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Electrochemical approach to the recycling of nitration waste concentrated sulphuric acid

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Electrolysis of nitration waste sulphuric acid, from the manufacture of trinitrotoluene, results in the formation of a dark solution in which the concentration of aromatics is reduced to much lower levels. The resulting acid can be decolourized by oxidation with H_2O_2 or by anodic oxidation in the cell. The H_2O_2-treated electrolysed acid has a nitroaromatic content of 107 p.p.m. and a total carbon content of 278 p.p.m., corresponding to a reduction of 98.7% and 90.3%, respectively. The dark intermediate product appears to result from the anodic oxidation of amines which are initially produced at the cathode, and is destroyed by further anodic oxidation on prolonged electrolysis.

1. Introduction

In recent years the purification of waste H_2SO_4 generated by many industrial processes has received a considerable amount of attention. This has largely been due to increasingly severe restrictions on the disposal of waste acids, which can create serious environmental problems [1, 2]. Methods for the purification of waste H_2SO_4 generally involve reconcentration of the acid which is usually diluted in chemical processes [2–4]. Subsequently, it is often necessary to remove non-volatile organic contaminants which would prevent the recycling of the acid in the original process or its use for other purposes.

The removal of organics can be achieved by thermal decomposition of the preconcentrated acid to SO_2 and water, followed by oxidation to SO_3 for conversion to H_2SO_4 [1, 2]. Organic compounds are largely decomposed by this process. Although H_2SO_4 of high purity can be obtained by this method, the disadvantage is the high cost involved. Alternative methods for the purification of waste H_2SO_4 often involve the removal of organic contaminants by oxidation. Oxidizing agents include HNO_3 [2, 4] and H_2O_2 or peroxydisulphate [5]. The use of electrochemical oxidation has also been reported [6–10]. It would appear that organics are removed as CO_2 [6] and that oxidation is achieved via formation of peroxysulphuric acids at the anode [8].

This paper describes an electrochemical method for the removal of nitroaromatics from waste H_2SO_4 recovered from nitration processes such as the manufacture of TNT. Waste H_2SO_4 from nitration processes has been purified by treatment with various reagents such as NH_4^+ salts [5, 11–13], urea [5] and absorbents such as carbon, silicate, bentonite and perlite [11, 13]. This is usually followed by oxidation with air or an oxidizing agent. Electrochemical methods for the removal of nitroaromatics do not, however, appear to have been investigated.

Preliminary work in Chemetics Laboratories [14] showed that electrolysis of nitrated toluenes in hot concentrated H_2SO_4 occurred rapidly, producing a black colloidal product. It was further shown that the black product could be decolourized by treatment with H_2O_2 resulting in almost complete removal of the nitroaromatics from the H_2SO_4. This was, therefore, the route adopted in the present investigation.

2. Experimental details

2.1. *Analysis*

Gas chromatography was performed using a

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* *Permanent address*: CIL Inc., CIL House, PO Box 200, North York, Ontario, Canada M2N 6H2.

Varian Aerograph 90-P gas chromatograph with a thermal conductivity detector and a stainless steel column, 3 m × 0.6 cm, containing 10% SE-30 on chromosorb W. GLC–mass spectrometry was carried out using a Searle Biospect chemical ionization quadrupole mass spectrometer with a Varian Aerograph series 1400 GLC inlet system. NMR spectra were recorded with a Varian T-60 NMR spectrophotometer, and IR spectra were recorded with a Beckmann AccuLab 1 double-beam spectrophotometer using a KBr disc. Concentrations of 2,4-DNT in H_2SO_4 were determined by a Hitachi Perkin–Elmer Coleman 124 double-beam UV spectrophotometer by correlation with a Beer's Law concentration – absorbance plot for 2,4-DNT (λ_{max} 245 nm). Samples were dissolved in a 12.5% (v/v) methanol–water mixture. Microanalyses were performed by Dr C. Daessle, Organic Microanalysis, Montreal, Quebec, Canada or by the microanalytical laboratory at the University of Alberta, Edmonton, Alberta, Canada. Analysis of nitration plant waste acid, both electrolysed and untreated, was carried out by ICD Chemicals Research Laboratory, Sheridan Park, Ontario, Canada.

2.2. *Electrolysis procedure*

2.2.1. Undivided cell. The electrolyses were carried out in a 400-ml beaker containing a carbon cathode (area 54.3 cm) and a cylindrical platinum gauze anode (2.5 × 5 cm). A Hewlett–Packard model 6274B d.c. power supply with a Simpson Canada model 270 ammeter was used.

In a typical procedure, the substrate to be electrolysed (1.9 g) was dissolved in concentrated H_2SO_4 (200 ml) and electrolysed at 100° C with a constant current of 1.0 A for 3 h, giving a dark brown or black solution (electrolysis for longer periods of time resulted in a gradual decolourization of the solution.) The solution was mixed with ice and water* (approximately 500 ml) and treated with sufficient NH_3 to raise the pH to 8. The precipitate (usually dark brown or black) was filtered and the filtrate extracted with ether. The extracts were dried using $MgSO_4$ and the ether evaporated. The residue (if present) was analysed by GLC, IR and NMR. The dark precipitate was washed with water, methanol and ether and dried in an oven at 90° C or under vacuum. Microanalyses were carried out on some of the electrolysis products.

2.2.2. Divided cell: electrolysis of nitrobenzene. The cathode compartment consisted of a 400-ml beaker and the anode compartment was a 50-ml glass tube containing a sinter at the base. The cathode was the same as in the undivided cell electrolysis and a platinum wire was used as the anode.

Nitrobenzene (1.9 g) dissolved in conc H_2SO_4 (200 ml) was introduced into the cathode compartment and the anode compartment which contained concentrated H_2SO_4 (40 ml) was suspended in the centre of the beaker containing the catholyte. The solution was electrolysed for 3 h using a constant current of 1 A. The catholyte soon became purple in colour and this colour intensified as the electrolysis proceeded, while the anolyte remained colourless. The catholyte was poured into a mixture of 500 ml H_2O and 300 g ice and extracted with ether. After drying (using $MgSO_4$) the ether was evaporated leaving an oily residue (0.26 g) which was shown by GLC to contain starting material. No other volatile products were detected. The aqueous layer was treated dropwise with NH_3 until the pH was 8.5, then cooled and filtered. Only a trace of a semi-solid dark residue was collected. The filtrate was extracted with ether, the extracts dried (using $MgSO_4$) and evaporated leaving a purple red residue (0.07 g). GLC analysis at 150° C showed that the residue contained aniline. No other appreciable GLC peaks were observed at column temperatures 150–220° C. The identity of the aniline was confirmed using GLC–mass spectrometry. No organic products were isolated from the anolyte.

2.2.3. Divided Cell: electrolysis of o-*nitrotoluene.* The above experiment was repeated using *o*-nitrotoluene (1.9 g) in concentrated H_2SO_4 (200 ml). During the electrolysis the catholyte became greenish-brown. The product was worked up as above. Ether extraction of the acidic solution gave a residue (0.06 g) which was shown by GLC to contain starting material.

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* In some experiments the solution was steam distilled to remove starting material prior to neutralization.

Neutralization with NH_3 followed by filtration gave a trace of a sticky black residue, and ether extraction of the neutralized solution gave a brown liquid (0.1 g) which was shown by GLC at 150° to contain mainly *o*-toluidene by comparison with an authentic sample.

3. Results and discussion

3.1. *Electrolysis of waste acid*

Waste H_2SO_4 obtained from the CIL plant in McMasterville, Quebec contains a variety of nitrated toluenes, the most abundant of which is usually 2,4-DNT whose concentration is typically about 5000 p.p.m. [14]. Electrolysis of a sample of this acid using the undivided cell reduced the concentrations of all of these compounds to low values. For example the concentration of 2,4-DNT was reduced from 5200 to 115 p.p.m. The black solution obtained from the electrolysis contained approximately half the original total carbon content. Oxidation of this black solution with H_2O_2 resulted in decolourization and a reduction in the carbon content to a low value (278 p.p.m.). The results, which are summarized in Table 1 indicate that the procedure is successful in destroying the wide range of nitroaromatics present in the waste acid.

Table 1. Analysis of electrolysed and untreated nitration plant waste acid

Component	*Concentration (p.p.m.)*		
	A	*B*	*C*
2,4-DNT	5200	115	0
2,5-DNT	70	3	3
2,6-DNT	760	10	0
3,4-DNT	120	2	0
3,5-DNT	30	1	0
2,4,6-TNT	1130	32	6
2,4,5-TNT	260	16	8
2,3,4-TNT	80	0	0
High boiling residues (as dinitrobenzoic acid)	500	70	90
Total C	2900	1300	278

A, Untreated waste acid.
B, Electrolysed waste acid.
C, Electrolysed waste acid treated with H_2O_2.

3.2. *Reaction optimization*

In order to optimize the electrolysis conditions, studies were carried out on solutions of the principal contaminant, 2,4-DNT, in concentrated H_2SO_4. The concentrations of the solutions used were approximately 5000 p.p.m., close to the usual values in the waste acid.

Possibly the most important factor in the development of this project was the selection of the most favourable cathode material, because of its influence on reaction rate and initial cost of the cell. Initial studies [14] showed that the best candidates as far as reaction rates are concerned were the mercury and lead cathodes, but the toxicity of the first and the high corrosion rate of the second at elevated temperatures render them impractical. Other cathode materials tested included stainless steel (254 SMO), tin, graphite and 5% tantalum–titanium. These had various drawbacks such as low H_2 overpotential or appreciable corrosion rates except for graphite, which demonstrated high stability and an acceptable cathodic range.

Many types of graphite electrode were tested including high density graphite, carbon arc graphite, porous graphite, silicon carbide-coated graphite, pyrolytic graphite and vitreous graphite. These behaved similarly under the test conditions (temperature, 100° C; current density, $0.25\,A\,dm^{-2}$), with high density graphite and carbon arc graphite having the highest activity in the group.

A graph illustrating the comparative activities of selected cathode materials is illustrated in Fig. 1. It can be seen that cathode materials such as tin and graphite are approximately equivalent, while platinum was less active (probably due to low H_2 overpotential) and mercury was the most active (high H_2 overpotential).

In order to determine other parameters which are important in the destruction of nitroaromatics the effects of temperature, current density and acid strength were investigated. It was found that the rate of the electrolysis increased with increasing current density. For example, using a 2,4-DNT concentration of 800 p.p.m.

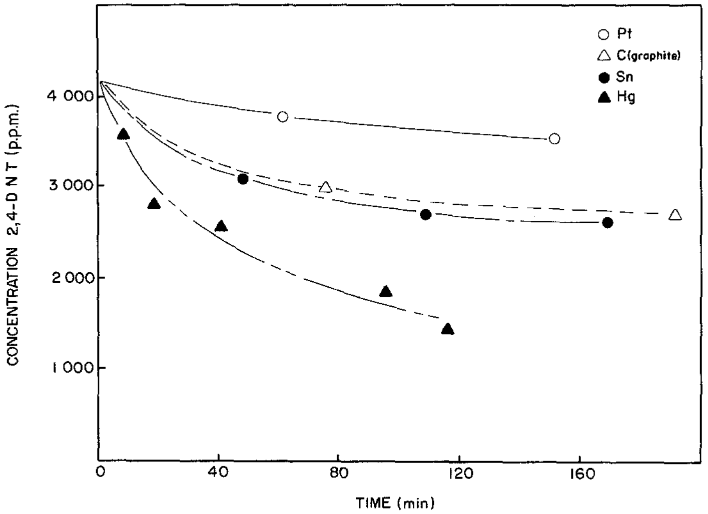

Fig. 1. Effect of the cathode material on the electrolysis rate of 2,4-DNT in 96% H_2SO_4.

and a temperature of 60 or 100° C, doubling the current density reduces the time required to destroy the nitroaromatic by about 50%. The relative rates of destruction of 2,4-DNT in 96% H_2SO_4 at 100° C using various current densities are shown in Fig. 2.

The relationship between the reaction rate and temperature was less obvious. It was observed that at a constant current density of 0.92 A dm^{-2} increasing the temperature had little effect on the rate. Unfortunately, it was found that at ambient temperature (22° C) current densities higher than about 1.0 A dm^{-2} were unsatisfactory due to increasing amounts of gas evolution. It was in fact shown that the cathodic potential was lower (more negative) at lower temperatures and, thus, reduction of hydrogen ions to hydrogen occurred more readily. Satisfactory rates of electrolysis were achieved at 60 and 100° C using current densities of 3.5–5.5 A dm^{-2}. Under these conditions the 2,4-DNT concentration was reduced to less than 500 p.p.m. in 2–4 h.

Electrolyses were also performed at three different acid strengths while maintaining a constant temperature of 100° C and a current density of 5.5 A dm^{-2}. It was found that the rate of the reaction was almost identical in 96% and 70% H_2SO_4 but there was a marked decrease in rate in 50% acid. The results are illustrated in Fig. 3. It is to be noted that waste H_2SO_4 from

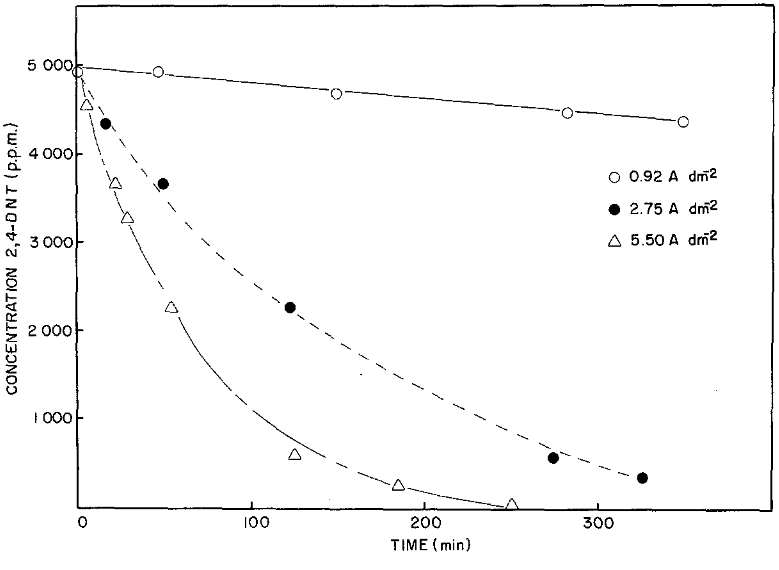

Fig. 2. Effect of the current density on the electrolysis rate of 2,4-DNT in 96% H_2SO_4.

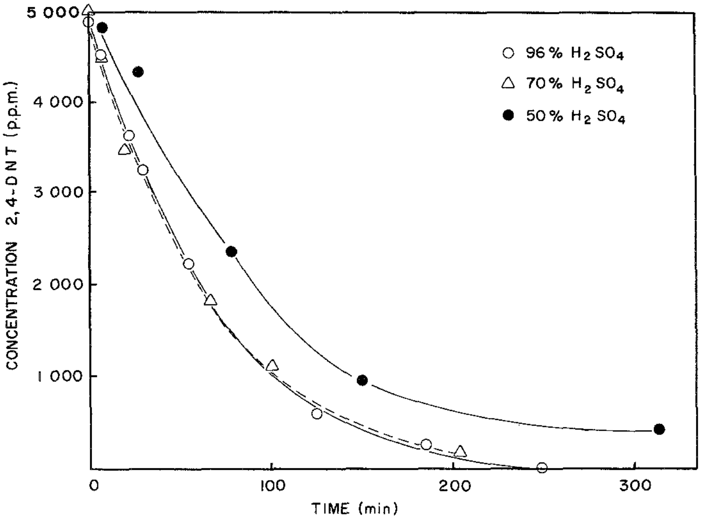

Fig. 3. Effect of H_2SO_4 concentration on the electrolysis rate of 2,4-DNT.

the nitration process has a concentration of approximately 70%.

3.3. *Reaction pathway*

Electrolysis of solutions of 2,4-DNT in concentrated H_2SO_4 resulted in the formation of dark brown or black solutions, which after more prolonged electrolysis underwent decolourization. In most electrolysis it was found possible to isolate a black, powdery product from the dark electrolysed solution by neutralization with NH_3 followed by filtration. The filtrate was still dark in colour, however, indicating that some of the black product remained in solution. This was also evident when the mass balance (products versus reactant) was considered. It was shown that little or no organic product could be isolated from the nearly colourless solution obtained by more prolonged electrolysis.

The black material isolated from the electrolysis of 2,4-DNT was found to be insoluble or only slightly soluble in organic solvents. It was, however, soluble in concentrated H_2SO_4 and HCl, indicating the presence of groups which could be protonated. It showed a high degree of thermal stability and did not melt below 300° C. Because of the low solubility of the product in organic solvents and its amorphous nature, useful IR and NMR spectra could not be obtained.

Oxidation of aniline under certain conditions produces aniline black [15, 16] and an analogous product is produced by the oxidation of *o*-toluidene [15]. The formation of aniline black has also been reported in the electrochemical oxidation of aniline [17], although it is not clear whether the electrolysis products described as 'aniline black' are the same as the 'aniline black' produced chemically. Over the years a number of different structures have been proposed for aniline black [17], but it would appear that it is a high molecular weight material containing C, H and N. It was initially supposed that a similar type of product might be formed in the electrolysis of 2,4-DNT via cathodic reduction to an amine followed by anodic oxidation. Microanalysis, however, showed the presence of an appreciable amount of oxygen (approximately 27%) in the dark coloured product and a chemical test for nitro groups [18] proved to be negative. (The analysis results were C, 55.4%; N, 14.2%; H, 2.9%; O, 27.5% (estimated by difference from 100%); S, <0.1%.)

It was found that when the electrolysis time or the current was reduced, an orange-brown solid could be isolated by extraction of the acidic electrolysis solution with CH_2Cl_2. This product was shown by GLC to contain some starting material. Neutralization of the electrolysis solution with NH_3 gave small amounts of a black precipitate, but no organic products were isolated by extraction of the filtrate with ether. It was concluded that any possible intermediates, such as amines, underwent further reactions under the electrolysis conditions and could not be isolated.

In order to shed further light on the reaction, electrolyses in H_2SO_4 were also carried out on nitrobenzene and *o*-nitrotoluene as well as on their reduction products, aniline and *o*-toluidene. It was thought that these compounds might give simpler products whose structures would be easier to interpret. It was observed that all of these compounds gave products with similar characteristics, i.e. dark brown or black with very high melting points and low solubility in organic solvents. Again, it was not found possible to obtain useful IR and NMR spectra. Microanalyses were carried out on some of these products and, as in the case of the product from DNT, showed the presence of oxygen as well as C, H and N. (In the microanalyses carried out at the University of Alberta, the analyst noted that some of the products were difficult to combust completely. As a result, consistent analysis results could not be obtained. A typical analysis of *o*-nitrotoluene electrolysis product showed C, 62.1%; N, 9.6%; H, 3.7%; O, 16.1% and S, 0.09%.) Yields of the isolated products varied considerably and were difficult to reproduce in repeated experiments. No volatile products (detectable by GLC) were formed in any of these electrolyses.

Divided cell electrolyses were then carried out on nitrobenzene and *o*-nitrotoluene in H_2SO_4 in order to isolate any products formed at the cathode which would have undergone oxidation in the undivided cell electrolyses. The corresponding amines, aniline and *o*-toluidene, were in fact detected in the ether extracts of the neutralized electrolysis solutions.

It was concluded that electrolysis of nitroaromatics such as 2,4-DNT in concentrated H_2SO_4 results in reduction to an amine which is then oxidized at the anode to give a high molecular weight, black product which can be further oxidized to CO_2 and oxides of nitrogen.

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