79. *Nitryl Chloride. Part II.* The Reaction with Alkylbenzenes.*

By F. P. Gintz, D. R. Goddard, and (in part) M. J. Collis.

Nitryl chloride, in various solvents at room temperature and below, chlorinates (rather than nitrates) toluene, *m*- and *p*-xylene, and mesitylene, although not benzene. The extent of chlorination was measured and the products isolated.

With polar solvents, in which nitryl chloride forms yellow solutions, the chlorinating agent is probably free chlorine produced by the reaction of nitryl chloride with traces of water. With the less polar solvents, in which nitryl chloride forms colourless solutions, it is probably the nitryl chloride molecule itself.

The kinetics of chlorination in nitromethane–ether were studied by dilatometric and chemical techniques. With the aromatic compound in excess, the reaction velocity was of the first order. The rate increased markedly with increase in the reactivity of the hydrocarbon and with increase in the polarity of the solvent. These facts are consistent with a mechanism involving a bimolecular attack by a chlorine molecule on the aromatic compound.

The formula of nitryl chloride, NO_2Cl, suggests that it could either nitrate or chlorinate aromatic compounds. Gillespie and Millen[1] predicted the following series of nitrating agents of increasing power, on the basis that the efficiency of $X{\cdot}NO_2$ depends on the electron affinity of X: $EtO{\cdot}NO_2 < HO{\cdot}NO_2 < AcO{\cdot}NO_2 < NO_3{\cdot}NO_2 < Cl{\cdot}NO_2 < H_3O^+{\cdot}NO_2 < NO_2^+$. The order is also that of the increasing strength of the acid HX. They expected, therefore, that nitryl chloride should be a very reactive nitrating agent, even more powerful than dinitrogen pentoxide. Similarly, chlorinating agents could be arranged in order of reactivity, the efficiency of the agent Y·Cl increasing with the electron

---

* Part I, preceding paper.

[1] Gillespie and Millen, *Quart. Rev.*, 1948, **2**, 277.

affinity of Y and hence with the strength of the acid HY: $HO{\cdot}Cl < AcO{\cdot}Cl < NO_2{\cdot}Cl < Cl{\cdot}Cl < H_2O^+{\cdot}Cl < Cl^+$. Thus nitryl chloride should be a moderate chlorinating agent, slightly weaker than molecular chlorine.

Steinkopf and Kuhnel,[2] who first studied the reaction of nitryl chloride with organic compounds, found that at room temperature nitryl chloride dissolved in benzene without reacting, and that when warmed the nitryl chloride evaporated off unchanged. When benzene and nitryl chloride were heated under pressure 1-chloro-2-nitro*cyclo*hexadiene was formed which decomposed producing nitrobenzene. Nitryl chloride reacted violently with naphthalene, forming both 1-nitro- and 1-chloro-naphthalene.

However, Price and Sears [3] reported that nitryl chloride reacts with benzene at room temperature to form nitrobenzene, although in only 30% yield, and that the nitrating action of nitryl chloride was enhanced by the presence of Lewis acids, *e.g.*, aluminium trichloride, in presence of which and in carbon disulphide as solvent benzene gave a 90% yield of nitrobenzene and toluene a mixture of *o*- and *p*-nitrotoluene in yields of 47 and 24% respectively. Similarly, naphthalene gave 1-nitronaphthalene in 31% yield.

We confirmed Steinkopf and Kuhnel's observation for benzene. The formation of nitrobenzene reported by Price and Sears [3] might have been caused by catalysis by impurities such as nitrogen dioxide or nitric acid. We could not confirm the formation of 1-chloro-2-nitro*cyclo*hexadiene when nitryl chloride and benzene are heated together, but only detected nitrobenzene.

The reaction of nitryl chloride with various alkylbenzenes was studied. At room temperature or below, it forms with toluene, *p*-xylene, and mesitylene chloro-derivatives, with little or no nitro-derivatives. The kinetics of chlorination were studied.

Extent of Chlorination and Nitration of Alkylbenzenes by Nitryl Chloride.—This work was mostly done before that on the nature of nitryl chloride solutions reported in Part I, the observation during it of the yellow colour of solutions of nitryl chloride in nitromethane leading to their study.

The alkylbenzene (*p*-xylene or mesitylene) was added to a cooled solution of nitryl chloride in the solvent. The course of the reaction was followed by withdrawing samples of the reaction mixture, hydrolysing them, and determining the chloride and total acid. The relative proportions of chlorination and nitration were determined by using a known amount of nitryl chloride with the alkylbenzene in excess and then estimating the quantity of organic chloro- and nitro-compounds produced. The extent of nitration, based on the initial nitryl chloride concentration, was never more than 3·5%. The results for chlorination given in Table 1 are typical.

TABLE 1. *Extent of chlorination of alkylbenzenes during* 3 *hr.*

[ArH] (in excess), 0·2—2·0 moles/l.; $[NO_2Cl]$, 0·05—0·40 mole/l.

			Chlorination (%) *					Chlorination (%) *	
Temp.	Aromatic cpd.	Solvent	Total	Side-chain	Temp.	Aromatic cpd.	Solvent	Total	Side-chain
0°	Toluene	$MeNO_2$–Et_2O (2 : 1)	40	—	−5°	Mesitylene	$MeNO_2$	55	—
					20	,,	,,	55	14
					20	,,	$Me{\cdot}CO_2H$	51	—
0	*p*-Xylene	,,	50	—	20	,,	MeCN	56	—
−5	,,	$MeNO_2$	57	—	20	,,	C_6H_6	60	—
20	,,	,,	51	11	20	,,	,,	63	23
20	,,	$Me{\cdot}CO_2H$	52	—	20	,,	$Me{\cdot}CO_2Et$	61	—
					20	,,	,,	65	30
					20	,,	CH_2Cl_2	65	—

* Based on initial concn. of NO_2Cl.

The products isolated are given in Table 2 for solutions in nitromethane (*n.i.*, not isolated; *d*, isolated as a derivative).

---

[2] Steinkopf and Kuhnel, *Ber.*, 1942, **75**, 1323.

[3] Price and Sears, *J. Amer. Chem. Soc.*, 1953, **75**, 3276.

TABLE 2.

Hydrocarbon:	*p*-Xylene	Mesitylene
Hydrocarbon in excess	2-Chloro- and 2-nitro-*p*-xylene	Nitro(*n. i.*) and chloro-mesitylene
Nitryl chloride in excess	2 : 5-Dichloro- and 2-nitro-*p*-xylene (*d*)	Trichloromesitylene

The Nature of the Chlorinating Agent.—(a) *Coloured solutions of nitryl chloride in nitromethane.* In Part I it was shown that these solutions were yellow owing to the hydrolysis of nitryl chloride by traces of moisture in the solvent:

$$3NO_2Cl + H_2O \longrightarrow NOCl + Cl_2 + 2HNO_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The reaction, which takes place only after an induction period of several minutes, is complete in solutions of strength of the order 0·05M. By comparing the action of an initially colourless solution with a coloured one, we showed that the coloration corresponds with the formation of a very reactive chlorinating agent which can only be chlorine itself.

If chlorine were the sole chlorinating agent in these solutions we should not expect the extent of chlorination to exceed one third. Yet in practice the percentage of chlorination in 2—3 hr. is of the order of 55. A careful check of the extent of chlorination against reaction time revealed that the initial rapid reaction of nitryl chloride solutions was followed by a slow reaction which proceeded for many hours. With initial *p*-xylene and nitryl chloride concentrations 2·0M and 0·25M in nitromethane, the extent of chlorination after 1 hr. at −10° was 43%, after a further 2 hr. at 20° was 51%, and after a further hr. at 20° was 58%. Corresponding figures for mesitylene were 42, 52, and 66%. We concluded that the additional chlorination must be due to the other constituents present in yellow solutions, *viz.*, nitrosyl chloride and nitric acid. Measurement of the extent of chlorination by nitrosyl chloride, and nitrosyl chloride in the presence of nitric acid, confirmed this (Table 3).

TABLE 3. *Extent of chlorination of mesitylene* (0·1—1·0 *mole/l., in excess*) *by nitrosyl chloride at* 20°.

Reagent (Molar ratios)	Solvent	ArCl (%) (total) after 3 hr.	19 hr.	ArCl (%) (side-chain) after 5 hr.	19 hr.
NOCl	$MeNO_2$	6	—	—	—
NOCl	MeCN	8	—	—	—
1·0 NOCl : 0·53 HNO_3	$MeCO_2H$	8	—	—	—
1·0 NOCl : 1·28 HNO_3	$MeNO_2$	15	—	—	—
1·0 NOCl : 2·0 HNO_3	$MeNO_2$	26	49	—	—
1·0 NOCl : 2·4 HNO_3	$MeNO_2$	—	—	6	7

(b) *Colourless solutions of nitryl chloride.* Nitryl chloride is unchanged when dissolved in benzene, methylene chloride, carbon tetrachloride, or ethyl acetate and when these solvents are used the nitryl chloride molecule or the chlorinium ion (Cl^+) derived from it is probably primarily responsible for the chlorination. That the extent of chlorination by such solutions is often considerably less than 100% can easily be explained as a result of the reaction of the nitrous acid, formed in the reaction, with unreacted nitryl chloride:

$$NO_2Cl + RH \longrightarrow RCl + HNO_2; \; NO_2Cl + HNO_2 \longrightarrow NOCl + HNO_3$$

Here again there is rapid chlorination followed by a slower one due to chlorination by nitrosyl chloride; for mesitylene in benzene the extent of chlorination at 20° after 1 hr., 3 hr., and 23 hr. is 61, 63, and 73% respectively, and the corresponding extents in ethyl acetate are 65, 65, and 71%.

The Kinetics of Chlorination.—The reaction of nitromethane solutions of nitryl chloride with the alkylbenzenes was too fast to follow even at −5°. The reaction was slowed down to a convenient rate by the use of 2 : 1 nitromethane–ether. A dilatometric method was employed, checked by a chemical one. The aromatic compound was always in excess (10-fold or more) to avoid the chlorination of the hydrocarbon being complicated by the further reaction of the chloro-aromatic product. The reaction was of first order with respect to the nitryl chloride (see Fig. 1). Unfortunately, the rate constants varied over a range of 25% and since we do not know why, the kinetics were of limited use. The lack of reproducibility might have been due to the catalytic effect of traces of water, but although elaborate precautions were taken to exclude moisture, subsequent results were no better.

Within the somewhat large experimental error, the first-order rate constant was independent of the initial nitryl chloride concentration; in 2 : 1 nitromethane–ether at −4·92° with an initial concentration of *p*-xylene 2·03M, *k*, for initial concentrations of nitryl chloride 0·07, 0·15, 0·17, 0·19, and 0·25 was 0·044, 0·060, 0·045, 0·052, and 0·053 respectively. However, the chemically determined rate constants were always slightly lower (*e.g.*, 0·044, 0·035, 0·035 min.$^{-1}$ in the same system at −5° and initial concentration of nitryl chloride 0·15M) than dilatometric ones (*e.g.*, 0·060, 0·045, 0·052 min.$^{-1}$). The reaction velocity was very dependent on the composition of the solvent; at −10° with initial concentration of *m*-xylene 2·0M, solvent ratios nitromethane : ether of 1 : 2, 3 : 10, and 1 : 10 gave k_1 0·10, 0·018, and 0·011 min.$^{-1}$ respectively. It varied with the aromatic compound; when the hydrocarbon was more reactive to electrophilic substitution than *p*-xylene, the reaction became too rapid to follow in 2 : 1 nitromethane–ether, and the proportion of ether had to be increased (Table 4).

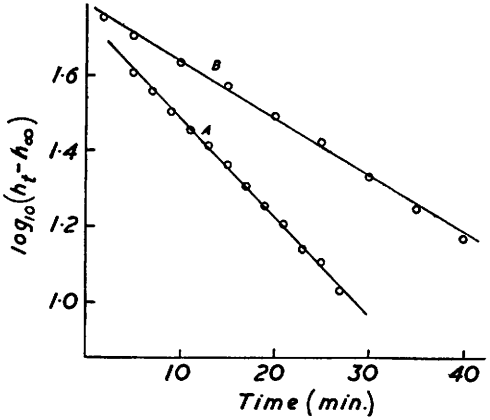


FIG. 1. *Rate of chlorination of* p-*xylene at* 5°.

A, Dilatometric, k_1 = 0·060 min.$^{-1}$.
B, Chemical, k_1 = 0·035 min.$^{-1}$.

TABLE 4. *Variations in* k_1 *with aromatic compound* (*initial concn. ca.* 2M).

Compound	Solvent $MeNO_2 : Et_2O$	Temp.	k_1 (min.$^{-1}$)
p-Xylene	2 : 1	−5°	0·050 (mean)
Toluene	2 : 1	−5	0·018 (mean)
m-Xylene	1 : 2	−10	0·10
,, ...	1 : 10	−10	0·011
Mesitylene	1 : 10	−10	0·088

An attempt was made to determine the order of reaction with respect to the aromatic compound by varying its initial concentration; the rate was unaffected, probably because the aromatic compound, being in excess, constitutes an appreciable fraction of the solvent. Thus an increase in rate caused by an increase in concentration of the aromatic compound might be compensated by a reduction in rate due to decrease in the polarity of the solvent.

All the results are consistent with a bimolecular attack on the aromatic compound by the chlorine molecule. Ultraviolet absorption spectra showed that nitryl chloride is hydrolysed similarly in nitromethane–ether as in pure nitromethane.

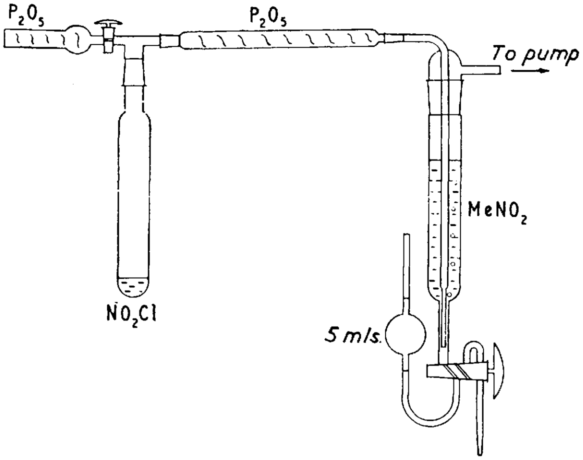
EXPERIMENTAL

Materials.—All compounds other than those in Part I were prepared and purified by standard methods.

Isolation of Reaction Products.—(a) *Nitryl chloride with excess of* p-*xylene. Separation of nitration product.* 150 ml. of *p*-xylene were added to 200 ml. of a 0·4M-nitryl chloride in nitromethane cooled to $-10°$. After 1 hr. the solution was allowed to warm to room temperature, and after a further hour was poured into water. The organic layer was separated, washed with water, and distilled at 15 mm. pressure. At 100° the distillation was stopped and the residue reduced with iron and hydrochloric acid. Last traces of *p*-xylene were extracted with ether. The aqueous layer was made alkaline and the amine product was ether-extracted. On evaporation of the ether a small residue of red oil was left which, acetylated with acetic anhydride, gave a product which, recrystallised from aqueous alcohol, had m. p. 137°, unchanged by admixture with 2-acetamido-*p*-xylene. The original reaction product therefore contained 2-nitro-*p*-xylene.

Separation of chlorination product. Another reaction mixture, obtained as above, was washed with water and evaporated at 100°/15 mm. The residue was dissolved in 100 ml. of light petroleum (b. p. 60—80°), filtered through a column of alumina, and eluted with light petroleum. The first portion of the eluate contained only traces of *p*-xylene. The next 200 ml. when evaporated left approximately 6 ml. of a colourless oil which distilled at 183° (b. p. of 2-chloro-*p*-xylene, 183°) (Found: C, 68·5; H, 6·70; Cl, 24·7. Calc. for C_8H_9Cl: C, 68·3; H, 6·45; Cl, 25·2%).

FIG. 2.



(b) p-*Xylene with excess of nitryl chloride.* A four-fold excess of nitryl chloride was used. The nitration and chlorination products were separated as above. The amine isolated was only sufficient to give an azo-dye test. The chloro-compound was large colourless plates, m. p. 70°, unchanged by admixture with 2 : 5-dichloro-*p*-xylene (Found: C, 54·5; H, 4·9; Cl, 39·4. Calc. for $C_8H_8Cl_2$: C, 54·9; H, 4·6; Cl, 40·5%).

(c) *Nitryl chloride with excess of mesitylene.* The method was similar to that for *p*-xylene. The amine was only sufficient for an azo-dye test. The chloro-compound was a colourless oil, b. p. 206° (b. p. of chloromesitylene, 204—206° (Found: C, 70·5; H, 7·31; Cl, 21·9. Calc. for $C_9H_{11}Cl$: C, 69·9; H, 7·12; Cl, 23·0%).

(d) *Mesitylene with excess of nitryl chloride.* 3 ml. of mesitylene were added to 200 ml. of *ca.* 0·5M-nitryl chloride in nitromethane. After 1 hr. the mixture was washed with water, then evaporated at low pressure to about 30 ml. On cooling, long white needles separated, m. p. 194°. Recrystallisation from alcohol to constant m. p. gave a product, m. p. 212° [2 : 4 : 6-trichloromesitylene prepared from chlorine and mesitylene had m. p. 209° (lit.,[4] m. p. 204—205°)] (Found: C, 47·6; H, 3·6; Cl, 47·6. Calc. for $C_9H_9Cl_3$: Cl, 48·2; H, 4·0; Cl, 47·7%).

Determination of Reaction Products.—*Aromatic nitro-compounds.* When nitromethane was solvent, the method was similar to that of Bird and Ingold,[5] the nitromethane being extracted

---

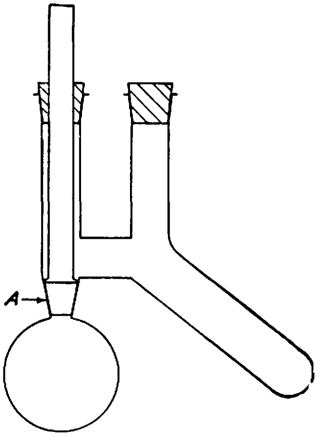
[4] Fittig and Hoogewerff, *Annalen*, 1869, **150**, 328.

[5] Bird and Ingold, *J.*, 1938, 918.

with alkali and the residual aromatic nitro-compound titrated with titanous chloride. However, in order completely to remove the nitromethane without loss of the aromatic nitro-compound (which appeared to be soluble in an alkaline solution of nitromethane) we had to use a large volume of 5N-sodium hydroxide (200 c.c. per 5 ml. of sample) in place of the N-alkali used by them. The procedure employed for the titanous chloride reduction was based on that of Augood, Hey, and Williams.[6]

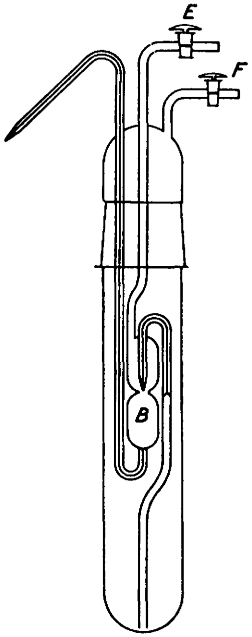
Organic chloro-compounds. Nitro-methane or -ethane was removed as above. With other solvents less vigorous treatment with alkali was required. The chloro-compound was then determined by a modification of Bacon's method.[7] *n*-Butanol was added to the aromatic residue and the mixture refluxed for 1½ hr. during the addition of metallic sodium. On cooling, diluting, and acidifying, the aqueous layer was separated and mixed with the washings of the butanol layer and the chloride present was titrated potentiometrically.

FIG. 3.



A, Ground stopper.

FIG. 4.



In some cases the extent of chlorination was estimated more simply from the reduction during the reaction of the hydrolysable chloride in the reaction mixture. Side-chain chlorination products were determined by the same method except that the aromatic residue was refluxed with sodium butoxide instead of metallic sodium.

Reaction Kinetics.—Dilatometry. A solution of nitryl chloride was prepared by distilling the oxyhalide over phosphoric oxide into nitromethane by using the apparatus shown in Fig. 2. The kinetic runs were carried out in groups of four. 5 ml. of the nitryl chloride solution were pipetted into the bulb of each mixing flask (Fig. 3), and a sample was analysed. 5 ml. of a solution of the aromatic compound in ether were placed in the other arm of each flask. One flask was placed in the thermostat and the others were cooled in solid carbon dioxide. After temperature equilibrium had been obtained, the bulb of the mixing flask was unstoppered by withdrawing the rod through the greased Polythene stopper. The solutions were mixed by tilting the flask, the stopper was withdrawn and a tapless dilatometer (Benford and Ingold [8] type *C*) filled.

Chemical determination of reaction velocities. A solution of nitryl chloride in nitromethane was placed in the tube of the apparatus illustrated in Fig. 4, and immersed in the thermostat

---

[6] Augood, Hey, and Williams, *J.*, 1952, 2097.
[7] Bacon, *J. Amer. Chem. Soc.*, 1909, **31**, 49.
[8] Benford and Ingold, *J.*, 1938, 929.

up to the ground joint. An equal volume of an ether solution of the aromatic hydrocarbon at the thermostat temperature was then rapidly added. Samples were withdrawn at intervals and hydrolysed, and the liberated chloride titrated with silver nitrate. The samples were withdrawn without exposure to the atmosphere as follows. The mixture was blown into the bulb *B* (capacity 2·45 ml.) by blowing dry air into *F* with tap *E* open. When the bulb was full, the pressure at *F* was released, and the excess of the solution in the upper bulb syphoned back into the bulk of the reaction mixture. By closing *F* and blowing dry air through *E*, the liquid in the bulb *B* was forced out through the capillary tube and collected in a flask containing a little water.

Check of the stability of chlorine and nitryl chloride in nitromethane and ether solvents. When it was realised that free chlorine was present in solutions of nitryl chloride in nitromethane the stability of solutions of chlorine was investigated. Solutions of chlorine (*ca.* 0·05M) were stable in pure nitromethane at −5°, but in pure ether they slowly reacted, losing 15% of oxidising power in 3 hr. although there was no loss of ionisable chlorine. Solutions in 2 : 1 nitromethane–ether were, surprisingly, much less stable, losing 70% of oxidising power in 1 hr.

When the stability of nitryl chloride in nitromethane and ether was originally investigated the total acid and chloride produced on hydrolysis were determined and there was no change with time. In view of the reaction of free chlorine, the reducing power of nitryl chloride solutions was determined. A solution of nitryl chloride in pure nitromethane was stable, that in ether very slowly developed reducing action at −5°, but again with the mixed solvent the development was more rapid. The rise in reducing power of the solution during 40 min. at −5° was equivalent to the removal of the oxidising power of one third of the chlorine originally present. Since most kinetic runs were over in under 30 min. the reaction with the solvent clearly would not invalidate the general conclusions from the kinetics.

THE CHEMISTRY DEPARTMENT, CHELSEA POLYTECHNIC,
LONDON, S.W.3.

[*Received, April* 25*th*, 1957.]