

THE EFFECT OF ELECTRIC FIELD AND TEMPERATURE ON THE ISOMER DISTRIBUTION FORMED DURING THE MONONITRATION OF CHLOROBENZENE

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The distribution of isomers in mononitration of chlorobenzene is shown to be dependent upon the temperature of the reaction mixture and the physical properties of the solvents involved. An empirical model which relates the isomer ratio with the dipole moments and dielectric constants of the solvents has been derived. Based on this observation, a study into the effect of electric field on the distribution of isomers in continuous mononitration of chlorobenzene has been undertaken.

INTRODUCTION

Mononitrochlorobenzene isomers are widely used as solvents or intermediates in various heavy organic industries. The technical applications of the three isomers are different and the demand for a particular one depends on the nature of the process concerned.

The distribution of monochloronitrobenzene isomers may be slightly affected by change in temperature of the reaction media or using certain additives [1]. However, variation in temperature could also promote the formation of certain byproducts and the use of the additives may impose difficulties in separation and purification of the isomers. These procedures are, therefore, not applicable to industrial plants.

However, the present method, described in later sections, may find application in related industries.

EXPERIMENTAL

The chemicals used in this study were all analytical grade. Chlorobenzene was purified by distillation at reduced pressure (15 Torr) with a glass column of 3 cm dia and 100 cm high, packed with glass rings of 3 mm dia.

Anhydrous nitric acid was prepared by a method similar to that of Hughes *et al.* [2].

Solutions of anhydrous nitric acid in organic solvents were prepared at the temperature of liquid nitrogen and the mixtures were allowed to warm to -15° , the temperature of storage. Solutions prepared in this way were stable for about a week, but then decomposed quickly.

The general kinetic methods for homogeneous batch nitration of aromatic compounds in organic solvents and in water have been discussed elsewhere [3].

Isomer distributions were determined by gas-liquid

chromatography. The instrument was a Beckman model GC 2160 linked to a recorder which was coupled with a disk integrator (Linear Instruments). The flame ionisation detector was used. A stationary phase of 1 g sodium hydroxide supported on 14 g Apiezon L on Chromosorb P of 80 - 100 mesh was packed in a 9-ft stainless-steel column. The operating temperature was 140° . Nitrogen was used as carrier gas with a constant flow rate of 30 ml/min.

The qualitative and quantitative analyses of the acidic byproducts formed during mononitration of chlorobenzene were achieved by a method similar to that of Kaghazchi *et al.* [4]. This consisted of alkali extraction of phenolic compounds from the reaction mixture, followed by acidification of the alkali solution, reextraction by ether and spectroscopic analysis. It was found that two phenolic compounds, namely 2,4-dinitro-6-chlorophenol and 2,6-dinitro-4-chlorophenol, formed the major quantity of the byproducts of chlorobenzene nitration. These compounds were identified by comparing the IR spectra of the isolated byproducts with the reference spectra of some polynitrochlorophenols (Infra Red Data Committee of Japan/Sadtler Research Laboratories Inc., Philadelphia, U.S.A.). The Instrument used was a Zeiss model IMR 25.

Further analysis of the organic phase product, using the KBr pressed disk technique, confirmed that neutral or basic organic impurities were not present in large amounts as no significant absorption peaks which could correspond to such compounds were observed.

RESULTS AND DISCUSSION

Effect of temperature. The ratio of *para/ortho* chloronitrobenzene is slightly dependent upon the temperature of the reaction mixture (Fig. 1). However, increase in temperature has the disadvantage of promoting the formation

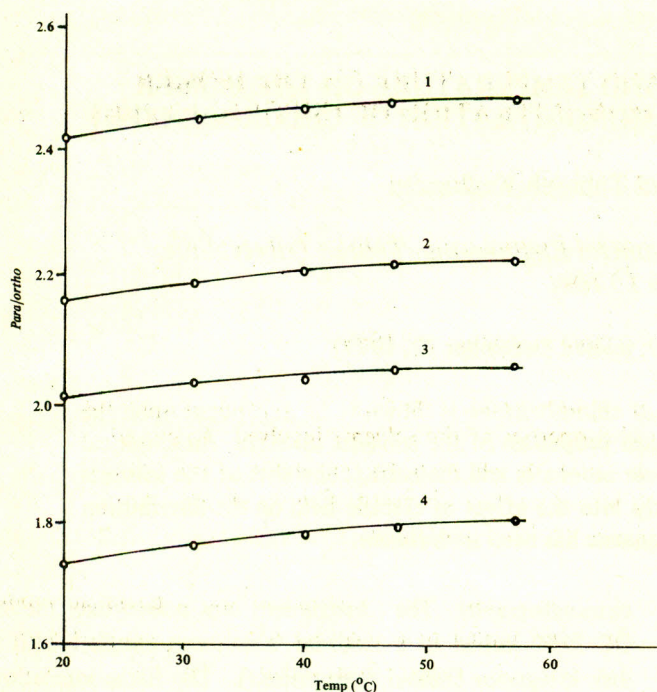


Fig. 1. The effect of temperature on the isomer ratio.

Nitration Conditions	Solvent
1. Homogeneous system	Nitromethane
2. Homogeneous system	Water
3. Two phase system (nitration by mixed acid)	---
4. Homogeneous system	Carbon tetrachloride

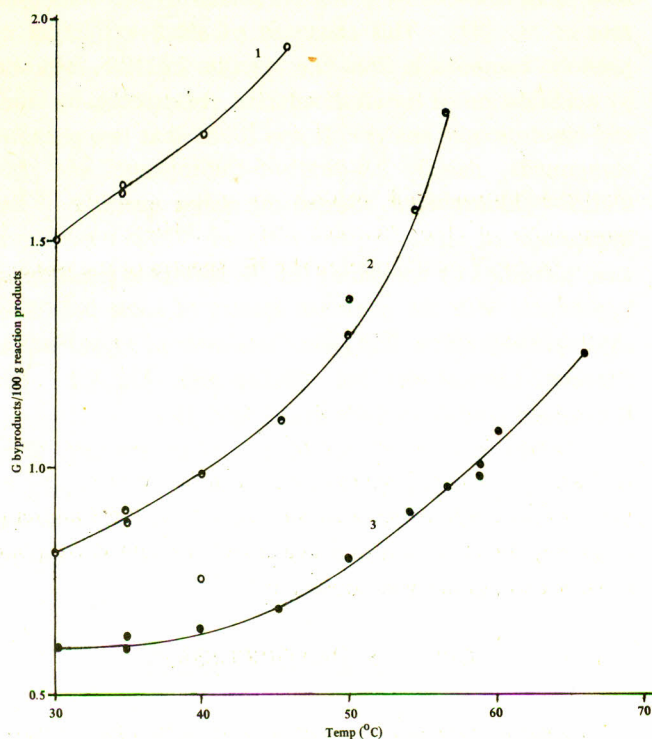


Fig. 2. The effect of temperature on the formation of acidic by-products: (1) two phase nitration by mixed acid, (2) homogeneous nitration in acetic acid, and (3) homogeneous nitration in carbon tetrachloride.

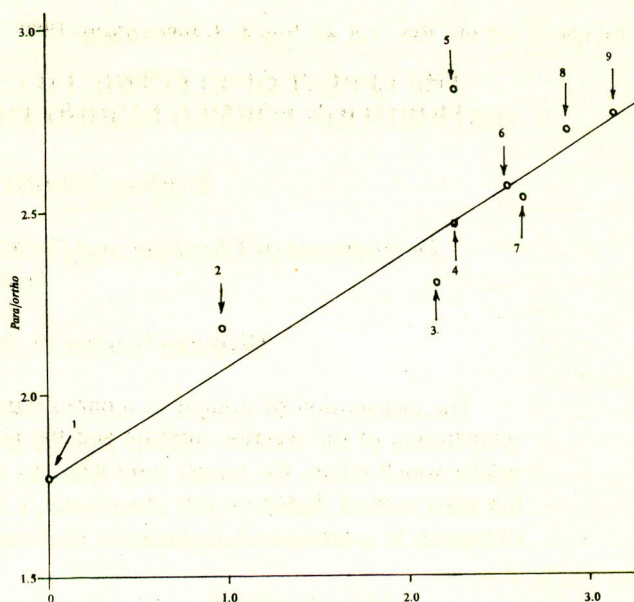


Fig. 3. The effect of physical properties of solvents on the isomer ratio: (1) carbon tetrachloride, (2) water, (3) acetonitrile, (4) Nitromethane, (5) acetic acid (6) *o*-dichlorobenzene, (7) nitrobenzene, (8) sulpholane, and (9) benzonitrile.

of phenolic byproducts. This is demonstrated in Fig. 2 from which it can be observed that, in several nitrating systems, a rapid increase in the total amounts of acidic byproducts occurs above 50 – 60°.

Effect of Electric Field. The present authors observed that the isomer distribution during chlorobenzene nitration is dependent upon the physical properties of the solvents involved. The effect of three types of solvents was considered: dipolar-aprotic, protic and nonpolar. The influence of the dipole moment and dielectric constant of the solvents on the *para/ortho* ratio was studied. The results are summarised in Table 1, from which it is found that the *para/ortho* ratio is dependent upon the nature of the solvents involved according to the relation:

$$Para/ortho = \frac{0.317 \mu}{\log \epsilon} + 1.766 \quad \epsilon \neq 1 \quad (1)$$

where μ is the dipole moment in Debye units, and ϵ is the dielectric constant of the solvent (Fig. 3).

This finding indicates that the isomer distribution varies with change in the dipole moment of the particular solvent involved.

It is possible to alter the dipole moment of a compound by means of an electric field, the effect of which on nonpolar molecules and on those with permanent dipole moment is known.

The induced dipole moment in a nonpolar molecule as the result of an electric field is:

$$m = \alpha F = \frac{3}{4N_0\pi} \cdot \frac{\epsilon - 1}{\epsilon + 2} \left(\frac{M}{\rho} \right) \cdot E \quad (2)$$

Table 1. Effect of the physical properties of solvents on the distribution of mononitrochlorobenzene isomers.

Solvents	Type of solvent [6]	ϵ	μ	Temp (°C)	Isomer proportions (%)			
					<i>o</i> -	<i>p</i> -	<i>m</i> -	<i>p</i> / <i>o</i>
Nitromethane*	Dipolar aprotic	35.87	3.46	31	28.5	70.5	1.0	2.47
<i>o</i> -Dichlorobenzene†	"	9.93	2.51	31	27.6	71.3	1.0	2.58
Sulpholane*	"	44.00	4.69	31	26.6	72.6	0.8	2.73
Acetonitrile*	"	37.50	3.37	31	30.2	69.2	0.5	2.29
Nitrobenzene**	"	34.82	3.98	31	28.0	71.1	0.9	2.54
Benzonitrile*	"	25.20	4.39	31	26.3	72.7	0.9	2.76
Water‡	Protic	78.54	1.85	31	31.0	67.9	1.0	2.19
Acetic acid*	"	6.15	1.74	31	25.8	73.2	1.0	2.84
Carbon tetrachloride†	Nonpolar	2.24	0.00	31	35.9	63.6	0.5	1.77

* [HNO₃] = 9.02 mole/l† [HNO₃] = 0.22 mole/l** [HNO₃] = 0.98 mole/l‡ [HNO₃] = 17.02 mole/l

Table 2. Effect of electric field on the distribution of monochloronitrobenzene isomers.

Nitration conditions	DC voltage	Distribution of isomers (%)			
		<i>o</i> -	<i>p</i> -	<i>m</i> -	<i>p</i> / <i>o</i>
Homogeneous nitration by anhydrous nitric acid	0	25.8	73.2	0.9	2.837
Temp 31°	107	25.8	73.2	0.9	2.837
	210	25.8	73.2	0.9	2.837
	405	25.8	73.2	0.9	2.837
[HNO ₃] = 9.2 mole/l	562	25.8	73.2	0.9	2.837
	750	25.6	73.5	0.9	2.871
Flow rates:	830	25.5	74.1	0.7	2.917
10 ml/min 18.4 mole/l. HNO ₃ in acetic acid	905	25.1	74.4	0.7	2.964
10 ml/min. 0.1 mole/l chlorobenzene in acetic acid	1500	23.4	75.8	0.8	3.239
Conversion = ca. 80%	3000	20.6	78.7	0.7	3.820
Two phase nitration by 6.1 mole/l. HNO ₃ in 70% H ₂ SO ₄	0	32.7	66.3	0.8	2.027
Temp = 31°	110	32.7	66.3	0.8	2.027
	344	32.7	66.3	0.8	2.027
rev/min = 2000 ± 200	580	32.7	66.3	0.8	2.027
Flow rates:	655	32.6	66.5	0.8	2.039
20 ml mixed acid/min (continuous phase)	732	32.1	66.9	0.9	2.084
10 ml chlorobenzene/min (dispersed phase)	835	31.9	67.3	0.8	2.109
Conversion = ca. 90%	901	31.2	67.9	0.8	2.176
	1500	29.8	69.4	0.8	2.328
	3000	26.2	72.9	0.9	2.782

where F is the electric field within the dielectric, E is the applied field, M is the molecular weight, ρ is the density, N_0 is Avogadro's number and α is the distortion polarisability.

The dipole moment of a polar molecule placed in an electric field will be the sum of two terms: (a) the orientation polarisability due to permanent dipole which is given by: $\mu^2 / 3kT.F$; and (b) the induced dipole moment due to

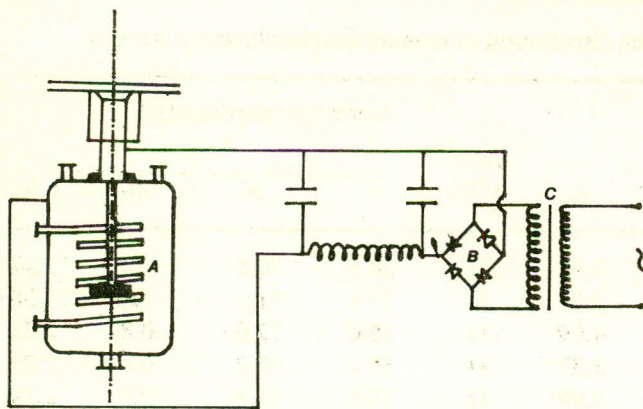


Fig. 4 The reactor and the rectifier's circuit (not to scale): (a) cooling coils, (b) zener diodes, and (c) transformer.

the electric field acting on it, αF where F is the strength of the local field, T is the absolute temperature and k is the Boltzman constant.

It is clear from the present observation that the electric fields have some effect on the distribution of mononitrochlorobenzene isomers. However, it is not possible to estimate the extent of such an effect theoretically. Further experiments were, therefore, conducted.

A small continuous-stirred-tank reactor was designed and constructed. The reactor was made of stainless-steel and its main features were the same as those of Wilson's apparatus [5], with the exception of baffles and agitator. The reactor had no baffles and was fitted with a 20-mm dia straight blade turbine impeller which was being driven by a $\frac{1}{4}$ h.p. motor at a speed of 2000 ± 200 rev/min.

To produce an electric field within the reactor, a direct current of a known voltage was connected to the outer

wall of the vessel and the impeller's shaft. Low voltage direct current was produced by means of a circuit consisting of a transformer and four 'zener' diodes (Philips) (Fig. 4). With such a circuit direct currents of less than 900 volts can be generated. To study the effect of stronger electric fields, a rectifier was used. The instrument was a Griffin L96-100 E.H.T. model.

The results are presented in Table 2.

Owing to instrumental limitations it was not possible to obtain a sufficiently strong induced field. Nevertheless, the present results clearly indicate that the ratio *para/ortho* is increased by means of a strong electric field.

This procedure, in contrast to most other methods, does not involve the use of any catalysts or change in the reaction conditions and hence additional problems in separation and purification of the isomers can be avoided.

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