone is formed together with 2-nitroanthraquinone and various dinitroanthraquinone isomers. The microkinetics of the nitration were studied in the classical manner of carrying out reactions at constant temperatures in laboratory equipment. Samples of reaction mixture were withdrawn after given reaction times and these immediately added to an ice-water mixture. This dilution causes immediate stopping of the reaction and precipitation of the solid anthraquinone compounds. The resulting suspension was filtered, the filter cake washed, dried and then analysed by means of a gas chromatographic method developed in these laboratories.

 The absolute concentrations (weight %) of anthraquinone, 1- and 2-nitroanthraquinone and the sum of all dinitro-anthraquinone isomers were determined in each sample. At the time this kinetic study was carried out, we were unable to analyse the separate dinitro-isomers and consequently they were treated as one compound. We now know that the 1,5-, 1,8-, 1,6- and 1,7-isomers are formed in the ratio 40, 40, 10, 10 . The other six possible dinitroanthraquinone isomers and trinitroanthraquinone

compounds are not formed in detectable amounts, i.e. less than
0.3 weight %. Thin layer chromatographic analysis of the reaction
products has shown that the amount of oxy-anthraquinone compounds
formed through oxidation reactions is also very small (0 - 2
weight %). These side reactions have not been incorporated in our
model.

A series of 21 experiments were carried out using technical
grade anthraquinone and nitric acid. The following reaction
parameters were varied in the ranges and with the accuracies
given below:

- Weight ratio : nitric
  acid to anthraquinone   6:1 to 12:1   (± 0.1   )

- Reaction temperature   0 to 20°C   (± 0.5°C   )

- Water content of nitric
  acid (weight %-H_2O)   0.2 to 2.9   (± 0.05   )

- Nitrous acid content of
  nitric acid (weight %-N_2O_3) 0.06 to 0.6   (± 0.03   )

- Reaction time   0 to 180 min.   (± 0.5 min.)

The amounts of water and nitrous acid in the nitric acid were
determined by titration of the acid with standard caustic soda
and potassium permanganate solutions. We have assumed that the
amount of nitrous acid remains constant during the reaction and
is present in the form N_2O_3 (3). The results of a typical kinetic
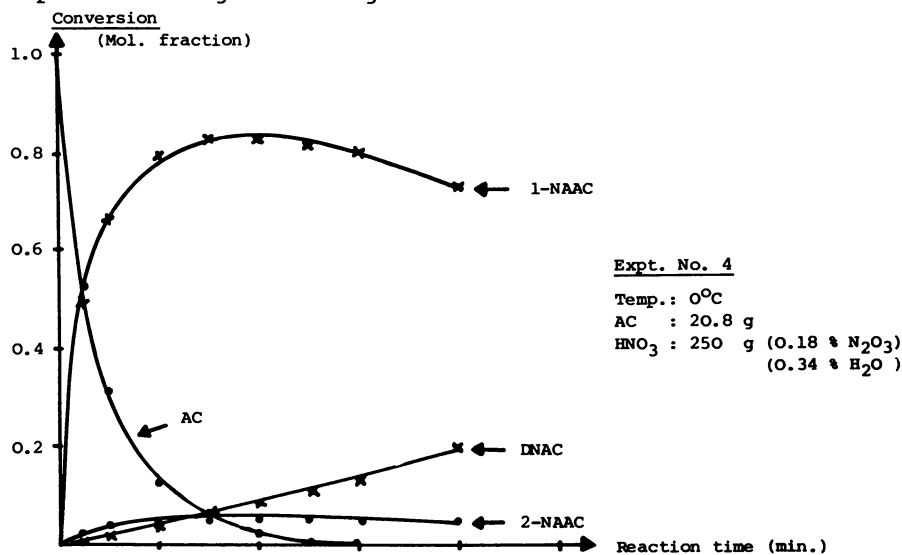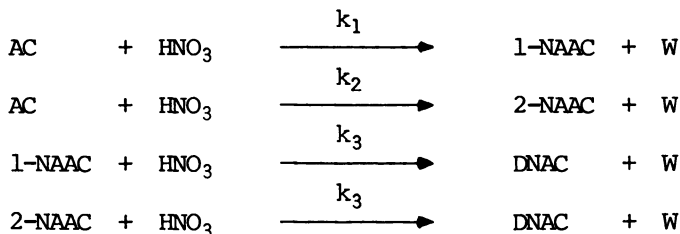experiment are given in figure 1 .

Figure 1.   Typical kinetic experimental results

Kinetics of reaction.

Model. The following model is proposed for the nitration of anthraquinone in nitric acid:

Reactions

$$AC \quad + \quad HNO_3 \quad \xrightarrow{k_1} \quad 1\text{-NAAC} \quad + \quad W$$

$$AC \quad + \quad HNO_3 \quad \xrightarrow{k_2} \quad 2\text{-NAAC} \quad + \quad W$$

$$1\text{-NAAC} \quad + \quad HNO_3 \quad \xrightarrow{k_3} \quad DNAC \quad + \quad W$$

$$2\text{-NAAC} \quad + \quad HNO_3 \quad \xrightarrow{k_3} \quad DNAC \quad + \quad W$$

Mass balance equations

$$[AC_O] \quad = \quad [AC] \quad + \quad [1\text{-NAAC}] \quad + \quad [2\text{-NAAC}] \quad + \quad [DNAC]$$

$$[W] \quad = \quad [W_O] \quad + \quad [1\text{-NAAC}] \quad + \quad [2\text{-NAAC}] \quad + \quad 2\,[DNAC]$$

$$[N_2O_3] \quad = \quad \text{constant during the reaction}$$

Kinetic equations

$$\frac{d\,[1\text{-NAAC}]}{dt} \quad = \quad (k_1\,[AC] - k_3\,[1\text{-NAAC}]) \cdot F$$

$$\frac{d\,[2\text{-NAAC}]}{dt} \quad = \quad (k_2\,[AC] - k_3\,[2\text{-NAAC}]) \cdot F$$

$$\frac{d\,[DNAC]}{dt} \quad = \quad k_3\,([1\text{-NAAC}] + [2\text{-NAAC}]) \cdot F$$

$$\text{where } F \quad = \quad e^{-P(7)\,[W] - P(8)\,[N_2O_3]} \cdot [AC_O]^{P(9)}$$

$$k_1 \quad = \quad e^{(P(1) - P(2)/T)}$$

$$k_2 \quad = \quad e^{(P(3) - P(4)/T)}$$

$$k_3 \quad = \quad e^{(P(5) - P(6)/T)}$$

From the approximately 500 experimental numerical values the best values of the nine reaction parameters P(1)....P(9) were determined using a multivariant non-linear regression programme.

For simplicity, the dimensionless units of mol. fraction conversions were used in the model instead of absolute values of the concentrations (conversion to 1-NAAC = $[NAAC]/[AC_O]$ etc.).
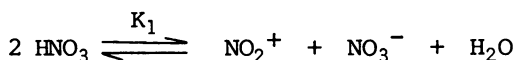The values obtained were:

P(1)	P(2)	P(3)	P(4)	P(5)	P(6)	P(7)	P(8)	P(9)
24.30	7262	25.17	8217	24.22	8115	1.165	12.85	-2.594

The standard deviation between the calculated and experimentally found values was 0.02, the maximum deviation was 0.115 .

Comments on the kinetic model. The proposed model has the following characteristics: With a given starting concentration of anthraquinone, the nitration reactions are first order with respect to the anthraquinone compounds and independent of the nitric acid concentration which is in large excess. The strong inhibiting effects of water and nitrous acid (N_2O_3) on the reaction rates are explained quantitatively by means of exponential functions. Neither the cubic relationships proposed by Ingold et. al. in their classical studies of nitration in nitric acid (4) or any other higher power function of the type $[water]^n$, $[N_2O_3]^m$ · can quantitatively explain the very large inhibiting effects of these two compounds over wide ranges of concentrations.

On the other hand, the effect of the starting concentration of anthraquinone can be interpreted by means of a power function, $[AC_O]^{P(9)}$. We belive that this unusual effect is caused by the formation of a chemical complex between the nitronium ion which is the effective nitration agent in nitric acid and all of the anthraquinone compounds in the reaction mixture.

$$2\ HNO_3 \underset{}{\overset{K_1}{\rightleftharpoons}} NO_2^+ + NO_3^- + H_2O$$

$$2\ NO_2^+ + AC\text{-compounds} \underset{}{\overset{K_2}{\rightleftharpoons}} complex$$

$$\text{Hence } [NO_2^+] = \frac{[complex]\ [NO_3^-]\ [H_2O]}{K_2 \cdot K_1 \cdot [AC\text{-compounds}]\ [HNO_3]^2}$$

With the assumption that the rate of reaction is proportional to some function of $[NO_2^+]$, it is not surprising to find the rate of reaction inversely proportional to the concentration of all anthraquinone compounds, i.e. proportional to $[AC_O]^{P(9)}$, with P(9) being negative.

Since completion of our studies, several patent publications concerning this nitration have appeared (5, 6). Using our model, we have simulated the reaction under the published conditions and compared the calculated results with those reported. The ranges

	This work	German Patent Publication 2 252 013	German Patent Publication 2 241 627 2 232 464
Weight Ratio (HNO_3/AC	6 – 12	3.6	0.91 – 15.1
Temperature (^oC)	0 – 20	25 – 55	45 – 80
Reaction time (min.)	0 – 180	20 – 4320	0.5 – 40
Water in HNO_3 (wt. %)	0.2 – 2.9	3.6	2 – 3.6
Nitrous acid in HNO_3 (wt. 4)	0.06 – 0.6	? (= 0)	? (= 0)
No. of experimental points	172	3	24
Simulation { Sum of squares of residuals }	0.186	0.057	0.268
Standard deviation between simulation and reported values }	0.019	0.08	0.103

Table I . Patent publications and model-simulations

Temp. (^oC)	HNO_3/AC (wt. ratio)	H_2O (wt. %)	N_2O_3 (wt. %)	k_1F	k_1/k_2	k_1/k_3
0	12	0	0	.562	13.8	24.6
	12	3	0	.038	13.8	24.6
	12	0	.5	.175	13.8	24.6
	4	0	0	.047	13.8	24.6
50	12	0	0	34.58	8.05	15.2
	12	3	0	2.34	8.05	15.2
	12	0	.5	10.8	8.05	15.2
	4	0	0	2.91	8.05	15.2

Table II . Comparison of rate constants under various conditions

of reaction conditions given in these examples and a summary of
the differences between simulated and published results are given
in table I . The concentration of nitrous acid during the reaction
is not given in these publications, consequently we have assumed
a zero value for this variable. It can be seen that the model is
able to predict the end products of reaction with a reasonable
degree of accuracy under a very wide range of conditions,
including those far removed from our experimental conditions.
        Given the values of the kinetic constant parameters P(1)....

....P(6) one can calculate the best conditions for obtaining maximum yields of l-nitroanthraquinone. As the activation energy for the formation of this compound is lower than the activation energies for the other two reactions the process should be carried out at as low a temperature as possible (table II).

Reactor design.

For the industrial application of this nitration the design of the reactor is of utmost importance. The reaction must be carried out under controlled conditions so that the amount of main product produced in the reactor is a maximum. Because of the potentially hazardous nature of the reaction and the necessity of rapidly stopping the reaction after a given degree of nitration, only a continuous type of reactor can be used in a large plant.

   Ideal tubular reactor. The simplest type of continuous reactor is the tubular reactor operating under the condition of plug flow (7), consequently we developed a computer simulation programme for this type of reactor. The model included the three kinetic and two mass balance equations together with a differential equation for the heat balance (increase of temperature) along the reactor. The model was tested by carrying out simulations under the isothermal conditions (heat of reaction zero) used in the kinetic studies. Then, using a measured value of the heat of nitration (36 kcal mol^{-1}), we calculated the end products obtainable with the plug flow adiabatic reactor. A typical reaction product would be: AC 4.0 weight %, 1-NAAC 79.0 %, 2-NAAC 6.5 %, DNAC 10.5 %.

   Cascade of stirred-tank-reactors. Our first pilot plant experiments were carried out in an existing cascade reactor system consisting of 4-stirred vessels with volumes of 0.25, 3.07, 3.04 and 3.17 litres coupled together in series. Each vessel was equipped with a cooling system, thus the temperature of each tank could be varied as desired. Residence time distribution studies of this system had shown that, under the conditions of interest, the flow characteristics of each tank were those of an ideal stirred tank (7).

   The nitration was carried out by pumping nitric acid of known concentration and temperature at given rate (28 liter/hour) continuously through the cascade and adding anthraquinone by means of a weigh-belt feeder at a rate of 1.38 kg/hour to the first vessel. The reaction mixture leaving the last vessel and any samples taken from either of the vessel, were immediately diluted with ice-water to stop further reaction. These samples were then treated and analysed as described in section 2 .

   A computer programme was written which simulated the nitration in a series of n-stirred tanks. With given conditions

Experiment No. 14: AC : 0.023 kg min.$^{-1}$

HNO$_3$: 0.28 kg min.$^{-1}$ (H$_2$O = 1.0 wt.%, N$_2$O$_3$ = 0.8 %)

Vessel No.	Temp. in vessel (°C)	Product-analysis (mol. %)				
			1-NAAC	2-NAAC	DNAC	AC
1	- 4.9	Expt.	5	1	0	93
		Model	5.5	0.7	0	94
2	3.0	Expt.	48	8	1	35
		Model	54	7.4	2.5	36
3	6.6	Expt.	71	6	8	25
		Model	72	9.7	7.2	11
4	7.2	Expt.	77	10	8	6
		Model	74	10	13	3.4

Table III . Nitration in a cascade of 4 stirred tanks

Reaction conditions:

AC/HNO$_3$ = 1/12 (wt.)
H$_2$O in HNO$_3$ =   2.0 wt.%
N$_2$O$_3$ in HNO$_3$ =   0.01 wt.%
Reaction time   = 20   min.
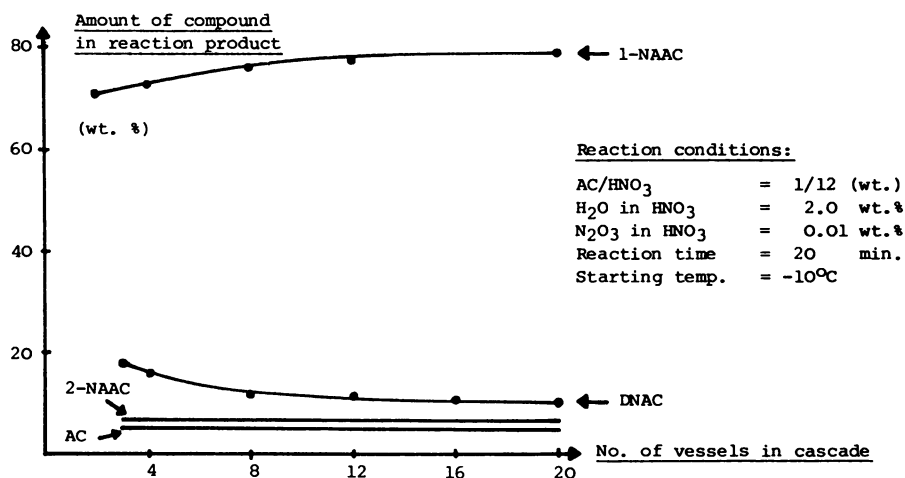Starting temp.   = -10°C

Figure 2.   Stimulation of nitration in cascade reactor

(flow rates, composition of nitric acid, temperatures and volumes of each tank) the programme calculated the composition of the reaction product in each tank in turn, starting with tank 1 .

Some of the results obtained experimentally are compared in table III with those predicted by the model. The agreement is excellent and, as expected, the amounts of dinitroanthraquinone formed in this reactor system are higher than in the plug flow reactor. Using this model we were able to show that for this nitration a cascade of at least 20 stirred vessels are required in order to obtain the same product-mixture as with the ideal tubular reactor (fig. 2).

Final pilot plant reactor. Following the sucessful operation of the cascade reactor, a new pilot plant was designed and used. In this reactor the nitric acid and anthraquinone were fed continuously at given rates into a stirred tank vessel (internal volume 1.3 liter) and the overflow from this vessel was allowed fo flow continuously through a tubular reactor (internal volume, 3.98 liter, diameter 15.8 mm) and then immediately diluted with water to stop the reaction. Samples of this suspension were filtered, dried and analysed as previously described. Both stirred tank and tubular vessel were well insulated, i.e. the reaction was carried out adiabatically.

In order to improve the flow characteristics through the tubular reactor, 10 lengths (each 50 cm) of static mixer elements were inserted at 100 cm internals along the tube. Residence-time distribution studies using a pulse of potassium chloride as tracer showed that this tubular reactor had the flow characteristics equivalent to a cascade of 35 stirred tanks in series. Thus for practical purposes, this tube can be considered to have flow characteristics equivalent to those of a plug flow reactor.

We have simulated the complete (stirred tank and tube) reactor system by combining our model for the cascade reactor, with only one stirred tank, with the model for the adiabatic ideal tubular reactor. An example of the excellent fit between simulated and experimentally found results is given in fig. 3 .

AC (3.5 kg/h)
(20°C)   HNO$_3$ (42 kg/h, -1°C)
          (H$_2$O = 2.3 wt. %, N$_2$O$_3$ = 0.07 wt. %)
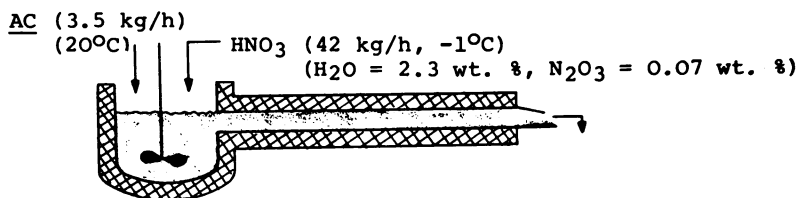
		Temp. (°C)	Product-analysis (wt. %)			
			AC	1-NAAC	2-NAAC	DNAC
In stirred tank	measured	7.3	70	26	2.8	0.9
	calculated	7.0	73	24.6	1.9	0.4
At end of reactor	measured	28.1	8.4	75.1	6.6	6.3
	calculated	30.3	6.3	78.1	6.8	8.7

Figure 3.   Pilot plant reactor (adiabatic)

With this reactor system we have been able to achieve our goal of obtaining the product-mix of the ideal tubular reactor.

Finally, a sensitivity analysis of this reactor system was carried out using the results of a series of simulations. This showed that the following limits of operating conditions must be maintained,in order to maintain the concentration of anthraquinone at the end of the reaction within the range of 2.5 - 4.5 weight %.

a) Temperature of imput nitric acid: limits ± 0.35°C

b) Nitric acid/anthraquinone ratio : limits ± 0.35 (weight basis)

c) Water content in nitric acid   : limits ± 0.04 weight %

d) N_2O_3-content in acid   : limits ± 0.01 weight %

e) Flow of nitric acid
                (resisdence time): limits ± 5.8 volume/hour %

Our experience with the pilot plant showed that it was very difficult to maintain this required degree of consistency. It was therefore necessary to devise a special control system for this reactor and we hope to report on the use of the model in developing this controller at a later date.

Conclusion

An empirical mathematical model for a nitration which involves both simultaneous and consecutive reactions has been obtained from simple experiments. The model has been used to simulate various types of nitration reactors. These simulations are invaluable in predicting, correlating and understanding the results obtained from the various reactors.

Acknowledgment

Notation

AC   : anthraquinone

1-NAAC: 1-nitroanthraquinone

2-NAAC: 2-nitroanthraquinone

DNAC   : dinitroanthraquinone, all isomers

W   : water

N_2O_3 : nitrous acid in nitric acid (as N_2O_3)

$[AC_o]$: starting concentration of anthraquinone

$[W_o]$: starting concentration of water

$[AC]$, $[1-NAAC]$, etc.: concentration in $gmol.1^{-1}$

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