Toluene Mono-nitration in a Semi-batch Reactor

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Abstract: Toluene mono-nitration in a semi-batch reactor was investigated with reaction calorimeter (RC1). The mixed acid $HNO_3/H_2SO_4/H_2O$ (wt%) was used in proportion 13/66/21, which is similar to industrial parameters. The exothermic rates at different reaction temperatures were compared, and then the curves of heat generation rate after dosing were analyzed. The Maximal Temperature attainable by runaway of the desired Synthetic Reaction (MTSR) under different conditions were calculated for the course hazard evaluation. The results showed that the average reaction heat of mono-nitration was between $169.07{\sim}177.11$ kJ mol^{-1}, and the special heat of reactant was about 2 kJ kg^{-1} K^{-1}. Average Ea of second order kinetic was about 30 kJ mol^{-1}, and reaction rate was 10^{-4} mol s^{-1} l^{-1} order of magnitude when the strength of sulphuric acid was about 73.5%. It was also found that when temperature or stirring speed increases, the potential heat accumulation decreases.

Keywords: toluene mono-nitration, apparent activation energy, semi-batch reaction, thermal hazard

Introduction

Nitrotoluene is an important organic material, which has a wide use in synthesis of medicine, pesticide, dyestuff, explosives and others [1, 2]. The mono-nitration of toluene with mixed acid is a complex heterogeneous reaction, and the overall reaction rate is dependent on mass transfer and chemical reaction

[3]. C. Hanson and co-workers studied this reaction extensively, and proved that diffusion resistances play more important part in reaction rates at high sulphuric acid concentration [4, 5]. In recent years, J.M. Zaldivar *et al.* studied the mass transfer and kinetics using film model, and experimentally validated this mathematic approach [6, 7]. Chun-Yu Chen and Kuo-Ming Luo *et al.* drew out kinetic parameters from reaction calorimetry experiments, and evaluated thermal stability of this reaction [8, 9]. Flavio Augusto D'Angelo *et al.* developed a methodology for toluene mono-nitration which was carried out batch-wise, and gave an optimum procedure to maximize conversion [10].

Considering the high sulphuric acid and nitric acid system in industry, semi-batch experiments have been conducted using reaction calorimeter (RC1) with high stirring speed to avoid sharp heat generation and high potential accumulation. The data were analyzed by using the fast rate model presented by the fore workers [11, 12] to derive the apparent activation energy. The course severity was estimated as well.

Experimental

Equipment

RC1 is an appropriate tool for information on the desired reaction, since chemical reactions always occur with heat exchange, the measurement of heat flow with RC1 serves as a direct indicator of reaction rate [13]. RC1e, used here, comprises MP10 (a 1 liter glass reactor with jacket), Pt100 temperature sensors, calibration heater, dosing system (a balance, a pump and so on) and a controller unit for dosing control.

Reagents and experimental conditions

Materials, such as nitric acid, sulphuric acid, toluene, and sodium bicarbonate, were all analytically pure, and all produced by Nanjing Chemical Reagent Co., Ltd, Jiangsu province, P R China.

Mixed acid was prepared in a 500 ml round flask before reaction calorimetry, which was cooled by ice-water mixture. The mixed acid comprise $HNO_3/H_2SO_4/H_2O$ (wt%) = 13/66/21, which is similar to the concentration of mixed acid in industry.

The mixed acid was charged to RC1e reactor, and heated up to a given temperature under Tr mode. After a calibration and Cpr determination, 100 g toluene were dosed into the reactor at a constant speed 2 g min^{-1}, then the reaction system was hold for 100 min before another calibration and Cpr determination.

After reaction, the acid and organic phases were separated from each other, and measured volumes and masses separately. The organic phase was cleaned using sodium bicarbonate solution (2 wt%) and distilled water, then analyzed by gas chromatography.

Results and Discussion

Thermodynamic parameters

To separate the heat of contact of toluene and sulphuric acid, from the heat of nitration, blank experiment was performed first. The initial concentration of sulphuric acid used here was 83.5%, which is the same as that in the prepared mixed acid containing pure nitric acid. As shown in Figure 1, the maxim heat flow is about 2.4 W, and the enthalpy is about 0.96 kJ as 1 mol toluene contact the aqueous solution of sulphuric acid, and it is small enough to be neglected when compared to the nitration enthalpy shown in Table 1.
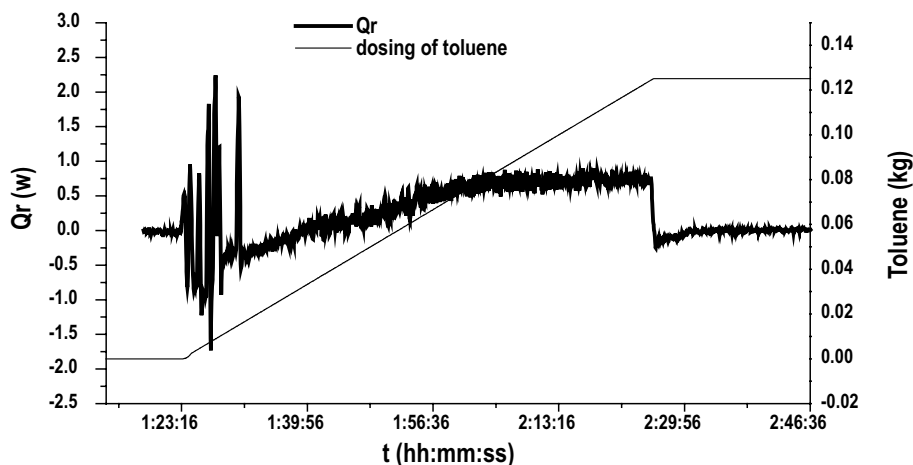
Figure 1. Qr curve when toluene is dosed to sulphuric acid.

In China, most of toluene mono-nitration processes are carried out between 30~50 °C. Hence, isothermal nitrations at 30, 35, 40, 45, 50 °C are tested using RC1e, in order to estimate this nitration under industry condition. Some thermodynamic parameters, such as specific heat, obtained from experiments are listed in Table 1. The results indicate that the reaction heat per mol of mono-nitration is in the scale of 169.07~177.11 kJ mol^{-1}, and the special heat of reactant is about 2 kJ kg^{-1} K^{-1}.

Table 1. Thermodynamic parameters under different conditions

Set temperature (°C)	30	35	40	40	45	50
Stirring speed (rpm)	350	350	250	350	350	350
ΔH_r (10^3 J)	185.383	183.77	186.86	188.85	192.51	191.60
ΔH_m (10^3 J mol^{-1})	170.55	169.07	171.91	173.74	177.11	176.27
ΔT_{ad} (°C)	146.47	148.40	149.20	145.77	151.53	147.16
Cpr1 (kJ kg^{-1} K^{-1})	2.01	2.02	1.95	2.06	2.07	2.07
Cpr2 (kJ kg^{-1} K^{-1})	1.83	1.90	1.84	1.88	1.94	1.89

Although these thermodynamic parameters were close to each other, the reaction system at 50 °C changed from yellow to rufous after dosing, while other systems kept yellow. It indicates that side reactions such as oxidation occur at 50 °C [3].

To ensure the intensity of agitation, the viscosity of acid phase and organic phase from product mixture were tested to calculate the stirring Re number. And the results in Table 2 indicate that the temperature affects not only the chemical reaction, but also the physical properties.

Table 2. The stirring Re number

| Set temperature (°C)	30	35	40	40	45	50
Stirring speed (rpm)	350	350	250	350	350	350
Dynamic viscosity (mPa·s)	6.58	5.81	5.19	5.19	4.65	4.20
Stirred Re number	7977	9030	7513	10102	11299	12499

Apparent activation energy

All experiments were conducted in a semi-batch reactor, and these entire heat flow curves were similar. Let's take the reaction under 30 °C, 350 rpm for example. As shown in Figure 2, the exothermic rate increases sharply as toluene mixes with acid, and then slow down (part 1 of the Qr curve). Then the rate falls down more quickly for the moment the dosing is finished (part 2 of the Qr curve).
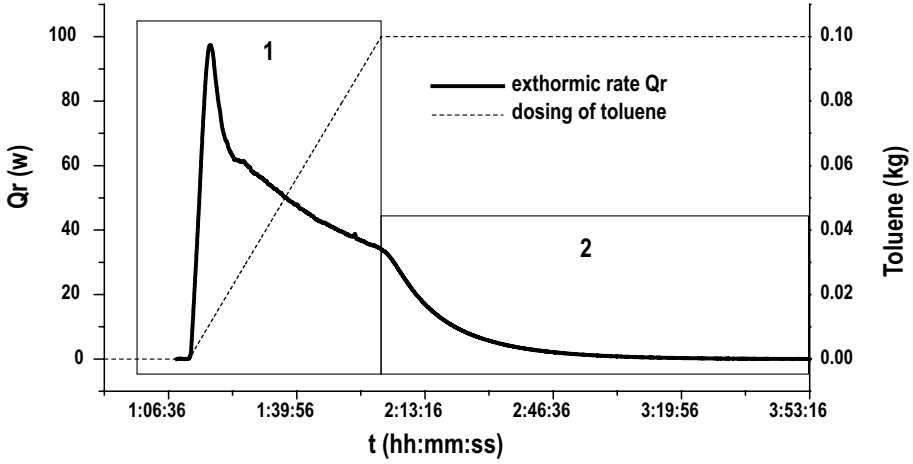
Figure 2. The exothermic rate and dosing of toluene under 30 °C, 350 rpm.

Considering all parameters such as concentration, interfacial area and diffusivity all change during dosing, and the volume of acid phase is comparably stable after dosing, part 2 of Qr curve is selected and analyzed for apparent activation energy, when this reaction processed more than 85%.

Toluene mono-nitration is described as:

$$C_7H_8 + HNO_3 \rightarrow MNT + H_2O$$
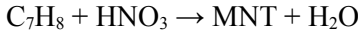
Considering that the volume is constant, the reaction rate can be described as follows:

$$r = -\frac{1}{V}\frac{d[HNO_3]}{dt} = -\frac{Q_r}{V\Delta H_m} \tag{1}$$

As shown in many papers [11, 12], the fast toluene nitrate can be expressed as follows:

$$r = a'\sqrt{Dk_2[HNO_3]}[T]_a^s \Rightarrow 2\ln r = 2(\ln a' + \ln[T]_a^s) + \ln D + \ln[HNO_3] + \ln k_2 \tag{2}$$

Based on Arrhenius equation $\ln k = \ln A - \dfrac{E_a}{RT}$, equation (2) can be expressed as:

$$\ln r = \ln a' + \ln[T]_a^s + 0.5\ln D + 0.5\ln[HNO_3] + 0.5\ln A - 0.5\frac{E_a}{RT} \tag{3}$$

If nitration performed at T_2 and T_1 ($T_2 > T_1$) separately, equation (4) will be obtained.

$$E_a = R(\frac{1}{\frac{1}{T_1} - \frac{1}{T_2}})[2(\ln r_2 - \ln r_1) - (2\ln\frac{a'_2}{a'_1} + 2\ln\frac{[T]^s_{a2}}{[T]^s_{a1}} + \ln\frac{D_2}{D_1} + \ln\frac{[HNO_3]_2}{[HNO_3]_1} + \ln\frac{A_2}{A_1})] \quad (4)$$

All the experiments were conducted using the same mixed acid and toluene. Thus when at the same fraction conversion *x,* the concentrations of sulphuric acid and nitric acid could be recognized equal to the ones at other temperatures. To minimize the influence of temperature to physical properties, such as *a'*, D, and $[T]^s_a$, smaller temperature interval (2-3 °C) was selected. Together with the constant, frequency factor A, finally, the apparent activation energy can be expressed:

$$E_a = 2R\frac{\ln r_2 - \ln r_1}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (5)$$

Fractional conversion *x* can be calculated by RC1 software automatically:

$$x = \left.\int_{t_0}^{t} Q_r(t)dt \middle/ \int_{t_0}^{t_f} Q_r(t)dt\right. = \left.\int_{t_0}^{t} Q_r(t)dt \middle/ \Delta H_r\right. \quad (6)$$

Gas chromatography data show that there are very little toluene in product, so the *x* from the RC1 can be treated as real fraction conversion.

The exothermal rates between the fractional conversions 0.86-0.91 are calculated by equation (5). This scale can ensure the end of dosing. Reaction at 50 °C isn't calculated in Table 3 for the apparent side reactions.

From Table 3, it can be found that the reaction rate is 10^{-04} mol l^{-1} s^{-1} order of magnitude. Values of Ea are more than 20 kJ mol^{-1} when tests are performed at the temperature lower than or equal to 40 °C, while Ea alternate in a large scale at 45 °C. It's because side reactions are more active at high temperature. And the value 0.47 kJ mol^{-1} may come from a test error. The average Ea is 30 kJ mol^{-1} as exclude values less than 10 kJ mol^{-1}.

There are no obvious relation between the Ea and temperature. Because *a'*, D, $[T]^s_a$ and viscosity change as temperature arise; no simple models can be used to express these relations between these parameters and temperature. Besides, isomer proportion changes as reaction conditions alternate, what will lead to an enthalpy's alternation, and influence Ea calculation finally.

Table 3   Apparent activation energy under different fractional conversions

| Fractional conversion x	Set temperature (°C)	r (mol l⁻¹ s⁻¹)	Ea (10³ J mol⁻¹)	Fractional conversion x	Set temperature (°C)	r (mol l⁻¹ s⁻¹)	Ea (10³ J mol⁻¹)
0.86	30	4.90E-04	-	0.87	30	4.53E-04	-
	32	5.04E-04	22.26348		32	4.69E-04	26.34855
	35	5.35E-04	31.37674		35	4.98E-04	30.77932
	37	5.64E-04	41.59382		37	5.25E-04	43.16865
	40	5.86E-04	20.63147		40	5.55E-04	29.30506
	42	5.86E-04	0.471676		42	5.67E-04	18.17342
	45	6.16E-04	27.7794		45	5.85E-04	17.37957
0.88	30	4.21E-04	-	0.89	30	3.87E-04	-
	32	4.32E-04	21.11782		32	3.97E-04	20.15033
	35	4.59E-04	30.63609		35	4.15E-04	23.29189
	37	4.84E-04	42.96008		37	4.40E-04	46.17372
	40	5.16E-04	34.9722		40	4.74E-04	39.87359
	42	5.33E-04	25.20932		42	4.90E-04	26.16582
	45	5.41E-04	8.493005		45	4.97E-04	8.402718
0.90	30	3.48E-04	-	0.91	30	3.09E-04	-
	32	3.60E-04	25.21868		32	3.23E-04	33.85421
	35	3.77E-04	24.8346		35	3.36E-04	20.67281
	37	3.96E-04	37.09154		37	3.51E-04	35.77569
	40	4.27E-04	41.5693		40	3.80E-04	42.08103
	42	4.40E-04	24.91865		42	3.90E-04	20.30632
	45	4.45E-04	6.179777		45	3.91E-04	2.290809

Otherwise, Ea here obtained is less than 16100 ± 100 cal reported by P.R. Cox and A.N. Strachan [14]. There are two major factors contribute to this result. First, it is well known that the decrease of Ea follows the increased concentration of sulphuric acid. And here the strength of sulphuric acid used for calculation is about 73.5%, which is stronger than 70.2% used in the literature. Another influence comes from the pure toluene, as reported in literature [15], the nitration of pure toluene may be controlled by the nitronium ion NO_2^+ generating step, not the nitronium ion attacking step. Besides, for this complex reaction, there are some uncertain factors contribute to this situation as well, such as errors from mathematic model.

Thermal hazard evaluation

Severity and probability are crucial to evaluate the risk of an exothermal process. Severity can be estimated from MTSR (Maximum Temperature attainable

the runaway of the desired Synthetic Reaction) and $\Delta T'_{ad}$ while ΔT_{dec} (how long will it take from the reaction reaching MTSR until the thermal explosion takes place) reflects probability of an incident [13]. The former can be obtained from RC1 experiments, and the latter won't be discussed here.

A balance between potential input and output is calculated as follows: the potential input is proportional to the actual feed of toluene, and corresponds to the overall heat of reaction. The potential output is simply the integration of exothermal rate Qr. The difference between potential input and output represents the potential accumulated momentarily present. It is divided by the specific heat and reactant mass in the reactor in order to obtain MTSR and $\Delta T'_{ad}$ [13] (Figure 3 and 4).
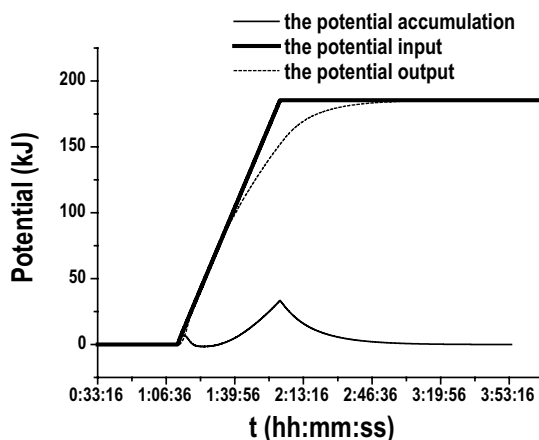
Figure 3.   The thermal accumulation under 30 °C, 350 rpm.
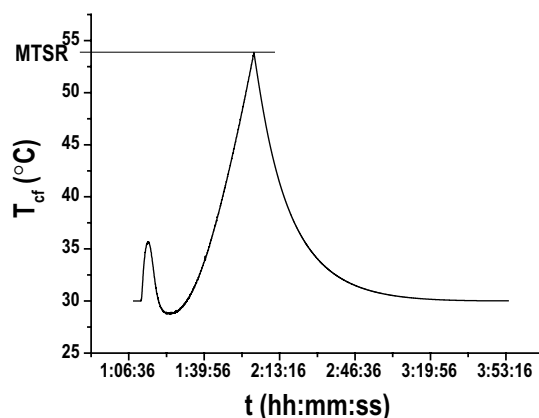
Figure 4.   MTSR under 30 °C, 350 rpm.

The potential accumulation and T_{cf} curve show that soon after the feed of toluene, there is a small peak of thermal accumulation. After that, the largest accumulation appears at the moment when the feed is completed.

Apparently, MTSR and the maximal $\Delta T'_{ad}$ are going to be reached if an adiabatic cooling failure occur at this moment. The thermal risk parameters such as MTSR are listed in Table 4.

Table 4.   Thermal hazard parameters

Set temperature (°C)	Stirring speed (rpm)	maximal potential accumulation (kJ)	Correspond conversion	MTSR (°C)	Maximal $\Delta T'_{ad}$ (°C)
30	350	33.4	0.8194	53.87	23.87
35	350	33.6	0.8170	58.56	23.56
40	250	40.4	0.7845	69.23	29.23
40	350	29.2	0.8447	60.34	20.34
45	350	28.0	0.8539	64.12	19.12
50	350	24.6	0.8955	67.03	17.03

The results in Table 4 indicate that the accumulation and $\Delta T'_{ad}$ are reduced when temperature or stirring speed increases. It also can be founded that at 50 °C, although maximal $\Delta T'_{ad}$ is lowest; MTSR is high, because this reaction is operated at a comparatively high temperature. Considering there are more side-reactions occurring at this higher temperature, toluene mono-nitration must be operated at a lower temperature for the consideration of safety and the minimal side reactions.

Conclusions

Toluene mono-nitration in semi-batch reactor was carried out, 100 g toluene was charged into 630 g mixed acid at different temperature (30, 35, 40, 45, 50 °C). All these experiments were performed using the same mixed acid: $HNO_3/H_2SO_4/H_2O$ (wt%) = 13/66/21, and stirred Re number was more than 7900. The experiments data showed the enthalpy of reaction was between 169.07~177.11 kJ mol^{-1}, and the special heat of the reaction mixture was about 2 kJ kg^{-1} K^{-1}.

The exothermic rates were analyzed using the fast nitration model, and average apparent activation energy of second order nitration was about 30 kJ mol^{-1} while wipe off Ea values less than 10 kJ mol^{-1}. There was no certain relationship

between temperature and Ea for complex reaction conditions.

From the determination of MTSR and $\Delta T'_{ad}$, the potential accumulation reduces as reaction temperature rises, or agitator speed up. However, this reaction should be performed at a lower temperature, because there are more potential hazard and side-reactions at 50 °C.

This paper gives fundamental information for course prevention under given condition. However, large of further work should be done for this complex reaction.

List of abbreviations and symbols
A frequency factor
a' interfacial area per unit of volume of acid phase, cm^{-1}
Cpr   special heat (kJ kg^{-1} K^{-1})
Cpr1   the special heat measured before dosing (kJ kg^{-1} K^{-1})
Cpr2   the special heat measured after reaction (kJ kg^{-1} K^{-1})
D   diffusivity of toluene in the acid phase, cm^2 s^{-1}
$[T]_a$ concentration of toluene in acid phase (mol l^{-1})
$[T]_a^s$ saturation concentration of toluene in acid phase (mol l^{-1})
$[HNO_3]$ concentration of nitric acid in acid phase (mol l^{-1})
E_a apparent activation energy (J mol^{-1})
ΔH_r overall heat generated in reaction (J)
ΔH_m reaction heat of consuming 1 mol toluene or generating 1 mol MNT
            (J mol^{-1})
k_2 second order rate constant, (l mol^{-1} s^{-1})
MTSR Maximum Temperature attainable by runaway of the desired Synthetic
            Reaction (°C)
Qr   heat flow, exothermic rate (W)
R gas constant (J K^{-1} mol^{-1})
r reaction rate (mol s^{-1} l^{-1})
T temperature (K)
ΔT_{ad} adiabatic temperature rise, $\Delta Tad = \Delta Hr\ m^{-1}\ Cpr^{-1}$ (K)
$\Delta T'_{ad}$ adiabatic temperature rise momentarily present in semi-batch reaction
            (K)
T_{cf} temperature after cooling failure (°C), the maximal T_{cf} is equal to
            MTSR
ΔT_{dec} how long will it take from the reaction reaching MTSR until the thermal
            explosion takes place (s)
V volume of acid phase
x fractional conversion of toluene

References

[1] Dong Y., Improvement of Manufacture Technics in Toluene Mononitration, *Modern Chemistry Engineering*, **1998**, (5), 20-21.

[2] Cai C., Lu C.X,. Nitration of Toluene with NO_2 -O_2 System, *Chinese Journal of Explosives & Propellants*, **2003**, *26*(2), 1-2,21.

[3] Lu C.X., *Nitration Theory,* Jiangsu Science and Technology Publishing House, Nanjing **1993**, 125-131.

[4] Hanson C., Marsland J.G., Macrokinetics of toluene nitration, *Chem. Eng. Sci.*, **1971**, *26*, 1513-1520.

[5] Hanson C., Ismail H.A.M., Macrokinetics of toluene and benzene nitration under laminar condition, *ibid.*, **1977**, *32*, 775-777.

[6] Zaldivar J.M., Molga E., Alos M.A., Hernandez H., Westerterp K.R., Aromatic Nitration by Mixed Acid. Fast Liquid-Liquid Reaction Regime, *Chemical Engineering and Progressing*, **1996**, *35*, 91-105.

[7] Zaldivar J.M., Molga E., Alos M.A., Hernandez H., Westerterp K.R., Aromatic Nitration by Mixed Acid. Slow Liquid-Liquid Reaction Regime, *ibid.*, **1995**, *34*, 543-559.

[8] Chun-Yu Chen, Chia-Wei Wu, Thermal Hazard AssessmentaAnd Macrokinetics Analysis of Toluene Mononitration in a Batch Reactor, *J. Loss Prevent. Industries*, **1996**, *9*(5), 309-316.

[9] Kuo-Ming Luo, Jih-Guang Chang, The Stability of Toluene Mononitration in Reaction Calorimeter Reactor, *ibid.*, **1998**, *11*, 81-87.

[10] D'Angelo F.A., Brunet L., Cognet P., Cabassud M., Modeling and Constraint Optimisation of an Aromatic Nitration in Liquid-Liquid Medium, *Chem. Eng. J.*, **2003**, *91*, 75-84.

[11] Field J.P., Strachan N., Dependence of the Rate Constanta and Activation Energy of Aromatic Nitration on Mixed Acid Composition, *Ind. Chem. Prod.,* **1982**, *21*, 352-355.

[12] Albright L.F., Hanson C., *Industrial and Laboratory Nitrations*, ACS, Washington, **1976**, 210-211.

[13] Gygax R., Chemical Reaction Engineering for Safety, *Chem. Eng. Sci.*, **1988**, *43*(8), 1759-1771.

[14] Cox P.R., Strachan A.N., Two Phase Nitration of Toluene-I, *ibid.*, **1972**, *21*, 457-463.

[15] Chapman J.W., Cox P.R., Strachan A.N., Two Phase Nitration of Toluene-III., *ibid.,* **1974**, *29*, 1247-1251.