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Adiabatic calorimetry for safety studies in nitration processes [1]

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Abstract

The thermal and chemical evolution of the benzonitrile nitration process under adiabatic conditions were investigated for the reacting mixture: 5.1% benzonitrile 30.9% HNO_3 55.4% H_2SO_4 and 8.6% H_2O at a starting temperature of 300 K. Two different reaction stages were identified: the first is the result of complete nitration of benzonitrile only; the second is generated by both the hydrolysis of benzonitrile nitroderivatives and ammonium nitrate decomposition.

The reactive behaviour of a 3-nitrobenzonitrile/sulphonitric mixture (6.2% 3-nitrobenzonitrile, 30.6% HNO_3, 54.7% H_2SO_4 and 8.5% H_2O) was also investigated independently under the same experimental conditions. The results were used with a mathematical model to evaluate the thermokinetic parameters regulating the development of the entire reaction process.

INTRODUCTION

Nitration of benzonitrile is commonly employed in the chemical industry to produce mono-nitroderivatives as basic materials for the manufacture of dye stuffs, polymers and drugs.

A temperature range of 283–293 K up to complete reactant conversion is usually employed and gives rise to a mixture of isomeric compounds, 3-nitrobenzonitrile being the most abundant [1].

Hazards [2,3] exist owing to exothermicity and the possible occurrence of secondary reactions leading to the formation of gaseous products. The explosion of a benzonitrile nitration plant has been reported [4].

Adiabatic calorimetry combined with chemical analysis was used to investigate the nitration of benzonitrile in this study with a view to

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elaborating a mathematical model to describe the system behaviour under varying process conditions and, thus, to provide quantitative criteria for the assessment of safe operating procedures.

EXPERIMENTAL

All the adiabatic runs were performed with a Sikarex 3 calorimeter equipped with a modified glass-stirred reactor, as previously described [5].

For each experiment, 22.4 g of sulphonitric mixture (58.4% H_2SO_4, 32.6% HNO_3 and 9% H_2O) were heated with stirring at the desired temperature, and 1.2 g of benzonitrile or 1.5 g of 3-nitrobenzonitrile were then added.

Samples of the reacting solution withdrawn from the reactor at different times were rapidly quenched with a known amount of cold water, and then extracted with dichloromethane. After the evaporation of the solvent, the organic material recovered was treated with an ethereal solution of diazomethane to convert the organic acids into the corresponding methyl esters. The samples were then analysed with a Carlo Erba Mega gas chromatograph equipped with an SPB-5 capillary column (length, 30 m; i.d., 0.32 mm; film thickness, 0.25 μm; initial temperature, 308 K (1 min); final temperature, 453 K; heating rate, 18 K min^{-1}; carrier gas, helium; flow rate 2.0 ml min^{-1}) and a flame ionization detector.

The presence of ammonia was checked by means of a modified Berthelot colorimetric method [6].

Gases collected during the adiabatic run were analysed with an HP 5700A gas chromatograph equipped with a CTR I concentric column from Alltech (outer column, 1.8 m × 6 mm, packed with activated molecular sieve; inner column, 1.8 m × 3 mm, packed with Poropak mixture) used in isothermal conditions (303 K) with helium as carrier gas (30 ml min^{-1}) and with a thermal conductivity detector.

RESULTS AND DISCUSSION

The thermal evolution of benzonitrile (BN) nitration, starting from an initial temperature of 300.3 K under adiabatic conditions, is shown in Fig. 1.

Two different reaction stages can be clearly distinguished: the first characterized by a relatively fast heat-release rate, and the second, smoother in the initial part, being responsible for the explosive behaviour of the system. The chemical analyses showed that the first stage corresponds to a complete conversion of benzonitrile to 70.2% 3-nitrobenzonitrile, 21.1% 2-nitrobenzonitrile and 3.9% 4-nitrobenzonitrile. The adiabatic temperature rise ($\Delta T = 28.8$ K) is in close agreement with that calculated from the nitration enthalpy ($\Delta H = -145.2$ kJ mol^{-1}).

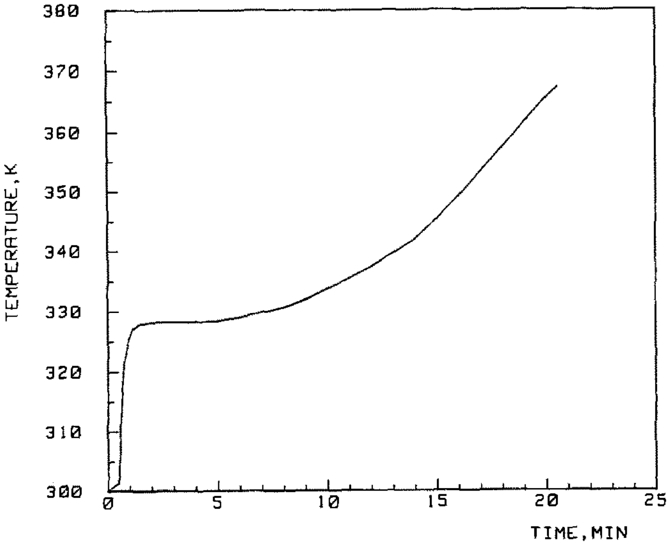

Fig. 1. Temperature–time plot for benzonitrile nitration.

During the second stage, the intermediate nitroderivatives are hydrolysed to the corresponding nitrobenzoic acids with the simultaneous occurrence of other reactions, as indicated by the absence of ammonia from the reaction products and by the evolution of gas.

The adiabatic temperature rises in the second stage indicate that the thermal effect of these reactions is remarkable compared with that evaluated for the hydrolysis alone.

For the sake of simplicity, chemical characterization of the second stage was first attempted through adiabatic runs with 3-nitrobenzonitrile (NBN) and mixed acid as reactants. The temperature and concentration profiles of the chemical species against time are shown in Fig. 2. It can be seen that the reactant is completely converted into the corresponding nitrobenzoic acid (NBA) through the intermediate 3-nitrobenzamide (NBAM), thus revealing that gaseous products (N_2O, 3.0×10^{-3} mol; O_2, 1.9×10^{-3} mol; and N_2, 8.5×10^{-3} mol) are formed from ammonia reactions only. The product distribution of the gas phase is referable to [7]

$$16NH_4NO_3 \xrightarrow{a} 14N_2 + 3O_2 + 30H_2O + 4HNO_3$$

$$\Delta H_a = -237.2 \text{ kJ per mol } NH_4NO_3$$

$$NH_4NO_3 \xrightarrow{b} N_2O + 2H_2O$$

$$\Delta H_b = -152.3 \text{ kJ per mol } NH_4NO_3$$

Consistency with this scheme is underlined by the N_2/O_2 molar ratio observed (14/3), and by the attainment of nitrogen and heat balances.

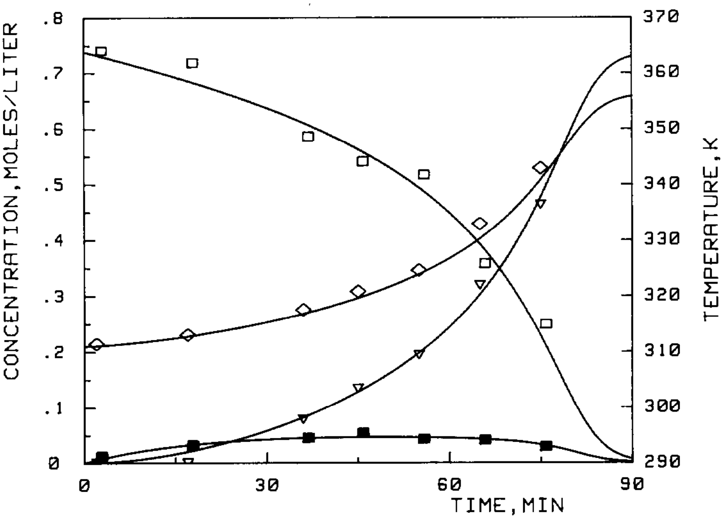

Fig. 2. 3-Nitrobenzonitrile/sulphonitric mixture system. Experimental results from Sikarex runs and model results: □, 3-nitrobenzonitrile; ■, 3-nitrobenzamide; ▽, 3-nitrobenzoic acid; ◇, temperature; ———, model. C_0 3-nitrobenzonitrile = 0.74 M.

The following reaction network can therefore be proposed to explain the reactive behaviour of the 3-nitrobenzonitrile/sulphonitric mixture under adiabatic conditions

$$\mathrm{NBN} \xrightarrow{(1)\,\mathrm{H_3O^+}} \mathrm{NBAM} \xrightarrow{(2)\,\mathrm{H_3O^+}} \mathrm{NBA} + \mathrm{NH_4^+}$$

$$\Delta H_1 = -94.1\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H_2 = -37.2\ \mathrm{kJ\ mol^{-1}}$$

A mathematical model can be elaborated by assuming for the NH_4NO_3 decomposition fast reaction steps with respect to reaction (2)

$$\mathrm{d[NBN]}/\mathrm{d}t = -k_1^0 \exp(-E_1/RT)[\mathrm{NBN}]$$

$$\mathrm{d[NBAM]}/\mathrm{d}t = k_1^0 \exp(-E_1/RT)[\mathrm{NBN}] - k_2^0 \exp(-E_2/RT)[\mathrm{NBAM}]$$

$$\mathrm{d[NBA]}/\mathrm{d}t = k_2^0 \exp(-E_2/RT)[\mathrm{NBAM}]$$

$$\mathrm{d}T/\mathrm{d}t = V(mc_p + MC_p)^{-1}[(\mathrm{d[NBN]}/\mathrm{d}t)(-\Delta H_1) + (\mathrm{d[NBAM]}/\mathrm{d}t)(-\Delta H_2 - a\Delta H_\mathrm{a} - b\Delta H_\mathrm{b})]$$

Parameters k_1^0 (1.34×10^{13} $\mathrm{min^{-1}}$) and E_1 (92.3 kJ $\mathrm{mol^{-1}}$) were determined experimentally in separate isothermal experiments of 3-nitrobenzonitrile hydrolysis in the range 328–348 K; the selectivity coefficients a (0.70) and b (0.30) were obtained from the gas analyses.

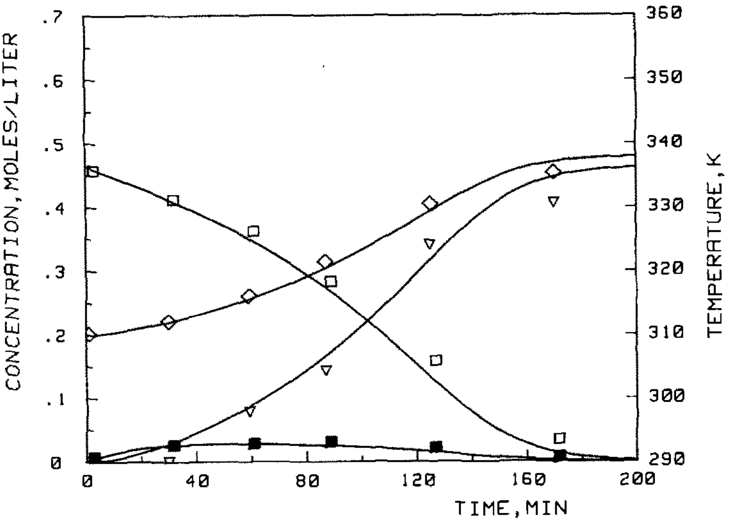

Fig. 3. 3-Nitrobenzonitrile/sulphonitric mixture system. Experimental results from Sikarex runs and model results: □, 3-nitrobenzonitrile; ■, 3-nitrobenzamide; ▽, 3-nitrobenzoic acid; ◇, temperature; ———, model. C_0 3-nitrobenzonitrile = 0.45 M.

The enthalpies of reaction were derived from the enthalpies of formation of the single compounds, with the additional aid of the group contributing method, where necessary.

The values of k_2^0 (1.1×10^{11} min^{-1}) and E_2 (72.8 kJ mol^{-1}) were determined by parametric optimization (Fig. 2).

The reliability of the model was checked by comparing simulated (solid line) and experimental (symbols) behaviours of the reacting system for a different initial substrate concentration (0.45 mol dm^{-3}) (Fig. 3). The good fit confirms the soundness of the model.

CONCLUSION

Thermal analysis by adiabatic calorimetry, combined with chemical characterization of the reacting system, shows that benzonitrile nitration comprises two reaction stages.

The first corresponds to fast nitration of the organic substrate, whereas in the second both the hydrolysis of the intermediate benzonitrile derivatives and ammonium nitrate decomposition are involved.

Thermokinetic parameters regulating the reactive behaviour of the 3-nitrobenzonitrile/sulphonitric mixture system can be evaluated with a mathematical model.

Work is in progress to attain a complete thermokinetic characterization of the reacting system that will also include the initial nitration stage and thus provide the basis for total modelling of the complete benzonitrile nitration process.

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